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Photoenolization with α-Chloro Substituents

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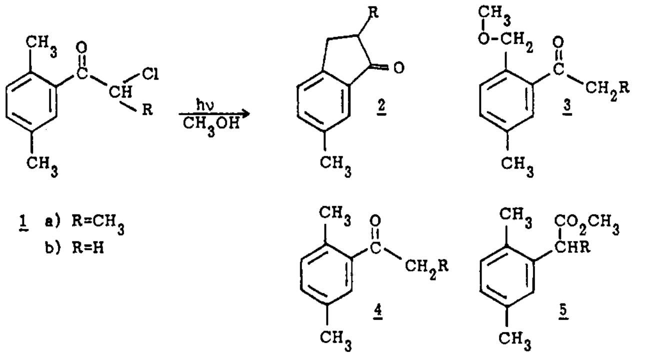
Irradiation of a methanol solution of 2,5-dimethyl-α-chloropropiophenone (**1a**) produces 2,6-dimethyl-1-indanone (**2a**), 2-(methoxymethyl)-5-methylpropiophenone (**3a**), 2,5-dimethylpropiophenone (**4a**), and methyl 2-(2,5-dimethylphenyl)propionate (**5a**). It is proposed that the first two products arise from hydrogen abstraction followed by chlorine loss, the latter two from initial loss of chlorine. Making the chlorine-bearing carbon primary suppresses the formation of the latter two products, while maintaining the carbonyl nearly planar with the ring suppresses all product formation. Other examples are presented.

Aryl ketones with *o*-alkyl groups are known to undergo a highly efficient photoinduced enolization. The resulting photoenol normally undergoes a rapid reketonization such that no net chemical change occurs. It has been long recognized that if this reketonization could be diverted, these reactions could be very useful and interesting.[1] With this thought in mind we attached a chloro group to the α-carbon and observed efficient chloride displacement and cyclization derived from the resultant photoenols as noted in Scheme I. In previous studies photoenols have also been diverted by way of elimination[3] reactions as well as trapped by dienophiles.[1] All of this chemistry has been reasonably attributed to ground-state chemistry derived from the photogenerated enols. In contrast it has also been demonstrated that chlorine atoms are eliminated from the 1,4-biradical intermediate of the type II reaction of δ-chlorovalerophenone.[4,5] This raises the issue of whether the Cl is lost as chloride from the photoenols or as a chlorine atom from the excited-state precursor. In the latter case a subsequent electron-transfer step would provide ions to account for products that are apparently ion derived.

Another major issue deals with the stereochemistry of the photoenolization process. Both *E* and *Z* isomers (Scheme II) are generated in the process,[1,6] and as a further complication restricted rotation in the excited state adds additional intermediates to sort out.[6] This has led to much confusion and controversy especially to structural assignments of flash photolysis transients.[7-9] This seems to be reasonably well understood now with the general conclusion that the *Z* photoenols (with the H near the site of its original abstraction) undergo extremely fast reversion so that other processes cannot compete. The *E* isomers, on the other hand, are much longer lived and serve as the source of other chemistry.

Scheme I



Scheme II. Mechanism Where H Abstraction Is First Step, Cl May Be Lost from Enol b or Biradical (Excited State) c

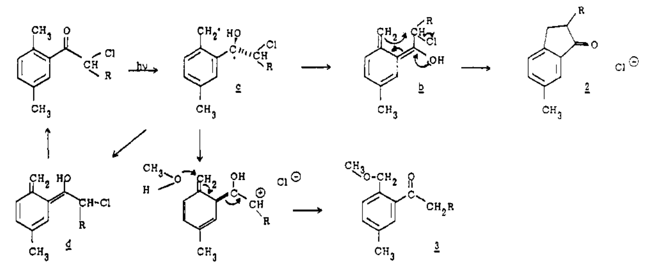
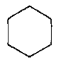


Table I. Chemical and Quantum Yields of Various Photoproducts

solvent	Φ	product distribn 2	3	4	5
		For 1a			
CH_3OH	0.42	42	28	4	24
t-BuOH	0.39	81		6	
	0.11	87		6	
		For 1b			
CH_3OH	0.76	39	57		
C_6H_6	0.11	62			

With the inclusion of a chloro group the possibility of photofragmentation and/or photosolvolysis presented itself. Indeed this competed with photoenolization in some cases as illustrated in Scheme I. In general, alkyl halides produce radical, carbocation, and carbene intermediates on photolysis. There has been much recent experimental work and discussion about how mechanistically all this comes about.[10-15] One favored view is that the initial step is bond homolysis followed by, in some cases, an electron-transfer step involving the radical pair to produce ionic intermediates.[10] The distinction between this and

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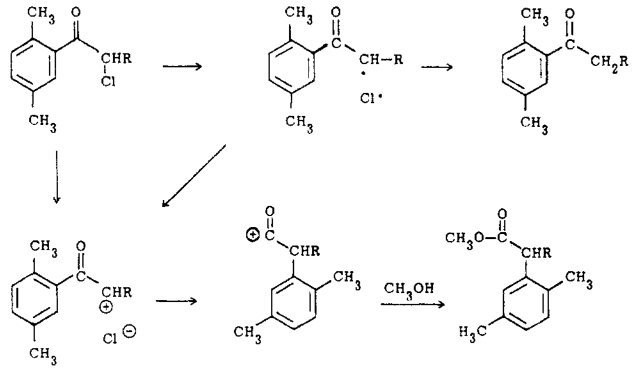
Scheme III. Mechanism Where Cl Leaves before H Abstraction. Both Radical and Ionic Products Observed



a mix of both homolytic and heterolytic cleavage is difficult to make either experimentally or theoretically. At any rate we have observed radical behavior in the form of hydrogen abstraction (e.g., product 4) and cationic in the form of rearranged products (e.g., product 5). An early report[17] of this rearrangement involved phenacyl halides (without *o*-methyl groups). If the aromatic ring had electron-donating groups, rearrangement was observed, otherwise not. Radical-like hydrogen abstraction from solvent was generally observed, and the results were interpreted as being radical derived. Later four-ring chloro ketones were found to undergo an efficient ring-contraction rearrangement termed a "photo-Favorskii" rearrangement.[18] The result was not a general one, however, in that other ring sizes do not produce this cationic rearrangement.[19]

Results

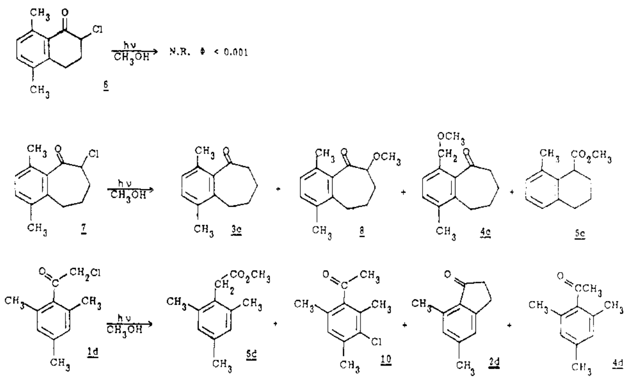
When irradiated in methanol, 2,5-dimethyl-α-chloropropiophenone (**1a**) produces products **2a**–**5a** as indicated in Scheme I. When the bulky *tert*-butyl alcohol is used as a solvent, the products incorporating the solvent (**3** and **5**) are no longer observed, just as when cyclohexane is used. When the chloro position is changed from secondary to primary as in **1b** the products **4** and **5** are no longer observed. These results are summarized in Table I. When the chloro ketone function is incorporated into a six-membered ring as in **6** the structure is photostable. When the ring size is increased to seven (**7**), photochemical reactivity is restored with the formation of **3c**, **4c**, and **5c** and one new product, **8**, a result of chloride displacement. When two *o*-methyl groups are present as in **1d**, the observed products are **2d**, **4d**, and **5d** along with a ring-chlorinated product, **10**. When Cl is changed to Br, only **3a** is observed as a product. When the *o*-methyl group is moved to the para position, **4e** and **5e** are observed.

The reactions of **1a** and **1b** are weakly quenched by dienes (2,5-dimethyl-2,4-hexadiene and 1,3-cyclohexadiene), and linear, single-line Stern–Volmer plots are produced which gave k_qt = 7.4 for **1a** in CH_3OH and 1.02 for **1b** in CH_3OH and ~0.1 for **1b** in benzene.

Discussion

The behavior of *o*-methyl α-chloro ketones can be interpreted as a mix of two efficient primary photoprocesses: hydrogen abstraction by the n,π* excited carbonyl (photoenolization) and ejection of chlorine either as an atom or as an anion (photolytic cleavage). Schemes II and III illustrate these features in detail.

Scheme IV



Hydrogen-Abstraction Step. It is apparent from the small value (1.0) of k_qt compared with the value of 1.0 for *o*-methylacetophenone itself that H abstraction is occurring at an essentially undiminished rate and that chlorine does not play a role until after the *o*-hydrogen is abstracted. The linear Stern–Volmer plots indicate that, in contrast to *o*-methylacetophenone,[6] there is no relatively long-lived triplet (that is a *Z* or anti photoenol, b in Scheme II). The implication here is either that the anti photoenol is also short-lived or that syn–anti rotation is rapid (or that the anti isomer is photochemically unreactive, an unlikely possibility). At the photoenol stage the presence of the chlorine serves to very effectively divert the normal course of photoenolization, i.e. reversion to the starting ketone. In the present case the indanone, **2**, must arise either from cyclization of the ground-state *anti*-dienol (b) or the departure of chloride from the biradical (triplet state of c) precursor and cyclization of the resulting cation. Similarly the methoxy structure **3** can arise by a S_N1 displacement of a photoenol or, again, an earlier departure resulting in a cation that partitions between cyclization and capture by solvent.

Chloride-Ejection Step. When the chlorine is attached to a secondary site when a methyl group is added (**1a**), dramatic changes take place. Two new products appear (**4**, **5**) that are characteristic of radical and carbocation intermediates, respectively. The product **4** is characteristic of the generation of an acyl radical that then abstracts hydrogen from the medium. The ester, **5**, is a result of a Favorskii-type rearrangement and apparent ionic process. This kind of photochemical process has been observed in a few other cases.[17,18]

In the present case the lifetime of the excited state is substantially enhanced; relative to **1a**, the k_qt of the Stern–Volmer plot increased to 7.4 from 1.0 (in CH_3OH). Apparently conformational and electronic effects served to enhance the interaction between the carbonyl group and the C–Cl bond, producing a degree of stabilization.[18] The n,π* carbonyl group is less reactive toward H abstraction. The reduction of carbonyl reactivity is associated with the incidence of C–Cl reactivity. Converting the Stern–Volmer data into rate constants, one has for **1a** a rate constant for hydrogen abstraction of $5 \times 10^9\ s^{-1}$ (assuming k_q to be $5 \times 10^9\ M^{-1}\ s^{-1}$). For **1b** the $k_H = 4.9 \times 10^8$, a 10-fold reduction with the rate of chlorine loss determined to be $1.9 \times 10^8\ s^{-1}$.[21]

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(21) α-Methoxy-2,5-dimethylacetophenone (**8**) was prepared by Friedel–Crafts addition of methoxyacetyl chloride to *p*-xylene. On photolysis it produced only the acetophenone (in high quantum efficiency, 0.6) and none of the other observed photoproducts of **1**. Prolonged treatment of **1** with methanol (in the dark, under a variety of conditions) failed to produce **8**.

Incorporating the Carbonyl in a Ring. Results with the six- and seven-membered ring analogues are revealing with regard to the question of when the chloride leaves after hydrogen abstraction; the possibilities include the syn and anti dienols (d and b) or the common excited state (the diradical c, Scheme II). The six-membered ring ketone, **6**, has a rigid geometry that maintains the carbonyl and the ring near-planar in configuration. The result is that only the syn configuration d is achievable and that both forward *and* reverse hydrogen transfer are so rapid that none of the other rapid processes can compete. In contrast the seven-membered ring (**7**) has a twisted configuration. The syn dienol is strained and the anti is unachievable. The fact that this compound undergoes hydrogen abstraction followed by chloride loss indicates that a planar ground-state anti dienol isomer is not necessary for product formation. That the syn isomer does not lead to product formation suggests that chlorine is lost from the common excited-state precursor of these isomers, the twisted biradical structure c. This biradical (excited state) is probably quite similar to the well-known 1,4-biradical intermediate of the type II process. When a chlorine substituent is incorporated into that structure, as in the case of δ-chlorovalerophenone, chlorine loss resulting in elimination is known to occur. The rate of chlorine atom ejection is estimated[4] to be $1.7 \times 10^6\ \mathrm{s}^{-1}$. Our failure to observe elimination products (for **1b**, for example) leads us to believe that, to the extent that radicals are involved in the present photochemistry, they eventually become ions.[22]

It seems clear that the C–Cl bond breaking is the first step for the rearrangement reaction. When the methyl groups on the ring are not present, the hydrogen abstraction and rearrangement occur in an entirely similar way. Thus, α-chloropropiophenone produced 41% of rearrangement product **5e** and 27% of hydrogen-abstraction product propiophenone. The ratio of rearrangement/abstraction is lower, probably reflecting the enhancement of rearrangement afforded by the two ring methyl groups. In an attempt to determine whether the product ratio was a sensitive function of solvent polarity, the reaction was carried out with varying amounts of water as cosolvent. Up to 20 mol % water could be included with no detectable change in product ratio. A similar result was obtained by adding up to 50% cyclohexane.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 337 or 237 infrared spectrophotometer. NMR spectra were recorded on a Varian T-60 spectrometer or a Bruker 300 MHz instrument at Cornell University. Mass spectra were recorded on a Cary 14 spectrophotometer. Gas chromatography was performed on a Perkin-Elmer 900 or Varian 1700 gas chromatograph using a 6-ft 3% SE30 or 12-ft 10% SE30 column unless otherwise specified. Photochemical reactions were performed on a Rayonet photochemical reactor equipped with 3000 or 3500 RUL lamps. Quantum yield data were obtained with a merry-go-round device. Preparative photolyses were carried out with a medium-pressure mercury lamp (Hanovia).

2,5-Dimethyl-α-chloroacetophenone (1b). Under nitrogen atmosphere, $AlCl_3$ (1.1 equiv, 41.2 g 0.308 mol) was slowly added to a solution of *p*-xylene (excess, 80 mL) and chloroacetyl chloride (21.2 mL, 0.28 mol) and the resultant mixture stirred at 0 °C. The reaction mixture was allowed to warm to room temperature and then poured over 500 mL of crushed ice containing 8 mL of concentrated HCl. The mixture was then extracted twice with 75-mL portions of petroleum ether, the resulting organic layer twice with 75 mL portions of H_2O. The organic layer was dried ($MgSO_4$), evaporated, and distilled at 142–143 °C (18 mm): NMR (CCl_4) δ 2.4 (3 H, s), 2.5 (3 H, s), 4.5 (2 H, s), 7.3 (3 H, m); IR (film). Anal. Calcd for $C_{10}H_{11}ClO$: C, 65.76; H, 6.07. Found: C, 65.68; H, 6.17.

Other α-chloro phenones were synthesized similarly. 2,5-Dimethyl-α-chloropropiophenone (**1b**) was prepared in 72% yield with the following spectral data: IR (neat) 1715, 875, 835, 775 cm^{-1}; ^1H NMR (CCl_4) δ 2.4 (6 H, d), 5.1 (1 H, q), 1.65 (3 H, d), 7.3 (3 H, d). Anal. Calcd for $C_{11}H_{13}ClO$: C, 67.17; H, 6.66. Found: C, 67.22; H, 6.74.

Irradiation of 2,5-Dimethyl-α-chloroacetophenone in CH_3OH. A solution of 2.0 g (11.0 mmol) in 0.6 L of CH_3OH was irradiated 12 h by a Pyrex-filtered Hanovia lamp. Evaporation of methanol followed by preparative GLC (column A, 210 °C) afforded four fractions identified as follows. For **2b**, 6-methyl-1-indanone: mp 60–61 °C (lit.[24] mp 63 °C); NMR (CCl_4) δ 2.37 (3 H, s), 3.00 and 2.55 (2 H and 2 H, A_2B_2 pattern nearly identical with that of authentic 1-indanone), 7.40 (3 H, m); IR (CCl_4). For 2-(methoxymethyl)-5-methylacetophenone: NMR ($CDCl_3$) δ 2.38 (3 H, s), 2.53 (3 H, s), 3.38 (3 H, s), 4.67 (2 H, s), 7.40 (3 H, m). In CD_3OD with a trace of base the singlet at δ 2.53 disappears, a fact that distinguishes this structure from the isomer α-methoxy-*o*-methylacetophenone. IR (CCl_4) 1705 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.98; H, 8.01.

Irradiation of 1a. A 1.0-g sample of **1a** was dissolved in 600 mL of methanol and irradiated with a medium-pressure Hanovia lamp with Pyrex filtering. After 16-h irradiation the solvent was evaporated and the residue analyzed by GLC. Four products were identified as follows.

Compound **2a**: IR (CCl_4) 2960, 1720, 1622, 1497, 1448, 1375, 1330, 1283, 1249, 1160, 1121, 1045, 975, 900, 855 cm^{-1}; ^1H NMR (CCl_4) δ 7.35 (3 H, d), 2.4 (3 H, s), 1.2 (3 H, d), 3.3 (1 H, q), 2.7 (2 H, d); mass spectrum, *m/e* 160 (M^+), 132, 144, 116, 91. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.61; H, 7.58.

Compound **3a**: IR (CCl_4) 2950, 1785, 1700, 1620, 1575, 1500, 1460, 1380, 1350, 1285, 1250, 1198, 1175, 1110, 1010, 980, 875, 838 cm^{-1}; ^1H NMR (CCl_4) δ 7.3 (3 H, m), 2.4 (3 H, s), 1.2 (3 H, t), 2.8 (2 H, m), 3.3 (3 H, s), 4.6 (2 H, s); mass spectrum, *m/e* 192 (M^+), 177, 163, 159. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.37. Found: C, 74.90; H, 8.55.

Compound **5a**: IR (CCl_4) 2960, 1740, 1500, 1460, 1433, 1375, 1332, 1199, 1173, 1080, 863, 850 cm^{-1}; ^1H NMR (CCl_4) δ 7.0 (3 H, d), 2.3 (6 H, s), 1.4 (3 H, d), 3.6 (3 H, s), 3.9 (1 H, q); mass spectrum, *m/e* 133, 105. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.71; H, 8.29.

A similar procedure was used for the irradiation of **1d**. The spectral properties of the various products follow along with the percent yield (determined by GC) are as follows:

1d, starting material: NMR ($CDCl_3$) δ 6.76 (2 H, s), 4.22 (2 H, s), 2.27 (3 H, s), 2.17 (6 H, s); IR (CCl_4) 1710. Anal. Calcd for $C_{11}H_{13}ClO$: C, 67.17; H, 6.66. Found: C, 67.14; H, 6.56.

2d: 16% yield; NMR ($CDCl_3$) δ 6.93 (1 H, s) 6.79 (1 H, s), 2.97 (2 H trip, J = 2 Hz), 2.50 (2 H trip, J = 2 Hz), 2.49 (3 H, s), 2.33 (3 H, s); IR (CCl_4) 1715 cm^{-1}. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.41; H, 7.51.

5d: 18% yield; NMR ($CDCl_3$) δ 6.94 (2 H, s), 3.82 (3 H, s), 3.73 (2 H, s), 2.47 (6 H, s), 2.43 (3 H, s); IR (CCl_4) 1712 cm^{-1}. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.80; H, 8.33.

4d: 12% yield; NMR ($CDCl_3$) δ 6.51 (2 H, s), 2.31 (3 H, s), 2.21 (3 H, s), 2.14 (6 H, s); IR (CCl_4) 1705 cm^{-1}.

6,9-Dimethylbenzsuberone (3a) was prepared by the method of Kadesch.[23]

2-Chloro-6,9-dimethylbenzsuberone was prepared by refluxing **3c** (229 mg, 1.2 mmol) and *tert*-butyl hypochlorite (213 mg, 1.9 mmol) in 7.5 mL of CCl_4 with a trace of *p*-toluenesulfonic acid. The reaction is monitored by NMR, and maximum yield is achieved after 30-min reflux. The resulting solution was extracted with saturated aqueous $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated. The resulting pale yellow liquid was demonstrated to be nearly pure **7** by NMR. The liquid was evaporatively distilled at 190 °C in a Kugelrohr apparatus, 240 mg obtained

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[22] An indication that a radical course (not involving an electron-transfer step) for the reaction is not operative comes from results with α-(phenylthio)-2,5-dimethylacetophenone. The only observed products are the acetophenone, **4b**, and diphenyl disulfide. Data from Wagner's studies of elimination with 1,4-biradicals indicate that there is a strong preference for loss of phenylthio radicals.[4]

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(90%): NMR (CCl_4) δ 7.00 (2 H, AB pattern, J = 7 Hz), 4.41 (1 H, triplet, J = 7 Hz), 2.62 (2 H, m), 2.35 (3 H, s), 2.30 (3 H, s), 1.67 (4 H, m); IR (film) 1695 cm^{-1}. Anal. Calcd for $C_{13}H_{15}ClO$: C, 70.11; H, 6.79. Found: C, 70.02; H, 6.87.

Irradiation of 2-chloro-6,9-dimethylbenzsuberone (7) was carried out with a 0.33-g sample (1.5 mmol) in 300 mL of methanol and irradiated under N_2 for 8 h with a Pyrex-filtered medium-pressure Hanovia lamp. The solvent was evaporated, and the residue was analyzed by GLC (170 °C, SE 30). One of the peaks was too small to be successfully analyzed. The four that were determined along with yields and spectral data are as follows:

2-Methoxy-6,9-dimethylbenzsuberone (8): 6% yield; NMR (300 Hz, $CDCl_3$) δ 1.69 (2 H, m), 1.90 (2 H, m), 2.16 (3 H, s), 2.23 (3 H, s), 2.61 (2 H, m), 2.90 (3 H, s), 4.70 (2 H, d of d, J = 1.4 and 3.0 Hz), 6.98 (2 H, s). The multiplets above include appropriate splitting for cis, trans, and geminal coupling: J = 1.4, 3.0, and 15.0 Hz; m/e = 218 (21, M^+), 190 (18, M − CO), 186 (45, M − CH_3OH), 175 (33, M − CO − CH_3); IR (film) 1695 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.05; H, 8.20.

5-Carbomethoxy-1,4-dimethyltetralin (5c): 34% yield; NMR ($CDCl_3$, 300 Mz) δ 1.81 (4 H, m), 2.09 (3 H, s), 2.17 (3 H, s), 2.51 (2 H, m), 2.70 (1 H, d of d), 3.62 (3 H, s), 6.78 (1 H, d), 6.84 (1 H, d); m/e 218 (20, M^+), 159 (100, M − CO_2Me); IR (film) 1740 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.32; H, 7.82.

α-Chloropropiophenone: 68% yield; bp 160–162 °C (16 torr); IR (neat) 1695 cm^{-1}; NMR (CCl_4) δ 1.70 (3 H, d), 5.11 (1 H, q), 7.47 (3 H, m), 7.96 (2 H, m).

Irradiation of α-Chloropropiophenone. A 1.0-g sample was dissolved in 400 mL of methanol and irradiated with a Pyrex-filtered Hanovia lamp for 15 h. Evaporation of methanol, solution in hexane, extraction with aqueous bicarbonate solution, and drying ($MgSO_4$) afforded crude material that was separated by preparative gas chromatography. Two major products were obtained: propiophenone, identified through identity of IR and NMR spectra and methyl α-phenylpropionate (**5e**), identified from spectra properties: IR 1735 cm^{-1}; NMR (CCl_4) δ 1.37 (3 H, d) 3.66 (3 H, s) 3.70 (1 H, q) 7.27 (5 H, m). Up to 20 mol % water causes no change in product distribution.

Acknowledgment. We thank the Research Corp. for their support of this work.

Registry No. **1a**, 88632-72-8; **1b**, 50690-11-4; **1d**, 50690-12-5; **2a**, 66309-83-9; **2b**, 24623-20-9; **2d**, 6682-69-5; **3a**, 99356-69-1; **3b**, 66521-22-0; **3c**, 16198-27-9; **4a**, 35031-52-8; **4c**, 99356-71-5; **4d**, 1667-01-2; **5a**, 99356-70-4; **5c**, 99356-68-0; **5d**, 41841-19-4; **5e**, 31508-44-8; **6**, 99356-65-7; **7**, 99356-66-8; **8**, 99356-67-9; **10**, 99376-43-9; p-$C_6H_4(CH_3)_2$, 106-42-3; $ClCH_2COCl$, 79-04-9; $C_6H_5COCHClCH_3$, 6084-17-9; $C_6H_5COCH_2CH_3$, 93-55-0.

Reaction of Fluoroxytrifluoromethane with Ring-Substituted Styrenes: A Structure-Reactivity Study

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The reaction of fluoroxytrifluoromethane (FTM) with a group of ring-substituted styrenes has been studied. Reaction products have been determined, and relative rates for addition to the double bond have been measured by a competition method. The data give a straight line when plotted as log (k/k_H) vs. Hammett σ values with a ρ of −2.48. A similar plot vs. σ^+ gave less satisfactory agreement with linearity and a ρ of −2.18. A mechanism is proposed in which a spin-paired free-radical pair is formed that is converted by electron transfer into an ion pair.

Despite the high electronegativity of fluorine, there are some reagents that, in their reactions with organic compounds in solution, appear to behave as sources of the fluorine cation. These include fluorine,[2a] oxygen difluoride,[2c] fluoroxytrifluoromethane (FTM),[3] and fluoroxypentafluoroethane.[4] The reagent for which the most extensive experiments have been performed is fluoroxytrifluoromethane (FTM), which has been used by Barton and his co-workers to introduce fluorine into organic compounds by reactions both with the carbon–carbon double bond and, to a lesser extent, with the carbon–hydrogen bond. The evidence that the FTM–alkene reactions studied by Barton et al. proceed by an electrophilic fluorination mechanism has been summarized by Hesse.[3] A study of the reaction of FTM with ring-substituted styrenes has been carried out in this laboratory in order to examine quantatively the reaction of FTM with a group of alkenes in which a greater range of polar nature exists then has been the case in previous studies. The results are reported below.

Results

In choosing an experimental method for this study an important consideration was the question of the supply of FTM. The reagent is expensive and, for a time, was commercially unavailable, necessitating its synthesis for use in some of the experiments. Accordingly, a procedure using large amounts of this reagent such as bubbling it through a solution was ruled out. Attempts at preparing stable solutions of FTM in inert solvents were unsuccessful and a competition method was finally chosen (cf. the similar situation for fluorine).[5] This involved admitting gaseous FTM to a vigorously stirred solution of two styrenes in fluorotrichloromethane solvent. The amount of FTM was chosen so that the amounts of styrenes consumed would allow accurate measurement of C_0/C_f (C = concentration) for each. These experiments allowed the determination of the nature of the reaction products and of the relative rate constants. The styrenes used were styrene and p-chloro-, m-chloro-, p-methyl-, m-nitro-, and p-methoxystyrene. For the last one, reaction product structures could be determined but rate data could not.

Nature of the Reaction Products. FTM–Styrene Reaction. The identification of the products of the re-

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[1] Taken in part from the Ph.D. dissertation of D.M.S., The George Washington University, 1981.

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