K): δ 7.2–7.6 (c, 15 H, Ph), 1.87 (s, 6 H, Me), 1.84 (s, 6 H, Me), 0.83 (s, 6 H, Me), δ –5.40 (t, 7.4 Hz, 1 H, Re–H$_A$), –5.70 (d, 7.4 Hz, 2 H, Re–H$_B$). ^{31}P$\{^1$H$\}$ NMR (298 K): δ –20.2. ^{31}P$\{^1$H$\}$ NMR (193 K): δ –15.4 (d, 29 Hz, 2 P, P$_B$), –30.4 (t, 29 Hz, 1 P, P$_A$). ^{13}C$\{^1$H$\}$ NMR (298 K): δ 203.2 (q, $^2J_{PC}$ = 9.2 Hz, CO), 142.8 (d, $^1J_{PC}$ = 38.8 Hz, C$_1$ of Ph), 130.5 (d, $^2J_{PC}$ = 11.1 Hz, C$_2$ of Ph), 128.8 (s, C$_4$ of Ph), 128.0 (d, $^3J_{PC}$ = 7.4 Hz, C$_3$ of Ph), 25.6 (d, $^1J_{PC}$ = 31.5 Hz, Me). ^{13}C$\{^1$H$\}$ NMR (193 K): δ 202.6 (dt, $^2J_{PC}$ = 51.8, 10.1 Hz, CO), 141.7 (t, $^1J_{PC}$ = 42.5 Hz, C$_1$ of P$_B$Me$_2$*Ph*), 140.3 (d, $^1J_{PC}$ = 35.1 Hz, C$_1$ of P$_A$Me$_2$*Ph*), 130.1 (d, $^2J_{PC}$ = 9.0 Hz, C$_2$ of P$_A$Me$_2$*Ph*), 129.3 (t, $^2J_{PC}$ = 11.0 Hz, C$_2$ of P$_B$Me$_2$*Ph*), 128.1 (s, C$_4$ of P$_B$Me$_2$*Ph*), 127.9 (s, C$_4$ of P$_A$Me$_2$*Ph*), 127.4 (t, $^3J_{PC}$ = 8.4 Hz, C$_3$ of P$_B$Me$_2$*Ph*), 127.1 (d, $^1J_{PC}$ = 7.4 Hz, C$_3$ of P$_A$Me$_2$*Ph*), 25.7 (t, $^1J_{PC}$ = 37.0 Hz, P$_B$*Me*$_2$Ph), 24.3 (t, $^1J_{PC}$ = 33.3 Hz, P$_B$*Me*$_2$Ph), 21.4 (d, $^1J_{PC}$ = 25.9 Hz, P$_A$*Me*$_2$Ph).

ReD$_3$(CO)(PMe$_2$Ph)$_3$ was prepared similarly by treatment of ReCl$_3$(CO)(PMe$_2$Ph)$_2$ with LiAlD$_4$ followed by hydrolysis with D$_2$O. The isotopomeric mixture of ReH$_{3-x}$D$_x$(CO)(PMe$_2$Ph)$_3$ (x = 0–3) was prepared by treatment of ReCl$_3$(CO)(PMe$_2$Ph)$_2$ with LiAlD$_4$ and hydrolysis with H$_2$O/D$_2$O (1:1 molar ratio).

Tetrahydridocarbonyltris(dimethylphenylphosphine)rhenium(V) Tetrafluoroborate (2a) and Dihydrido(dihydrogen)carbonyltris(dimethylphenylphosphine)rhenium(III) Tetrafluoroborate (2b). ReH$_3$(CO)(PMe$_2$Ph)$_3$ (1; 25 Mg) was dissolved in CD$_2$Cl$_2$ (0.4 mL) in a 5-mm NMR tube. The sample was cooled to –80 °C (dry ice/acetone). HBF$_4$·OEt$_2$ (6 μL) was added via a microsyringe. The sample was shaken and then quickly introduced into an NMR probe precooled to –80 °C. ^{1}H NMR (193 K): δ 6.8–7.7 (c, Ph), 2.17 (d, $^2J_{PH}$ = 9 Hz, Me, 2b), 1.92 (d, $^2J_{PH}$ = 5 Hz, Me, 2a), 1.90 (d, $^2J_{PH}$ = 5 Hz, Me, 2a), 1.72 (d, $^2J_{PH}$ = 7 Hz, Me, 2b), 1.55 (d, $^2J_{PH}$ = 7 Hz, Me, 2b), 1.19 (d, $^2J_{PH}$ = 7 Hz, Me, 2a), –3.91 (q, $^2J_{PH}$ = 17.9 Hz, Re–H, 2a), –4.90 (pseudo t, $^2J_{PH}$ = 55 Hz, Re–H, 2b). ^{31}P$\{^1$H$\}$ NMR (193 K): δ –26.6 (t, $^2J_{PP}$ = 15 Hz, P$_A$, 2a), –27.9 (d, $^2J_{PP}$ = 15 Hz, P$_B$, 2a), –27.6 (t, $^2J_{PP}$ = 11 Hz, P$_A$, 2b), –27.7 (d, $^2J_{PP}$ = 11 Hz, P$_B$, 2b). After the NMR experiments, excess NEt$_3$ was added and NMR spectra were taken again to show that 1 was regenerated quantitatively.

Photo-Heterolysis and -Homolysis of Substituted Diphenylmethyl Halides, Acetates, and Phenyl Ethers in Acetonitrile: Characterization of Diphenylmethyl Cations and Radicals Generated by 248-nm Laser Flash Photolysis

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Abstract: Para-substituted diphenylmethyl halides, acetates, and ethers RPh(R'Ph)CH-X (R, R' = CF$_3$ to OCH$_3$), upon photolysis with ~250-nm light in acetonitrile solutions, undergo homolysis and heterolysis of the C–X bond to give the radicals, RPh(R'Ph)CH$^\bullet$ (abbreviated as C$^\bullet$), and the cations, RPh(R'Ph)CH$^+$ (C$^+$). Whereas the quantum yields for homolysis (0.2–0.4) are rather independent of the nature of the substituent on the benzene ring, those for heterolysis increase with increasing electron-donor strength from $\leq$0.07 for CF$_3$ to 0.3 for OMe. The cation:radical ratios are also dependent on the nucleofugal properties of X. For the halides, the observed heterolysis:homolysis ratios correlate with the pK_a values of the conjugate acids HX and *not* with the electron affinities of X$^\bullet$. In acetonitrile, heterolysis is much less endothermic than homolysis. Homolysis and heterolysis can also be effected *indirectly* by reaction with triplet acetophenone (produced by 308-nm photolysis). Unless stabilized by one or more MeO, the cations decay predominantly by reaction with acetonitrile to give nitrilium ions. However, since this reaction is reversible (shown for the benzhydryl cation), the nitrilium ion contributes only to an insignificant degree to the formation of the final (cation-derived) products, which result from reaction with trace water (main product, benzhydryl alcohol; minor, benzhydrylacetamide). The rate constants for addition of C$^+$ to CH$_3$CN are in the range 3.5 × 10^5 to 3.8 × 10^7 s^{-1} for the cations with R = R' = Me to R = H, R' = CF$_3$. The rate constants for reaction of C$^+$ with halides (ion recombination) are ~2 × 10^{10} M^{-1} s^{-1} (diffusion control). The radicals C$^\bullet$ disappear by dimerization and disproportionation, for which a complete mass balance has been achieved by product analysis for the case of the benzhydryl system. At laser-pulse powers > 10 mJ electronically excited radicals, C$^{\bullet*}$, are additionally formed in many cases, via absorption of a light quantum by ground-state C$^\bullet$.

Introduction

Carbocationic structures exist as intermediates or transition states in nucleophilic substitutions, in elimination reactions, in electrophilic addition and substitution, in amide, ester, ortho ester, and acetal solvolyses, in (C–C and C–H) rearrangements, and in polymerization, to name some of the more important types of reaction.[4] Carbocations can readily be generated in superacids

and studied by physical methods such as NMR, and an enormous wealth of information has thus been accumulated on the structures and also reactions of these species.[5,6] With carbocations to some extent stabilized, production from appropriate precursors (C–X) is also possible in non-nucleophilic solvents, using Lewis acids[6]

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Characterization of Diphenylmethyl Cations and Radicals

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or radiation–chemical methods[7] to effect the heterolysis of the C–X bond. Cation reactivities with nucleophiles such as halides, alcohols, amines, or alkenes have thus been determined.[7-9]

Carbocations have also been produced photochemically,[10-22] and this method has the advantage of allowing one to work in nucleophilic solvents, such as those typically used in studies of solvolysis reactions. This approach has recently been taken to explore the electrophilic reactivity of the triphenylmethyl ("trityl") cation in acetonitrile–water mixtures,[23] and similar studies on diphenylmethyl ("benzhydryl") cations have been undertaken with use of "bad" anionic leaving groups such as *p*-cyanophenolate.[24,25] The present work is concerned with the 248-nm photolysis of substituted diphenylmethyl *halides* (RPh)(R′Ph)CH–X, particularly chlorides. These compounds as precursors are not stable in aqueous solvents because of their high ground-state hydrolytic reactivity, which is the consequence of the *good* leaving group properties of the halides.[26] In solvents less ionizing than water, however, the halides are expected to be useful carbocation precursors since it should be possible to enhance heterolysis by electronic excitation of the molecule. If the period of production of cations via this path is short as compared to their lifetime, the physical properties and the chemical reactivities can be determined. By use of this method, a series of mainly para-substituted diphenylmethyl cations has now been produced from the corresponding halides. In the present paper attention is focused on (1) the identification of the *transient* photochemical products, i.e. the cations (formed by heterolysis) and the radicals (from homolysis), and on the dependences of cation:radical ratios on structure and

solvent, (2) the identification of the *final* photoproducts, (3) the *thermodynamics* of the C–X bond cleavage, and (4), on the photochemical *mechanism* of C–X homolysis and heterolysis. *Reactivities* of the diphenylmethyl cations with nucleophiles, including carbon nucleophiles (olefins and aromatics), will be reported in a forthcoming paper.[27]

Experimental Section

The diphenylmethyl (benzhydryl) chlorides were prepared by treatment of the corresponding alcohols with HCl in CH_2Cl_2 in the presence of anhydrous $CaCl_2$, and they were purified by recrystallization or fractional distillation.[28] Unless commercially available, the alcohols were obtained from the ketones by reduction with Zn/KOH[29] or $NaBH_4$ in ethanol. Diphenylmethyl bromide was from Aldrich and was purified by recrystallization or vacuum distillation. Phase-transfer catalyzed reaction of diphenylmethyl bromide with KF[30] yielded the corresponding fluoride. Diphenylmethyl acetate, diphenylmethyl trifluoroacetate, diphenylmethyl 4-cyanophenolate, and diphenylmethyl 4-nitrophenolate were synthesized as described for similar systems.[25] Para-substituted $Ph_2CH^{+-}O_3SCF_3$ salts were produced by adding a $\geq$10-fold excess of $CF_3SO_3SiMe_3$ to the benzhydryl chlorides in acetonitrile. The main solvent was spectroscopic grade acetonitrile (Merck "Uvasol", water content $\leq$10 mM). For measurements of cation lifetimes, the water content was reduced to $\leq$2 mM by in situ treatment with neutral Al_2O_3. Further solvents were dichloromethane (Merck; purified by successive treatment with concentrated H_2SO_4, aqueous carbonate, $CaCl_2$, and final column chromatography over basic Al_2O_3), cyclohexane (Merck, analytical grade) and spectroscopic grade tetrahydrofuran (Merck "Uvasol") (both passed over basic Al_2O_3), and analytical grade aliphatic alcohols (Merck). 1,3-Cyclohexadiene (Fluka, >97%) was chromatographed over basic Al_2O_3. Tetra-*n*-butylammonium chloride (Fluka), after drying in vacuo, was recrystallized from CH_2Cl_2–Et_2O-*n*-pentane mixtures under N_2 to exclude moisture.

Two types of standards for quantum yield measurements were used: (a) For the time-resolved experiments, aqueous solutions of KI with $OD/cm \sim 1$ served to count the number of photons delivered by the laser by measuring the concentration of e^-_{aq} from the photoionization of I^- ($\Phi(e^-_{aq}) = 0.29$[31]), taking $\epsilon(e^-_{aq})$ at 650 nm to be 16 400 M^{-1} cm^{-1}.[32] (b) For the calibration of product yields from 248-nm laser or from irradiation with 254-nm light (from a mercury lamp using a monochromator to filter out undesired wavelengths), ferrioxalate actinometry was used assuming $\Phi(CO_2) = 1.25$.[33] Before photolysis, the acetonitrile solutions that contained 0.84 mM Ph_2CHCl (OD(248 nm)/cm = 1.0) and 0.049 mM *n*-octadecane together with 6.2 mM *n*-octane as an internal reference (or, respectively, scavenger for reactive radicals such as Cl•), were deoxygenated by bubbling with 99.998% Ar. The solutions (in 1 × 1 cm Suprasil quartz cells) were then subjected to the 248-nm laser pulses or to 254-nm light from a low-pressure Hg lamp, while being stirred with a magnetic stirring bar. After photolysis, 3–5 μL samples were injected into a Varian 1400 gas chromatograph (injector block at 170 °C) using a temperature program in the range 70–240 °C with a gradient of 10 °C/min, a split of ~1:30, and FI detection, and passed (using 0.8 bar H_2 as carrier gas) over a 23-m Carbowax 20 M column. The retention times of all the products were $\leq$20 min. The following products were identified by using authentic material as reference: Ph_2CH_2, Ph_2CHOH, $Ph_2CHNHCOCH_3$, $Ph_2CHCHPh_2$. The compounds Ph_2CHCH_2CN and $Ph_2CHC_8H_{17}$ (four isomers) were identified by mass spectrometry (70-eV ionization) on the basis of their molecular peaks and characteristic fragmentations. For the quantum yield measurements, aqueous solutions containing ferrioxalate with the same optical densities at 248 or 254 nm as those of the Ph_2CHCl solutions were used, with the same quartz cells under identical conditions.

For the laser experiments, the solutions (optical densities/cm were typically ≈ 0.2–2) were deoxygenated by bubbling with 99.998% Ar and photolyzed at 20 ± 2 °C with a flow system (flow rate ~ 100 mL/h), using 20-ns pulses (5–100 mJ) of 248-nm (KrF*) or 308-nm (XeCl*) light from a Lambda Physik EMG103MSC excimer laser. For the

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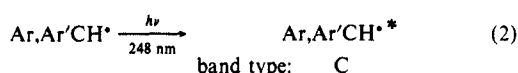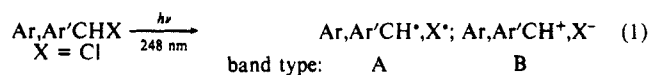
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248-nm light, a pulse power of 60 mJ (measured at the position of the cell) corresponds to 7 × 10^{16} photons hitting the active cell area of 4 × 5 mm. The optical absorption signals of the transients were digitized simultaneously by Tektronix 7612 and 7912 transient recorders interfaced with a DEC LSI11/73[+] computer which was also used for process control of the apparatus and to on-line (pre)analyze the experimental data. Final data analysis was performed on a Microvax II connected with the LSI via Ethernet.

Pulse radiolysis experiments were conducted in a way analogous to that described for the laser. A 3 MeV van de Graaff accelerator was used[34] that delivered 100-ns pulses with doses such that ~1–2 μM radicals were produced. The absorption spectrum of $Ph_2CH^•$, produced[35] via the reaction $SO_4^{•-} + Ph_2CHCO_2^- \rightarrow SO_4^{2-} + Ph_2CH^• + CO_2$, was measured in a deoxygenated aqueous solution and is used as the ε standard for the other benzhydryl radicals (see equations 6 and 7 and discussion in section 1).

Results and Discussion

1. Identification of the Photochemically Produced Transients. In Figure 1 are shown the absorption spectra observed at ~70 ns after photolysis (with the 20-ns 248-nm laser pulse delivering 20–60 mJ of energy per pulse) of ~0.1 mM solutions in acetonitrile (AN) of the diphenylmethyl chlorides $4\text{-}RC_6H_4(4\text{-}R'C_6H_4)CHX$, abbreviated as (RPh)(R'Ph)CHX[36] or Ar,-Ar'CHX. The spectra contain three types of bands: A, narrow

$$\underset{X = Cl}{Ar,Ar'CHX} \xrightarrow[248\ nm]{h\nu} \underset{\text{band type:}\quad A\qquad\quad B}{Ar,Ar'CH^•,X^•;\ Ar,Ar'CH^+,X^-} \quad (1)$$

$$Ar,Ar'CH^• \xrightarrow[248\ nm]{h\nu} \underset{\text{band type:}\quad C}{Ar,Ar'CH^{•*}} \quad (2)$$

bands with λ_{max} in the range 325–350 nm; B, similarly strong but broader bands in the range 430–500 nm; and C, weaker bands between 350 and 400 nm. It is evident that the positions of the bands depend on the substituent(s) at the phenyl ring(s). Also, the ratio of the intensities (amplitudes) of band B to band A increases with increasing electron-releasing ability of the substituent(s). The spectroscopic data of all the transients are collected in Table I.

Cations. On the basis of the similarity of the absorption spectra with the known[37] spectra of diarylmethyl cations (mainly in concentrated sulfuric acid solutions), the type B absorptions are identified as ground-state substituted diphenylmethyl cations. This assignment is corroborated by the observation that identical spectra were obtained by dissolving the corresponding trifluoromethanesulfonates $Ar,Ar'CHOSO_2CF_3$ in AN. The assignment of the type B absorptions as due to cations is further supported by the reactivity of these species with nucleophiles such as water, alcohol and ether (see Table II),[27] and by their nonreactivity with typical radical or triplet quenchers, such as O_2.

The dependence of the photochemical cation yield from reaction 1 was studied by varying the intensity of the exciting laser light (with the use of filters placed in the beam) and found to be strictly linear in the range 3–60 mJ/pulse, which demonstrates that the production of cation by eq 1 is a *monophotonic* process.

Radicals. The type A transients are also produced by a monophotonic process. These are identified as the corresponding diphenylmethyl radicals $Ar,Ar'CH^•$. This assignment is based on the identity of the spectra of the photochemically generated species and those produced by pulse *radiolysis* in tetrahydrofuran.[38] In this solvent, the radicals are formed by reaction of
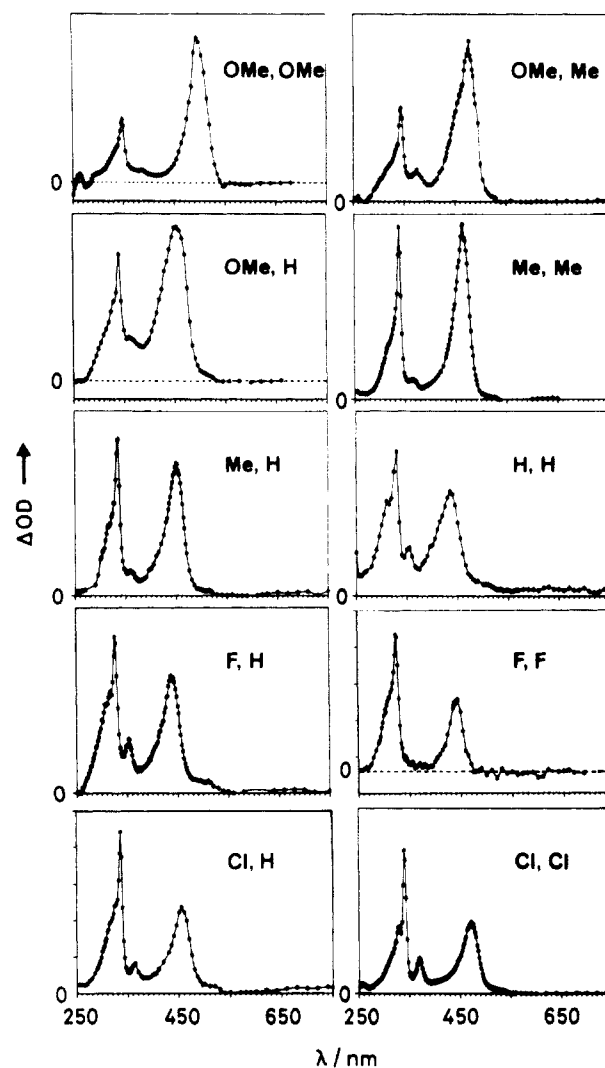

Figure 1. Absorption spectra of transients observed on photolysis (λ = 248 nm) of ~0.1 mM solutions of substituted diphenylmethyl chlorides in acetonitrile. The optical densities were measured ~70 ns after the laser pulse. The power per pulse was 20–60 mJ. The para substituents are indicated in the figures.
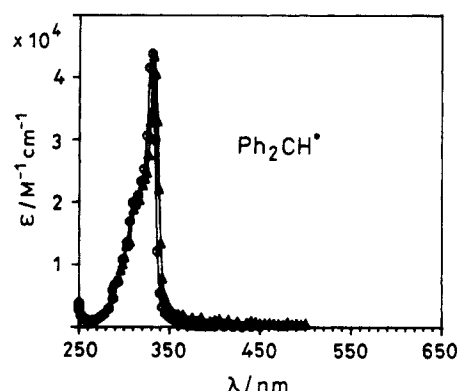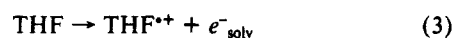

Figure 2. Absorption spectra of $Ph_2CH^•$ obtained on reaction (a) of e^-_{solv} with Ph_2CHCl in THF (triangles) and (b) of $SO_4^{•-}$ with $Ph_2CHCO_2^-$ in H_2O at pH ≈ 8, [2-methyl-2-propanol] = 50 mM (circles). With b, the ε scale is based on $G(Ph_2CH^•) = G(SO_4^{•-}) = 3.0$.

the radiation chemically generated e^-_{solv} with the parent chlorides, cf. eqs 3–5.

$$THF \rightarrow THF^{•+} + e^-_{solv} \quad (3)$$

$$THF^{•+} \rightarrow \overline{CH_2CH_2O}\dot{C}HCH_2 + H^+ \quad (4)$$

$$e^-_{solv} + Ar,Ar'CHCl \rightarrow Ar,Ar'CH^• + Cl^- \quad (5)$$

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(36) Unless specified otherwise, the substituent is always in the para position.

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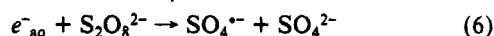
(38) Essentially identical spectra were obtained in 2-propanol as solvent.

Table I. Spectroscopic Data for the Cations, Radicals, and Excited Radicals Produced by 248-nm (and Acetophenone-Sensitized 308-nm) Photolysis of Di- (and Tri-)arylmethyl Chlorides in Acetonitrile

| ArAr'CHCl | | | | radical C· | | radical C·* | cation C+ | | OD(C+): | [C+]: | | |
Ar (para substituents)	Ar'	Σσ+/(R,R')a	pKR+	λ, nm⁻¹	log ε M⁻¹ cm⁻¹	λ, nm⁻¹	λ, nm⁻¹	log ε, M⁻¹ cm⁻¹	OD(C·)	[C·]	Φ(C+)b	Φ(C·)b
4-methoxyphenyl (OMe,OMe)	4-methoxyphenyl	-1.56	-5.71c -5.56d	348 ~350e 352f	4.67f	385	500 ~512e 507c 503e 501k	5.04c 5.10k	3.04	1.29 1.13	0.31 0.15h,j 0.27	0.24 0.23h,j
4-methoxyphenyl (OMe,OPh)	4-phenoxyphenyl	-1.28		350 354f	4.63f	395	500 516l	5.20l	2.82	0.73	0.16	0.22
4-methoxyphenyl (OMe,Me)	4-methylphenyl	-1.09	-8.32m -7.36d	344 346f	4.63f	375	478 482m 476k	4.92m	1.60	0.81	0.22	0.27
4-methoxyphenyl (OMe,H)	phenyl	-0.78	-7.9n -8.12d	340 344f	4.53f	360	455 466n 463o 457k	4.52n 4.79o	1.23	1.23 0.65	0.32 0.17	0.26
4-methylphenyl (Me,Me)	4-methylphenyl	-0.62	-10.4c -9.53d	338 340f	4.72f	364	464 472c 462k	4.87c	0.96	0.67	0.18 0.06h,p	0.27 0.1h,p
4-methylphenyl (Me,H)	phenyl	-0.31	-11.6n -12.29m -10.59d	336 338f	4.65f	360	450 456n 456m 455o 449k	4.43n 4.87m 4.86o	1.03	0.62	0.11	0.18
phenyl (H,H)	phenyl	0	-13.3c -13.56m -11.77d	330 331q 332f 330s	4.64q ≈4.64f 4.64s	350	435 453r 440c 442m 449i 435k	4.64c 4.74m 4.58i	0.57	0.57	0.13	0.23
4-fluorophenyl (F,H)	phenyl	-0.07	-11.55d	326 330f	4.61f	352	436 450d 445o 439k	4.72o	4.45	0.35	0.09	0.26
4-fluorophenyl (F,F)	4-fluorophenyl	-0.14	-13.03u	324 327f	4.65f		444 452u 448o 453v 442k	4.87u 4.86o	0.47	0.29	0.085	0.29
4-chlorophenyl (Cl,H)	phenyl	0.114	-12.08d -13.7n	336 336f	4.76f	365	456 463o 464d 467v	4.73o	0.52	0.56	0.15	0.27
4-chlorophenyl (Cl,Cl)	4-chlorophenyl	0.23	-13.96c	340 344f	4.76f	370	472 485c 483o 489v	5.14c 5.00o	0.61	0.25	0.052 0.05h,w	0.20 0.245h,w
4-(trifluoromethyl)phenyl (CF3,H)	phenyl	0.61		334 336f	4.50f	360	425 430o	4.5o	<0.18	<0.18	<0.07	0.39
mesityl	mesityl	-0.82	-6.6c	350 354f	4.34f		524 527o 522r 528c	4.50o	1.1	0.73	0.11	0.12
Ph3C			-6.63c	338 334x 339y	4.56x 4.61y		410 404/431c 404/432z 432z	4.60c 4.58z	1.43			

a Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979. b Obtained by comparison with the yield of e⁻aq (Φ = 0.29)[31] from 248-nm photolysis of aqueous KI solutions and taking ε(e⁻aq) at 650 nm to be[32] 16400 M⁻¹ cm⁻¹. Obviously, Φ(C+) depends on the choice of ε(C+). c Solvent H₂SO₄. Deno, N. C.; Jaruzelski, J. J.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3044. d Reference 70. e Photolysis in the solvent CH₂Cl₂. This work. f From electron irradiation of 1.4 mM solutions of substituted benzhydryl chloride in the solvent THF. The ε values are based on that for Ph₂CH· (43850 M⁻¹ cm⁻¹). This value is that measured in H₂O (see footnote s) and assumed to be the same in THF. g Solvent H₂SO₄. Arnett, E. M.; Bushick, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 1564. h λ(excitation) = 308 nm. Values are corrected for the unsensitized formation of C+ and C·. i [Acetophenone] = 110 mM; [substrate] = 20 mM. k Thermal dissociation of ArAr'CHCl in CH₃CN by trimethylsilyl trifluoromethanesulfonate. This work. l BCl₄⁻ salt in CH₂Cl₂. Schneider, R. Ph.D. Thesis, Friedrich-Alexander-University Erlangen-Nürnberg, FRG, 1987. m Solvent H₂SO₄. White, W. M.; Stout, C. A. *J. Org. Chem.* **1962**, *27*, 2915. n Solvent H₂SO₄. Deno, M. C.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3051. o Solvent H₂SO₄ (95-97%, p.A., Merck). This work. p [Acetophenone] = 75 mM; [substrate] = 9.5 mM. q Reference 40. r SbCl₆⁻ salt in nitromethane. Volz, H.; Schnell, H. W. *Angew. Chem.* **1965**, *19*, 864. s Produced by electron irradiation in the solvent H₂O, pH 7.4 (1 mM phosphate), 2 mM K₂S₂O₈, 0.1 M tert-butyl alcohol, 0.5 mM Ph₂CHCO₂H argon saturated. The ε value was calculated by assuming G(Ph₂CH·) = G(SO₄·⁻) = 3.0 and using N₂O saturated 10 mM KSCN for dosimetry, taking G(OH) = 6.0 and ε(SCN)₂·⁻) at 480 nm to be 7600 M⁻¹ cm⁻¹. t Wang, Y.; Tria, J. J.; Dorfman, L. M. *J. Phys. Chem.* **1979**, *83*, 1946. u Deno, M. C.; Evans, W. L. *J. Am. Chem. Soc.* **1957**, *79*, 5804. v SbCl₆⁻ salt in CH₂Cl₂. Volz, H.; Mayer, W. D. *Liebigs Ann. Chem.* **1975**, 835. w [Acetophenone] = 21 mM; [substrate] = 52 mM. x Reference 42. y From electron irradiation of aqueous solutions, pH 8.9 (1 mM phosphate), 1 mM K₂S₂O₈, 0.1 M tert-butyl alcohol, 0.5 mM Ph₃CCO₂H, argon saturated. Calculation of ε as described in footnote s. z Solvent H₂SO₄. Harmon, K. M.; Hesse, L.; Kleemann, L. P.; Kocher, C. W.; McKinley, S. V.; Young, A. E. *Inorg. Chem.* **1969**, *8*, 1054.

The extinction coefficients of the *substituted* radicals Ar,Ar'CH· (listed in Table I) as produced via eq 5 in THF were measured with reference to a solution containing *the parent*, diphenylmethyl chloride (Ar=Ar'=Ph). The ε value for Ph₂CH·, however, was measured in *aqueous* solution (at λ_{max} = 332 nm) with use of the oxidative decarboxylation of diphenylacetic acid[35] with SO₄·⁻, eq 7,[39] SO₄·⁻ being produced by e⁻aq reaction with S₂O₈²⁻, eq 6. The

$$e^-_{aq} + S_2O_8^{2-} \rightarrow SO_4^{\cdot -} + SO_4^{2-} \qquad (6)$$

$$SO_4^{\cdot -} + Ph_2CHCO_2^- \rightarrow SO_4^{2-} + Ph_2CH^\cdot + CO_2 \qquad (7)$$

spectrum measured in this sytem is shown in Figure 2, together with that produced in THF via reaction 5. The spectra are virtually identical. The ε value at 332 nm obtained for Ph₂CH· in H₂O (using G = 3 SO₄·⁻ per 100 eV of absorbed energy for the radiation–chemical yield) is 4.38 × 10⁴ M⁻¹ cm⁻¹, in excellent

(39) The advantage of H₂O as a solvent is that the radiation–chemical yield of e⁻aq is accurately known (see, e.g., Henglein, A.; Schnabel, W.; Wendenburg, J. *Einführung in die Strahlenchemie*; Verlag Chemie: Weinheim, 1969. Spinks, J. W. T.; Woods, R. J. *An Introduction to Radiation Chemistry*; Wiley: New York, 1976.

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Table II. Second-Order Rate Constants (M^{-1} s^{-1}) for Quenching the Transients from $(4\text{-ClPh})_2\text{CHCl}$

solvent	quencher	transient		
		cation	radical	excited radical
aceto-nitrile	Cl⁻	2.0×10^{10}	a	a
		$2.2 \times 10^{10\,b}$		
	ethanol	1.1×10^{9}	a	a
		$8.5 \times 10^{8\,b}$		
	H_2O	1.7×10^{8}	a	a
		$1.2 \times 10^{8\,b}$		
	tetrahydrofuran	$1.0 \times 10^{9\,c}$	a	
	$O_2{}^d$	a	1.3×10^{9}	9.4×10^{9}
	1,3-cyclohexadiene		a	5.5×10^{9}
	ferrocene		a	1.7×10^{10}
2-propanol	O_2		9.0×10^{8}	(3.2×10^{9})
	1,3-cyclohexadiene			4.3×10^{9}

^{a}No effect of quencher observed on the decay of the transient. ^{b}Refers to Ph_2CH^+. ^{c}Reversible reaction, rate constant given refers to the forward direction, $K_{equil} = 170$ M^{-1}. ^{d}In AN, the solubility of O_2 at 1 atm pressure is 8.5 mM (Smith, G. J. *J. Photochem.* **1983**, *22*, 51. Osburn, J. O.; Markovic, P. L. *Chem. Eng.* **1969**, *76*, 105).
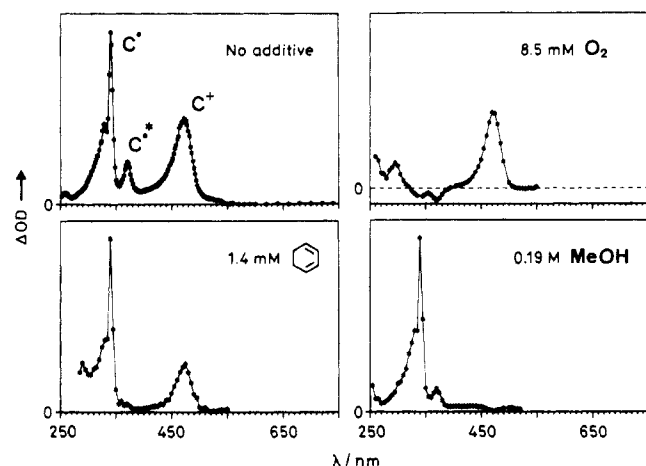
Figure 3. Effect of scavengers on the absorption spectra of the transients from bis(*p*-chlorophenyl)methyl chloride $((\text{ClPh})_2\text{CHCl})$ in acetonitrile: (a) no scavenger, 70 ns after pulse; (b) oxygen saturated (8.5 mM O_2), 200 ns; (c) 1.4 mM 1,3-cyclohexadiene, 80 ns; (d) 0.19 M methanol, 90 ns.

agreement with that (4.4×10^4) measured[40] in AN.[41] This procedure was checked by determining λ_{max} and ϵ of triphenylmethyl radical, produced analogously to eq 7 from triphenylacetic acid. The ϵ obtained is 4.1×10^4 at $\lambda_{max} = 339$ nm, in good agreement with a previously measured value in ethanol $((3.6 \pm 0.7) \times 10^4$ M^{-1} $cm^{-1})$.[42]

The assignment of the type A transients as radicals is further supported by the fact that they can easily be scavenged by O_2 (rate constants $\sim 1 \times 10^9$ M^{-1} s^{-1}) (see Figure 3 and Table II).

Excited Radicals. The type C bands (λ_{max} between 350 and 400 nm) are considerably weaker than those of the cations or radicals. In fact, in some cases the bands are apparent only as shoulders on the long-wavelength side of the radical bands (see Figure 1). The position and intensity of the bands depends on the substituent(s). The intensity of the bands is dependent also on solvent. The type C absorptions decay by first-order kinetics with rate constants k_0 of the order 10^6 s^{-1} (see Table III). The exponential decay of the transients can be accelerated considerably by the addition of compounds (quenchers) such as 1,3-cyclo-

(40) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1985**, *107*, 83. Bromberg, A.; Meisel, D. *J. Phys. Chem.* **1985**, *89*, 2507.

(41) It is therefore assumed that $\epsilon(Ph_2CH^{\bullet})$ is the same in the solvents H_2O, THF, and acetonitrile.
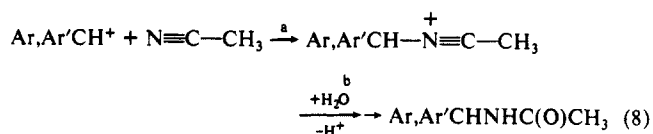
(42) Taub, I. A.; Harter, D. A.; Sauer, M. C.; Dorfman, L. M. *J. Chem. Phys.* **1964**, *41*, 979.

Table III. Rate Constants for the Decay of the Transients from Para-Substituted Diphenylmethyl Chlorides in Acetonitrile^a

para substituent	transient		
	cation^b	radical^c	excited radical^d
CF_3, H	3.8×10^7		$\sim 3 \times 10^6$
Cl, Cl	$2.8\ (\pm0.2) \times 10^6$ $>10^{8\,f}$	2.2×10^9	$6.8 \times 10^6\ (5.6 \times 10^6)^e$
Cl, H	$2.8\ (\pm0.2) \times 10^6$		$5.5 \times 10^6\ (5.1 \times 10^6)^e$
H, H	$2.5\ (\pm0.2) \times 10^6$	2.0×10^9	$3.7 \times 10^6\ (3.9 \times 10^6)^e$
F, H	$1.8\ (\pm0.1) \times 10^6$		3.6×10^6
F, F	$1.1\ (\pm0.1) \times 10^6$		1.1×10^7
Me, H	$5.9\ (\pm1.2) \times 10^{5\,g}$		$5.2 \times 10^6\ (4.6 \times 10^6)^e$
Me, Me	$3.5\ (\pm0.7) \times 10^{5\,g}$		4.7×10^6
OMe, H	h		
OMe, OMe	h		

^{a}Rate constants for the decay at 20 ± 1 °C in acetonitrile containing ≤ 2 mM H_2O. ^{b}Units s^{-1}, standard deviation in parentheses. ^{c}Units M^{-1} s^{-1}, calculated by using the ϵ values of the radicals given in Table I. ^{d}Units s^{-1}, standard deviation $\pm 10\%$. ^{e}In cyclohexane, from ref 44b. ^{f}In the solvent 2-propanol. ^{g}The error is larger due to admixture of non-exponential decay kinetics (see text). ^{h}Decay is predominantly by second order.

hexadiene, ferrocene, or O_2, with the rate constant for transient decay, k_{obsd}, described by $k_{obsd} = k_0 + k_q[\text{quencher}]$. The second order rate constants k_q measured are 10^9–10^{10} M^{-1} s^{-1} for the dienes, and $\sim 10^{10}$ M^{-1} s^{-1} for O_2 (see Table II).

The dependence of the signal amplitudes of the type C bands on the intensity of the laser pulse was measured for Ph_2CHCl and $(\text{ClPh})_2\text{CHCl}$ in the range 0–40 mJ/pulse. In both cases, the signal amplitude was found to increase with the *square* of the laser power, which indicates that the production of the species requires *two* photons. It was also found that the decay of the species C resulted in an additional formation of the radicals $Ar,Ar'CH^{\bullet}$, on top of the "spontaneously" produced amount present immediately after the pulse. The rates of this "delayed" radical production were the same (and the amplitudes were similar)[43] as those for decay of the type C species (as determined for $(\text{MeOPh})_2\text{CHCl}$ and Ph_2CHCl at a laser power of ~ 60 mJ/pulse). In the case of Ph_2CHCl the λ_{max} of the type C species is the same as that (355 nm) observed[40,44] for the electronically excited state of $Ph_2CH^{\bullet}$ (denoted as $Ph_2CH^{\bullet*}$),[45] and the chemical reactivity is also similar. On this basis and on that of its biphotonic formation, the type C species is identified as $Ph_2CH^{\bullet*}$, and, by analogy, the similar bands with the other systems are given the same assignment, i.e. as the electronically excited radicals. Their formation by photon absorption by the radical is described by eq 2.[46] This explains why type C transients were always relatively prominent when conditions (substituents, solvent, anionic leaving group) were favorable for *homolysis* rather than heterolysis of the benzhydryl C–X bond.

Photochemical Yields of the Transients. As mentioned above, the amplitudes of the signals due to cation and ground-state radical were found to be linearly related to laser pulse intensity, varied in the range 3–60 mJ, indicating that the transients are produced in a monophotonic process. Since the ϵ values of the cations are known from measurements in concentrated H_2SO_4 or AN (see Table I), and those of the radicals from the pulse radiolysis experiments, not only can the experimentally observed OD(cat-

(43) In ref 40, the ϵ for $Ph_2CH^{\bullet*}$ is estimated to be similar to that of $Ph_2CH^{\bullet}$. This explains the approximately equal amplitudes for decay at 355 nm and buildup at 330 nm.

(44) (a) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396. (b) Weir, D.; Scaiano, J. C. *Chem. Phys. Lett.* **1986**, *128*, 156.

(45) Meisel, D.; Das, P. K.; Hug, G. L.; Bhattacharyya, K.; Fessenden, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 4706.

(46) In the case of $(\text{ClPh})_2\text{CHCl}$, a "two-color" experiment (cf. ref 40, 44, and 45) was performed with use of a 248-nm pulse to produce $(\text{ClPh})_2\text{CH}^{\bullet}$ followed (after 2 μs) by a 308-nm pulse to excite the radical. This led to a strong formation of the 370-nm band, supporting its identification as due to $(\text{ClPh})_2\text{CH}^{\bullet*}$, and it led also to $(\text{ClPh})_2\text{CH}^{+}$ (with λ_{max} at 472 nm), by 308-nm photoionization of $(\text{ClPh})_2\text{CH}^{\bullet}$ (cf. Faria, J. L.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 1277).

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ion):OD(radical) ratios be converted into the corresponding concentration ratios [cation]:[radical],[47] but also the quantum yields for their formation can be determined. The results obtained by using low-intensity pulses (to ensure linearity of response and to minimize production of C[•]*) are summarized in Table I. It is evident that the [cation]:[radical] (= heterolysis:homolysis) ratio increases with increasing electron-donor properties of the para-substituents. This dependence is shown in Figure 4, where the quantum yields for cation formation are plotted versus the σ^+ or the pK_{R^+} values (the latter are a measure of the stability of the cations). The slope of the dependence is not very steep: The quantum yield for cation formation from $(MeOPh)_2CHCl$ is only a factor of 6 larger than that from $(ClPh)_2CHCl$.[48] This may indicate that a positive charge in the transition state is not *fully* developed. However, for such a conclusion to be creditable, data from analogous photochemical systems would have to be available for comparison. This type of data does not seem to exist.[49]

It is interesting that the quantum yields for *radical* formation, $\Phi(C^•) \approx 0.2–0.3$, are rather independent of substituent (from MeO to Cl). This suggests that radical stabilization by the para-substituent is unimportant in the transition state of the C–X bond homolysis. The overall decrease in the cation:radical ratio in going from electron-releasing to -withdrawing substituents is thus due to the decrease in this direction of the quantum yield for *cation* formation.

Decay of the Transients. In Figure 5 it is shown that in AN the excited radical $(ClPh)_2CH^{•*}$ (at 370 nm) and the cation $(ClPh)_2CH^+$ (at 472 nm) decay by first-order kinetics, while the ground-state radical $(ClPh)_2CH^•$ disappears in a second-order fashion. For the different systems, the rate constants for $R^{•*}$ and R^+ decay are listed in Table III. It is evident that the substituents have only a small effect on the rate constants for excited-radical decay. In contrast to this is the pronounced effect the substituent has on the cation kinetics: With the substituents CF_3, Cl, F, and H the cation was found to decay in a clean first-order reaction,[50] with rate constants that decrease with decreasing electron demand of the substituent. On going to strongly electron-donating substituents such as OMe, the decay is predominantly by second order.[51]

The first-order decay of the cations with not more than one Me or with no OMe group ($\sum\sigma^+ > -0.5$) is explained by their reaction with acetonitrile to give nitrilium ion, eq 8a. As pointed

$$Ar,Ar'CH^+ + N\equiv C—CH_3 \xrightarrow{a} Ar,Ar'CH—\overset{+}{N}\equiv C—CH_3$$

$$\xrightarrow[-H^+]{\overset{b}{+H_2O}} Ar,Ar'CHNHC(O)CH_3 \quad (8)$$

out in section 2, there is evidence that this reaction is reversible.

Nitrilium ion formation is also indicated by conductance measurements. In Figure 5d it is shown that the laser flash produces a steep increase of conductance which decreases by only ~40% over a period of ~5 μs, a period in which the benzhydryl cation is quantitatively gone, as observed optically (Figure 5c). The fact that the total concentration of ions decreases much more slowly than that of Ph_2CH^+ proves that this ion is converted to a longer-lived one, and this is identified as the nitrilium ion.

(47) The greatest amount of uncertainty in the ratios is due to that in the ε values of the cations, see ref 37 and Table I.

(48) In the *ground*-state solvolysis of Ar,Ar'CHCl in ethanol at 25 °C, the rate constant increases by 10^6 in going from Ph_2CHCl to $(MeOPh)_2CHCl$ (Schade, C. Ph.D. Dissertation, University of Lübeck, 1988. See also ref 68.).

(49) As a somewhat analogous case a weak sensitivity to substituents has been observed for photo*protonation* of styrenes, cf. McEwen, J.; Yates, K. *J. Am. Chem. Soc.* **1987**, *109*, 5800.

(50) Due to reaction of the cation with water (see Table II), the first-order rates are sensitive to the water-content of AN. The AN used contained ≤2 mM H_2O, obtained by in situ treatment with neutral Al_2O_3. At ≤2 mM H_2O, the contribution of H_2O to the decay rates of the cations is ≤10%.

(51) Observed slight deviations from ideal second-order kinetics can be explained in terms of reaction of the cations with traces of water. Reversible addition to AN (with the equilibrium shifted to the left, see eq 8a) is also a possibility.
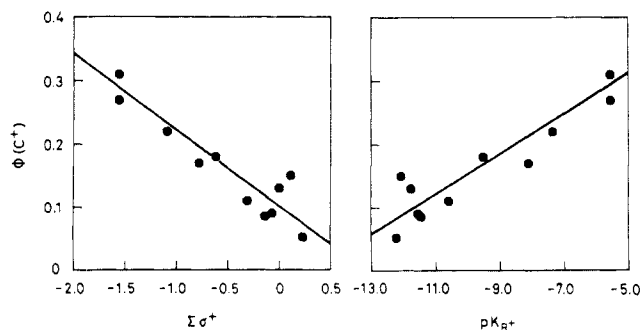

Figure 4. The dependence of the quantum yield for heterolysis on the electrofugal leaving group properties of the para-substituted benzhydryl cations as expressed by $\sum\sigma^+$ and pK_{R^+}.

Table IV. Quantum Yields of Products from 248-nm Photolysis of Ph_2CHCl in Acetonitrile

products	Φ	products	Φ
$Ph_2CHCHPh_2$	0.06	Ph_2CHOH	0.10_5
($\equiv 2 \times Ph_2CH^•$	0.12)	Ph_2CHNH-	0.01_8
Ph_2CHCH_2CN	0.01_6	$COCH_3$	
$Ph_2CHC_8H_{17}$	$0.04_8{}^a$		
Ph_2CH_2	0.01_5		
$\sum\Phi(precursors)^b$	$\sum\Phi(Ph_2CH^•)$ 0.20	$\sum\Phi(Ph_2CH^+)$	0.12_3
transients^c	$Ph_2CH^•$ 0.23	Ph_2CH^+	0.13

^{a}The values are the sum of the yields of the four isomers detected, whose concentration ratio was ~1:1:1:0.7. ^{b}Yields of the precursors calculated from the product yields. ^{c}The values are from the time-resolved experiments, see Table I. They are based on log ε(440 nm) = log ε(330 nm) = 4.64 for cation and radical, respectively.

The second-order decay of the *stabilized* cations such as $(MeOPh)_2CH^+$ is suggested to involve ion recombination,[52] eq 9, the reverse of the heterolysis reaction. Rate constants for this

$$Ar,Ar'CH^+ + Cl^- \xrightarrow{k_{comb}} Ar,Ar'CHCl \quad (9)$$
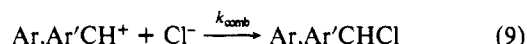
reaction were obtained by photolyzing the benzhydryl chlorides in the presence of excess amounts (compared to $[Ar,Ar'CH^+]$) of Cl^- (as the tetra-*n*-butylammonium salt) and measuring the pseudo-first-order rate of decay of the cation as a function of $[Cl^-]$. The rate constants thus determined (see Table II)[53] are equal to ~2×10^{10} M^{-1} s^{-1}, which corresponds to diffusion control in AN. Diffusion-controlled reaction of Ph_2CH^+ with halides has previously been reported for other solvents such as chlorinated hydrocarbons and alkanes.[7] All the reactivity data are in full agreement with the cationic nature of the type B transients.

2. Final Photoproducts and Mechanism of Their Formation. AN solutions containing ~0.1 mM Ph_2CHCl in the presence of 6.2 mM *n*-octane were photolyzed at room temperature with (a) 254-nm light from a low-pressure or from a medium-pressure mercury lamp, and (b) with the 248-nm light from the laser. At substrate conversions ≤10% six photochemical products were identified $Ph_2CHCHPh_2$, Ph_2CHCH_2CN, $C_8H_{17}CHPh_2$, Ph_2CH_2, $Ph_2CHNHC(O)CH_3$, and Ph_2CHOH (see Table IV). The yield of the first four products was reduced to ≤3% of the original values when O_2 was present during photolysis, but the yields of the latter two products remained the same.[54] This indicates that the former are derived from radical precursors and the latter from cation which typically have a low reactivity with O_2. In the presence of 0.4 M 2-methyl-2-butene (as an efficient scavenger for reactive radicals such as Cl[•] and a moderate trap for carbocations[55]) Ph_2CHCH_2CN was undetectable, the yield of Ph_2CHOH was

(52) For a review on cation–anion combination reactions see: Ritchie, C. D. *Can. J. Chem.* **1986**, *64*, 2239.

(53) For more complete information see ref 27.

(54) In the presence of O_2, the initial yield of $Ph_2CH^•$ was not lower than in its absence, indicating that the precursor of the radical is not scavenged by O_2. O_2 led to a large yield of Ph_2CO.

(55) $k(Ph_2CH^+ + 2$-methyl-2-butene) ≈ 5×10^7 M^{-1} s^{-1}, see ref 27.

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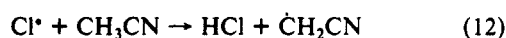
Bartl et al.
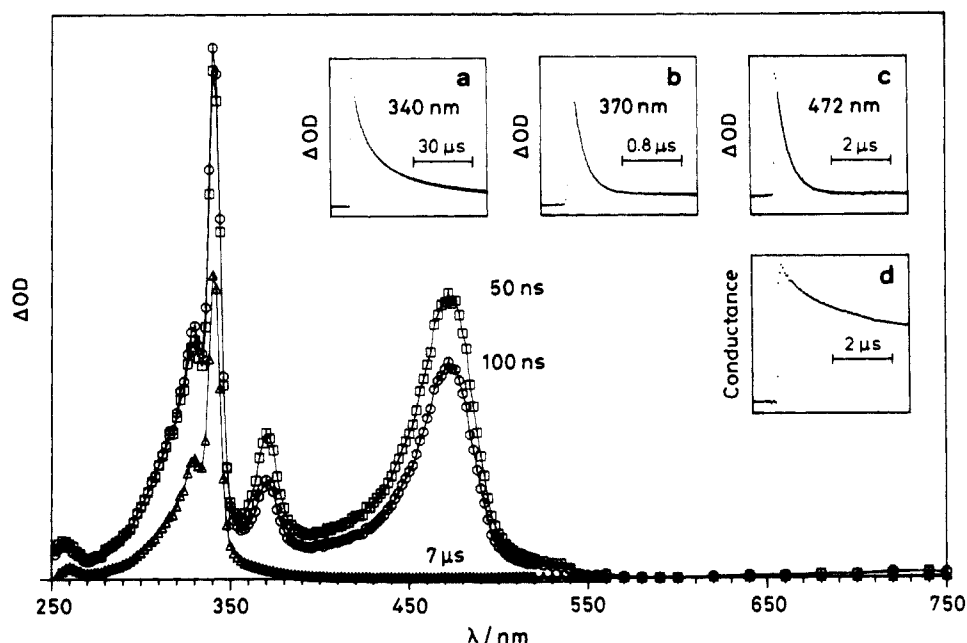
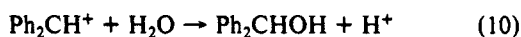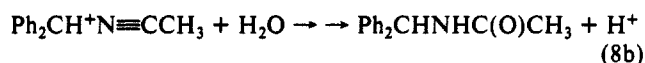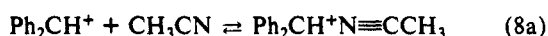**Figure 5.** Dependence on time of the absorptions measured after photolysis of a 0.2 mM solution of $(ClPh)_2CHCl$ in acetonitrile. Key is as follows: □, 50 ns; O, 100 ns; △, 7 μs. Insets are as follows: (a) decay of radical at 340 nm; (b) decay of excited radical at 370 nm; (c) decay of cation at 472 nm; (d) decay of conductance. The smooth curve through the experimental points is from a computer analysis assuming first-order (for cation and excited radical) and second-order kinetics (for radical).

reduced to 35% whereas that of $Ph_2CHCHPh_2$ was unchanged. Addition of 10 mM of Cl^- (as the n-Bu_4N^+ salt) resulted in the reduction of the yield of Ph_2CHCH_2CN to 4% and that of Ph_2CHOH to 10%, whereas that of $Ph_2CHCHPh_2$ remained unchanged.

These results can easily be explained in terms of photoheterolysis and homolysis of benzhydryl chloride (eq 1') to yield the cation and radical already identified by laser spectroscopy, and chloride and chlorine atom

$$Ph_2CHCl \xrightarrow[\text{248 nm}]{h\nu} \begin{cases} Ph_2CH^+ + Cl^- \\ Ph_2CH^\bullet + Cl^\bullet \end{cases} \quad (1')$$

followed by eq 8–16

$$Ph_2CH^+ + CH_3CN \rightleftarrows Ph_2CH^+N\equiv CCH_3 \quad (8a)$$

$$Ph_2CH^+N\equiv CCH_3 + H_2O \rightarrow \rightarrow Ph_2CHNHC(O)CH_3 + H^+ \quad (8b)$$

$$Ph_2CH^+ + H_2O \rightarrow Ph_2CHOH + H^+ \quad (10)$$

$$2 Ph_2\dot{C}H \rightarrow Ph_2CHCHPh_2 \quad (11)$$

$$Cl^\bullet + CH_3CN \rightarrow HCl + \dot{C}H_2CN \quad (12)$$

$$Cl^\bullet + C_8H_{18} \text{ (octane)} \rightarrow HCl + C_8H_{17}^\bullet \text{ (octane(-H)}^\bullet) \quad (13)$$

$$Ph_2\dot{C}H + \dot{C}H_2CN \rightarrow Ph_2CHCH_2CN \quad (14)$$

$$C_8H_{17}^\bullet + Ph_2CH^\bullet \rightarrow C_8H_{17}CHPh_2 \text{ (combination)} \quad (15)$$
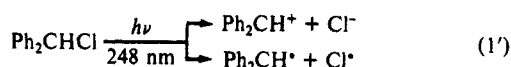
$$\rightarrow C_8H_{16} \text{ (octene)} + Ph_2CH_2 \text{ (disproportionation)} \quad (16)$$
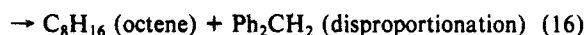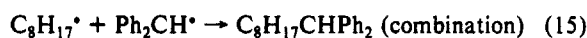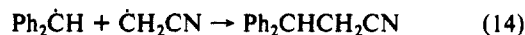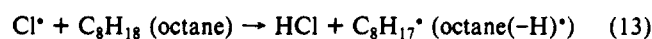
The reversibility of nitrilium ion formation via eq 8a is concluded from the fact that not the Ritter[56] product $Ph_2CHNHC(O)CH_3$ is the main cation-derived product but it is Ph_2CHOH, the product of the reaction of Ph_2CH^+ with H_2O. This carbinol is *not* the product of the *primary* reaction of the cation, since the cation is much shorter lived than can be explained by its reaction with H_2O. With a water content of ≤ 2 mM and $k(H_2O + Ph_2CH^+) = 1.2 \times 10^8$ M^{-1} s^{-1} (see Table II), k_{obsd} for reaction with water of the cation is $\leq 2.4 \times 10^5$ s^{-1}, to be compared with 2.5×10^6 s^{-1} for its reaction with AN. Thus, if formation of the nitrilium ion was

irreversible, the acetamide would be the main cation-derived product and not the carbinol.

The scavenger experiments described above are almost self-explanatory. As shown in Table II, Cl^- scavenges the cation very efficiently. Chloride is also able to trap $Cl^\bullet$ to yield $Cl_2^{\bullet-}$[57] which is much less powerful in abstracting $H^\bullet$ from CH_3CN. The resulting decrease in the yield of $^\bullet CH_2CN$ leads to a drastic reduction in that of $Ph_2CH_2CH_2CN$, formed by cross-termination of the radicals (eq 14).[58] Alkenes such as 2-methyl-2-butene are even better traps for $Cl^\bullet$ than is Cl^-, and therefore $Ph_2CH_2CH_2CN$ is undetectable in their presence. The alkene leads to a reduction in the Ph_2CH^+-derived product yields as well, in agreement with the known electrophilic reactivity of Ph_2CH^+ with C–C double bonds.[8] Oxygen admission to solutions under photolysis removes all radical-derived products without affecting those derived from cation, in line with the nonreactivity of O_2 with cations.

The quantum yields for product formation may be compared with those for production of the transients (see Table IV). For the case of C–Cl *homolysis*, from the products $\Phi(Ph_2CH^\bullet) = 2\Phi(Ph_2CHCHPh_2) + \Phi(Ph_2CHCH_2CN) + \Phi(C_8H_{17}CHPh_2) + \Phi(Ph_2CH_2) = 0.12 + 0.016 + 0.048 + 0.015 = 0.20$, to be compared with $\Phi = 0.23$ from the laser experiments. The similar numbers mean that there is little recombination of $Ph_2CH^\bullet$ and $Cl^\bullet$ occurring, indicative of a short lifetime of $Cl^\bullet$ (as a result of reactions 12 and 13). Similarly, from product analysis the cation-derived yields add up to 0.12, within experimental error the same as the value ($\Phi = 0.13$) measured for the cation by laser spectroscopy. This shows that with the Ph_2CHCl system ion recombination (competing with trapping of the cation by water) is unimportant. In summary, the product data are qualitatively and quantitatively in full support of C–X bond homolysis and heterolysis as described in section 1.

As mentioned in section 1, the *stabilized* cations such as $(MeOPh)_2CH^+$ decay predominantly by combination with Cl^-, rather than by reaction with solvent. It is therefore to be expected that the yields of cation-derived *stable* products will be *less* than that of cation as determined immediately after the laser pulse.

3. Thermochemical Aspects of Bond Cleavage. With Ph_2CHCl in AN, on excitation with 266 nm a weak fluorescence was measured with $\lambda_{max} = 290$ nm, which corresponds to an energy

(56) In the Ritter reaction amides are produced from nitriles by reaction with (tertiary) alcohols under acidic conditions.

(57) Fornier de Violet, P. *Rev. Chem. Intermed.* **1981**, *4*, 121.
(58) The dimer of $^\bullet CH_2CN$ was not detected.

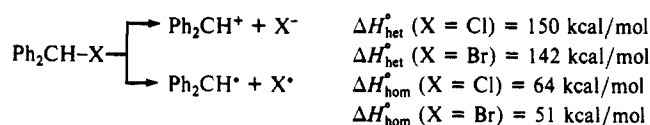**Table V.** Dependence of the Cation:Radical on the Nucleofugal Leaving Group X ($\lambda_{excitation}$ = 248 nm) and Thermodynamic Parameters[a] for C-X Bond Dissociation in the System Ph_2CH-X ($=R-X$) in Acetonitrile

X	$[C^+]:[C^\bullet]$[b]	$\Phi(C^+)$[c]	$\Phi(C^\bullet)$[c]	EA(X•)/ eV[d]	pK_a (H-X) in H_2O (25 °C)	in DMSO[e]	$\Delta H°$ (H-X)[f]	$\Delta H°_f$ (R-X)[g]	$\Delta H°_{hom}$ (R-X)[h]	$\Delta H°_{het}$ (R-X)[i]	ΔG (solv)[k] for X⁻ (g → AN)	ΔG_{het} (solv)[l]
Br	0.63	0.12	0.19	3.36	-8	0.9	323.6	44.8	51 (44)[m]	142	-69	7
Cl	0.59	0.13	0.23	3.61	-7	1.8	333.3	32.6	64 (56)[m]	150	-73	11
F	0.26	0.05	0.20	3.40	3.16	15	371.5	-1.8	89	179	-96	17
CF_3CO_2	0.14	0.04	0.31		0.52	3.45	322.7					
CH_3CO_2	<0.08[n]			3.26[o]	4.76	12.3	348.5	-54.7	76	170	-62[p]	42
4-NO_2PhO	<0.1[n]			3.55[q]	7.16	10.8						
4-CNPhO	0.22 0.16[r] 0.49[t]	0.02 0.01[s]	0.09 0.13[r]	3.33[q]	7.97		332.0					
HO	<0.03[n,u]		0.04	1.83	15.7	32	390.8	0.9	77	204	≤-84	54
H	<0.02[n,u,v]		≤0.1[v]	0.756			400.4	40.3	81	232		
PhO				2.37[w]	10	18	349.8					

[a] The free energies (ΔG) and bond dissociation enthalpies (ΔH) are in kcal/mol. Except for $\Delta H°$(H-X), all values related to 298 K. [b] Calculated from the measured optical densities at λ_{max} of C^+ or $C^\bullet$ and taking log $\epsilon(C^+)$ = log $\epsilon(C^\bullet)$ = 4.64 (see Table I). [c] The quantum yield Φ was determined with reference to an aqueous KI solution with the same OD at 248 nm, assuming $\Phi(e^-_{aq})$ = 0.29 (ref 31) and $\epsilon(e^-_{aq})$ at 650 nm = 16 400 M⁻¹ cm⁻¹ (ref 32). The error is estimated to be ±10%. [d] From ref 60. [e] From Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456. [f] $\Delta H°$(H-X) is the gas-phase enthalpy for deprotonation of H-X to yield H^+ + X^-. The values are from Bartmess, J. E.; McIver, R. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2, p 87. [g] See ref 61. [h] Based on $\Delta H_f(R^\bullet)$ = 69 kcal/mol, from ref 59. [i] IP(Ph₂CH•) = 7.32 eV, see ref 63. [k] Calculated from the values given by ref 66. [l] Calculated by using $\Delta H°_{het}$(R-X), ΔG(solv)(X⁻), and the value 67 kcal/mol for solvation of Ph_2CH^+, cf. ref 65. [m] Sehon, A. H.; Szwarc, M. *Annu. Rev. Phys. Chem.* **1957**, *8*, 439. [n] Formation of cation is not established; however, Ph₂CH• was seen. [o] The value is from Bartmess et al., see footnote f. [p] Derived from the ΔG(solv) in H_2O given by Ritchie, C. D. *J. Am. Chem. Soc.* **1985**, *105*, 7313. [q] Lind, J.; Shen, X.; Eriksen, T. E.; Merenyi, G. *J. Am. Chem. Soc.* **1990**, *112*, 479. [r] Value obtained by using the maximum OD(C•) after completion of the "delayed rise" of radical. Energy per pulse = 30 mJ. [s] Value obtained by subtracting from the initial OD the OD that does not decay within 5 μs. [t] In the solvent CF_3CH_2OH. [u] The cation yield was measured in the presence of O_2 (in order to scavenge potential radical and triplet species that absorb at λ(cation)). The yield of cation has been corrected for cation decay occurring over the time period necessary for O_2 to scavenge the noncationic species. The radical yield was determined in the absence of O_2. [v] Radical formation is possibly biphotonic. [w] Average of the value given by Richardson, J. H.; Stephenson, L. M.; Brauman, J. T. *J. Chem. Phys.* **1975**, *62*, 1580, and that in footnote q.

of the excited singlet, S_1, of 99 kcal/mol (see Scheme I).

For the gas-phase *homolysis* of Ph_2CHCl a value of 64 kcal/mol is obtained from a thermochemical cycle based on $\Delta H°_{formation}(Ph_2CH^\bullet)$ = 69 kcal/mol,[59] $\Delta H°_{formation}(Cl^\bullet)$ = 29 kcal/mol,[60] and $\Delta H°_{formation}(Ph_2CHCl)$[61] = 32.7 kcal/mol. With EA(Cl•) = 3.61 eV,[62] and IP(Ph₂CH•) = 7.32 eV,[63] $\Delta H°$ for *heterolysis* is obtained as 150 kcal/mol. The corresponding (lower) values for the bromide are indicated below (see also Scheme I in section 6)

$$Ph_2CH-X \begin{cases} Ph_2CH^+ + X^- & \Delta H°_{het} (X = Cl) = 150 \text{ kcal/mol} \\ & \Delta H°_{het} (X = Br) = 142 \text{ kcal/mol} \\ Ph_2CH^\bullet + X^\bullet & \Delta H°_{hom} (X = Cl) = 64 \text{ kcal/mol} \\ & \Delta H°_{hom} (X = Br) = 51 \text{ kcal/mol} \end{cases}$$

The value $\Delta H°_{het}$ = 150 kcal/mol means that even after excitation with a 248-nm photon, which yields 115 kcal/mol, in the gas-phase heterolysis is not possible, in contrast to homolysis. So, if heterolysis is to occur, energy has to be gained, and solvation of the product ions is a possibility to achieve this.

In the following, the effect of solvation on the thermodynamics of bond cleavage of the Ph_2CHX system will be considered from two different points of view. For both cases, it is assumed—as usual—that the thermochemical data from the gas phase describe the situation in solution as well, as long as no ions are formed, i.e. for the case of homolysis. This is justified since the solvation energies of *noncharged* (odd and even electron) species are usually small.

In the first approach, the situation that results from complete mutual separation and solvation of the separate ions in AN is considered.[64] In this medium, which has an excellent solvating power for cations,[9a] a solvation enthalpy of 67 kcal/mol is estimated for Ph_2CH^+.[65a,b] The solvation energies of the anions were calculated with use of the free energies of hydration $\Delta G°(g \rightarrow H_2O)$[66] and of transfer $\Delta G°(H_2O \rightarrow AN)$[66] and the resulting values are collected in column 12 of Table V. If these values and that for Ph_2CH^+ (67 kcal/mol) are combined with the (gas phase) heats of heterolysis $\Delta H°_{het}$ (R-X), the (liquid phase) heats of heterolysis ΔG_{het}(solv) are obtained, as shown in column 13. The interesting result is that the values for *heterolysis* of ground-state Ph_2CH-X (X = F, Cl, Br) in acetonitrile are endothermic by only 7-17 kcal/mol, to be compared with as much as 51-64 kcal/mol for *homolysis* (for X = Br and Cl). Heterolysis is thus more favored than homolysis.

In the second approach, bond heterolysis is assumed to result in an ion *pair*, in the solvent CH_2Cl_2, and linear free energy relationships are employed to estimate heterolysis energies in solution.

The free energy $\Delta G°$ for ionization of trityl chloride in CH_2Cl_2 to give the ion pair has been determined to be +7.0 kcal/mol at 25 °C.[67]

$$Ph_3CCl \underset{}{\overset{CH_2Cl_2}{\rightleftharpoons}} Ph_3C^+Cl^- \qquad K = 7 \times 10^{-6}$$
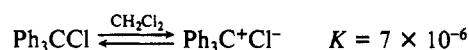
Since chloride affinities of carbenium ions have been shown to be proportional to OH⁻ affinities (as defined by pK_{R^+}),[68] the free

(59) Rossi, M. J.; M. Millen, D. F.; Golden, D. M. *J. Phys. Chem.* **1984**, *88*, 5031.

(60) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516.

(61) Result of force-field calculation using MMPMI, cf. Gajewski, J. J.; Gilbert, K. E. Molecular Mechanics Package (MS-DOS Computers), Serena Software: Bloomington, IN, 1989.

(62) See ref 60, or Golden, D. M.; Rodgers, A. S.; Benson, S. W. *J. Am. Chem. Soc.* **1966**, *88*, 3196.

(63) Harrison, A. G.; Lossing, F. P. *J. Am. Chem. Soc.* **1960**, *82*, 1052.

(64) In AN, free ions do exist, cf. Gschwind, R.; Haselbach, E. *Helv. Chim. Acta* **1979**, *62*, 947.

(65) (a) By use of the Born equation and taking ϵ(AN) = 35.94 and the ion radius r(Ph₂CH⁺) = r(Ph₂CH) = 245 pm (see: Exner, O. *Correlation Analysis of Chemical Data*; Plenum: New York, 1988, p 152. Charton, M. *J. Am. Chem. Soc.* **1975**, *97*, 1552). (b) A value of 46 kcal/mol is given for the solvation enthalpy in AN of radical cations of methylated benzenes by Kochi, J. K. *Angew. Chem.* **1988**, *100*, 1331.

(66) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985.

(67) Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, 1979; p 33.
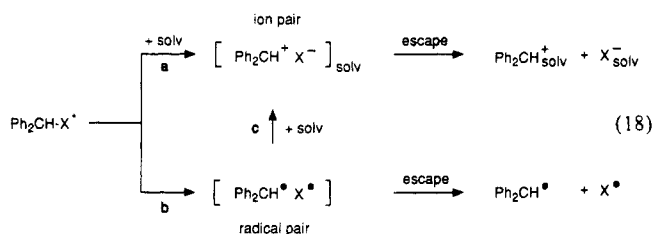
(68) Schade, C.; Mayr, H.; Arnett, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 567. Schade, C.; Mayr, H. *Tetrahedron* **1988**, *44*, 5761.

energy for ionization of compounds R–Cl can be described by eq 17[69]

$$R-Cl \xrightarrow{CH_2Cl_2} R^+Cl^- \quad \Delta G^°(\text{kcal/mol}) =$$
$$-1.79 \times pK_{R^+} - 4.86 \quad (17)$$
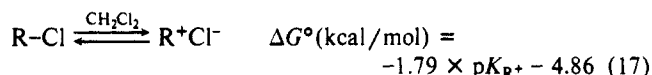
from which $\Delta G^°$(ionization) = +16.2 kcal/mol for Ph_2CHCl (pK_{R^+} = –11.7).[70] If $\Delta S^°$(ionization) is assumed to be of similar magnitude as that determined[71] for tritylchloride (–23.3 ± 1.9 cal/(Kmol)), $\Delta H^°_{het}(Ph_2CHCl)$ can be estimated to be +9.3 kcal/mol. This value, which refers to formation of an ion *pair* in CH_2Cl_2, indicates that with ground-state benzhydryl chloride in dichloromethane, the *heterolytic* cleavage of the C–Cl bond ($\Delta H^°_{het}$ = 9.3 kcal/mol) is *less* endothermic than the *homolytic* cleavage ($\Delta H^°_{hom}$ = 64 kcal/mol), a result which is qualitatively in agreement with the first approach ($\Delta G^°_{het}$ = 11 kcal/mol), which, however, relates to the more polar solvent AN in which the ions exist as free, solvated species.

4. Effects of Nucleofugal Leaving Group and of Solvent on Heterolysis/Homolysis. Concerning the family of the halogens X as anionic leaving groups, it is evident from Table V that the quantum yields for cation formation, $\Phi(C^+)$, and also the $[C^+]:[C^·]$ (= $[X^-]:[X^·]$) ratios correlate with the acidities (pK_a values and gas-phase enthalpies for deprotonation of the conjugate acids HX) and *not* with the electron affinities of the halogen atoms, $EA(X^·)$. The dependence of $[C^+]:[C^·]$, i.e. of heterolysis/homolysis, on the anionic leaving group properties of the halide (expressed by $pK_a(HX)$) and the lack of correlation with the EAs of $X^·$ suggests that the photophysical process leading to C^+ and X^- has the characteristics of a heterolysis (eq 18a). Homolysis followed by electron transfer in the resulting radical pair, eq 18b,c, would be

ion pair

$$Ph_2CH\text{-}X^· \longrightarrow \begin{cases} \xrightarrow{+solv}_{a} [\; Ph_2CH^+\; X^- \;]_{solv} \xrightarrow{escape} Ph_2CH^+_{solv} + X^-_{solv} \\ c \uparrow +solv \\ \xrightarrow{}_{b} [\; Ph_2CH^·\; X^· \;] \xrightarrow{escape} Ph_2CH^· + X^· \end{cases} \quad (18)$$

radical pair

an alternative if and only if *solvation* of the incipient ions was *concerted* with the electron transfer. In this case it would be the reduction potentials (which parallel the pK values of the halides) which determine the driving force of the electron transfer. On the basis of the results presented in section 3 and shown in Scheme I, electron transfer *without* ion solvation is thermodynamically strongly *uphill*, and it is therefore not surprising that the electron affinities, which of course do not take account of solvation, do not allow the heterolysis yields to be predicted. It is obvious that heterolysis (with ion solvation) and homolysis followed by electron transfer (with simultaneous ion solvation) cannot be distinguished on the basis of the data presented in Table V.

It is interesting that the quantum yields for radical formation are similar for all the halides (Φ = 0.21 ± 0.02).

As shown by a comparison of $CF_3CO_2^-$ with Br^- as anionic leaving groups, the pK_a values of the conjugate acids are of greater predictive value with respect to the cation/radical ratio than are the *gas-phase* deprotonation enthalpies, $\Delta H(H-X)$, which are essentially the same for the two systems, $\approx$323 kcal mol^{-1}. The fact that the liquid-phase parameter (pK_a) describes the dependence on leaving group of the cation yield better than does the gas-phase parameter (deprotonation enthalpy) may be taken as evidence for solvent assistance already in the very early stages of the C–X bond fragmentation. On the other hand, the pK_a value
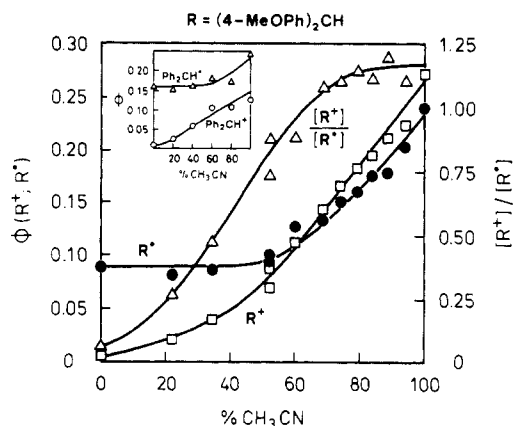

Figure 6. Dependence of the quantum yields for formation of cation and radical on the composition of the binary solvent mixture acetonitrile–dichloromethane. The main figure shows the dependence for $(MeOPh)_2CHCl$, the inset that for Ph_2CHCl.

is not *sufficient* for predicting the leaving group properties. An example is the couple fluoride as an anionic leaving group (pK_a(HF) = 3.16) and trifluoroacetate ($pK_a(CF_3CO_2H)$ = 0.52): Although HF is a considerably weaker acid than CF_3CO_2H, the $C^+:C^·$ ratio for the fluoride is twice that for the trifluoroacetate.

The leaving groups *p*-nitro- and *p*-cyanophenolate deserve special comment: they are the only aromatic nucleofuges and therefore able to absorb light at 248 nm. With these compounds, not only the electrofuge (the cation-to-be), but also the nucleofuge (the anion-to-be) can absorb a photon, in contrast to the case of the aliphatic or inorganic leaving groups. This additional pathway for excitation is probably the reason why *p*-cyanophenolate is a much better anionic leaving group than would be expected on the basis of its pK value. By the same token, *p*-nitrophenolate should be an even better nucleofuge; however, there is *no* evidence for cation formation in this case. This can be explained by the well-known[72] tendency of nitroaromatics to intersystem cross to T_1 efficiently and the assumption of a very low rate of heterolysis from T_1.

The phenolates are additional examples to show that electron affinity is not a good indicator for anionic leaving group behavior: The EAs of $Br^·$ and 4-$NCPhO^·$ are very similar (3.36 and 3.33 eV, respectively), but the cation yields are quite different. This is even more so for the couple $Cl^·$ and 4-$O_2NPhO^·$ (3.61 and 3.55 eV).

In Figure 6 it is shown that the quantum yields for cation and radical production from $(MeOPh)_2CHCl$ in acetonitrile–dichloromethane mixtures increase strongly with increasing CH_3CN content, demonstrating that both heterolysis and homolysis profit from the increase in the polarity of the medium.[73] Similar, but less pronounced effects were seen with Ph_2CHCl (see inset in Figure 6) and with $(ClPh)_2CHCl$. In a qualitative way, the same phenomenon was also observed in going to other low-polarity solvents, such as cyclohexane or tetrahydrofuran.[74]

To summarize, it appears that there does not exist a single parameter that describes the heterolysis:homolysis ratio as a function of the anionic leaving group. On the whole, *solution*-phase parameters such as pK_a seem to be of greater predictive value than *gas*-phase values such as EA. A complication is that, as shown in section 5, homolysis, as well as heterolysis, can proceed not only from the singlet but also from the triplet excited state, and for its decay the cation:radical ratio may be different from

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(69) Correlation of $\Delta\Delta G^°(Ar_2CH^+ + Ar'_2CHCl \rightleftharpoons Ar_2CHCl + Ar'_2CH^+)$ from ref 68 with Mindl's pK_{R^+} values[70] yields the slope of 1.79 kcal mol^{-1}. From $\Delta G^°$(ionization of Ph_3CCl) = +7.0 kcal mol^{-1}, an intercept of –4.86 was obtained.

(70) pK_{R^+} value taken from Mindl, J.; Vecera, M. *Collect. Czech. Chem. Commun.* **1971**, *36*, 3621.

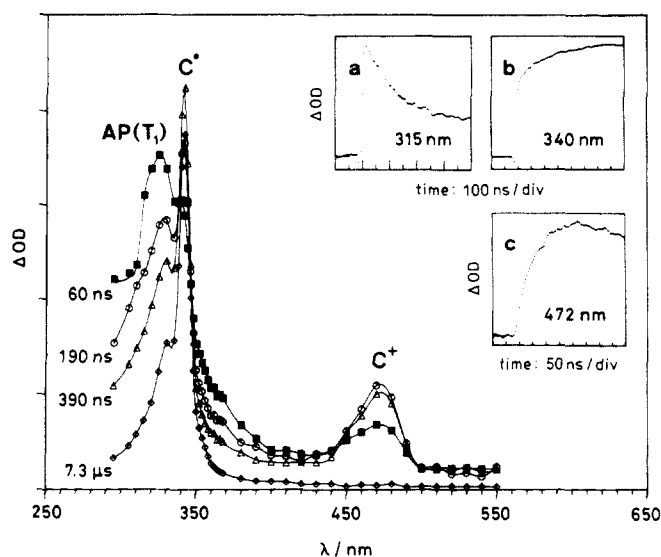(71) Heublein, G.; Bauerfeind, D. *J. Prakt. Chem.* **1984**, *326*, 81.

(72) Morrison, H. A. In *The Chemistry of the Nitro and Nitroso Group*; Feuer, H., Ed.; Wiley: New York, 1969, Chapter 4. Döpp, D. *Top. Curr. Chem.* **1975**, *55*, 49.

(73) However, the situation is more complicated: It was found that the fluorescence intensity (λ_{max} = 313 nm) of $(MeOPh)_2CHCl$ in CH_2Cl_2 is only 33% of that in acetonitrile. This suggests that the excited singlet state is quenched by CH_2Cl_2, giving it less chance to relax by bond cleavage. It would obviously be interesting to know the lifetimes of the singlet in the two solvents.

(74) In the case of THF, the low cation yield observed is at least in part due to scavenging by the solvent, see ref 27.

Characterization of Diphenylmethyl Cations and Radicals

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Figure 7. Absorption spectra observed on excitation of acetophenone (21 mM, OD/cm = 1.1) with a 308-nm laser pulse in the presence of 52 mM bis(4-chlorophenyl)methyl chloride (OD/cm ≤ 0.05). Key is as follows: ■, 60 ns; O, 190 ns, Δ, 390 ns; ◇, 7.3 μs after pulse. Insets are as follows: (a) decay of the acetophenone triplet at 315 nm, (b) buildup of the radical at 340 nm, (c) buildup of the cation at 472 nm.

that for bond fragmentation from the excited singlet. Therefore, a full understanding of the effect of X on the heterolysis:homolysis ratio requires the knowledge of the nature of the electronically excited state from which the bond fragmentation occurs and of the rates of all the relevant processes. However, at present most of these data are not known.

5. Sensitized Bond Cleavage. Phosphorescence experiments were performed at 77 K in 2-methyltetrahydrofuran glass with 270-nm light for excitation of deoxygenated samples containing Ph_2CHCl, $(MeOPh)_2CHCl$, or $(ClPh)_2CHCl$ (OD/cm ≈ 0.4). In each case broad emission bands (half-band widths 100 nm) were observed with λ_{max} = 450 ± 10 nm which are assigned to the triplets of the benzhydryl chlorides. The λ_{max} values correspond to triplet energies of 64 ± 1.5 kcal/mol. The lifetime of the triplets at 77 K was measured to be ≈0.5 ms.

In order to test whether the triplet state is able to undergo C–X homolysis and/or heterolysis, it is necessary to produce the triplet *without* producing the singlet excited state. This is possible by selective excitation of the chlorides into their triplet states by triplet energy transfer from, e.g., acetophenone (AP). This ketone has a triplet energy of 74.1 kcal/mol,[75] compared to 64 kcal/mol for the chlorides. Thus, energy transfer is exothermic by 10 kcal/mol, a value sufficient to expect rate constants approaching the diffusion limit.[75,76]

Experiments were performed by photolyzing solutions containing AP at 308 nm (emission from XeCl*), and AP concentrations such that at 308 nm OD(AP) ≥ 10 × OD(benzhydryl chlorides).[77] Since at 308 nm the extinction coefficients of the chlorides are low, AP can be selectively excited even in the presence of large concentrations of aromatic chloride.[78] In Figure 7 are shown results from an experiment involving triplet transfer to $(ClPh)_2CHCl$. From the spectrum recorded at 60 ns after the pulse the acetophenone triplet $(AP(T_1))$ is recognizable (at 315–325 nm), and there is a band at 472 nm which is that of the cation $(ClPh)_2CH^+$. At 190 ns the cation band has *increased*, whereas the triplet band is *decreased*, and there has developed a band at 340 nm, which is due to the radical $(ClPh)_2CH^•$. The

insets show the decay of triplet (a) and the synchronous[79] formation of radical (b) and of cation (c). The rate of radical buildup was found to be proportional to the concentration of $(ClPh)_2CHCl$, giving a k_q value of 1 × 10⁹ M⁻¹ s⁻¹.

The quantum yields for the AP-sensitized production of radical and cation were determined by comparing the OD values due to $AP(T_1)$ immediately after the pulse with those of $(ClPh)_2CH^•$ and of $(ClPh)_2CH^+$ after completion of the energy transfer reaction.[80] Taking the quantum yield for $AP(T_1)$ formation as 1, its $\epsilon(320$ nm) = 12600 M⁻¹ cm⁻¹,[81] and the ϵ values for the radical and the cation from Table I, the quantum yields for the sensitized radical and cation formation were found to be 0.24 and 0.05, practically the same as those for the direct, 248-nm photolysis (see Table I).

Also with the other systems such as $(MeOPh_2)$-, $(MeOPh)Ph$-, $(MePh)_2$-, $(MePh)Ph$-, and Ph_2-CHCl, sensitized radical and cation production was observed. In some of these systems, such as, e.g., $(MePh)_2CHCl$, the radical band is overlapped strongly by the $AP(T_1)$ band, so that a buildup at λ_{max}(radical) cannot be seen, in contrast to the case of the cation. However, after disappearance of $AP(T_1)$, a clean radical spectrum, undistorted by other species, was observed. Analysis of the OD at the appropriate wavelengths gave quantum yields for sensitized radical and cation formation for $(MePh)_2CHCl$ of 0.1 and 0.06, respectively, values that are considerably smaller than those for the 248-nm direct photolysis (see Table I). In the case of $(MeOPh)_2CHCl$, the quantum yield for sensitized *radical* formation was measured to be 0.24, the same as that for the "direct" 248-nm photolysis. The yield for sensitized *cation* formation, however, is only 0.15, about half of that for 248 nm excitation. This type of complicated dependence on substituent of the pattern of heterolysis/homolysis from singlet or triplet makes it difficult to compare the excited-state chemistry of these compounds with their ground-state[48] solvolytic behavior.

6. Comments on the Mechanism of the Photochemical C–X Bond Rupture. As seen from the examples given above, the substituents appear to influence not only the rates of homolysis and heterolysis from S_1, but also the rates of intersystem crossing (ISC) $S_1 \rightarrow T_1$, those for homolysis and heterolysis from T_1, and probably the internal conversion and emission rates. In the case of $(ClPh)_2CHCl$, the quantum yields for homolytic and heterolytic bond cleavage were found to be the same for the direct and for the sensitized case. It is tempting to interpret this situation in terms of faster $S_1 \rightarrow T_1$ intersystem crossing than homo- or heterolytic bond rupture from S_1, this then being followed by bond rupture from T_1. This could be due to promotion of ISC by the "heavy" atom effect of the chlorines. In contrast, with $(MePh)_2CHCl$, the quantum yields of homolysis and heterolysis are much lower for the sensitized than for the direct photolysis, suggesting that in this case the $S_1 \rightarrow T_1$ rate is smaller than those for homolysis and heterolysis from S_1.

It is very interesting that triplet sensitization of bond *heterolysis* does *at all* occur. If it is assumed that both the heterolysis products, the cation and the anion, are in the singlet ground states, their direct formation from triplet is spin forbidden. In agreement with this view, photoheterolysis of *tri*phenylmethyl–X (X = anionic leaving group) could not be sensitized by triplets.[12] On the other hand, with corresponding *benzyl* systems, triplet-sensitizer-induced photoheterolysis has been frequently observed.[14,17] The occurrence of heterolysis on interaction with triplet sensitizers has found various explanations, e.g., Schuster[17] and Arnold[21a] suggested an exciplex between sensitizer and substrate, Cristol[82] proposed a vibrationally excited ground state, and McKenna[83] advanced the

(75) Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 301.

(76) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232. Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966; p 348.

(77) Blank experiments (no acetophenone present) were run to determine the amount of directly formed radical and cation. The values for the sensitized formation of radical and cation have been corrected for the contribution due to direct production.

(78) This is *not* possible with Ph_2CHBr, whose $\epsilon(308$ nm) ≈ 145 M⁻¹ cm⁻¹.

(79) The buildup of cation looks as if it is faster than that of the radical. This appearance is caused by decay of cation (by reaction with solvent, eq 8a) being almost as fast as its formation (by triplet energy transfer).

(80) The OD(cation) at 472 nm was corrected to take account of the first-order decay according to eq 8a.

(81) Lutz, H.; Breheret, E.; Lindquist, L. *J. Phys. Chem.* **1973**, *77*, 1758.

(82) Cristol, S. J.; Schloemer, G. C. *J. Am. Chem. Soc.* **1972**, *94*, 5916. Cristol, S. J.; Bindel, T. H. *J. Org. Chem.* **1980**, 951; *J. Am. Chem. Soc.* **1981**, *103*, 7287.

Scheme I[a]

Ph₂CHCl in CH₃CN
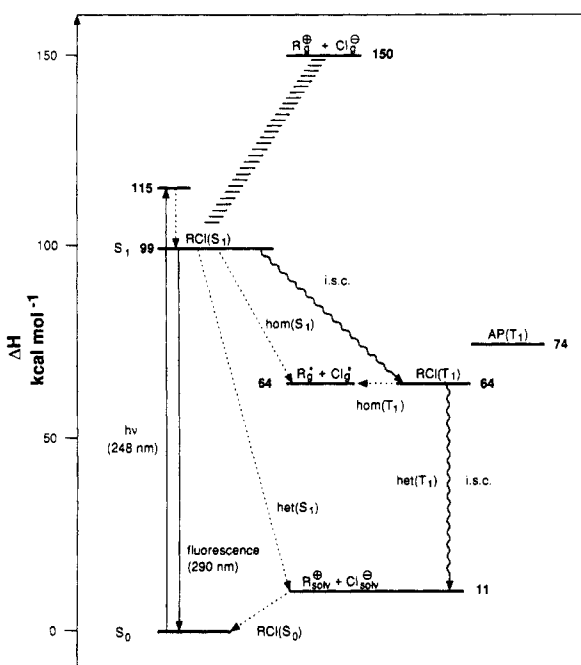
[a] AP = acetophenone.

hypothesis that both singlet and triplet excited states undergo exclusive homolysis, followed by intersystem crossing and electron transfer in the radical pair (eq 18b → 18c).[84] As pointed out in section 4, electron transfer requires solvation of the ions in order to be thermodynamically possible.[85]

Also the anionic leaving group X is expected to have an influence on the ISC rates, the internal conversion rates, the emission rates, and, of course, on the homolysis and heterolysis rates from S_1 and T_1. For example, in the series X = F, Cl, and Br the S_1 → T_1 rate will increase, due to the heavy-atom effect. If it is assumed that with the triplet state, heterolysis is less favored than homolysis, the [cation]:[radical] ratio is expected to *decrease* in going from F to Br. Since the opposite is observed, the better anionic leaving group properties of Br⁻ as compared to F⁻ (see Table V) overrule the "leveling effect" resulting from presumably higher S_1 → T_1 ISC rates for the bromide.

Concerning the solvent, it can obviously influence the rates of all the possible transitions and transformations of the electronically excited and of the ground states of the system,[86] the most relevant of which are indicated in Scheme I which summarizes the observations presented with benzhydryl chloride as a model.

Even on excitation with a 248-nm photon, *without ion solvation*, C–Cl heterolysis is not possible since it is at least 35 kcal/mol endothermic. The degree to which in practice heterolysis occurs as compared to homolysis depends therefore on the extent of solvation of the incipient ions in the bond fragmentation process. Solvation of ions requires a reorientation of the solvent molecules (time domain picosecond).[87] If this process is slower than bond

fission, the bond will break homolytically. If, however, solvation occurs on the same time scale as bond fragmentation, heterolysis is possible and it is *likely* to occur since the energy of the transition state of heterolysis is lowered considerably by solvation of the ions. Bond fragmentation is the result of conversion of electronic excitation energy into vibrational energy, and the time scale of (re)distribution of vibrational energy in molecules of the size of diphenylmethane derivatives is in the picosecond domain and similar to that for intermolecular transfer of vibrational excess energy to solvent molecules.[88] The fact that in acetonitrile in all cases heterolysis is observed along with homolysis means that in this solvent ion solvation is concerted with bond scission. In contrast, in cyclohexane ion solvation is unefficient and heterolysis therefore cannot compete with homolysis. In borderline cases such as, e.g., CH_2Cl_2, ion formation may occur, but only to give ion *pairs*[89] with typical lifetimes <1 ns[87] which means they cannot be observed with the present apparatus since they decay within the 20-ns pulse.

7. Summary and Conclusions. It has been shown that photolysis of substituted benzhydryl halides, acetates, and ethers yields the corresponding benzhydryl radicals and cations. The (homolytic and heterolytic) bond fragmentations proceed from the triplet or singlet excited states. Substituents on the benzhydryl system and anionic leaving groups appear to influence the heterolysis–homolysis yields by their effects on the rates of intersystem crossing, hetero- and homolysis and probably emission and internal conversion. The same is probably true for the solvent. In acetonitrile and apparently also in CH_2Cl_2 heterolysis is thermodynamically more favored than homolysis, which is the result of the large solvation energies of the ions. Heterolysis must be a solvent-assisted process, since heterolysis *without* ion solvation is uphill even with 115 kcal/mol of excitation energy provided. The extent to which the transition state for bond cleavage profits from solvation of the incipient ions is suggested to depend on the relative rates of solvent reorientation and of bond breaking.

(83) Appleton, D. C.; Bull, D. C.; Givens, R. S.; Lillis, V.; McKenna, J.; McKenna, J. M.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Perkin Trans 2* **1980**, 77. Appleton, D. C.; Brocklehurst, B.; McKenna, J.; McKenna, J. M.; Thackeray, S.; Walley, A. R. *Ibid.*, 80. Lillis, V.; McKenna, J.; McKenna, J. M.; Smith, M. J.; Taylor, P. S.; Williams, I. H. *Ibid.*, 83.

(84) A homolysis–electron transfer mechanism has recently also been suggested for the photolysis of 1-naphthylmethyl esters, cf. ref 21d.

(85) For the related *tri*arylmethanes in AN, Manring and Peters[18] suggested photo-*heterolysis* followed by electron transfer, eq 18a, reverse c, in order to explain the dependence on anionic leaving group of the cation–radical yields. However, in analogy to the *diaryl* systems, such a process is expected to be thermodynamically *uphill*, since it requires desolvation of the ions.

(86) Solvent effects similar to those described for the benzhydryl systems have been observed for the photodissociation of triarylmethanes, see ref 18. See also refs 24 and 25.

(87) Simon, J. D.; Peters, K. S. *Acc. Chem. Res.* **1984**, *17*, 277. Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 1441. Masnovi, J. M.; Kochi, J. K. *Ibid.*, 7880.

(88) Seilmeier, A.; Kaiser, W. In *Ultrashort Laser Pulses*; Kaiser, W., Ed.; Springer: Berlin, 1988; p 294.

(89) An exception is the stabilized (MeOPh)₂CH⁺, see Figure 6.