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ASPECTS OF RADICAL CATION CHEMISTRY AND POSSIBLE APPLICATIONS TO COAL MODEL COMPOUND REACTIONS

Dissertation
Submitted to the College of Arts and Sciences
as partial fulfillment
of
the Doctor of Philosophy Degree
in Chemistry
West Virginia University
Department of Chemistry

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1994

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PREFACE

The following manuscript is a description of our efforts over the last five years to investigate and elucidate the chemical parameters and mechanisms that lead to the C-C bond cleavage reactions in organic compounds.

Motivation to perform this work was provided by the reactions of certain coal model compounds under coal liquefaction conditions. These coal model compounds were found to cleave the bond connecting the naphthalene ring to the remainder of the molecule and the reactivity was attributed to be due to radical cation behavior. This behavior was different than the reactivity of radical cations of similar phenyl-containing compounds. Our contribution to this field involves the investigation of the C-C bond cleavage reactions of the radical cations of naphthyl-containing compounds.

Chapter I illustrates the generation of the radical cations of naphthyl-containing compounds in solution and gas phase and their bond cleavage reactions. Their reactivity was compared to the corresponding reactivity under catalytic conditions.

Chapter II examines the general oxidation reactions of the above-mentioned compounds. The purpose was to investigate the effects of counterion on the reactions. The remainder of this chapter is devoted to the investigations of the dehydrogenation reactions of related compounds. There has been interest recently in the development of new and milder dehydrogenating reagents.

Three Fe compounds were found to produce the desired dehydrogenation reactivity at relatively low temperatures (130 ^{0}C).

The final chapter of this manuscript discusses the results and conclusions derived from the sensitized irradiation of a series of esters by a triphenylpyrylium salt and oxygen. These esters were found to undergo C-C bond cleavage reactions and these reactions were found to arise by a oxygen-induced radical chain autoxidation reaction and not by radical cationic behavior as has been proposed in the literature.

It is my hope that future work will be devoted to further our understanding of the general oxidations and dehydrogenations of some substrates by Fe compounds. What role does the ClO_4^- play in these reactions? Is a radical cation intermediate involved here? These are only a few of the potential avenues that can be examined by using this manuscript as a guide. I am sure that there are more unexpected and exciting reactions waiting to be observed in the systems such as those described in this text.

Acknowledgements

I wish to express my sincere appreciation and great gratitude to Dr. John H. Penn. Dr. Penn has provided his time, encouragement and guidance in this research. He is not only the advisor, but also a good friend. He helped me a lot in both chemistry and daily life. Without his help, the completion of my graduate work would not be success.

I would also like to thank the members of my research committee (Dr. Dady Dadyburjor, Dr. Nar S. Dalal, Dr. William R. Moore, Dr. Kung K. Wang) for their suggestions, time and services with special appreciation to Dr. Dalal for his great assistance to acquire the ESR spectrum. I would also like to express my thanks to Dr. Plato Magriotis, who had been a committee member for several years.

I would also like to thank my mother, Afeng, my brothers and sisters, Yuhai, Yuqian, Yuzhen and Yudi for their constant support and caring over these years. The ultimate appreciation is due to Luna for her persistent love and support.

Dedicated to the memory of

my father, Zhongchu

CHAPTER I

Radical Cation Bond Cleavage Pathways for Naphthyl-Containing Coal Model Compounds[A]

Abstract

A series of naphthyl-containing compounds has been synthesized. The radical cations of these compounds were generated in solution using three independent techniques. These compounds were found to undergo bond cleavage reactions in exact analogy to the corresponding phenyl-containing compounds. The radical cations of these compounds were also generated in the gas phase in a mass spectrometer and show the same reactivity patterns as was observed in solution. ESR spectroscopy was used to try to identify the radical cations of these compounds. Under coal liquefaction conditions, a different reactivity pattern of these compounds has been previously observed, but ascribed to reactions of radical cations. Since the radical cations of naphthyl-containing model compounds react differently than the naphthyl-containing model compounds under coal liquefaction conditions, a reinterpretation of catalyst-initiated bond cleavage mechanisms in naphthyl-containing coal model compounds should be undertaken.

[A] i) Penn J. H.; Wang, J. *Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem.*, **1992**, 1650. ii) Penn J. H.; Wang J. *Energy and Fuels*, **1994**, 8, 421.

Introduction

To liquify or gasify coal, the carbon-carbon bonds of the organic structure must be broken. Thermal cleavage requires temperatures so high that other, mostly undesirable, reactions take place. However, chemical bonds can be selectively cleaved by use of catalysts, at temperatures where thermal reactions are not important. There has been much recent interest in the development of new and improved catalysts designed for coal liquefaction.[1,2,3,4] Iron catalysts composed of $Fe(CO)_5$ or $Fe(CO)_5$-S had high activity for hydrogenation of aromatic species. A bimetallic catalyst that incorporated Mo with Fe was active for coal conversion.[2] Slurry-phase catalyst precursors like iron (III) acetylacetonate, that form finely divided catalysts during reactions, have been shown to be active for coal liquefaction and coprocessing.[9] Carbon blacks, which are often used as supports for catalysts[5] and as molecular sieves[6] have been reported to catalyze the cracking of pure hydrocarbons.[8] Combined with these studies has been the desire to find new and improved compounds that can better chemically model the reactions experienced by the coal polymer as it undergoes the bond cleavage reactions necessary for coal gasification and liquefaction reactions.[7,8,9] Especially intriguing to us were the class of compounds containing both naphthyl and phenyl aromatic moieties with various alkyl linkages interconnecting these aromatic moieties. These compounds, exemplified by 4-(1-naphthylmethyl)-bibenzyl (compound 1 in Scheme 1),[3, 7] contain several desirable features for coal model studies. The model compound should be liquid or solid under the reaction conditions to mimic the conditions prevalent during coal liquefaction. This usually means that the model compound should have a high molecular weight. The model compounds should contain several types of potentially reactive structural units. The presence of different functionality in the same molecule permits the study of various proposed chemical reaction mechanisms and competitive kinetics in the presence of intramolecular interactions. Because competitive reactions certainly occur in coal liquefaction process, a study of model compounds with only one type of bond that cleaves affords limited information. Compound **1** was the model compound designed for the above features. It contains both a methylene and an ethylene bridge as well as monocyclic and bicyclic aromatic units. There are five potential sites in which the reaction may take place (i.e., a, b, c, d, and e). Particularly attractive for model compound studies was the hypothesis that cleavage of various bonds (i.e., bond a, b, c, d, or e) would indicate the operative reaction mechanism in the complex situation represented by coal catalysis conditions.

Of particular interest to our research group was the fact that **1** has been reported to cleave the bond connecting the naphthyl group to the remainder of the molecule (i.e., bond a in **1**, also referred to in the literature as *α*-cleavage) when subjected to a variety of catalysts under a variety of conditions.[10,11] Farcasiu studied the bond cleavage reactions of compound **1** under catalytic conditions and found that essentially bond a cleavage regioselective after omitting the thermal component (see Table I).[10] Curtis's results for model 1 study were similar (Table II) in that the bond a was the predominant bond to be cleaved under

Table I. Selectivity of Bond Breaking of **1** at X% Black Pearls 2000 Catalyst

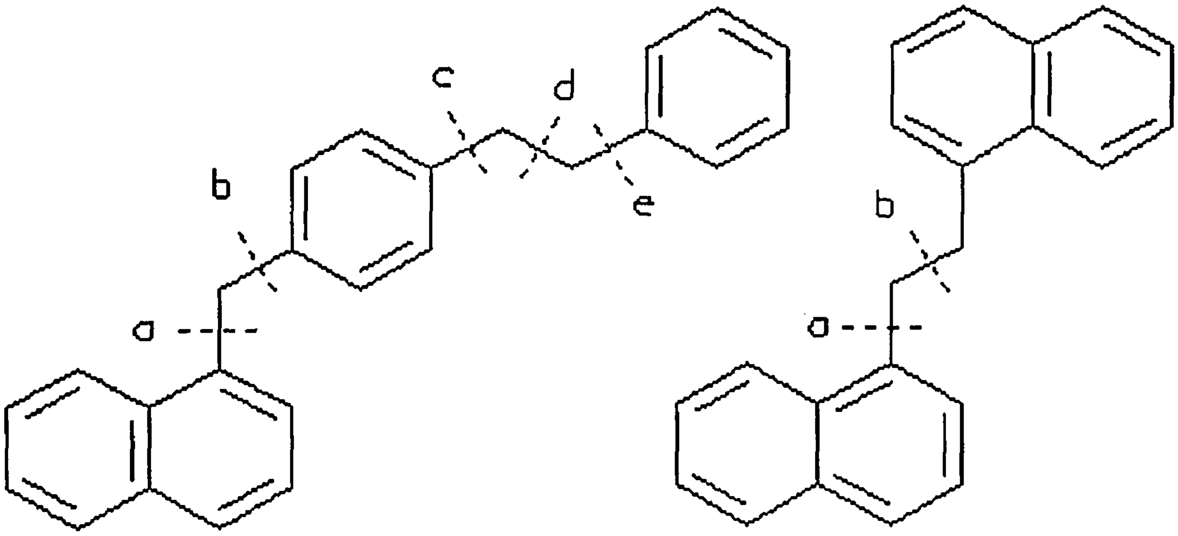
bond booken	% of total product at X% catalyst			
	0	2	5	10
a	40	82	87	90
b	4.2	5	5	5
d	56	13	8	5

Table II. Selectivity of Iron and Molybdenum Catalysts for Hydrocracking **1**

Catalyst Precursor	Selectivity X 100%		
	a/(a+b+d)	(a+b)/(a+b+d)	d/(a+b+d)
Thermal	61	61	39
Sulfur	64	67	33
FeNaph	74	74	26
FeNaph+S	79	86	14
MoNaph	72	72	28
FeAcAc+S	82	82	18
FeAcAc+Mo Naph+S	92	92	8

slurry phase catalysis conditions.[11] These results were made more intriguing when it was reported that 1,2-(di-1-naphthyl)ethane (2c) and a number of other naphthyl-containing compounds underwent bond a cleavage under catalytic conditions.[12] The reaction of 1,2-dinaphthylethane (2c), under the same catalytic reaction conditions yields naphthalene and ethylnaphthalene, indicating specific cleavage of the bond between the polycyclic naphthyl unit and the adjacent ethylene substituent. Based on the fact that a CDA (Charge Distribution Analysis) study[13] of the Black Pearls 2000 catalyst developed a surface charge at exactly the same temperature as the catalytic behavior began and that a naphthyl-group should be the easiest part of 1 from which to remove an electron, the hypothesis was advanced that bond a cleavage was due to radical cation reactions. This hypothesis has been supported by ASED-MO quantum chemical calculations[14] which suggest that bond a is the bond weakened most by the loss of electron density and the most susceptible to breaking when the radical cation is formed.

This theory concerning the regiochemistry of the naphthyl-radical cation cleavage pathway is in contradiction with a large number of studies of the bond cleavage reactions of phenyl-containing radical cations. In phenyl-containing compounds, bond b (often referred to as β-cleavage in the literature, see Scheme 2) has been found to preferentially cleave in mass spectrometric studies in which the radical cations are generated in a gas phase non-polar environment[15] and a variety of solution studies in which the solvent polarity had little impact upon the preferred bond cleavage pathway.[16] The preference for bond b cleavage

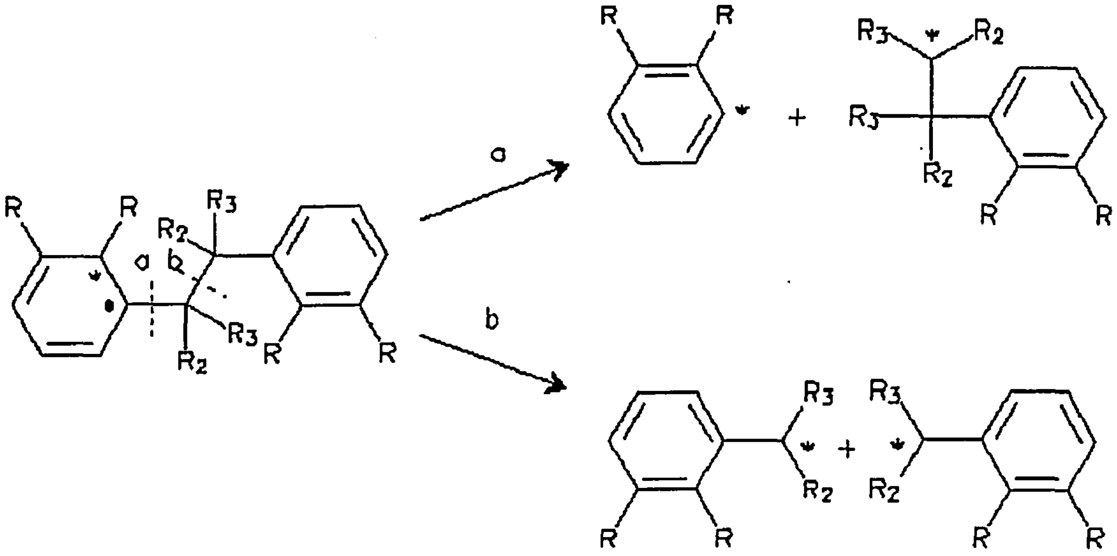


1

2c

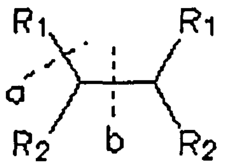
Scheme 1

(rather than bond a) in radical cations has been rationalized as resulting from the hyperconjugation of bond b with the aromatic system from which the electron is removed and from the resonance stabilization of the intermediates formed via bond b cleavage. Both intermediates from bond b cleavage are resonance stabilized. In contrast, neither intermediate resulting from bond a cleavage is stabilized, with an aryl and a primary radical being formed. The result is that path b in **2c** is predicted thermodynamically by simple back-of-the-envelope thermochemical calculations to be lower in energy than path a by ca. 30 kcal/mole for both the neutral and radical cationic species. These pathways are shown in Scheme 2 where * indicates either a radical or a cation on one of the intermediates and a cation or a radical on the other intermediate.



Scheme 2

The simplest way to reconcile these contrasting viewpoints of radical cation reactivity would be to argue that the more extended π-system of the naphthyl group has an altered radical cation reactivity which would result in bond a cleavage. We have performed an extensive chemical study to investigate whether the naphthyl-group has an altered reactivity consistent with the results presented above. For this purpose, we have independently generated the radical cations of various polyarylethanes (see Scheme 3) containing both phenyl- and naphthyl-groups in order to verify their reactivity. The phenyl-containing compounds were specifically chosen because the reactivity patterns of their radical cations is well-understood. The naphthyl-containing compounds were specifically chosen to have structures identical to those of the phenyl-containing compounds. This leaves the reactivity of the naphthyl-group as the single reaction variable. The radical cations of each compound have been generated by several independent techniques, each of which has been previously demonstrated to generate radical cations via one electron oxidation. We report here that the radical cations of naphthyl-containing compounds react in the same fashion as the corresponding phenyl-containing radical cations. This result indicates that a new chemical mechanism must be advanced to explain the results of bond cleavage reactions of naphthyl-containing coal model compounds.



2a: $R_1 = R_2 =$ 1−Np
2b: $R_1 =$ Ph, $R_2 =$ 1−Np
2c: $R_1 =$ H, $R_2 =$ 1−Np
2d: $R_1 =$ H, $R_2 =$ Ph
2e: $R_1 = R_2 =$ Ph

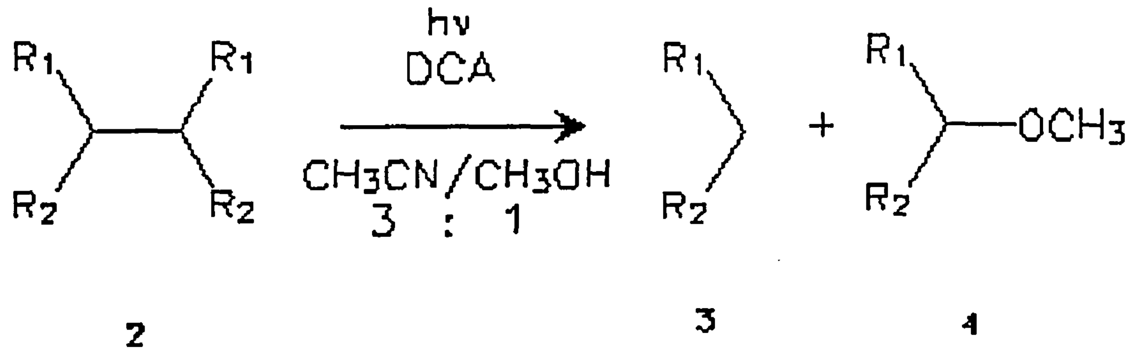
Scheme 3

Results

Radical Cation Formation in Solution: The radical cations of **2** (i.e., $2^{\bullet+}$) have been generated using three independent methods. The first method uses a photochemically excited state to perform a single electron transfer. For those radical cations with fast bond cleavage reactions, the bond cleavage reactions may compete favorably with the energetically favorable back electron transfer and result in a chemical reaction. In our studies, we have used the excited-state of 9,10-dicyanoanthracene (**DCA***) which is well-known to be a strong one electron oxidant.[17] **DCA** possesses the advantage that long wavelength irradiation produces only photoexcitation of the **DCA** and no photoexcitation of the other molecules in solution. Despite the fact that **DCA** has a long wavelength absorption tail, the naphthyl-groups also possess long wavelength absorption tails which may potentially absorb light. The possible complication of light absorption by the naphthyl-groups can be easily tested, since **2c** would be expected to undergo bond cleavage reactions if it absorbs light. In contrast, **2e** would not undergo bond cleavage via radical cation formation (as evidenced by the non-reactivity of **2d**). Our results are shown below in eq (1) with quantitative data about the reaction being given in Table III.

The reactivity of **2d** and **2e** have been previously explored using this technique.[16a] Our results for these compounds are in exact agreement with literature results. The radical cation of **2e** (i.e., $2e^{\bullet+}$) is reactive, yielding **3e** from the radical and **4e** from the cation (Note Scheme 2). A high mass balance is

(1)



obtained in the reaction, indicating that other reaction pathways (e.g., bond a

Table III. Results of DCA Irradiation Using a Sunlamp for Photoexcitation

Compound			Yields (mole %)	
	R_1	R_2	3	4
2a	Np	Np	-[a]	-[a]
2b	Ph	Np	95	96
2c	H	Np	-	-
2d	H	Ph	-	-
2e	Ph	Ph	87	91

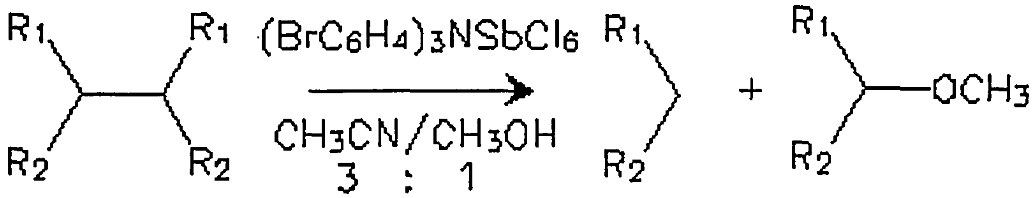
a) The insolubility of **2a** prevented a quantitative analysis of this reaction. However, quantities of **3** and **4** were observed as described in the text.

cleavage) comprise only a minor amount of the total reaction. Compound **2d**, also previously studied,[16a] shows little reactivity under these conditions. The rationale for the nonreactivity of **2d**$^{\bullet+}$ is that diaryl substitution does not stabilize the radicals sufficiently to have bond b cleavage (or any other potential reaction) compete with the back electron transfer which yields neutral **DCA** and **2d**.

The reactivity of naphthyl-containing analogues (i.e., **2b** and **2c**) exactly parallels the known reactivity of the phenyl-containing analogues. Dinaphthyl-diphenyl **2b** cleaves to yield **3b** and **4b** in high yields. Dinaphthyl **2c** is unreactive under these conditions. This result clearly denotes that light is not being absorbed by the naphthyl group under these conditions, signifying that the reactivity of **2b** must originate from the radical cation which is produced by **DCA*** oxidation. Tetranaphthyl **2a** was relatively insoluble in this solvent system. The insolubility of **2a** prevented our experimental studies to be extended to the same level of detail as was performed with **2b**-**2e**. However, analysis of the reaction solutions of **2a** which had been subjected to the same conditions as the other compounds of **2** showed identifiable amounts of **3a** and **4a** with no other observable products. This observation is consistent with bond b cleavage of **2a**$^{\bullet+}$ with little or no bond a cleavage.

Independent generation of **2**$^{\bullet+}$ was accomplished by two additional techniques. In the first technique, tris-(4-bromophenyl)aminium hexachloroantiminate ($(BrC_6H_4)_3NSbCl_6$) was used as a single electron transfer

(2)



2 3 4

oxidizing reagent.[18] The results for formation of $2^{\bullet+}$ in 3:1 CH_3CN/CH_3OH are depicted in eq (2) with quantitative information about the reaction being given in Table IV.

Table IV. Results of Amminium Oxidation Reactions

Compound			Yields (mole %)	
	R_1	R_2	3	4
2b	Ph	Np	89	93
2c	H	Np	-	-
2d	H	Ph	-	-
2e	Ph	Ph	91	89

Analogous to the results obtained by the DCA* oxidation technique, $2b^{\bullet+}$ and $2e^{\bullet+}$ are reactive and undergo bond b cleavage to form 3 and 4. $2c^{\bullet+}$ and $2d^{\bullet+}$ are unreactive and no reaction is seen within a reasonable length of time. These results for radical cation bond cleavage again indicate that only bond b is cleaving, regardless of whether the important groups are phenyl or naphthyl.

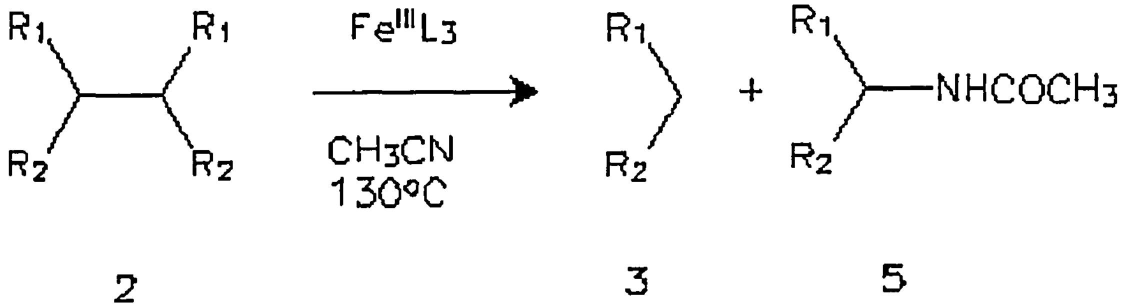
A third independent method of radical cation formation was to use the one electron oxidant Fe(1,10-phenanthroline)$_3$(PF$_6$)$_3$ (Fe^{III}L$_3$(PF$_6$)$_3$). This oxidant has the advantages that it is a strong oxidant (E_R=1.09 V vs SCE in CH_3CN)[19] and is sterically crowded enough that the Fe nucleus cannot be used for chemical bonding as might occur in an inner-sphere electron transfer reaction. It has the disadvantage that it is rapidly reduced by alcoholic solvents. Since the reactions must be performed in CH_3CN, the carbocation formed in this reaction will be

Table V. Results of Fe^{III} Oxidation Reactions

Compound			Yields (mole %)	
	R_1	R_2	3	5
2b	Ph	Np	minor	84
2c	H	Np	-	-
2d	H	Ph	-	-
2e	Ph	Ph	minor	85

trapped by CH_3CN to form amide **5**. The trapping of carbocations by CH_3CN is well-known and is known as the Ritter reaction.[20] The results of this reaction are presented in eq (3) with quantitative information about the reaction being given in Table V.

(3)



The results from this reaction are less conclusive than the reactions above, since incomplete mass balances were obtained. However, relatively high yields of the cation from the bond cleavage of bond b are indicated for **2b** and **2e**, in exact analogy to the reactions reported above. The radical which would have been formed in this reaction was not observed. However, this is not surprising since Kochi[21] has previously shown that generation of radicals in the vicinity of this reagent results in addition of the radical to the phenanthroline ligand and would be unobservable using our methodology.

Gas Phase Generation of $2^{\bullet+}$: As a further verification of the reactivity of $2^{\bullet+}$, we have generated $2^{\bullet+}$ in a mass spectrometer in order to observe the relative importance of the different reaction pathways (i.e., bond a or bond b cleavage). The amounts of each pathway can be estimated by the relative ion abundance for each pathway (Note the reaction possibilities in Scheme 2). For all compounds in this study, we were able to observe fragment ions from both reaction pathways. Therefore, we have gathered the results as a ratio of the two reaction pathways (Table VI).

Although the ionization energy is high by solution phase measurements (35 ev), the molecules were all measured under identical conditions, using the minimum amount of energy to observe both the molecular ions and their fragmentation pathways. Note that two possible bond a fragmentation pathways are available for **2b**. If bond a cleavage occurs in the direction of the naphthyl

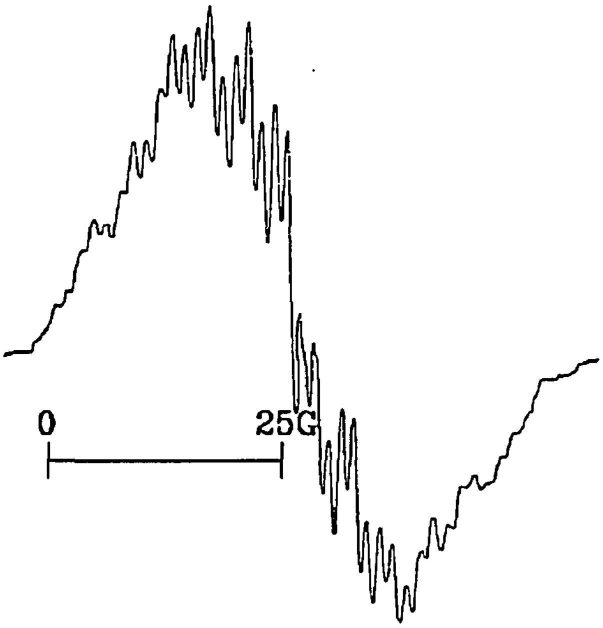
Table VI. Results of Gas Phase Radical Cation Generation

Compound			Bond b/Bond a
	R_1	R_2	
2a	Np	Np	28/1
2b	Ph	Np	588/1 (714/1)[a]
2c	H	Np	166/1
2d	H	Ph	91/1
2e	Ph	Ph	80/1

a) Bond a cleavage in the direction of the naphthyl group

group, one would expect to see fragments of 127 and 307. If bond a cleavage were to occur in the direction of the phenyl group, one would observe fragments of 77 and 327. Both pathways were observed in addition to the predominant amount of bond b cleavage, with their ratios given in Table IV. For all other compounds, only one bond a cleavage pathway is possible. While it is impossible to be certain that all ions with these molecular weights have the correct structure for either the bond a or the bond b reaction pathway, we rely on these results to give an approximation of the relative amounts of each pathway observable in the gas phase.

Radical Cation identification By ESR spectroscopy: Our second approach to



Scheme 4

understanding the reactions of radical cations is to identify them by electron spin resonance (ESR). In order to identify the radicals, appropriate methods of generation must be determined and the structures of easily identifiable intermediates must be conclusively identified. Representative of our efforts in this area is the spectrum of 1-methylnaphthalene radical cation shown above (Scheme 4). It is apparent that sufficient fine structure exists to enable us to conclusively identify the radical when the resolution is optimized. However, the large number of nonequivalent hydrogens in this compound make an exact identity uncertain (other possible species in solution are the 1-methylnaphthalene radical or a dimeric radical cation species). We have attempted to reduce the number of nonequivalent hydrogens by introducing symmetry into the molecule (e.g., 2,6-dimethylnaphthalene, 1,8-dimethylnaphthalene). However, producing spectra at this resolution has not been successful yet.

Discussion

Previous studies of the reactivity of phenyl-containing radical cations have demonstrated that bond b cleavage is dramatically preferred to bond a cleavage. The results presented here demonstrate conclusively that naphthyl radical cations exhibit no special reactivity and behave exactly like phenyl radical cations. This is demonstrated by the similarity of the reactivities of phenyl- and naphthyl-containing radical cations in solution and in the gas phase. For example, there is only a slow bond cleavage of the radical cations of naphthyl-containing **2c** and phenyl-containing **2d**, as evidenced by their lack of reactivity with the three independent oxidants. Tetraphenyl **2e** undergoes exclusive cleavage of bond b by all three methods. Diphenyl-dinaphthyl **2b** also undergoes bond b cleavage in the presence of all three single electron oxidants. Our interpretation of this result is that the naphthyl group behaves exactly like a phenyl group. This interpretation is justified by the oxidation potentials ($E_{1/2}^{ox}$) of toluene[22] and 1-methylnaphthalene[23] which have been reported to be 2.64 and 1.55 V *vs* NHE, respectively. This clearly indicates that the radical cation of **2b** should be localized primarily on the naphthyl-group. The bond cleavage of $\mathbf{2b}^{\bullet+}$ is, thus, more consistent with the requirement that bond cleavage only occurs for tetraaryl-substituted radical cations and does not indicate any special property of the phenyl-group of **2b**. Further support for this argument concerning the tetraaryl-substitution comes from the results of $\mathbf{2a}^{\bullet+}$ which was generated by the $\mathbf{DCA}^{*}$ oxidation. Trace amounts of **3a** and **4a** were observable with no other products being observable. Although the solubility problems of **2a** prevented a proper quantitative analysis in solution, the gas phase reactivity of all compounds (including **2a** and **2b**, Note Table IV) shows a clear preference for bond b cleavage as the predominant cleavage pathway. We conclude that there is a clear and unequivocal reactivity preference of naphthyl-containing radical cations to cleave bond b in polar solution (i.e., the 3:1 CH_3CN/CH_3OH solution) and in a nonpolar environment (i.e., the gas phase).

A skeptic who views the complete selectivity of the radical cation's choice for bond b cleavage might still question whether the reactions of the model

$$\frac{k_B}{k_A} = \frac{A_B}{A_A} e^{-(E_B - E_A)/RT} \qquad (4)$$

compounds would be as selective at the higher temperatures used under normal processing conditions (i.e., ≥ 275°C) as has been observed in our ambient temperature studies. To be sure, competing reactions are always less selective at higher temperatures. This is easily shown in the following manner. The relative rates of bond a and bond b cleavage can be represented by the Arrhenius equation in eq (4), where k_A and k_B are the rate constants for cleavage of bond a and bond b, A_A and A_B are the Arrhenius preexponential factors for these cleavages, and E_A and E_B are the activation energies for these cleavages. Making the reasonable assumption that the pre-exponential factors for bond a and bond b cleavage are similar means that as the temperature approaches infinity, k_B/k_A will approach 1. In other words, at higher temperatures, bond a cleavage may become more important depending on the activation energy difference between path A and path B. However, the reaction can not become more selective in the opposite sense. We conclude that bond b cleavage will be the major bond cleavage pathway of radical cations at any temperature and that the amount of bond a cleavage should be less than the amount of bond b cleavage for naphthyl-containing radical cations, unless there is a breakdown in the normal and reasonable assumptions used in this model.

The results obtained in this study clearly demonstrate that bond b is cleaved preferentially when there is a choice between the bond b pathway and the bond a pathway. However, it may be argued that the radical cations of **1** or other naphthyl-containing compounds cleave bond a when no other choices are available. For this purpose, we have independently generated $\mathbf{1}^{\bullet+}$, $\mathbf{3a}^{\bullet+}$ and $\mathbf{3b}^{\bullet+}$ under conditions identical to our studies with **2** (i.e., DCA irradiation, $(BrC_6H_4)_3NSbCl_6$, and $Fe^{III}L_3(PF_6)_3$). As expected, absolutely no reaction was observed, to the limits of our detection by the use of internal standard methodology as described above. This confirms the expectation that the kinetic barriers to bond a cleavage are much higher than for bond b cleavage. Further data concerning potential bond a cleavage reactivity is available from mass spectral results. In the initial report concerning the preparation and use of **1** as a coal model compound,[8] the MS spectrum of **1** was reported to have a base peak of 213. This peak corresponds to bond d cleavage (see Scheme I). Interestingly, no peak corresponding to bond a cleavage (i.e., 127 or 195) was reported, although ions with relative intensities as low as 8% were reported. Another analysis of the MS[14a] of **1** reported that the ratio of bond a : bond b : bond d cleavage was 26 : 34 : 40. We have specifically remeasured the MS of **1** using 35 eV electron ionization and find the ratio of bond a : bond b : bond d is maximally 2 : 16 : 100. Although the absolute values of our peak intensities are not identical to the earlier studies, the sum total of these MS experiments indicate that bond d cleavage in $\mathbf{1}^{\bullet+}$ is the preferred cleavage pathway in a mass spectrometer. This occurs, despite the fact that the electron should be removed from the naphthyl-moiety of **1**. This is not to say that bond a cleavage cannot occur from naphthyl-containing model compounds. The MS of **3a** and **3b** show that bond a cleavage can occur. The mass spectrum of **3a** shows that bond a cleavage fragments are a maximum of 31% of the base peak which is the parent ion. More interesting is the MS of **3b** which shows that bond a cleavage (i.e., *α*- to the naphthyl group) is only a maximum of 11% as compared to the base peak (again, the parent ion) while bond b cleavage (i.e., *α*- to the phenyl group) is a maximum of 39%. Thus, bond a cleavage is a minor pathway in **3b**. This further indicates the energetic disadvantage for bond a cleavage in naphthyl-containing radical cations relative to other reaction pathways.

Several studies have demonstrated bond a cleavage as the predominant bond cleavage pathway for 1 under catalytic conditions.[8,9,10] The interpretation of these results has been that $1^{\bullet+}$ was the important intermediate in determining which bond cleaved under catalytic conditions.[8] We believe that the current results demonstrate that the bond a cleavage of the radical cations of naphthyl-containing compounds is an extremely energy demanding process and that a reinterpretation of bond cleavage mechanisms under catalytic conditions should be undertaken. It is beyond the scope of the present work to be able to present a complete mechanistic picture which will correctly explain the mechanism of bond cleavage of naphthyl-containing compounds under these catalytic conditions. Alternative mechanisms which may be partly or totally responsible for the reactivity of these naphthyl-containing compounds include a radical hydrogen transfer mechanism,[24] an acid-catalyzed mechanism,[25] specific intermediates with chemical bonding between the catalyst and naphthyl groups,[26] or charge-transfer complex formation. The correct mechanism will be one which can accommodate the reactivity of naphthyl-groups in the presence of unreactive phenyl-groups.

While there is insufficient evidence at present to identify the exact mechanism followed under these conditions, we rule out charge-transfer complexes as a viable alternative mechanism. This argument is based upon our bond cleavage studies[27] of benzylic ether charge-transfer complexes with quinones where a 60 kcal/mole C-O bond is not cleaved via a demonstratable charge-transfer complex. Instead, the compounds are cleaved by an alternative mechanism (i.e., hydride transfer) which requires changes in bonding between the quinone and the ether. The naphthyl-C bond which is cleaved under these catalytic conditions has a higher bond strength than the C-O bonds of our earlier work. Since the charge-transfer complexes in these studies were insufficiently strong to cause bond cleavage, we believe that similar interactions in naphthyl-compounds would be insufficient to cause the observed bond cleavages. Further research will be necessary to address the issue of the true intermediates(s) in these reactions.

Summary

Taken together, the results described above conclusively demonstrate that radical cation reactivity of naphthyl- and phenyl- compounds are the same and result in bond b cleavage. A reinterpretation of catalyst behavior towards naphthyl-containing compounds should be undertaken.

Experimental Section

Melting points were determined on a Laboratory Devices Mel-Temp apparatus and were uncorrected. High-Performance Liquid Chromatographic analyses were carried out on a Waters Protein Peptide I System, equipped with a Resolvex C-18 reversed phase column. Integration of the signals was performed by a Hewlett-Packard Model 3392A digital integrator. Gas-liquid chromatographic analyses were conducted on a Hewlett-Packard Model 5890A GC equipped with a 10 m 5% phenylmethylsilicone or a Carbowax 20 m Megabore column. Integration of the signals was performed by a Hewlett-Packard Model 3390A digital integrator. GC-MS were measured with a HP 5980 mass spectrometer with a 5890 gas chromatograph equipped with a 25-m 5% phenylmethylsilicone column. ^{1}H NMR spectra δ (ppm) and J (hertz) and ^{13}C NMR were measured in the indicated solvent with TMS (δ=0.0 ppm) or $CDCL_3$ (δ=77.0 ppm) as an internal standard on a JEOL GX-270 Spectrometer. All ESR measurements were made at the X-band (9.5 GHz) microwave frequencies utilizing the modified Brunker ER300D ESR spectrometer system. In this system, the microwave frequency is measured with a Hewlett-Packed digital frequency counter, model 5430A, whereas the magnetic field is calibrated with an NMR gaussmeter.

Acetonitrile was predried over CaH_2 and then distilled from P_2O_5 shortly before use. Unless otherwise specified, all chemicals were purchased from Aldrich. **2c** was purchased from Lancaster and recrystallized from ethanol.

Identification of reaction products was accomplished by GC/MS analysis and by comparison with an authentic chemical sample. Reported product yields and overall conversion are based on GC measurements using octyl cyanide as an internal standard or authentic samples of **3b** and **4b** as external standards.

Synthesis of Fe(III) (1,10-phen)$_3$(PF$_6$)$_3$: 6.950 g of $FeSO_4*7H_2O$ (25.0 mmol) in 250 mL of distilled water was added to 1.49 g of 1,10-phenanthroline (7.50 mmol) resulting in a deep red solution. 1.00 g of $NaPF_6$ (5.95 mmol) was added to the reaction mixture and stirred for 1 hr. The red precipitate was collected by vacuum filtration to yield 2.05 g (2.18 mmol, 87%) of Fe(II) (1,10-phen)$_3$ (PF$_6$)$_2$. Oxidation of 2.35 g (2.50 mmol) Fe(II) (1,10-phen)$_3$ (PF$_6$)$_2$ with 1.01 g of $Ce(SO_4)_2*4H_2O$ (2.50 mmol) in 250 mL of 6 N H_2SO_4 gave a blue solution. Addition of 1.00 g of $NaPF_6$ (5.95 mmol) to this solution gave 1.15 g (1.06 mmol, 42%) of blue crystals of Fe(III) (1,10-phen)$_3$(PF$_6$)$_3$ which were collected by vacuum filtration and washed with water.

Synthesis of 3a and 3b: **3a** and **3b** and were synthesized by a literature method.[28] A Grignard reagent was prepared from 1.14 g (0.048 mol) of magnesium turnings and 9.94 g (0.048 mol) of bromonaphthalene in 20 mL of dry ether. When the reaction was complete, the ether was replaced with dry benzene. To this hot solution was added 5.06 g (0.04 mol) of benzylchloride or 7.06 g (0.04 mol) of 1-(chloromethyl)naphthalene dissolved in 10 mL of dry benzene. The mixture was refluxed for 1 hr, cooled to room temperature, and decomposed with 20 mL of cold 4 N hydrochloric acid. The organic layer was separated, washed with water, dried over anhydrous sodium sulfate, concentrated, distilled under vacuum and repeatly recrystallized from ethanol. **3a**: mp 107-108 ^{0}C; ^{1}H NMR (270 MHz, $CDCl_3$) δ (ppm) 4.87 (s, 2H), 7.07-7.54 (m, 8H), 7.76-8.06 (m, 6H); ^{13}C NMR (270 MHz, $CDCl_3$) δ (ppm) 136.1, 133.8, 132.2, 128.7, 127.1, 126.9, 126.1, 125.7, 125.6, 123.9, 35.7; **3b**: mp 54-55 ^{0}C; ^{1}H NMR (270 MHz, $CDCl_3$) δ (ppm) 4.46 (s, 2H), 7.18-7.47 (m, 9H), 7.75-8.01 (m, 3H); ^{13}C NMR (270 MHz, $CDCl_3$) δ (ppm) 140.6, 136.6, 133.9, 132.1, 128.7, 128.6, 128.4, 127.3, 127.1, 126.0, 125.9, 125.5, 124.3, 39.0.

Synthesis of 4-(1-naphthylmethyl)-bibenzyl (1): Ferric chloride (57 mg), 0.35 mmol) was transferred into a flame dried 50 mL round-bottomed flask in a glove box followed by addition of dry CS_2 (8 mL). The resulting mixture was stirred for 10 minutes and cooled to 0^{0}C. Solid bibenzyl was added and stirred for 10 min. A solution of 1-chloromethylnaphthalene (706.6 mg, 4.0 mmol) in dry CS_2 (5 mL) was added dropwise into the reaction flask to bring out excess HCl formed during the reaction. The reaction mixture was poured into ice water (20 mL) containing concentrated HCl (3 mL), diluted with CH_2Cl_2 (20 mL), shaken thoroughly, and transferred into a separatory funnel. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic extracts were decolorized with activated charcoal, filtered and evaporated in vacuo to give a clear oil (1048 mg). Silica gel column chromatography eluted with 1 : 4 CH_2Cl_2 /hexane was used to recover bibenzyl (802 mg, 80.1 %) and the desired **1** (127 mg, 9.9 %) as a colorless solid, mp 64.0-64.5 ^{0}C (hexane); NMR (270 MHz,

$CDCl_3$) δ (ppm) 7.98 (t, 1H), 7.83 (t, 1H), 7.73 (d, 1H), 7.43 (m, 1H), 7.38 (d, 1H), 7.24 (m, 3H), 7.16 (m, 3H), 7.08 (q, 4H), 4.39 (s, 2H), 2.85 (s, 4H).

Synthesis of Tetra-1-naphthylethane (2a) and 1,2-Di-(1-naphthyl)-1,2-diphenylethane (2b): **2a** and **2b** were prepared by the McMurry method.[29] Titanium trichloride (8.9 g, 58 mmol) was weighed under dry nitrogen in a glove bag and placed under nitrogen in a 250 mL three-neck flask with 100 mL of dry glyme. $LiAlH_4$ (750 mg, 9.7 mmol) was quickly added to the stirred $TiCl_3$ slurry, and the resulting black suspension was stirred for 10 min before use. Naphthyl phenyl methanol or dinaphthyl methanol (3.6 mmol) in several mL of glyme was then added, and the reaction mixture was refluxed for 16 h. After cooling, the reaction mixture was quenched by addition of dilute aqueous HCl, further diluted with water, and extracted with ether. The ether extracts were combined, washed with brine, dried ($MgSO_4$), filtered, concentrated *in vacuo*, and purified by crystallization from ethanol to yield colorless crystals of the desired compound. **2a**, mp: 276°C (decompn); lit., 277°C (decompn)[30]; ^1H NMR (270 MHz, $CDCl_3$) δ (ppm) 7.94 (d, 4H), 7.11-7.60 (m, 24H), 6.65 (s, 2H); ^{13}C NMR (270 MHz, $CDCl_3$) δ (ppm) 139.5, 133.4, 131.8, 128.3, 127.1, 126.8, 125.5, 124.9, 124.7, 123.0, 45.9; **2b**, mp: 220-222°C, lit., 223-224°C[31]; ^1H NMR (270 MHz, $CDCl_3$) δ (ppm) 8.31 (d, 2H), 6.79-7.81(m, 22H), 5.61 (s, 2H); ^{13}C NMR (270 MHz, $CDCl_3$) δ (ppm) 142.9, 138.2, 134.0, 131.9, 129.0, 128.9, 128.7, 128.5, 127.8, 126.8, 126.0, 125.6, 125.2, 125.0, 124.8, 123.5, 52.1.

Synthesis of Methyl Di-1-naphthylmethyl ether (4a) and Methyl

Naphthylphenylmethyl ether (4b): 2.72 mmol of 1-naphthylphenylmethanol or di-1-naphthylmethanol in dry THF was added to 200 mg (8.3 mmol) of NaH. The solution was stirred for 2 hr before 500 mg (3.52 mmol) of methyliodide was added. The solution was stirred overnight. Work up, followed by flash column chromatography yielded colorless crystals of pure product. 4a, mp: 136-137°C, lit., 138°C[32]; ^{1}H NMR (270 MHz, $CDCl_3$) δ (ppm) 7.25-8.05 (m, 14H), 6.73 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (270 MHz, $CDCl_3$) δ (ppm) 135.9, 133.9, 131.8, 128.8, 128.6, 126.3, 125.8, 125.6, 125.4, 123.7, 79.4, 57.9; 4b, mp: 64-66°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ (ppm) 7.6 (m, 12H), 5.90 (s, 1H), 3.44 (s, 3H); ^{13}C NMR (270 MHz, $CDCl_3$) δ (ppm) 141.3, 136.8, 133.9, 131.1, 128.7, 128.4, 127.5, 127.3, 126.9, 125.9, 125.5, 125.4, 125.2, 124.1, 83.2, 57.3; low-resolution MS: M/Z 248 M+ (intensity) (100), 217 (94), 202 (32), 171 (40), 155 (18), 127 (18), 121 (16), 107 (17), 105 (33), 95(8), 77 (19), 51 (6).

Photochemical Generation of Radical Cations: Photochemical reactions were carried out in a Southern New England Ultraviolet Rayonet RPR-100 photochemical reactor at 350 nm. A solution of DCA (0.1 mmol) and **2** (0.5 mmol) in 10 mL of CH_3CN/CH_3OH (3:1) was degassed by bubbling N_2 for 15 min prior to irradiation, sealed with latex septa, irradiated for 18 h and analyzed as described above.

Aminium Salt Radical Cation Generation: A solution of **2** (0.05 mmol) and tris-(4-bromophenyl)aminium hexachloroantimonate (0.1 mmol) in CH_3CN/CH_3OH (3:1) was added to a 5 mL conical vial with N_2 bubbled through the solution and allowed to stir for 5 h and analyzed as described above.

Fe(1,10-phenanthroline)$_3$(PF$_6$)$_3$ Generation of Radical Cations: A solution of **2** (0.02 mmol) and Fe^{III}L$_3$(PF$_6$)$_3$ (0.04 mmol) in 1 mL of CH$_3$CN was prepared and added to several pyrex tubes. These tubes were degassed by using three freeze-pump-thaw degassing cycles, sealed under vacuum, and placed in a Neslab Model EX 250-HT constant temperature bath maintained at 130°C for 24 h and analyzed as described above.

Gas Phase Radical Cation Generation: Gas phase generation of **1**$^{\bullet+}$, **2**$^{\bullet+}$, **3a**$^{\bullet+}$ and **3b**$^{\bullet+}$ were carried out on a Finnigan Model 4021 Quadrapole mass spectrometer equipped with a Model 9610 data reduction system. Electron ionization (35 ev) was used to ionize the compounds by direct injection using the solid probe attachment.

Electron Spin Resonance Studies of Radical Cations: The direct observation of radical cations of coal model compounds with iron (III) was carried out as follows: separate trifluoroacetic acid solution of 6.3 mM coal model compounds and Fe(III)(Phen)$_3$(ClO$_4$)$_3$ (prepared from 11 mg of complex and 2.0 mL of solvent by heating over a steam bath until complete dissolution) were added to an ESR tube with a side arm affixed. The tube was sealed in vacuo and the contents were mixed by rapid shaking immediately prior to insertion into the ESR cavity.

Mass Spectral Data for 1, 2, 3a, and 3b:

Gas Phase Radical Cation Generation: Gas phase generation of **1**$^{\bullet+}$, **2**$^{\bullet+}$, **3a**$^{\bullet+}$, and **3b**$^{\bullet+}$ carried out on a Finnigan Model 4021 Quadrapole mass spectrometer equipped with a Model 9610 data reduction system. Electron ionization (35 ev) was used to ionize the compounds by direct injection using the solid probe attachment.

4-(1-naphthylmethyl)-bibenzyl (1): MS: m/z M+ (intensity) 65 (4.15), 77 (6.81), 78 (1.73), 79 (14.59), 89 (1.01), 91 (45.31), 92 (3.10), 103 (5.14), 104 (4.44), 105 (2.17), 115 (8.93), 116 (1.00), 127 (2.31), 128 (1.46), 139 (1.90), 141 (16.57), 142 (1.84), 152 (2.80), 153 (8.40), 154 (1.09), 165 (5.48), 166 (1.46), 178 (3.02), 179 (1.59), 181 (1.12), 189 (4.09), 190 (2.62), 191 (4.17), 195 (2.36), 202 (15.56), 203 (9.16), 204 (1.65), 213 (1.15), 215 (56.45), 216 (33.06), 217 (9.92), 218 (2.11), 226 (1.81), 227 (2.66), 228 (7.99), 229 (13.98), 231 (100.00), 232 (33.50), 233 (3.07), 322 (72.14), 323 (23.79), 324 (3.01).

Tetra-1-naphthylethane (2a): MS: m/z M+ (intensity) 45 (100.00), 58 (20.69), 59 (12.50), 60 (32.40), 61 (1.24), 89 (1.41), 90 (13.30), 91 (2.52), 127 (0.22), 267 (6.05), 268 (2.23).

1,2-Di-(1-naphthyl)-1,2-diphenylethane (2b): MS: m/z M+ (intensity) 77 (0.17), 127 (0.14), 202 (12.53), 203 (2.41), 204 213 (1.01), 215 (25.84), 217 (100.00), 218 (19.76), 219 (2.19), 307 (0.07), 434 (0.36).

1,2-Di-(1-naphthyl)ethane (2c): MS: m/z M+ (intensity) 127 (0.05), 139 (1.51), 141 (100.00), 142 (15.62), 153 (1.28), 155 (0.60), 282 (2.62).

1,2-Diphenylethane (2d): MS: m/z M+ (intensity) 65 (7.80), 77 (1.10), 89 (1.09), 91 (100.00), 92 (7.94), 103 (1.17), 104 (1.98), 105 (0.81), 182 (6.98).

1,1,2,2-Tetraphenylethane (2e): MS: m/z M+ (intensity) 51 (1.32), 77

(1.25), 115 (1.96), 128 (1.43), 139 (1.23), 152 (14.3), 153 (1.91), 163 (1.21), 165 (23.9), 167 (100.00), 168 (14.5), 178 (1.08), 334 (0.18).

Di-(1-Naphthyl)methane (3a): MS: m/z M+ (intensity) 77 (2.62), 89 (1.93), 91 (1.32), 101 (1.72), 113 (1.55), 114 (3.08), 115 (31.45), 116 (3.45), 120 (3.61), 121 (1.22), 126 (13.62), 127 (15.25), 128 (3.67), 133 (16.23), 134 (15.37), 139 (17.69), 140 (7.16), 141 (31.29), 142 (3.61), 152 (1.91), 153 (1.86), 165 (2.06), 189 (2.21), 190 (1.13), 191 (1.20), 226 (2.55), 228 (1.07), 237 (1.57), 239 (9.03), 240 (2.63), 241 (2.13), 250 (3.55), 252 (54.32), 253 (50.55), 254 (10.14), 255 (1.07), 263 (11.91), 265 (48.51), 266 (18.61), 267 (76.18), 268 (100.00), 269 (48.58), 270 (5.05).

1-Naphthylphenylmethane (3b): MS: m/z M+ (intensity): 51 (1.33), 63 (1.50), 65 (5.30), 77 (3.37), 89 (6.13), 90 (1.91), 91 (10.72), 95 (3.34), 96 (2.30), 101 (5.26), 102 (1.71), 108 (15.08), 109 (10.72), 115 (23.34), 116 (2.43), 126 (2.55), 127 (6.59), 128 (2.03), 139 (13.55), 140 (5.90), 141 (39.36), 142 (4.79), 151 (1.34), 152 (2.92), 163 (1.53), 164 (1.69), 165 (5.94), 176 (2.35), 178 (3.84), 187 (1.01), 189 (14.12), 190 (4.37), 191 (4.54), 200 (2.54), 202 (4.81), 202 (77.29), 203 (69.75), 204 (11.80), 213 (11.54), 214 (4.00), 215 (74.78), 216 (29.80), 217 (99.10), 218 (100.00), 219 (54.76), 220 (4.74).

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CHAPTER II

Dehydrogenation and Bond Cleavage Reactions of Hydroaromatic Compounds by Fe Complexes[B]

Abstract

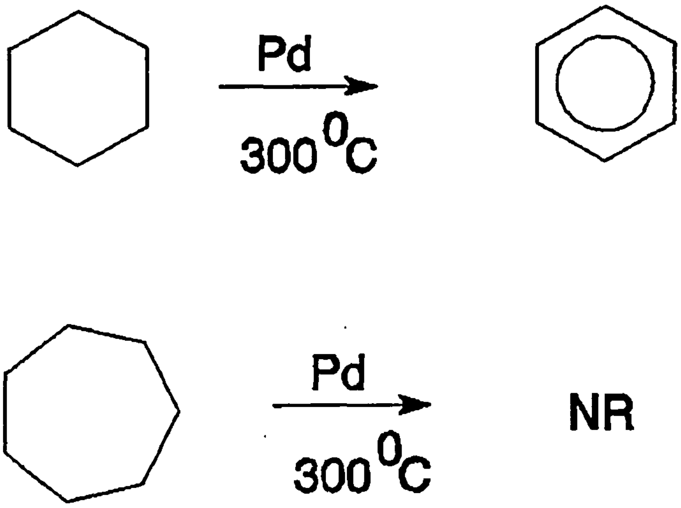
Iron (III) and iron (II) compounds have been developed as novel dehydrogenation reagents for hydroaromatic compounds. The reaction proceeds to give high yields with 6-membered ring substrates. In contrast, the dehydrogenation reaction failed with five-membered ring systems, except for the 2,3-dihydrobenzofuran which gave benzofuran as the product. These iron (III) compounds were also reacted with naphthyl or phenyl-containing compounds under conditions favoring electron transfer reactions. These compounds were found to undergo bond cleavage reactions. The products were found to be dependent on the counterion of the ion complex, a phenomenon which has not been observed previously.

[B] i) Penn, J. H.; Wang, J. *J. Chem. Soc. Chem., Comm.* submitted. ii) Penn, J. H.; Wang, J. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel & Petroleum Chem.*, in press.

Introduction

1. Dehydrogenation reactions

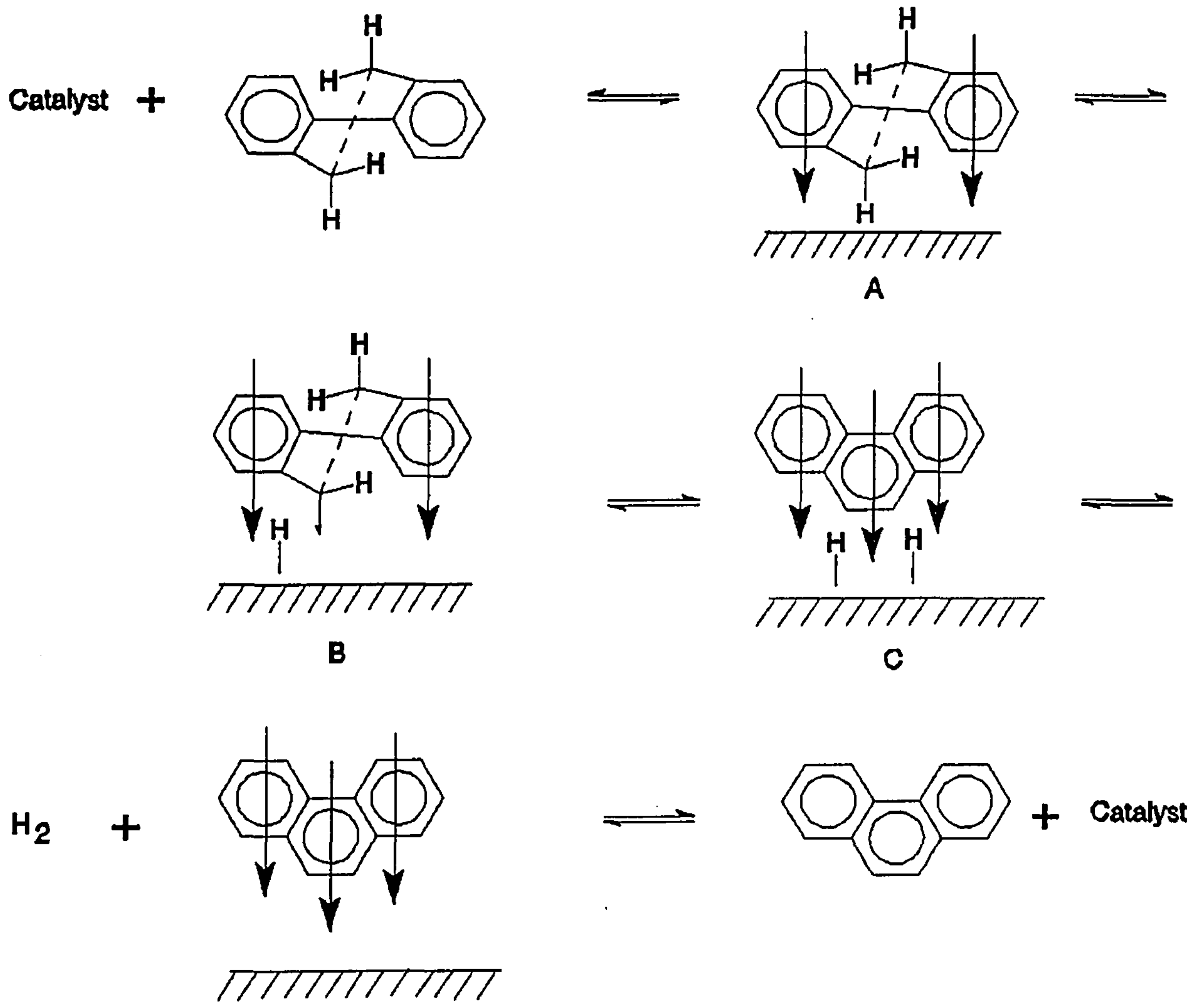
Dehydrogenation reactions[1,2,3,4] are very useful in organic synthesis. By definition, dehydrogenation involves removal of one or more pairs of hydrogen atoms to provide an unsaturated bond or bonds. Dehydrogenation is frequently the last step in



Scheme 1

the synthesis of polycyclic aromatic hydrocarbons and their derivatives.[5,6] Dehydrogenation of hydroaromatic systems is facilitated by the resonance energy derived in forming an aromatic system. For example, cycloheptane is relatively stable under conditions under which cyclohexane is converted readily to benzene[7] (see Scheme 1). A second, and perhaps more important, feature of aromatization is the delimiting of dehydrogenation to defined, predictable portions of the molecule. This together with the thermal stability of the resulting aromatic systems allows fair to excellent yields in many reactions.

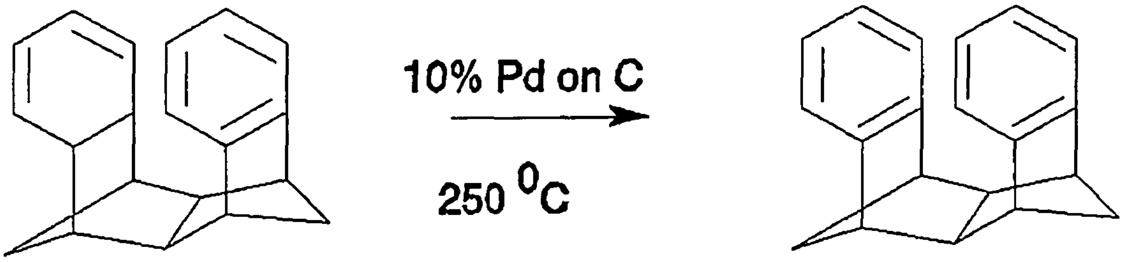
Catalytic dehydrogenation of hydroaromatic compounds is one of the classic methods of synthesis of polycyclic aromatic molecules. The most generally satisfactory catalysts are platinum, palladium, nickel, etc. As a rule, catalytic dehydrogenation must be carried out at elevated temperatures to displace the equilibrium in favor of the dehydrogenated product. The reactions can often be carried out under milder conditions if a hydrogen acceptor, such as maleic acid, cyclohexene, oxygen or nitrobenzene, is present to remove hydrogen as it is formed. The acceptor is reduced to the saturated compound. The usually vigorous conditions of dehydrogenation promote various side reactions in proportions that depend on the substrate structure (as a whole), the reaction conditions, and the catalyst. Catalytic dehydrogenation reactions are usually carried out by heating a mixture of substrate and catalyst, with or without solvent, to reflux. In the absence of solvent, the reaction temperature is in the range of 300-400^{0}C. Reactions in solutions are often carried out at reflux and high-boiling solvents are usually employed, such as cumene, p-cymene, decalin, naphthalene, or quinoline. Optimum temperatures vary widely, dependent principally upon the structure of the hydroaromatic compound and the nature of the catalysts. Tetralin has been smoothly dehydrogenated at temperatures as low as 185^{0}C while decalin and 9-methyldecalin require temperatures exceeding 300^{0}C.[8,9] Catalytic dehydrogenation is in essence the reverse of catalytic hydrogenation, and presumably the mechanism is also the reverse.[10] A considerable weight of experimental evidence supports the generalization that hydrogenation involves the cis-addition of two hydrogen atoms from the less hindered side of the double bond or polycyclic ring systems.[11,12] Conversely, dehydrogenation appears to involve predominantly cis-hydrogen abstraction.[13,14] A mechanistic picture[15] has been proposed to explain the essential facts concerning dehydrogenation of hydroaromatic compounds. According to this scheme (Scheme 2), dehydrogenation of a dihydroarene, such as dihydrophenanthrene, may be depicted as a series of equilibria involving π-bonded and σ-bonded intermediates. The substrate is initially adsorbed on the catalyst surface by π bonds to one or more aromatic rings. The number of rings associated in this manner will be dependent in individual cases upon the ease of adoption of a favorable planar conformation and steric factors, such as the presence of bulky substituents. Transfer of an axially oriented hydrogen



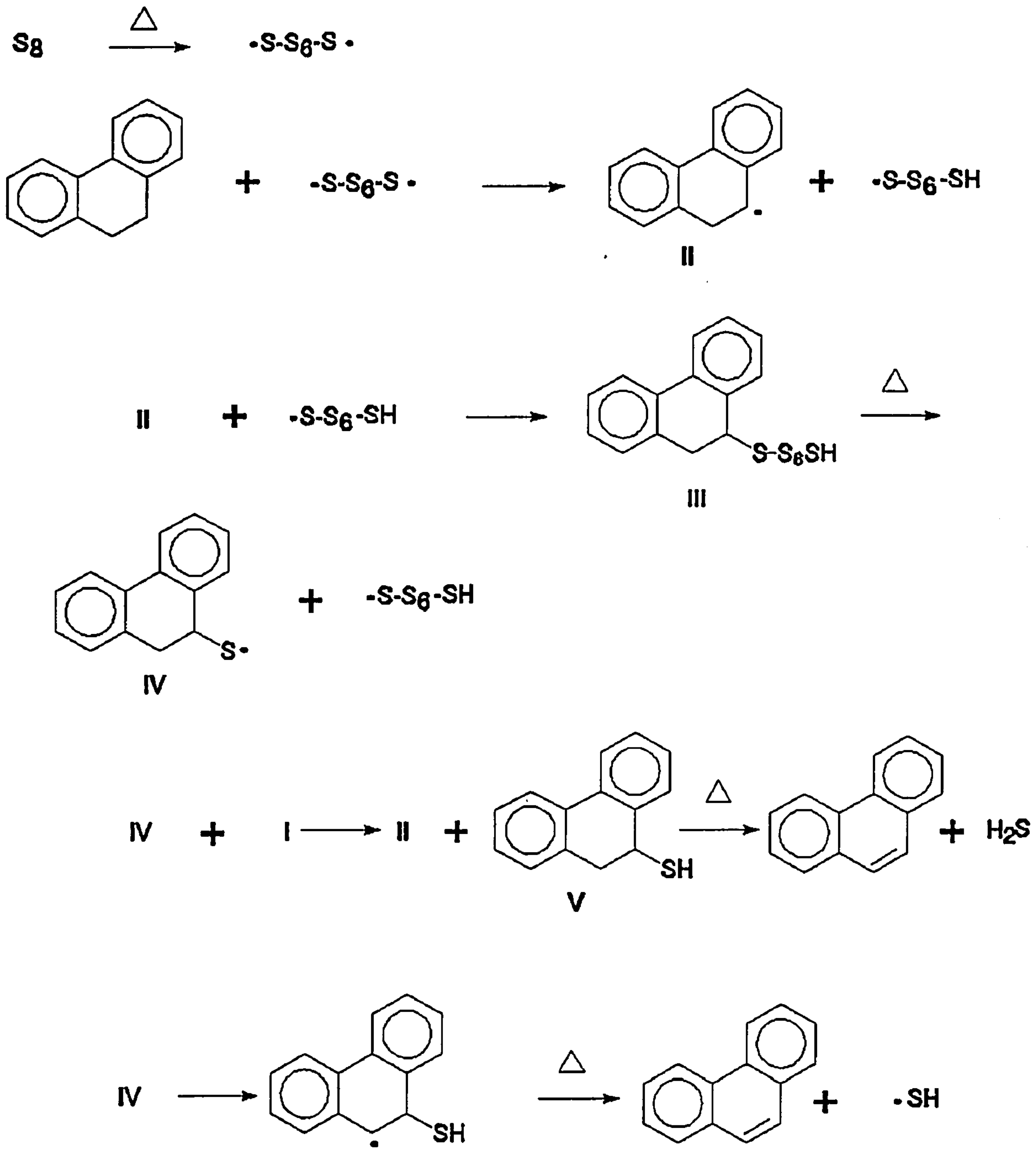
Scheme 2

atom from the partially saturated central ring of the π-bonded intermediate A to the catalyst leads to a σ-bonded intermediate B. Loss of a second hydrogen provides a fully aromatic polycyclic ring system C still closely associated with the catalyst surface by π bonds. Alternatively, an intermediate having two σ bonds to the ring undergoing reaction is also conceivable. Desorption of molecular hydrogen from the catalyst surface and its loss from solution shift the equilibria to favor formation of the fully aromatic molecule, e.g., phenanthrene. Desorption of the aromatic product into the solution frees the catalyst for repetition of the cycle. There are a lot of applications of these catalytic dehydrogenation reactions.[16] Sometimes they are a must for the dehydrogenation of substrate.[17] In this case, the inner hydrogen atoms to be eliminated are sterically so efficiently shielded they resisted numerous oxidizing reagents, like MnO_2, DDQ, or chloranil (eq 1).

(1)



Elemental sulfur and selenium, like the platinum metals, are classical dehydrogenation reagents.[18] Sulfur exists in a large number of molecular forms including a stable eight-membered ring in a crown conformation[19] and linear chains of widely variable length.[20] Selenium also exists in various forms, including a cyclic Se_8 structure; however, the latter, in contrast to sulfur, is less stable than the infinite chain form.[21] Their facility as dehydrogenation reagents is a consequence of their tendency to complete the inert gas configuration by acquisition of two



Scheme 3

electrons with formation of the respective hydrides, H_2S and H_2Se.

Since sulfur is considerably cheaper and less toxic than selenium, it is usually the first choice for preliminary exploratory studies. On the other hand, selenium is a milder reagent, and reactions are often cleaner with fewer side products. Similar to catalytic dehydrogenation, dehydrogenation by use of sulfur and selenium is often carried out at high temperatures. The mechanism of dehydrogenation of hydroaromatic compounds by means of sulfur and selenium is not well established. The evidence is consistent with radical mechanisms involving abstraction of hydrogen atoms from allylic or benzylic positions, although other possibilities are not conclusively ruled out[6] (Scheme 3).

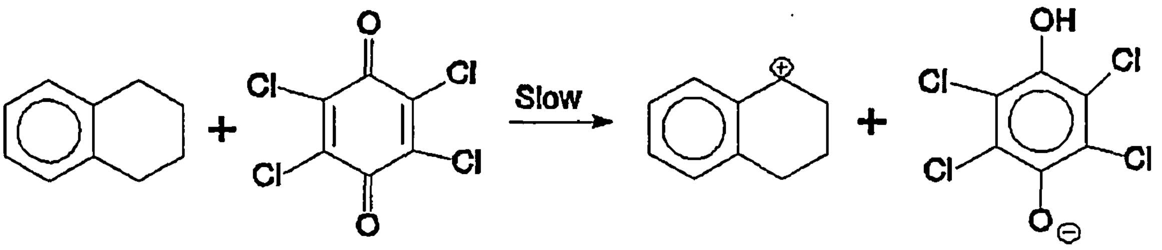
Unlike palladium, platinum, sulfur or selenium, high oxidation potential quinones are new milder dehydrogenation reagents.[22] Two important quinones often used for aromatizations are chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) and DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) (Scheme 4). The choice of quinone reagent is dictated by the oxidation potential of the quinone, the anticipated ease of dehydrogenation of the substrate, and the probability of side reactions. Quinones of high oxidation potential are more powerful electron or anion acceptors than are those of low oxidation potential, and the rates of dehydrogenation reactions reflect these differences. Electron-withdrawing groups enhance the potential of a quinone, while electron-donating groups decrease it. For example, DDQ, the most powerful quinone reagent in routine use, dehydrogenates

P-Chloranil DDQ

Scheme 4

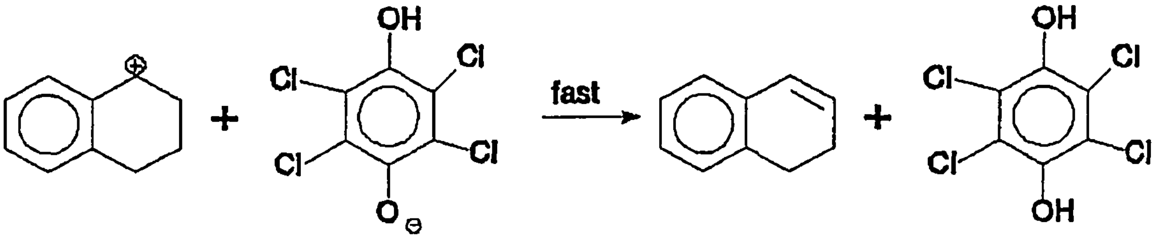
1,2-dihydronaphthalene 5500 times faster than p-chloranil at 100°C, while o-chloranil reacts 4200 times faster than p-chloranil under the same conditions.[23] The generally greater reactivity of the o-quinones compared to the p-quinones is presumed to be a consequence of strong hydrogen bonding in the transition state leading to a catecholate monoanion.[24] Dehydrogenation reactions using quinones are normally carried out by heating substrate with one equivalent of quinone at reflux temperature in an inert solvent such as benzene, dioxane, toluene, chlorobenzene, or xylene selected according to the desired operating temperature when the insoluble quinol byproduct precipitates out and this can be used to follow the reaction. The mechanism for the dehydrogenation of hydroaromatic compounds put forward by Braude, Jackman and Linstead,[25] and supported by the investigation[26] using tritium-labelled substrate, involves the transfer of a hydride ion to the quinone in the rate-determining step (eq 2):

(2)



In agreement with the rate-determining step of the reaction (eq 2), Lewis et al found in the quinone oxidation of deuterated Leuco triphenylmethane dyes k_H/k_D values ranging from 7 to 14 which are the observed large isotope effects.[27,19] Rapid proton transfer from the conjugate acid to the hydroquinone anion then leads to dehydrogenated product A and the hydroquinone QH_2 (eq 3):

(3)



Supporting this mechanism, the dehydrogenation of hydroaromatic compounds by low-potential quinones (E_0<600 mV) has been found to be subject to proton catalysis according to reactions (4-6) in which the protonated quinone QH^+ acts as an efficient hydride ion acceptor.

Further evidence is derived from work from the Penn laboratories, where rate constants for the bond cleavage reaction of high potential quinones with substituted benzyl ethers have been shown to correlate with the Hammett σ^+ constant[28] and thermal and photochemical reactions for related compounds have been shown to correlate over a large temperature range (eq 7).[29] Recent evidence for such an ionic mechanism has been obtained from trapping of the intermediate carbocations with nucleophilic solvents such as water[30] and methanol.[31]

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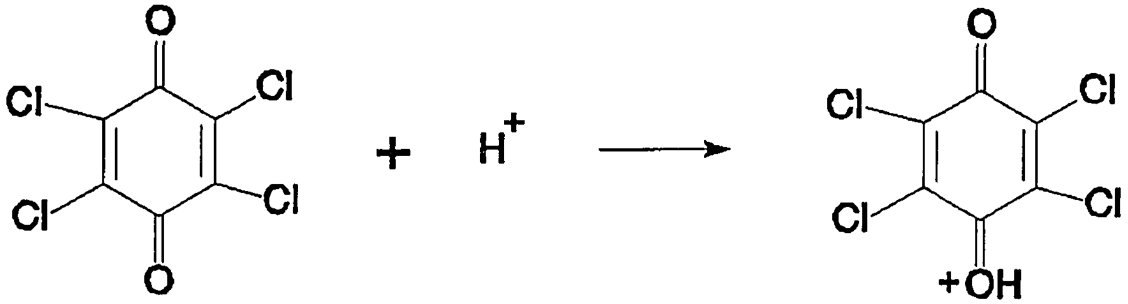
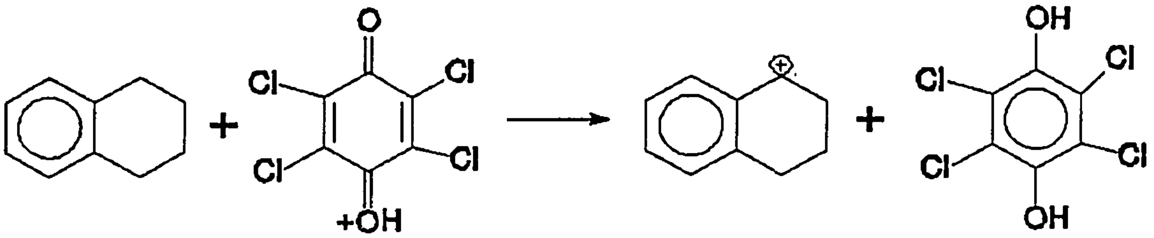


Further light has been shed on the mechanism of hydrogen transfer by a study of the dehydrogenation of cis-1,2-dideuterioacenaphthene by DDQ and o-chloranil.[32] In benzene solution, the dehydrogenation proceeds with predominantly cis-elimination. This result has been explained by the involvement

(5)



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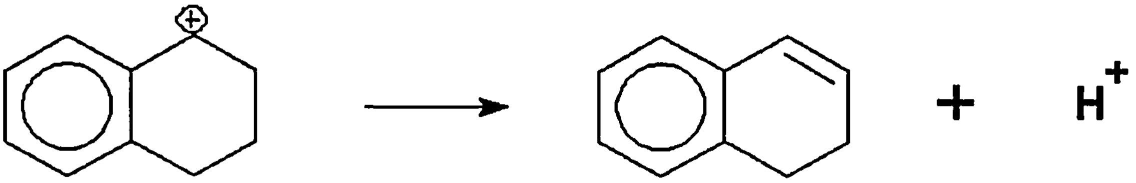
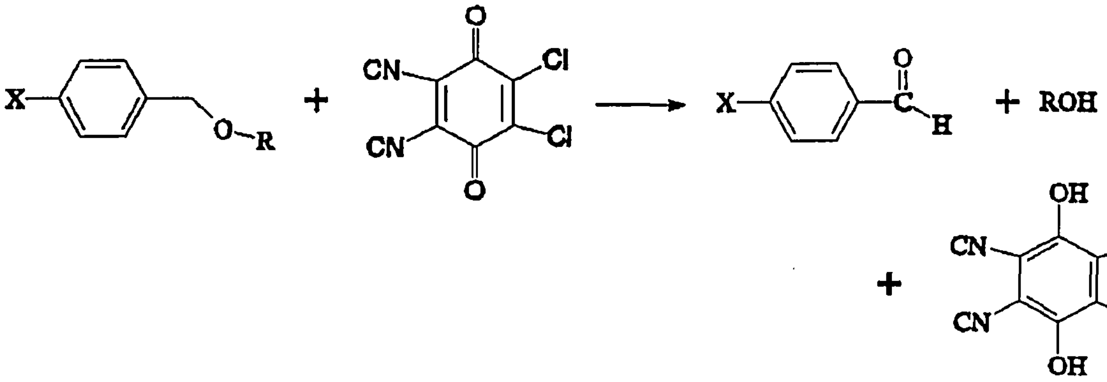


of ion pairs which may collapse to give the hydroquinone and the cis-dehydrogenated product acenaphthylene-d_0 and acenaphthylene-d_2. Dissociation into the free ions leads to both cis and trans dehydrogenated products. Polar solvents such as dimethylformamide favor dissociation of the ion pair, thus affecting the cis-trans ratio. Several cases have been described which do not accord entirely with an ionic bimolecular mechanism. Hashish and Hoodless[33] report that dehydrogenation of 1,4-

(7)



dihydronaphthalene by p-chloranil in phenetole appears to follow second-order kinetics only in the later stages of reaction. They suggest that electron transfer within an initially formed charge-transfer complex may be the rate-determining step in this reaction. More evidence has been obtained which suggests that reaction of 1,4-cyclohexadiene with DDQ may involve simultaneous rather than stepwise hydrogen transfer.[34,35] One of the most useful applications of dehydrogenations by quinone has been in steroid chemistry, particularly for the synthesis of ring A cyclohexadieneones.[36]

Other reagents that have been used for dehydrogenation are trityl salts[37,38], alkyllithium-TMEDA complexes[39], metal complexes such as Wilkinson catalyst[40], MnO_2[41], Lewis acids such as aluminum chloride[42] and antimony pentachloride[43] and activated charcoal.[44] The last-mentioned reagent also dehydrogenates cyclopentanes to cyclopentadienes.

2. C-C bond cleavage reactions[c]

Cleavage of radical cations to the fragments (i.e., a radical and a carbocation) is an important general reaction.[45]

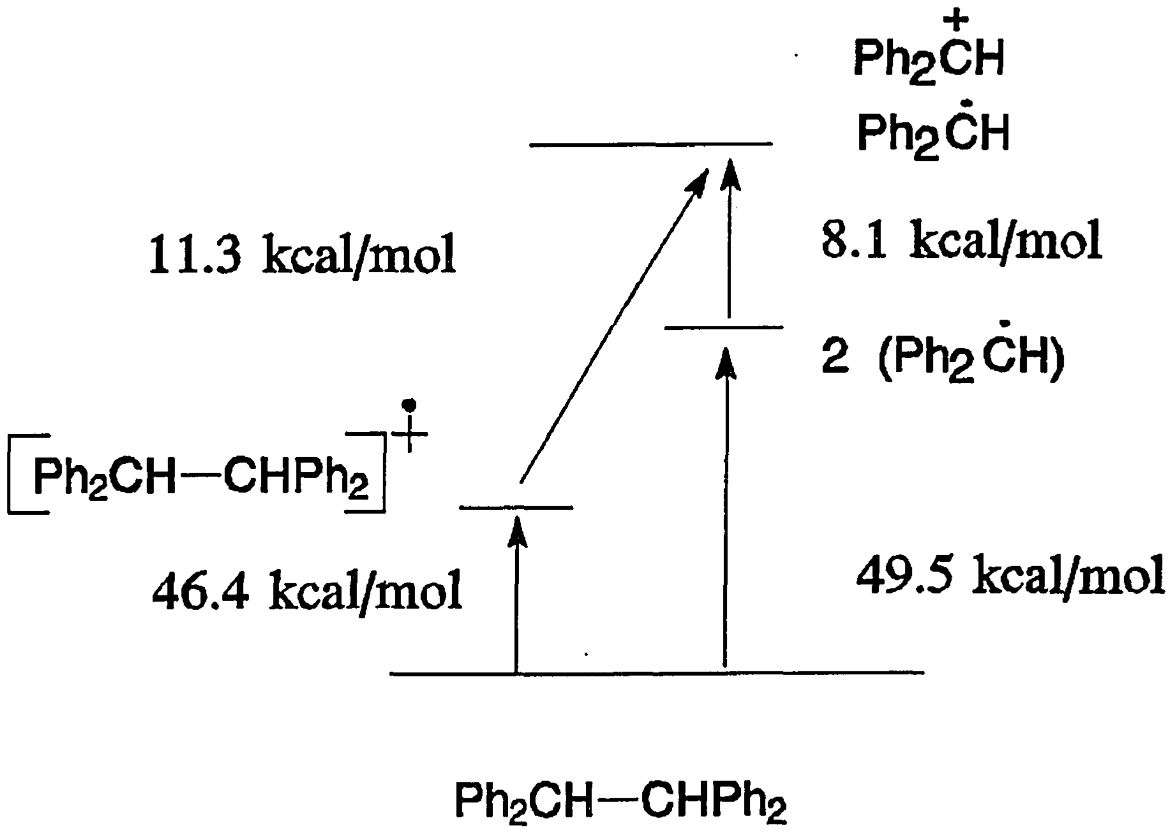


Fig. 1 Thermochemical Cycle for the Cleavage of Tetraphenylethane

This process is well understood in the gas phase where it accounts for many fragments in the mass spectrum of a molecule.

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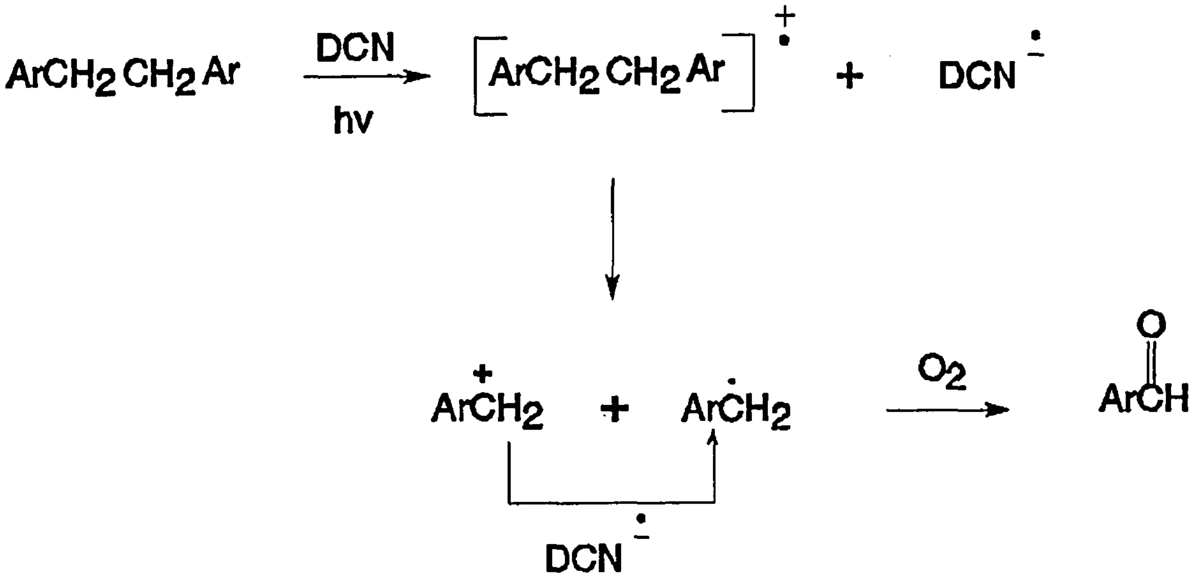
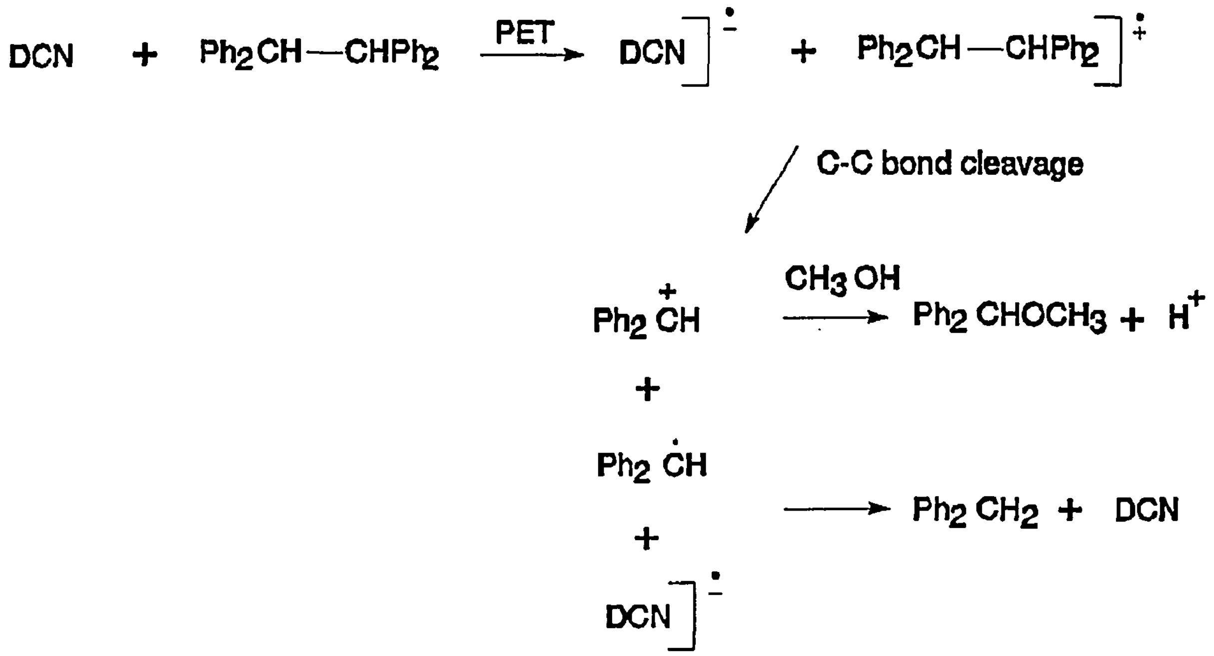
[c] Here is just a brief review of C-C bond cleavage reactions, see Chapter III for more details.

This evidence strongly suggests that certain bonds in radical cations are substantially weaker compared to their neutral counterparts. A representative example is shown in Fig. 1, where relevant data for 1,1,2,2-tetraphenylethane are presented. Thus, using the oxidation potentials of 1,1,2,2-tetraphenylethane ($E_{1/2}$=2.01 V = 46.4 kcal/mol) and the diphenylmethyl radical (0.35 V = 8.1 kcal/mol)[46], the heats of formation of 1,1,2,2-tetraphenylethane and the diphenylmethyl



Scheme 5

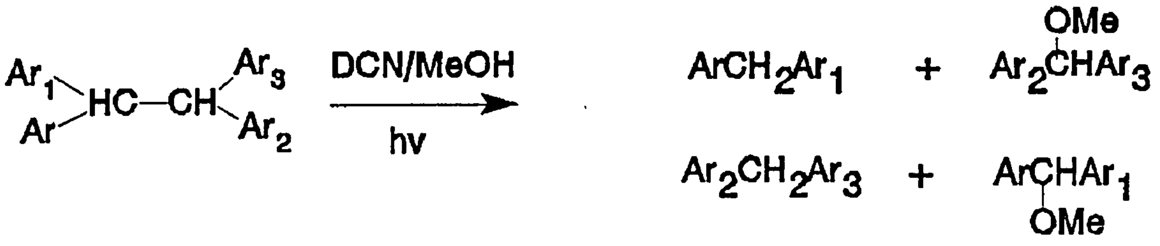
radical calculated using molecular mechanics force field (MM2) calculation,[47] and by assuming that the solvation energy of neutral species is negligible, a value of the bond dissociation energy of 11.3 kcal/mole is obtained for the radical cation of 1,1,2,2-tetraphenylethane. This value compares to the value of



Scheme 6

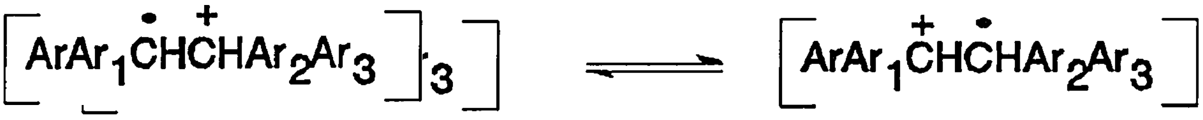
49.5 kcal/mole for the neutral molecule. This difference in activation energies explains the very fast bond cleavage reactions observed for this radical ion. The C-C bond cleavage reactions of bibenzyl was first reported by Das, Griffin and co-workers.[48] 1,4-Dicyanonaphthalene (DCN) was used as the photosensitizer. Upon irradiation of DCN, the diarylethanes were oxidized to form the corresponding radical cation, as observed by time-resolved laser flash photolysis. In the absence of oxygen, no fundamental cleavage products were found, because the short lifetime of the radical cations prevented the C-C bond cleavage. In contrast, in an oxygen saturated solution, the major products were the corresponding arylaldehydes. The radical anion of DCN can transfer an electron to O_2 to form the radical anion of O_2 which is more reluctant to give an electron to the radical cations. This process causes a longer lifetime for the radical cations and allows the bond cleavage reaction to occur (Scheme 5). The photoinduced electron transfer (PET) reaction of 1,1,2,2-tetraphenylethane has been reported by Arnold and co-workers[49] to provide C-C bond cleavage through an intermediate tetraphenylethane cation radical. The radical cation intermediate fragments to diphenylmethyl radical and diphenylmethyl carbocation (Scheme 6). In general, the electron donor substrate is oxidized by PET to a cation radical which undergoes C-C bond cleavage to form the most stable radical and

(8)



cation pair. These species react further with solvent and with the reduced acceptor to form hydrocarbon and ether products. Popielarz and Arnold[50] have studied the electron transfer initiated C-C bond cleavage of an extensive series of 1,1,2,2-

(9)



$$\left[\left[ArAr_1\overset{\bullet}{C}H\overset{+}{C}HAr_2Ar_3\right]_3\right] \rightleftharpoons \left[ArAr_1\overset{+}{C}H\overset{\bullet}{C}HAr_2Ar_3\right]$$

tetraarylethanes and 1,1,2-triarylethanes or 1,1,2-triarylpropanes. In a solution of acetonitrile-methanol (3:1), radical cations of these aryl alkanes were generated by transferring an electron to excited state 1,4-dicyanobenzene. For a radical cation of these compounds, the fragmentation would give a cation and a radical. The cation would be trapped by methanol to form a methyl ether while the radical would undergo back electron transfer from radical anion of dicyanobenzene forming an carbanion which would be subsequently protonated to give a hydrocarbon as the final product (eq. 8). The fragmentation of some unsymmetrical compounds could lead to four products (i.e., a pair of ethers and a pair of hydrocarbons). The ratio of products would be expected to be dependent on the oxidation potentials of the two possible radical fragments. In accord with expectations, an excellent linear relationship of the logarithm of the observed ratio of products and the electrochemically determined reversible oxidation potentials with an almost unit slope led the author to propose that the product ratio is determined by the relative rates of cleavage in the two possible modes or by equilibria of the radicals and cations before separation of the geminate radical cation pair (eq. 8).

Further research in dehydrogenation reactions is very important in organic synthesis, especially in natural product synthesis, since very mild reaction conditions are desirable. However, most methods used today require drastic reaction conditions and some of the reagents are toxic and very expensive.

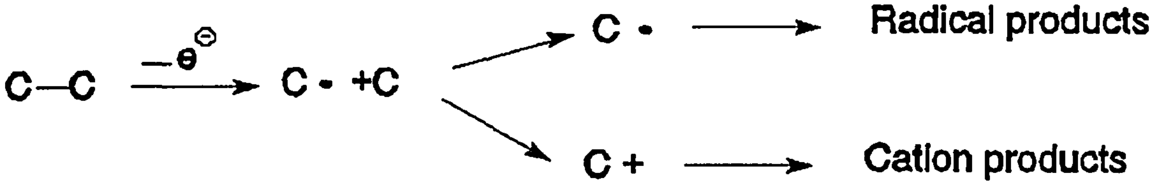
To circumvent these problems, new reagents for dehydrogenation reactions need to be developed. The iron (III) perchlorate is non-toxic, inexpensive and soluble in most organic solvents. This reagent has been used recently for a variety of organic functional group transformations, including oxidative cleavage of carbon-nitrogen double bonds,[51] the coupling reaction of electron rich aromatic compounds[52] and the conversion of alcohol and halides to amides.[53] Iron (III) (1,10-Phen)$_3$ complex has been used by Kochi[54] for the oxidation of various methylarenes. In this study we attempt to employ these iron compounds to react with a variety of organic substrates which have been traditionally used to test for dehydrogenation and/or radical cation reactivity.

Results and Discussion

Carbonyl Formation from Tris-1,10-phenanthroline Iron(III) Perchlorate, a Standard Radical Cation Generating Reagent: The importance of radical cations in a variety of organic reactions (e.g., cycloaddition reactions, bond cleavage[55]) is well documented. A number of recent studies have attempted to examine the reactivity of radical cations as generated under a variety of conditions.[56] Since the primary event leading to the generation of a radical cation is the transfer of an electron from the organic donor molecule to a suitable substrate, and since the electron transfer event normally requires contact or a close proximity of the reagents, the subsequent reactivity of the radical cation may be highly dependent on the species which is the electron acceptor.

In Chapter I of this thesis, the radical cation reactivity of a number of di- and tetraarylethanes was examined in order to determine potential reactivity differences between naphthyl and phenyl groups.[57] 1,1,2,2-Tetraphenylethane (**1c**) was specifically chosen for the previous study because its radical cation, and its subsequent reactivity, has been studied under a variety of conditions.[58] Naphthyl groups were found to react similarly,[56] giving the products expected from the cleavage of a radical and a cation (eq 10). We were therefore surprised to find a different product in the reactions of tris-1,10-phenanthroline iron(III) perchlorate ($FeL_3(ClO_4)_3$) which has previously been used exclusively as a one electron oxidant.[59] $Fe(ClO_4)_3$ produces

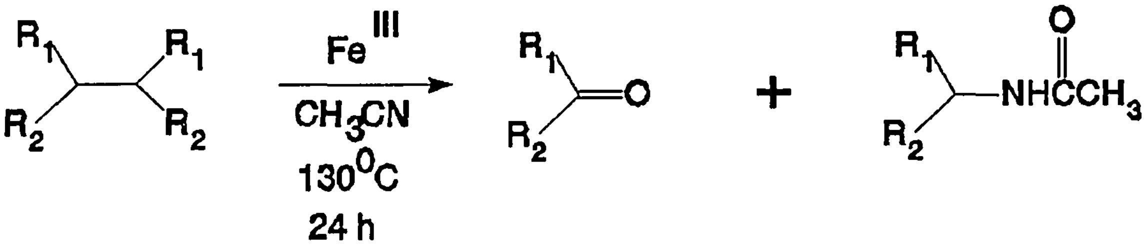
(10)



similar products.

Fe(1,10-phen)$_3$(ClO$_4$)$_3$ was prepared by a published procedure[60]

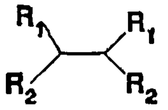
(11)



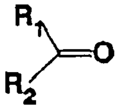
while Fe(ClO$_4$)$_3$ was obtained from Aldrich. The reactions observed are shown in eq (11) and the specific structures and reaction yields are given in Table I. The standard conditions for these reactions were to heat a degassed solution of the Fe^{III} compound (0.03 M) and the organic compound (0.02 M) in freshly dried and distilled CH$_3$CN at 130^{0}C for twenty four hours. The products were analyzed as previously.

In contrast to the FeL$_3$(PF$_6$)$_3$ results reported earlier,[56] 2 was observed in high yields from the "radical" cleavage product of 1 (note eq 10). The appearance of this compound must be

Table I. Oxidation reaction by Fe^{III}



1



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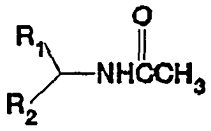


3

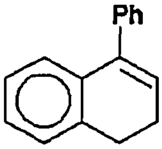
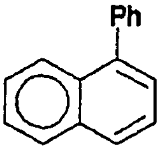
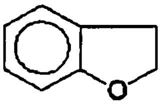
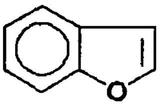
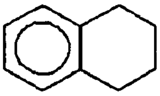
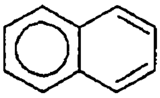
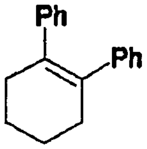
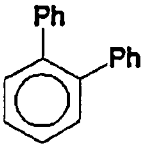
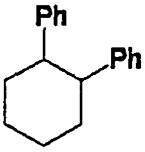
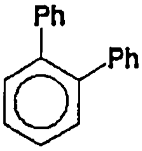
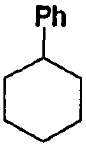
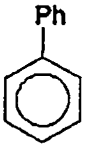
1	R_1	R_2	Oxidant	2	3	Conversion
a	Np	H	$Fe^{III}L_3(ClO_4)_3$	75%	trace	69%
b	Np	Ph	$Fe^{III}L_3(ClO_4)_3$	86%	82%	65%
			$Fe^{III}(ClO_4)_3$	83%	84%	70%
c	Ph	Ph	$Fe^{III}L_3(ClO_4)_3$	80%	84%	70%

dependent on having both Fe^{III} and ClO_4^- in the oxidant species. This conclusion is based upon the following experiments. A solution of **1b**, $LiClO_4$, and $(BrC_6H_4)_3NSbCl_6$ (0.01, 0.04, and 0.02 mM) in 3:1 CH_3CN/CH_3OH yielded the normally expected radical cation products of naphthylphenylmethane and methyl naphthylphenylmethyl ether. Similarly, heating a solution of **1b**, $Fe(1,10\text{-phen})_3(PF_6)_3$ and $LiCLO_4$ (0.02, 0.04, and 0.12 mM) in CH_3CN yielded the radical cation products (i.e., naphthylphenylmethane and **3b**). In contrast, a solution of **1b**, $Fe(1,10\text{-phen})_3(ClO_4)_3$ and $NaPF_6$ (0.02, 0.03, and 0.1 mM, respectively) in CH_3CN yields **2b** and **3b** as noted earlier in Table I. Therefore, the ClO_4^- must be present in the oxidant and it is not sufficient for the ClO_4^- to be in the reaction solution in order to obtain the carbonyl products.

Possible rationales for the origin of the carbonyl oxygen include the incorporation of an oxygen from the ClO_4^-, trace amounts of water in the acetonitrile, or unexpected iron oxo species formed in the reaction solution of the Fe^{III} species.

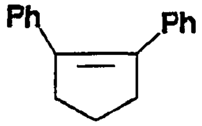
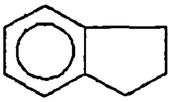
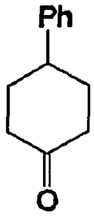
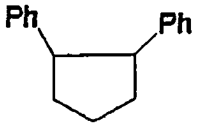
Dehydrogenation Reaction by Iron (III) Perchlorate: Iron (III) perchlorate ($Fe(ClO_4)_3$) has been reacted with a variety of organic substrates which have been traditionally used to test dehydrogenation reactivity. These substrates are shown in Table II along with other data concerning the quantitative aspects of these reactions. Typical reaction conditions for these reactions utilize our standard sealed tube methodology.[61] In this technique, $Fe(ClO_4)_3$ (0.03 M) and the starting substrate (0.02 M) were dissolved in a CH_3CN solution at room temperature. Following three freeze-pump-thaw degassing cycles, the reaction tubes were sealed under vacuum and placed in an oil bath at 130°C for 24 hours. The reaction yields and product distributions were determined by GC/MS methodology using octyl cyanide as an internal standard. The results of these experiments are gathered in Table II. The conversion amount signifies the amount of the starting material which has reacted during the indicated time. The yield data in Table II signify the amount of product which was observed based on unreacted starting material and assuming

Table II. Dehydrogenation Reaction Of $Fe(ClO_4)_3$

Substrate Number	Substrate	Product	Conversion of Substrate	Yield of Product
5			100%	84%
6			61%	85%
7			33%	88%
8			85%	78%
9			17%	91%
10			46%	87%

that only a single product is formed in the reaction.

Table II. Dehydrogenation Reaction of $Fe(ClO_4)_3$ (continued)

Substrate Number	Substrate	Product	Conversion of Substrate	Yield of Product
11		—	0%	0%
12		—	0%	0%
13		—	0%	0%
14		—	0%	0%

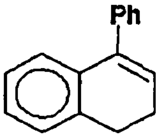
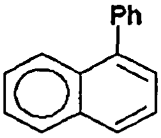
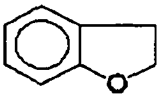
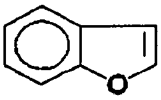
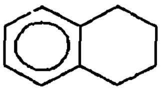
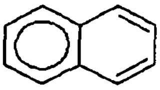
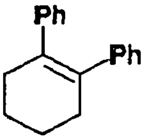
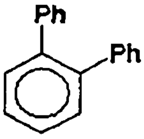
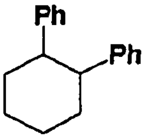
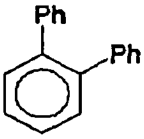
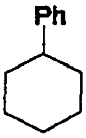
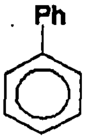
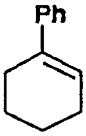
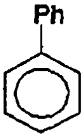
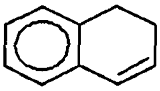
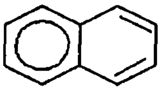
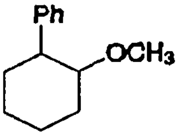
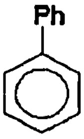
The compounds in Table II have been grouped according to the numbers of hydrogen atoms which must be removed to make an aromatic structure. In this classification scheme, 5 and 6 require removal of two electrons (and subsequently two protons) to make an aromatic structure. Compound **7** and **8** are characterized by the necessity to remove four electrons (and subsequently four protons), while compound **9** and **10** require the removal of six electrons (and subsequently six protons) to make an aromatic structure. The reactions are clean leading to a single product in all cases as detected by GC analysis. The yields of these products are also all very high (≥ 80%) based upon the amount of unreacted starting material. In contrast to these results, compounds **11-14** are characterized by the fact that the dehydrogenation product is not an aromatic structure. For example, 1,2-diphenylcyclopentene (**11**) would only be able to form a cyclopentadiene structure and not become fully aromatic. The fact that no product is seen in these reactions is not necessarily a bad sign for the dehydrogenation of potentially aromatic species since this has been observed many times previously.[62] Compound **12** was particularly studied in some detail as the reaction product (i.e., indene) would be clearly observable by GC. Independent GC injections of indene clearly established that no product was formed under our reaction conditions. Similar statements can be made about **14** where the retention times of **14** and **11** were clearly different than those of any potential dehydrogenation products under our GC conditions. No product was observed for the reactions of either **11** or **14**.

As a further point of note concerning these reactions, **5** shows the interesting phenomenon that its conversion to form 1-phenylnaphthalene was greater than expected, given the number of electrons which should have been removed from **5**. This observation may signal a catalytic action of the Fe(II) product of the reaction. In accord with this observation, Fe(II) (1,10-phen)$_3$ has been shown to cause dehydrogenation reactivity, with 40% conversion of **5** to 1-phenylnaphthalene being observed under similar conditions. The detailed results of the catalytic potential of Fe(II) will be examined later in this chapter.

Additional testing with **9** was performed to evaluate the source of the low reactivity of this compound as observed by its low conversion yield. When the concentration of Fe(ClO$_4$)$_3$ in the reaction solution was doubled, approximately twice the amount of the product o-terphenyl was formed. The amount of reaction time had no influence on the reaction since heating the reaction for 48 hours (as opposed to only 24 hours) still resulted in the same amount of conversion to products. These results seem to indicate an additional pathway for the Fe(III) complexes in these solutions, since high conversion yields are noted in the reaction of **10** which is structurally similar to **9**.

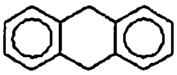
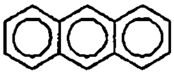
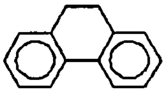
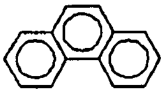
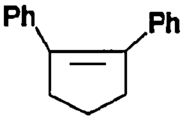
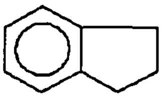
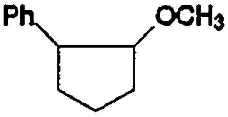
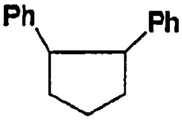
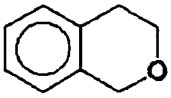
Dehydrogenation Reaction by Fe(III)(1,10-phen)$_3$(ClO4)$_3$: Iron (III) (1,10-phen)$_3$ (ClO4)$_3$ has been tested with a variety of organic substrates for its dehydrogenation reactivity. These substrates are shown in Table III along with other data concerning the quantiative aspects of these reactions. Dehydrogenation reactions were carried out in CH$_3$CN solution. The substrate and the Fe(1,10-phen)$_3$(ClO4)$_3$ were heated together at 130^{0}C for 24 hours. The color of the solution changed from

Table III. Dehydrogenation Reaction of Fe(III) (1,10-phen)$_3$(ClO$_4$)$_3$

Substrate Number	Substrate	Product	Conversion of Substrate	Yield of Product
5			100%	88%
6			100%	82%
7			96%	90%
8			100%	93%
9			15%	92%
10			20%	85%
15			100%	91%
16			75%	89%
17			49%	65%

green to red which means the Fe(III) may be reduced to Fe(II).

Table III. Dehydrogenation Reaction of Fe(III) (1,10-phen)$_3$(ClO$_4$)$_3$ (continued)

Substrate Number	Substrate	Product	Conversion of Substrate	Yield of Product
18			100%	87%
19			100%	83%
11		—	0%	0%
12		—	0%	0%
20		—	0%	0%
14		—	0%	0%
21		—	0%	0%

The detailed results of these experiments are presented in Table III. The substrates are the ones that are often used in the dehydrogenation reactions. The reaction yields and product distributions were also listed. The first six substrates in Table III have also been grouped according to the number of hydrogen atoms which must be removed to make an aromatic structure. The other substrates were selected to test the dehydrogenation reactivity of these substrates with other functionality. The reactions with 6-membered ring systems proceeded with good yields as expected. In contrast, the reactions failed with the 5-membered ring substrate. The only exception was 2,3-dihydrobenzofuran (**6**) which gave benzofuran as the product. This is not surprising since the product formed (i.e., benzofuran) has an aromatic structure while the other 5-membered ring substrates did not give the products with the aromatic structures. Compound **21** also failed in the dehydrogenation reaction although it has six-membered ring system. This can be explained by the lack of fully aromatic structure of the product. Compound **17** was studied in some detail since the reaction product was biphenyl. The methoxy group was somehow lost during the reaction.

It can also be noted that **5**, **18** and **19** show the interesting phenomenon that their conversion to form products was greater than expected, given the number of protons which should have been removed from these substrates. This observation may also signal a catalytic behavior of the Fe(II) product of the reaction. As can be seen later in this chapter, Fe(II) (1,10-phen)$_3$ (ClO$_4$)$_2$ does show dehydrogenation reactivity.

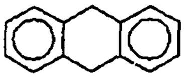
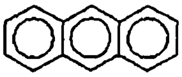
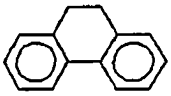
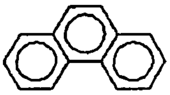
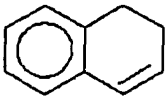
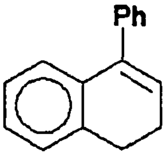
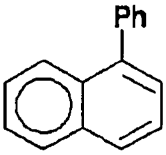
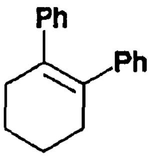
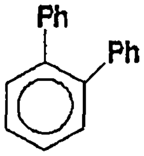
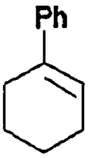
Additional testing with **9** was performed to evaluate the effect of the substrate concentration and reaction time on the reaction. When the concentration of Fe(1,10-phen)$_3$(ClO4)$_3$ in the reaction was increased, the amount of the product was also increased. The amount of the reaction time had no influence on the reaction since heating the reaction for 48 hours (as opposed to only 24 hours) still resulted in the same amount of conversion to products.

Another interesting result is that some of the reaction can even occur at room temperarure. **5**, **16**, and **18** can be dehydrogenated to phenylnaphthalene, naphthalene and anthracene, with conversions of 21%, 12% and 30%, respectively. This may suggest that Fe(1,10-phen)$_3$(ClO$_4$)$_3$ is a useful reagent for the dehydrogenation of some biological compounds which require only very mild reaction conditions.

Another thing needed to be pointed out is that the dehydrogenation reaction is counterion dependent. This conclusion is based on the following experiment. When **9** and Fe(1,10-phen)$_3$(PF$_6$)$_3$ was heated together at 130^{0}C for 24 hours, no dehydrogenation reaction was observed. ClO$_4^-$ plays an important role in the dehydrogenation reactions.

Dehydrogenation Reaction by Fe(II) (1,10-phen)$_3$(ClO$_4$)$_2$: As was indicated earlier that Fe(II) may show dehydrogenation reactivity, Fe(II) (1,10-phen)$_3$(ClO$_4$)$_2$ has been used to react with several organic substrates. The reaction conditions were the same as those for the Fe(ClO$_4$)$_3$ and Fe(III) (1,10-phen)$_3$(ClO$_4$)$_3$

Table IV. Dehydrogenation Reaction of Fe(II) (1,10-phen)$_3$(ClO$_4$)$_3$

Substrate Number	Substrate	Product	Conversion of Substrate	Yield of Product
18			19%	78%
19			4%	75%
16		—	0%	0%
5			41%	71%
8			42%	86%
15		—	0%	0%

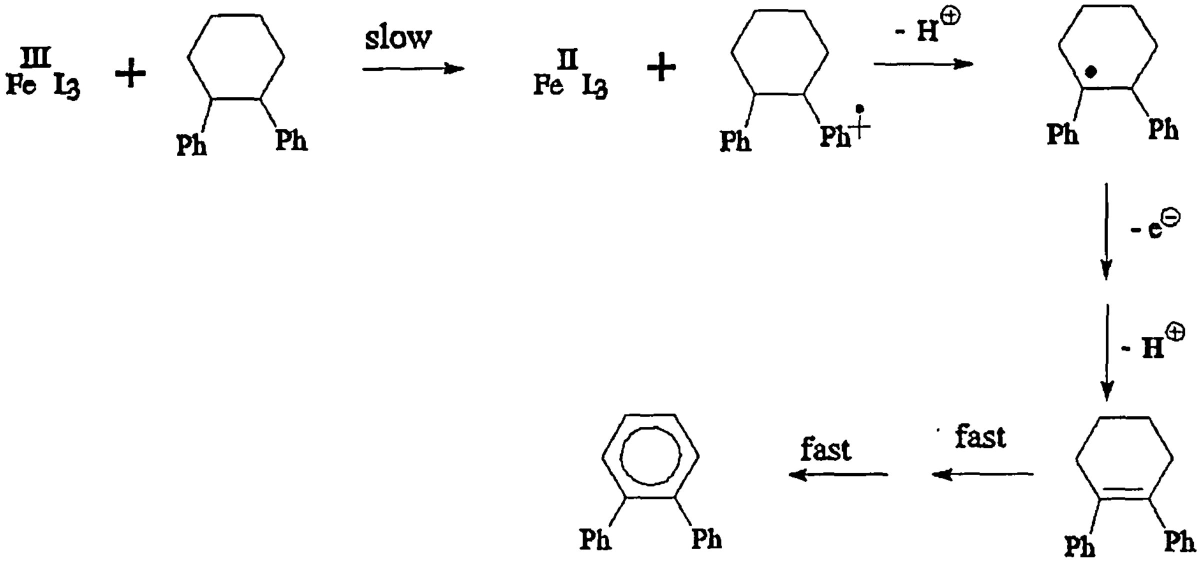
dehydrogenation. The substrates and Fe(II) (1,10-phen)$_3$(ClO$_4$)$_2$ were heated together in CH$_3$CN in a sealed tube at 130^{0}C for 24 hours. The results of the experiments are presented in Table IV. It can be seen that Fe(II) (1,10-phen)$_3$(ClO$_4$)$_2$ does demonstrate dehydrogenation reactivity, although it apparently shows no oxidation ability when compared to Fe(III) dehydrogenating reagents. The results in Table IV show that Fe(II) (1,10-phen)$_3$(ClO$_4$)$_2$ only dehydrogenates a limited number of organic substrates and the dehydrogenation products of these substrates have at least three phenyl rings.

The dehydrogenation by Fe(II) (1,10-phen)$_3$(ClO$_4$)$_2$ is also counterion dependent. When **8** was treated with Fe(II) (1,10-phen)$_3$(PF$_6$)$_2$ under same condition, no dehydrogenation reaction was observed.

Fe^{III} as a Dehydrogenation Reagent: The results presented in Tables II through III demonstrate that Fe(III) can act as a dehydrogenating reagent. These dehydrogenation reactions are similar to the dehydrogenation reactions reported previously.[62a] In these systems, dehydrogenation is observed in all 6-membered ring systems studied here and fails in the case of 5- or 7-membered ring systems. The single exception to this behaviour is given by 2,3-dihydrobenzofuran (**6**) which did indeed yield a dehydrogenated product. The failure of the dehydrogenation of indane (**12**) to indene can be explained by the lack of aromatic structure of the dehydrogenated product.

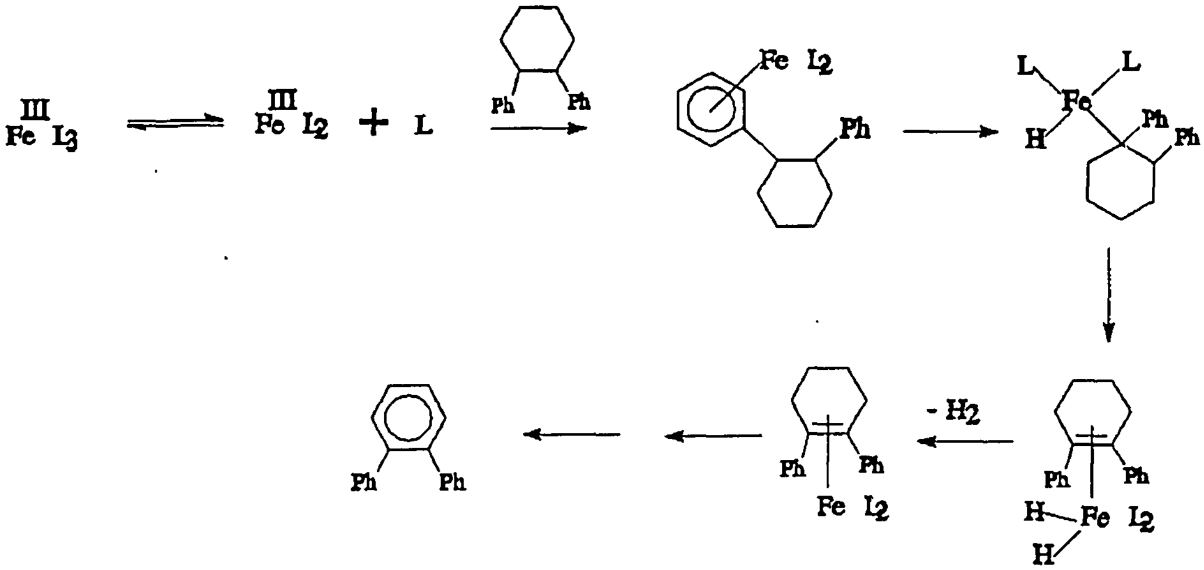
Several mechanisms may be possible for the dehydrogenation reaction. The key intermediate in each mechanism is postulated to be an initial alkene. In the case of 1,2-diphenylcyclohexane, the key intermediate would be 1,2-diphenylcyclohexene. This intermediate is postulated since it is a natural intermediate on the route to o-terphenyl and 1,2-diphenylcyclohexene undergoes dehydrogenation with these reagents at a much faster rate than does the parent 1,2-diphenylcyclohexane itself.

In mechanism 1 (Scheme 7), Fe(III) can serve as a one electron oxidant[57] which can transfer one electron from the substrate to Fe(III). This radical cation of the substrate formed by this electron transfer, can lose a proton followed by either a hydrogen atom transfer or sequential electron and proton loss to give an alkene which is converted at a much faster rate than the original cycloalkane to yield dehydrogenated product.



Scheme 7

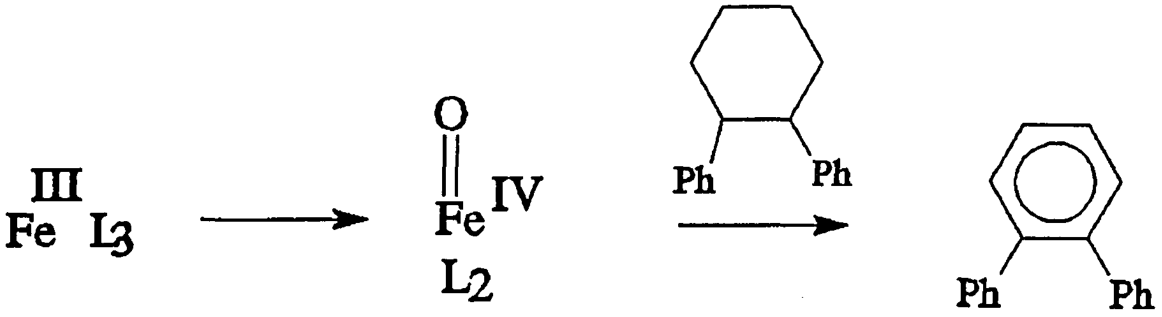
In mechanism 2 (Scheme 8), Fe(III)L_3 may form a complex with



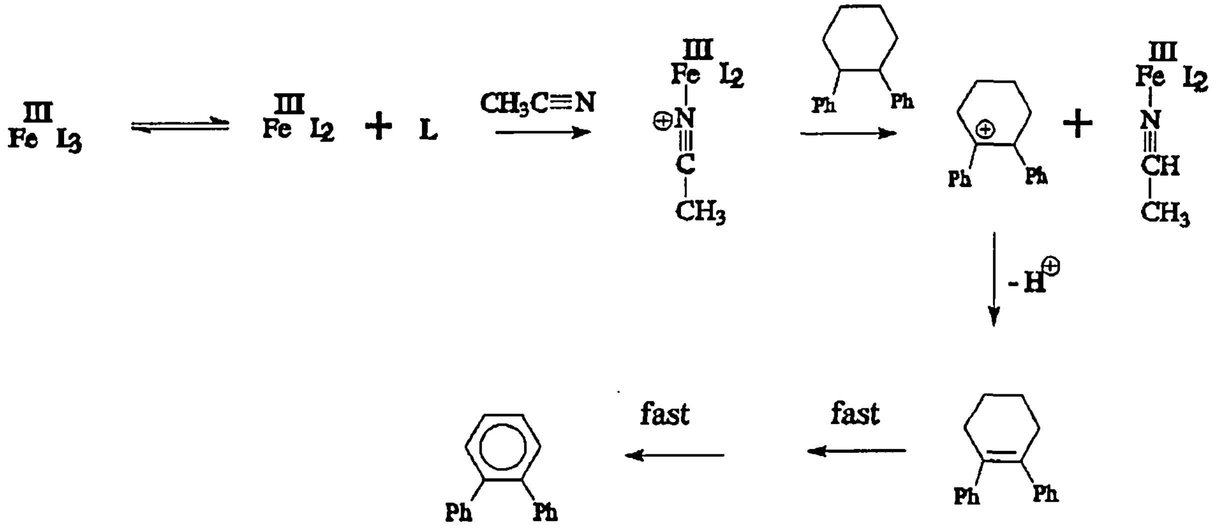
Scheme 8

the substrate after initial loss of the 1,10-phenanthroline ligand. Oxidative addition of the coordinately unsaturated iron to a phenyl ring may be followed by a series of oxidative addition/reductive elimination[63] reactions to yield the dehydrogenated product. This mechanism may be also used to explain the dehydrogenation reactivity of Fe(II).

In mechanism 3 (Scheme 9), an iron oxo intermediate is formed during the reaction. It has been reported that iron (IV) oxo species show dehydrogenation reactivity.[64] Another mechanistic possibility is that of hydride abstraction in which the hydride of the substrate can be abstracted by the Fe(III) complex as shown in mechanism 4 (Scheme 10). Precedent for this reaction has been obtained by Bunting who interpreted a kinetic



Scheme 9



Scheme 10

isotope effect in an oxidation of a hydro pyridinium by ferricyanide ion to be due to a hydride transfer.[65] Evidence for any or all of the mechanisms shown above has been seen in our studies, since 1,10-phenanthroline has been found in solutions after the reactions and electron transfer from these systems is well-precedented for oxidants with similar oxidation potentials.

Regardless of the exact mechamism, Fe(III) can serve as a cheap and mild dehydrogenation reagent as seen from its reactions with the substrates which has been used to test the dehydrogenation reactivity.

Counterion Effects in Dehydrogenation and Oxidation Reactions: It is very interesting that an counterion effect was observed in both dehydrogenation and oxidation reactions. This finding is unprecedented in these reactions. As mentioned above, only ClO_4^- worked as an counterion for these reactions. It must also be noted that both Fe(III) or Fe(II) and ClO_4^- must come from the starting reagents and both act as a whole part. ClO_4^- must participate in these reaction processes.

Future work should be focused on the investigation of the mechanism of the dehydrogenation and oxidation reactions. The detailed study of counterion effect will also be important.

Summary

Iron oxidants containing ClO_4^- have been shown to give different products than those normally expected for radical cation generating reagents. Caution should be used in the interpretation of products as originating from radical cations when using oxidants containing ClO_4^-.

$Fe(ClO_4)_3$, Fe(III) (1,10-phen)$_3$(ClO_4)$_3$ and Fe(II) (1,10-phen)$_3$(ClO_4)$_2$ have been found to perform dehydrogenation reactions under relatively mild conditions (i.e., 130^0C). Thus, these complexes can be observed to do more than oxidation of alcohols or related structures.

Experimental Section

Melting points were determined on a Laboratory Devices Mel-Temp apparatus and were uncorrected. Gas-liquid chromatographic analyses were conducted on a Hewlett-Packard Model 5890A GC equipped with a 10 m 5% phenylmethylsilicone or a Carbowax 20 m Megabore column. Integration of the signals was performed by a Hewlett-Packed Model 3390A digital integrator. GC-MS were measured with a HP 5980 mass spectrometer with a 5890 gas chromatograph equipped with a 25-m 5% phenylmethylsilicone column. ^1H NMR spectra δ (ppm) and J (hertz) and ^{13}C NMR were measured in the indicated solvent with TMS (δ=0.0 ppm) or $CDCl_3$ (δ=77.0 ppm) as an internal standard on a JEOL GX-270 Spectrometer.

Acetonitrile was predried over CaH_2 and then distilled from P_2O_5 shortly before use. THF was distilled from sodium benzophenone ketyl under argon before use. 1,2-Dinaphthylethane (**1a**) was purchased from Lancaster and recrystalized from ethanol. Unless otherwise specified, all chemicals were purchased from Aldrich.

Identification of reaction products was accomplished by GC/MS analysis and by comparison with an authentic chemical sample. Reported product yields and overall conversion are based on GC measurements using octyl cyanide as an internal standard.

Synthesis of Fe(III) (1,10-phen)$_3$(PF$_6$)$_3$: 6.950 g of $FeSO_4$*$7H_2O$ (25.0 mmol) in 250 mL of distilled water was added to 1.49 g of

1,10-phenanthroline (7.50 mmol) resulting in a deep red solution. 1.00 g of $NaPF_6$ (5.95 mmol) was added to the reaction mixture and stirred for 1 hr. The red precipitate was collected by vacuum filtration to yield 2.05 g (2.18 mmol, 87%) of Fe(II) (1,10-phen)$_3$ $(PF_6)_2$. Oxidation of 2.35 g (2.50 mmol) Fe(II) (1,10-phen)$_3$ $(PF_6)_2$ with 1.01 g of $Ce(SO_4)_2*4H_2O$ (2.50 mmol) in 250 mL of 6 N H_2SO_4 gave a blue solution. Addition of 1.00 g of $NaPF_6$ (5.95 mmol) to this solution gave 1.15 g (1.06 mmol, 42%) of blue crystals of Fe(III) (1,10-phen)$_3(PF_6)_3$ which were collected by vacuum filtration and washed with water.

Synthesis of Fe(III) (1,10-phen)$_3(ClO_4)_3$: 6.950 g of $FeSO_4*7H_2O$ (25.0 mmol) in 250 mL of distilled water was added to 1.49 g of 1,10-phenanthroline (7.50 mmol) resulting in a deep red solution. 0.633 g of $LiClO_4$ (5.95 mmol) was added to the reaction mixture and stirred for 1 hr. The red precipitate was collected by vacuum filtration to yield 2.30 g (2.01 mmol, 81%) of Fe(II) (1,10-phen)$_3$ $(ClO_4)_2$. Oxidation of 1.99 g (2.50 mmol) Fe(II) (1,10-phen)$_3$ $(ClO_4)_2$ with 1.01 g of $Ce(SO_4)_2*4H_2O$ (2.50 mmol) in 250 mL of 6 N H_2SO_4 gave a blue solution. Addition of 0.633 g of $LiClO_4$ (5.95 mmol) to this solution gave 1.23 g (1.37 mmol, 55%) of blue crystals of Fe(III) (1,10-phen)$_3(ClO_4)_3$ which were collected by vacuum filtration and washed with water.

Synthesis of 1,2-Di-(1-naphthyl)-1,2-diphenylethane (1b): **1b** was prepared by the McMurry method.[66] Titanium trichloride (8.9 g, 58 mmol) was weighed under dry nitrogen in a glove bag and placed under nitrogen in a 250 mL three-neck flask with 100 mL of dry glyme. $LiAlH_4$ (750 mg, 9.7 mmol) was quickly added to the stirred $TiCl_3$ slurry, and the resulting black suspension was stirred for 10 min before use. Naphthyl phenyl methanol (3.6 mmol) in several mL of glyme was then added, and the reaction mixture was refluxed for 16 h. After cooling, the reaction mixture was quenched by addition of dilute aqueous HCl, further diluted with water, and extracted with ether. The ether extracts were combined, washed with brine, dried ($MgSO_4$), filtered, concentrated *in vacuo*, and purified by crystallization from ethanol to yield colorless crystals of the desired compound. **1b**, mp: 220-222°C, lit., 223-224^{0}C[67]; ^{1}H NMR (270 MHz, $CDCl_3$) δ (ppm) 8.31 (d, 2H), 6.79-7.81 (m, 22H), 5.61 (s, 2H); ^{13}C NMR (270 MHz, $CDCl_3$) δ (ppm) 142.9, 138.2, 134.0, 131.9, 129.0, 128.9, 128.7, 128.5, 127.8, 126.8, 126.0, 125.6, 125.2, 125.0, 124.8, 123.5, 52.1.

Synthesis of 1,2-Diphenylcyclopentene and 1,2-Diphenylcyclohexene : The preparation of 1,2-Diphenylcyclopentene and 1,2-Diphenylcyclohexene was carried out by the method of Mc Murry.[68] 2.05 g of $LiAlH_4$ was added to 19.5 g of $TiCl_3$ in about 500 mL of dry THF under N_2. The resulting black mixture was heated under reflux for 15 min. 7.0 g of 1,3-dibenzoylpropane or 6.0 g of 1,4-dibenzoylbutane was added and the mixture was heated under reflux for 24 hr. The reaction mixture was diluted with water and extracted with diethyl ether. The organic layer was washed with water, saturated NaCl, and dried with Na_2SO_4. Removal of solvent at reduced pressure yielded a crude oil which was purified by column chromatography (silica gel, petroleum to yield desired product. Diphenylcyclopentene, mp: 63-64 °C, lit., 62.5-63 °C[69]; NMR (270 MHz, $CDCl_3$) δ (ppm) 2.1 (m, 2H), 2.9 (t, 4H), 7.19 (s, 10H); low-resolution MS, base and parent 220. Diphenylcyclohexene, mp: 47-48 °C, lit., 48-48.5 °C[70]; NMR (270 MHz, $CDCl_3$) δ (ppm) 1.8 (m, 4H), 2.43 (m, 4H), 7.0 (s, 10H); low-resolution MS, base and parent 234.

Synthesis of Cis-1,2-Diphenylcyclopentane (14) and 1,2-Diphenylcyclohexane (9): A solution of 1,2-Diphenylcyclopentene or 1,2-Diphenylcyclohexene (500 mg) in absolute ethanol (20 mL) was hydrogenated[71] at ambient temperature and pressure using 10% palladium on charcol (100 mg) as catalyst. The mixture was filtered after the hydrogenation was over, evaporated to dryness. The residue was purified by column chromatography (silica gel, petroleum ether) to yield desired product. Diphenylcyclopentane, mp:45-47 °C, lit., 45.8-47 °C[72] ; ^{1}H NMR (270 MHz, $CDCl_3$) δ (ppm) 2.08 (m, 6H), 3.42 (t, 2H), 6.91 (m, 10H); ^{13}C NMR (270 MHz, $CDCl_3$) δ (ppm) 142.5, 128.5, 127.4, 125.5, 50.9, 30.4, 23.8; low-resolution MS, parent 234. Diphenylcyclohexane, mp: 46-47 °C, lit., 46 °C[73]; ^{1}H NMR (270 MHz, $CDCl_3$) δ (ppm) 1.98 (m, 8H), 3.20 (t, 2H), 7.07 (10H); ^{13}C NMR (270 MHz, $CDCl_3$) δ (ppm) 142.8, 128.6, 128.2, 126.8, 48.3, 29.1, 22.9; low-resolution MS, parent 236.

Synthesis of methyl 2-phenylcyclopentyl ether (20) and methyl 2-phenylcyclohexyl ether (17): The methyl 2-phenylcyclopentyl ether and methyl 2-phenylcyclohexyl ether were prepared from 1-phenylcyclopentene and 1-phenylcyclohexene using the photochemical method.[74] A solution of 1-phenylcyclopentene or 1-phenylcyclohexene (200 mg) and 1,4-dicyanobenzene (150 mg) in acetonitrile-methanol (10 mL, 3:1) were degassed by bubbling nitrogen through the solution for 15 min prior to irradiation and irradiated in Pyrex tubes using a Honovia 450 W medium-pressure mercury vapor lamp for 24 hr. Flash column chromatography of the photolysate, using ethyl acetate-hexanes (5%) as eluent, yield the desired products. Methyl 2-phenylcyclopentyl ether, NMR (270 MHz, $CDCl_3$) δ (ppm) 1.65-2.01 (m, 6H), 2.98 (m, 1H), 3.82 (m, 1H), 3.15 (s, 3H), 7.18-7.30 (m, 5H); low-resolution MS, parent 176. Methyl 2-phenylcyclohexyl ether, (270 MHz, $CDCl_3$) δ (ppm) 1.35-2.06 (m, 8H), 3.04 (m, 1H), 3.09 (s, 3H), 3.49 (m, 1H), 7.21-7.29 (m, 5H); low-resolution MS, parent 190.

Carbonyl Formation Reaction from $Fe(ClO_4)_3$, Fe(1,10-phenanthroline)$_3(ClO_4)_3$: A solution of substrates (0.02 mmol) and Fe(II) or Fe(III) complex (0.04 mmol) in 1 mL of CH_3CN was prepared and added to several pyrex tubes. These tubes were degassed by using three freeze-pump-thaw degassing cycles, sealed under vacuum, and placed in a Neslab Model EX 250-HT constant temperature bath maintained at 130°C for 24 h and analyzed as described above.

Dehydrogenation of Substrates by $Fe(ClO_4)_3$, Fe(1,10-phenanthroline)$_3(ClO_4)_3$ and Fe(1,10-phenanthroline)$_3(ClO_4)_2$: A solution of substrates (0.02 mmol) and Fe(II) or Fe(III) complex (0.04 mmol) in 1 mL of CH_3CN was prepared and added to several pyrex tubes. These tubes were degassed by using three freeze-pump-thaw degassing cycles, sealed under vacuum, and placed in a Neslab Model EX 250-HT constant temperature bath maintained at 130°C for 24 h and analyzed as described above.

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CHAPTER III

2,4,6-Triphenylpyrylium Salt-Sensitized Oxygenation of Esters[D]

Abstract

A number of esters have been synthesized. Sensitized irradiation of these compounds using 2,4,6-triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$) in acetonitrile in the presence of O_2 resulted in C-C bond cleavage reactions, yielding the corresponding aldehydes or ketones. A radical chain mechanism has been proposed for the reactions.

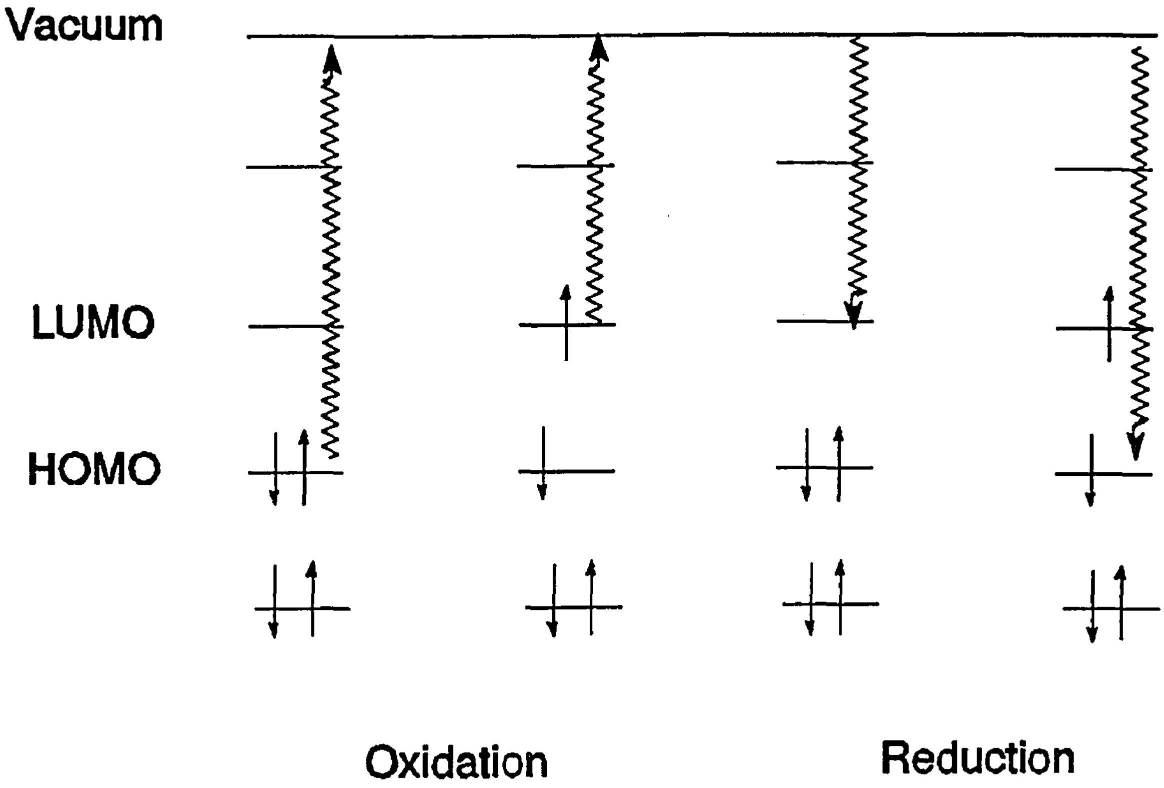
[D] Penn, J. H.; Wang, J. *J. Am. Chem. Soc.* submitted.

Introduction

1. Radical Cation Chemistry

Radical cations, their structures and their reactions have been attracting ever increasing attention over the last decade.[1] They are important intermediates in a wide variety of chemical and biological processes, encompassing photosynthesis[2] and interstellar chemistry[3] and ranging from conducting polymers[4] to synthetically useful reactions, such as electron transfer induced anti-Markovnikov additions[5], cation radical Diels-Alder reactions,[1g] or nucleophilic substitution reactions.[6] In addition, they command attention because of a multitude of unusual structure types and a variety of interesting reactions.

Radical cations are formed by the removal of one electron from a neutral molecule. One electron oxidations may be achieved with a variety of chemical oxidants,[7] electrochemical techniques, [8] pulse radiolysis,[9] electron impact ionization,[10] and photoinduced electron transfer. The latter is a mild and versatile method for the generation of radical cation-radical anion pairs in solution.[11] This method utilizes the fact that the oxidative power of an acceptor and the reductive power of a donor are substantially enhanced by photoexcitation (Scheme 1). Thus, for donor-acceptor pairs with negligible or weak interactions in the ground state, electronic excitation of either reactant may lead to the generation of radical ion pairs via electron transfer. For the study of radical cations it is advantageous to excite an acceptor (eq 1, Scheme 2). Depending on the nature of the acceptor and its lifetime, it will be quenched before or after intersystem crossing to the triplet state. In Scheme 2, the reaction is formulated for triplet quenching (eq 2), which



Scheme 1

generates radical ion pairs of triplet spin multiplicity. Even so, the resulting radical ions have limited lifetimes since the pairs readily undergo intersystem crossing (eq 3), followed by recombination of the singlet pairs (eq 4) or separation by diffusion (eq 5) to generate "free" radical ions. The most common triplet state electron acceptors are ketones and quinones, where aromatic hydrocarbons, often bearing one or more cyano groups, are the most frequently used singlet state electron acceptors. For the generation of radical cations from a given donor it is important that the exothermicity of the electron transfer be adjusted to fall within an appropriate range, typically between 0.2 and 1.0 eV. The change in free

$$A \longrightarrow {}^{1}A^{*} \longrightarrow {}^{3}A^{*} \tag{1}$$

$${}^{3}A^{*} + D \longrightarrow {}^{3}\overline{A^{\bullet -}D^{\bullet +}} \tag{2}$$

$${}^{3}\overline{A^{\bullet -}D^{\bullet +}} \longrightarrow {}^{1}\overline{A^{\bullet -}D^{\bullet +}} \tag{3}$$

$${}^{1}\overline{A^{\bullet -}D^{\bullet +}} \longrightarrow A + D \tag{4}$$

$${}^{3}\overline{A^{\bullet -}D^{\bullet +}} \longrightarrow {}^{2}A^{\bullet -} + D^{\bullet +} \tag{5}$$

Scheme 2

energy (ΔG) for an electron transfer reaction is given by the Rehm-Weller equation[12] (eq 6)

$$\Delta G = -E_T - E_{red} + E_{ox} - e^2/\epsilon a \tag{6}$$

where E_T is the excited state energy (0-0 transition), E_{ox} is the one-electron oxidation potential of the donor, E_{red} is the one-electron reduction potential of the acceptor, and $e^2/\epsilon a$ is the Coulomb term which accounts for ion pairing. Alternatively, one can define the

Table 1. Reduction potential of selected electron acceptors

Acceptor	$E_{A/A}$[b]	$E_{(0,0)}$[c]	$^3E^*$[d]	$^*E_{A/A}$[e]
Singlet acceptors				
2,4,6-Triphenylpyrilium tetrafluoroborate	-0.29[13]	2.8[14]		2.5
2,6,9,10-Tetracyanoanthracene	-0.45[14]	2.82[14]		2.35
1,2,4,5-Tetracyanobenzene	-0.65[14]	3.83[14]		3.2
9,10-Dicyanoanthracene	-0.89[14]	2.88[14]		2.0
1,4-Dicyanonaphthalene	-1.28[14]	3.45[14]		2.15
9-Cyanoanthracene	-1.39[14]	2.96[14]		1.55
p-Dicyanobenzene	-1.60[14]	4.29[15]		2.7
9-Cyanophenanthrene	-1.88[16]	3.42[14]		1.55
1-Cyanophthalene	-1.98[17]	3.75[14]		1.75
2-Cyanonaphthalene	-2.13[17]	3.68[14]		1.55
Naphthalene	-2.50[18]	3.97[14]		1.45
Phenanthrene	-2.45[18]	3.58[14]		1.15
Anthracene	-1.96[18]	3.28[14]		1.3
Triplet acceptors				
Chloranil	+0.02[18]		2.7[19]	2.7
Benzoquinone	-0.54[18]		2.95[19]	2.4
Anthraquinone	-0.94[20]		2.72	1.8
Benzil	-1.50		2.36	0.85
Benzophenone	-2.16		2.95	0.8

---

[b] Half wave reduction potential (V) vs SCE

[c] Singlet energy (eV) from the 0,0 transition of the fluorescence spectrum

[d] Triplet energy (eV)

[e] Excited state reduction potential

the reduction potential of the acceptor excited state: (eq 7)

$$E^{*}_{red} = -E_{T} + E_{red} \tag{7}$$

The application of PET is limited to the oxidation of substrates with oxidation potentials well below the threshold value defined by E_{red}. According to eq (6), the change in free energy of the reaction can be tuned by variation of the solvent (polarity) and of the acceptor (reduction potential, excited-state energy). For a given class of acceptors, the excited state energies typically vary over a narrow range, whereas the reduction potentials can be altered substantially by the introduction of appropriate substituents (Table 1). Therefore, it does not generally present a problem to adjust the exothermicity to an appropriate range.

Radical cations have been involved in carbon-carbon bond cleavage reactions.[21] The photoinduced electron transfer (PET) reaction of 2,2-diphenylethyl-2-propylmethylether in acetonitrile-methanol solution using 1,4-dicyanobenzene as a sensitizer has been reported by Arnold and co-workers[22,23] to provide heterocyclic C-C bond cleavage to give the benzhydryl radical and an α-alkoxy carbocation (Figure 1). The benzhydryl radical is then reduced to the benzhydryl anion by back electron transfer from the dicyanobenzene radical anion. Protonation then forms diphenylmethane.

Pinacol derivatives also undergo cleavage in the presence of an Fe(III) complex[24] or singlet 1,4-dicyanonaphthalene:[25] (Scheme 3)

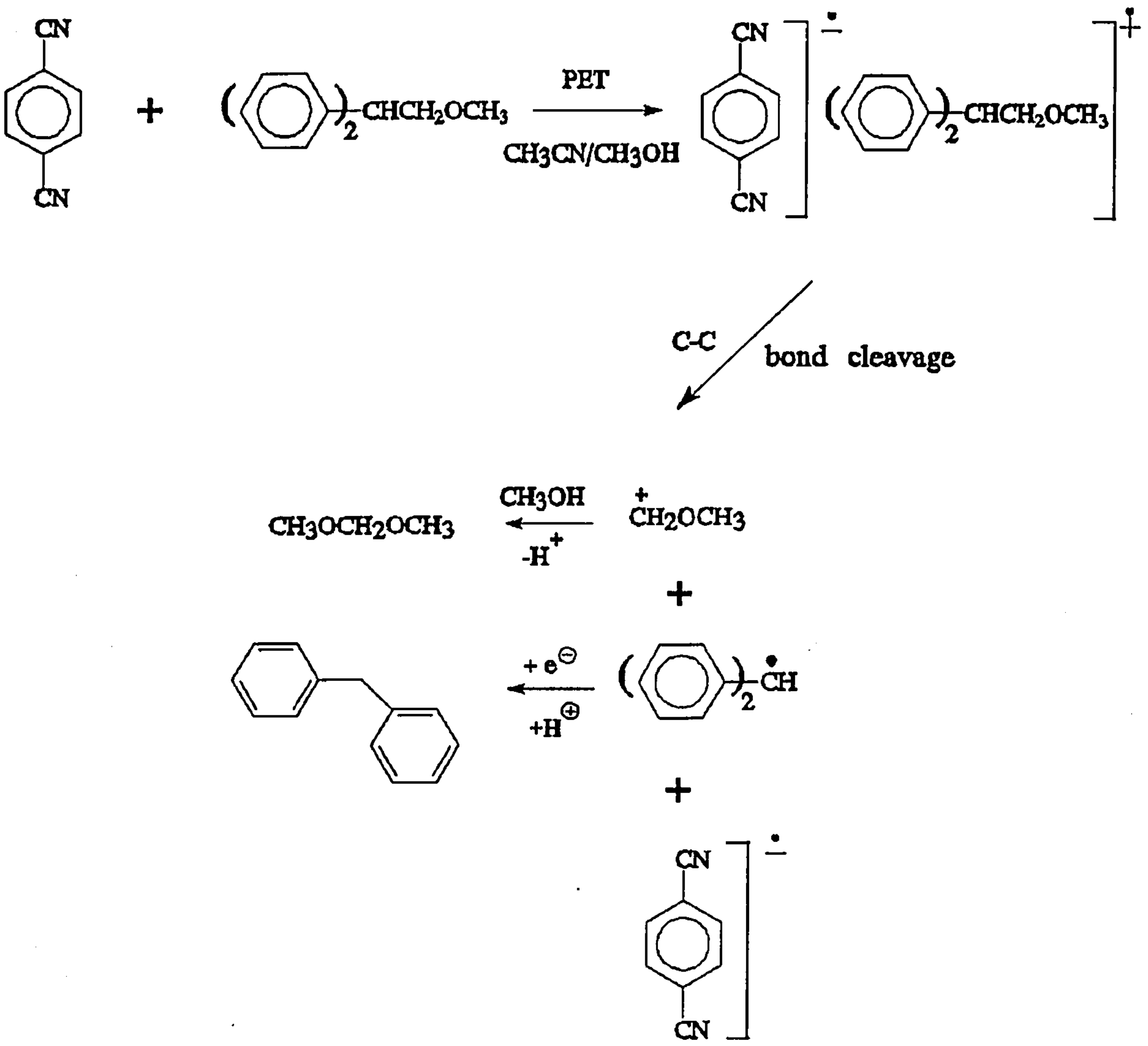
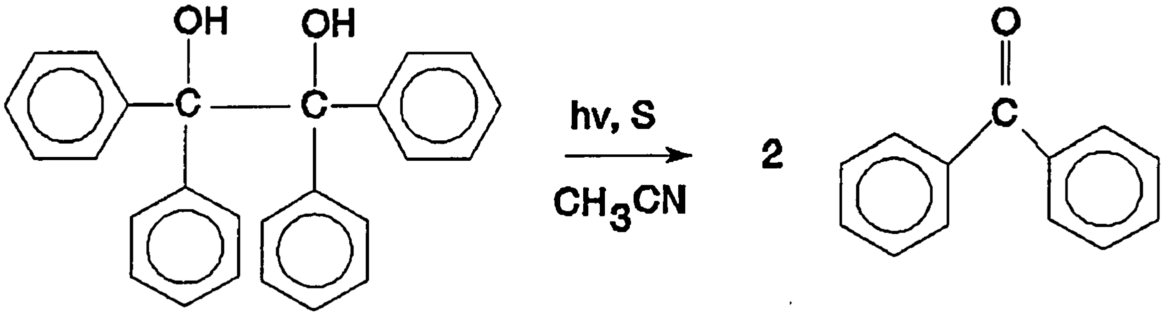
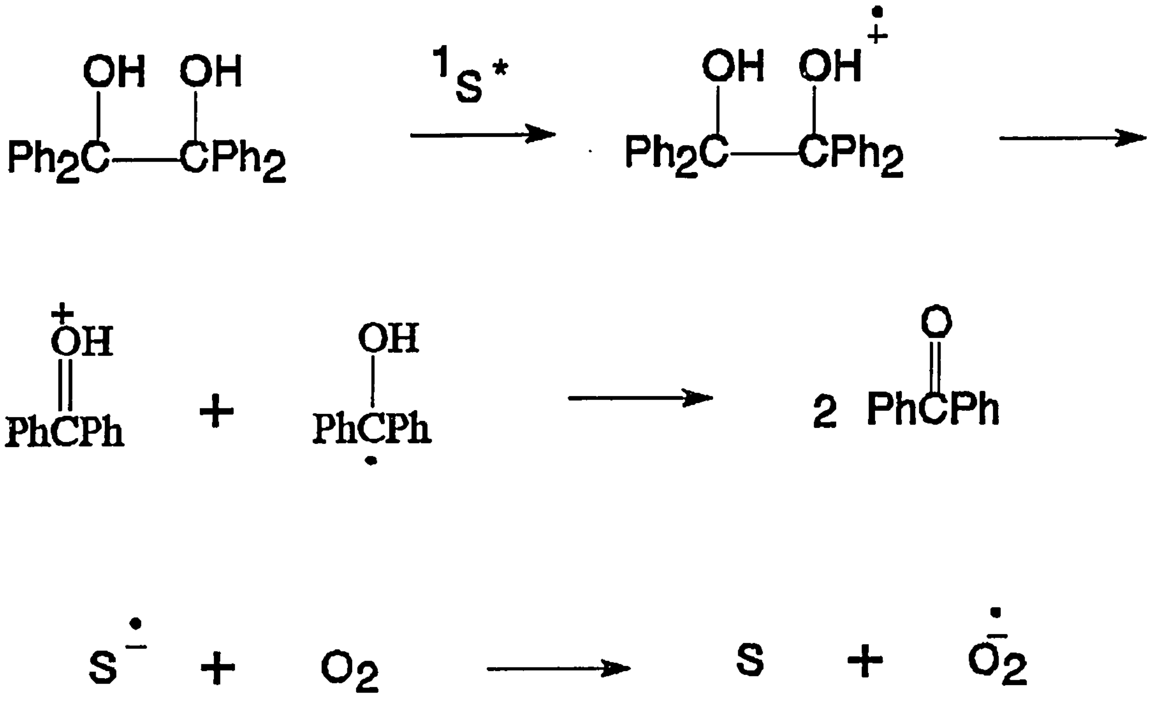


Figure 1. Photoinduced Electron Transfer Reaction of 2,2-Diphenylethyl-2-propylmethylether



S=1,4-dicyanonaphthalene

Scheme 3

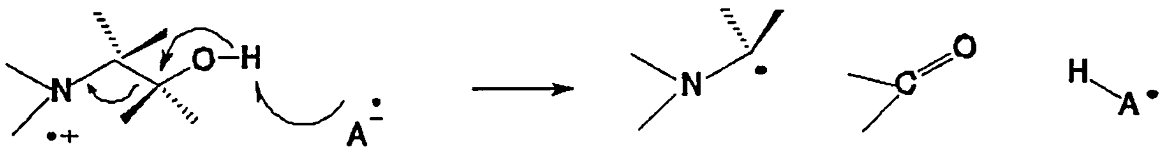


Scheme 4

The effeciency of the above reaction is enhanced in the presence of O_2 because electron transfer from the radical anion of dicyanonaphthalene to oxygen produces the superoxide ion ($O_2^{\bullet-}$), which is a less efficient electron donor to the radical. This increases the opportunity for fragmentation by prolonging the lifetime of the radical cation because back electron transfer is made less feasible (Scheme 4).

More recently, a variety of C-C cleavage reactions were discovered in α, β-bifunctional substrates, viz., diamines or aminoalcohols, and their benzologs.[26] These reactions are initiated by electron transfer from the substrate to a photoexcited acceptor. Subsequently, the acceptor radical anion abstracts a proton from the functional heteroatom in the γ-position, leading to fragmentation. A moderate isotope effect on the fragmentation efficiency and a correlation with the radical (eq 8) anion basicity suggest that

(8)

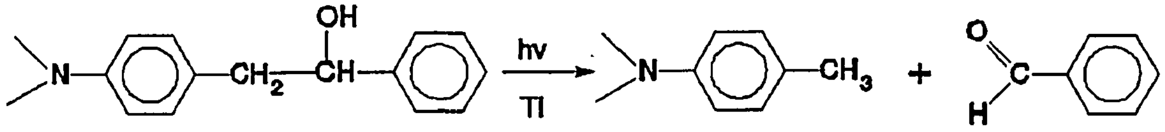


the proton is removed in the rate-determining step, possibly concerted with C-C cleavage, although not necessarily synchronous with it. The relative fragmentation rates of chiral aminoalcohols (erythro substrates undergo fragmentation more readily than threo compounds) support an anti-coplanar conformation as the optimum geometry for the fragmentation.[18b,c]

The fragmentation leads to the simultaneous generation of two neutral radicals in close proximity, separated only by the carbonyl product. Depending on the nature of the substrate, these fragments may react by hydrogen atom transfer, either to the aminoalkyl(benzyl)radical or to the sensitizer derived radical. Accordingly, the acceptor can act either as a sensitizer or undergo two-electron reduction. In general, the increased efficiency of C-C bond cleavage observed for these substrates can be ascribed to two features: a weakened C-C bond in the radical cation due to the presence of the second functional group; and the greater acidity of the N-H or O-H functions compared to the α-C-H acidity of the aminium radical cation.

These reactions are illustrated with the fragmentation of two isomeric aminoalcohols

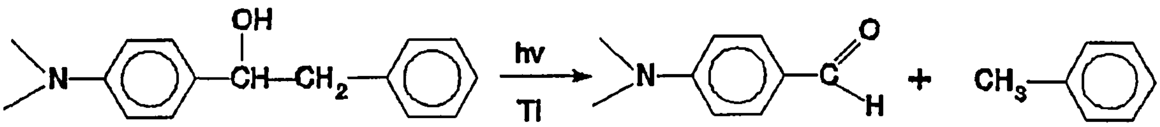
(9)



and one aminodiol (eq 9), which have been observed upon thioindigo sensitized irradiation in benzene solution.[18c] Under these conditions, the (p-N,N-dimethyl-aminobenzyl) benzyl alcohol suffers fragmentation with apparent internal disproportionation; the benzyl alcohol function is oxidized, whereas the p-aminobenzyl function is reduced, giving rise to N,N-dimethyl-p-toluidine and benzaldehyde. The acceptor is involved only as a sensitizer and, hence, remains unchanged.

The benzyl p-dimethylaminobenzyl alcohol is fragmented similarly with formation of p-(N,N-dimethylamino)benzaldehyde and toluene. Once again, the benzyl alcohol function is oxidized, the second benzyl function is reduced, and the acceptor remains unchanged; it is involved only as a sensitizer (eq 10).

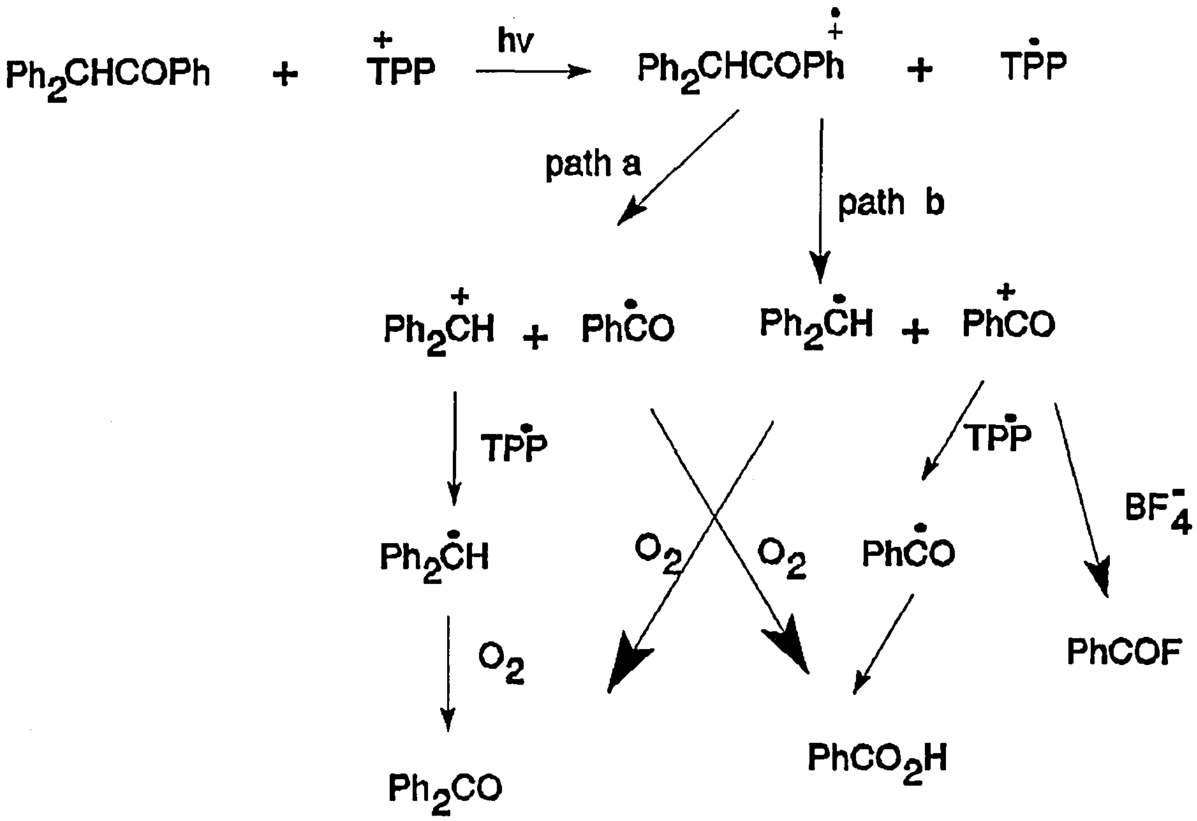
(10)



It has also been recently reported that a radical cation was involved in the photoinduced electron transfer C-C bond cleavage of ketones and aldehydes.[27] In this work, a 2,4,6-triphenylpyrylium salt was used as a sensitizer. The photoinduced electron transfer of 1,2,2-triphenylethanone with the 2,4,6-triphenylpyrylium salt gave rise to to a radical cation of the ketone which was observed by laser flash photolysis. The radical cation of the ketone was rationalized to undergo C-C bond cleavage in CH_2Cl_2 to afford the diphenylmethyl radical or cation and the benzoyl radical or cation. The benzoyl cation or diphenylmethyl cation would then be reduced by TPP• to yield the benzoyl radical and diphenylmethyl radical. The benzoyl radical or diphenylmethyl radical can react with the oxygen to give the corresponding benzoic acid and benzophenone (Scheme 5).

2. C-C Bond Cleavage of Esters

Esters and lactones give α-cleavage of either the carbonyl-oxygen bond or the carbon-carbonyl bond on irradiation. Simple alkyl esters yield carbonyl-carbon bond cleavage as the



Scheme 5

major primary processes.[28] For example, γ-butyrolactone undergoes α-cleavage on either side of the carbonyl group as shown in Fig. 2.[29] Cleavage of the oxygen-carbonyl bond gives a dialdehyde as a minor reaction product. α-Cleavage of the carbonyl-carbon bond is much more efficient than cleavage of the carbonyl-oxygen bond as was shown by the quantum yield of both reactions.

Dihydrocoumarin[30] undergoes only carbonyl-oxygen cleavage to yield a ketene which subsequently reacts with water to give a carboxylic acid (eq 11).

Photoreaction of phenyl esters gives o- and p-acylphenols together with some of the parent phenol. This reaction is known as the photo-Fries rearrangement.[31] The reaction is an intramolecular process proceeding by way of homolytic α-cleavage, followed by in-cage recombination of the radicals. Phenoxyl radicals can escape from the cage and abstract hydrogen to form phenol as shown in Fig. 3.

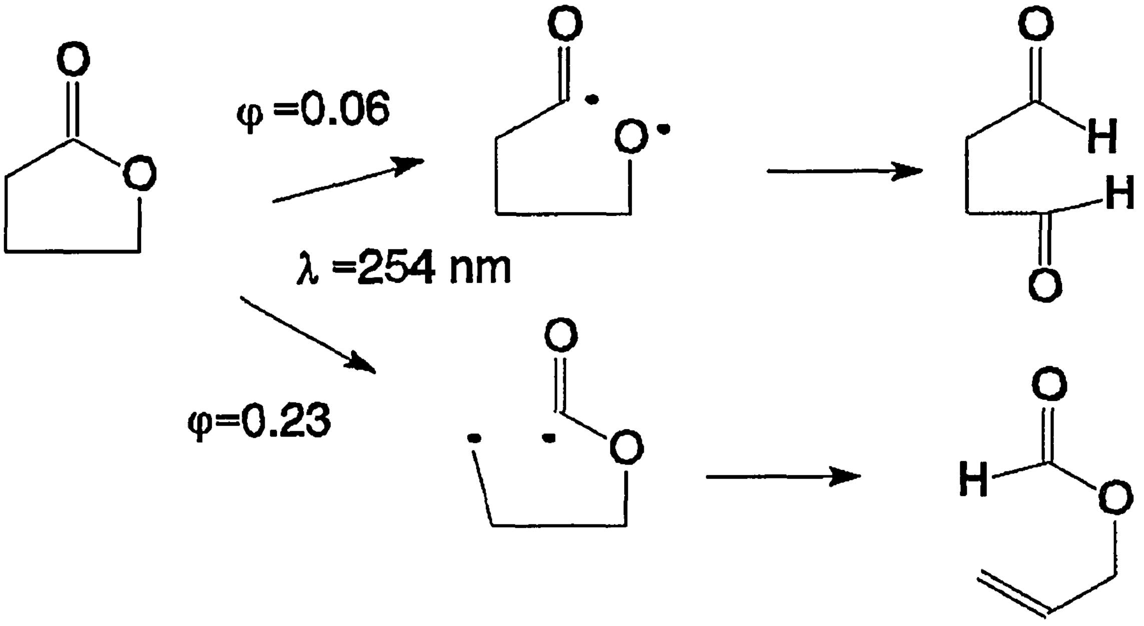
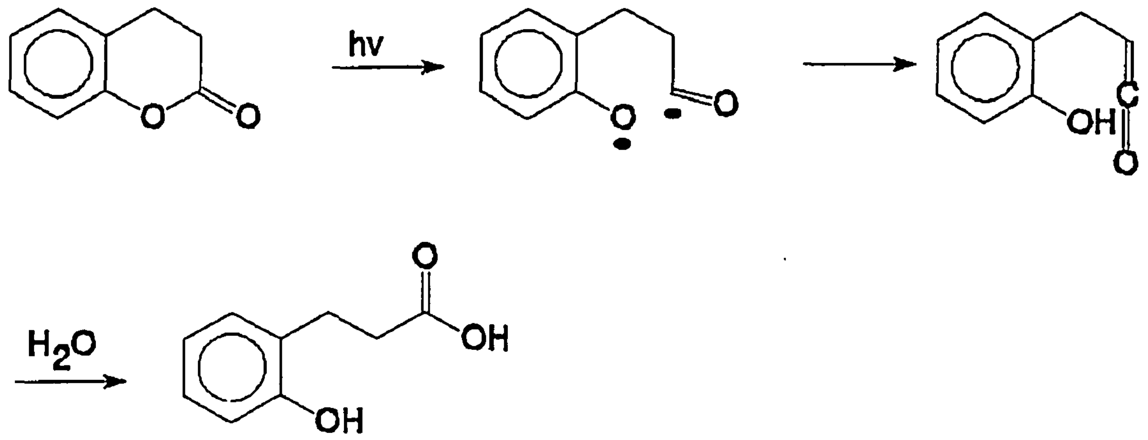


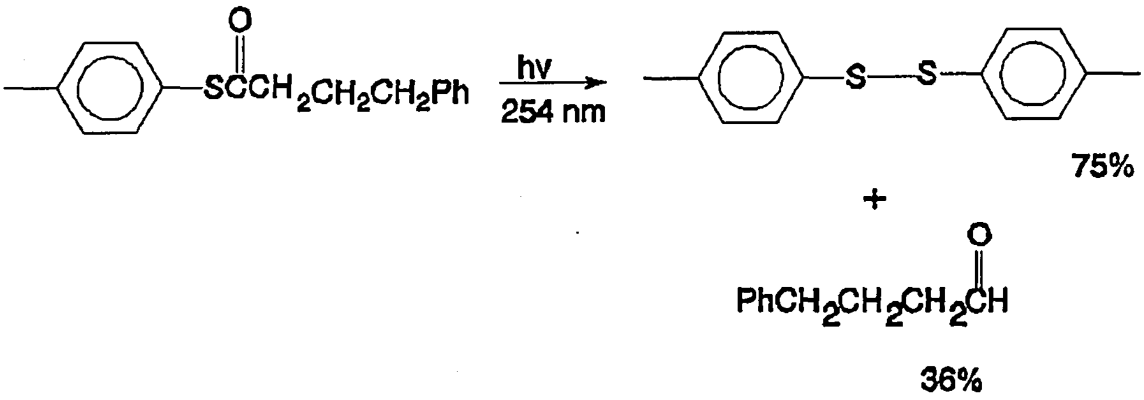
Figure 2. Photochemical Reactions of γ-Butyrolactone.

Thioesters provide another example of compounds where α-bond fission is the predominant photochemical process. The major products are usually[32] an aldehyde formed by hydrogen abstraction of the acyl radical and a disulfide formed by combination of two thio radicals (eq 12).

(11)



(12)



Like esters, amides undergo α-cleavage reactions on irradiation. The carbonyl-nitrogen bond cleaved when N,N-dimethylbenzamide was irradiated[33] in the presence of 1,1-diphenylethylene, and the product is formed by trapping of the benzoyl radical with 1,1-diphenylethylene (eq 13).

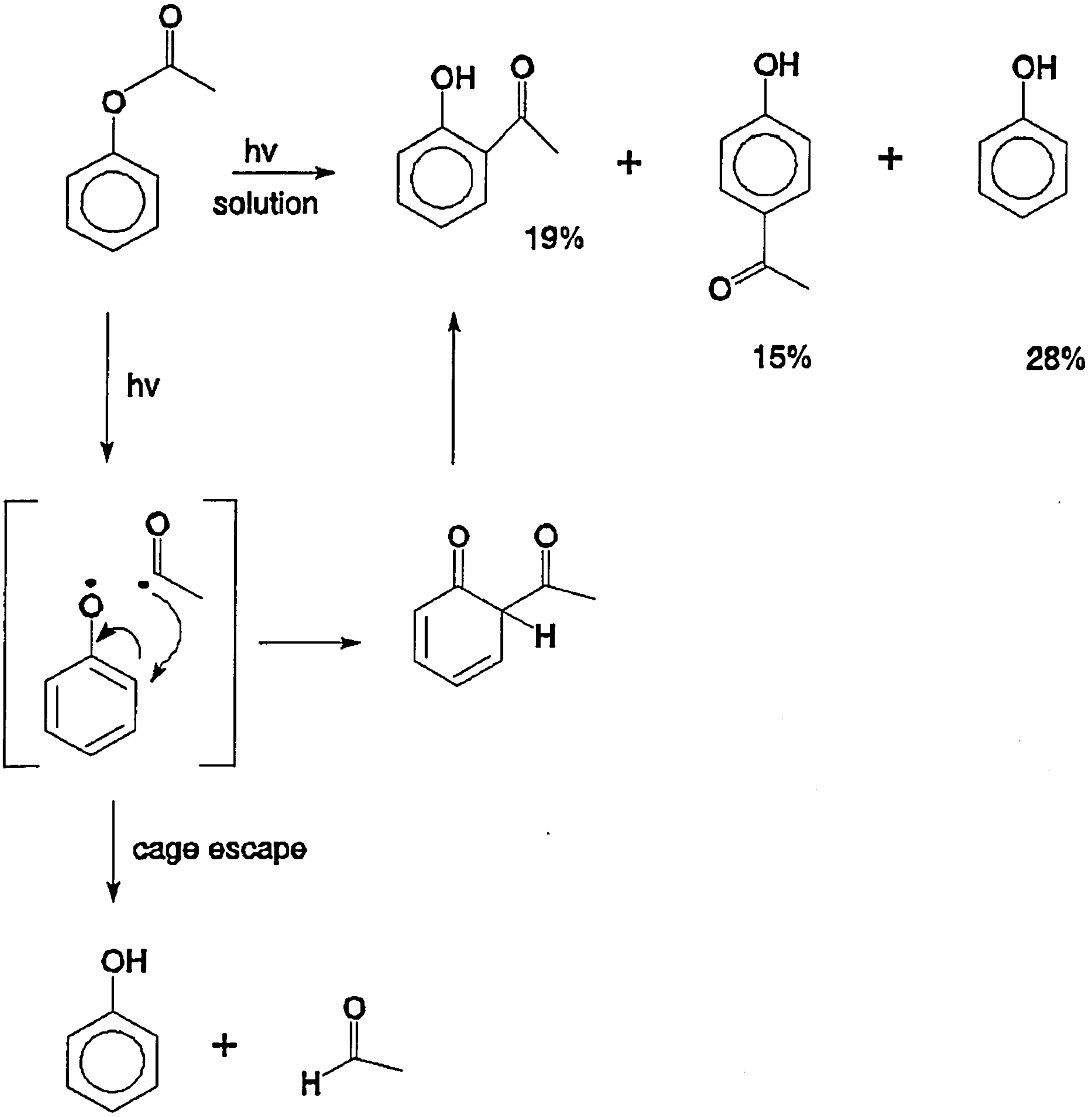
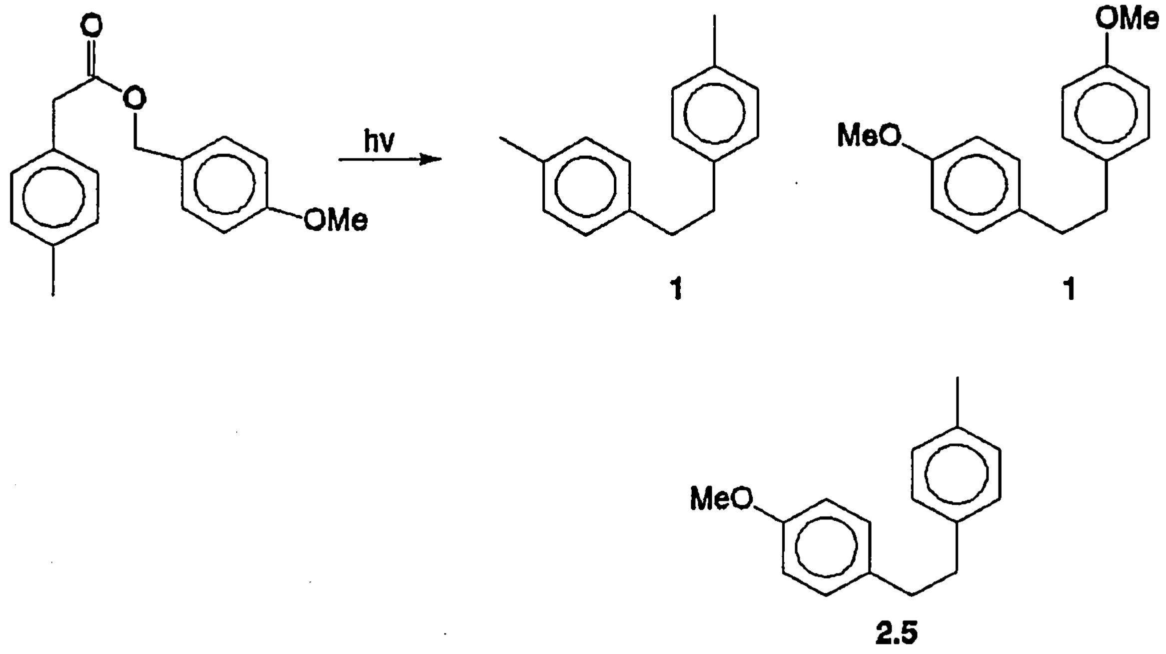


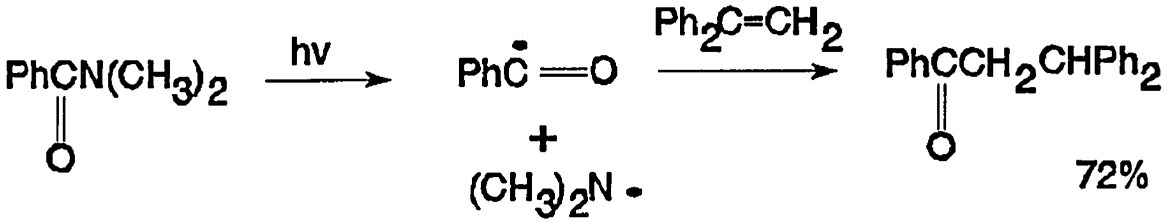
Figure 3. Photo-Fries Rearrangement of Phenylesters.

Esters have also shown to undergo the cleavage of the bonds β to the carbonyl group. For example, p-methoxybenzyl p-methylphenylacetate gives a β-cleavage reaction followed by the lose of CO_2 resulting in a variety of hydrocarbon products[34] as shown

(14)



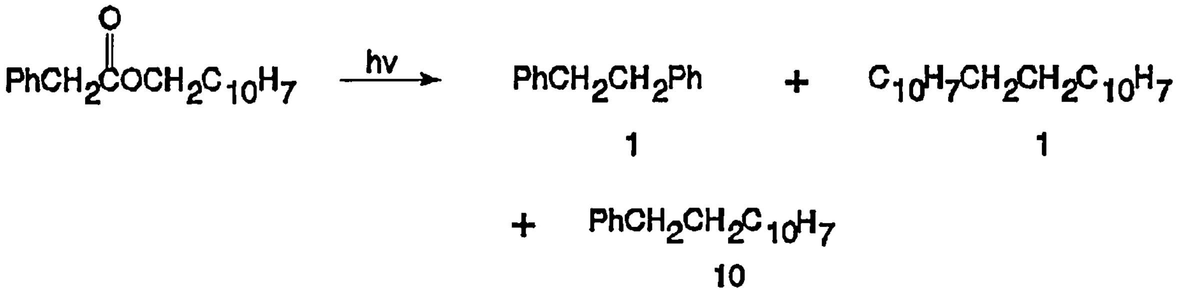
(13)



$$\mathrm{PhC(=O)N(CH_3)_2} \xrightarrow{h\nu} \mathrm{Ph\dot{C}{=}O} + \mathrm{(CH_3)_2N\cdot} \xrightarrow{\mathrm{Ph_2C{=}CH_2}} \mathrm{PhC(=O)CH_2CHPh_2}\quad 72\%$$

in eq 14. The reaction follows a pathway which involves a β-cleavage followed by decarboxylation to form two radicals that can combine to form a mixed product or can diffuse into the solvent to combine in a statistical fashion. The driving force for this reaction is related to two factors. The radical formed by the β-cleavage is stabilized by the extended resonance capabilities for the benzyl and the carboxyl portions of the molecule. The loss of CO_2 provides for an entropic factor and allows for an aditional thermodynamic driving force. Some esters, such as α- or β-naphthylmethyl phenylacetates, give a mixture of hydrocarbons which consists mainly of the unsymmetrical compound.[35] In this case the reaction cannot be quenched by triplet quenchers, and it is likely that a solvent cage effect is operating with the majority of radicals combining within the cage (eq 15).

(15)



$$PhCH_2\overset{O}{\overset{\|}{C}}OCH_2C_{10}H_7 \xrightarrow{hv} \underset{1}{PhCH_2CH_2Ph} + \underset{1}{C_{10}H_7CH_2CH_2C_{10}H_7} + \underset{10}{PhCH_2CH_2C_{10}H_7}$$

The reactions of these esters show a different reactivity when a different solvent was used. Pincock and DeCosta[36] have recently described photoinduced bond cleavage reactions in a series of naphthylmethyl esters to produce both ionic and radical products. The authors

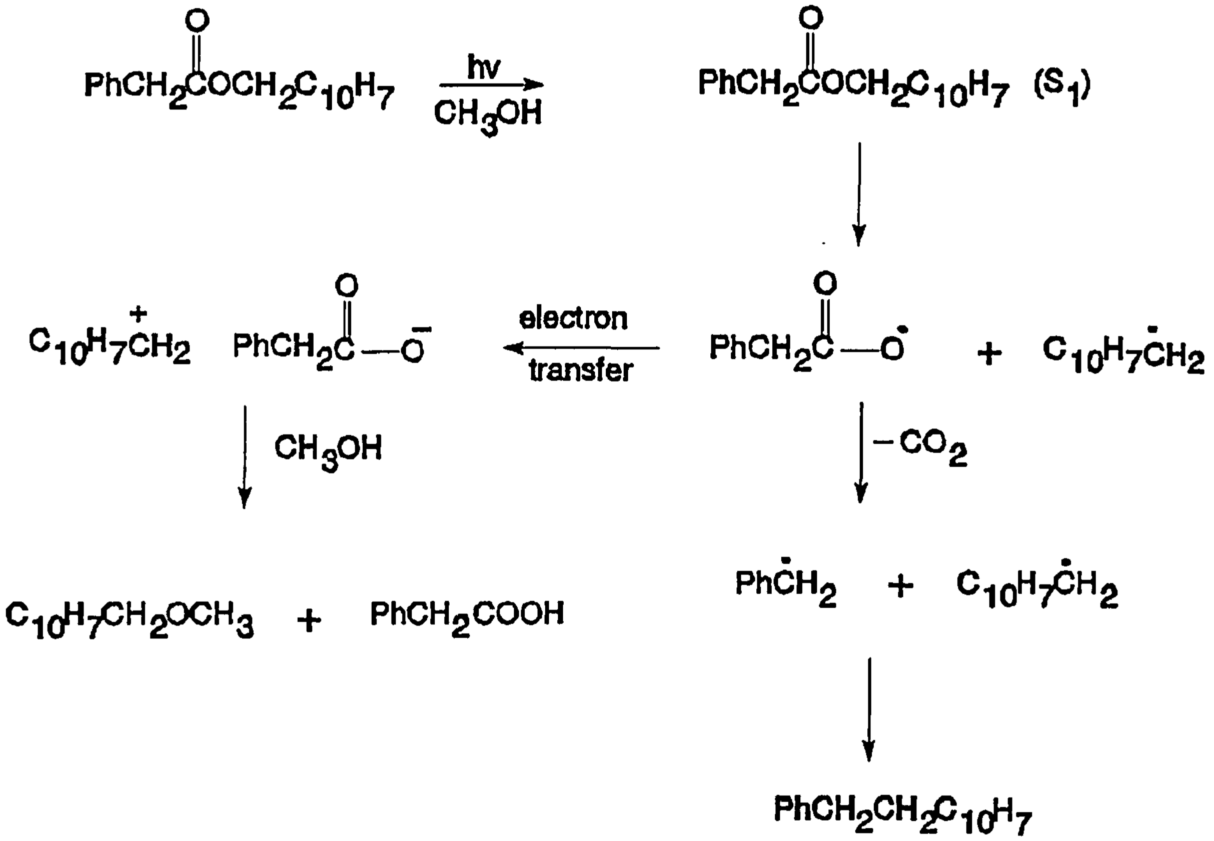
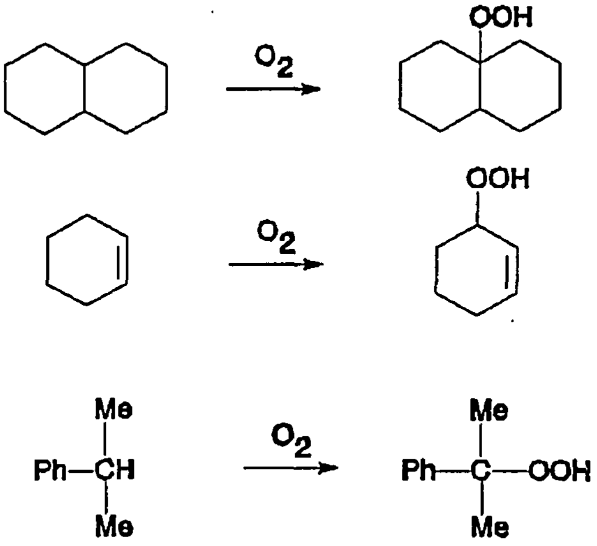


Figure 4. Photochemical Reactions of naphthylmethyl benzylacetate.

attributed their results to excited state homolysis to form a caged radical pair (the 1-naphthylmethyl radical/acyloxy radical pair) and electron transfer between the radicals to form an ion pair (1-naphthylmethyl cation/carboxylate anion ion pair). The radical pair results in formation of the in-cage coupled products after loss of carbon dioxide from the acyloxy radical. The ion pair leads to the methyl ethers and the carboxylic acids. The competition between the radical and ionic pathways is very dependent upon the substituents on the naphthalene ring. Analysis of these substituent effects resulted in a proposed mechanism of initial homolytic cleavage of the carbon-oxygen bond of the ester from the excited singlet state. The radical pair then partitions between two pathways: decarboxylation of the acyloxy radical and electron transfer converting the radical pair to the ion pair. The rates of electron transfer were shown to fit Marcus theory in both the normal and the inverted region (Fig. 4).

3. Autoxidation

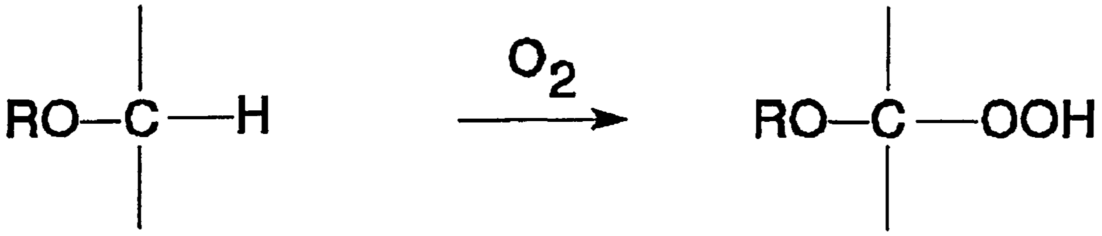
The slow atmospheric oxidation of a wide variety of organic compounds in the liquid phase under mild conditions (less than 150 to 200 ^{0}C) to hydroperoxides is called autoxidation.[37] The reactions occur when compounds are allowed to stand in air and are catalyzed by light, so that unwanted autoxidations can be greatly slowed by keeping the compounds in dark places. The hydroperoxides produced often react further to alcohols, ketones, aldehydes, acids and more complicated products, so that the reaction is not often used for preparative purposes, although in some cases hydroperoxides have been prepared in good yield.[38] It is because of autoxidation that foods, rubber, paint, lubricating oils, etc. deteriorate on exposure to the atmosphere over periods of time. On the other hand, a useful application of autoxidation is the atmospheric drying of paints and varnishes. As with other free-radical reactions of C-H bonds, some bonds are attacked more readily than others,[39] aithough the selectivity is very low at high temperatures and in the gas phase. The reaction can be carried out successfully at tertiary (to a lesser extent, secondary(, allylic (though allylic rearrangements are common), and benzylic R.[40] Scheme 6 shows actual examples:



Scheme 6

Another susceptible position is aldehyde C-H, but the peracids so produced are not easily isolated[41] since they are converted to the corresponding carboxylic acids. The α positions of ethers are also easily attacked by oxygen: (eq 16)

(16)



$$RO-C-H \xrightarrow{O_2} RO-C-OOH$$

but the resulting hydroperoxides are almost never isolated. However, this reaction constitutes a hazard in the storge of ethers since solutions of these hydroperoxides and their rearrangement products in ethers are potential spontaneous explosives.[42]

Oxygen itself (a diradical) is probably unreactive to be the species that actually abstracts the hydrogen. But if a trace of free radical is produced by some initiating process, it reacts with oxygen to give peroxy radical which does abstract hydrogen. Autoxidation can be described by the following free-radical chain sequence,

Initiation: production of free radicals

Propagation: (eq 17 and 18)

$$R\bullet + O_2 \longrightarrow ROO\bullet \tag{17}$$

$$ROO\bullet + RH \xrightarrow{k_p} ROOH + R\bullet \text{ (or } ROORH\bullet\text{)} \tag{18}$$

Termination: (eq 19)

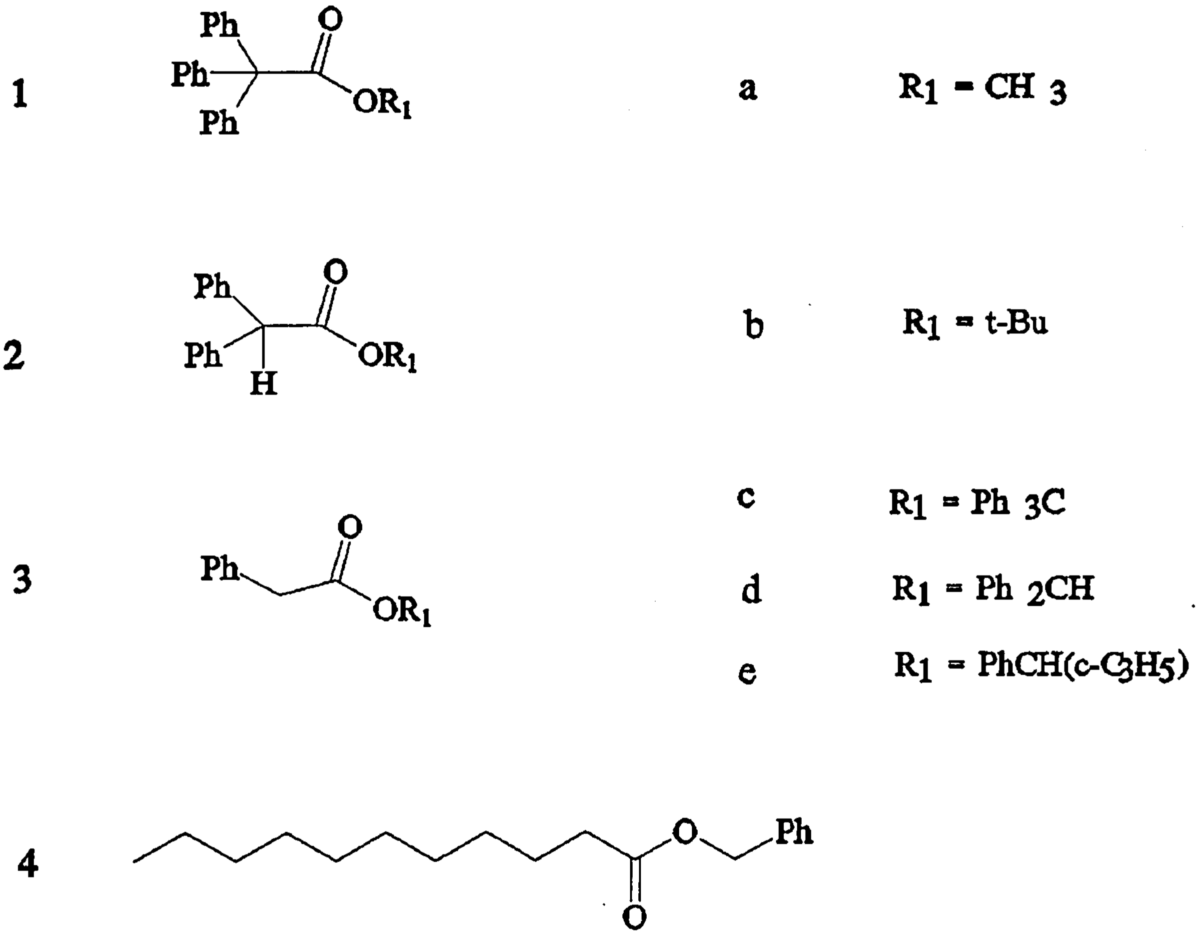
(19)

$$2\,ROO\bullet \xrightarrow{2\,k_t} \text{molecular products}$$

where RH represent an organic substrate, R● is an alkyl radical derived from the substrate, and ROO● is the peroxy radical produced by reactions of R● with molecular oxygen.

Prevention of the oxidative degradation of organic materials such as food-stuffs, petroleum products, and synthetic polymers is of considerable technological importance because desirable properties of the original material are lost by reaction with atmospheric oxygen. Inhibition[43] is usually achieved by the addition of relatively low concentrations of antioxidants which function by interfering with chain propagation, chain initiation, or more rarely, chain termination. Phenols and aromatic amines are widely used for inhibition of oxidation of hydrocarbons. They are chain-breaking antioxidants which influence the normal propagation processes either by reaction with peroxy radicals or occasionally by reaction with alkyl radicals. Reaction with a chain-propagating radical can take place by hydrogen transfer, by addition, or by electron transfer to terminate the chain or more usually to produces a new radical which either continues the chain at a reduced rate or terminates a second chain.[44] Since phenols and aromatic amines begin to lose their antioxidant efficiency at temperatures above about 100 °C, a second class of antioxidants has been developed which reduce the rate of chain initiation. These compounds are known as preventive antioxidants and can be metal ion deactivators, ultraviolet light deactivators, or peroxide decomposers. Metal ion deactivators form strong chelate complexes with metal ions and prevent the formation of the coordination complexes between metal ions and hydroperoxides or oxidizable substrates that are necessary for the transfer of an electron in the initiation reactions. Ultraviolet light deactivators are compounds such as ortho-hydroxybenzophenones which when added to an organic compound protect it from photochemical degradation by preferentially absorbing irradiation without initiating autoxidation. Peroxide decomposers react with hydroperoxides to give molecular products by a nonradical process. Organic compounds containing at least one sulfur atom are the most important antioxidants of the class.[45]

Radical cations generated by photoinduced electron transfer undergo a variety of chemical reactions. Among the competing reaction pathways, C-C bond cleavage is of particular interest since it may provide a unique opportunity to study the chemistry of free radicals and carbocations generated simultaneously. Recently it has been reported that radical cations are intermediates in the photoinduced C-C bond cleavage reactions of ketones and aldehydes and the cations formed from radical cation cleavage have been detected by the laser flash photolysis. The reaction required irradiation of these ketones and aldehydes in the presence of triphenylpyrilium salt and oxygen. However, the irradiation of these substrates in the presence of DCA did not give any sign of the reactions. This is surprising since the excited state of DCA is a very strong one electron oxidant and has been used for the C-C bond cleavage reactions of phenyl or naphthyl-containing compounds. In order to understand what really happen to these ketones and aldehydes, a series of esters were synthesized and irradiated in the presence of triphenylpyrilium salt and oxygen.



a $R_1 = CH_3$

b $R_1 = t\text{-}Bu$

c $R_1 = Ph_3C$

d $R_1 = Ph_2CH$

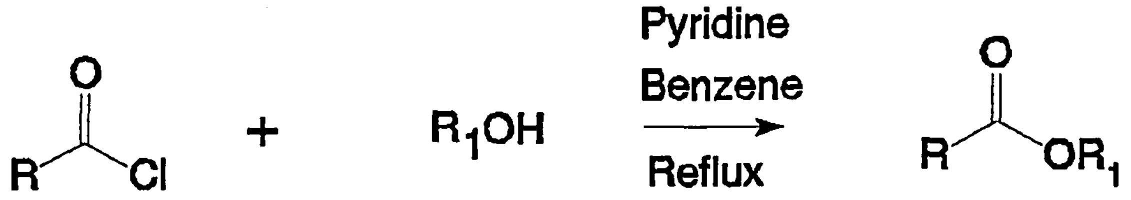
e $R_1 = PhCH(c\text{-}C_3H_5)$

Scheme 7

Results and Disscussion

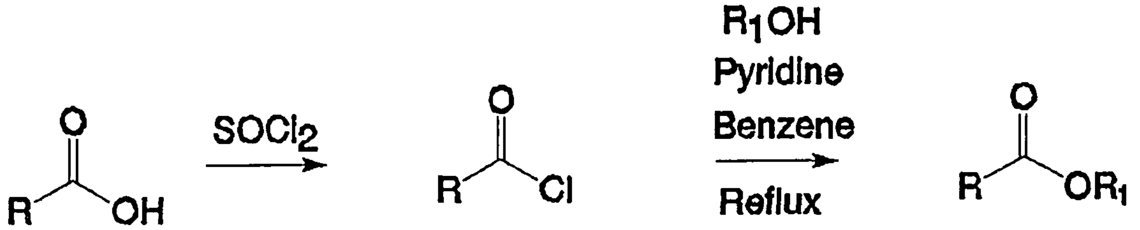
Ester Synthesis: Esters for this study were readily prepared using standard methodology.[46] When the acid chloride was commercially available, the desired esters were readily obtained in high yields by refluxing the acid chloride and the alcohol in pyridine-containing benzene solution (eq 20).[47]

(20)



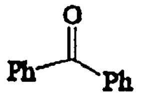
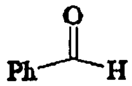
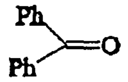
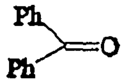
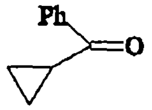
For those compounds with more sensitive functionality and for which the acid chloride was not available commercially, thionyl chloride was used to generate the acyl chloride[48] which was treated in-situ with alcohol to afford the ester with good yield (eq 21). The full range of functionality for this study is shown in Scheme 7. Further details concerning the syntheses of these compounds can be found in the Experimental Section.

(21)



Bond Cleavage Reactions of the Esters: The results of the bond cleavage reaction

Table II. Results of TPP$^+$-Sensitized Irradiation of Esters

Compound	Conversion (percent)	Cleavage Products (Yield in mole%)		
				
1a	9%	small amount		
2a	77%	88%		
2b	89%	75%		
				
3c	90%	75%		73%
3d	95%	66%		72%
3e	85%	65%		71%

for this series of esters are shown in Table II. Standard reaction conditions for these experiments were to prepare an acetonitrile solution of the ester (0.025 M), TPP$^+$ (0.015M), together with an appropriate internal standard. These solutions were irradiated with a sunlamp for three hours. Analysis of the reaction mixtures was performed by GC and GC/MS.

In the case of compound 1, only a low conversion amount (ca. 8%) was observed. The observed product (i.e., benzophenone) was exactly analogous to the product observed previously in the irradiation of 1,2,2,2-tetraphenylethanone which has been studied previously.[27] No additional products were observed. The amount of reaction from **1** was markedly different from the amount of reaction for **2** and **3**, for which high conversion amounts of oxygenated products were observed. In the case of diphenylmethyl **2**, benzophenone was the only observed product. The expected formate and/or t-butyl compounds were observed by the large solvent peak in the GC. No further effort was made to isolate the compounds arising from this part of the molecule. Benzyl compound **3** gives high yields of products corresponding to both portions of the molecule. For example, both triphenylmethyl **3c** and diphenylmethyl **3d** yield benzophenone from the O-ester portion of the molecule. Similarly, the phenylcyclopropylmethyl **3e** yields phenyl cyclopropyl ketone in high yield.

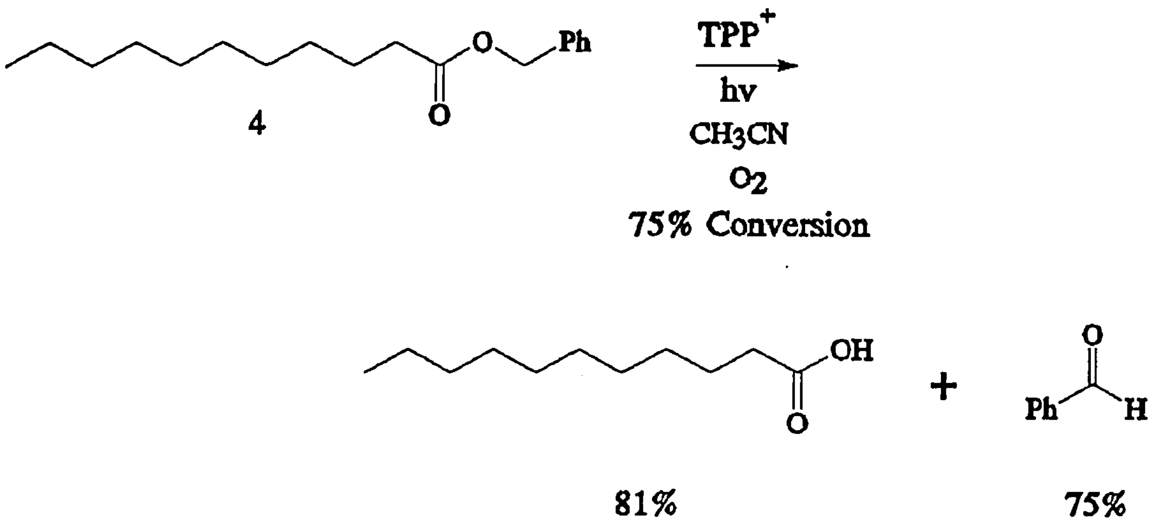
To establish several details of the reaction mechanism, control experiments were undertaken. In all cases, **2a** was used for these control experiments. When the reaction was run with the oxidizing reagent 9,10-dicyanoanthracene (**DCA**), no products were observed and the starting material was observed to be unreacted, irregardless of whether the solution was oxygenated or not. This result signifies that $\mathbf{2a}^{\bullet+}$ cannot be responsible for the bond cleavage reactivity observed. This follows from the fact that 1,1,2,2-tetraphenylethane is easily cleaved by irradiation of **DCA** under similar conditions, as we[49] and others[21b] have observed previously. Irradiation of an oxygenated solution of **2a** produced no products, signifying that a sensitizer was required for the observed bond cleavage reactions. The viability of $^1O_2$ as an intermediate in these reactions was ruled out by the fact that no products resulted from the irradiation of Rose bengal in an oxygenated solution of **2a**. The requirement for O_2 in the reaction was shown by the fact that absolutely no bond cleavage product was observed when a TPP^+ solution which had been degassed by bubbling N_2 prior to and then during the reaction. The conclusions that can be drawn from these control experiments are that TPP^+ and O_2 are required for the bond cleavage reaction and that **2a**$^{\bullet+}$ is not directly responsible for the bond cleavage products formed in these reactions.

Further constraints upon the character of the reaction can be determined from an analysis of the reactivity of **4**. In this reaction which was performed under identical conditions as the previous reactions, benzaldehyde and undecanoic acid were observed as the sole products. No decrease in the chain length of this product is observed. A high conversion amount was noted, as was a reasonable mass balance in this reaction. This result indicated to us that the phenyl group was the important directing group in the observed reactivity (eq 22).

This reactivity was reminiscent of autoxidation reactions,[37] which are controlled by a radical chain mechanism. In order to investigate the possible role of a radical chain mechanism as the origin of the bond cleavage pathways, phenol was added as a radical chain scavenger. In one set of experiments, phenol was added in a concentration approximately

equal to that of substrate **2a** (0.025 and 0.03 M, respectively). The purpose of this experiment was to ensure that most of the $TPP^{+\bullet}$ would be quenched by phenol and not by **2a**. As expected, there was absolutely no conversion of 2a to bond cleavage products. **2a** was observed to be unchanged in the reaction. Since no bond cleavage products are

(22)



observed, the phenol radical cation does not initiate the bond cleavage reaction pathway. In a second experiment with phenol, phenol was added in a concentration lower than that of **2a** (0.006 and 0.025 M, respectively). In contrast to the high conversion yield of **2a** when no phenol was added to the solution (77% conversion), only an 8% conversion of **2a** was observed under these reaction conditions. All of the phenol was completely consumed during this time. Therefore, the 8% conversion represents a maximum amount of conversion, since the bond cleavage could have begun after the phenol had been consumed in the reaction. Since phenol is well known to be a very good radical chain process terminator, we conclude that a radical chain process is involved in the bond cleavage reactions observed here.

Further support for the radical chain character of the reaction was obtained by a study of the conversion amount as a function of concentration of the substrate. These results are gathered in Table III. The chain length of a radical reaction would be expected to be

Table III. Conversion Yield as a Function of **2a** Concentration

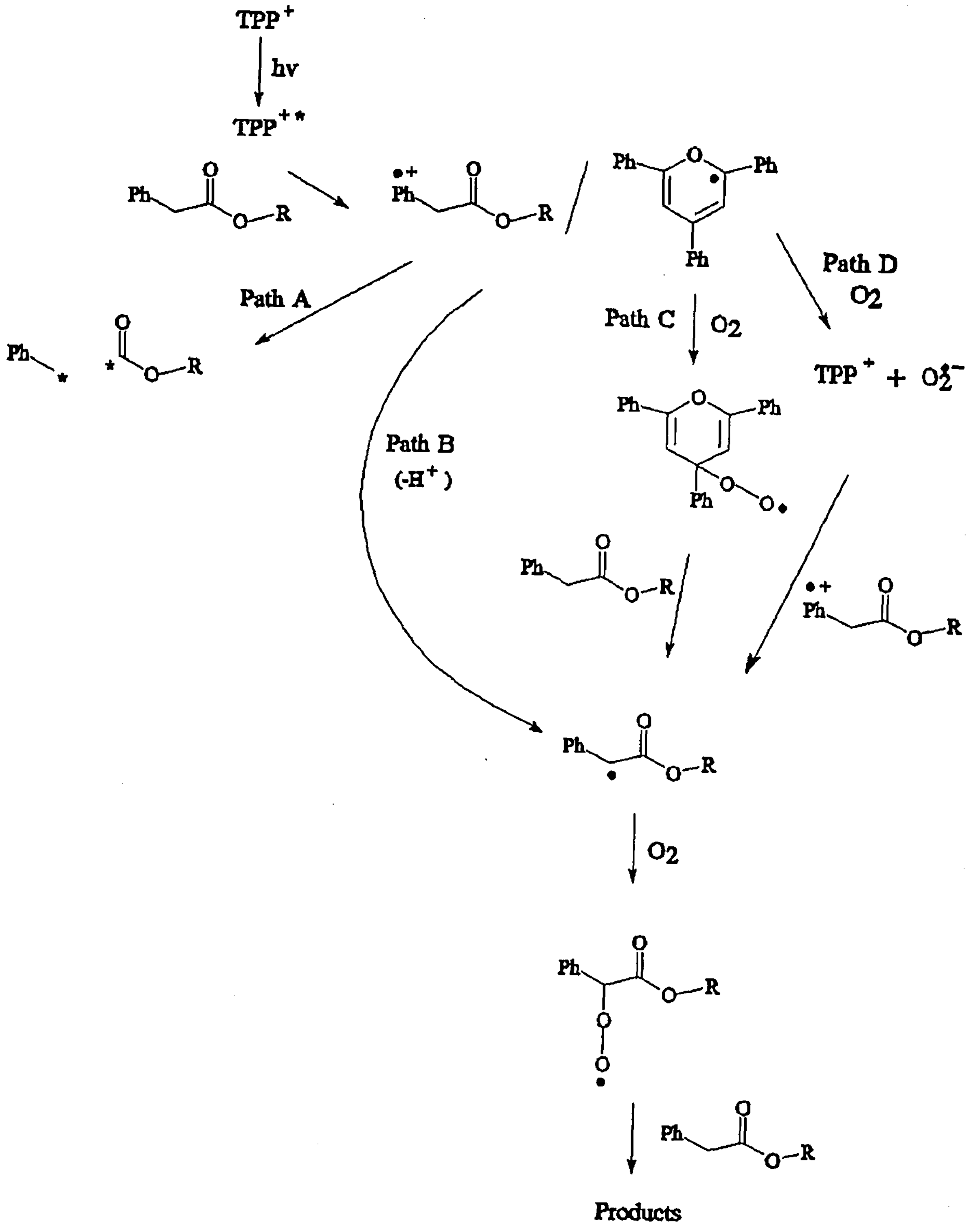
[**2a**] (M)	Conversion
0.007	28%
0.013	43%
0.017	57%
0.024	69%

affected by the concentration of substrate. Higher concentrations of substrate would be intercepted more often in the chain process and would lead to higher amounts of bond cleavage. In accord with these expectations, the conversion amounts upon irradiation of 0.015 M TPP^+ solutions were found to be highly sensitive to the **2a** concentration. Higher concentrations of **2a** underwent more reaction, as expected from a radical chain process.

A final experiment in support of the radical chain mechanism was to independently start this process. The generation of a radical chain was initiated photochemically by reacting of 25 mM of **2a** with 9 mM benzoylperoxide in the presence of O_2. Although the conversion yield (16%) was not as great as in the TPP^+ sensitized experiments, benzophenone was observed as a product. We conclude that the reaction can be quenched and can be initiated exactly as autoxidation reactions.

Reaction Mechanism: Possible mechanisms for the radical chain mechanism leading to the bond cleavage reactions of **2** and **3** are shown in Scheme 8. Compound **4** is expected to react in a similar fashion, although the site of deprotonation must be considered to be α to the phenyl group. All mechanisms begin with photoexcitation of TPP^{+} to yield TPP^{+*} which undergoes electron transfer with the organic substrate to yield a radical cation and the TPP$^{\bullet}$. In mechanism A, the radical cation reacts directly to yield a radical and a cation which proceed onward to the observed products. We specifically do not specify where the electron resides and denote the site of the radical and cation by *. In mechanism B, the radical cation loses an H^{+} to some base, generating the α-phenyl radical which can be trapped by O_2 to yield a hydroperoxy radical. This radical participates as part of the radical chain mechanism which ultimately results in the observed products. In mechanism C, the TPP●, formed by electron transfer from organic substrate, may add a molecule of O_2 at either the 2, 4, or the 6 positions of the pyrylium ring through the resonance possibilities of the radical to yield a hydroperoxy radical. This hydroperoxy radical is suited to initiate a radical chain mechanism by interaction with a molecule of the starting substrate. In mechanism D, the TPP● can undergo an electron transfer with the O_2 in the solution to yield an $O_2^{\bullet-}$. The $O_2^{\bullet-}$ can accept an H^{+} from the substrate radical cation to yield HOO● and an α-phenyl radical. Both of these species may then participate in the radical chain autoxidation mechanism. Pathway A can be ruled out on the basis of the DCA-sensitized irradiations. Since no product was observed in the DCA reactions, and since **2a** can quench the DCA*, the direct bond cleavage of **2a**$^{\bullet+}$ cannot explain the observed reactivity. Pathway D can also be ruled out since DCA$^{\bullet-}$ is known to undergo electron transfer with O_2 to yield DCA and $O_2^{\bullet-}$ at the diffusion controlled rate. Since DCA$^{\bullet-}$ is formed in the reactions of **2a**, and no products are observed in the DCA irradiations, pathway D is not a viable pathway.

A close look at Paths B and C reveals that the only difference between these paths is



Scheme 8

which side of the initial radical cation/radical pair interacts with its surroundings in a way to generate the radical chain. We believe that both pathways are likely and cannot differentiate between these mechanistic pathways based upon the available data.

Summary

An understanding of the TPP$^+$ sensitized bond cleavage pathways of esters has been obtained. In contrast to previous reports of radical cation behavior from these systems, a radical chain autoxidation pathway must also be considered as a viable pathway for certain functionalities. The esters in this study were found to undergo C-C bond cleavage reactions by this radical chain mechanism. Characteristic of radical chain pathways, the C-C bond cleavage reaction can be inhibited by the addition of phenol and can be initiated by other radical sources.

Experimental Section

Melting points were determined on a Laboratory Devices Mel-Temp apparatus and were uncorrected. Gas-liquid chromatographic analyses were conducted on a Hewlett-Packard Model 5890A GC equipped with a 10 m 5% phenylmethylsilicone or a Carbowax 20 m Megabore column. Integration of the signals was performed by a Hewlett-Packed Model 3390A digital integrator. GC-MS were measured with a HP 5980 mass spectrometer with a 5890 gas chromatograph equipped with a 25-m 5% phenylmethylsilicone column. ^{1}H NMR spectra δ (ppm) and J (hertz) and ^{13}C NMR (270 MHz) were measured in the indicated solvent with TMS (^{1}H δ 0.0 ppm), $CHCl_3$ (^{1}H δ 7.26 ppm), or $CDCl_3$ (^{13}C δ 77.0 ppm) as internal standards on a JEOL GX-270 Spectrometer.

Acetonitrile was predried over CaH_2 and then distilled from P_2O_5 shortly before use. THF was distilled from sodium benzophenone ketyl under argon before use. Benzene was distilled from $LiAlH_4$ prior to use. Pyridine was dried over potassium alkoxide (KOH). 2,4,6-Triphenylpyrylium tetrafluoroborate was commercially available and was recrystallized twice from ethanol before use. Unless otherwise specified, all chemicals were purchased from Aldrich.

Identification of reaction products was accomplished by GC/MS analysis and by comparison with an authentic chemical sample. Reported product yields and overall conversion are based on GC measurements using octyl cyanide as an internal standard.

Synthesis of Esters: Two general methods for the syntheses of the esters.

Method A: Into a solution of the acid chloride (3.0 mmol) in benzene (3.0 mL) in a dry 10 mL round bottomed flask equipped with a stirring bar, a condenser and a drying tube was added alcohol or amine (2.0 mmol) in benzene (1.0 mL), followed by pyridine (2 drops). The solution was refluxed for 1 hr. After cooling to ambient temperature, the mixture was poured into 10 mL of benzene, and 10 mL of saturated aqueous sodium bicarbonate was added. The aqueous solution was extracted with benzene (2 X 10 mL). The combined organic phases were washed with saturated ferric aqueous sulfate and NaCl and dried over anhydrous sodium sulfate. The solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, 10% acetate/hexane) to afford the desired product.

Method B. Thionyl chloride (10 mmol) was added slowly to the carboxylic acid (1.5 mmol) in a flask equipped with a stirring bar, a condenser, and a drying tube at room temperature, the solution was then refluxed for 3 hr. The excess of thionyl chloride was removed by distillation. To the remaining solution was added 3 mL of benzene and 1.0 mmol of the alcohol or amide, followed by pyridine (1.0 mL). After being stirred for 1 hr, the mixture was poured into 10 mL of benzene and 10 mL of saturated sodium bicarbonate was added. The same work-up procedure as described in Method A afforded the desired product.

Data are gathered in the following manner for each of the compounds synthesized:

Compound name: method of synthesis; yield; physical properties; mp; spectral data.

Methyl 2,2-diphenylacetate (2a): method A; 90%; colorless crystal; 58-60 ^{0}C, Lit: 60-61 ^{0}C[50]; ^{1}H NMR (270 MHz, $CDCl_3$) δ (ppm) 3.75 (s, 3H), 5.04 (s, 1H), 7.25-7.33 (m, 10H); ^{13}C NMR (270 MHz, $CDCl_3$) δ (ppm) 172.8, 138.6, 128.5, 128.4, 127.2, 56.9, 52.8;

low-resolution MS, parent 226.

T-butyl diphenylacetate (2b): method A; 91%; colorless crystal; 81-82 ^{0}C, Lit: 80-81 ^{0}C[51]; ^{1}H NMR (270 MHz, CDCl$_3$) δ (ppm) 1.45 (s, 6H), 1.56 (s, 3H), 4.92 (s, 1H), 7.26-7.32 (m, 10H); ^{13}C NMR (270 MHz, CDCl$_3$) δ (ppm) 172.6, 139.2, 128.6, 128.5, 127.0, 58.1, 52.6, 27.9.

Methyl 2,2,2-triphenylacetate (1a): method B; 85%; colorless crystal; 184-185 ^{0}C, Lit: 182-184 ^{0}C[52]; ^{1}H NMR (270 MHz, CDCl$_3$) δ (ppm) 3.79 (s, 3H), 7.14-7.36 (m, 15H); ^{13}C NMR (270 MHz, CDCl$_3$) δ (ppm) 174.2, 143.5, 130.2, 127.7, 126.9, 52.3.

Diphenylmethyl benzylacetate (3d): method A; 83%; crystal; 43-44 ^{0}C, Lit: 45 ^{0}C[53]; ^{1}H NMR (270 MHz, CDCl$_3$) δ (ppm) 3.72 (s, 2H), 6.87 (s, 1H), 7.23-7.32 (m, 15H); ^{13}C NMR (270 MHz, CDCl$_3$) δ (ppm) 170.4, 140.0, 133.7, 129.3, 128.5, 128.4, 127.8, 127.0, 126.9, 77.1, 41.5.

Triphenylmethyl benzylacetate (3c): method B; 86%; crystal; 123-125 ^{0}C; ^{1}H NMR (270 MHz, CDCl$_3$) δ (ppm) 3.66 (s, 2H), 7.26-7.32 (m, 20H); ^{13}C NMR (270 MHz, CDCl$_3$) δ (ppm) 177.1, 146.8, 133.2, 129.3, 128.6, 127.9, 127.3, 127.2, 82.2, 40.9.

Cyclopropylphenylmethyl benzylacetate (3e): method A; 89%; liquid; ^{1}H NMR (270 MHz, CDCl$_3$) δ (ppm) 0.30-0.56 (m, 4H), 1.22-1.29 (m, 1H), 3.62 (s, 2H), 5.24 (d, 1H), 7.21-7.29 (m, 10H); ^{13}C NMR (270 MHz, CDCl$_3$) δ (ppm) 170.8, 140.0, 133.9, 129.2, 129.1, 128.4, 128.2, 127.7, 126.9, 126.4, 77.8, 41.5, 16.4, 3.9, 2.9.

Benzyl undecanotate (4): method B; 84%; liquid; ^{1}H NMR (270 MHz, CDCl$_3$) δ (ppm) 0.85-1.64 (m, 19H), 2.34 (t, 2H), 5.1 (s, 2H), 7.32-7.35 (m, 5H); ^{13}C NMR (270 MHz, CDCl$_3$) δ (ppm) 173.6, 136.1, 128.7, 128.5, 128.4, 128.3, 128.1, 65.9, 34.2, 31.8, 31.5, 29.5, 29.4, 29.3, 29.0, 24.9, 22.6, 14.1. low-resolution MS, parent 214.

Photochemical Reactions: Photosensitized electron transfer reactions were carried out in acetonitrile solution in a substrate concentration of 0.025 M and a sensitizer concentration of 0.015 M. The solution was placed in a Pyrex tube and oxygen was bubbled through the solution for 15 min prior to irradiation. The solution was irradiated in a sunlamp (500 nm) for 3 hr and analyzed as described above. The results are summarized in Table II.

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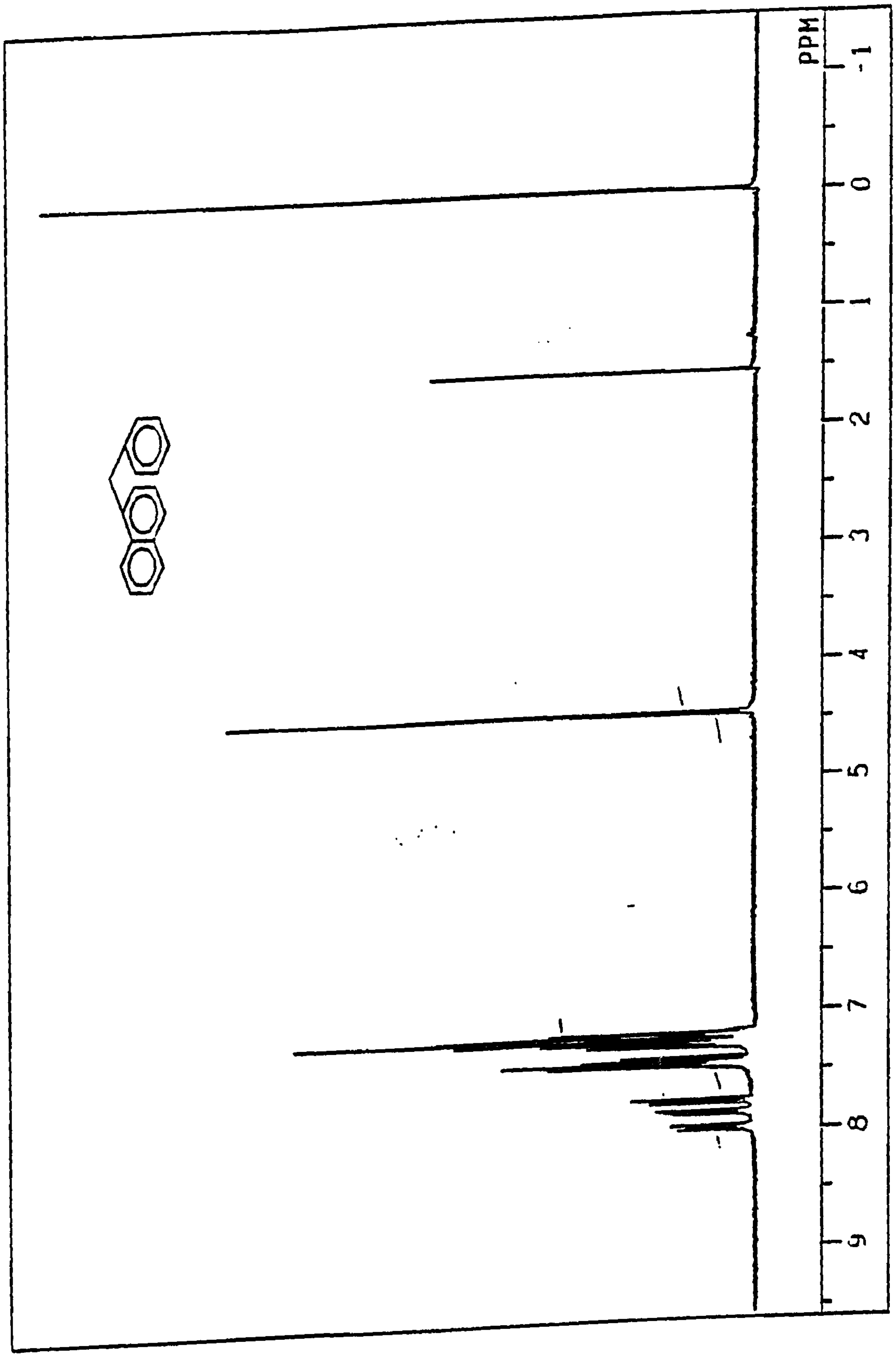
Appendix: ^{1}H NMR and ^{13}C NMR of the Starting Materials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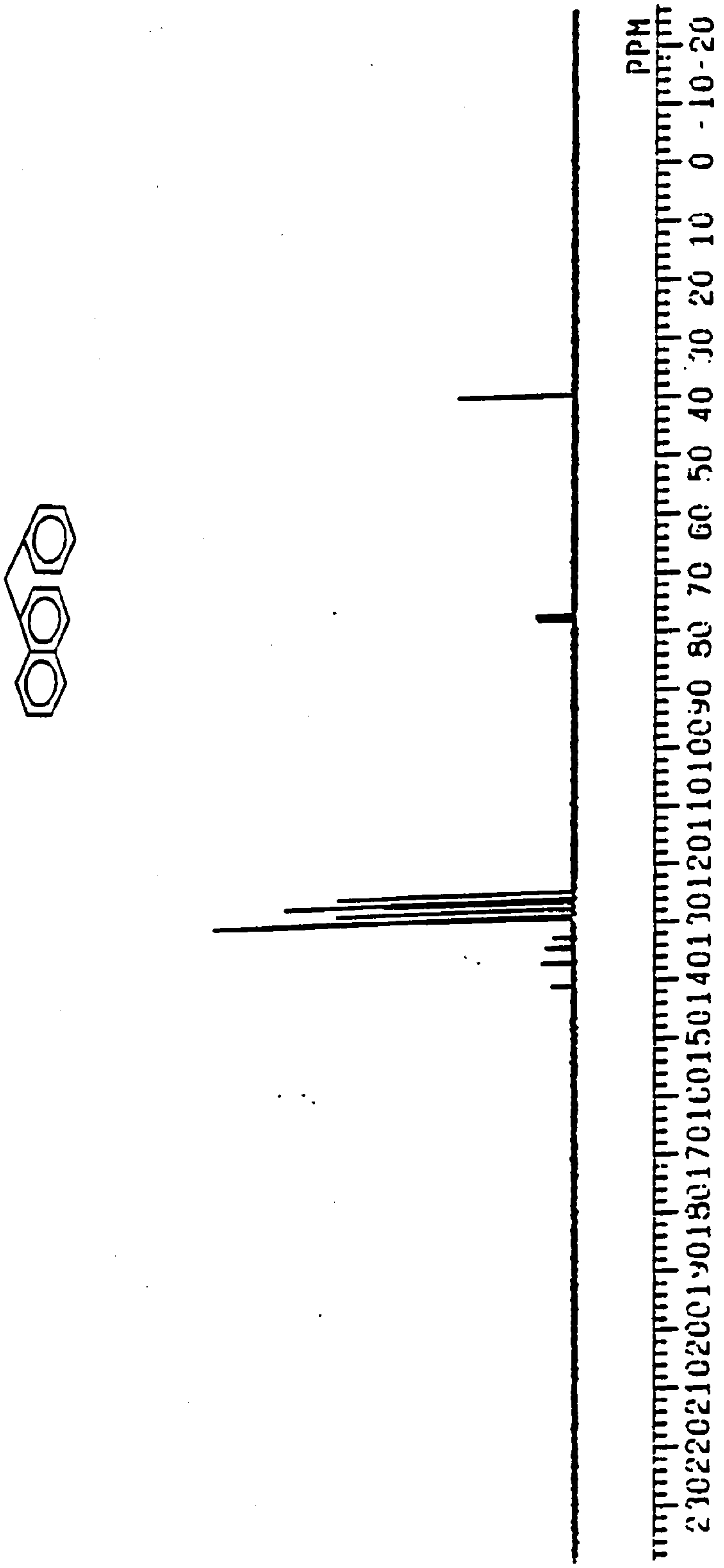
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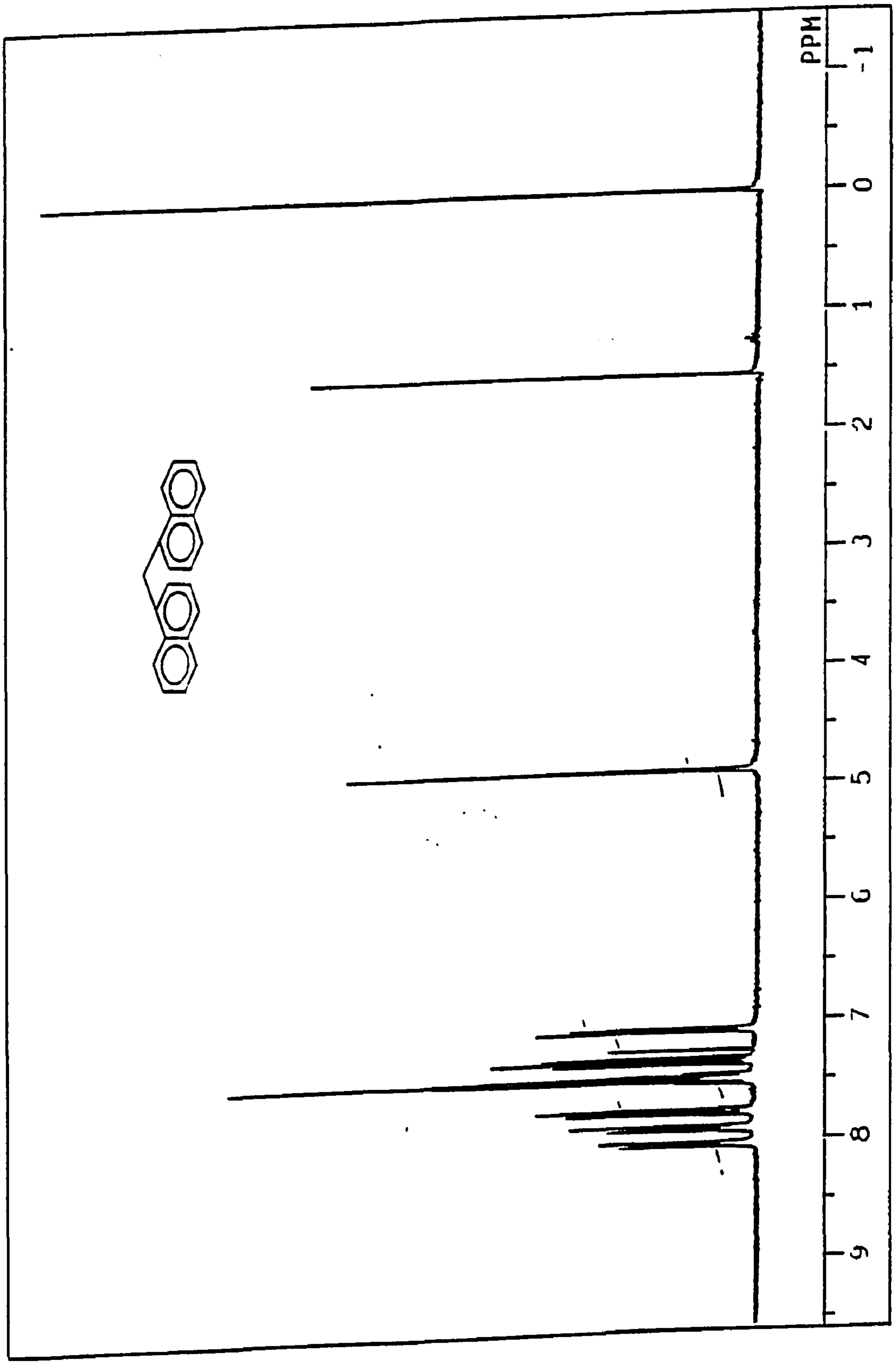
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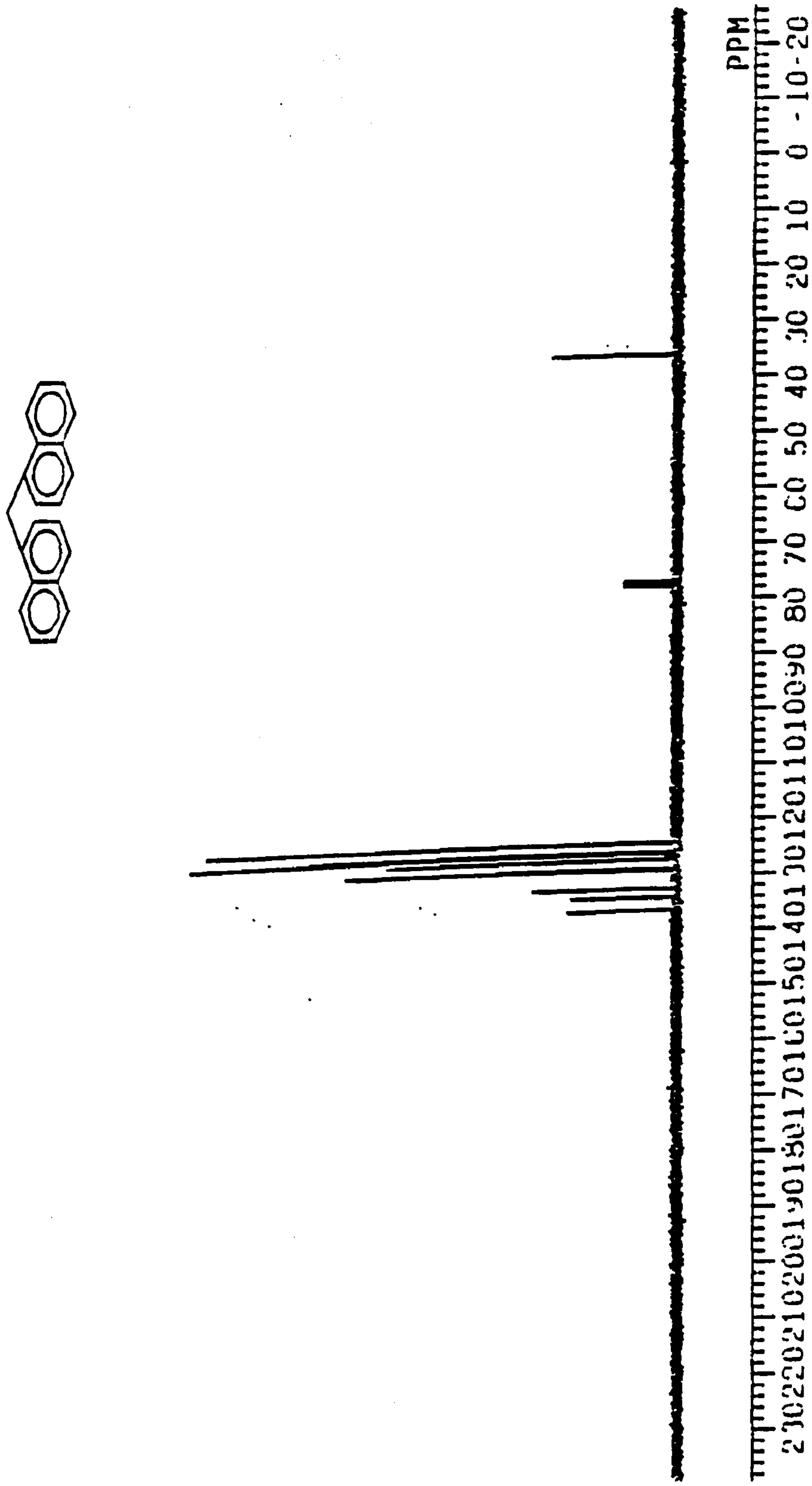
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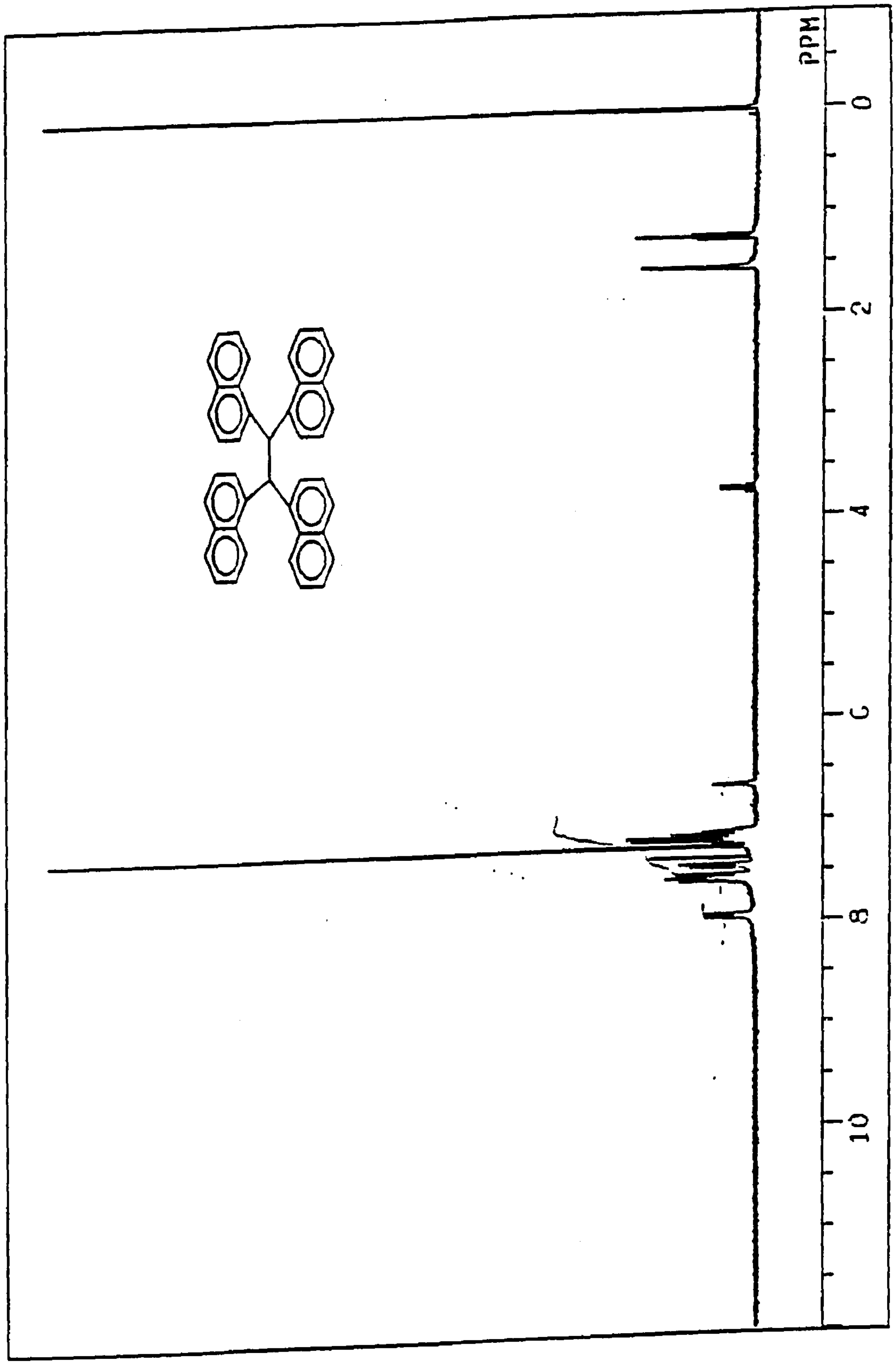
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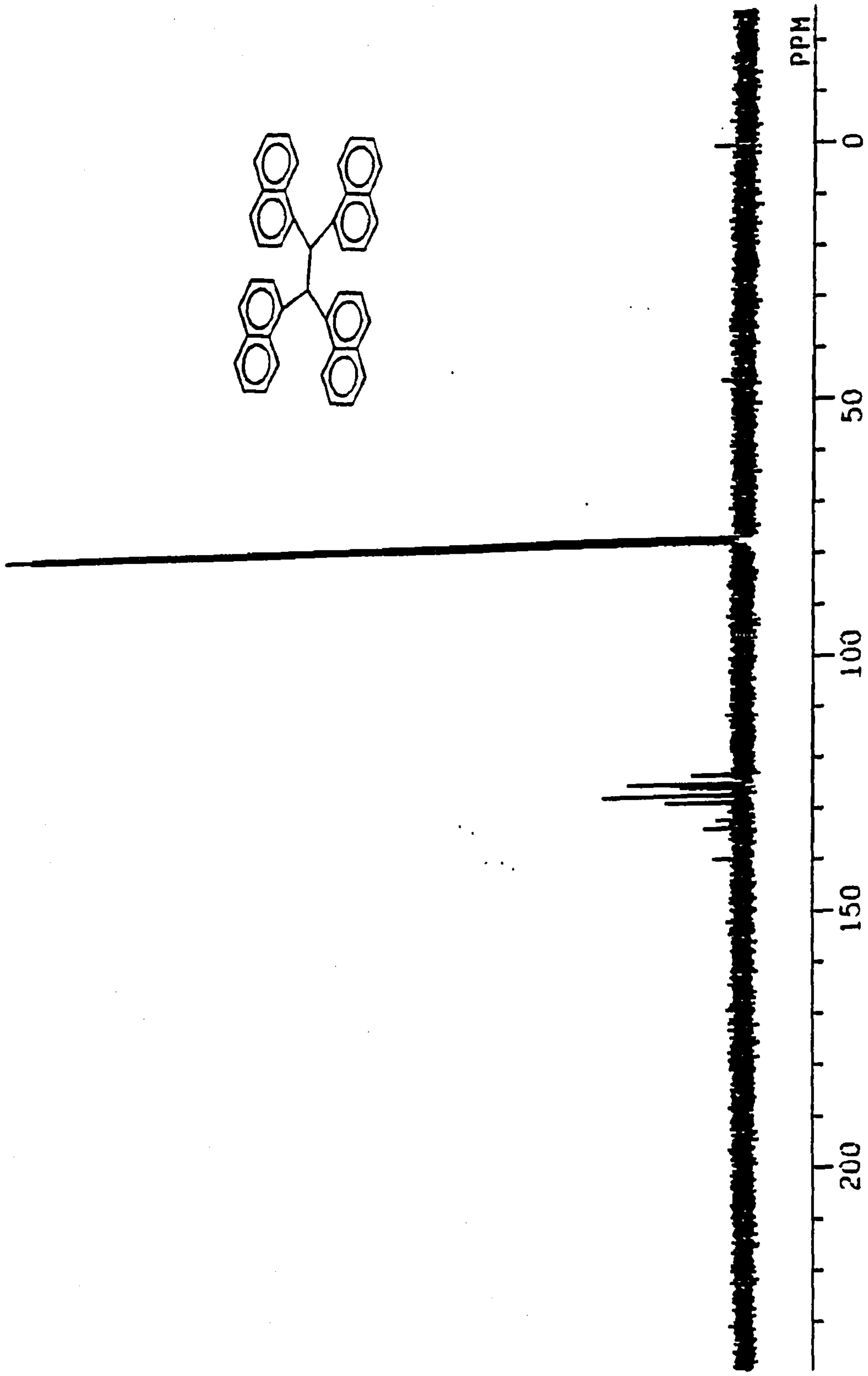
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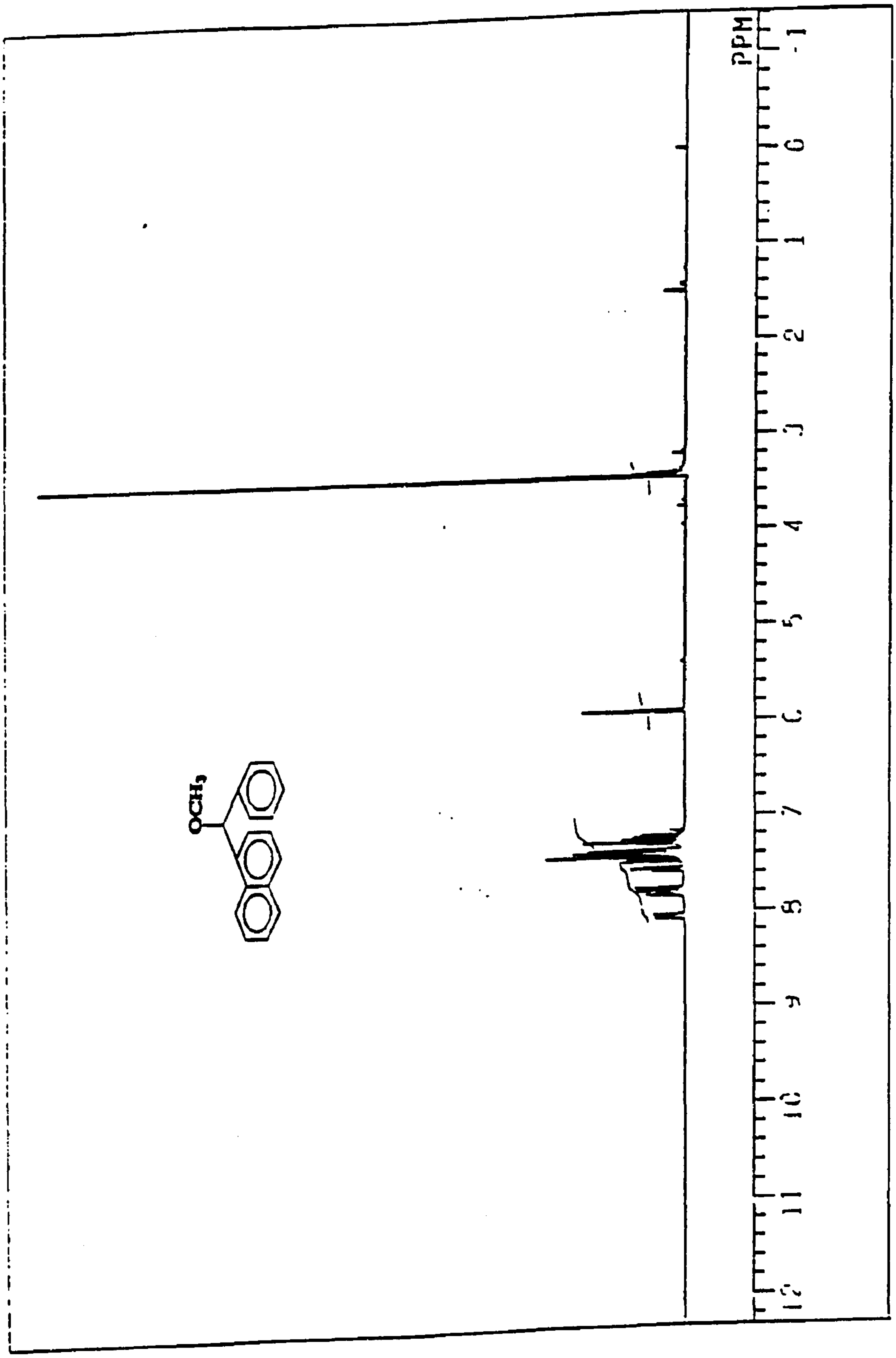
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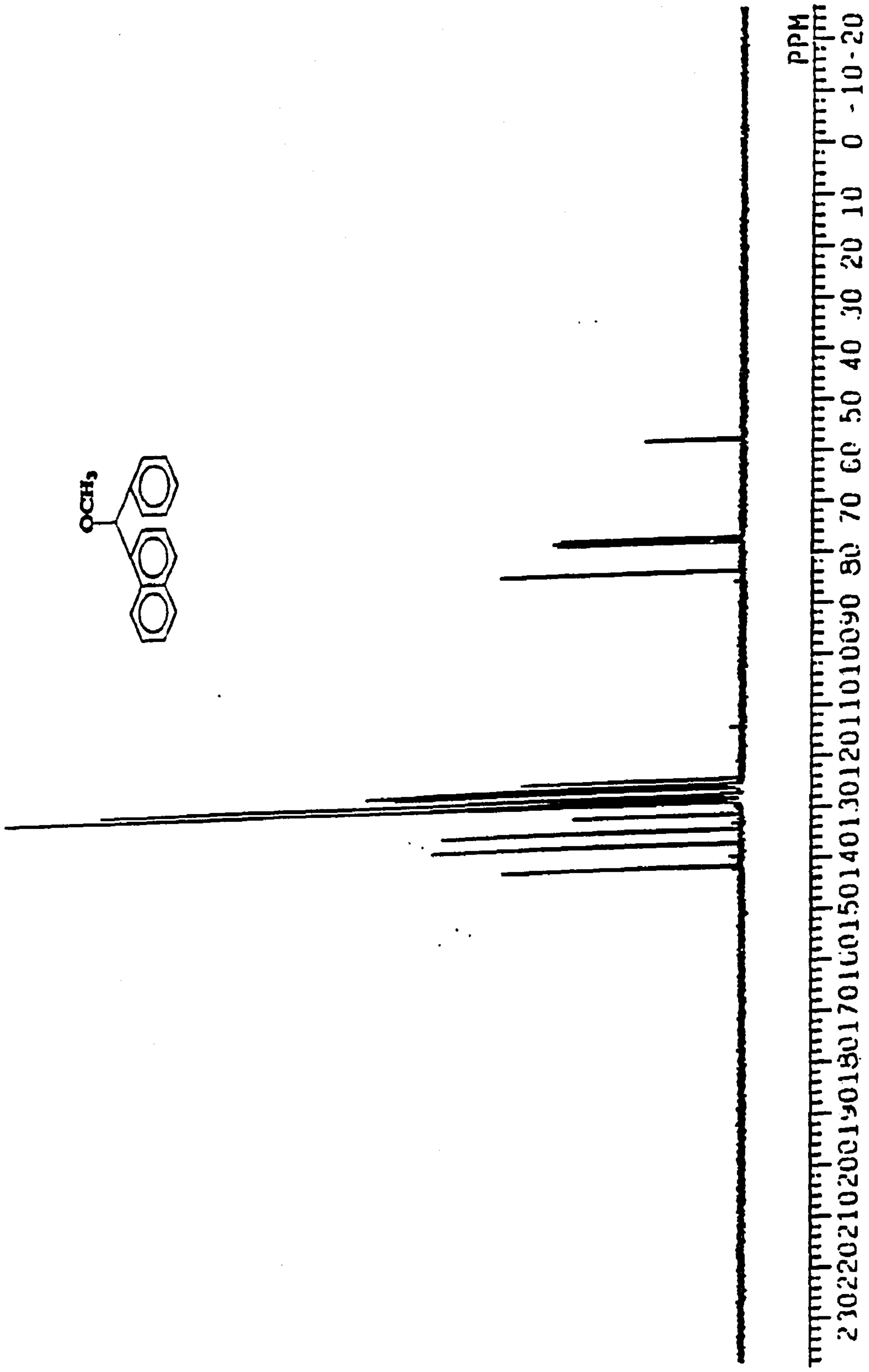
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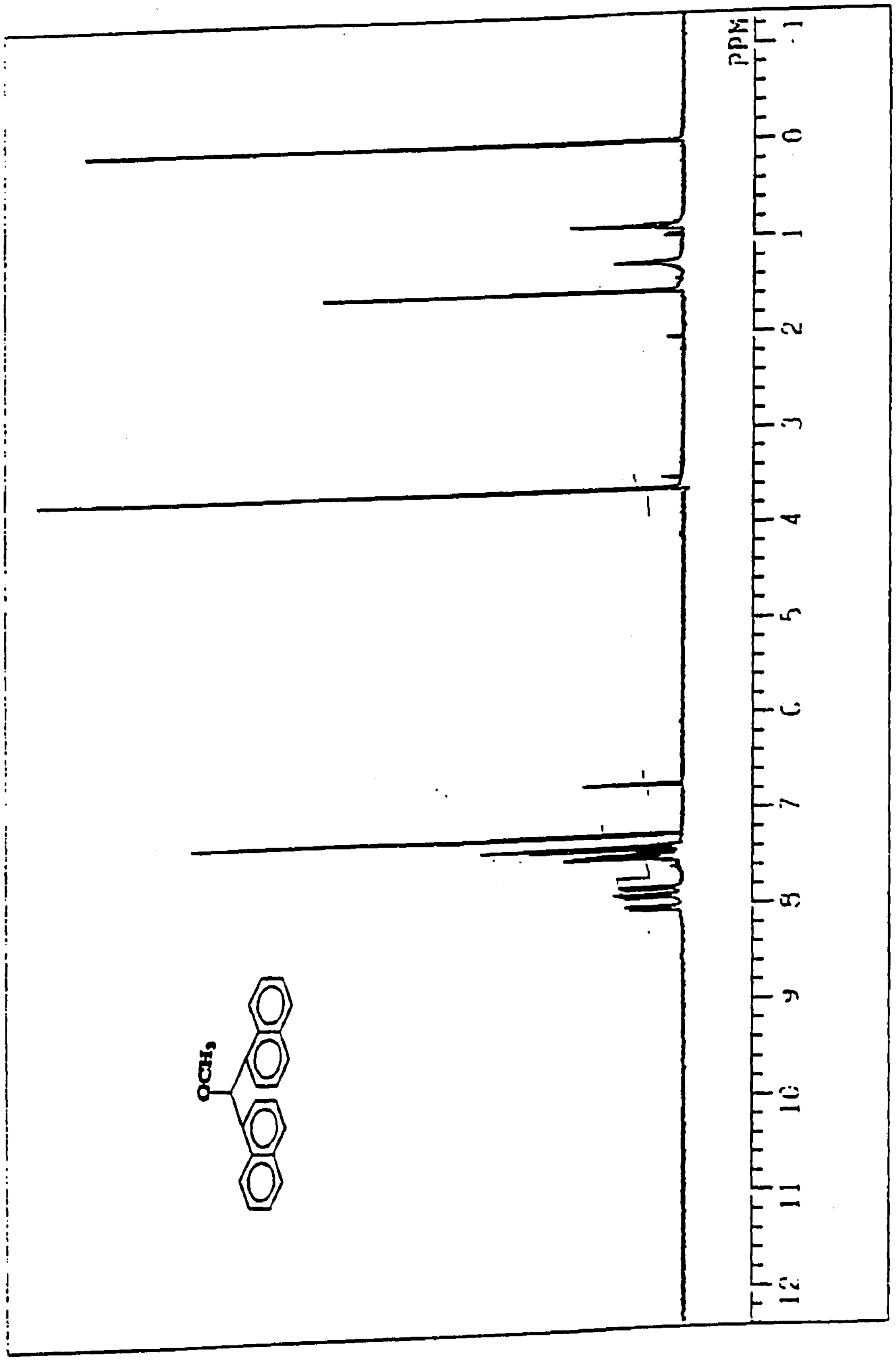
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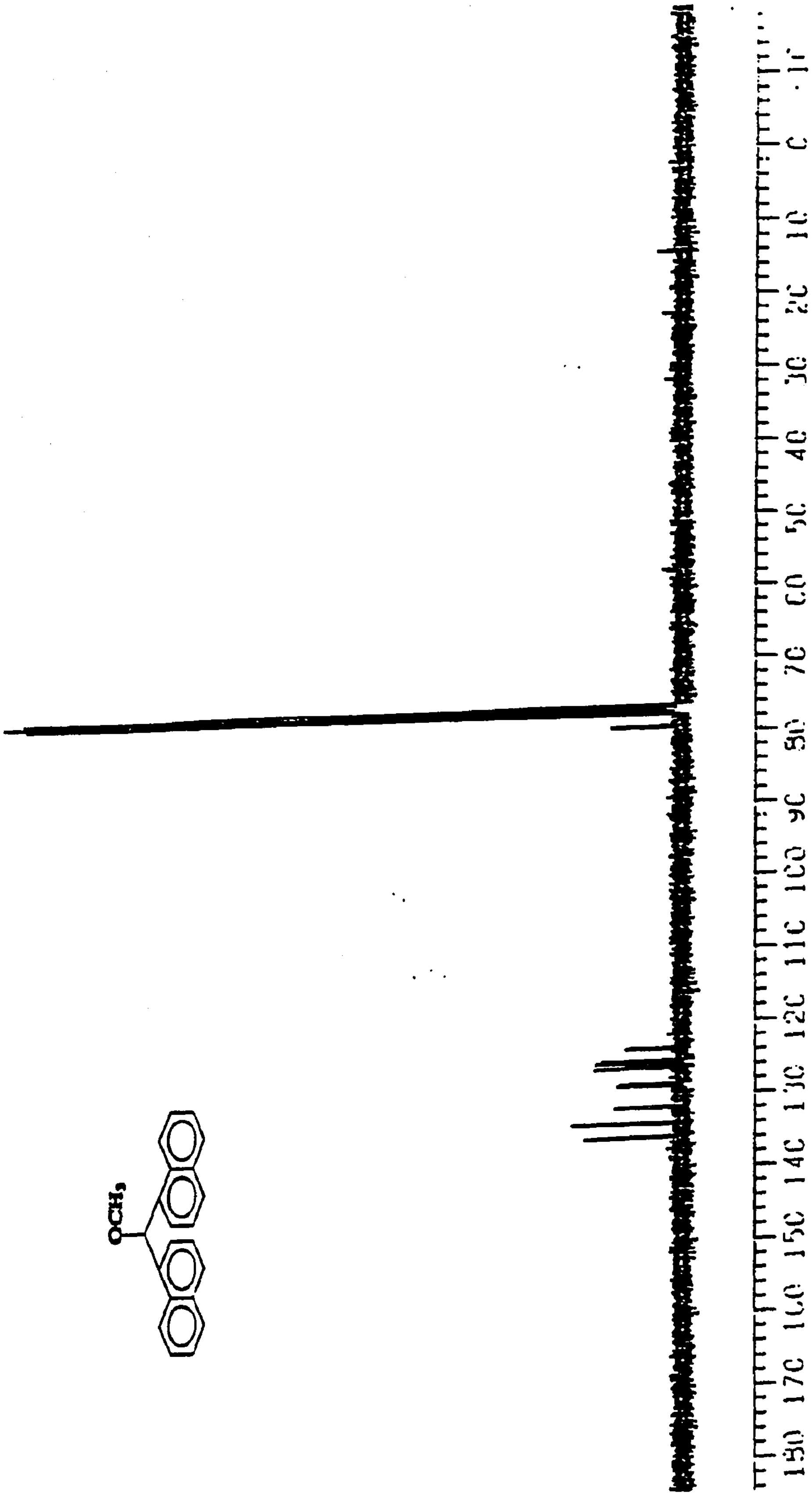
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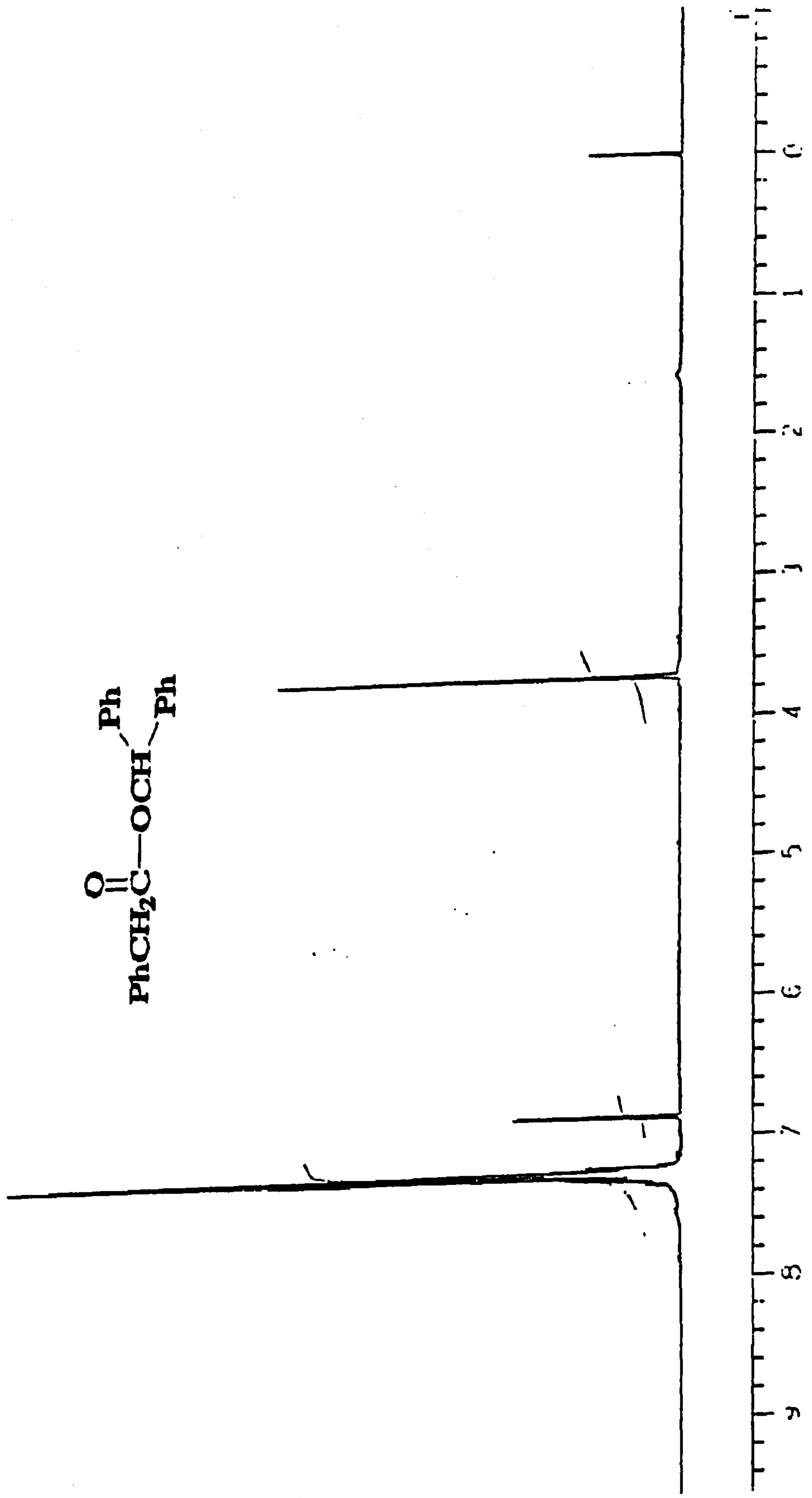
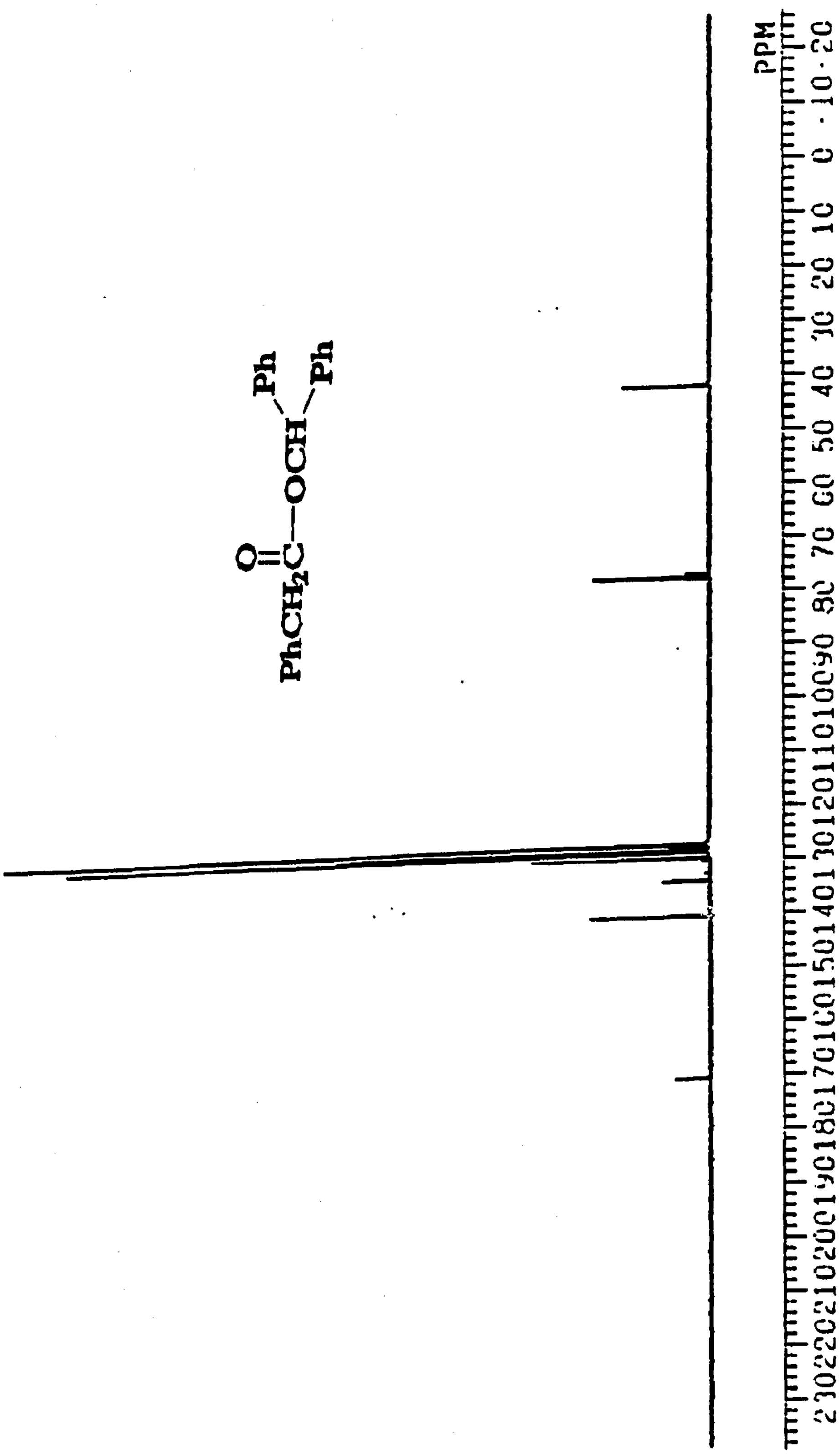
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


PhCH₂C(=O)—OCH(Ph)Ph
0
1
2
3
4
5
6
7
8
9


PhCH$_2$C(=O)—OCH(Ph)Ph
PPM
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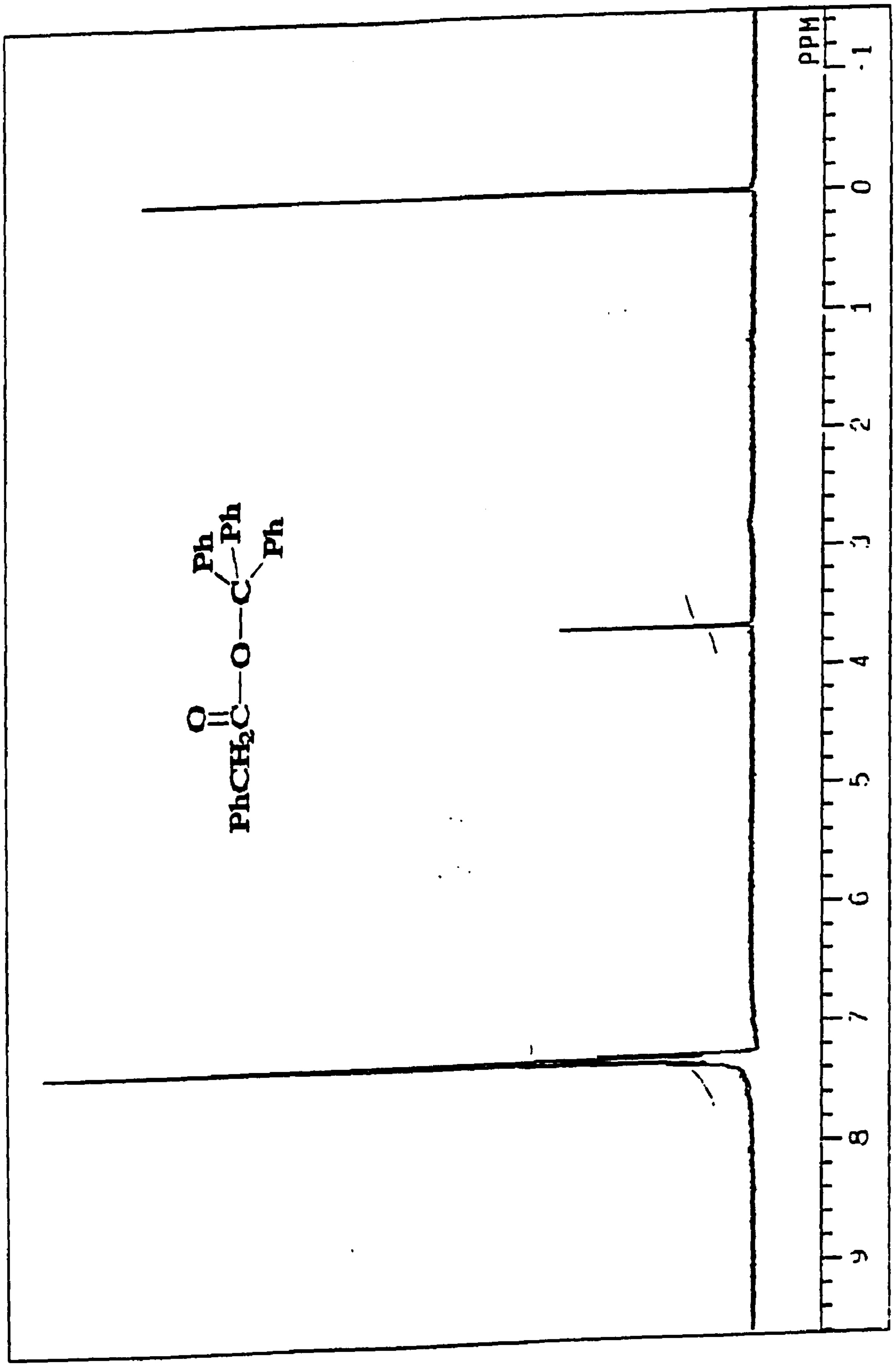
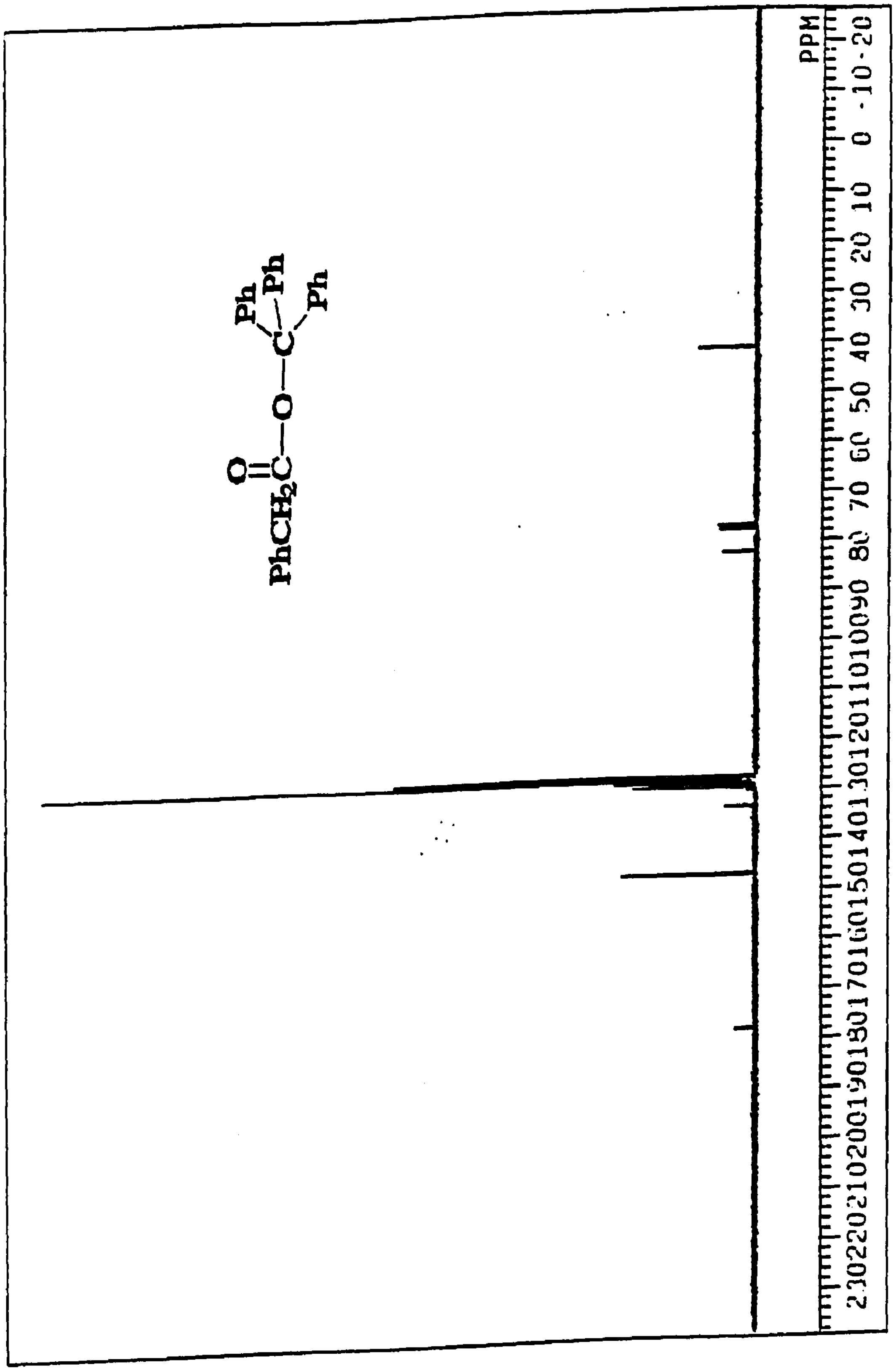

PPM
-1
0
1
2
3
4
5
6
7
8
9
PhCH2C(=O)—O—C(Ph)(Ph)(Ph)


PhCH2C(=O)—O—C(Ph)3
PPM
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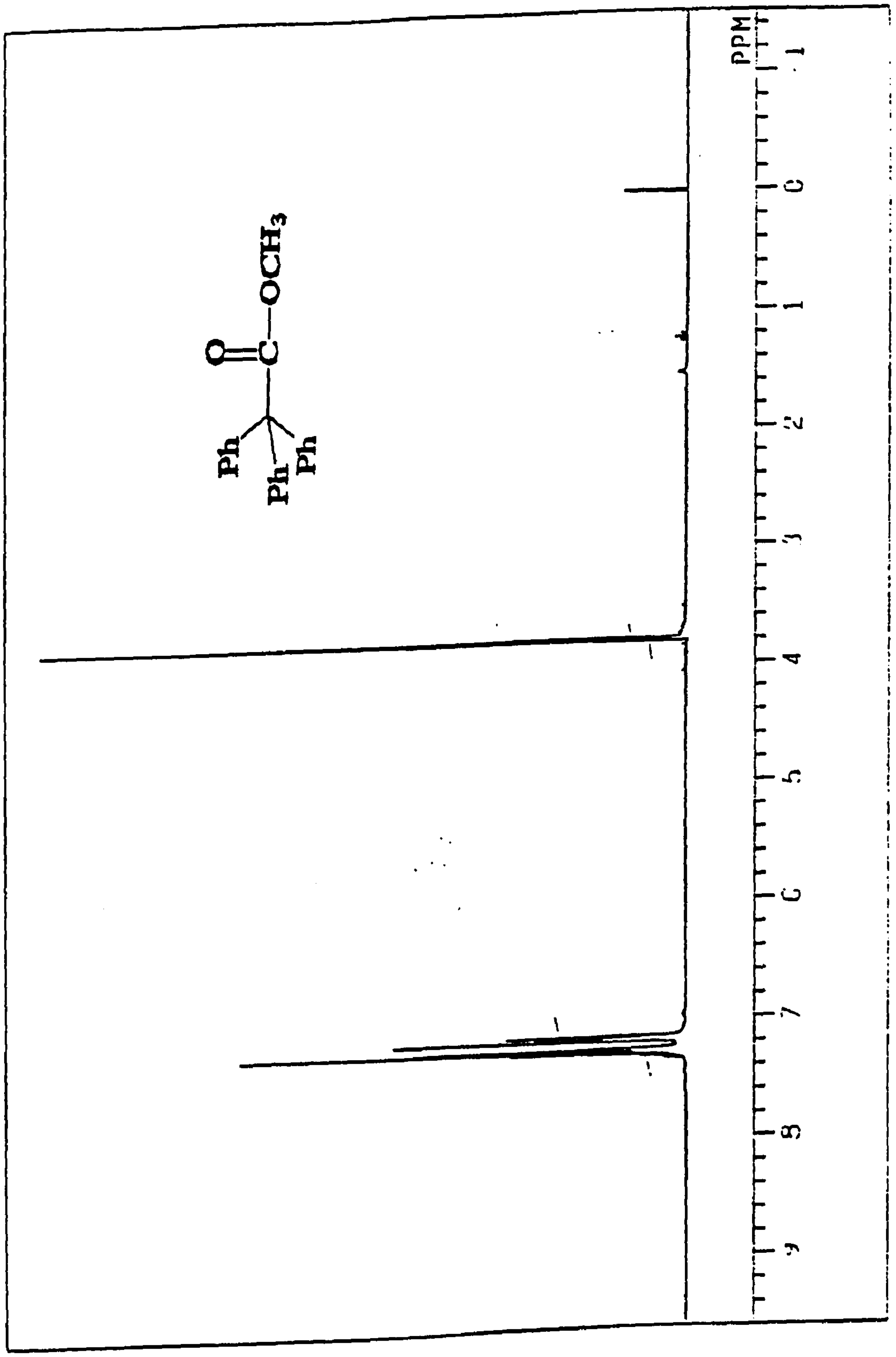
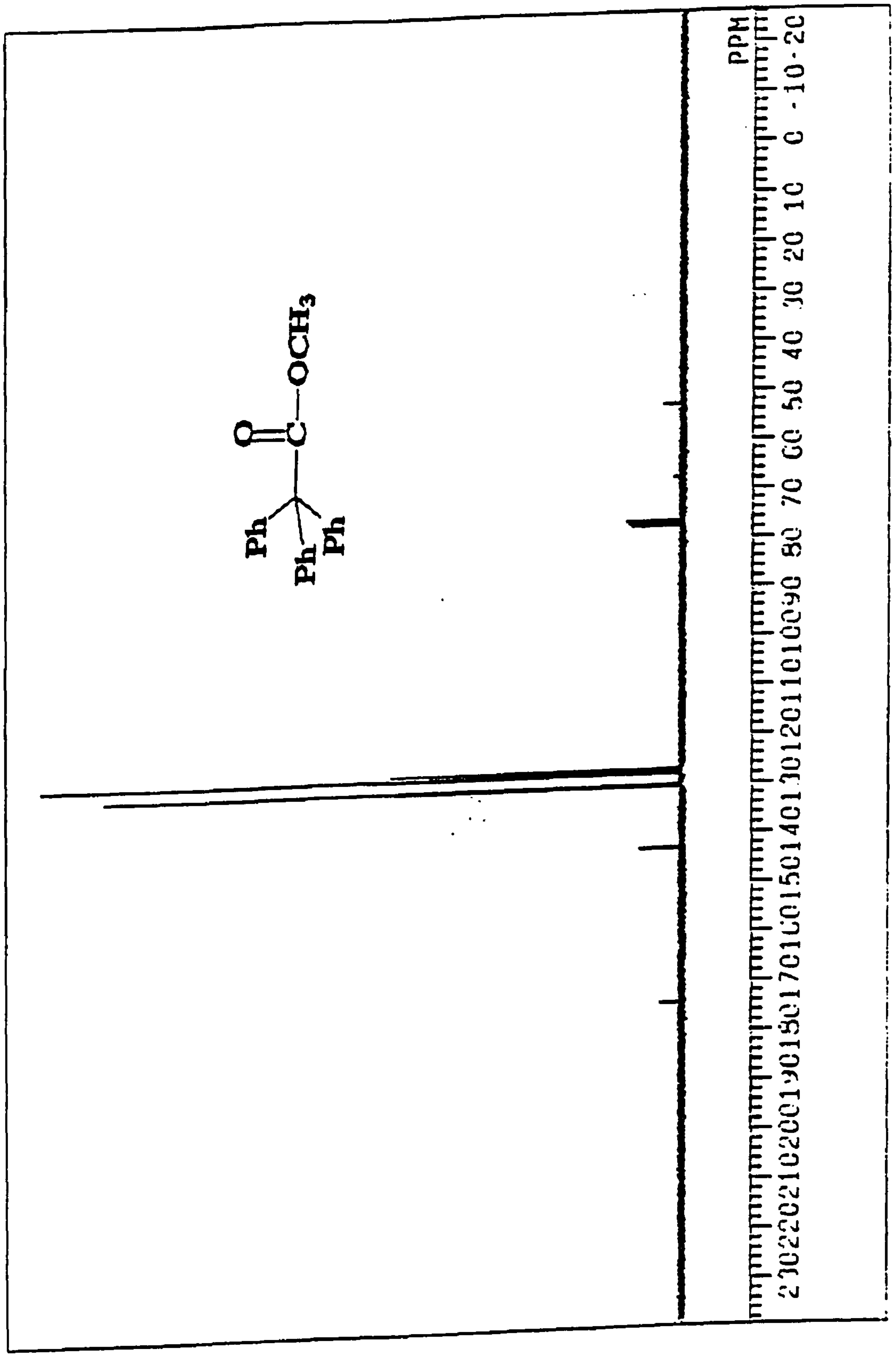
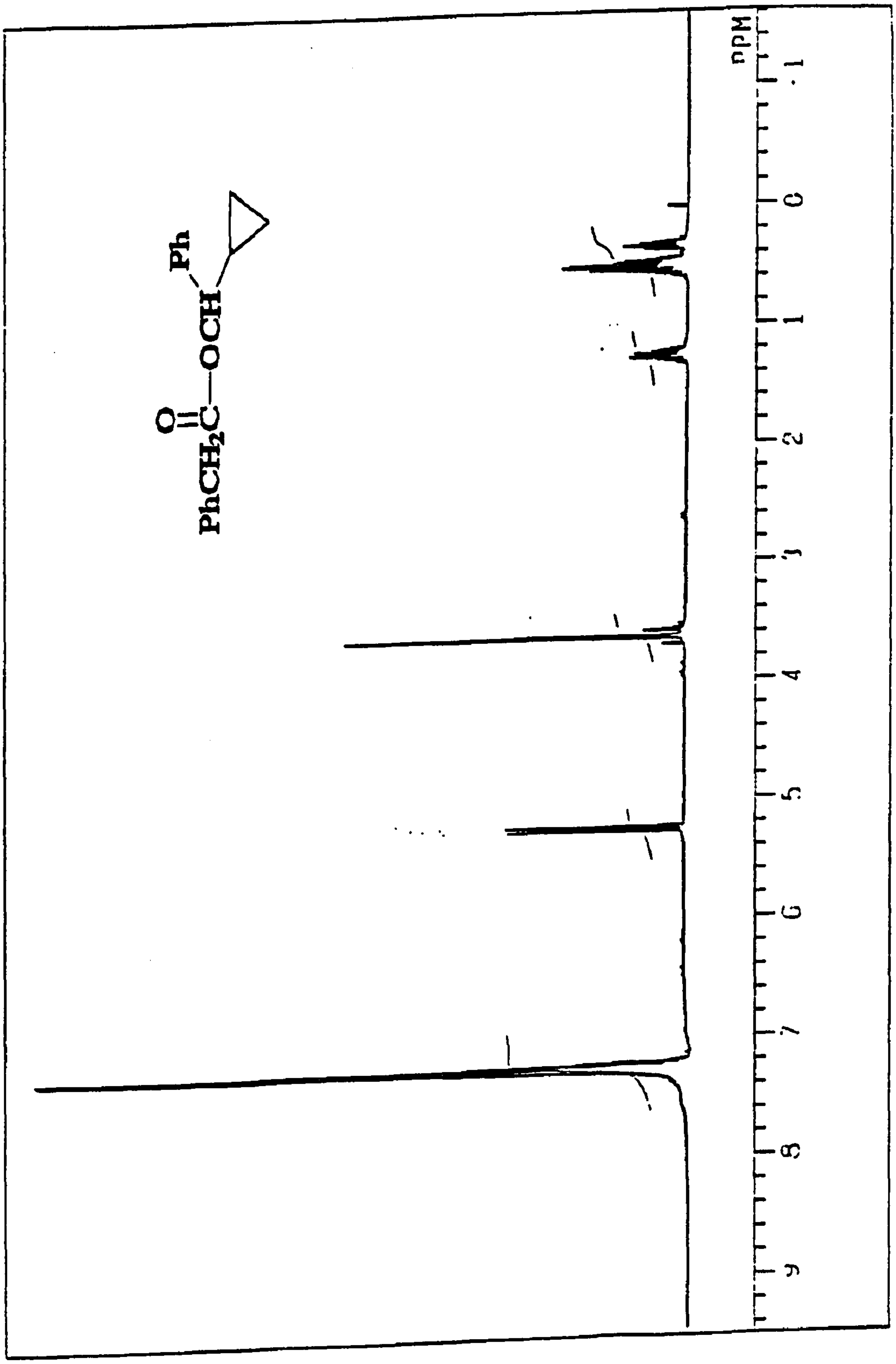
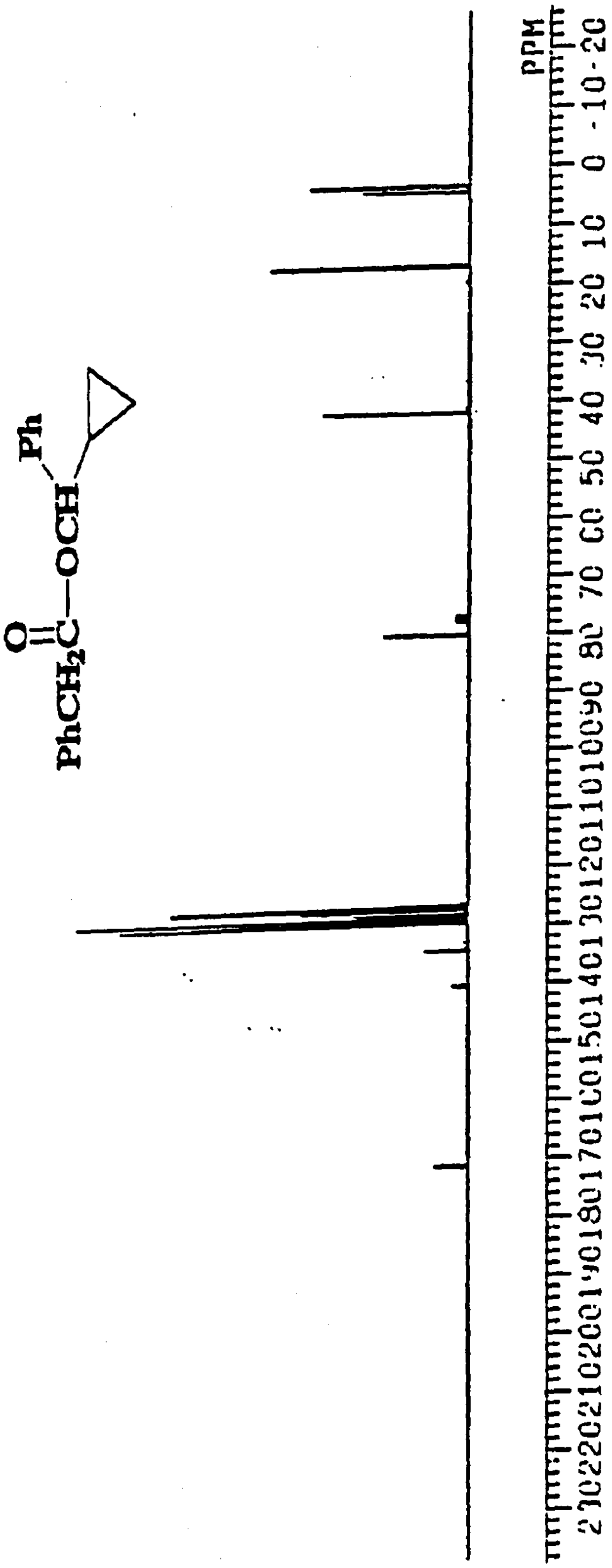
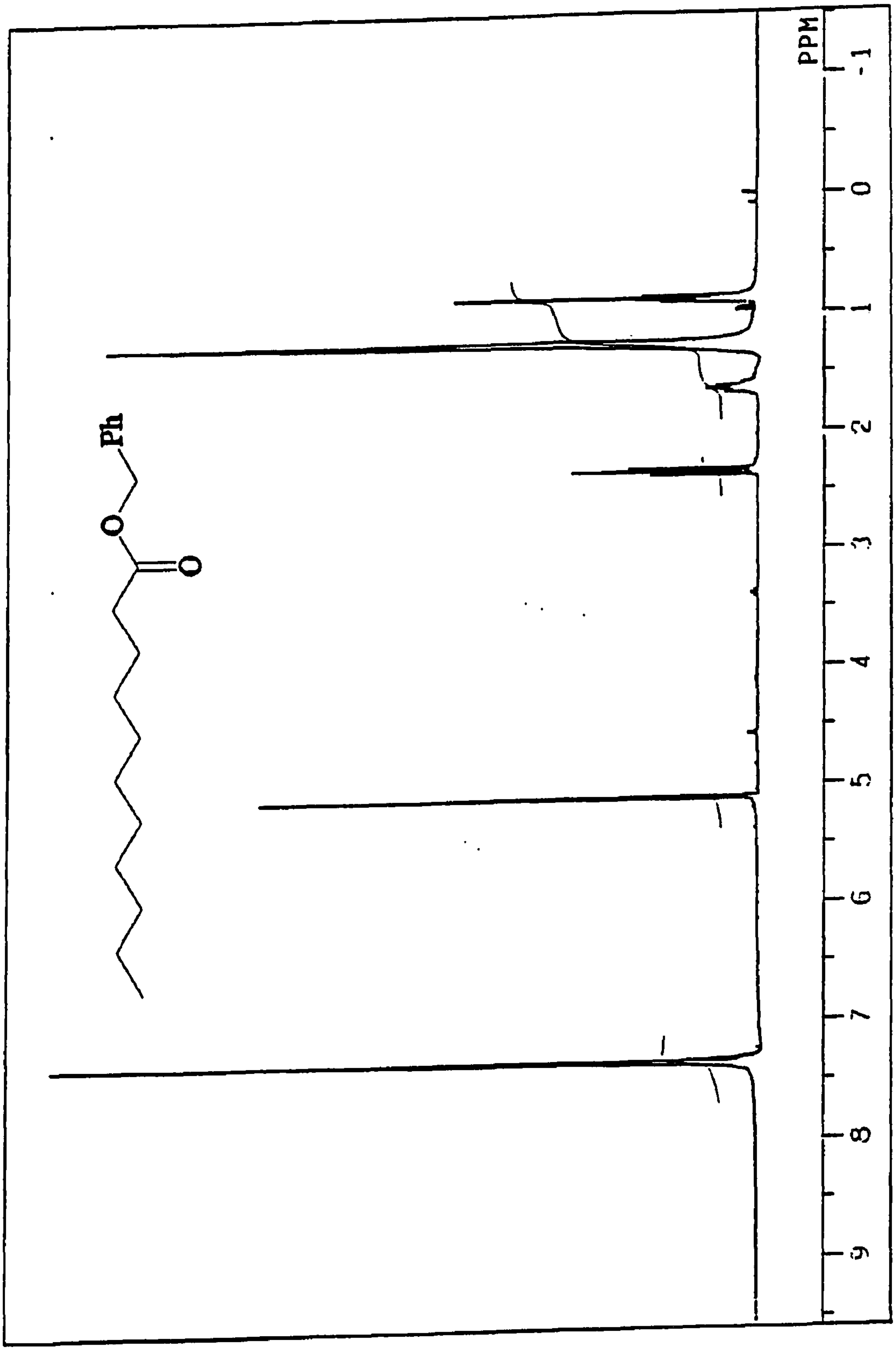
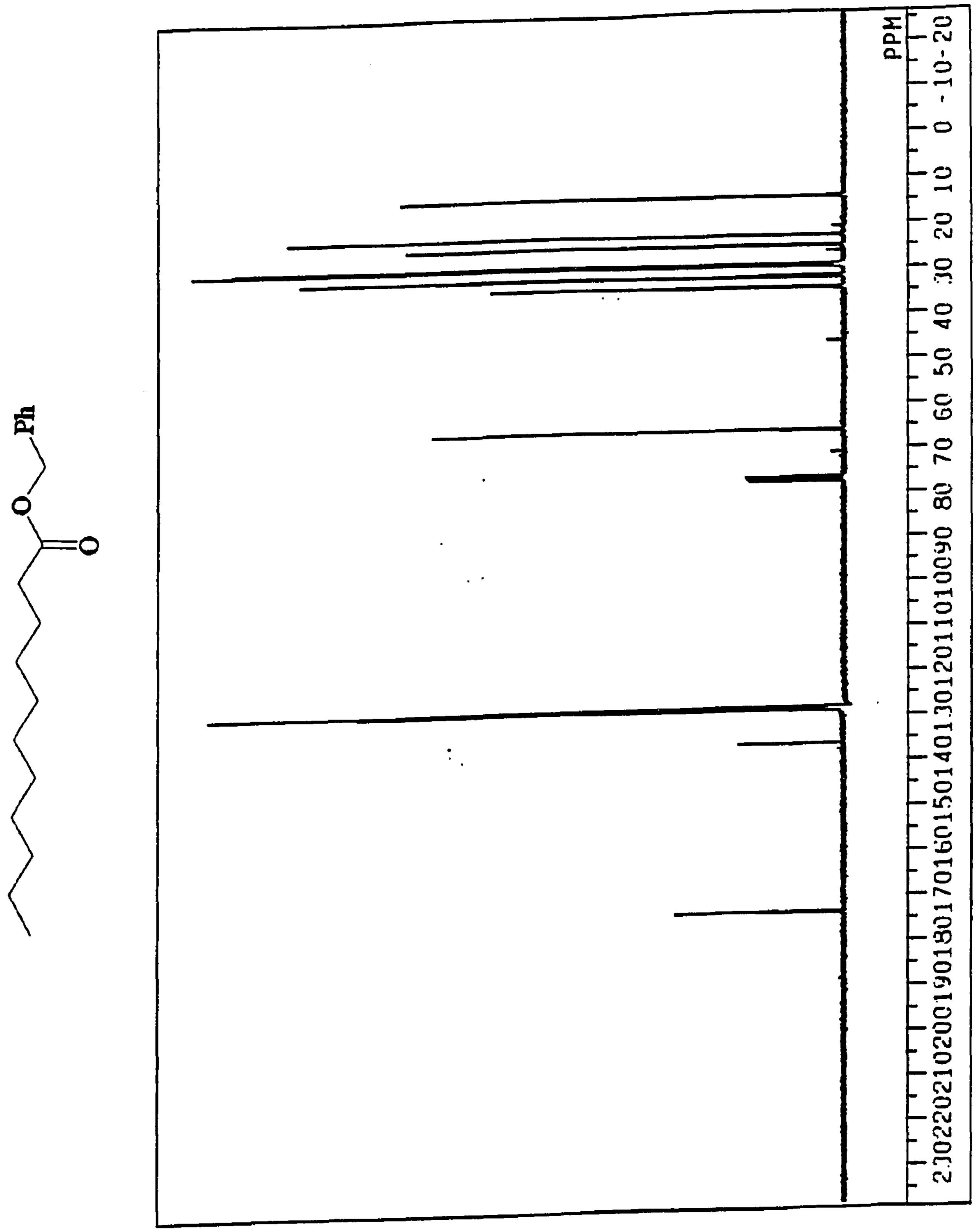

Ph
Ph
Ph
O
C
OCH3
PPM
-1
0
1
2
3
4
5
6
7
8
9


Ph
Ph
Ph
C
O
OCH3
PPM
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20


PhCH2C(=O)—OCH(Ph)
ppm
-1
0
1
2
3
4
5
6
7
8
9


PhCH2C(=O)—OCH(Ph)
PPM
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20


PPM
-1
0
1
2
3
4
5
6
7
8
9
O
O
Ph


Ph
O
O
PPM
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

Approval of Examining Committee

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Naresh Dalal

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6/10/94

Date

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