

SYNTHESIS AND NMR INVESTIGATION  
OF ALKYLATED INDANS

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OF ALKYLATED INDANS

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## CHAPTER I

### INTRODUCTION

During the course of an extensive and continuing investigation of the structures of liquid and soluble materials derived from coal, the need arose for a collection of  $^{13}\text{C}$  NMR spectra of pure compounds representative of structures thought to be present in coal and coal liquids. For this purpose,  $^{13}\text{C}$  NMR spectra of a large number of hydrocarbons were obtained and analyzed.<sup>1</sup> Recently, alkylated indans also received attention in view of their possible occurrence, along with other organic compounds, as trapped components in coals.<sup>2</sup> However, the supply of  $^{13}\text{C}$  NMR spectral data on alkylated indans was meager and in part prompted this study.<sup>1,3</sup>

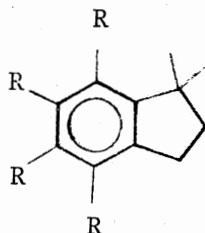
In cooperation with the Air Force Office of Scientific Research (U.S.), the Bartlesville Energy Technology Center has been studying the enthalpies of formation of hydrocarbons including alkylated indans, naphthalenes, anthracenes, etc., that impart specific properties to fuels.<sup>4</sup> Knowledge gained from the study of these pure compounds will be used in tailoring high energy fuels of the future. In view of this need, we began the synthesis and purification of selected alkylated indans for use in thermodynamic studies by the U.S. Department of Energy, Bartlesville Energy Technology Center in Bartlesville, Oklahoma.

## CHAPTER II

### HISTORICAL

Alkyl derivatives of indan have been prepared by the reduction of derivatives of indene,<sup>5</sup> cyclodehydration of some phenylalkanols<sup>6-8</sup> and cyclization of alkyl-3-phenylpropanoic acids or butanoic acids to the alkylindanones followed by reduction to the corresponding indan.<sup>9,10</sup> Elsner and Parker<sup>9</sup> described the synthesis of methylated indans by the cyclization procedure shown in Figure 1. The 3-arylpropanoic acid (3) is obtained either by the reaction of 1 with malonic ester or by the reaction of 2 by Reformatsky reaction. Cyclization of 3 gives the alkyl derivatives of indanone 4 which is converted to the corresponding indan. Using this procedure, twelve indans were synthesized.<sup>9</sup> However, this procedure gives a very low yield when both R<sub>1</sub> and R<sub>4</sub> are methyl groups and prohibits the synthesis of indan with two alkyl groups at the 1,7 position.

Mattox<sup>11a</sup> reported that the cyclialkylation reaction of benzene or other aromatic homologs with isoprene in sulfuric acid provides a convenient one-step procedure for the synthesis of 1,1-dimethylindans of the type shown below.



where R = H or alkyl

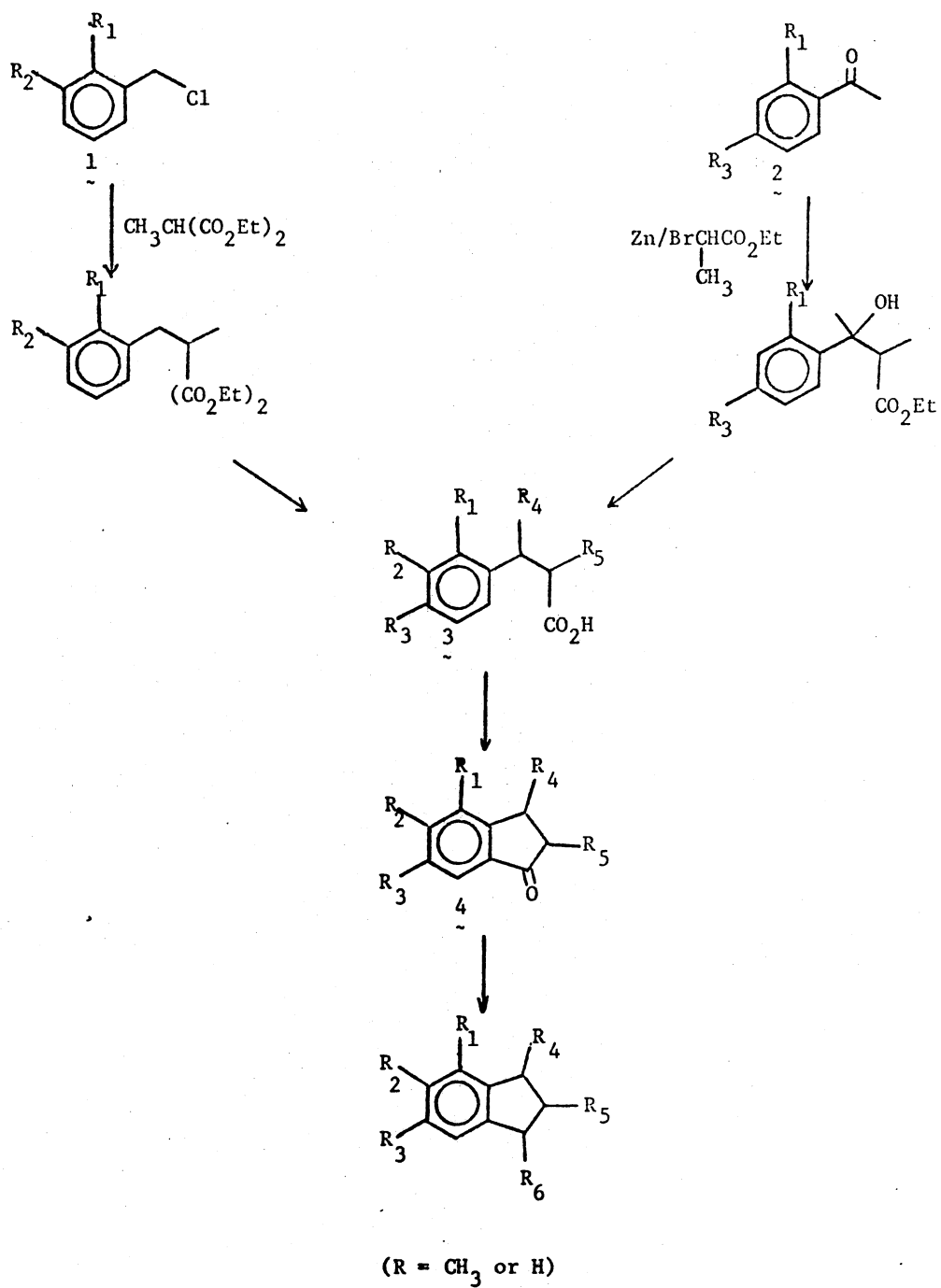
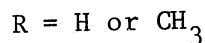
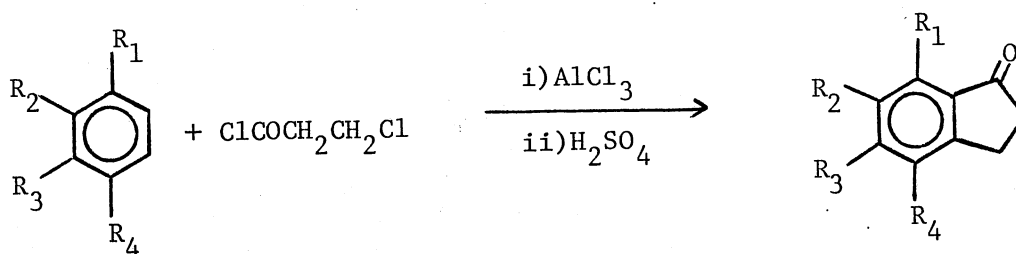


Figure 1. Synthesis of Methylated Indans by Cyclization Procedure

Entel and coworkers reported the synthesis of methyl-substituted indans for use in IR and UV spectral studies.<sup>12</sup> Munavalli and Ourisson described the synthesis of isomeric methylisopropylindans by the reaction of methylindanones with isopropylmagnesium bromide.<sup>13</sup>

Hart and Tebbe<sup>14</sup> synthesized a series of alkylated indanones, the precursors for indans, by the condensation of a bifunctional molecule with an aromatic nucleus in a one-step reaction involving acylation and alkylation of the nucleus as shown below.



Other synthetic routes for alkylated indans are described in the literature.<sup>15-19</sup> Although several methods are available for the synthesis of alkylated indans, a general route for the synthesis of the peri-substituted analogs was not available. Recently, Vickery and coworkers<sup>20</sup> reported the synthesis of 1,7-dimethylindan (6) in 44% yield by the four-step procedure shown in Figure 2. However, the final product did not show the required purity for thermodynamic studies.

An attempt to prepare pure 6 starting from p-cresol and crotonic acid, as shown in Figure 3, also was not successful since an impure final product resulted.<sup>21</sup> This sequence has disadvantages. The first

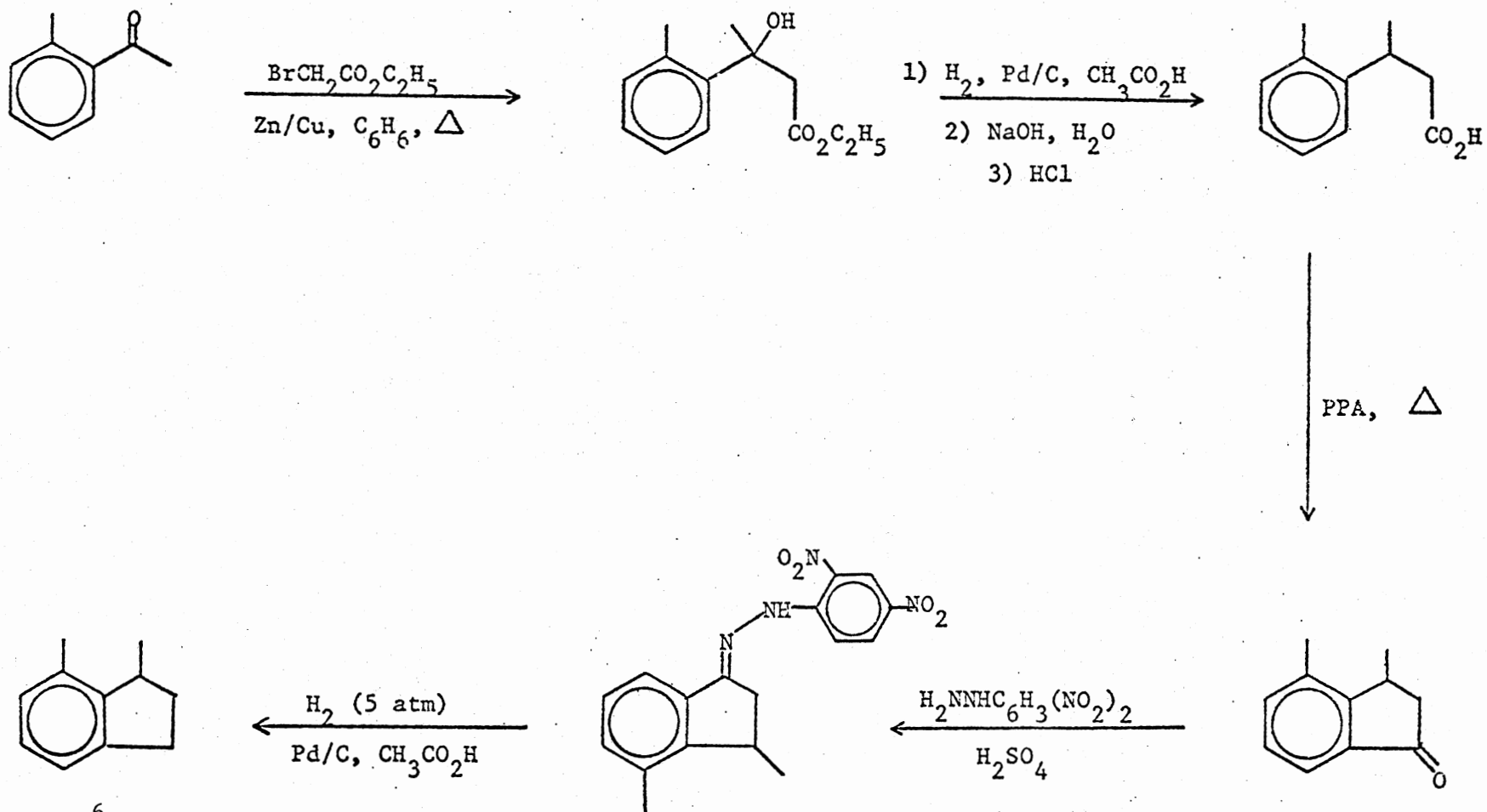


Figure 2. Synthesis of 1,7-Dimethylindan from 2'-Methylacetophenone

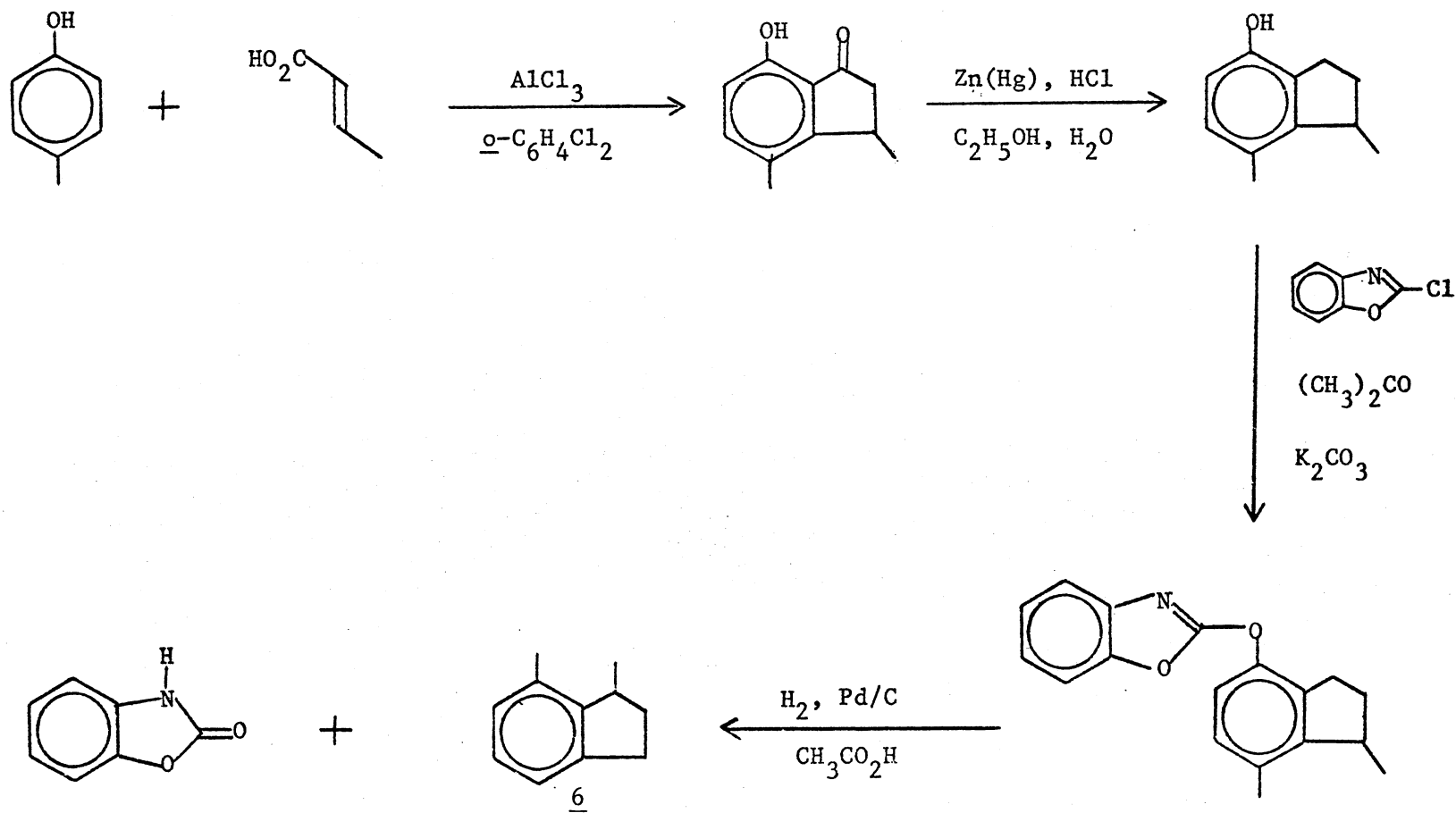


Figure 3. Reaction Scheme for the Synthesis of 1,7-Dimethylindan from p-Cresol

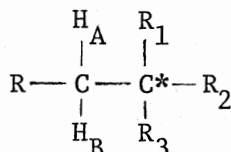
step is an exothermic reaction which is difficult to control. The reaction mixture becomes so viscous as to prevent stirring and consequently a severe foaming problem results. Upon cooling, the mixture forms a difficultly soluble glass which greatly complicates the work-up.

The synthesis of 1-ethyl-7-methylindan (7a) and 1-isopropyl-7-methylindan (8) have not been previously described. Hydrocarbon 8 has been suggested as one of the products by Bey and Ourisson during the rearrangement of 1,1,8-trimethyl- $\Delta^8$ -2-octalone in ethylene glycol containing *p*-toluenesulfonic acid,<sup>22</sup> but no physical data was offered for the product.

Magnetic nonequivalence of geminal protons and geminal methyl groups has been observed in the NMR spectra of a variety of chemical structures,<sup>23</sup> and is frequently observed in compounds containing a methylene or an isopropyl group adjacent to a chiral carbon.<sup>24-30</sup>

Magnetic nonequivalence results in an observable chemical shift depending on fulfillment of three conditions.<sup>31</sup> These conditions apply equally well whether the species be pairs of protons or magnetic nuclei other than protons. However, it is true that a large part of the literature is concerned with geminal protons or geminal methyl groups.

The first of these conditions is that there be no symmetry element between the species on the NMR time scale. So long as there is no molecular motion that corresponds to a symmetry operation for the species of a frequency of about  $10^3$ /sec, the species may be observably nonequivalent. This is easily seen for a molecule such as

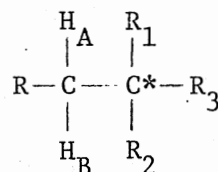




The methylene protons,  $H_A$  and  $H_B$  have no symmetry element between them. The chiral carbon atom denies a symmetry plane, and the protons are nonequivalent.<sup>32</sup>

The second condition for observable nonequivalence is that there be a field gradient (electrical and/or magnetic) between the species. The species may be geometrically nonequivalent (condition one), but still be in so nearly the same field that the chemical shift between them is beyond the limits of resolution of the NMR spectrometer.

The third condition for observation of nonequivalence is the absence of molecular motion(s) that simulates a symmetry operation. However, suppose that in the molecule



the field at the methylene proton is very much the same irrespective of the angle of rotation around the bond, then free rotation around this bond may so effectively reduce the chemical shift as to render it undetectable. Rotation is not a true symmetry operation since  $H_A$  and  $H_B$  have no symmetry axis; however, this may approximate a symmetry operation such that full rotation makes nonequivalence unobservable.

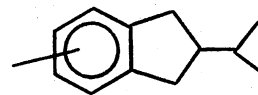
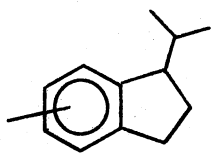
Compounds containing an isopropyl group adjacent to a chiral carbon can show a magnetic nonequivalence of geminal methyl groups in their NMR spectra.<sup>33-35</sup> The chemical shift difference between the geminal groups in conformationally mobile systems may be partitioned into a "conformational" term  $\Delta\delta_c$ , dependent on differences in conformer

populations and an "intrinsic" term,  $\Delta\delta_i$ , that is independent of these conformer populations.<sup>36</sup>

$$\Delta\delta_{\text{obs}} = \Delta\delta_c + \Delta\delta_i \quad (1)$$

Since populations of excited vibrational and solvation states probably influence chemical shifts and coupling constants only slightly, the intrinsic asymmetry effect is generally assumed to be temperature-independent.<sup>37</sup> The temperature dependent effect which results from unequal populations of the conformers must however be allowed for. Since the conformer populations will vary with temperature, there results a temperature-dependent contribution. Therefore, at infinite temperature, the populations of all the rotomers would be expected to be equal so that the contribution from the "conformational" term,  $\Delta\delta_c$  would become zero and hence  $\Delta\delta_{\text{obs}}$  is expected to be equal to  $\Delta\delta_i$ . Hence,  $\Delta\delta_i$  could be extracted through extrapolations to high temperature. However, Franzen and Binsch<sup>36</sup> specify that the conformer populations tend toward equality on increase of temperature only if entropy differences are zero. Also, they showed that in certain cases  $\Delta\delta_c$  and  $\Delta\delta_i$  may differ in relative sign. In particular,  $\Delta\delta_{\text{obs}}$  may accidentally be zero, despite  $\Delta\delta_c$  and  $\Delta\delta_i$  having a substantial magnitude. Extrapolations rely on a hypothesis of monotonic behavior of measured quantity as a function of temperature and hence cannot be applied in cases where  $\Delta\delta_c$  and  $\Delta\delta_i$  differ in relative sign.

Based on these facts, the chemical shift nonequivalence in  $^1\text{H}$  NMR spectra of compounds of the following type will be discussed in Chapter III.



Hydrocarbons have been important in  $^{13}\text{C}$  NMR spectroscopy since the earliest studies. The striking advantages of  $^{13}\text{C}$  NMR spectroscopy for the characterization of hydrocarbons was one of the initial discoveries of Lauterbur<sup>38</sup> in his pioneering studies of  $^{13}\text{C}$  spectra. Subsequently Grant and coworkers examined a variety of aliphatic<sup>39</sup> and aromatic<sup>40,41</sup> systems in detail to establish clearly the utility of  $^{13}\text{C}$  shieldings for hydrocarbon identification and as a probe for assessing the electronic structure of aromatic compounds.<sup>42</sup>

During the last decade, a great deal of attention has been focused on the effect of substituents on  $^{13}\text{C}$  chemical shifts.<sup>43,44</sup> The study of substituent effects has afforded empirical correlations and additivity models that have proven to be extremely useful in  $^{13}\text{C}$  peak assignments. Empirical correlations describing the influence of substituents on chemical shifts have been established for example in paraffins,<sup>45</sup> methylcyclohexanes,<sup>44</sup> methyldecalins<sup>46</sup> as well as for many other types of compounds.

By comparing the shielding of the monosubstituted compound with those for the parent hydrocarbon, one can obtain substituent effects for a given substituent. For a disubstituted derivative, the individual effects of each substituent can be used along with the shieldings of the parent hydrocarbon to estimate the shieldings for that derivative.<sup>47</sup> In many systems, this simple additivity method works very

well if the substituents are well separated; the predicted shieldings are generally within  $< 1$  ppm of the observed values. Also, because of their reproducibility, a knowledge of these substituent effects for a given system often can permit the direct assignment of  $^{13}\text{C}$  signals in the spectra of related compounds.<sup>48,49</sup>

Using spectral accumulation and complete proton decoupling,<sup>50</sup> the measurement of carbon chemical shifts has become relatively routine. These measurements require more sophisticated equipment than does  $^1\text{H}$  NMR spectroscopy, and  $^{13}\text{C}$  spectra are often difficult to interpret, as is evidenced by extensive discussions usually associated with the assignment of peaks.<sup>51</sup>

Attempts to overcome the problems of assignments have led to the development of a number of methods, the most important and often used being "off-resonance decoupling," which has the effect of reducing the one-bond  $^{13}\text{C}$ -H coupling to a fraction of its actual value while generally removing long range couplings. This provides information regarding the number of protons attached directly to the carbon.<sup>52</sup>

The use of deuterium substitution for assignment of resonance in  $^1\text{H}$  NMR spectroscopy has its parallel in  $^{13}\text{C}$  NMR spectroscopy. Carbons bonded to deuterium generally display no NOE and are split by residual C-D coupling. This results in resonance lines for carbons substituted with deuterium that are substantially less intense than those of bearing protons.<sup>53</sup> Hence, comparison of spectra of specifically deuterated materials with the spectra of the corresponding protio compounds allows ready assignment of resonances.

Among other techniques employed for carbon-13 assignments, the gated decoupling technique which provides information about long range

carbon-proton coupling is found to be very useful. In aromatic systems, the geminal long-range coupling  $^2J_{\text{CCH}}$  as well as the four bond coupling  $^4J_{\text{CCCCCH}}$  are found to be small (1-2 Hz), in contrast to the vicinal coupling  $^3J_{\text{CCCH}}$  (7-12 Hz).<sup>52</sup>

Other techniques which are employed in carbon-13 chemical shift assignments are the use of fully proton-coupled (non-decoupled) spectra<sup>54-56</sup> and selective  $^{13}\text{C}$  [ $^1\text{H}$ ] decoupling.<sup>55,56</sup>

Although many structural characteristics of molecules are clearly revealed by the  $^{13}\text{C}$  chemical shifts and coupling constants in NMR spectra, additional structural information as well as insight into dynamic molecular processes can be gained from relaxation time measurements.<sup>57,58</sup> The two characteristic times,  $T_1$  for spin-lattice relaxation, and  $T_2$  for spin-spin relaxation, describe different time-dependent processes occurring in the nuclear system.<sup>52,59,60</sup> The development of Fourier transform NMR has encouraged a strong interest in  $^{13}\text{C}$  spin-relaxation measurements and their application to organic chemistry problems. Usually,  $T_1$  measurements yield the desired information; therefore, the more difficult  $T_2$  measurements are used less often, especially in studies of organic compounds.<sup>52</sup>

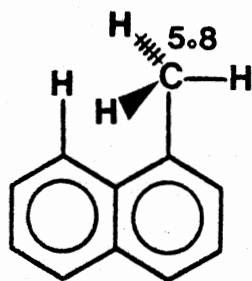
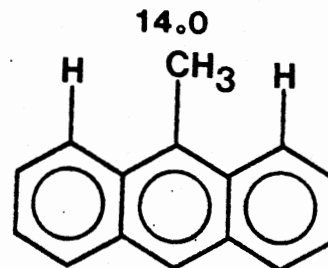
The process of spin-lattice relaxation is an energy exchange between nuclear spins and the "lattice," tending toward establishment of an equilibrium state of the populations of the nuclear spin energy levels. For nuclei of spin 1/2, this energy exchange results from the perception by these spins of fluctuating localized magnetic fields. There are four sources of these fluctuating fields, corresponding to four spin-lattice relaxation mechanisms: dipole-dipole interactions, spin-rotation, scalar interaction, and chemical shift anisotropy. In

many organic compounds,  $^{13}\text{C}$ - $^1\text{H}$  dipole-dipole (DD) interactions dominate carbon  $T_1$  processes. Of the remaining three mechanisms, only spin-rotation is commonly encountered, and then only in small molecules or with freely spinning groups in larger molecules.<sup>62</sup>

Spin-lattice relaxation phenomena primarily reflect the dynamics rather than structures of molecules. However, there is an intimate relation between the two and hence  $T_1$  values can be used indirectly as an aid to spectral assignments or more directly in studies of hindered rotation, axes of rotation, segmental motion, association, and complexation.<sup>57,64,65</sup>

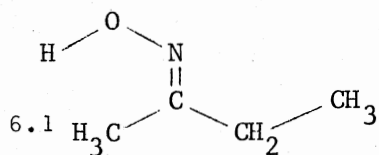
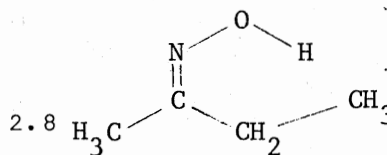
Among all carbons in a  $^{13}\text{C}$  NMR spectrum, the quaternary substituted ones are undoubtedly the most difficult to assign. The single resonance spectra frequently fails for reasons of complexity of spin-spin coupling patterns. In such cases relaxation data may provide unequivocal assignment.<sup>66</sup> Besides the designation of quaternary carbons, relaxation times are equally suited for the assignment of proton substituted carbons, particularly in those instances where the off-resonance spectrum cannot be distinguished because of numerous signal overlaps.<sup>67</sup> Furthermore,  $T_1$  values may serve to discriminate carbons which undergo internal re-orientation from those which belong to the rigid skeleton of the molecule.<sup>63</sup>

An interesting example of the study of dynamic molecular processes is the effect of the hindered rotation on methyl  $^{13}\text{C}$   $T_1$  values as found for 1-methylnaphthalene (9) and 9-methylanthracene (10), which give values of 5.8 and 14.0 sec, respectively.<sup>58</sup>

910

In 1-methylnaphthalene (9) the interaction with the peri-proton causes the methyl group to adopt a staggered conformation, thereby hindering its rotation and leading to a smaller  $T_1$  value, compared to  $T_1$  values of the methyl group in 10. In 9-methylanthracene, however, the existence of two peri-hydrogens means that there is no longer any preferred conformation of the methyl group, thus decreasing the rotation barrier and facilitating free rotation which, in turn, leads to a marked increase in  $T_1$ , as observed.

Similar behaviors are used to account for the differences in the  $^{13}\text{C}$  relaxation times of the syn and anti methyl groups in 2-butanone oxime (11a and 11b). Steric interaction between the syn-methyl group and the hydroxyl proton in 11a leads to a lowering of torsional barrier and enhanced rotation for the methyl group. This, in turn, causes a decrease in the effectiveness of the dipolar mechanism, leading to an increase in methyl  $T_1$ -value.

11a11b

This interaction is removed in the anti-isomer 11b, where the methyl group undergoes normal rotation, leading to more effective dipolar relaxation and a considerably shortened  $T_1$ -value relative to that of syn-methyl carbon of 11a.<sup>68</sup>

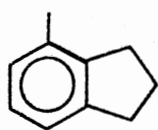


## CHAPTER III

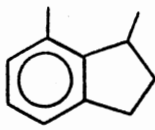
### RESULTS AND DISCUSSION

General. This study is divided into four parts. The synthesis of peri-substituted indans 6-8, along with nine unhindered analogs constitutes the first part. The second part is concerned with a comprehensive analysis of magnetic nonequivalence of isopropyl methyls through  $^1\text{H}$  NMR spectroscopy. The third area of concentration is concerned with the study of  $^{13}\text{C}$  chemical shift assignments for alkylated indans and from the resulting assignments an attempt is made to deduce substituent shift parameters for methylated indans. The fourth and final area of concentration concerns the study of peri interaction in 1,7-dialkylated indans through  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral studies and also through  $^{13}\text{C}$  spin lattice relaxation studies.

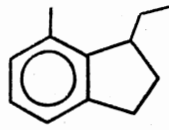
Synthesis. The syntheses of alkylated indans 5, 6, 7a, 8 and 12-20 were carried out for  $^{13}\text{C}$  NMR spectral studies and for use in thermodynamic studies by the U.S. Department of Energy, Bartlesville Energy Technology Center.



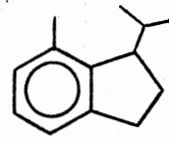
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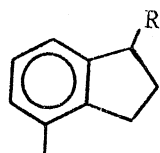
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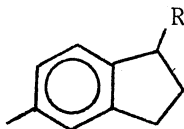
7a



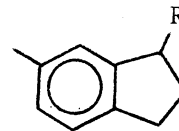
8



12, R=CH<sub>3</sub>  
13, R=C<sub>2</sub>H<sub>5</sub>  
14, R=i-C<sub>3</sub>H<sub>7</sub>



15, R=CH<sub>3</sub>  
16, R=C<sub>2</sub>H<sub>5</sub>  
17, R=i-C<sub>3</sub>H<sub>7</sub>

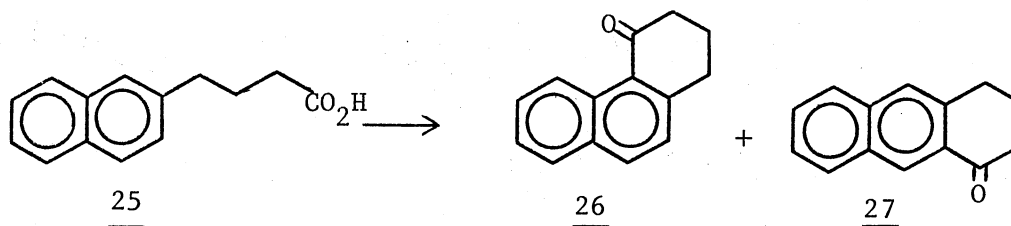


18, R=CH<sub>3</sub>  
19, R=C<sub>2</sub>H<sub>5</sub>  
20, R=i-C<sub>3</sub>H<sub>7</sub>

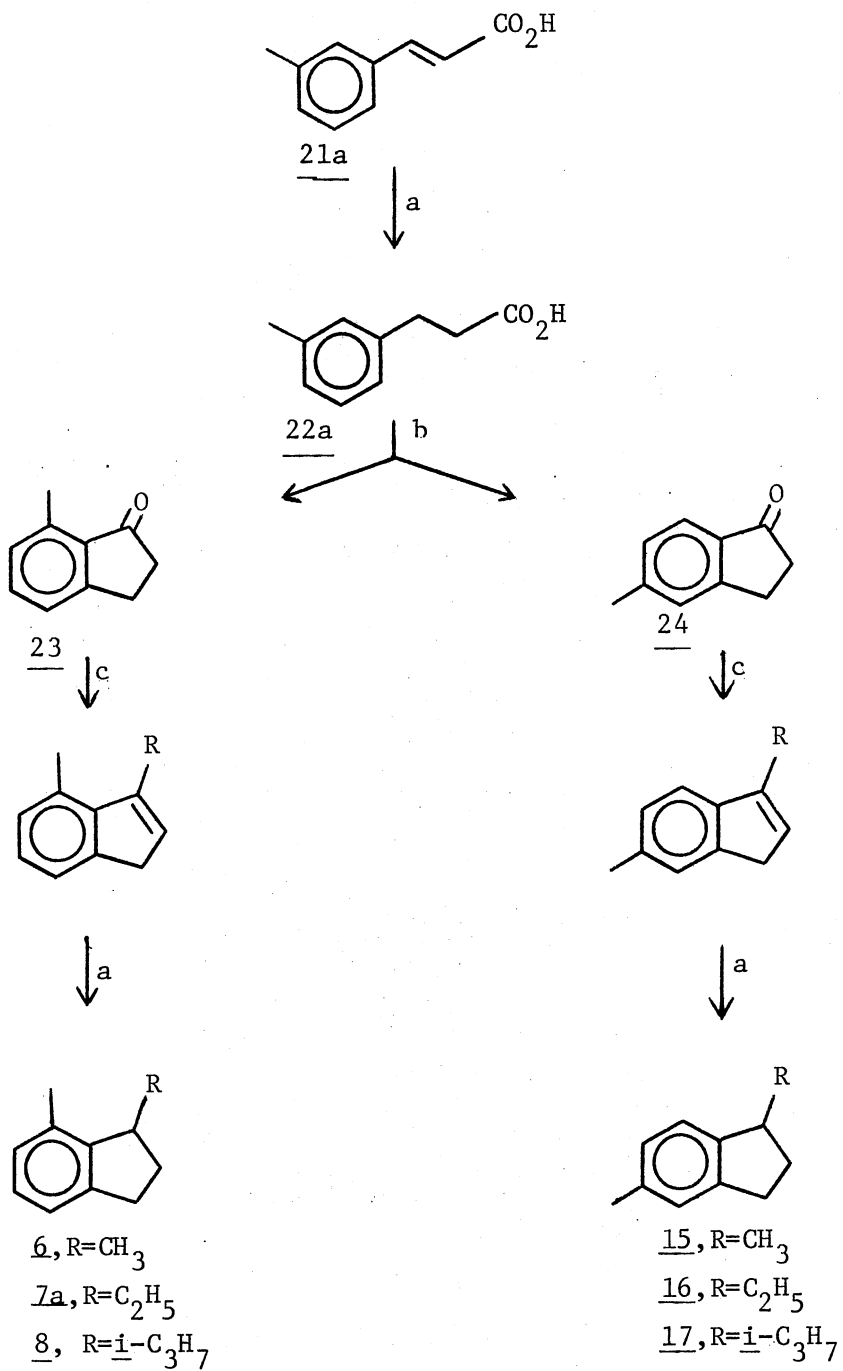
The indans 5, 6, 7a and 8 are of interest because of the synthetic challenge and because the bulk of the alkyl substituents at the peri-positions have a pronounced effect on the <sup>1</sup>H and <sup>13</sup>C NMR spectra. The synthesis provided an excellent method to obtain the three peri-substituted indans 6, 7a and 8 through a common route as shown in Figure 4.

Knoevenagel<sup>68</sup> condensation of 3-methylbenzaldehyde with malonic acid in pyridine solvent yielded 21a in 90-95% yield. Hydrogenation in presence of 5% Pd/C in acetic acid gave 3-(3-methylphenyl)propanoic acid (22a) in 95% yield.

Vuppalapaty<sup>69</sup> reported selectivity in cyclization of 4-arylbutanoic acids depending on the acidic reagent used for cyclization. For example, as shown below, cyclization of 25, resulted in different ratios of 26 and 27, depending on the cyclization reagent.<sup>69</sup>



However, as shown in Figure 4, similar cyclizations of 22a leading to 23 and 24, using hydrogen fluoride (HF), polyphosphoric acid (PPA) and methanesulfonic acid (MSA) did not show any selectivity and gave the same ratio of isomeric indanones (23:24; 1:1). Each of the three



<sup>a</sup> Pd/C, H<sub>2</sub>, CH<sub>3</sub>CO<sub>2</sub>H. <sup>b</sup> PPA, Δ. <sup>c</sup> RMgx, -H<sub>2</sub>O.

Figure 4. Reaction Sequence for Synthesis of Indans

reagents gave high yields for the cyclization of 22a.

Use of HF has the advantage that there is practically no work-up involved after reaction since the excess HF can be easily evaporated using a gas stream or steam bath leaving the crude product. However, the hazard in using this reagent is a distinct disadvantage.

With PPA, the reaction time and temperature are critical. At high temperature and longer reaction time, self-condensation causes decrease in yields. Koo<sup>70</sup> has developed guidelines for optimizing reaction temperature in PPA cyclization.

Eaton and Carlson<sup>71</sup> have described a cyclization procedure using a hot mixture of MSA and P<sub>2</sub>O<sub>5</sub>. Since MSA ordinarily does not cause sulfonation of aromatic rings, we considered that neat MSA should be a superior cyclizing agent at elevated temperatures because of its acidity and excellent solvent properties. The performance of a neat anhydrous MSA exceeded our expectations and the easy handling and simple work up procedure suggested MSA may be superior to hot PPA as a cyclizing agent.<sup>72</sup>

The critical step in the synthesis shown in Figure 4 is obviously the separation of the isomeric indanones 23 and 24 which are formed approximately in 1:1 ratio during the cyclization of the acid 22a. Partial separation was accomplished by fractional crystallization in n-hexane, during which about 10-15% of the pure indanone 24 was isolated as white crystals. Ketone 23 was separated completely from the enriched mother liquor by the use of preparative HPLC as described in the following chapter.

Ourisson and Munnavalli<sup>13</sup> reported the synthesis of several alkylated indans from the reaction of indanones and alkylmagnesium

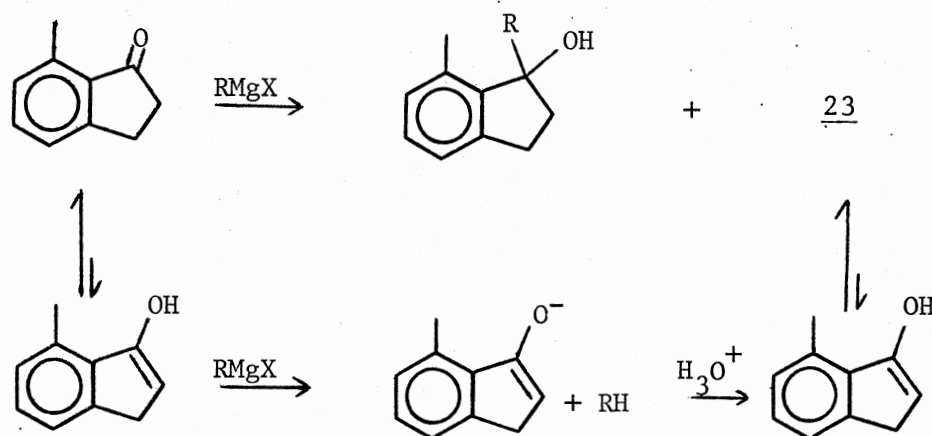
halides. However, our experience showed that these reactions do not go to completion and hence result in a product contaminated with unreacted starting material. With bulkier alkyl Grignards (isopropyl) the amount of unreacted indanones is considerable as is recorded in Table I which shows the percent unreacted indanones 23 and 24 found in the product of their reactions with alkylmagnesium halides.

TABLE I  
PERCENT UNREACTED INDANONES

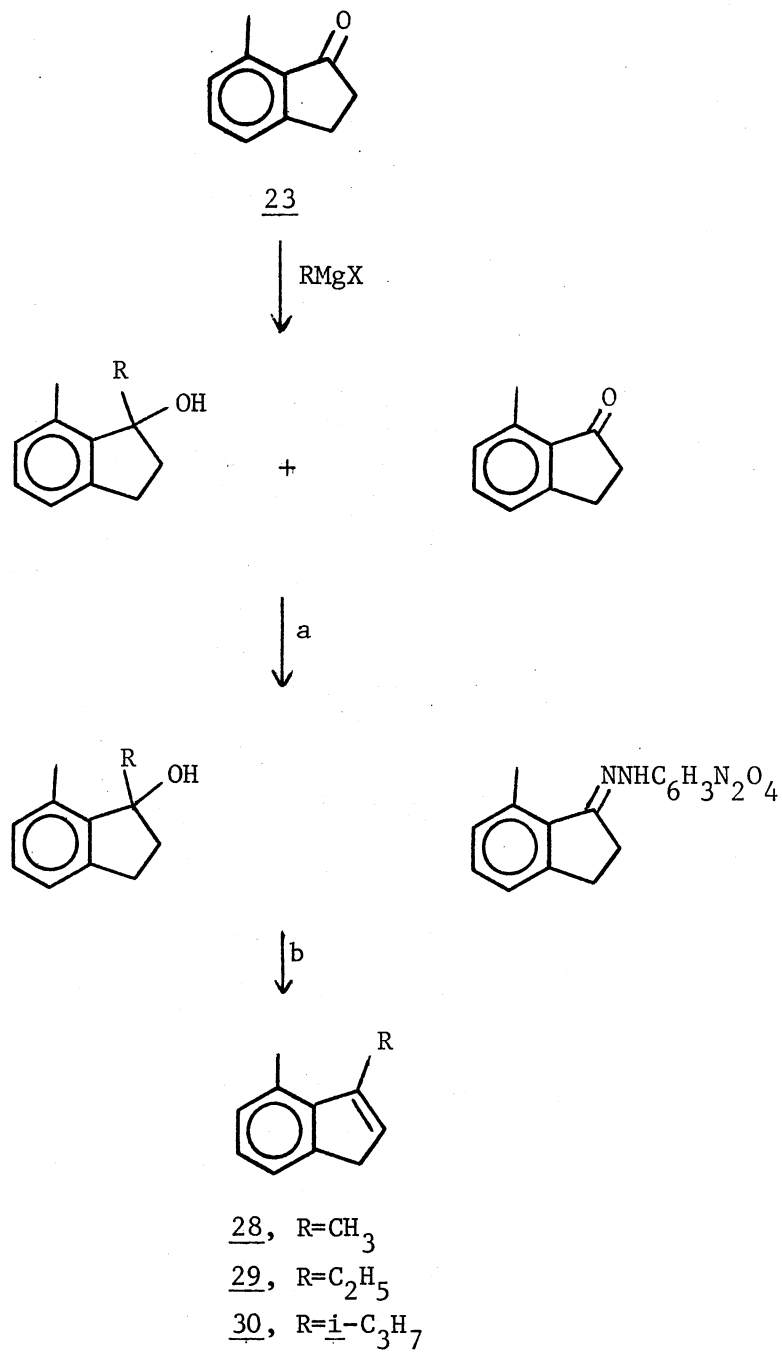
Indanone	RMgX	% Unreacted Ketones
<u>23</u>	i) CH <sub>3</sub> MgBr	4
	ii) C <sub>2</sub> H <sub>5</sub> MgBr	8
	iii) <u>i</u> -C <sub>3</sub> H <sub>7</sub> MgCl	74
<u>24</u>	i) CH <sub>3</sub> MgBr	3
	ii) C <sub>2</sub> H <sub>5</sub> MgBr	7
	iii) <u>i</u> -C <sub>3</sub> H <sub>7</sub> MgCl	47

The higher percentage of recovered 23 (74%) vs 24 (47%) results from the steric effect of the peri-methyl group at C-7 of 23. Because of this steric hindrance, the addition of isopropylmagnesium chloride to the carbonyl group of 23 is slower than addition to 24. Consequently, there is more time for enolization as shown below, to take place. Once enolization occurs, there is rapid reaction with Grignard reagent

to form the enolate anion and propane. Reversal of this anion to 23 does not take place since there is no source of proton while the Grignard reagent is present. Once the Grignard reagent is destroyed during the work-up with dilute acid, ketone 23 is formed from the enolate as shown below and then appears as a contaminant in the product mixture.



We devised an efficient method for the removal of unreacted indanones, based on formation of the 2,4-dinitrophenylhydrazone. Figure 5 shows the scheme employed for the removal of unreacted indanone, 23. The same scheme was also employed for removing indanones 24, 31 and 32 from reaction mixtures. The procedure for this separation involves mixing a catalytic amount of oxalic acid, ethanol and 2,4-dinitrophenylhydrazine to form the red-orange 2,4-dinitrophenylhydrazone which precipitates from solution. The precipitate is filtered out and the filtrate on steam distillation in presence of catalytic amount of oxalic acid gives the indenenes 28-30, completely free of the



<sup>a</sup> 2,4-Dinitrophenylhydrazine. <sup>b</sup> Steam distillation of filtrate in presence of  $\text{H}_2\text{C}_2\text{O}_4$ .

Figure 5. Scheme for the Separation of Unreacted 23

corresponding indanone. A major advantage of this method is that the 2,4-dinitrophenylhydrazones may be purified by recrystallization in nitroethane and then converted to indanone by various published procedures.<sup>73</sup> This method should be widely applicable for removing unreacted ketones after their reactions with alkylmagnesium halides.

The indanones 31 and 32 were prepared separately from 2-methyl and 4-methylbenzaldehydes respectively, by a procedure similar to that used for the preparation of 23 and 24. The indans 12-20 were prepared from 24, 31 and 32 by a procedure identical to that described for the preparation of indans 6, 7a and 8. Table II summarizes the percent unreacted ketones and the percentage yields of the corresponding indenenes. Catalytic hydrogenation of the indenenes to the corresponding indans took place in excellent yields (90-95%).

Chemical Shift Nonequivalence of Isopropyl Methyl Groups. Compounds containing an isopropyl group adjacent to a chiral carbon show magnetic nonequivalence of geminal methyls in their NMR spectra.<sup>33-35,74</sup> As stated earlier, the chemical shift difference between the geminal groups ( $\Delta\delta_{\text{obs}}$ ) in conformationally mobile systems may be positioned into a "conformational" term ( $\Delta\delta_{\text{c}}$ ) depending on the difference of conformer populations and a temperature independent "intrinsic" term ( $\Delta\delta_{\text{i}}$ ) that is independent of these conformer populations.<sup>74</sup> The intrinsic nonequivalence results from the dissymmetric environment created by the asymmetric centers in these compounds.

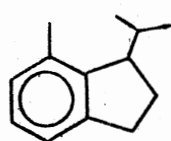
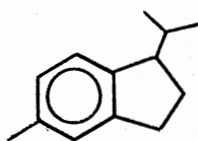
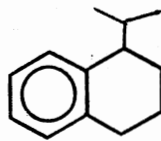
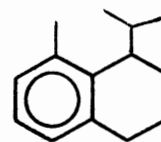
$$\Delta\delta_{\text{obs}} = \Delta\delta_{\text{c}} + \Delta\delta_{\text{i}} \quad (1)$$



TABLE II  
 PERCENT UNREACTED KETONES AND THE PERCENTAGE YIELD OF INDENES

Indanone	Alkylmagnesium halide	% Unreacted Ketone	% Yield
<u>23</u>	CH <sub>3</sub> MgBr	3-5	85-90
	C <sub>2</sub> H <sub>5</sub> MgBr	8	75-80
	<u>i</u> -C <sub>3</sub> H <sub>7</sub> MgCl	74	15-20
<u>24</u>	CH <sub>3</sub> MgBr	3-5	85-90
	C <sub>2</sub> H <sub>5</sub> MgBr	7	75-80
	<u>i</u> -C <sub>3</sub> H <sub>7</sub> MgCl	47	25-30
<u>31</u>	CH <sub>3</sub> MgBr	3-5	85-90
	C <sub>2</sub> H <sub>5</sub> MgBr	6	75-80
	<u>i</u> -C <sub>3</sub> H <sub>7</sub> MgCl	45	25-30
<u>32</u>	CH <sub>3</sub> MgBr	3-5	85-90
	C <sub>2</sub> H <sub>5</sub> MgBr	7	75-80
	<u>i</u> -C <sub>3</sub> H <sub>7</sub> MgCl	47	25-30

The hydrocarbons 8, 17, 33 and 34 were investigated to seek an understanding of the contributions from "conformational" term  $\Delta\delta_c$  and "intrinsic" term  $\Delta\delta_i$  as given in equation (1). As expected, the  $^1\text{H}$  NMR spectra of hydrocarbons 8, 17 and 33 show an extensive magnetic non-equivalence of the isopropyl methyl groups at temperatures between 30 and 150 °C.

8173334

An increase in temperature results in a decrease of  $\Delta\delta_{\text{obs}}$  in all three cases (Table III). However, hydrocarbon 34 exhibits unusual magnetic nonequivalent isopropyl methyl signals. Binsch and Franzen<sup>36a</sup> suggested that  $\Delta\delta_c$  and  $\Delta\delta_i$  terms in equation (1) may differ in relative sign. Therefore, in case of 34 the  $\Delta\delta_i$  term in equation (1) has a contribution to  $\Delta\delta_{\text{obs}}$  opposite in sign as compared to compounds 8, 17 and 33. However, Reisse and coworkers<sup>36b</sup> have an opposing view about the concept of intrinsic and conformational anisochronism and they suggest that the differences in the screening constants between diastereotopic groups (e.g., the two isopropylmethyl groups in compounds 8, 17, 33 and 34) could be the reason for observed nonequivalence. This is discussed in detail elsewhere.<sup>75,76</sup>

In all the four hydrocarbons, one methyl resonance ( $\delta_A$ ) remains unaffected by temperature change as shown in Table III. This may result from one methyl group spending more time in the shielding zone of the aromatic ring and consequently its doublet appears at higher field and it is subject to temperature dependence ( $\delta_B$ ) whereas the

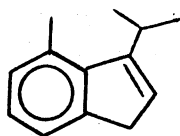
TABLE III  
 CHEMICAL SHIFT VALUES FOR ISOPROPYL METHYL SIGNALS IN  
 HYDROCARBONS 8, 17, 33 AND 34

Hydrocarbon	Temperature (°C) <sup>b</sup>	$\delta_A$ (Hz) <sup>a</sup>	$\delta_B$ (Hz) <sup>a</sup>	$\delta_A - \delta_B$ ( $\Delta\delta_{\text{obs}}$ )
<u>8</u>	30	104.0	63.5	40.5
	60	104.0	65.5	38.5
	90	104.0	67.5	36.5
	120	104.0	69.5	34.5
	150	104.0	71.5	32.5
<u>17</u>	30	98.0	76.5	21.5
	60	98.0	78.5	19.5
	90	98.0	80.0	18.0
	120	98.0	81.5	16.5
	150	98.0	82.5	15.5
<u>33</u>	30	98.0	70.0	28.0
	60	98.0	72.5	25.5
	90	98.0	75.5	22.5
	120	98.0	78.0	20.0
	150	98.0	80.0	18.0
<u>34</u>	30	87.0	84.0	3.0
	60	87.0	85.3	1.7
	90	87.0	87.0	0
	120	87.0	87.9	-0.9
	150	87.0	88.5	-1.5

<sup>a</sup> From Me<sub>4</sub>Si (indirect) in 1,2,4-trichlorobenzene. <sup>b</sup> Temperature accurate to  $\pm 2$  °C.

other methyl group shows the usual chemical shift value and its resonance signal is stationary.

The indene 30 was chosen to study the contribution of  $\Delta\delta_c$  term for the nonequivalence of isopropyl methyl group. The  $\Delta\delta_i$  term in equation (1) is completely removed in 30, as the isopropyl group is no longer attached to a chiral carbon.

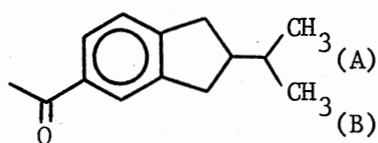
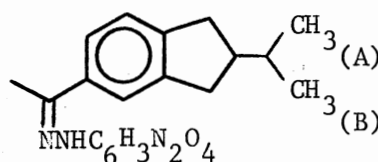


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Low temperature NMR spectra of indene 30 were examined with the expectation that steric interference would lead to restricted rotation of the isopropyl group. However, the low temperature NMR spectra of 30 indicates the rotation of the isopropyl group is fast on the NMR time scale even at  $-150\text{ }^\circ\text{C}$ , hence nonequivalence is not observable. The absence of nonequivalence even at very low temperature ( $-150\text{ }^\circ\text{C}$ ) suggests that the "intrinsic" term ( $\Delta\delta_i$ ) arising from chirality rather than the "conformational" term ( $\Delta\delta_c$ ) arising from steric factors is responsible for the large chemical shift nonequivalence ( $\Delta\delta_{\text{obs}}$ ) displayed by the isopropyl methyl groups in 8. Further, the temperature dependence of the spectrum of 8 could be a result of differences in the conformer populations. These two observations suggest that  $\Delta\delta_c$  and  $\Delta\delta_i$  might always occur lumped together and the magnitude and relative sign of these two terms depend on the compound in question. At this time, we do not have a rationalization for their magnitude and relative sign.

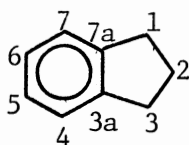
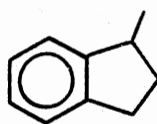
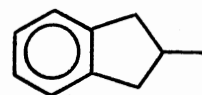
The  $^1\text{H}$  NMR spectra of 35 and 36 did not show any chemical shift

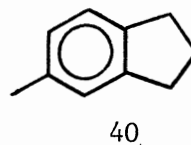
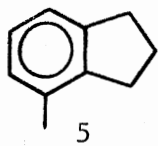
nonequivalence between the two isopropyl methyl groups. Since the

3536

the isopropyl group is attached in each case to a chiral carbon chemical shift nonequivalence due to intrinsic asymmetry is expected. There is no contribution from the "conformational" term ( $\Delta\delta_c$ ) as there cannot be any pronounced barrier for the rotation of the isopropyl group. The complete absence of chemical shift nonequivalence indicates, the  $\Delta\delta_i$  term is also negligible. One of the conditions for observation of nonequivalence is that there be no molecular motions that simulates a symmetry operation.<sup>31</sup> In compounds 35 and 36, the field at both isopropyl methyl protons is very much the same irrespective of the angle of rotation around the bond. This may effectively reduce the chemical shift such that it is no longer detectable. Rotation is not a true symmetry operation since  $\text{CH}_3_{(A)}$  and  $\text{CH}_3_{(B)}$  have no symmetry axis; however, this may sufficiently approximate a symmetry operation as to render nonequivalence unobservable through full rotation.<sup>31</sup>

Discussion of  $^{13}\text{C}$  NMR of Alkylated Indans. Table IV includes  $^{13}\text{C}$  chemical shifts of indans and all four isomeric monomethylindans. The numbering system along with the structures are shown below.

373839



The C-13 chemical shifts for indan (37) have been reported by several workers.<sup>3b,48,77</sup> The assignments of resonance positions for the other hydrocarbons were accomplished by various techniques.<sup>48,52-56</sup> The chemical shift assignments for 38 were made by taking into consideration the known substituent effect of  $\alpha$  and  $\beta$  carbons (deshielding) and  $\gamma$ -carbon (shielding).<sup>57,78</sup> Observation of a doublet in the SFORD experiment at 39.4 ppm made the assignment for C-1 possible. Triplets were observed in the off-resonance spectrum for the resonance lines at 34.7 and 31.4 ppm. The value 31.4 ppm is assigned to C-3 as the methyl group at C-1 which is  $\gamma$  to C-3 should shield it as compared to the value of 32.8 ppm for indan (37). The signal at 34.7 is assigned to C-2. The peak assignments for the six aromatic carbons were made by comparison with 37 and taking into consideration the  $\beta$ -deshielding effect of methyl group at C-1 and  $\gamma$ -shielding effect on C-7.<sup>70</sup>

By comparison with model compound 37 and from the observed multiplicities of signals in the off-resonance spectrum, the assignment of the signals for hydrocarbon 39 were made without ambiguity. Also the symmetry present in the molecule makes the assignment fairly straightforward.

In indan 5, with the methyl group at C-4 ortho or  $\beta$  to C-3, permitted assigning the upfield signal of 31.4 to C-3 and the downfield signal (33.1 ppm) to C-1. As the C-7 carbon is para to the methyl group, the upfield signal at 121.5 ppm in the aromatic region is

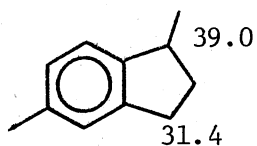
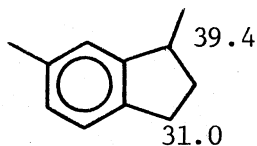
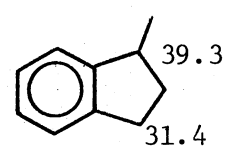
TABLE IV  
 $^{13}\text{C}$  CHEMICAL SHIFTS OF MONOMETHYLINDANS<sup>a</sup>

Compound	C-1	C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	CH <sub>3</sub>
<u>37</u>	32.8	25.4	32.8	143.6	124.1	125.8	125.8	124.1	143.6	-
<u>38</u>	39.4	34.7	31.4	143.3	124.0	125.9	125.9	122.8	148.2	19.8
<u>39</u>	41.1	34.4	41.1	143.2	124.2	125.8	125.8	124.2	143.2	20.6
<u>5</u>	33.1	24.7	31.4	142.5	133.3	126.7	126.1	121.5	143.3	19.1
<u>40</u>	32.4	25.6	32.8	143.8	124.8	135.0	126.6	123.8	140.6	21.1

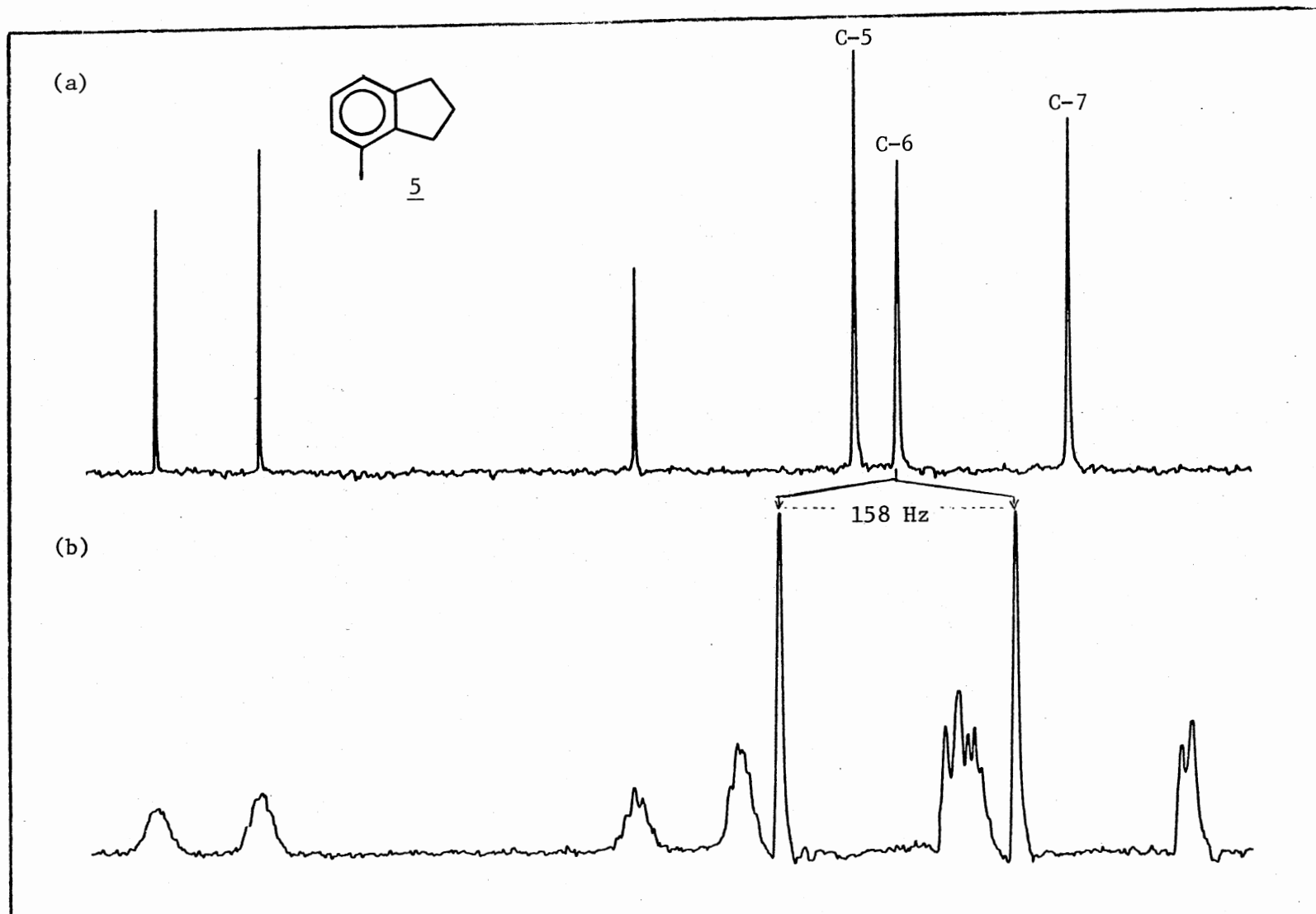
<sup>a</sup> 2 M solutions in CDCl<sub>3</sub> relative to Me<sub>4</sub>Si in ppm.

assigned to it. The assignments for C-5 and C-6 carbons are based on the information obtained from the gate-decoupled spectrum of 5 (Spectrum 1). Only the aromatic region is shown in this spectrum. The gate-decoupled spectrum gives information about long-range carbon coupling with protons on the aromatic ring. In aromatic systems the geminal  $^2J_{\text{CCH}}$  as well as the four-bond coupling  $^4J_{\text{CCCH}}$  are found to be small (1-2 Hz), in contrast to vicinal coupling  $^3J_{\text{CCCH}}$  (7-12 Hz).<sup>50-52</sup> In the indan 5, C-6 cannot experience any three-bond coupling and its splitting from two-bond C-H coupling are often too small to be resolved. Therefore its signals appear as a pair of sharp but unresolved doublets,  $^1J_{\text{C-6, H-6}} = 158$  Hz, which can be distinguished from other signals. On the other hand, C-5 experiences one directly bonded coupling with hydrogen,  $^1J_{\text{C-5, H-5}} = 156$  Hz, which is then split by H-7,  $^3J_{\text{C-5, H-7}} = \sim 8$  Hz. A very small splitting by H-6 is also observed and this results in further fine splitting of the peaks. Thus, analysis of gate-decoupled spectra of 5 aids the assignment of peaks for C-5 and C-6 carbons. The assignments for other carbons are simple and are given in Table IV.

The chemical shift assignments for C-1 and C-3 carbons in hydrocarbon 40 requires caution as the methyl group at C-5 is remote from C-1 and C-3 which removes any concern based on steric effects. The assignments for them are made using 15, 18 and 38 as model compounds.

151838





Spectrum 1. The Aromatic Portion of (a) Full-Decoupled, and (b) Gate-Decoupled  $^{13}\text{C}$  NMR of 5

The  $\alpha$ -shielding and  $\gamma$ -shielding effects<sup>57,58</sup> of the methyl group at C-1 and the observed multiplicities of signals in off-resonance spectra of 15, 18 and 38 made possible the assignments for C-1 and C-3. Comparison of  $^{13}\text{C}$  NMR spectra of 15 and 38 shows that the presence of methyl group at C-5 shields C-1 by 0.4 ppm with the C-3 resonance unaffected. Similarly, comparison of 18 and 38 reveals the methyl group at C-6 shields C-3 by 0.4 ppm and again the C-1 resonance remains unaffected. Based on these observations, the presence of methyl group at C-5 in 40 is expected to shield C-1 as compared with C-3. Hence the signal at 32.4 ppm is assigned to C-1 and 32.8 ppm to C-3. The assignments for other carbons are fairly simple and are shown in Table IV. However the resonances for C-4 and C-7 were assigned using gated-decoupling technique.

Dimethylindans. The  $^{13}\text{C}$  chemical shift values of dimethylindans are summarized in Table V. In appropriate cases, methods such as off-resonance proton decoupling, gated decoupling, and comparison with model compounds were used to make assignments. Also, the  $\alpha$ - and  $\beta$ -deshielding and  $\gamma$ -shielding effects of methyl substituent (attached to C-1 or C-2 or C-3 carbons) are taken into account.

For 1,1-dimethylindan (43), based on peak intensity, the signal at 28.6 ppm is assigned to the geminal methyl carbons. Because of the  $\beta$ -deshielding effect on each other, a downfield displacement of the methyl carbon resonance occurs as compared to the methyl carbon resonance of 38. Similar  $\beta$ -effect is also observed for 2,2-dimethylindan (44).

The results of C-13 NMR studies of cis- and trans-1,2-dimethylindans (41a and 41b respectively) give an insight into their stereochemistry. On the basis of known dependence of the vicinal coupling constants on

TABLE V

 $^{13}\text{C}$ -CHEMICAL SHIFTS FOR DIMETHYLINDANS<sup>a</sup>

Indan	C-1	C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	R(CH <sub>3</sub> )
1,1-Dimethyl-(43) <sup>b</sup>	43.8	41.4	30.1	142.1	124.2	126.0	126.0	121.3	152.0	R <sub>1</sub> , R <sub>1</sub> '=22.6
cis-1,2-Dimethyl-(41a) <sup>b</sup>	42.4	37.8	39.4	142.4	124.3	(126.0)	(125.9)	123.3	148.3	R <sub>1</sub> -14.6; R <sub>2</sub> =15.1
trans-1,2-Dimethyl-(41b) <sup>b, c</sup>	46.7	44.0	40.2	142.7	123.9	125.9	125.9	122.8	148.1	R <sub>1</sub> =17.6; R <sub>2</sub> =18.5
cis-1,3-Dimethyl- <sup>b</sup>	38.1	45.1	38.1	148.0	122.5	126.0	126.0	122.5	148.0	R <sub>1</sub> , R <sub>3</sub> =19.3
trans-1,3-Dimethyl- <sup>b, c</sup>	37.6	43.1	37.6	147.9	123.1	126.2	126.2	123.1	147.9	R <sub>1</sub> , R <sub>3</sub> =20.5
1,4-Dimethyl-(12)	39.6	34.2	29.9	142.2	133.2	126.8	126.2	120.3	148.1	R <sub>1</sub> =20.5; R <sub>4</sub> =18.9
1,5-Dimethyl-(15)	39.0	34.9	31.3	143.7	124.9	135.4	126.7	122.7	145.5	R <sub>1</sub> =20.0; R <sub>5</sub> =21.2
1,6-Dimethyl-(18)	39.3	34.9	31.0	140.5	123.7	126.7	135.3	123.8	148.6	R <sub>1</sub> =19.8; R <sub>6</sub> =21.2
1,7-Dimethyl-(6)	38.3	33.5	30.8	142.9	121.8	126.3	127.4	133.2	147.1	R <sub>1</sub> =19.3; R <sub>7</sub> =18.6
2,2-Dimethyl-(44) <sup>b</sup>	47.6	39.9	47.6	142.9	124.4	125.8	125.8	124.4	142.9	R <sub>2</sub> , R <sub>2</sub> '=28.7
4,6-Dimethyl- <sup>b</sup>	33.0	42.0	30.9	139.4	132.8	127.5	135.3	122.2	143.5	R <sub>4</sub> =18.9; R <sub>6</sub> =21.0
4,7-Dimethyl- <sup>b</sup>	31.6	24.2	31.6	142.0	130.4	126.9	126.9	130.4	142.0	R <sub>4</sub> , R <sub>7</sub> =18.8
5,6-Dimethyl- <sup>b</sup>	32.6	25.7	32.6	141.3	125.4	133.6	133.6	125.4	141.3	R <sub>5</sub> , R <sub>6</sub> =19.6

<sup>a</sup> In ppm from internal Me<sub>4</sub>Si in 2 M solution. Values in Parentheses may be interchanged. <sup>b</sup> Reference 11b.

<sup>c</sup>  $^{13}\text{C}$  spectra were taken as a mixture of cis and trans isomers.

the dihedral angle, the stereochemistry of conformers can generally be established through  $^1\text{H}$  NMR spectral investigation.<sup>59,80</sup> Because of the complexity of the splitting of resonance signals in the  $^1\text{H}$  NMR spectra of 41a and 41b, the coupling constants and hence the dihedral angle

41a41b

could not be calculated. However, the  $^{13}\text{C}$  chemical shift values of 41a and 41b reported in Table V might suggest their stereochemistry. The downfield shift observed for the methyl carbons in 41b as compared to the methyl carbons in 41a reveals the predominance of pseudodiequatorial, conformation for trans isomer (41b). This is in accordance with the fact that the resonance of an equatorial substituent in a  $^{13}\text{C}$  NMR spectrum occurs downfield as compared to an axial substituent.<sup>48,78</sup> Comparison of the chemical shifts of C-1 and C-2 in the trans isomer also shows evidence for diequatorial conformation as equatorial substituents deshields  $\alpha$ - and  $\beta$ -carbons more than axial substituents.<sup>48,78</sup>

Volkov and Fedorova<sup>81</sup> examined the  $^1\text{H}$  NMR spectra of cis- and trans-1,3-dimethylindans (42a and 42b respectively) and established that the cis isomer 42a exists predominantly in pseudoequatorial conformation and the trans isomer 42b shows equilibration between pseudo axial-equatorial and pseudo equatorial-axial conformations.



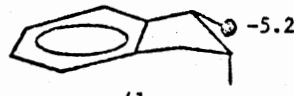
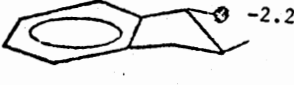
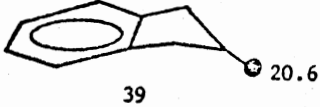
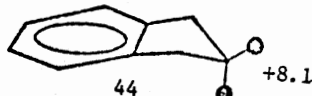
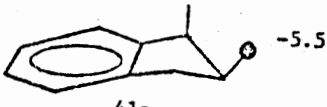
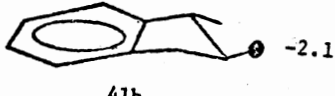
42a42b

The  $^{13}\text{C}$  NMR data presented in Table V also supports this. Thus the observation of increased deshielding for the methyl carbons as well as for C-1, C-2 and C-3 in 42a as compared to those in the trans isomer (42b) is in accordance with the findings deduced from  $^1\text{H}$  NMR data by Volkov and Fedorova.<sup>81</sup>

Table VI summarizes the effect of geminal and vicinal methyl groups on the  $^{13}\text{C}$  chemical shift values of each other as compared with the methyl resonance in the corresponding monomethylindan (parent). Vicinal methyl groups will have  $\gamma$ -shielding effect on each other.<sup>48,49,78</sup> The  $\gamma$ -effect of an axial substituent is increased shielding<sup>48,49,78</sup> as compared to an equatorial substituent. In cis-1,2-dimethylindan (41a), one of the methyl groups has to be in pseudo axial conformation, whereas in trans-1,2-dimethylindan (41b), both methyl groups are predominantly in pseudo-equatorial conformation. This leads to the observed upfield chemical shift for the methyl carbons in cis-1,2-dimethylindan. The  $\gamma$ -effect of equatorial substituent is quite small<sup>48,49,78</sup> and this is in accordance with the observed downfield shift for the methyl carbons in the trans isomer, 42b, as compared with the cis isomer, 41a. The effect of two ortho methyl groups on the C-13 chemical shift values of each other has been reported.<sup>40</sup>

By comparing the shielding of the monosubstituted compound with those for the parent hydrocarbon, one can obtain substituent effects for a given substituent. Alternatively, by comparing the suitable di- and monosubstituted derivatives, the substituent effects for a given substituent also can be obtained.<sup>47</sup> Thus a set of "substituent parameters" has been derived for methylated indans from the chemical shift reported in Tables IV and V. The average substituent parameters are

TABLE VI  
 EFFECT OF GEMINAL AND VICINAL METHYL GROUPS ON THE  
 CHEMICAL SHIFT VALUES OF EACH OTHER<sup>a,b</sup>

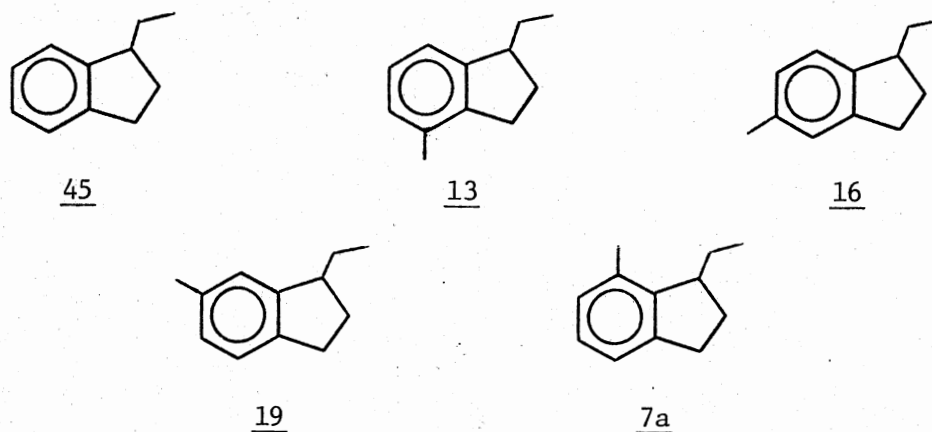
Parent	Geminal ( $\beta$ -effect)	Vicinal ( $\gamma$ -effect)
 38	 43	 41a
		 41b
 39	 44	 41a
		 41b

<sup>a</sup> The carbon under consideration is denoted by heavy dot.

<sup>b</sup> Positive values indicate the extent of deshielding compared to the methyl carbon of the parent compound, and the negative values the extent of shielding.

summarized in Table VII. The presence of methyl group at C-1 deshields C-1, C-2, C-4, C-5, C-6 and C-7a compared to the chemical shift values of the same carbons in indan (parent hydrocarbon). The carbons C-3, C-3a and C-7 are shielded. Similarly the shift parameters when the methyl group present at the remaining positions also are shown in Table VII. One can predict the chemical shifts of a dimethylindan by adding the perturbations (shift parameters) caused by each individual substituent onto the basic skeleton. This simple additivity method works very well for the indans where the methyl substituents are not sterically interacting, the experimentally observed values and those predicted using additivity, are in an excellent agreement for all carbons.

Ethylindans. The C-13 chemical shift values for the five ethylindans shown below are summarized in Table VIII.



The  $^{13}\text{C}$  chemical shift assignments for C-1 carbons of the above five indans were made by thorough analysis of off-resonance proton-decoupled spectra, which gave doublets for the corresponding signals. The assignments for carbons C-2 and C-3 of indan 13 were made by taking

TABLE VII  
 SUBSTITUENT PARAMETERS FOR METHYLINDANS<sup>a</sup>

Position of CH <sub>3</sub> group	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>3a</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>7a</sub>
C <sub>1</sub>	+6.5	+9.4	-1.4	-0.3	+0.1	+0.1	+0.1	-1.3	+4.6
C <sub>2</sub>	+8.3	+9.0	+8.3	-0.4	+0.1	0	0	+0.1	-0.4
C <sub>4</sub>	+0.3	-0.7	-1.4	-1.1	+9.2	+0.9	+0.3	-2.6	-0.3
C <sub>5</sub>	-0.4	+0.2	0	+0.2	+0.7	+9.2	+0.8	-0.3	-3.0

<sup>a</sup> In ppm; positive values denote downfield shifts relative to indan (37).



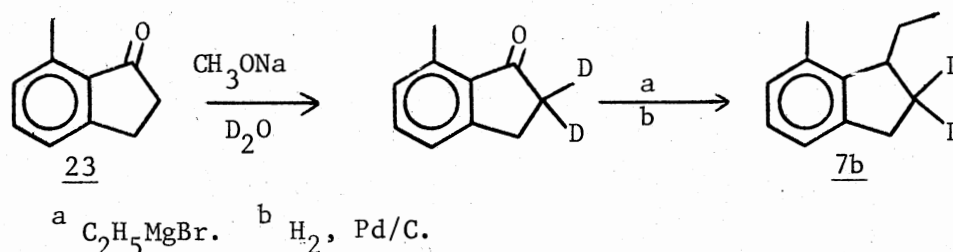
TABLE VIII  
 C-13 CHEMICAL SHIFT VALUES FOR THE ETHYLINDANS<sup>a,b</sup>

Carbon	<u>45</u>	<u>13</u>	<u>16</u>	<u>19</u>	<u>7a</u>
C-1	46.4	46.7	46.1	46.4	45.5
C-2	(31.5)	31.8	31.8	31.8	29.6
C-3	(31.4)	29.9	31.3	30.9	31.2
C-3a	143.7	142.6	(144.1)	140.7	143.2
C-4	124.1	133.1	124.9	123.8	121.7
C-5	125.7	126.9	135.5	126.8	126.2
C-6	125.9	126.0	126.5	135.0	127.4
C-7	123.4	120.8	123.2	124.1	133.3
C-7a	147.2	147.0	(144.4)	147.3	146.1
C-8	27.7	27.9	27.8	27.7	26.2
C-9	11.9	12.0	12.0	11.9	12.5
ArCH <sub>3</sub>	-	19.0	21.2	21.2	18.8

<sup>a</sup> 2 M solutions in CDCl<sub>3</sub> relative to Me<sub>4</sub>Si in ppm.

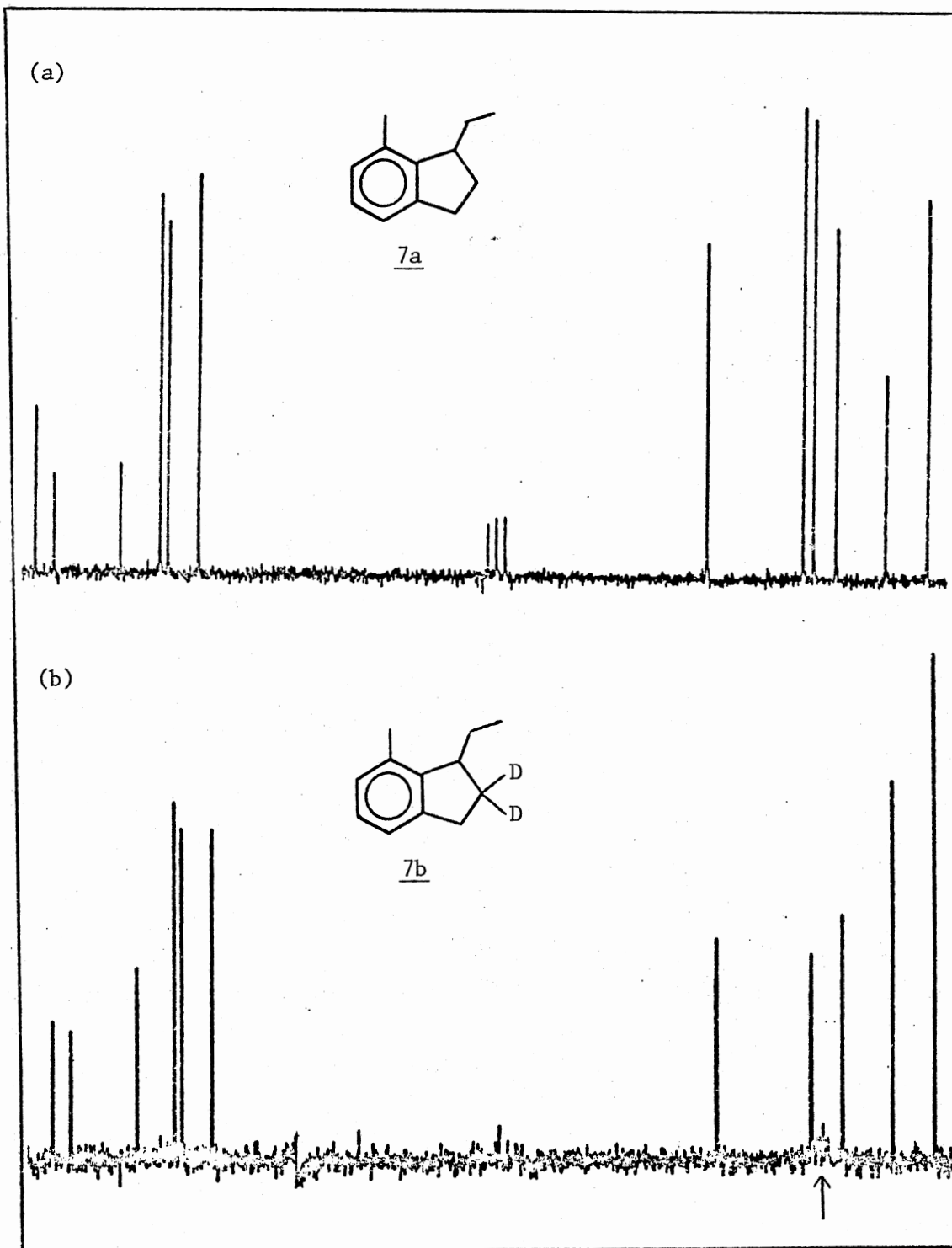
<sup>b</sup> Values in parentheses in the same column may be interchanged.

into consideration the shielding effect of C-4 methyl on C-3. The downfield value (amongst 29.9 and 31.3 ppm) is assigned to C-2 and the signal at 29.9 ppm is assigned to C-3. For compounds 16 and 19 the assignments for C-2 and C-3 are made by comparison with the chemical shift values of the C-2 and C-3 carbons of model compounds; 12, 13, 15, 16, 18 and 19. The assignments for C-2 and C-3 carbons of 7a were made through deuterium labeling. The protons attached to C-2 in indanone 23 were replaced with deuterium as shown below by the exchange procedure reported by Reich and coworkers.<sup>82</sup>



Carbons bonded to deuterium generally display no NOE effects and are split by residual C-D coupling.<sup>48,52,82</sup> This results in resonance lines for deuterated carbons that are substantially less intense than those of protonated ones. Comparison of the spectra of 7a and 7b (Spectrum 2) reveals that resonance at 29.6 ppm in 7b is converted to a triplet and almost lost in the noise and hence this resonance is assigned to C-2.

A Dreiding model of the indan 7a indicates that the peri-inter-action between the methyl and ethyl groups becomes severe when the latter adopts a pseudo-equatorial conformation. Hence, the ethyl group attains pseudo-axial conformation as compared to 13, 16, 19 and 45. This is reflected in the upfield chemical shift values observed for C-1 (45.5) and C-2 (29.6) carbons of 7a as compared to the



Spectrum 2.  $^{13}\text{C}$  NMR Spectra of 7a and 7b

chemical shift values of C-1 (46.7, 46.1, 46.4, 46.4) and C-2 (31.8, 31.8, 31.8, 31.5) in 13, 16, 19 and 45 respectively.

The assignments for the six aromatic carbons were made by comparison with model compounds viz. benzene, toluene, 37 and 45. A methyl group attached to a benzene nucleus shields the para carbon considerably and deshields the ipso carbon extensively. The ortho carbons are slightly deshielded and its effect on meta carbons are very small.<sup>52,83</sup> This fact is also taken into account while making the assignments for the aromatic carbons. The results from gate-decoupled and off-resonance proton decoupled experiments were also used to complete the assignments.

Isopropylindans. The  $^{13}\text{C}$  chemical shift values of the five isopropylindans 8, 14, 17, 20 and 46 are summarized in Table IX.

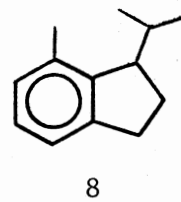
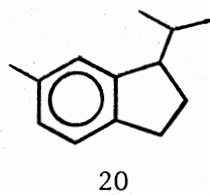
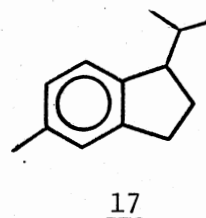
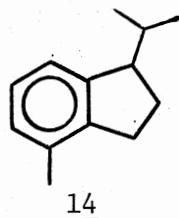
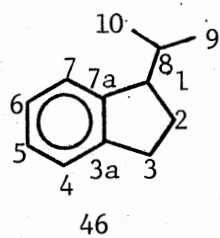


TABLE IX  
 C-13 CHEMICAL SHIFT VALUES OF ISOPROPYLINDANS<sup>a,b</sup>

Carbon	<u>46</u>	<u>14</u>	<u>17</u>	<u>20</u>	<u>8</u>
C-1	51.1	51.3	50.8	51.0	50.0
C-2	26.6	26.0	26.9	26.8	25.1
C-3	31.6	31.0	31.5	31.3	31.2
C-3a	144.2	142.9	143.1	141.1	143.8
C-4	124.1	133.1	124.8	123.8	121.5
C-5	(125.9)	126.8	135.4	126.8	126.2
C-6	(125.7)	125.9	126.4	134.8	127.4
C-7	(125.6)	121.4	123.8	124.7	133.4
C-7a	146.0	145.6	144.5	146.0	144.9
C-8	30.8	30.6	30.8	30.8	30.8
C-9	21.1	21.0	21.1	21.1	21.1
C-10	17.6	17.2	17.8	17.7	16.6
ArCH <sub>3</sub>	-	18.9	21.2	21.2	19.1

<sup>a</sup> 2 M solutions in CDCl<sub>3</sub> relative to Me<sub>4</sub>Si in ppm.

<sup>b</sup> Values in parentheses in the same column may be interchanged.

The assignment for C-1 and C-8 carbons of the above five indans were made from a thorough analysis of the off-resonance proton-decoupled spectra which showed doublets for the signals corresponding to those carbons. The presence of isopropylmethyl groups  $\gamma$ - with respect to the C-2 carbons explains the observed upfield shift as compared to the methyl and ethyl analogs. The presence of the methyl group at C-7 in indan 8 would force the isopropyl group more towards pseudo-axial conformation. This is in accordance with the observed upfield shifts for C-1 and C-2 carbons (50.0 and 25.1 ppm respectively) as compared to the C-1 and C-2 chemical shift values of those unhindered analogs (14, 17, 20 and 46).

As the isopropyl group is attached to a chiral carbon, the two methyl carbons show nonequivalent chemical shift values in their  $^{13}\text{C}$  NMR spectra also. In case of all five indans, the most upfield signal in the aliphatic region of their  $^{13}\text{C}$  spectra is assigned to one of the two methyls of the isopropyl group as it is believed to be influenced by the shielding cone of the benzene nucleus. The assignments for the other isopropyl methyl carbons and the arylmethyl carbons require caution as their  $^{13}\text{C}$  chemical shift values are very close and off-resonance proton-decoupled spectra would give quartets for both methyl signals. However, we made use of the spin-lattice relaxation ( $T_1$ ) values to identify both kinds of methyl signals. Relaxation studies can sometimes be applied for the assignment of C-13 signals; particularly in those instances wherein the off-resonance spectrum cannot be used.<sup>63,84</sup> Taking into account that the methyl group attached to the benzene nucleus does not have a vicinal proton, whereas the isopropyl methyl has one, the latter is anticipated to relax faster.<sup>84</sup> Table X

TABLE X  
CHEMICAL SHIFTS<sup>a</sup> AND RELAXATION TIMES  
OF THE METHYL CARBONS

Compound	Carbon	T <sub>1</sub> (sec)	δ <sub>c</sub> (ppm)
<u>14</u>	ArCH <sub>3</sub>	12.9	18.9
	9	2.8	21.0
<u>17</u>	ArCH <sub>3</sub>	12.1	21.2
	9	2.4	21.1
<u>20</u>	ArCH <sub>3</sub>	11.9	21.2
	9	2.5	21.1
<u>8</u>	ArCH <sub>3</sub>	14.0	19.1
	9	2.4	22.1

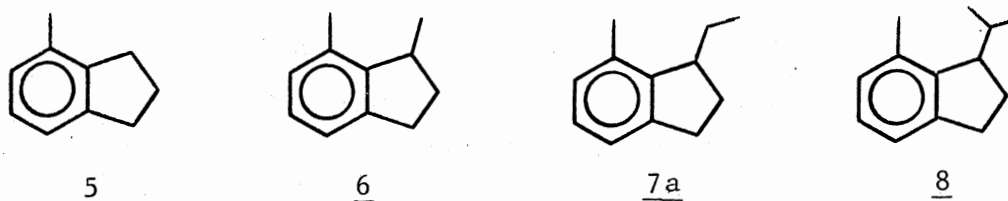
<sup>a</sup> In ppm from Me<sub>4</sub>Si in CDCl<sub>3</sub>.

summarizes the C-13 spin lattice relaxation times of the kinds of the methyl carbons in question.

The signal corresponding to the carbon which relaxes slowly is assigned to the methyl carbon attached to the benzene nucleus and the fast relaxing ones are assigned to the isopropyl methyl carbons.

The assignments for the six aromatic carbons were made by comparison with model compounds viz. benzene, toluene, 37 and 46 and also through analysis of gate-decoupled and off-resonance proton decoupled spectra of all the five compounds.

Discussion of peri-Interaction Through  $^1\text{H}$  and  $^{13}\text{C}$  NMR Studies. The compounds 5-8 were chosen to study the peri interaction through  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral studies.



Cheney<sup>85</sup> reported that hydrogen atoms which are subject to significant steric compression, generally exhibit a downfield shift relative to TMS. This effect is rationalized in terms of induced charge polarization in the C-H bond as a result of nonbonded hydrogen-hydrogen repulsive forces.<sup>85,86</sup> It has also been shown that the same effect is responsible for an increase in shielding experienced by the associated  $^{13}\text{C}$  nuclei.<sup>86,87</sup> The magnitude of these shifts however, exhibits a strong dependence upon the conformational geometry existing between the C-H bond in the two interacting groups.

Based on the above discussion, it is reasonable to expect that in



the series of indans 5-8, the downfield shift of the methyl group at the peri-position will increase as the bulk of the other substituent increases. The  $^1\text{H}$  NMR chemical shifts for the methyl protons in indans 5-8 are given in Table XI. These results given in Table XI show a deshielding effect on methyl proton signal by increase of the bulk of the peri-substituent at C-1. However, this effect is not very pronounced and this may result from conformational preference of the alkyl group at C-1, such that the peri-interaction is minimized.

TABLE XI  
 $^1\text{H}$  NMR CHEMICAL SHIFTS<sup>a</sup> OF  
 C-7 METHYL GROUP IN 5-8

Compound	$\delta_{\text{CH}_3}$	$\Delta\delta^b$
<u>5</u>	2.22	0.00
<u>6</u>	2.27	0.05
<u>7a</u>	2.29	0.07
<u>8</u>	2.30	0.08

<sup>a</sup> In ppm from  $\text{Me}_4\text{Si}$  in 2 M solution  
 in  $\text{CDCl}_3$ . <sup>b</sup> Relative to 5.

The  $^{13}\text{C}$  chemical shift arising from interaction of nuclei separated by more than three bonds is often small and variable. Thus less attention has been given to detailed study of such interactions, although nuclei separated by more than three bonds can exist in orientations in which nonbonded internuclear distances are comparable to or shorter than those for butane gauche arrangements. Based on the theory proposed by Grant and Cheney,<sup>86</sup> it was generally believed that  $^{13}\text{C}$  shieldings increase as the extent of steric crowding increases, until Grover, et. al.<sup>88</sup> reported that the substitution in cyclic compounds of hydroxyl having  $\delta$  syn-axial steric interactions with methyl carbons produces downfield shifts ~3 ppm. This long-range  $\delta$ -deshielding was further considered by Stothers et. al.<sup>89</sup> and they found that only a syn-axial arrangement of neighboring  $\delta$  nuclei produces appreciable downfield shifts while all other possible arrangements result in a small shielding effect. It was also shown<sup>88</sup> that the magnitude of these syn-axial interactions appear to be larger for those cases in which deflection of the ring system, which could increase the nonbonded interatomic distance of  $\delta$  substituents less likely. This kind of  $\delta$ -deshielding effect is found in acyclic systems too, however, its magnitude is small due to a low population of g(+) and g(-) orientation<sup>90</sup> (analogous orientation to syn-axial in cyclic compounds).

The  $^{13}\text{C}$  NMR studies of hydrocarbons 5-8 indicated that the orientation dependent effects can be extended to neighboring  $\epsilon$ -nuclei also. Our studies also verify the logic of earlier foundation for orientation dependent deshielding or shielding effect of neighboring  $\delta$ -nuclei. The C-13 chemical shift values of compounds 5-8 are summarized in Table XII. To make the comparison easier, we use the numbering system shown in the

TABLE XII  
 $^{13}\text{C}$  CHEMICAL SHIFTS<sup>a</sup> FOR peri-SUBSTITUTED INDANS

Carbon				
	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
C-1	33.1	38.3	45.5	50.0
C-2	24.7	33.5	29.6	25.1
C-3	31.4	30.8	31.2	32.6
C-3a	142.5	142.9	143.2	143.8
C-4	133.3	121.8	121.7	121.5
C-5	126.7	126.3	126.2	126.2
C-6	126.1	127.4	127.4	127.4
C-7	121.5	133.2	133.3	133.4
C-7a	143.3	147.1	146.1	144.9
C-8	19.1	18.6	18.8	19.1
C-9	-	19.3	26.2	30.8
C-10	-	-	12.5	22.1
C-11	-	-	-	16.6

<sup>a</sup> In ppm from  $\text{Me}_4\text{Si}$  in  $\text{CDCl}_3$ .

table. The NMR samples for these compounds were prepared in the same molar concentration (1.1 mmol/0.4 mL) to eliminate any concentration effect on chemical shift difference. The  $^{13}\text{C}$  chemical shift assignments for the compounds 5-8 are discussed in the earlier part of this chapter.

The  $^{13}\text{C}$  chemical shift data given in Table XI show that C-8 is shielded in compound 6 as compared to 5. Examination of Dreiding models for compounds 6-8 reveals that an equatorial substituent feels a severe steric interaction against the substituent at C-7 (methyl group). Therefore, a geometry in which the substituent at C-1 is pseudo-axial is preferred over pseudoequatorial. A shielding effect is produced on C-3 (indan 6) by the C-1 methyl group due to  $\gamma$ -gauche interaction. Since this kind of  $\gamma$ -shielding is only possible with an axial methyl substituent, a conformation with methyl group in axial position is favored in indan 6. This pseudo-axial arrangement of C-1 methyl group results in a gauche type orientation of the two methyl groups. This explains the observed shielding of C-8 in indan 6 as compared with C-8 in indan 5.

In compounds 7a and 8, however, C-8 is deshielded in 7a (0.2 ppm) and 8 (0.5 ppm) as compared to 6. Examination of models reveals that the methyl groups separated by five bonds in 7a and 8 can adopt spacial arrangements similar to a syn-axial arrangement (pseudo-parallel) as shown below for the indan 7a.



7a

Assuming the same shielding (for gauche type through space interaction) or deshielding (for syn-axial type through space interaction) trend for  $\delta$ -effect is also true for nuclei separated by five bonds, the observed chemical shifts of C-8 for the indans (7a and 8) can be explained. The examination of the models also reveals that the methyl groups separated by five bonds in 7a and 8 can adopt an arrangement from which only one orientation (pseudo-parallel) may have a deshielding effect while the other orientation has a shielding effect, similar to that found for neighboring  $\delta$ -nuclei.<sup>112,113</sup> Low population of the pseudo-parallel arrangement in 7a and relatively higher probability of this kind of orientation in 8 may explain further deshielding of C-8 in 8 compared to the same position in 7a.

The origin of this effect is not very well understood. Undoubtedly, the interpretation relating steric crowding with upfield shifts through steric polarization of interacting bonds<sup>86</sup> is inadequate to account for those syn-axial type effects. Batchelor<sup>90</sup> suggested that a second contribution to  $^{13}\text{C}$  steric shifts must be postulated. This hypothetical mechanism must produce deshielding as the distance between the interacting groups decreases, the distance dependence being steeper than that of the shielding mechanism which dominates  $\gamma$ -steric shifts. According to Batchelor,<sup>90</sup> a possible deshielding mechanism is the second order electric field effect due to fluctuating molecular dipoles.<sup>90</sup>

The effect of peri-interaction in compounds 5-8 may be discussed in terms of  $^{13}\text{C}$  spin-lattice relaxation times ( $T_1$  values) of the C-7 methyl carbons. Although quantitative information concerning dynamic molecular motions can be obtained from  $^{13}\text{C}$  spin-lattice relaxation times, it requires a detailed study of the mechanisms by which relaxa-

tion takes place.<sup>91,92</sup> However, a qualitative idea may be drawn from comparison of  $T_1$  values of identical substituents in similar environment, wherein major deviation in mechanism of spin-lattice relaxation is not expected.  $T_1$  values for methyl group (C-8) in compounds 5-8 are given in Table XIII.

TABLE XIII  
SPIN-LATTICE RELAXATION TIMES ( $T_1$ )<sup>a</sup> FOR C-8 METHYL SUBSTITUENT IN 5-8

	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
$T_1$	15.8	14.7	12.3	12.2

<sup>a</sup> Seconds.

Often hindrance to rotation is manifest in the relative  $T_1$  values for a molecule.<sup>65</sup> Since steric interaction can hinder the rotation of a methyl group, it can effectively relax by dipolar mechanism and this is reflected in shorter  $T_1$  values as compared with the unhindered one.<sup>57,65</sup> Thus in o-xylene, the methyl carbons have a shorter  $T_1$  of 10.8 sec<sup>93</sup> compared to a typical value of 11.3 sec (toluene) for freely rotating methyl carbons.<sup>65</sup> In compounds 5-8, by increasing the size of the peri-substituent at C-1 carbon, a higher rotation barrier for methyl group at C-7 results. This is reflected in the observed decrease in the  $T_1$  values as we go from indan 5 to 8 (Table XII).

Summary of Significance of the Research. The synthesis of peri-substituted indans 6-8 and the unhindered analogs 12-20 have been attained from the corresponding indanones 23, 24, 21 and 32. The scheme developed for the recovery of unreacted indanones by the use of 2,4-dinitrophenylhydrazine should be widely applicable for removing unreacted ketones, after their reactions with alkyl magnesium halides, and make them available for reuse.

The  $^{13}\text{C}$  chemical shift assignments, as reported in this thesis for the alkylated indans, have been successfully achieved. The substituent shift parameters, derived for the methylated indans by simple additivity methods, has been found to work very well for the indans where the methyl substituents are sterically noninteracting. In such cases, the experimentally observed data and those predicted using additivity values are in excellent agreement for all carbons.

The  $^{13}\text{C}$  NMR data for the indans 5-8, as shown in Table XII, indicate the orientation dependent effect similar to syn-axial arrangement of  $\delta$ -nuclei can be extended to neighboring  $\epsilon$ -nuclei. This is the first case to be reported regarding orientation dependent effect of neighboring  $\epsilon$ -nuclei.

The U.S. Department of Energy, Bartlesville Energy Technology Center in Bartlesville, Oklahoma, is now carrying out thermodynamic studies on peri-substituted indans and the corresponding unhindered analogs. Knowledge gained from the study of these pure compounds will be used in tailoring high energy fuels of the future.

## CHAPTER IV

### EXPERIMENTAL

General Information. Proton NMR spectra were recorded at 100.1 MHz on a Varian XL-100A NMR spectrometer. The  $^{13}\text{C}$  NMR spectra (fully decoupled, single frequency off-resonance proton-decoupled and gate decoupled) were recorded at 25.2 MHz in the FT mode on Varian XL-100A interfaced with a 12 K Nicolet 1080 computer system. Chemical shifts are reported in parts per million downfield from internal  $\text{Me}_4\text{Si}$  as standard. Infrared spectral data were collected from a Perkin-Elmer 681 spectrometer. Mass spectra were recorded with a CEC 21-110B high resolution mass spectrometer with Data General DS-50S data system at 70 ev. Melting points were determined with a Thomas-Hoover Capillary melting point apparatus. Melting and boiling points are uncorrected. Gas chromatographic analyses were obtained with a Varian Model 3700 capillary gas chromatograph, and a Varian Aerograph model 550. Analytical and preparative high-pressure LC were conducted on a Waters Associates Micro-porosil (silica gel) column with a Waters Associates analytical or Prep LC/System 500 liquid chromatographs, equipped with UV and index of refraction detectors. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

General Procedure for Synthesis of 3-Tolylpropenoic Acids (21a-c).

The synthesis of 3-(3-methylphenyl)propenoic acid (21a) is used as an example to illustrate the general procedure. 3-Methylbenzaldehyde



(240 g, 2 mol) and 800 mL of pyridine were placed in a 3-L, two-necked, round-bottomed flask fitted with a condenser and thermometer. The solution was warmed to 50 °C and malonic acid (416 g, 4 mol) was added in portions, with magnetically stirring. Heating was continued and at 80–85 °C piperidine (15 mL) was added. The mixture was stirred for 1 h and then for 3 h at 100–105 °C. The reaction was cooled to room temperature and most of the pyridine was evaporated under reduced pressure. The pasty residue was diluted with water and acidified with 1:1 HCl until strongly acidic. The solid product was filtered by suction, washed with 3 x 300 mL portions of water and purified by crystallization from acidified sodium hydroxide solution. Recrystallization from 2-propanol gave 287 g (88%) of white, crystalline 21a, mp 117–118 °C (lit.<sup>94</sup> mp 119 °C): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 11.6 (s, 1, CO<sub>2</sub>H), 7.76 (d, 1, CH=CHCO<sub>2</sub>H), 7.40–7.14 (m, 4, ArH), 6.42 (d, 1, ArCH=CH), 2.37 (s, 3, ArCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) ppm 172.49 (CO<sub>2</sub>H), 146.96, 138.37, 133.79, 131.34, 128.80, 128.60, 125.36, 116.96 (aromatic and vinylic), 21.22 (ArCH<sub>3</sub>); IR (KBr) cm<sup>-1</sup> 2990 (CO<sub>2</sub>H), 1690 (CO).

Preparation of 3-(2-Methylphenyl)propenoic Acid (21b). 2-Methylbenzaldehyde (120 g, 1 mol) was condensed with malonic acid (208 g, 2 mol) as described in the general procedure. Recrystallization of the crude product in 2-propanol gave 145 g (89%) of white, crystalline 21b, mp 175–176 °C (lit.<sup>94</sup> mp 169 °C): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 11.3 (s, 1, CO<sub>2</sub>H), 8.10 (d, 1, CHCO<sub>2</sub>H), 7.28 (m, 4, ArH), 6.38 (d, 1, ArCH), 2.48 (s, 3, ArCH<sub>3</sub>); IR (KBr) cm<sup>-1</sup> 2985 (CO<sub>2</sub>H), 1690 (CO).

Preparation of 3-(4-Methylphenyl)propenoic Acid (21c). Acid 21c was prepared in 93% yield from 4-methylbenzaldehyde (240 g, 2 mol) as described in the general procedure. Recrystallization, once with

2-propanol and then with 2-butanone gave 21c as white crystalline solid, mp 198-199 °C (lit.<sup>94</sup> mp 199 °C): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 12.1 (s, 1, CO<sub>2</sub>H), 7.76 (d, 1, CHCO<sub>2</sub>H), 7.20 (m, ArH, 4), 6.38 (d, 1, ArCH), 2.38 (s, 3, ArCH<sub>3</sub>), IR (KBr) cm<sup>-1</sup> 2990 (CO<sub>2</sub>H), 1690 (CO).

General Procedure for the Catalytic Hydrogenation of Acids 21a-c.

The catalytic hydrogenation of 3-(3-methylphenyl)propenoic acid (21a) is used as an example to illustrate the general procedure. A 70 g (0.432 mol) sample of 21a was added to a 1 L stainless steel hydrogenation vessel containing 500 mL of acetic acid and 7 g of 5% Pd/C catalyst. The vessel was evacuated, hydrogen was introduced, and then shaken (Parr Model 3920 hydrogenation apparatus) at 40-45 psig and 50-60 °C until hydrogen uptake ceased. Excess hydrogen was vented and the vessel contents were filtered through Dicalite to remove the catalyst. The filtrate was diluted with water to precipitate the product as colorless solid. The product was filtered and purified by reprecipitation (CH<sub>3</sub>CO<sub>2</sub>H - water) to give 61.6 g (87%) of 3-(3-methylphenyl)propanoic acid (22a), mp 45-47 °C (lit.<sup>94</sup> mp 43 °C): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 11.8 (s, 1, CO<sub>2</sub>H), 7.24-7.00 (m, 4, ArH), 2.88 (t, 2, ArCH<sub>2</sub>), 2.64 (t, 2, CH<sub>2</sub>CO<sub>2</sub>H), 2.30 (s, 3, ArCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) ppm 179.32 (CO<sub>2</sub>H), 139.78, 137.73, 128.74, 128.16, 126.81, 124.95 (aromatic), 35.51, 30.34, 21.21 (aliphatic); IR (KBr) cm<sup>-1</sup> 3005 (CO<sub>2</sub>H), 1710 (CO); mass spectrum, m/e (relative intensity) 165 (M+<sup>+</sup>, 10.7), 164 (M<sup>+</sup>, 100), 119 (67.8), 117 (31.6), 91 (44.6).

Catalytic Hydrogenation of 21b to 3-(2-Methylphenyl)propanoic Acid (22b). Acid 21b (35 g, 0.216 mol) was hydrogenated in the Parr apparatus as described in the general procedure. The crude product was recrystallized from 40% aqueous acetic acid to give 34.5 g (97%)

of 22b, mp 102–103 °C (lit.<sup>94</sup> mp 102 °C): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 12.0 (s, 1, CO<sub>2</sub>H), 7.20–7.06 (m, 4, ArH), 2.98 (m, 2, ArCH<sub>2</sub>), 2.64 (m, 2, CH<sub>2</sub>CO<sub>2</sub>H), 2.12 (s, 3, ArCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) ppm 179.40 (CO<sub>2</sub>H), 138.02, 135.72, 130.15, 128.22, 126.33, 126.00 (aromatic), 34.35, 27.93, 19.17 (aliphatic); IR (KBr) cm<sup>-1</sup> 3000 (CO<sub>2</sub>H), 1710 (CO); mass spectrum, m/e (relative intensity) 165 (M+1<sup>+</sup>, 12.3), 164 (M<sup>+</sup>, 100), 146 (27.7), 119 (20.8), 118 (41.5), 106 (30.8), 91 (76.2).

Catalytic Hydrogenation of 21c to 3-(4-Methylphenyl)propanoic Acid (22c). Catalytic hydrogenation of 200 g (1.23 mol) of acid 21c as described in the general procedure and recrystallization of the crude product from 50% aqueous acetic acid gave 188 g (96%) of 22c, mp 114–116 °C (lit.<sup>94</sup> mp 122 °C): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 10.34 (s, 1, CO<sub>2</sub>H), 7.16–7.04 (m, 4, ArH), 2.92 (m, 2, ArCH<sub>2</sub>), 2.66 (m, 2, CH<sub>2</sub>CO<sub>2</sub>H), 2.32 (s, 3, ArCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) ppm 179.28 (CO<sub>2</sub>H), 136.83, 135.57, 128.98 (x2), 127.87 (x2) (aromatic), 35.69, 30.08, 20.89 (aliphatic); IR (KBr) cm<sup>-1</sup> 3000 (CO<sub>2</sub>H), 1710 (CO); mass spectrum, m/e (relative intensity) 165 (M+1<sup>+</sup>, 8.7), 164 (M<sup>+</sup>, 100), 119 (22.2), 118 (54.9), 115 (17.7), 106 (28.5), 91, (46.4).

General Procedure for the Cyclization of 3-(Methylphenyl)propanoic Acids (22a-c) Using Polyphosphoric Acid (PPA). The cyclization of 22a is used as an example. Polyphosphoric acid (PPA) (350 mL) was heated in a 500 mL, 3-necked flask fitted with a mechanical stirrer, and a thermometer; the third neck being open. When the temperature of the PPA reached 100 °C, 50 g (0.308 mol) of acid 22a was added in small amounts over a period of 15 min. The mixture was stirred at 100–105 °C for 1.5 h. The cooled mixture was poured over 1500 g of ice to hydrolyze the PPA. The solution was extracted twice with 200 mL portions

of ether. The combined ether extracts were washed with saturated  $\text{NaHCO}_3$  solution (no unreacted 22a was recovered from this) and then with water. The ether layer was filtered through Dicalite and dried ( $\text{MgSO}_4$ ). The solvent was removed and the yellow oil was distilled (Kugelrohr, 105 °C, 3 mm) to give 38.5 g (86%) of colorless oil, which solidified on standing. The GC analysis of the distilled material showed two peaks 49:51 later assigned to 23 and 24 respectively.

Polyphosphoric Acid Cyclization of 22b. The acid 22b (50 g, 0.304 mol) was cyclized using 350 mL of PPA at 100 °C for 1.5 h as described in the general procedure. The crude product was distilled (Kugelrohr, 95 °C, 1 mm) to give 4-methyl-1-indanone (31) as a colorless solid. Recrystallization using *n*-hexane gave 32.9 g (74%) of white, crystalline 31, mp 98–99 °C (lit.<sup>13</sup> mp 95–96 °C):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.56 (d, 2, ArH at C-7), 7.40–7.16 (m, 2, ArH at C-5 and C-6), 2.98 (m, 2,  $\text{ArCH}_2$ ), 2.64 (m, 2,  $\text{ArCOCH}_2$ ), 2.34 (s, 3,  $\text{ArCH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) ppm 206.89 (CO), 153.87, 136.59, 135.66, 134.73, 127.22, 120.77 (aromatic), 36.09, 24.57, 17.65 (aliphatic); IR (KBr)  $\text{cm}^{-1}$  1710 (CO); mass spectrum,  $m/e$  (relative intensity) 146 ( $\text{M}^+$ , 100), 118 (55.6), 117 (85.0), 115 (40.2), 91 (14.5).

Polyphosphoric Acid Cyclization of 22c. Cyclization of 22c (50 g, 0.304 mol) was performed at 100–105 °C for 1.5 h using the general procedure. Crude 6-methyl-1-indanone (32) was distilled (Kugelrohr, 60 °C, 0.6 mm) and recrystallized using *n*-hexane to yield 36.0 g (81%) of pure 32, mp 61–63 °C (lit.<sup>13</sup> mp 62 °C):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.52 (s, 1, ArH at C-7), 7.36 (narrow m, 2, ArH at C-4 and C-5), 3.08 (m, 2,  $\text{ArCH}_2$ ), 2.62 (m, 2,  $\text{ArCOCH}_2$ ), 2.40 (s, 3,  $\text{ArCH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) ppm 206.53 (CO), 152.20, 136.82, 135.82, 135.54, 126.11, 123.28 (aromatic), 36.44, 25.32, 20.95 (aliphatic); IR (KBr)  $\text{cm}^{-1}$  1710 (CO); mass spectrum,  $m/e$

(relative intensity) 147 ( $M+1^+$ , 8.1), 146 ( $M^+$ , 100), 118 (69.2), 117 (68.2), 115 (23.4), 91 (15.8).

Separation of 7-Methyl-1-indanone (23) and 5-Methyl-1-indanone (24).

From 35 g of the mixture of 23 and 24 obtained by PPA cyclization of the acid 22a, 7 g of pure ketone 24 was isolated by fractional crystallization in *n*-hexane. The ketones were then recovered from the mother liquor and separated using the Waters Prep LC/System 500 liquid chromatograph equipped with a silica gel column and using  $CH_2Cl_2$  solvent, at a flow rate of 150 mL per min. In a typical LC run, 9.23 g of the indanone mixture (23 and 24) were separated. Fractions were collected and analyzed using analytical high-pressure LC ( $\mu$ . Porosil, 10  $\mu$  particle size,  $CH_2Cl_2$  solvent at a flow rate of 2 mL/min). The fractions on evaporation afforded: (i) 4.5 g of pure indanone 23, mp 54–56 °C (lit.<sup>95</sup> mp 54–55 °C):  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.46–6.98 (m, 3, ArH), 3.03 (m, 2,  $ArCH_2$ ), 2.6 (s, 3,  $ArCH_3$ ; m, 2,  $ArCOCH_2$ );  $^{13}C$  NMR ( $CDCl_3$ ) ppm 206.77 (CO), 155.42, 138.20, 134.08, 133.49, 128.72, 123.73 (aromatic), 36.51, 25.20, 18.05 (aliphatic); IR (KBr)  $cm^{-1}$  1708 (CO); mass spectrum,  $m/e$  (relative intensity) 147 ( $M+1^+$ , 9.2), 146 ( $M^+$ , 100), 118 (46.8), 117 (69.5), 115 (30.1), 91 (28.2), 69 (40.4). (ii) 0.8 g of mixture, and (iii) 3.2 g of indanone 24. Recrystallization of the indanone 24 in *n*-hexane yielded 3 g of pure 24, mp 71–73 °C (lit.<sup>95</sup> mp 70–71 °C):  $^1H$  NMR ( $CDCl_3$ )  $\delta$  7.54 (d, 1, ArH at C-7), 7.20–7.10 (m, 2, ArH at C-4 and C-6), 3.02 (m, 2,  $ArCH_2$ ), 2.61 (m, 2,  $ArCOCH_2$ ), 2.40 (s, 3,  $ArCH_3$ );  $^{13}C$  NMR ( $CDCl_3$ ) ppm 205.75 (CO), 155.28, 145.29, 134.52, 128.16, 126.80, 123.05 (aromatic), 36.18, 25.47, 21.91 (aliphatic), IR (KBr)  $cm^{-1}$  1708 (CO); mass spectrum,  $m/e$  (relative intensity) 147 ( $M+1^+$ , 10.4), 146 ( $M^+$ , 100), 118 (60.8), 117 (86.6), 115 (37.8), 91 (32.0), 69 (25.8).

Methanesulfonic Acid Cyclization of 22a. Anhydrous methanesulfonic acid (40 mL) was magnetically stirred at 110 °C in a 100 mL, round-bottomed flask equipped with a condenser, nitrogen inlet and outlet and thermometer. The acid 22a (5.0 g, 0.03 mol) was added in one batch and the mixture was stirred for 2.5 h. The dark mixture was poured slowly into 400 mL of stirred ice-water and extracted with about 200 mL of ether in two portions. The ether layer was washed with saturated NaHCO<sub>3</sub> solution and water, dried (MgSO<sub>4</sub>), and concentrated. The crude product was distilled (Kugelrohr, 80-85 °C, 0.4 mm) to give 3.7 g (85%) of a mixture of 23 and 24 as a colorless oil which solidified on standing. The GC ratio was 47:53 (23:24).

Hydrogen Fluoride Cyclization of 22a. Hydrogen fluoride (150 mL) was condensed into a plastic bottle and then the acid 22a (10 g, 0.061 mol) was added in small quantities with constant shaking. The bottle was kept in an ice bath during the addition. When the addition was complete, the mixture was allowed to react for 15 min and the excess hydrogen fluoride was evaporated (overnight) in a stream of nitrogen into a trap containing alkali. The residue was then poured into 500 mL of stirred ice water, extracted with ether, and worked up as described for the methanesulfonic acid cyclization of 22a. The crude product was distilled (Kugelrohr, 80-85 °C, 0.4 mm) to give 7.7 g (87%) of a mixture of 23:24 (47:53) as shown by gas chromatography.

Synthesis of 1,7-Dimethylindan (6). To a dry 3-necked, 250 mL, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser and N<sub>2</sub> inlet and outlet tubes, was taken a solution of 3.2 M methylmagnesium bromide in ether (Aldrich, 24 mL, 0.076 mol). This solution was cooled and indanone 23 (10 g, 0.068 mol) in 75 mL ether

was slowly added with stirring. After the addition was complete, the mixture was stirred at room temperature for 2 h and then under reflux for 45 min; cooled to room temperature, and then poured into 200 mL of ice cold dilute hydrochloric acid. The solution was extracted twice with 150 mL portions of ether. The combined ether layers were washed twice with 100 mL portions of saturated NaCl solution and once with 100 mL of water. The ether layer was dried ( $\text{MgSO}_4$ ) and the solvent evaporated to give a colorless solid. GC analysis showed about 2-3% of the unreacted starting material. The crude product was dissolved in 100 mL of 95% ethanol and 5 mL of 2,4-dinitrophenylhydrazine was added and kept for 2-3 h. The resulting suspension was filtered. Oxalic acid (3 g) was added to the filtrate and the solution was steam distilled. The product was isolated from the steam distillate by ether extractions. The product was eluted through basic alumina using *n*-hexane. The solvent was evaporated under reduced pressure, and the product was recrystallized in 75% aqueous ethanol to give 8.3 (84%) of pure 28, mp 50-51 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.26-6.90 (m, 3, ArH), 6.08 (m, 1, ArC=CH), 3.16 (m, 2, ArCH<sub>2</sub>), 2.56 (s, 3, ArCH<sub>3</sub>), 2.30 (d, 3, CH<sub>3</sub>C=CH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) ppm 145.09, 143.04, 141.17, 130.56, 129.41, 128.51, 124.34, 121.42 (aromatic and vinylic), 37.12, 19.75, 17.53 (aliphatic); mass spectrum m/e, calcd. for  $\text{C}_{11}\text{H}_{12}$ : 144.0939; Found:  $\text{M}^+$  144.0937.

The indene 28 (8.0 g, 0.05 mol) was hydrogenated over 0.8 g of 5% Pd/C catalyst in glacial acetic acid at room temperature and 30-35 psig. The product was isolated by ether extraction and distilled (Kugelrohr, 40-45 °C, 2.6 mm) [lit.<sup>20</sup> 88 (16 mm)] to give 7.4 g (91%) of 6 which was found to be 99.97% pure by high-pressure LC (silica column, *n*-hexane):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.08-6.84 (m, 3, ArH), 3.30 (m, 1, ArCH),

2.88 (m, 2, ArCH<sub>2</sub>), 2.27 (s, 3, ArCH<sub>3</sub>), 1.7 (m, 2, ArCH<sub>2</sub>CH<sub>2</sub>); <sup>13</sup>C NMR: see Table V; mass spectrum, m/e (relative intensity) 146 (M<sup>+</sup>, 32.4), 131 (100), 115 (18.2), 91 (18.8), 65 (15.3).

Synthesis of 1-Ethyl-7-methylindan (7a). Indanone 23 (10 g, 0.068 mol) in 75 mL of anhydrous ether was reacted with a solution of 3 M ethylmagnesium bromide (Aldrich, 24 mL, 0.072 mol). The unreacted indanone (8-10%) was removed from the crude product by treatment with 2,4-dinitrophenylhydrazine and steam distillation (as described in the synthesis of 6) to give 8.1 g of pale yellow oil. The yellow oil was eluted through basic alumina using n-hexane to remove color. GC analysis and <sup>13</sup>C NMR investigation showed the oil is a mixture of two isomeric indenenes (29 and the isomer with an exocyclic double bond). The indene mixture (8.0 g) was hydrogenated over 5% Pd/C catalyst in glacial acetic acid at room temperature and 35-40 psig. The product was isolated by ether extraction and distilled (Kugelrohr, 85-90 °C, 0.1 mm) to give 7.7 g (71% overall yield) of 7a: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.08-6.90 (m, 3, ArH), 3.10 (m, 1, ArCH), 2.86 (m, 2, ArCH<sub>2</sub>), 2.29 (s, 3, ArCH<sub>3</sub>), 2.02 (m, 2), 1.64-1.20 (m, 2), 0.96 (t, 3, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR: see Table IV; IR (neat) cm<sup>-1</sup> 2960, 1430; mass spectrum m/e, Calcd. for C<sub>12</sub>H<sub>16</sub>: 160.1252. Found: M<sup>+</sup> 160.1250.

Anal. Calcd. for C<sub>12</sub>H<sub>16</sub>: C, 90.00; H, 10.00. Found: C, 89.82; H, 9.94.

Synthesis of 1-Isopropyl-7-methylindan (8). Indanone 23 (10 g, 0.068 mol) in 74 mL of ether was reacted with 25 mL of 2.9 M (0.072 mol) isopropylmagnesium chloride (Alfa Products). The unreacted indanone (70%) from the crude product was removed by treatment with 2,4-dinitrophenylhydrazine, and steam distilled as described in the



synthesis of 6 to give 2.0 g of pale yellow oil (mixture of two indenenes; 30 and the isomer with exocyclic double bond). The oil was eluted through basic alumina using n-hexane to remove color. The solvent was evaporated and the indene mixture was hydrogenated over 5% Pd/C catalyst in glacial acetic acid at room temperature and 35-40 psig. The product was isolated by ether extraction and distilled (Kugelrohr, 110-115 °C, 0.8 mm) to give 1.6 g (13% overall yield) of 8:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.04-6.84 (m, 3, ArH), 3.16 (m, 1, ArCH), 2.80 (m, 2, ArCH<sub>2</sub>), 2.30 (s, 3, ArCH<sub>3</sub>), 2.18-1.86 (m, 3), 1.05 (d, 3, CHCH<sub>3</sub>);  $^{13}\text{C}$  NMR: see Table IX; IR (neat)  $\text{cm}^{-1}$  2800, 1380; mass spectrum m/e, Calcd. for  $\text{C}_{13}\text{H}_{18}$ : 174.1408. Found:  $\text{M}^+$  174.1405.

Anal. Calcd. for  $\text{C}_{13}\text{H}_{18}$ : C, 89.65; H, 10.35. Found: C, 89.19; H, 10.25.

Synthesis of 1,5-Dimethylindan (15). Indan 15 was synthesized from 5 g (0.034 mol) of indanone 24 and 12 mL of 3.2 M methylmagnesium bromide in ether by the same procedure described in the synthesis of indan 6. The crude product was distilled (Kugelrohr, 60-62 °C, 1 mm) to give 4.1 g (82%) of 15:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.10-6.89 (m, 3, ArH), 3.13 (m, 1, ArCH), 2.82 (m, 3, ArCH<sub>2</sub>), 2.31 (s, 3, ArCH<sub>3</sub>), 1.62 (m, 2, ArCH<sub>2</sub>CH<sub>2</sub>), 1.5 (d, 3, CHCH<sub>3</sub>);  $^{13}\text{C}$  NMR: see Table V.

Synthesis of 1-Ethyl-5-methylindan (16). This was prepared from 24 (6 g, 0.04 mol), and 14 mL of 3 M ethylmagnesium bromide (0.042 mol). The crude product was distilled (Kugelrohr, 70-73 °C, 1.6 mm) to give pure 16 (yield 71%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.12-6.92 (m, 3, ArH), 3.04 (m, 1, ArCH), 2.90 (m, 2, ArCH<sub>2</sub>), 2.30 (s, 3, ArCH<sub>3</sub>), 1.98-1.2 (m, 4), 0.98 (t, 3, CH<sub>2</sub>CH<sub>3</sub>);  $^{13}\text{C}$  NMR: see Table VIII.

Synthesis of 1-Isopropyl-5-methylindan (17). Indan 17 was prepared from 7 g (0.048 mol) of indanone 24 and 2.9 M isopropylmagnesium chloride in ether (14.5 mL, 0.05 mol). Distillation (Kugelrohr, 90-93 °C, 1 mm) gave pure 17 in 23% yield:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.08-6.88 (m, 3, ArH), 3.02 (m, 1, ArCH), 2.80 (m, 2.80,  $\text{ArCH}_2$ ), 2.16-1.70 (m, 3), 0.98 (d, 3,  $\text{CHCH}_3$ ), 0.76 (d, 3,  $\text{CHCH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): see Table IX.

1,4-Dimethylindan (12). This was prepared from 31 (5 g, 0.034 mol) and 3.2 M solution of methylmagnesium bromide (12 mL, 0.036 mol). Distillation (Kugelrohr, 66-69 °C, 5 mm) gave pure 12 (82% yield):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.16-6.90 (m, 3, ArH), 3.18 (m, 1, ArCH), 2.78 (m, 2,  $\text{ArCH}_2$ ), 2.24 (s, 3,  $\text{ArCH}_3$ ), 1.60 (m,  $\text{ArCHCH}_2$ ), 1.28 (d, 3,  $\text{CHCH}_3$ );  $^{13}\text{C}$  NMR: see Table V.

1-Ethyl-4-methylindan (13). Indan 13 was prepared from 7.5 g (0.05 mol) of 31 and 17.5 mL of 3 M ethylmagnesium bromide (0.052 mol). Distillation (Kugelrohr, 89-92 °C, 2 mm) gave pure 13 in 69% yield:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.06-6.88 (m, 3, ArH), 3.02 (m, 1, ArCH), 2.74 (m, 2,  $\text{ArCH}_2$ ), 2.22 (s, 3,  $\text{ArCH}_3$ ), 1.98-1.20 (m, 4), 0.96 (t, 3,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR: see Table VIII.

1-Isopropyl-4-methylindan (14). Indanone 31 (10 g, 0.068 mol) and 2.9 M *i*-PrMgCl (25 mL, 0.072 mol) were used to prepare 14. The crude product was distilled (Kugelrohr, 58-60 °C, 0.06 mm) to give pure 14 (24% yield):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.08-6.90 (m, 3, ArH), 3.10 (m, 1, ArCH), 2.78 (m, 2,  $\text{ArCH}_2$ ), 2.25 (s, 3,  $\text{ArCH}_3$ ), 2.22-1.79 (m, 3), 1.00 (d, 3,  $\text{CHCH}_3$ ), 0.78 (d, 3,  $\text{CHCH}_3$ );  $^{13}\text{C}$  NMR: see Table IX.

1,6-Dimethylindan (18). This hydrocarbon was prepared from 32 (6 g, 0.04 mol) and 3.2 M  $\text{CH}_3\text{MgBr}$  (13 mL, 0.042 mol). Distillation (Kugelrohr, 60-62 °C, 1 mm) gave 5 g (83%) of pure 18:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )

$\delta$  7.08–6.88 (m, 3, ArH), 3.10 (m, 1, ArCH), 2.78 (m, 2, ArCH<sub>2</sub>), 2.30 (s, 3, ArCH<sub>3</sub>), 1.60 (m, ArCH<sub>2</sub>CH<sub>2</sub>), 1.24 (d, 3, CHCH<sub>3</sub>); <sup>13</sup>C NMR: see Table V.

1-Ethyl-6-methylindan (19). Indan 19 was prepared from 32 (5 g, 0.034 mol) and 3.0 M C<sub>2</sub>H<sub>5</sub>MgBr (12 mL, 0.036 mol). Distillation (Kugelrohr, 70–73 °C, 1.6 mm) gave pure 19 (69% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.10–6.88 (m, 3, ArH), 3.00 (m, 1, ArCH), 2.80 (m, 2, ArCH<sub>2</sub>), 2.30 (s, 3, ArCH<sub>3</sub>), 2.14–1.20 (br m, 4), 0.97 (t, 3, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR: see Table VIII.

1-Isopropyl-6-methylindan (20). This was prepared from indanone 32 (9 g, 0.060 mol) and 2.9 M *i*-PrMgCl (22 mL, 0.063 mol). Distillation (Kugelrohr, 55–58 °C, 0.05 mm) gave 20 in 26% yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.70–6.88 (m, 3, ArH), 3.02 (m, 1, ArCH), 2.88 (m, 2, ArCH<sub>2</sub>), 2.32 (s, 3, ArCH<sub>3</sub>), 2.28–1.10 (br m, 3), 0.98 (d, 3, CHCH<sub>3</sub>), 0.76 (d, 3, CHCH<sub>3</sub>); <sup>13</sup>C NMR: see Table IX.

Synthesis of 2-Isopropyl-5-acetylindan (35). 2-Isopropylindan (35) was prepared from 2-indanone (2.0 g, 13 mmol), and 2.9 M *i*-PrMgCl (5 mL, 14 mmol) by the usual method to give 0.37 g (18%) of 2-isopropylindan as a colorless solid; mp 38–40 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.20–7.02 (m, 4, ArH), 3.10–2.48 (m, 4), 2.18 (m, 1), 1.60 (m, 1), 0.96 (d, 6, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) ppm 143.52 (x2), 125.73 (x2), 123.99 (x2) (aromatic), 48.06, 37.58 (x2), 33.47, 21.27 (x2) (aliphatic); mass spectrum *m/e*, Calcd. for C<sub>12</sub>H<sub>16</sub>: M<sup>+</sup> 160.1250. Found: M<sup>+</sup> 160.1242.

In a dry 3-necked, 50 mL flask equipped with a condenser, and N<sub>2</sub> inlet and outlet tube, and magnetically stirred Teflon-coated stirring bar, were taken 0.2 g of anhydrous AlCl<sub>3</sub> in 7 mL of dichloromethane. The reaction was cooled to ice temperature, and 0.12 g of acetyl

chloride was introduced. 2-Isopropylindan (0.1 g, 0.6 mmol), dissolved in 1.5 mL of dichloromethane and was added to the mixture using a Pasteur pipette. The reaction was stirred at room temperature for 30-35 min and then poured into 2 mL of 1:1 HCl containing ice. 2-Isopropyl-5-acetylindan (35) was isolated in 85% yield by extraction with dichloromethane to give colorless solid 35, mp 40-41 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.76-7.68 (m, 2, ArH at C-4 and C-6), 7.22 (d, 1, ArH at C-7), 3.18-2.50 (m, 4), 2.56 (s, 3,  $\text{COCH}_3$ ), 2.22 (m, 1), 1.64 (m, 1), 0.98 (d,  $\text{CH}(\text{CH}_3)_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) ppm 197.58 (CO), 149.58, 144.09, 135.42, 126.58, 123.87, 123.78 (aromatic), 49.97, 37.52, 37.11, 33.29, 26.46, 21.06 (aliphatic); mass spectrum  $m/e$ , Calcd. for  $\text{C}_{14}\text{H}_{18}\text{O}$ :  $M^+$  202.1357. Found:  $M^+$  202.1365. The 2,4-DNP derivative of 35 melted at 184-185 °C.

Deuteration of 7-Methyl-1-indanone (23). Indanone 23 (2 g, 13 mmol) was dissolved in 20 mL of dioxane, and 17 mL of deuterium oxide and 0.26 g of anhydrous sodium methoxide were added. After 14 h of stirring (under  $\text{N}_2$  atmosphere) at 80 °C, the solution was cooled to room temperature and poured into slightly acidified water, and the organic material extracted with water. The ethereal solution was washed with saturated NaCl, dried ( $\text{MgSO}_4$ ) and the solvent evaporated. The residue was purified by crystallization from *n*-hexane to give 1.8 g (88%) of 7-methyl-2,2- $\text{d}_2$ -1-indanone. The  $^{13}\text{C}$  NMR and high resolution mass spectra confirmed complete deuteration at the expected position.

1-Ethyl-2,2- $\text{d}_2$ -7-methylindan (7b). The deuterated derivative of 23 (1 g, 6.7 mmol) was reacted with 3 mL of 3 M ethylmagnesium bromide (9 mmol) by the usual procedure. After completion, the reaction mixture was poured into 75 mL of saturated  $\text{NH}_4\text{Cl}$  with stirring, and the organic material was extracted with ether. The ethereal solution was

washed with saturated NaCl, dried ( $\text{MgSO}_4$ ) and concentrated to a colorless solid, which was hydrogenated over 5% Pd/C catalyst in glacial acetic acid to give 0.9 g (82%) of 7b:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.02-6.90 (m, 3, ArH), 3.12 (m, 1, ArCH), 2.80 (m, 2, ArCH<sub>2</sub>), 2.24 (s, 3, ArCH<sub>3</sub>), 1.60-1.26 (m, 2, CH<sub>2</sub>CH<sub>3</sub>), 0.98 (t, 3, CH<sub>2</sub>CH<sub>3</sub>);  $^{13}\text{C}$  NMR: see Spectrum 2; mass spectrum m/e, Calcd. for  $\text{C}_{12}\text{H}_{14}\text{D}_2$ : 162.1378. Found:  $\text{M}^+$  162.1372.

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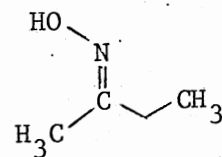
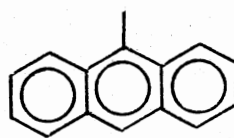
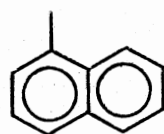
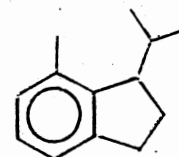
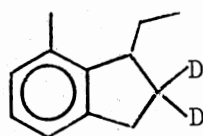
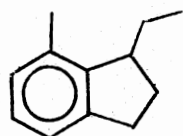
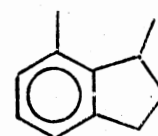
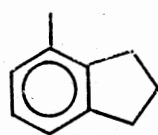
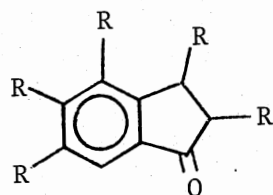
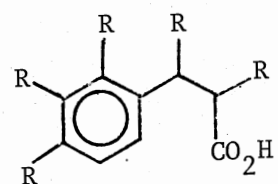
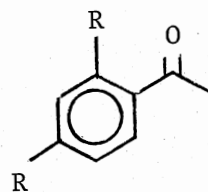
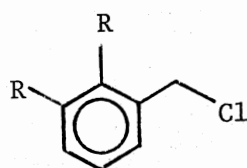


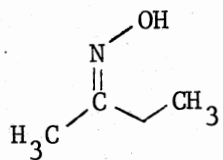
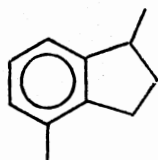
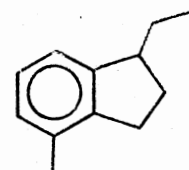
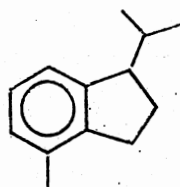
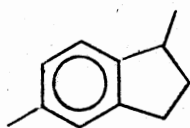
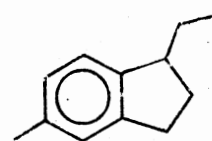
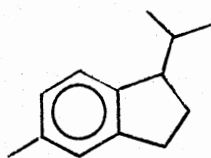
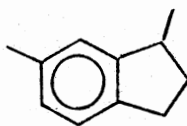
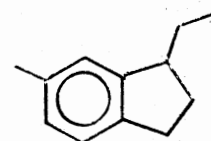
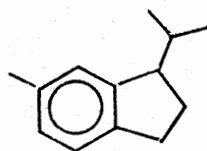
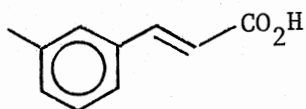
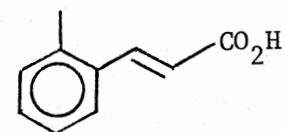
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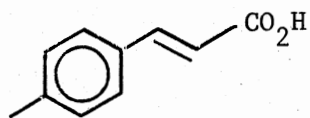
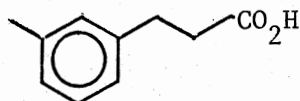
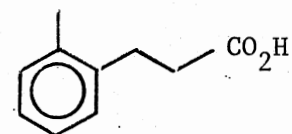
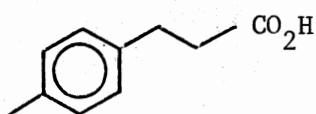
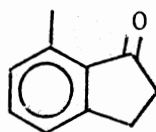
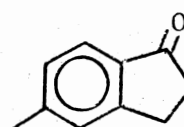
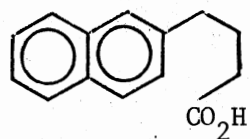
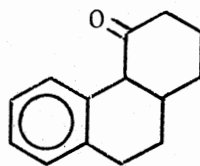
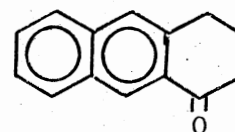
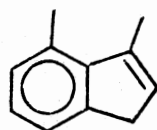
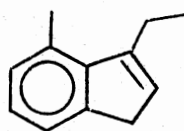
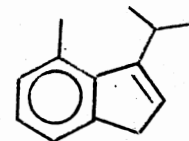
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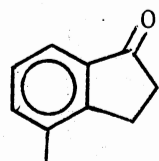
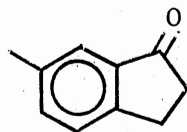
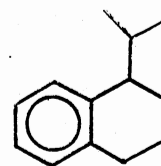
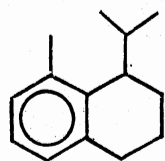
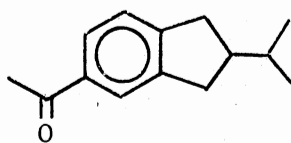
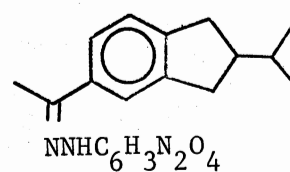
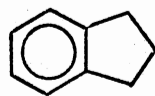
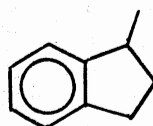
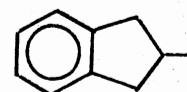
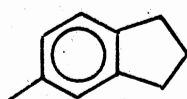
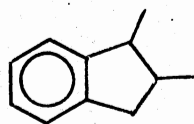
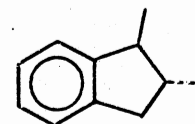
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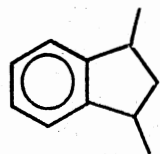
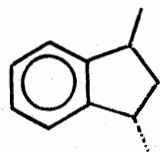
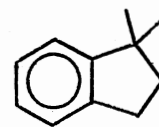
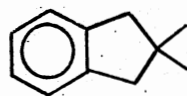
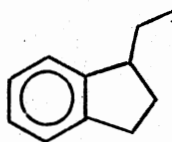
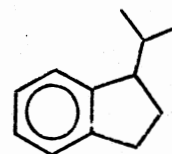
GLOSSARY OF STRUCTURES



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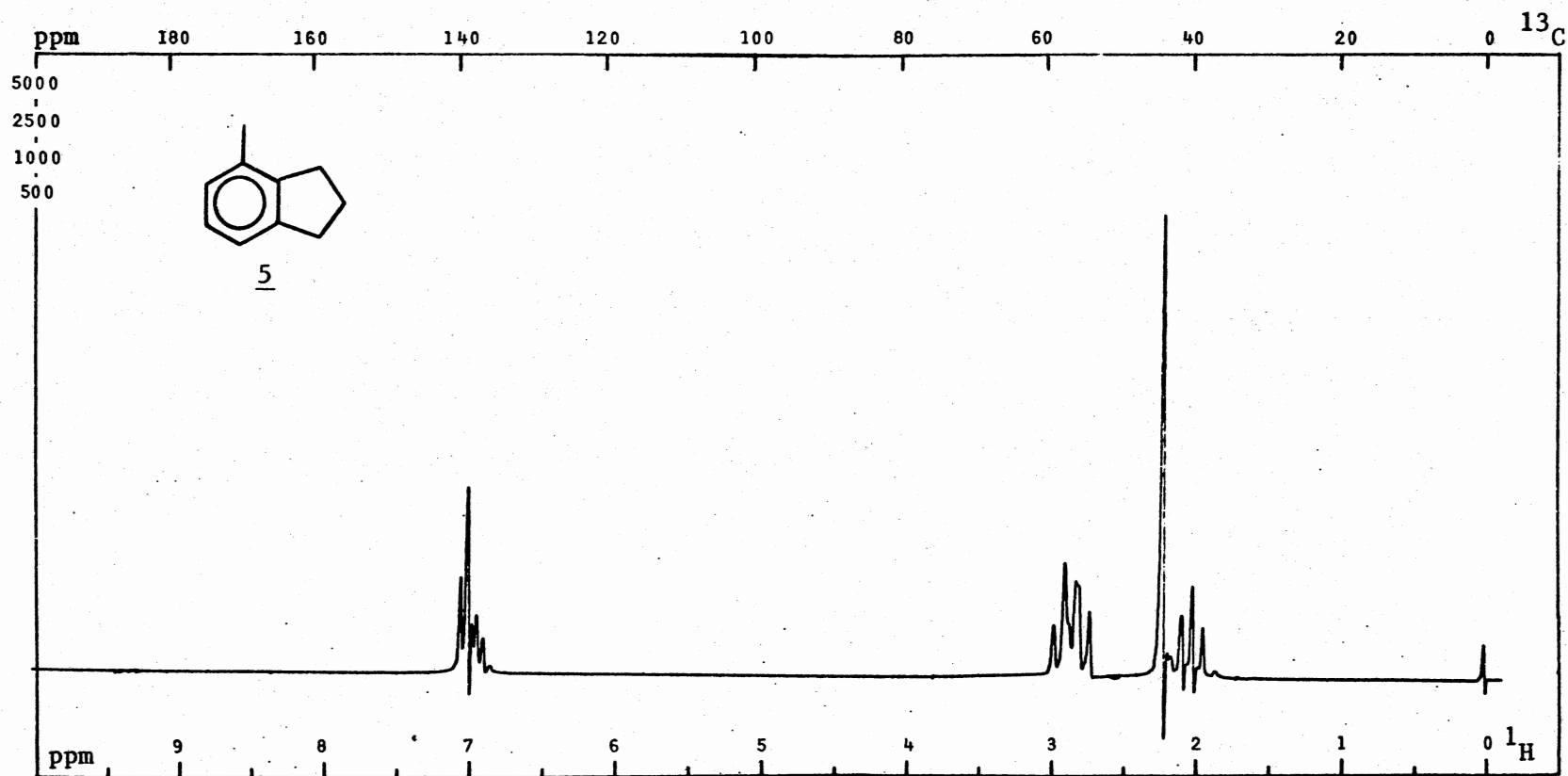
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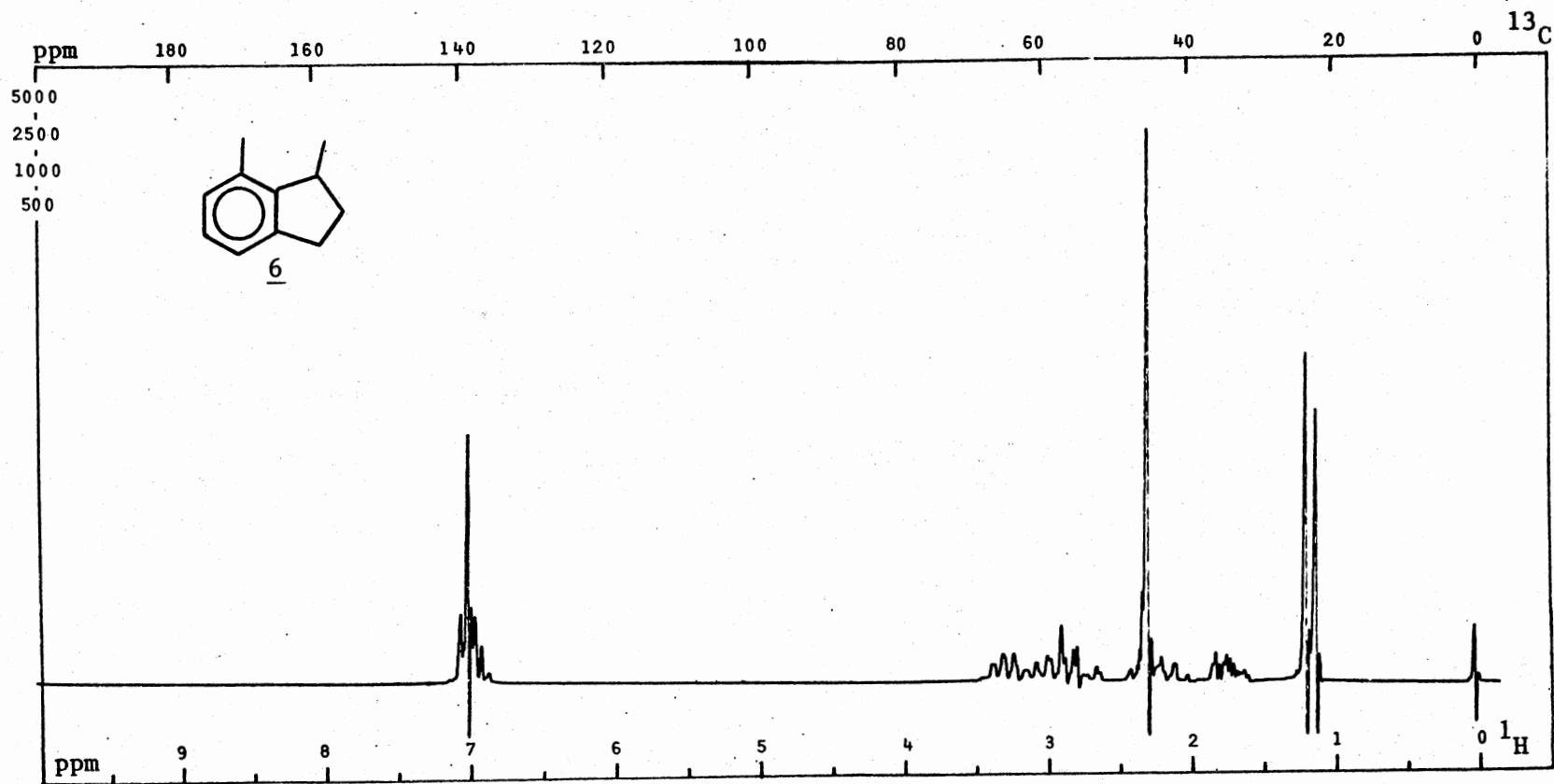


APPENDIX B

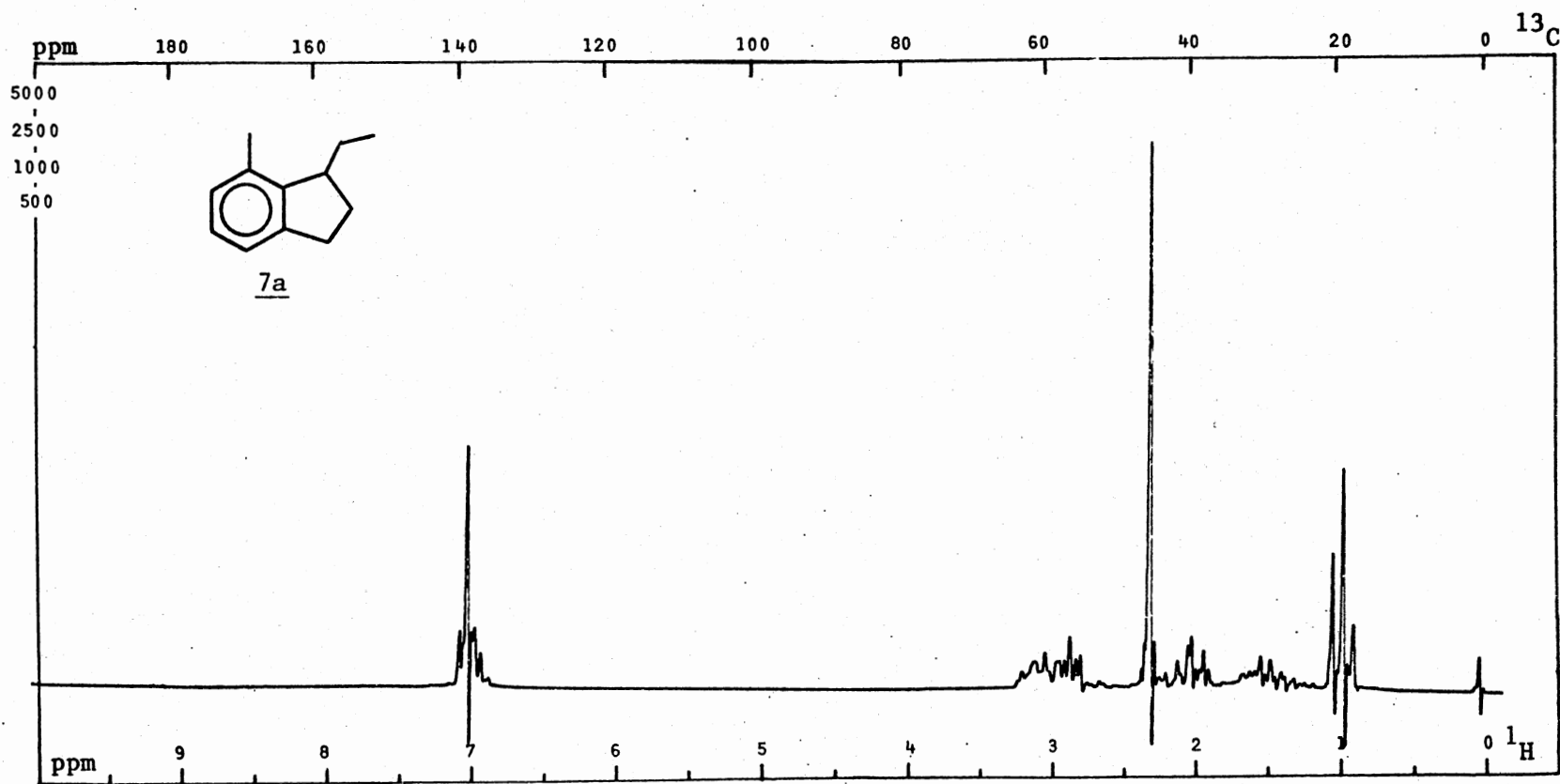
SELECTED SPECTRA



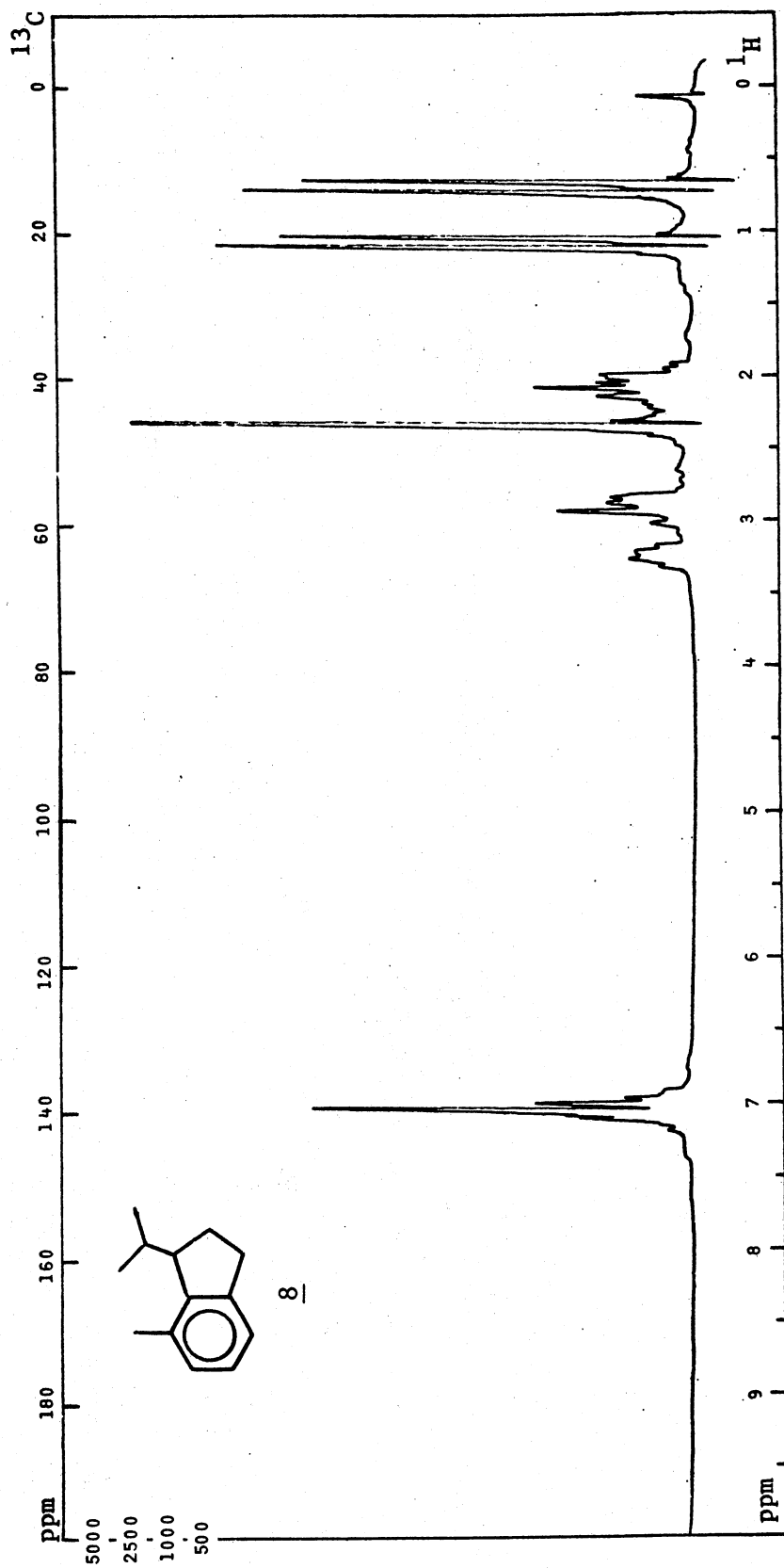
Spectrum 3.  $^1\text{H}$  NMR of 4-Methylindan (5)

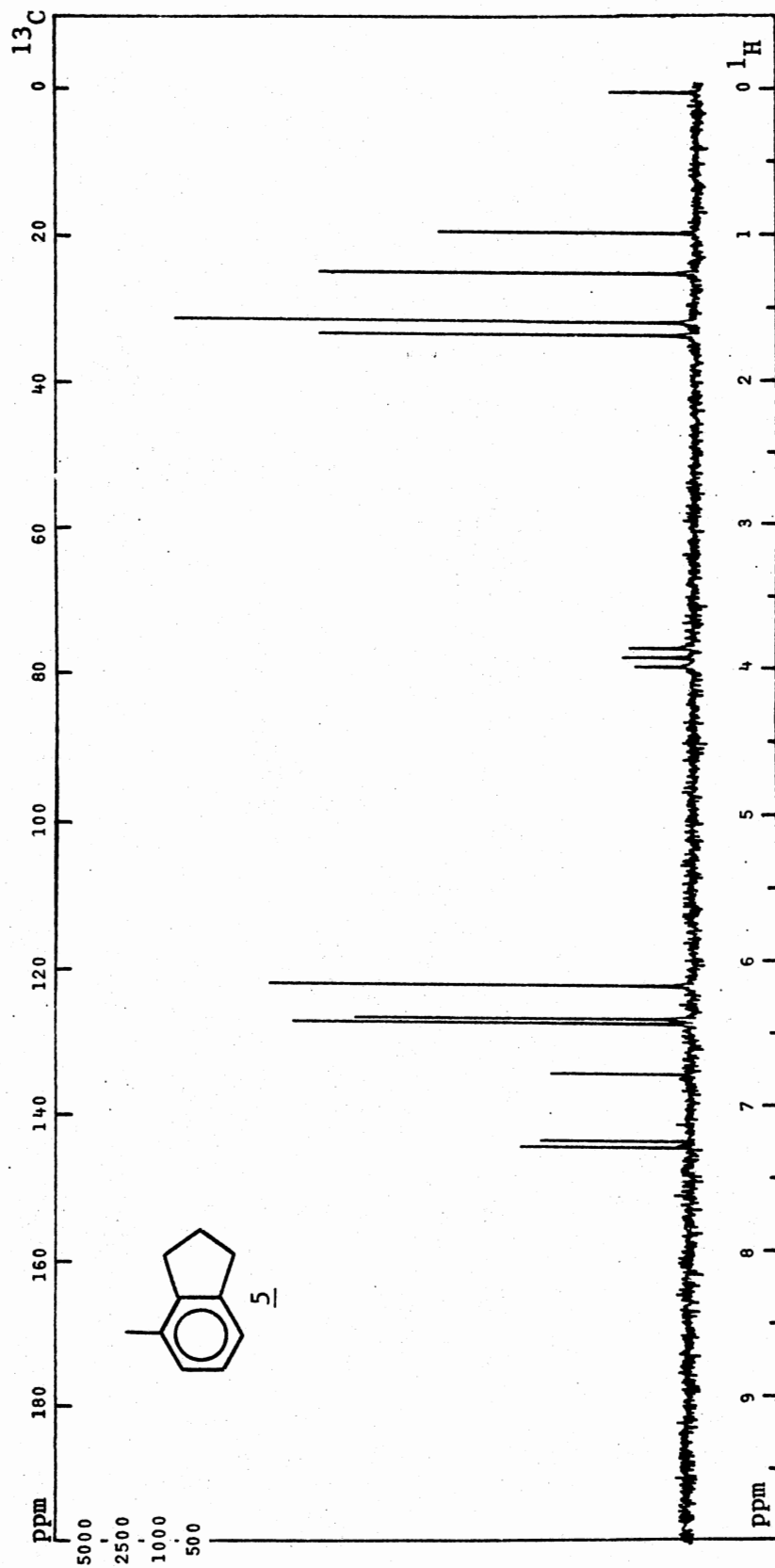


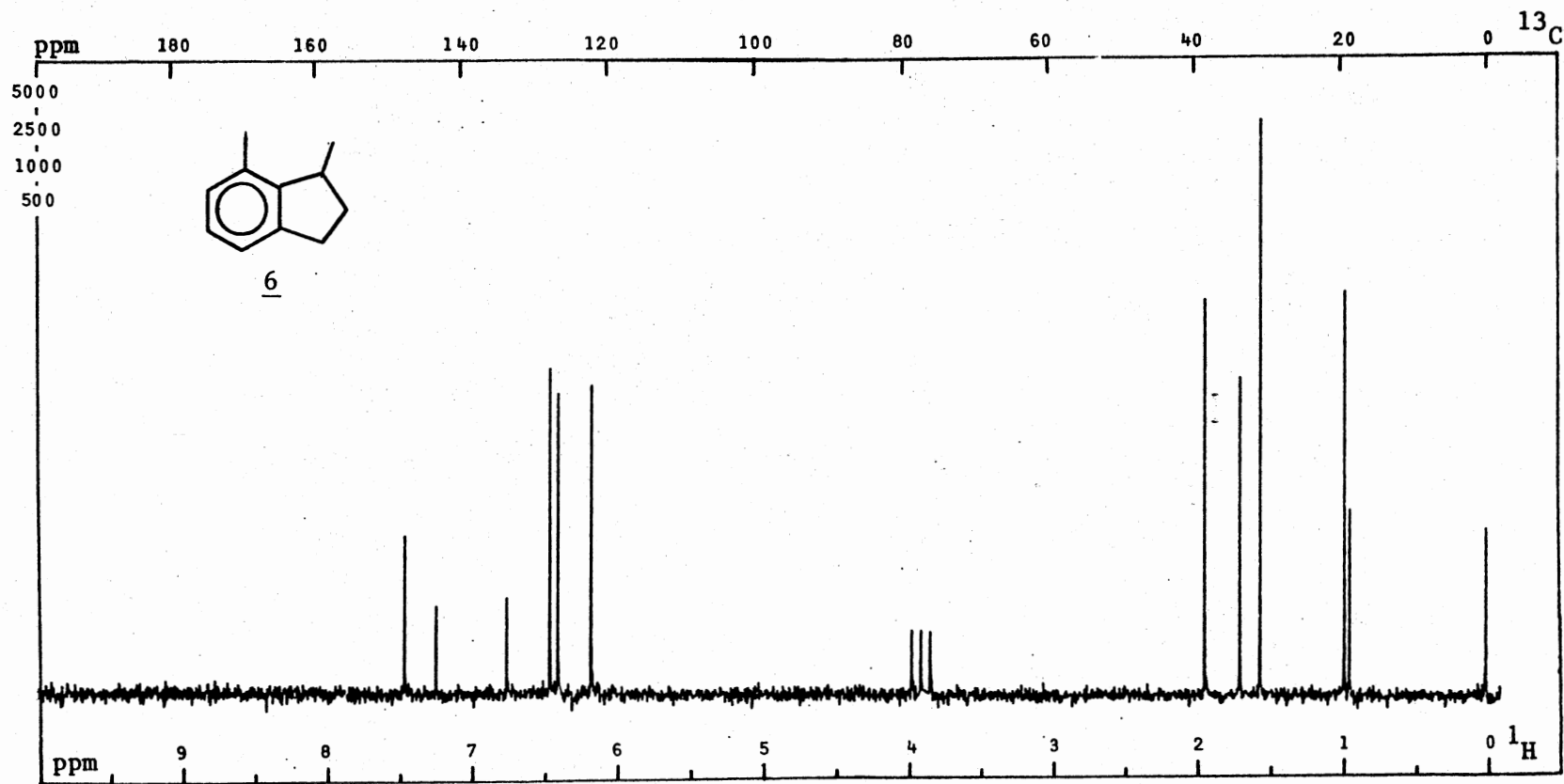
Spectrum 4.  $^1\text{H}$  NMR of 1,7-Dimethylindan (6)



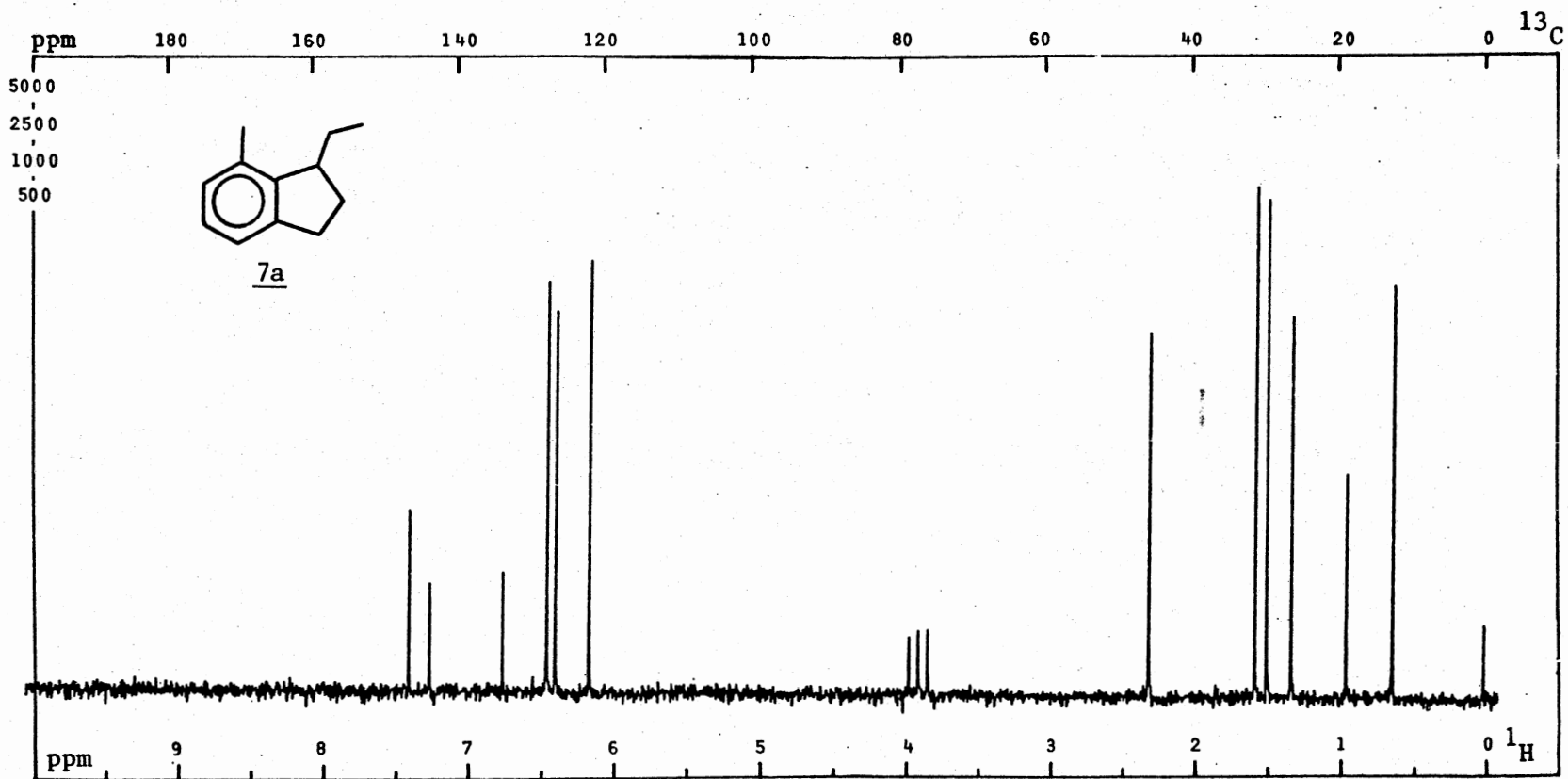
Spectrum 5.  $^1\text{H}$  NMR of 1-Ethyl-7-methylindan (**7a**)

Spectrum 6.  $^1\text{H}$  NMR of 1-Isopropyl-7-methylindan (8)

Spectrum 7.  $^{13}\text{C}$  NMR of 4-Methylindan (5)

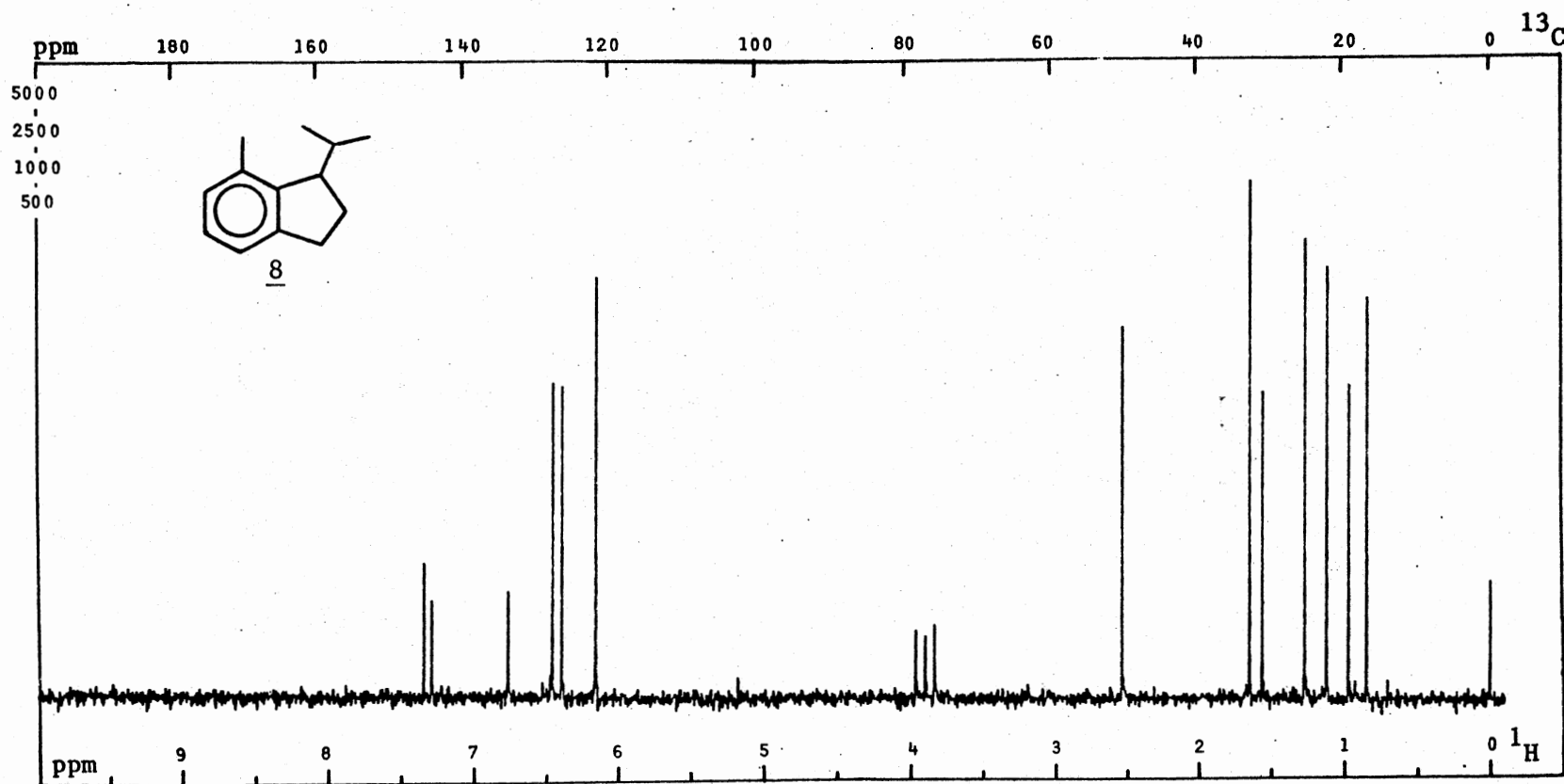


Spectrum 8.  $^{13}\text{C}$  NMR of 1,7-Dimethylindan (6)



Spectrum 9. <sup>13</sup>C NMR of 1-Ethyl-7-methylindan (**7a**)





Spectrum 10.  $^{13}\text{C}$  NMR of 1-Isopropyl-7-methylindan (8)

VITA<sup>2</sup>

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Doctor of Philosophy

Thesis: SYNTHESIS AND NMR INVESTIGATION OF ALKYLATED INDANS

Major Field: Chemistry

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