positions of the acidic hydrogen atoms. Selected intermolecular distances are included in Table VI.

The helices are stabilized by three important crystal packing forces: (1) The ethyl groups are organized in hydrophobic cores which run parallel to the *a* axis, thus providing separation of the crystal into hydrophobic and polar regions.

(2) The phosphoric acid groups participate in extensive networks of hydrogen bonds which run parallel to the *a* axis. A molecule with one acidic hydrogen atom relative position participates in a hydrogen bond to each of two molecules with the other acidic hydrogen atom position. One hydrogen bond is 1.688 Å in length and is formed between the H1 and O21 atoms of molecules located in adjacent helices related by a *c*/2 translation and the other is 1.758 Å in length and is formed between the H2 and O12 atoms of molecules located in adjacent helices related by both *a* and *c*/2 translations. This arrangement requires two molecules with differing acidic hydrogen atom positions and leads to a zigzag array of hydrogen-bonded molecules. In this way a given helix of molecules is hydrogen bonded directly to both adjacent antiparallel helices and indirectly through an antiparallel helix to the parallel helices directly above and below.

(3) Most importantly, the axial conformation of the molecule appears to be stabilized by dipolar interactions between adjacent molecules within a helix. Given the expected staggered rotameric conformation about the C2–O5 bond, 5-ethoxytrimethylenephosphoric acid could be found in any of four distinct conformations, two with the ethoxy group axial and two with the ethoxy group equatorial. According to a simple estimate of the dipole moments, these four conformations differ in dipole moment and, therefore, polarity. The two equatorial rotamers have calculated net dipole moments of 2.1 and 2.8 D and the two axial conformers have calculated net dipole moments of 1.9 and 3.6 D. The axial conformer has one rotameric conformation about the C2–O5 bond which is significantly more polar than the other axial and both equatorial conformations. This conformation of highest polarity is that found in the crystal; i.e., the O5–C4 bond is trans to the C2–C1 or, equivalent in polarity, the C2–C3 bond. Within a helix of molecules, the dipoles of adjacent molecules are arranged such that the positive and negative ends of a given molecule's dipole are stabilized by close proximity to the negative and positive ends of the dipole of two adjacent molecules. Therefore, an explanation for the polar axial conformation is that this conformation provides the highest attractive interaction with the polar environment provided by adjacent molecules.

Our NMR data[5] on the solution conformation of 5-ethoxytrimethylene phosphate indicate that in a nonpolar solvent the preferred conformation of the molecule is with the alkoxy group in an equatorial position; in a polar solvent such as deuterium oxide, the preferred conformation is with the alkoxy group in an axial position. Thus, both our solution and crystal studies indicate the importance of solute–solvent interactions in the observed conformations of this conformationally flexible polar molecule.

Acknowledgment. This work was supported by a grant from the Research Corp. and a research grant (GM-23026) from the National Institutes of Health.

Registry No. 1, 72844-26-9.

Supplementary Material Available: Positional parameters for all atoms in the asymmetric unit, anisotropic thermal parameters for the nonhydrogen atoms, and an ORTEP drawing of the second molecule in the asymmetric unit (4 pages). Ordering information is given on any current masthead page.

Photochemistry of Some Heteroatom-Substituted 5-Acylnorbornenes

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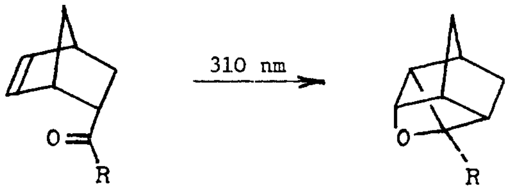
Received November 2, 1979

A series of 5-acylnorbornenes with hydroxyl, chloro, benzylthio, and diethylamino as α substituents was prepared as part of a study designed to evaluate the importance of lone-pair interactions in carbonyl photochemistry. Oxetanes were the primary photoproducts formed on irradiation of both the hydroxy ketone and the chloro ketone, but the thioketone and the amino ketone did not lead to detectable amounts of oxetanes. The results are discussed in terms of competitions between the three major competing processes: exciplex formation, intramolecular charge transfer, and bond homolysis.

Extensive studies in these laboratories have revealed the major features of photocyclizations of *endo*-5-acylnorbornenes to form oxetanes (eq 1).[1-4] These reactions are characterized by high chemical and photochemical efficiency even in systems in which side reactions, e.g., type I or type II photoelimination, might have been expected to be competitive with oxetane formation. These results and quenching studies have led us to conclude that the initial interaction, i.e., exciplex formation, between the carbonyl singlet state and the double bond occurs with a rate constant in excess of 10^{11} s^{-1}.[1,5-8] In an effort to define



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(1)

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(1) Sauers, R. R.; Rousseau, A. D.; Byrne, B. *J. Am. Chem. Soc.* **1975**, *97*, 4947.

(2) Sauers, R. R.; Kelly, K. W.; Sickles, B. R. *J. Org. Chem.* **1972**, *37*, 537.

(3) Sauers, R. R.; Schinski, W.; Mason, M. M.; O'Hara, E.; Byrne, B. *J. Org. Chem.* **1973**, *38*, 642.

(4) Sauers, R. R.; Henderson, T. R. *J. Org. Chem.* **1974**, *39*, 1850.

(5) For other examples of rapid intramolecular carbonyl–olefin interactions, see ref 6–8.

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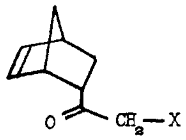
the *upper* limit to this rate, it became apparent that potentially competitive reactions might be initiated by electron transfer from lone-pair electrons which are more readily ionizable than the π electrons of the norbornene double bond since exciplex formation is believed to involve charge transfer.[9-13] To this end, we synthesized the heteroatom-substituted 5-acylnorbornenes **2a**–**d** and studied their photochemistry.



2a, X = OH

2b, X = Cl

2c, X = $SCH_2C_6H_5$

2d, X = $N(C_2H_5)_2$

2e, X = H

Results and Discussion

Syntheses. The key intermediate in the synthetic procedures was the hydroxy ketone **2a** which was prepared from 1,3-cyclopentadiene and hydroxymethyl vinyl ketone by a modification of the procedure of Utaka, Takeda, and Bender.[14] We found that the yield of this reaction could be raised to ca. 50% by avoiding the isolation of the highly unstable vinyl ketone and by careful attention to the other details (see Experimental Section).

The chloro ketone **2b** was obtained from **2a** on treatment with *p*-bromobenzenesulfonyl chloride in pyridine according to the classical procedure of Tipson.[15] Presumably, the initially formed *p*-bromobenzenesulfonate ester undergoes displacement by chloride ion, a reaction which is undoubtedly facilitated by the adjacent carbonyl group. In accord with this idea, the chloride **2b** served as the precursor for the thiobenzyl ether **2c** and the diethylamino derivative **2d**, both of which could be prepared from **2b** under relatively mild conditions by nucleophilic displacement reactions.

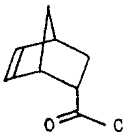
Photochemical Experiments. Irradiation of the hydroxy ketone **2a** in benzene proceeded cleanly to form one product to which structure **1** (R = CH_2OH) is assigned on the basis of spectral data and analogy with related systems.[1] In addition, the quantum yield for oxetane formation was found to be in the same range as those of simple alkyl substituted systems[1] (Table I). Thus, neither the lone-pair electrons nor the existence of an intramolecular hydrogen bond between the carbonyl group and the hydroxyl group[16] adversely affected the photochemistry of **2a**.

Table I. Quantum Yield Data

compd	concn, M^a	additive	concn, M	$\phi_{ox}{}^b$	$\phi_{-k}{}^b$
2e[1]	0.20			0.14	0.14
2a	0.21			0.18	
2b	0.070			0.29	
2b	0.079			0.24	
2b	0.075	piperylene	2.0		0.28
2b	0.075	piperylene	1.0		0.34
2b	0.075	piperylene	0.5		0.39
2b	0.094				0.84^c
2b	0.094	naphthalene	0.5	0.24	0.84^c

[a] Degassed benzene solutions. [b] Accuracy is estimated to be ±10%. [c] Nondegassed benzene solution.

In contrast, irradiations of exo, endo mixtures or pure *endo*-chloro ketone led to complex mixtures of products from which chlorooxetane **1** (R = CH_2Cl) could be isolated. The finding that these side reactions could be suppressed by piperylene (E_T = 58.5 kcal/mol) but not by naphthalene (E_T = 60.9 kcal/mol) was taken as an indication that free radicals were responsible for the side reactions and rapid loss of starting material. Photolyses were then carried out in the presence of butyl mercaptan in an effort to produce identifiable products by hydrogen-transfer reactions. Under these conditions, the chloro ketone was rapidly consumed, and a small amount of 5-acetylnorbornene (**2e**) was produced. In addition, when **2b** was irradiated in the cavity of an ESR spectrometer at 77 K, a triplet (a_H = 20 g) was observed. We conclude that **2b** undergoes homolysis to form **3**[17] in competition with oxetane formation and that



3

the radicals liberated react with starting material to produce side products.

In contrast, irradiations of both the thioketone **2c** and the amino ketone **2d** led to gradual disappearance of starting materials but no detectable amounts of oxetanes. Loss of thioketone is at least partly due to homolysis of the C–S bond as evidenced by the detection of dibenzyl disulfide in the photolysate. Small amounts (10%) of 5-acetylnorbornene (**2e**) were detected in the photolysate of the amino ketone.

In an effort to learn something about the inherent stability of **3**, we irradiated the chloro ketone in the presence of tributyltin hydride. This reaction was expected to be self-initiating,[18] and, in fact, we observed a very rapid loss of starting material coupled with formation of 5-acetylnorbornene (73%) but no oxetane. Evidently, **2b** is consumed by free-radical chain processes before significant conversion to oxetane can take place.

Discussion

A reasonably consistent interpretation of the above results requires a consideration of the relative importance of three competing primary processes: (a) exciplex formation, (b) heteroatom charge transfer, and (c) C–X bond homolysis. Unfortunately, the requisite parameters, i.e.,

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(6) Kurowsky, S. R.; Morrison, H. *J. Am. Chem. Soc.* **1972**, *94*, 507.

(7) Cowan, D. O.; Baum, A. A. *J. Am. Chem. Soc.* **1971**, *93*, 1153.

(8) Morrison, H.; Tisdale, V.; Wagner, P. J.; Liu, K.-C. *J. Am. Chem. Soc.* **1975**, *97*, 7189.

(9) Kochevar, I. E.; Wagner, P. J. *J. Am. Chem. Soc.* **1970**, *92*, 3742. Kochevar, I. E.; Wagner, P. J. *Ibid.* **1972**, *94*, 3859.

(10) Caldwell, R. A. *J. Am. Chem. Soc.* **1970**, *92*, 1439.

(11) Turro, N. J.; Lee, C.; Schore, N.; Barltrop, J.; Carless, H. A. J. *J. Am. Chem. Soc.* **1971**, *93*, 3079.

(12) Yang, N. C.; Hui, M. H.; Bellard, S. A. *J. Am. Chem. Soc.* **1971**, *93*, 4056.

(13) Yip, R. W.; Dogra, S. K. *Tetrahedron Lett.* **1977**, 2843.

(14) Utaka, M.; Takeda, A.; Bender, M. L. *J. Org. Chem.* **1974**, *39*, 3772.

(15) Tipson, R. S. *J. Org. Chem.* **1944**, *9*, 235.

(16) The blue shift (12 nm) and the enhanced intensity of the electronic absorption maximum is interpreted in terms of intramolecular hydrogen bonding.

(17) The observed hyperfine coupling constant is in agreement with literature data for similar systems. See: Paul, H.; Fischer, H. *Chem. Commun.* **1971**, 1038.

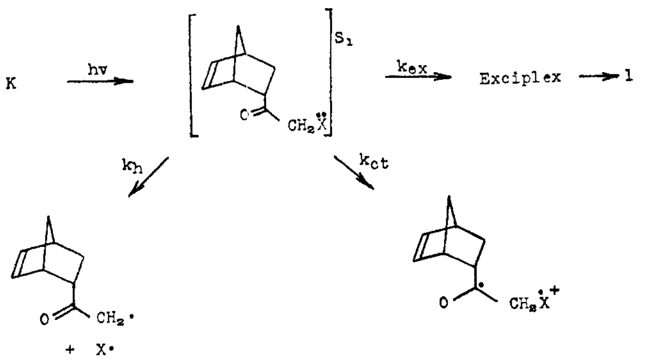
(18) Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299.

Table II. Estimated Bond Dissociation Energies (BDE) and Ionization Potential Data[21] for Model Compounds vs. Oxetane Formation

X	BDE, kcal/mol (for RCOCH$_2$X)	IP, eV (for CH$_3$X)	oxetane formation
H	98	na	+
OH	89	10.46[a]	+
Cl	79	11.26[b]	+
SCH$_2$C$_6$H$_5$	70	8.42[c]	–
N(CH$_3$)$_2$	67	7.82[d]	–
norbornene	na	8.97[e]	na

[a] Cocksey, B. J.; Eland, J. H. D.; Danby, C. J. *J. Chem. Soc. B* 1971, 790. [b] Dewar, M. J. S.; Worley, S. D. *J. Chem. Phys.* 1969, *50*, 654. [c] Bock, H.; Wagner G.; Kroner, J. *Chem. Ber.* 1972, *105*, 3850. [d] Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley-Interscience, New York, 1972. [e] Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* 1971, *54*, 783.

Scheme I



ionization potentials (IP's), and bond dissociation energies are not available for the appropriate model systems, CH$_3$C(O)CH$_2$X. Instead, we have chosen to estimate bond dissociation energies by making a small (~2 kcal/mol) correction[19] in the literature values for alkyl-X compounds[20] (cf. Table II).

The data in Table II suggest that oxetane formation can be frustrated by other processes if readily ionizable electrons or weak bonds are suitably positioned to interact with the excited carbonyl group. For the purpose of discussion, Scheme I will be used as an outline of the competing processes: exciplex formation (k_{ex}), heteroatom charge transfer (k_{ct}), and bond homolysis (k_h).

Rationalization of the clean formation of oxetane from the hydroxy ketone **2a** becomes a matter of noting that the IP of oxygen's lone pair is too high to compete with the double bond as a source of electrons and that there is insufficient energy in the single state of the carbonyl group (~80 kcal/mol[22]) to effect homolysis. On the other hand carbon–chlorine homolysis but not heteroatom charge transfer could proceed exothermically from the excited singlet state in competitition with exciplex formation, i.e., $k_{ex} > k_h >> k_{ct}$. If it is assumed that ϕ_h is the difference between ϕ_{ox} and ϕ_{-k} at high piperylene concentrations, it is possible to calculate a value of $\sim 10^{10}$ s^{-1} for k_h.[23,24] These results represent the chemical counterpart of the much discussed[25] spectroscopic phenomenon involving n,π^* absorptions of α-halo ketones, the rationalization of which is believed to involve mixing of the π^* orbital with the σ^* C–Cl orbital.

The failure of amino ketone **2d** to undergo either oxetane formation or homolysis must be the consequence of an extremely rapid intramolecular electron transfer from the nitrogen lone pair to the carbonyl singlet state. The lower limit for this event must be ca. 10^{12} s^{-1}, a value which is in agreement with that (10^{13} s^{-1}) estimated by Wagner and Jellinek[26] for intramolecular singlet quenching in α-(dimethylamino)acetophenone. The production of 5-acetylnorbornene (**2e**) is also consistent with the intermediacy of a charge-transfer state, given the analogies with both intramolecular[26] and intermolecular systems.[27]

Our results with thioketone **2d** are consistent with the following rate sequence, $k_h > k_{ct} \approx k_{ex}$, since we did not observe the formation of either oxetane or 5-acetylnorbornene. The estimated value of the rate of carbon–sulfur homolysis ($>10^{12}$ s^{-1}) is reasonable in view of the value estimated for carbon–chlorine homolysis (10^{10} s^{-1}) and, as expected, is significantly larger (100-fold) than the value of k_{ct} calculated by Padwa and Pashayan[28] for an α-benzylthioacetophenone.

Summary and Conclusions

A self-consistent, semiquantitative analysis of the interplay between the three major competing processes involved in the photochemistry of ketones **2a–e** has been presented. The results are consistent with a value of 10^{12} s^{-1} as an upper limit of exciplex formation in these systems. We plan to test further the underlying assumptions of the overall analysis and to exploit the utility of exciplex formation as an internal standard of reactivity. It is clear that heteroatoms make their presence known in at least two ways, and efforts to extend the synthetic generality of the intramolecular oxetane synthesis must take cognizance of possible complications induced by them.

Experimental Section

Infrared spectra were determined on a Perkin-Elmer Model 727B spectrometer. Nuclear magnetic resonance spectra were

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(19) (a) The correction represents an average of the differences in dissociation energy between the values obtained for various alkyl halides and the corresponding acetonyl halides. See: Egger, K. W.; Cocks, A. T. "The Chemistry of the Carbon—Halogen Bond", Patai, S., Ed.; Wiley: New York, 1973; pp 677–745. (b) King, K. D.; Golden, D. M.; Benson, S. W. *J. Am. Chem. Soc.* **1970**, *92*, 5541.

(20) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

(21) No attempt was made to "correct" the IP's reported in this table because of conflicting theories concerning inductive vs. conjugative and long-range effects. See: Worley, S. D. *Chem. Rev.* **1971**, *71*, 310–1. See also ref *a* of Table II. The differences are probably small (cf. quinuclidine, IP = 8.02 eV vs. 3-ketoquinuclidine, IP = 8.24 eV). See: Levin, C. C.; Hoffmann, R.; Hehre, W. J.; Hudec, H. *J. Chem. Soc., Perkin Trans. 2* **1973**, 210.

(22) All of the molecules in question absorb to the red of acetone which has $E_s \approx 83$ kcal/mol.

(23) It is assumed throughout that $k_{ex} \approx 10^{11}$ s^{-1} since the presence of electronegative substituents would, if anything, be expected to enhance the electrophilicity of the carbonyl group. For an analogy and discussion, see: Wagner, P. J.; Leavitt, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3669.

(24) For other examples of homolytic cleavages of chloro ketones, see: Taylor, R. P.; Blacet, F. E. *J. Am. Chem. Soc.* **1956**, *78*, 706. Strachan, A. N.; Blacet, F. E. *Ibid.* **1955**, *77*, 5254. Barltrop, J. A.; Thomson, A. *J. Chem. Soc. C* **1968**, 155.

(25) Allinger, N. L; Tai, J. C.; Miller, M. A. *J. Am. Chem. Soc.* **1966**, *88*, 4495. For a more comprehensive discussion of the orbital interactions in heteroatom substituted ketones see: Levin, C. C.; Hoffmann, R.; Hehre, W. J.; Hudec, J. *J. Chem. Soc., Perkin Trans. 2* **1973**, 210.

(26) Wagner, P. J.; Jellinek, T. *J. Am. Chem. Soc.* **1971**, *93*, 7328. See also: Padwa, A.; Eisenhardt, W.; Gruber, R.; Pashayan, D. *Ibid.* **1971**, *93*, 6998.

(27) Cohen, S. G.; Parola, A.; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141.

(28) Padwa, A.; Pashayan, D. *J. Org. Chem.* **1971**, *36*, 3550. Although these workers report only data for aromatic ketones, it is unlikely that the rates in question would be much different in the corresponding aliphatic system since the overall energy changes are similar. For a discussion and examples of the thermodynamics of these processes, see: Loutfy, R. O.; Dogra, S. K.; Yip, R. W. *Can. J. Chem.* **1979**, *57*, 342.

determined in deuteriochloroform on a Varian Model T-60 spectrometer using internal tetramethylsilane as a standard. Integration data are accurate to ±10%. Gas chromatographic data were obtained from an Aerograph Model A90P using the following columns and conditions: A, 3% SE-30 (10 ft × 0.25 in.) at 150 °C; B, 5% Versamid 900 (10 ft × 0.25 in.) at 155 °C; C, 3% FFAP–12% QF-1 (9 ft × 0.25 in.) at 105 °C; D, 10% Carbowax 20-M (5 ft × 0.25 in.) at 155 °C. The high-pressure liquid chromatographic equipment was a Waters Series 200 model equipped with a UV detector (254 nm) and a 10 cm × 8 mm radially compressed column of activated silica.

***endo*- and *exo*-5-(1-Keto-2-hydroxyethyl)bicyclo[2.2.1]hept-2-enes (2a).** A three-necked flask equipped with condenser, drying tube, and magnetic stirrer was charged in the following order with 6.71 g of red mercuric oxide, 6.71 g of ethyl acetate, 2.01 g of trichloroacetic acid, and 6.71 g of boron trifluoride etherate. The mixture was heated with stirring for 30 min at 55 °C and then cooled in an ice bath. The catalyst was added in portions to a stirred solution of 134.1 g (1.56 mol) of freshly distilled 2-butyne-1,4-diol in 670 mL of reagent-grade ethyl acetate. The temperature was maintained at 40–50 °C during the addition and for an additional hour afterward. The reaction mixture was cooled, decanted into a separatory funnel, extracted with sodium carbonate solution, and dried over sodium sulfate. After filtration the solution was cooled and treated with 40.23 g (0.61 mol) of freshly distilled cyclopentadiene with vigorous stirring. The resulting solution was allowed to warm to room temperature gradually over 17 h at which time the ethyl acetate was removed by rotary evaporation. Distillation of the residue at 70–75 °C (0.05 mm) gave 47.35 g (51%) of a slightly yellow liquid. Pure *endo*-**2a** could be obtained by careful distillation with a spinning-band column and was obtained as a waxy solid, bp 58–62 °C (0.075 mm) [lit.[14] bp 92 °C (8.5 mm)]. NMR and IR spectral data were in agreement with those given in ref 14: λ_{max} (C_6H_6) 275 nm (ϵ 50.5), λ_{max} (95% C_2H_5OH) 280 nm (ϵ 46), λ_{max} (C_6H_{12}) 273 nm (ϵ 48).

***endo*- and *exo*-5-(1-Keto-2-chloroethyl)bicyclo[2.2.1]hept-2-enes (2b).** A solution of 10 g (0.066 mol) of a mixture of alcohols **2a** in 100 mL of dry pyridine was cooled to 0 °C and treated in one portion with 18.47 g (0.0723 mol) of *p*-bromobenzenesulfonyl chloride. The resulting solution was stirred for 2 h at 0 °C. The reaction was quenched by slow addition of 10 mL of water, the temperature being kept below 5 °C. After addition of 100 mL of cold water, the product was extracted into chloroform which was washed with 6 N HCl until the pyridine had been removed. Evaporation of the chloroform gave an oil which on distillation gave 7.05 g (63%) of chloride **2b**: bp 52–55 °C (0.05 mm); NMR δ 6.3–5.8 (m, 2 H), 4.26 (s, 0.59 H), 4.23 (s, 1.4 H), 3.33 (m, 1 H), 2.96 (m, 1 H), 2.2–1.1 (m, 5 H); IR (neat) 3.25 (w), 5.78 (vs), 7.5 (s), 9.2 (s), 14.0 (s) μm^{-1}; λ_{max} (C_6H_6) 289 nm (ϵ 47).

Anal. Calcd for $C_9H_{11}OCl$: C, 63.35; H, 6.50; Cl, 20.78. Found: C, 63.63; H, 6.73; Cl, 20.59.

***endo*- and *exo*-5-[1-Keto-2-(benzylthio)ethyl]bicyclo[2.2.1]hept-2-enes (2c).** A mixture of 0.72 g (5.8 mmol) of benzyl mercaptan, 0.24 g (6.0 mol) of sodium hydroxide, and 10 mL of 50% ethanol was stirred until it became homogeneous. Addition of 1.0 g (5.9 mmol) of chloro ketone **2b** gave rise to a milky solution which was heated at reflux for 45 min. Water (20 mL) was added, and the product was extracted into ether. Drying (Na_2SO_4) and evaporation gave 1.1 g (72%) of an oil which gave a colorless oil on distillation: bp 147–153 °C (0.15 mm); NMR δ 7.4 (s, 5 H), 6.4–5.8 (m, 2 H), 3.77 (s, 2 H), 3.4–1.0 (m, 9 H); IR 3.75 (m), 3.70 (m), 5.87 (vs), 6.63 (s), 6.82 (s), 7.45 (s), 9.25 (s), 9.8 (s), 14.2 (s), μm^{-1}; λ_{max} (C_6H_6) 306 nm (ϵ 245), λ_{max} (C_6H_{12}) 307 nm (ϵ 252). An analytical sample was prepared by distillation in a molecular still at 100–110 °C (block temperature; 0.015 mm).

Anal. Calcd for $C_{16}H_{18}OS$: C, 74.37; H, 7.02; S, 12.41. Found: C, 74.50; H, 6.82; S, 12.65.

***endo*- and *exo*-5-[1-Keto-2-(diethylamino)ethyl]bicyclo[2.2.1]hept-2-enes (2d).** A solution containing 4.09 g (0.0240 mol) of **2b** and 3.51 g (0.0480 mol) of diethylamine in 100 mL of dry benzene was heated at reflux for 17 h. The precipitate was removed by filtration, and the benzene was evaporated in vacuo. The viscous oil was distilled in a molecular still at 90–100 °C (block temperature) and 0.05 mm to yield 1.0 g (20%) of a colorless oil which rapidly turned yellow on admission of air: NMR δ 6.3–5.8 (m, 2 H), 3.36 (s, 0.75 H), 3.3 (s, 1.25 H), 2.6 (q, J = Hz, 4 H), 1.05 (t, J = 7 Hz, 6 H); IR ($CHCl_3$) 3.36 (w), 5.83 (vs), 7.48 (s), 9.30 (s), 14.3 (s) μm^{-1}; λ_{max} (C_6H_6) 290 nm (ϵ 65). A picrate was prepared in ether and recrystallized from benzene–cyclohexane; mp 114–116 °C.

Anal. Calcd for $C_{19}H_{23}N_4O_8$: C, 52.41; H, 5.32; N, 12.87. Found: C, 52.32; H, 5.48; N, 12.76.

Irradiations of Ketones 2a. A solution of 18 g (0.12 mol) of **2a** in 1.1 L of benzene which contained 8 g (0.12 mol) of piperylene was irradiated for 4 days under nitrogen in an immersion apparatus using a Vycor filter and a 450-W Hanovia lamp. The volatile materials were removed on a rotary evaporator, and the residue was distilled at 79 °C (0.04 mm): yield 8.55 g (47%); NMR δ 4.71 (q, 1 H), 3.80 (AB q, J = 13 Hz, 2 H), 3.13 (m, 1 H), 3.06 (s, OH, 1 H), 2.73 (m, 1 H), 2.50 (m, 1 H), 2.3–1.4 (m, 5 H); IR (CCl_4) 2.77 (w), 2.90 (m), 7.68 (m), 9.15 (m), 9.60 (s), 10.2 (m) μm^{-1}. The analytical sample of **1** (R = CH_2OH) was obtained by GC (B).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95; O, 21.03. Found: C, 70.81; H, 7.67; O, 21.25.

Irradiations of Ketones 2b. The chloro ketone (7 g) was irradiated under similar conditions. Starting material was consumed within 17 h. The yield of distilled product **1** (R = CH_2Cl) was 3 g (43%): bp 110–114 °C (0.075 mm); NMR δ 4.77 (q, 1 H), 3.85 (s, 2 H), 3.17 (m, 1 H), 2.78 (m, 1 H), 2.60 (m, 1 H), 2.4–1.4 (m, 5 H); IR (CCl_4) 7.70 (s), 9.15 (s), 9.70 (s), 10.2 (s), 11.5 (s). An analytical sample was obtained by preparative GC (C).

Anal. Calcd for $C_9H_{11}OCl$: C, 63.35; H, 6.50; Cl, 20.78. Found: C, 63.30; H, 6.35; Cl, 20.59.

2b with Butyl Mercaptan. A solution comprised of 0.039 M **2b** (80% endo), 0.56 M butyl mercaptan, and 0.017 M hexadecane in benzene was irriadiated for 15 min with a Rayonet reactor with 3000-Å source. GC analysis (D) revealed complete loss of starting material and the formation of ca. 10% *endo*-5-acetylnorbornene. No oxetane was detected.

2b with Tributyltin Hydride. Similar irradiation of a solution comprised of 0.077 M **2b**, 0.114 M tributyltin hydride, and 0.017 M hexadecane gave rise to a 73% yield of *endo*-5-acetylnorbornene and a 39% yield of *exo*-5-acetylnorbornene. Oxetane **1** (R = CH_2Cl) could not be detected by GC analysis.

ESR Experiment. A sample of >99% pure *endo*-**2b** was collected and dissolved in dry hexane. The solution was placed in the cavity of a Varian Model E-12 ESR spectrometer which was cooled in liquid nitrogen. The resulting glass was irradiated with a collimated beam of light from a 200-W Osram superpressure mercury arc and a 5-mm plate of 9863 glass as a filter. Within 45 min a triplet spectrum developed in which the hyperfine splitting was found to be 20 G. The spectrum persisted after the light was removed but disappeared on thawing and refreezing.

Compound 2c. Irradiations of *exo-*/*endo*-thioketone mixtures were monitored by NMR and high-pressure LC. Long-term irradiation of benzene solutions did not reveal buildup of any adsorptions at ca. δ 4.6–4.8 which would be indicative of oxetane. Degassed solutions in Ultrex benzene showed equal rates of disappearance of the isomers and no new products of similar polarity (2:1 isooctane–methylene chloride eluent). Quantitative high-pressure LC using isooctane as eluent revealed the formation of a ca 6% yield of dibenzyl disulfide (triphenylmethane as internal standard).

Compound 2d. Irradiations of *exo-*/*endo*-amine mixtures were monitored by NMR spectroscopy and GC (D). No significant buildup of new products could be observed by NMR, especially in the δ 4.6–4.8 region expected for oxetanes. Long-term irradiation of a degassed sample revealed the development of peaks in the $CH_3C{=}O$ region. GC analysis confirmed the presence of *exo*- and *endo*-5-acetylnorbornenes in ca. 11% conversion.

Quantum Yield Determinations. Optically dense solutions of the pure endo ketones were prepared by using Ultrex benzene (Baker, 99.99% pure) and the appropriate internal standards. The solutions were placed in 13-mm quartz tubes to which high-vacuum stopcocks had been attached and subjected to four freeze-thaw degassing cycles at 0.05 mm. Irradiations were carried out on a merry-go-round apparatus which was suspended in a Rayonet factor equipped with a 3000-Å source. A Pyrex crystallizing dish surrounded the tubes and served to filter out the short-wavelength light. The actinometer used was hexachloroacetylnorbornene.[29]

Acknowledgment. We wish to thank Dr. J. Bell for valuable technical assistance with the high-pressure LC experiments and Professor J. San Filippo for the use of his high-pressure LC equipment. We also thank Dr. A. Hagedorn for his technical assistance and helpful comments throughout the course of this work and acknowledge the assistance of Dr. B. Wagner in obtaining the ESR spectrum.

Registry No. 1 (R = CH_2OH), 72784-93-1; 1 (R = CH_2Cl), 72784-94-2; *endo*-**2a**, 52747-94-1; *exo*-**2a**, 52747-95-2; *endo*-**2b**, 72784-95-3; *exo*-**2b**, 72784-96-4; *endo*-**2c**, 72784-97-5; *exo*-**2c**, 72784-98-6; *endo*-**2d**, 72784-99-7; *exo*-**2d**, 72785-00-3; *endo*-**2d** picrate, 72785-01-4; *exo*-**2d** picrate, 72785-02-5; *endo*-**2e**, 824-60-2; *exo*-**2e**, 824-61-3; 2-butyne-1,4-diol, 110-65-6; cyclopentadiene, 542-92-7; benzyl mercaptan, 100-53-8; diethylamine, 109-89-7; dibenzyl disulfide, 150-60-7.

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Fluorocarbanion Chemistry. Octafluorofluorene and Companions

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Received September 20, 1979

Octafluoro-9-fluorenone (**2**) is obtained by reaction of 2-bromooctafluorobiphenyl-2′-carboxylic acid (**4**) with *n*-butyllithium. The reaction illustrates an unusual intramolecular nucleophilic arylation involving attack at a carboxylate salt. Catalytic reduction gives octafluoro-9-fluorenol, rather than octafluorofluorene (**1**). **1** is synthesized by a six-step procedure from 2-bromononafluorobiphenyl (**7**). The key step involves an intramolecular nucleophilic alkylation to form ethyl octafluorofluorene-9-carboxylate (**12**), which rapidly undergoes decarboxylative hydrolysis in both alkaline and acidic media to form **1**. Relative to the 9-fluorenyl system and open-chain polyfluorinated analogues, **1** and **12** exhibit anomalous reaction chemistry, owing to the exceptional stabilities of their anions.

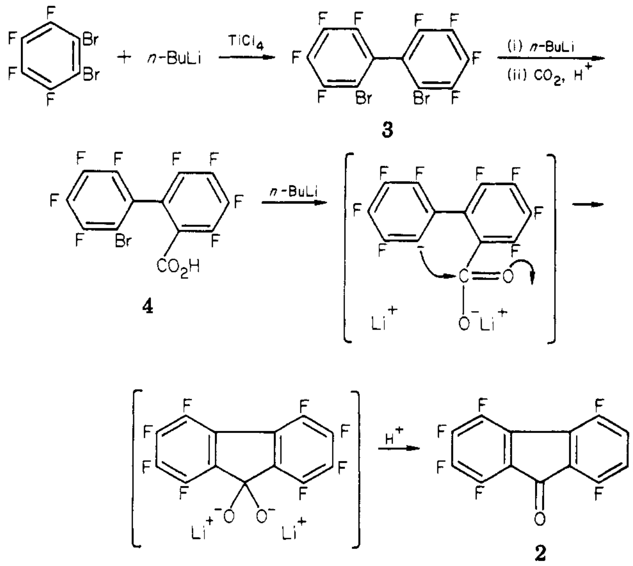
Introduction

The noteworthy effects of high aryl fluorination on reactivity have been elaborated in a recent review.[1] Of special relevance to this paper are the observations that polyfluoroaryl groups strongly stabilize carbanions by both inductive and resonance effects, as evidenced by marked enhancement of hydrocarbon acidities[2-4] and acceleration of carbanionic rearrangements.[5,6] This stabilization may also lead to anomalous reaction chemistry relative to all-hydrogen systems. One of the most revealing manifestations of this dichotomy between fluoro and hydrogen analogues is found in the chemistry of 1,2,3,4,5,6,7,8-octafluorofluorene (**1**) and its congeners.

Discussion

In preliminary communications[7,8] we described two synthetic routes to gain entry into the octafluorofluorene series. In the first approach,[7] we prepared octafluoro-9-fluorenone (**2**), as shown in Scheme I. The strategy required the availability of a suitable 2,2′-bifunctional octafluorobiphenyl which would readily undergo the desired cyclization. To this end, 2,2′-dibromooctafluorobiphenyl (**3**) was prepared from 1,2-dibromotetrafluorobenzene.[9]

Scheme I



Reaction of **3** with an equimolar concentration of *n*-butyllithium in ether at −78 °C gave the bromocarboxylic acid **4** after carbonation. This is a very sensitive reaction, since even under the most favorable conditions **4** was contaminated with small quantities of the octafluorodiphenic acid[10] (**5**), which, fortunately, did not interfere in the subsequent reaction. Rapid carbonation with dry ice favored formation of **4**, whereas slow bubbling of CO_2 gas provided only **5** and **3**, probably via metal–halogen ex-

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