pound (R_f 0.70, M^+ 392) precipitated from the solution while the propellanedione **6a** was observed by TLC of the mother liquor. This substance (R_f 0.70) was the product of reaction of one molecule of the 1,2-dione (**4a**) with another molecule of **4a** since it was also obtained by carrying out the same reaction in the absence of dimethyl β-ketoglutarate. No 1:1 adduct of **4a** and **5** could be found.

Acid-Catalyzed Reaction of Cyclododecane-1,2-dione and Dimethyl β-Ketoglutarate in Refluxing Benzene. Cyclododecane-1,2-dione (3.0 g, 0.015 mol), dimethyl β-ketoglutarate (**5**, 3.2 g, 0.018 mol), and *p*-toluenesulfonic acid (200 mg) were dissolved in benzene (70 ml). The solution was refluxed and water (0.4 ml) was removed by means of a Dean-Stark trap. Evaporation of the benzene afforded an oil (6 g) which was found to be a mixture of starting material and a *new compound* (R_f 0.42 in 10% ethyl acetate/benzene). The oil was chromatographed on silica gel which furnished a small quantity of the new compound (0.3 g, 6% yield). This substance was crystallized from methanol to provide white crystals: mp 85–86 °C; ir (CCl_4) 2940 and 2870 (C–H), 1740, 1715 with a shoulder at 1700 cm^{-1} (saturated and unsaturated ester functions); NMR ($CDCl_3$) δ 1.21–1.91 (12 H, broad multiplet), 2.2 (q, 2 H), 2.8 (t, 2 H), 3.62–3.7 (6 H, two overlapping singlets), 3.95 (s, 2 H), and 6.2 (m, 2 H); mass spectrum M^+ at *m/e* 334.1788; calcd for $C_{19}H_{26}O_5$, 334.1773; *m/e* 334 (100), 306 (14), 302 (57), 291 (816), 276 (20), 275 (100), 274 (40), 270 (1.4), 251 (14), 246)10.7), 245 (15), 231 (15), 228 (16), 219 (23), 218 (24), 205 (34), 203 (34), 192 (35), 191 (61.3), 189 (57), 173 (30), 159 (51), 149 (54), 145 (35), and 131 (65).

Anal. Calcd for $C_{19}H_{26}O_5$: C, 68.30; H, 7.8. Found: C, 68.00; H, 8.02. The structure of this compound is still undetermined.

Acknowledgments. We are greatly indebted to Mr. Paul Karges, Mr. William E. Comstock (NHLI), and Dr. Peter P. Roller (NCI) for mass spectra. Our thanks also go to Dr. Robert J. Highet and Mr. Robert B. Bradley for 220-MHz NMR spectra. We gratefully acknowledge a Faculty Research Grant from the Graduate School, University of Wisconsin—Milwaukee, and a grant from the Research Corporation (to J.M.C.). We wish to thank Mr. Steven H. Bertz (Harvard University) for information on related work. Our special thanks go to Dr. Ulrich Weiss (NIH) for pointing out to us the work in ref 4 and for many stimulating discussions.

Registry No.—**3**, 58602-52-1; **4a**, 3008-41-1; **4b**, 3008-37-5; **5**, 1830-54-2; **6a**, 58602-53-2; **6b**, 58602-54-3; **7a**, 58602-55-4; **7b**, 58602-56-5; **11**, 58602-57-6; **12**, 58602-58-7; **20**, 134-81-6; **21**, 16691-78-4.

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(22) Mr. Steven Bertz (Harvard University) has carried out this reaction on a related compound (unpublished results).

Photochemical Reactivity of Some Bridgehead Phenyl Ketones[1]

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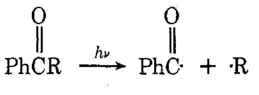
Received October 20, 1975

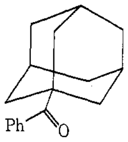
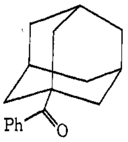
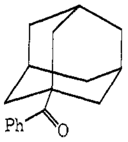
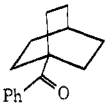
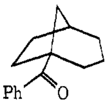
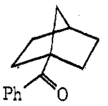
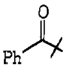
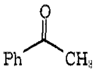
The photochemistry of several bridgehead phenyl ketones has been investigated. Bicyclo[2.2.2]octyl, 1-adamantyl, and 1- and 3-homoadamantyl phenyl ketones undergo efficient photochemical α-cleavage in benzene solution, whereas bicyclo[3.2.1]octyl and bicyclo[2.2.1]heptyl phenyl ketones do not. The rates for α-cleavage of ketones **1–4** are dependent upon bi- and tricycloalkane structure in a manner similar to that previously reported for the thermolysis of bridgehead peresters. The rate constant for α-cleavage is accelerated for 1- or 3-homoadamantyl vs. *tert*-butyl, but retarded by the smaller bicyclic ring systems. The kinetic results are indicative of an early transition state with polar character for photochemical α-cleavage. Quantum yields for product formation are larger for the bridgehead ketones than for pivalophenone owing to a decreased cage effect. The photoreduction of these ketones has also been investigated.

Reliable prediction of reactivity of an entire class of molecules is one of the ultimate goals of the investigation of reaction mechanisms. We have studied the reactivity of phenyl ketones toward photochemical α-cleavage (eq 1) with the above goal in mind.[3-5] We have established that the stability of the product free radicals does not correlate with photochemical reactivity. For example, pivalophenone (R = *tert*-butyl) is an order of magnitude more reactive than deoxybenzoin (R = benzyl).[3] We have also found that α substituents capable of stabilizing an adjacent positive charge are far more effective in accelerating α-cleavage than are substituents ca-



$$\mathrm{Ph}\overset{\overset{\displaystyle O}{\|}}{C}\mathrm{R} \xrightarrow{h\nu} \mathrm{Ph}\overset{\overset{\displaystyle O}{\|}}{C}\cdot + \cdot\mathrm{R} \qquad (1)$$

Table I. Absorption and Room-Temperature Phosphorescence Data for Bridgehead Ketones

Ketone		λ_{max}[a]	(ϵ)	Φ_P[b]	τ, μs[c]	τ_R, ms
1		316	(137)	$<10^{-5}$		
2		316	(129)	$<10^{-5}$		
3		317	(137)	$\sim 5 \times 10^{-5}$		5.9[d]
4		316	(140)	6.4×10^{-4}	5.4	8.3
5		319	(104)	2.8×10^{-4}	2.0	7.1
6		318	(106)	6.1×10^{-3}	30	5.0
7		317	(130)			
8		316	(63)	1.5×10^{-2}	56	3.7

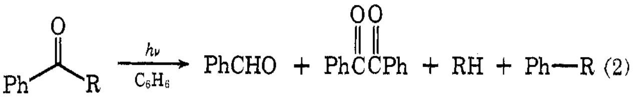
[a] Long wavelength absorption maximum in ethanol solution, 23 °C. [b] Phosphorescence quantum yield in degassed carbon tetrachloride, 23 °C. [c] Lifetime of room-temperature emission. [d] Calculated using the lifetime determined by Stern–Volmer product quenching (Table II).

pable of stabilizing free-radical centers.[4,5] In order to obtain further information about the photochemical α-cleavage process, the reactivity of six bridgehead bi- and tricycloalkyl phenyl ketones has been investigated. Studies of bridgehead reactivities have provided useful information about the mechanisms of carbonium ion[6] and free-radical[7,8] reactions. However, there are no previous reports of photochemical reactivities of bridgehead substrates.

Results

The bridgehead ketones 1–6 were synthesized via the reaction of the known carboxylic acids with phenyllithium or diphenylcadmium. Ketones 1–6 have n, π^* absorption and low-temperature emission spectra (E_T = 72 ± 1 kcal/mol) similar to that of pivalophenone (7, Table I) and have intersystem crossing quantum yields of 1.0 ± 0.05, as determined by comparison with benzophenone.[9] Room temperature phosphorescence was observed for ketones 3–6 in highly degassed, purified carbon tetrachloride solution. Phosphorescence quantum yields were measured by comparison to benzophenone (Φ = 0.015).[5,10] Lifetimes were determined either by single photon counting (4 and 5) or by signal-averaged flash kinetics (6).[5] The emission of ketone 3 was too weak to permit direct lifetime measurement. Radiative lifetime values for ketones 3–6 are intermediate between those for acetophenone (8, 3.7 ms) and benzophenone (10 ms).[5]

Irradiation of ketones 1–4 in degassed benzene results in formation of benzaldehyde, traces of benzil, bi- or tricycloalkane, and phenybi- or tricycloalkane (eq 2). These products



$$\mathrm{PhC(O)R} \xrightarrow[\mathrm{C_6H_6}]{h\nu} \mathrm{PhCHO} + \mathrm{PhC(O)C(O)Ph} + \mathrm{RH} + \mathrm{Ph{-}R} \quad (2)$$

1, R = 3-homoadamantyl
2, R = 1-homoadamantyl
3, R = 1-adamantyl
4, R = 1-bicyclo[2.2.2]octyl
5, R = 1-bicyclo[3.2.1]octyl
6, R = 1-bicyclo[2.2.1]heptyl

are derived from the benzoyl–alkyl radical pair formed upon α-cleavage (eq 1). Ketones 5 and 6 are relatively inert to photolysis in benzene. Under conditions sufficient for >90% conversion of ketones 1 or 2, ketone 5 is recovered ≳90% unchanged and ketone 6 is recovered quantitatively. Irradiation of 1–4 in 0.03 M dodecanethiol–benzene results in greatly increased yields of benzaldehyde, owing to efficient scavenging of benzoyl radicals.[3] Quantum yields for benzaldehyde formation (313-nm irradiation, benzophenone–benzhydrol actinometry) are given in Table II. Triplet lifetimes for ketones 1–4 were determined by the usual Stern–Volmer analysis using naphthalene as quencher both in benzene (λ >330 nm) and in 0.003 M thiol–benzene (λ 365 nm) solutions. The results obtained by the two methods are in good agreement. The lifetimes determined in benzene solution for ketone 4 are somewhat shorter than the value obtained by single photon counting in carbon tetrachloride solution (Table I). The longer lifetime is considered to be more accurate in light of the known

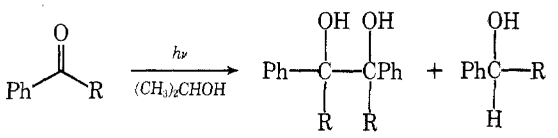
Table II. Quantum Yield and Kinetic Data for Bridgehead Ketones

Ketone	Φ^a	$k_q\tau$, M^{-1}	τ, s^d
1	0.65	24^b	4.9×10^{-9}
		25^c	5.0×10^{-9}
2	0.74	230^b	4.6×10^{-8}
		280^c	5.5×10^{-8}
3	0.68	1500^b	2.9×10^{-7}
		600^c	1.2×10^{-7}
4	0.13	5800^b	1.2×10^{-6}
		6500^c	1.3×10^{-6}
5	<0.01		
6	0		
7^e	0.30	447	9.1×10^{-8}

[a] Quantum yield for benzaldehyde formation in degassed 0.03 M dodecanethiol–benzene solution, 313 nm irradiation. [b] Slope of linear Stern–Volmer plot (λ 365 nm). [c] Slope of linear Stern–Volmer plot (λ >330 nm). [d] Calculated assuming $k_q = 5 \times 10^9\ M^{-1}\ s^{-1}$. [e] Data from ref 12.

ability of benzene to shorten the lifetime of aromatic ketones having lifetimes longer than 1 μs.[4,11]

Irradiation of ketones **1–3** in 2-propanol solution results in increased yields of tricycloalkane formation (55–71% isolated yields), but none of the products expected for aryl ketone photoreduction.[12] Ketones **4** and **5** give complex mixtures of α-cleavage products along with the corresponding pinacols and carbinols (eq 3). Photoreduction is the exclusive photochemical reaction for ketone **6** in 2-propanol. Isolated yields of photoreduction products are indicated in eq 3.

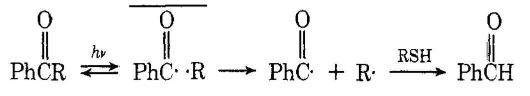


(3)

4	36%	9%
5	26%	11%
6	74%	17%

Discussion

For bridgehead ketones **1–4**, the only observed primary photoprocess in benzene solution is α-cleavage (eq 1). We have previously demonstrated that quantum yields less than 1.0 for product formation result from cage recombination of the initially formed radical pair (eq 4).[13] Low concentrations of



$$\mathrm{Ph\overset{\overset{O}{\|}}{C}R} \overset{h\nu}{\rightleftarrows} \overline{\mathrm{Ph\overset{\overset{O}{\|}}{C}\cdot\ \cdot R}} \longrightarrow \mathrm{Ph\overset{\overset{O}{\|}}{C}\cdot} + \mathrm{R\cdot} \xrightarrow{\mathrm{RSH}} \mathrm{Ph\overset{\overset{O}{\|}}{C}H} \quad (4)$$

thiol (RSH) can efficiently scavenge benzoyl radicals once they have escaped from the solvent cage in which they are formed. Quantum yields for benzaldehyde formation of 0.3–0.5 have been observed for a number of *tert*-alkyl and benzyl phenyl ketones.[3-5,12,13] Quantum yields for ketones **1–3** (Table II) are significantly higher than these values. The quantum yield for ketone **4** is 0.13, substantially lower than the values for ketones **1–3**. The lifetime of **4** is sufficiently long (5.4 μs in CCl_4) that quenching by benzene can occur.[4,11] Since the lifetime of **4** in benzene solution is approximately one-fourth as long as in carbon tetrachloride, ~75% of the excited states are quenched by benzene solvent. The resulting corrected quantum yield for ketone **4** is 0.52, nearly as large as those for ketones **1–3**. Thus we conclude that α-cleavage is the dominant decay process for ketone **4** in carbon tetrachloride solution.

The higher quantum yields for benzaldehyde formation from ketones **1–3** vs. pivalophenone (Φ = 0.3) indicates that a higher percentage of benzoyl radicals escape from the solvent cage. This decreased cage effect could result from either a decreased rate of radical pair recombination or an increased rate of diffusion. The apparent rate of diffusion out of the cage could increase owing to increased mass of the alkyl radical.[14] Larger radicals may migrate over longer distances before being slowed down by the frictional resistance of the solvent and beginning their random walk leading to recombination. The failure to observe CIDNP effects for the bridgehead phenyl ketones is in accord with this explanation.[15] Alternatively, cage recombination may be slower for the bridgehead vs. acyclic radicals since one face of the bridgehead radical is protected from attack by the benzoyl radical. This explanation can be valid only if alkyl radical rotation is not significantly faster than cage recombination or diffusion. We have observed similar rates of cage recombination, diffusion, and alkyl radical rotation for the benzoyl-1-phenylethyl radical pair.[13]

The lifetimes of the bridgehead ketone n, π* triplet states increase with decreased ring size (Tables I, II). Values of $1/\tau$ relative to that for pivalophenone are given in Table III. Since neither triplet energies nor radiative lifetimes (Table I) are dependent upon alkyl structure we assume that the variation in triplet lifetime reflects a decrease in the rate constant for α-cleavage with decreasing ring size. Only those ketones with lifetimes shorter than 1 μs undergo appreciable α-cleavage in benzene solution. The lifetime of **6** in CCl_4 is almost as long as that of acetophenone (Table I). Thus **6**, like acetophenone, would be expected to decay exclusively by radiative and nonradiative pathways to the ketone ground state. The absence of α-cleavage from ketone **5** is less readily explained. The lifetime of ketone **5** is actually shorter than that of **4**, which undergoes moderately efficient α-cleavage in benzene. In view of the apparent photochemical stability of ketone **5**, its short lifetime must be due either to a nondestructive decay pathway or to impurity quenching.

The effect of bridgehead bi- and tricycloalkane structure on reactivity for several types of homolytic and heterolytic reactions are given in Table III. Schleyer[16] has shown that a linear correlation exists between solvolysis rate constants and the calculated difference in strain energy of the bridgehead

Table III. Bridgehead Reactivities

R	$\mathrm{Ph\overset{\overset{O}{\|}}{C}R}^a$ $1/\tau$ 22 °C	$\mathrm{R\overset{\overset{O}{\|}}{C}OO\text{-}\mathit{t}\text{-}Bu}^b$ k_{therm} 80 °C	$\mathrm{R\text{-}N{=}N\text{-}R}^c$ k_{therm} 300 °C	RBr^d solvolysis
tert-Butyl	1	1	1	1
3-Homoadamantyl	20	15.2		0.5
1-Homoadamantyl	1.8	3.5		
1-Adamantyl	0.33	2.3	4.0×10^{-4}	10^{-3}
1-Bicyclo[2.2.2]octyl	0.017	0.16	5.1×10^{-5}	10^{-6}
1-Bicyclo[3.2.1]octyl	0.045	0.082	3.7×10^{-5}	10^{-6}
1-Bicyclo[2.2.1]heptyl	0.003	0.0025	2.0×10^{-6}	10^{-13}

[a] This work. [b] Data from ref 7, for R = *tert*-butyl, $k = 3.2 \times 10^{-4}\ s^{-1}$. [c] Data from ref 7. [d] Data from ref 6.

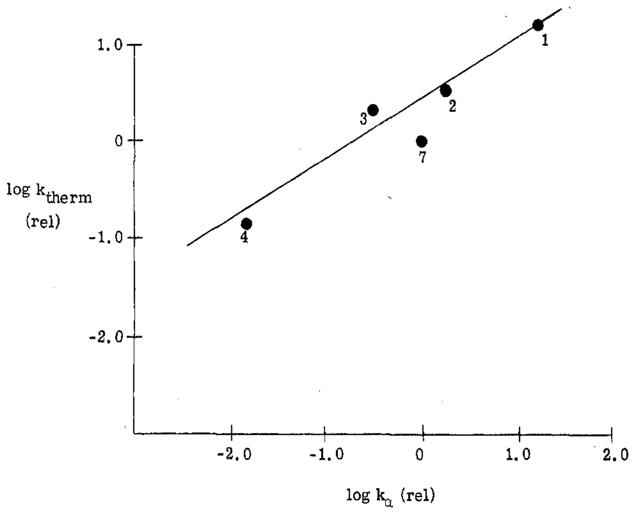


Figure 1. Linear free energy relationship for photochemical α-cleavage and perester thermolysis (Table III).

substrates and corresponding carbonium ions. Rüchardt[7,8] has found a good linear free energy relationship between the rate constants for bridgehead bromide solvolysis and perester thermolysis, the latter reaction being considerably less sensitive to ring strain (Table III). Rüchardt[8] attributes the variation in bridgehead perester reactivity to polar effects rather than ring strain. In support of this theory, a decrease of perester rate constants with increasing s character of the exocyclic bridgehead bond, as measured by the ^{13}C–H coupling constants of the corresponding polycyclic alkanes, is observed.

Both solvolysis of alkyl bromides[6] and thermolysis of azoalkanes[7,8] are subject to large rate retardation, even for 1-adamantyl vs. *tert*-butyl. These results are consistent with an almost planar transition state possessing considerable angle strain. In contrast, neither photochemical α-cleavage nor perester thermolysis[7] are subject to substantial retardation even for the bicyclo[2.2.2] substrates. Modest rate enhancements are observed for the homoadamantyl substrates, the effect being larger for the 3-homoadamantyl substrates.[17] The linear free energy relationship between ketone α-cleavage and perester thermolysis[7] is shown in Figure 1. We note that ketone α-cleavage is somewhat more sensitive to bridgehead alkane structure than is perester thermolysis, even though the rate constants for the photochemical reaction are 10^{10} faster. There is evidence that all of the peresters in Table III thermolyze via a one-step mechanism.[18] Therefore extrapolation of the data in Figure 1 to obtain values of k_α for ketones **5** and **6** appears justified. The estimated values of k_α for ketones **5** and **6** (10^4 and 10^2 s^{-1}, respectively) are substantially lower than typical values for alkyl phenyl ketone nonradiative decay in benzene solution ($\sim 3 \times 10^5$ s^{-1}).[12] Thus the insignificant α-cleavage of **5** and the complete lack of α-cleavage of **6** are not surprising. In view of the similar effects of structure on reactivity for ketone α-cleavage and perester thermolysis, Rüchardt's postulate of a polar transition state for homolysis may apply to photochemical α-cleavage. A polar transition state is consistent with our previous observations for deoxybenzoin derivatives.[4,5]

Photoreduction does not compete with α-cleavage of ketones **1–3** even in 2-propanol solvent. Scavenging of the bridgehead free radicals by 2-propanol provides another useful method of preparing the polycyclic hydrocarbons.[19] If the bridgehead phenyl ketones abstract hydrogen from 2-propanol with rate constants similar to that for pivalophenone (2.4×10^4 M^{-1} s^{-1}),[12] $\sim$5% photoreduction products would be expected for ketone **3** and <1% for ketones **1** and **2**. The lifetimes of ketones **4** and **5** are sufficiently long to allow photoreduction to compete efficiently with α-cleavage. Photoreduction is the exclusive reaction for ketone **6** in 2-propanol, as is the case for acetophenone.[12]

Experimental Section

General procedures for purification of materials,[3] quantum yield measurements,[3] Stern–Volmer quenching,[3] and room temperature phosphorescence lifetime and quantum yield measurements[4] have been previously described. Product analysis of preparative photolysis mixtures employed a Hewlett-Packard 5700 thermal conductivity gas chromatograph with a 3 m × 2.5 mm stainless-steel column containing 4% Apiezon L on DMCA-AW Chromosorb G. Mass spectra were recorded using a EAI Quad 150 spectrometer.

3-Benzoylhomoadamantane (1). To a solution of 68.0 g (0.35 mol) of homoadamantane-3-carboxylic acid[20] in 1 l. of absolute tetrahydrofuran at −60 °C was added a solution of phenyllithium (1.1 l., 0.76 M) within 4 h. After additional stirring for 1 h at 20 °C the reaction mixture was poured onto ice and extracted with ether. The ethereal phase was washed with 5% aqueous NaOH and water and yielded 120 g of viscous residue. Purification by treatment with Girard T[21] reagent and subsequent distillation yielded 37.6 g of pure 3-benzoylhomoadamantane which was once crystallized from CH_3OH: mp 68 °C; ir (KBr) 1675 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.86 (m, 17 H), 7.4 (m, 3 H), 7.64 (m, 2 H). Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.7; H, 8.47.

Oxime: mp 213–215 °C (from ethanol). Anal. Calcd for $C_{18}H_{23}NO$: C, 80.25; H, 8.61; N, 5.20. Found: C, 80.1; H, 8.66; N, 5.28.

2,4-Dinitrophenylhydrazone: mp 222–223 °C (from ethanol). Anal. Calcd for $C_{24}H_{26}N_4O_4$: C, 66.34; H, 6.03; N, 12.9. Found: C, 66.45; H, 5.94; N, 12.8.

1-Benzoylhomoadamantane (2). To a solution of 68.0 g (0.35 mol) of homoadamantane-1-carboxylic acid[20] in 1000 ml of absolute tetrahydrofuran at −60 °C was added a solution of phenyllithium (900 ml of ethereal solution, 0.8 M). After stirring for 2.5 h at 20 °C the reaction mixture was poured onto ice and extracted with ether. Workup as previously described yielded 100 g of residue. Purification by treatment with Girard T[21] and subsequent distillation yielded after crystallization from CH_3OH (twice) 40.7 g of pure 1-benzoylhomoadamantane: mp 55–56 °C; ir (KBr) 1675 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.83 (m, 17 H), 7.4 (m, 5 H). Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.85; H, 8.64.

Oxime: mp 195–196 °C (from ethanol). Anal. Calcd for $C_{18}H_{23}NO$: C, 80.24; H, 8.61; N, 5.20. Found: C, 80.25; H, 8.91; N, 5.21.

2,4-Dinitrophenylhydrazone: mp 238–239 °C (from ethanol/benzene). Anal. Calcd for $C_{24}H_{26}N_4O_4$: C, 66.34; H, 6.03; N, 12.90. Found: C, 66.8; H, 6.00; N, 12.85.

1-(α-Hydroxybenzyl)homoadamantane was prepared by $NaBH_4$ reduction of 1-benzoylhomoadamantane in CH_3OH at 20 °C. The alcohol did not crystallize. It was distilled bulb to bulb: bp 170 °C (0.1 mm); ^{1}H NMR ($CDCl_3$) δ 7.2 (s, 5 H), 4.17 (s, 1 H), 1.0–2.2 (m, 18 H, including OH). Anal. Calcd for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.6; H, 9.15.

1-Benzoyladamantane (3) was synthesized from adamantane-1-carbonic acid chloride and diphenylcadmium by the method of Stetter.[22] Separation of biphenyl was achieved by treatment of the crude ketone mixture with Girard T:[21] mp 55–56 °C; ^{1}H NMR (CCl_4) δ 1.76 (s, 6 H), 2.0 (s, 9 H), 7.4 (m, 5 H).

1-Benzoylbicyclo[2.2.2]octane (4). A. A mixture of 111.0 g (0.72 mol) of bicyclo[2.2.2]octane-1-carboxylic acid[23] and 130.0 g (1.08 mol) of $SOCl_2$ was refluxed for 2 h. Fractional distillation yielded 116.1 g (94%) of bicyclo[2.2.2]octane-1-carboxylic acid chloride: bp 101–103 °C (13 mm); n^{20}D 1.5005. Anal. Calcd for $C_9H_{13}ClO$: C, 62.61; H, 7.54; Cl, 20.58. Found: C, 62.55; H, 7.67; Cl, 20.90.

B. According to Stetter[22] a solution of 115.0 g (0.7 mol) of bicyclo[2.2.2]octane-1-carboxylic acid chloride in 500 ml of benzene was added within 15 min to a 500-ml benzene solution of diphenylcadmium, prepared from a Grignard solution of 1 mol of Mg and 1 mol of phenyl bromide in absolute ether and 0.53 mol of $CdCl_2$. After refluxing the mixture for 2 h ice/2 N H_2SO_4 was added. The organic layer was separated, washed with 2 N NaOH, 1 N HCl, and water, and then dried over Na_2SO_4. Crystalline material (134 g) was isolated, which on purification by Girard T treatment,[21] crystallization, and zone refining yielded 102 g of pure 1-benzoylbicyclo[2.2.2]octane: mp 57–58 °C; ir (KBr) 1660 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.71 (m, 13 H), 7.4 (m, 5 H). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.10; H, 8.38.

Oxime: mp 228–229 °C (from ethanol). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.30; H, 8.37; N, 6.07.

2,4-Dinitrophenylhydrazone: mp 248–249 °C (from ethanol/

benzene). Anal. Calcd for $C_{21}H_{22}N_4O_4$: C, 63.94; H, 5.62; N, 14.21. Found: C, 63.90; H, 5.70; N, 14.0.

1-(α-Hydroxybenzyl)bicyclo[2.2.2]octane was prepared by $NaBH_4$ reduction of 1-benzoylbicyclo[2.2.2]octane in CH_3OH at 20 °C: mp 99–101 °C (from *n*-hexane); ^1H NMR ($CDCl_3$) δ 9.56 (m, 13 H), 1.95 (s, OH), 4.22 (s, 1 H), 7.22 (m, 5 H). Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.15; H, 9.33.

1-Benzoylbicyclo[3.2.1]octane (5). A. Bicyclo[3.2.1]octane-1-carboxylic acid[24] (147.6 g, 0.96 mol) and 160.0 g (1.3 mol) of $SOCl_2$ were refluxed for 2 h. Fractional distillation yielded 152.3 g (93%) of bicyclo[3.2.1]octane-1-carboxylic acid chloride, bp 75–80 °C (1.3 mm). Anal. Calcd for $C_9H_{13}ClO$: C, 62.60; H, 7.53; Cl, 20.59. Found: C, 62.75; H, 7.51; Cl, 20.2. A small amount of the acid chloride was treated with CH_3OH and the methyl ester formed analyzed by GC for the presence of 2-carbomethoxybicyclo[2.2.2]octane. The methyl ester formed consisted only of 1-carbomethoxybicyclo[3.2.1]octane.

B. To a 600-ml benzene solution of diphenylcadmium, prepared from 1.1 mol of Mg and 1.1 mol of phenyl bromide in ether and 0.56 mol of $CdCl_2$, was added within 15 min a solution of 131.4 g (0.76 mol) of bicyclo[3.2.1]octane-1-carboxylic acid chloride in 600 ml of benzene. After refluxing for 2 h the mixture was worked up as usual. Unreacted bicyclic acid (29.0 g) and 175.1 g of ketonic material were obtained. Further purification by treatment with Girard T[21] and distillation yielded 149.2 g of pure 1-benzoylbicyclo[3.2.1]octane: bp 129–133 °C (0.4 mm); $n^{20}{}_D$ 1.5575; ir ($CHCl_3$) 1680 cm^{-1}; ^1H NMR (CCl_4) δ 1.7 (m, 10 H), 2.35 (m, 1 H), 7.4 (m, 3 H), 7.84 (m, 2 H). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.41. Found: C, 84.00; H, 8.48.

Oxime: mp 191–192 °C (from ethanol). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.70; H, 8.51; N, 6.03.

2,4-Dinitrophenylhydrazone: mp 217.5–219 °C (from ethanol). Anal. Calcd for $C_{21}H_{22}N_4O_4$: C, 63 94; H, 5.62; N, 14.21. Found: C, 64.00; H, 5.60; N, 14.40.

1-(α-Hydroxybenzyl)bicyclo[3.2.1]octane was prepared by $NaBH_4$ reduction of 1-benzoylbicyclo[3.2.1]octane in CH_3OH at 20 °C: mp 62–64 °C (from *n*-hexane); ^1H NMR ($CDCl_3$) δ 1.0–2.3 (m, 13 H), 2.1 (s, 1 H), 4.44 (s, 1 H), 7.25 (s, 5 H). Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.7; H, 9.49.

1-Benzoylbicyclo[2.2.1]heptane (6). To a solution of 91.0 g (0.72 mol) of bicyclo[2.2.1]heptane-1-carboxylic acid[25] in 1.8 l. of absolute tetrahydrofuran was added within 1 h under nitrogen and stirring a solution of phenyllithium in ether (1.1 M, 1.25 l.) at −60 °C. The mixture was stirred for another 1 h at 25 °C and poured onto ice. Usual workup yielded 11.5 g of unreacted acid and 135.0 g of yellowish oil. Further purification of the impure ketone by treatment with Girard T[21] and distillation yielded 96.4 g of pure 1-benzoylbicyclo[2.2.1]-heptane: mp 32–34 °C (from *n*-hexane/ether); bp 105–107 °C (0.25 mm); ir (CCl_4) 1675 cm^{-1}; ^1H NMR (CCl_4) δ 1.68 (m, 13 H), 7.23 (m, 3 H), 7.67 (m, 2 H). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.90; H, 8.14.

2,4-Dinitrophenylhydrazone: mp 174–175 °C (from ethanol) (lit.[26] mp 198–199 °C). Anal. Calcd for $C_{20}H_{20}N_4O_4$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.25; H, 5.39; N, 14.6.

1-(α-Hydroxybenzyl)bicyclo[2.2.1]heptane was prepared by $NaBH_4$ reduction of 1-benzoylbicyclo[2.2.1]heptane in CH_3OH at 20 °C: mp 99–101 °C (from *n*-hexane) (sublimation): ^1H NMR ($CDCl_3$) δ 0.85–1.75 (m, 10 H), 2.10 (s, OH), 2.2 (m, 1 H), 4.8 (s, 1 H), 7.27 (m, 5 H). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.8; H, 8.87.

Photolysis of Ketones 1–5. Solutions (0.01 M) of 1–5 in benzene were irradiated (Philips HPK 125 W, GWCa filter, transparent for λ > 330 nm under nitrogen atmosphere). The disappearance of ketone was followed by GC. After most of ketone 1 had disappeared, the photolyses were stopped and the reaction mixtures analyzed using a combination of GC and mass spectrometer. Yields are reported as uncorrected GC peak areas.

3-Benzoylhomoadamantane (1) gave besides unreacted 1 (5.8%), benzaldehyde (8.2%), homoadamantane (54.9%), benzophenone (2.8%), and 3-phenylhomoadamantane (3.5%).

1-Benzoylhomoadamantane (2) gave besides unreacted 2 (8%), benzaldehyde (9.0%), homoadamantane (39.7%), benzophenone (4.2%), and 1-phenylhomoadamantane (34.2%).

1-Benzoyladamantane (3) gave besides unreacted 3 (50%), benzaldehyde (10.8%), adamantane (12.8%), benzophenone (1%), and 1-phenyladamantane (25%).

1-Benzoylbicyclo[2.2.2]octane (4) gave besides unreacted 4 (~90%), bicyclo[2.2.2]octane (~1%), benzaldehyde (~1%), benzophenone (<0.5%), and 1-phenylbicyclo[2.2.2]octane (7%).

1-Benzoylbicyclo[3.2.1]octane (5) gave besides unreacted 5 (59%), bicyclo[3.2.1]octane (traces), benzaldehyde (traces), benzophenone (traces), and acetophenone (~2%).

Benzaldehyde from photolysis of ketones 1–4 was captured as its 2,4-dinitrophenylhydrazone and identified. For ketone 5 this procedure was unsuccessful; the only 2,4-dinitrophenylhydrazone isolated was the derivative of acetophenone. The hydrocarbons from photolysis of ketones 1–4 were isolated and identified by comparison with authentic samples after being separated from the reaction mixture by chromatography on silica gel with *n*-hexane, which provided a mixture of polycyclic alkane and its phenyl derivative. The polycyclic hydrocarbon was separated from the phenyl derivative by simple sublimation. Only in the case of photolysis of 1-benzoyladamantane was the corresponding 1-phenyladamantane isolated and identified by mixture melting point with an authentic sample.[27]

Photoreduction of 1-Benzoylhomoadamantane (2). A solution of 2.0 g of 1-benzoylhomoadamantane in 200 ml of 2-propanol was irradiated (Philips HPK 125 W, Pyrex) under nitrogen for 20 H. Control by TLC revealed no evidence for the formation of pinacols or 1-(α-hydroxybenzyl)homoadamantane. Evaporation of the solvent yielded a crystalline residue which on chromatography (silica gel) with *n*-hexane yielded 0.65 g of homoadamantane, mp 248–251 °C. Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.59; H, 11.87.

Photoreduction of 3-Benzoylhomoadamantane (1). Ketone (2.0 g) was reduced in 2-propanol as described above. Chromatography yielded 0.74 g of homoadamantane, which proved to be identical by ir spectrum with the material isolated from 1-benzoylhomoadamantane irradiation.

Photoreduction of 1-Benzoyladamantane (3). A solution of 2.0 g of 1-benzoyladamantane in 200 ml of 2-propanol was irradiated as described above. Monitoring by TLC showed that there was no formation of 1-(α-hydroxybenzyl)adamantane.[28] Evaporation of the solvent left a crystalline residue which on chromatography (silica gel elution with *n*-hexane) yielded 0.8 g of adamantane, identified by GC comparison with an authentic sample. Further elution with more polar solvents yielded no other identifiable products.

Photoreduction of 1-Benzoylbicyclo[2.2.2]octane (4). A solution of 5.35 g of 1-benzoylbicyclo[2.2.2]octane in 250 ml of 2-propanol was irradiated as described above for 24 h. Evaporation of the solvent yielded 4.85 g of brownish crystals which on treatment with 2-propanol yielded 0.12 g of crystals of unknown structure, mp 230–235 °C (sublimation). The filtrate was evaporated and residue separated by chromatography on silica gel to yield 1.7 g of pinacols, mp 137–139 °C. Anal. Calcd for $C_{30}H_{38}O_2$: C, 83.67; H, 8.90. Found: C, 83.55; H, 8.77.

Further elution yielded 0.65 g of unreacted 4. Qualitatively it was observed that the ketone even when irradiated in 2-propanol underwent α-cleavage. Bicyclo[2.2.2]octane was found by GC analysis.

Photoreduction of 1-Benzoylbicyclo[3.2.1]octane (5). A solution of 5.35 g of 1-benzoylbicyclo[3.2.1]octane in 250 ml of 2-propanol was irradiated as described above for 24 h. A precipitate (0.2 g, mp 177–178 °C, sealed capillary) was separated and the filtrate evaporated. The oily residue (4.55 g) was analyzed for pinacols and secondary alcohol by TLC. Chromatography on silica gel yielded 1.2 g of crystalline pinacols, mp 129–133 °C. Anal. Calcd for $C_{30}H_{38}O_2$: C, 83.67; H, 8.90. Found: C, 83.74; H, 8.63.

Further elution yielded 0.78 g of starting material, followed by 0.5 g of 1-(α-hydroxybenzyl)bicyclo[3.2.1]octane, identified by mixture melting point and TLC with an authentic sample. As for ketone 5, the photoreduction gave a complex mixture, α-cleavage products being detected by GC.

Photoreduction of 1-Benzoylbicyclo[2.2.1]heptane (6). A solution of 2.0 g of ketone in 200 ml of 2-propanol was irradiated (Philips HPK 125 W, Pyrex) under nitrogen for 16 h. Evaporation of the solvent yielded a crystalline residue which was separated on silica gel. Eluticn with benzene/*n*-hexane yielded 1.5 g of pincaols, mp 225–240 °C. Further elution with benzene yielded 0.35 g of 1-(α-hydroxybenzyl)bicyclo[2.2.1]heptane, identified by elemental analysis and by comparison of mixture melting point and ir spectroscopic data with an authentic sample. An attempt was made to separate the diastereomeric pinacols. One isomer was isolated in pure form, mp 233–234 °C (sealed capillary). Anal. Calcd for $C_{28}H_{34}O_2$: C, 83.54; H, 8.51. Found: C, 83.5; H, 8.50.

When a solution of 2.0 g of ketone in 200 ml of 2-propanol containing 2 ml of piperylene was irradiated under the same conditions, no photoreduction was observed. Similar results were obtained when 1-benzoylbicyclo[3.2.1]octane or -bicyclo[2.2.2]octane were irradiated in 2-propanol containing 2% piperylene.

Acknowledgment. We thank Professors C. Rüchardt and P. v. R. Schleyer for useful information and stimulating discussions.

Registry No.—**1**, 58541-21-2; **1** oxime, 58541-22-3; **1** 2,4-DNPH, 58541-23-4; **2**, 58541-24-5; **2** oxime, 58541-25-6; **2** 2,4-DNPH, 58541-26-7; **3**, 31919-47-8; **4**, 58541-27-8; **4** oxime, 58541-28-9; **4** 2,4-DNPH, 58541-29-0; **5**, 58541-30-3; **5** oxime, 58541-31-4; **5** 2,4-DNPH, 58541-32-5; **6**, 1015-14-1; **6** 2,4-DNPH, 58541-33-6; **7**, 938-16-9; **8**, 98-86-2; homoadamantane-3-carboxylic acid, 21898-91-9; homoadamantane-1-carboxylic acid, 31061-65-1; 1-(α-hydroxybenzyl)homoadamantane, 58541-34-7; adamantane-1-carbonic acid chloride, 2094-72-6; bicyclo[2.2.2]octane-1-carboxylic acid, 699-55-8, bicyclo[2.2.2]octane-1-carboxylic acid chloride, 21891-38-3; 1-(α-hydroxybenzyl)bicyclo[2.2.2]octane, 5818-96-2; bicyclo[3.2.1]octane-1-carboxylic acid, 2534-83-0; bicyclo[3.2.1]octane-1-carboxylic acid chloride, 58541-35-8; 1-(α-hydroxybenzyl)bicyclo[3.2.1]octane, 58541-36-9; bicyclo[2.2.1]heptane-1-carboxylic acid, 18720-30-4; 1-(α-hydroxybenzyl)bicyclo[2.2.1]heptane, 5818-94-0; homoadamantane, 281-46-9.

References and Notes

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Bridged Polycyclic Compounds. 82. Multiple Mechanisms for Oxymercuration of Some Dibenzobicyclo[2.2.2]octatrienes[1]

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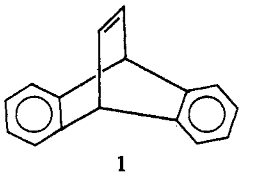
Received August 26, 1975

Addition of mercuric acetate to 1-methyldibenzobicyclo[2.2.2]octatriene, 1-methoxydibenzobicyclo[2.2.2]octatriene, and 1,4-dimethyldibenzobicyclo[2.2.2]octatriene has been carried out in a variety of solvent systems. With variation in substrate and in reaction conditions, cis addition, trans addition, and addition with rearrangement have been observed. The composition of the product mixtures have been rationalized in terms of these competing reaction paths for oxymercuration.

There has been much recent interest in oxymercuration reactions because of their usefulness in synthesis and their interesting mechanistic possibilities.[2] It has been suggested that oxymercuration proceeds via mercurinium ions, via concerted additions, and via β-mercuricarbocations, and a good deal of effort has been extended to prove or disprove the intervention of one or more of these intermediates or processes.

It seemed to us that a conservative viewpoint would assume that there are many mechanisms for oxymercuration reactions, just as for other electrophilic addition reactions. Our experience with dibenzobicyclo[2.2.2]octatriene (**1**) and related compounds suggested that this would be a useful system to investigate, as small modifications of structure or of reaction conditions often lead to mechanistic changes. The results of a portion of our studies are reported in this paper.



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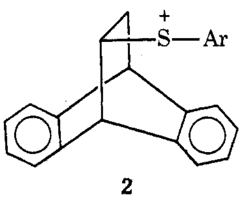

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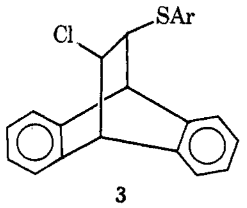

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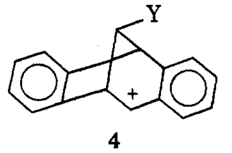

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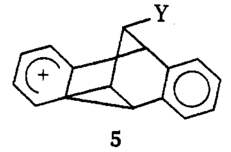

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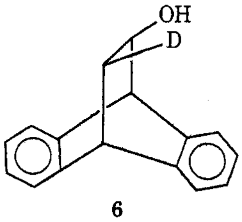

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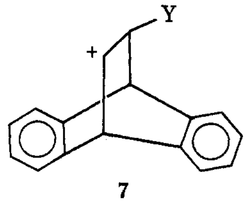

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