Mechanism of Photoacetylation of Substituted Adamantanes

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Mechanism of photoacetylation of adamantanes with biacetyl is discussed. The reaction proceeded via triplet biacetyl and had a large ρ^* value (−0.71). Thermolysis of *tert*-butyl 1-adamantaneperoxycarboxylate in biacetyl gave 1-acetyladamantane while *tert*-butyl 2-adamantaneperoxycarboxylate gave both 1- and 2-acetyladamantanes. The exclusive bridgehead substitution in the present photoacetylation is not determined by the radical transfer step, but mostly by the regiospecific abstraction of the bridgehead hydrogen by triplet biacetyl, probably due to the large nonbonded repulsion in a transition state of secondary hydrogen abstraction.

In our current studies on free-radical reactions[1-4] from mechanistic and preparative viewpoints, the authors have drawn a conclusion that adamantane is one of the most appropriate "probes" for radical reactions of saturated hydrocarbons because of its degeneracy (i.e., only two kinds of reaction sites are possible) and of the finding that neither (or least) cleavage nor intramolecular rearrangements take place.

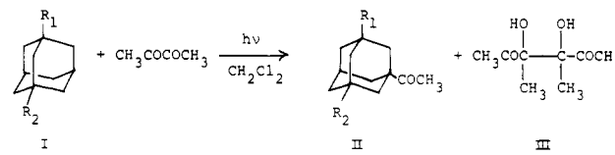
Although many direct functionalizations of adamantane have been successfully carried out via ionic[5-8] as well as free-radical[9-15] routes, no appropriate procedure is known for direct acetylation. Recently the authors have found that the photoacetylation is one of the most excellent procedures for the preparation of bridgehead acetyladamantanes[4,14] regiospecifically. The regiospecific bridgehead substitution is interesting and noteworthy because the photoacetylation proceeds via hydrogen abstraction from adamantanes by excited triplet state of biacetyl,[14] which leads to the simple expectation of nonregiospecific (bridgehead and bridge) product distribution. In this article, mechanistic study is made on the photoacetylation and a possible origin of the unusual regiospecificity, a plausible mechanism, or relative reactivities of substituted adamantanes are discussed.

Results

Products. Irradiation of a methylene chloride solution of adamantane (Ia) and excess biacetyl in a Pyrex vessel with a high-pressure 100-W mercury lamp gave 1-acetyladamantane (IIa) regiospecifically, in 92% preparative yield based on the consumed adamantane, and the coupling product of acetoin radical (III) was also formed in approximately equimolar amount to IIa.[14] The structure of IIa was determined on the basis of melting point and spectral data as well as the chemical conversions to the known compounds. Thus, IIa was converted to 1-adamantanol by the Baeyer–Villiger reaction followed by hydrolysis[5] or to 1-adamantanecarboxylic acid by the bromoform reaction. Any trace of 2-acetyladamantane, or its plausible derivative, was not detected. Substituted adamantanes (I) also gave bridgehead acetyladamantanes (II) regiospecifically and in excellent to good yields as shown in Scheme I. In the case of 1-methoxyadamantane (Ic), expected 1-acetyl-3-methoxyadamantane (IIc) was accompanied by adamantyloxyacetone (**IV**) in the ratio of 10/1.

Relative Reactivities. Sets of competitive reactions between two bridgehead-substituted adamantanes appropriately selected gave a series of relative reactivities of the three positions of 1-substituted adamantanes as shown in Table I. From a plot of the relative rates against σ^*[2] values, −0.71 was

Scheme I



I: (a) $R_1 = R_2 = H$.
(b) $R_1 = CH_3$, $R_2 = H$.
(c) $R_1 = OCH_3$, $R_2 = H$.
(d) $R_1 = CO_2CH_3$, $R_2 = H$.
(e) $R_1 = Br$, $R_2 = H$.
(f) $R_1 = R_2 = CH_3$

obtained as a ρ^* value of the present reaction. Adamantane was photoacetylated more than 100 times as fast as cyclohexane, so the latter was chosen as a relevant standard compound of secondary C–H, since the formation of bridge-substituted adamantanes is negligibly small.

Quenching and Quantum Yield. As shown in Table II, pyrene or oxygen showed a large influence on the reaction, the former quenched the photoacetylation completely and the latter, interestingly, accelerated the product formation in comparison with the run carefully deoxygenated and irradiated under nitrogen. Under oxygen, 1-acetyladamantane, 2-acetyladamantane, and 1-adamantanol[1] were obtained in the ratio of 3.4:1.5:1.

Quantum yields of the formation of 1-acetyladamantane and disappearance of biacetyl was found to be ca. 0.03 and 1.0, respectively, according to the standard method[15] utilizing

Scheme II

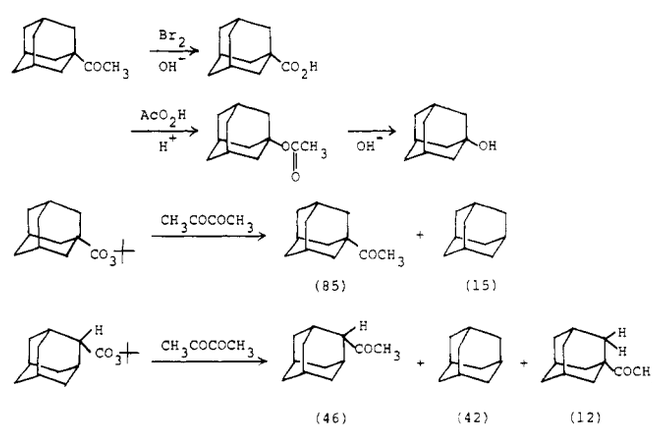


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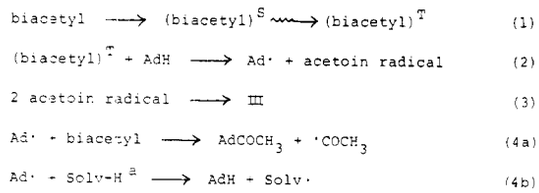
Table I. Relative Rates of Bridgehead Hydrogen Abstraction from Ad(1)X by the Photoexcited Biacetyl

X	Registry no.	σ^{*a}	k_X/k_H
CH_3, CH_3	702-79-4	−0.20	1.016 ± 0.012
CH_3	768-91-2	−0.10	0.879 ± 0.008
H	281-23-2	0.00	1.00 ± 0.028
OCH_3	6221-74-5	0.52	0.403[b]
CO_2CH_3	711-01-3	0.71	0.220 ± 0.0036
Br	768-90-1	1.00	0.0528 ± 0.0004[c]

[a] Inductive effects estimated from Taft's σ^* values for a series of CH_2X were adopted in ref 2. [b] Taken as a standard, k was statistically corrected. [c] This value was not considered in the calculation of ρ^* because of low yield.

Scheme III



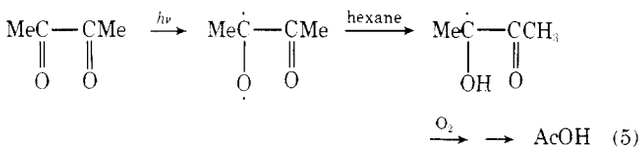
potassium ferrioxalate actinometer.[16] The concentrations employed were 8.4×10^{-2} mol/L of adamantane and 1.66 mol/L of biacetyl.

Decomposition of *tert*-Butyl Adamantaneperoxycarboxylates in Biacetyl. In similar procedure to the general perester preparation,[17] *tert*-butyl 1- and 2-peroxyadamantanecarboxylates were prepared and these peresters were decomposed in biacetyl. Results were shown in Scheme II. 1-Adamantyl perester gave adamantane and 1-acetyladamantane in a ratio of 15:85 and the combined yield was 56% based on *tert*-butyl 1-peroxyadamantanecarboxylate used. 2-Adamantyl perester gave adamantane and 1- and 2-acetyladamantane in a ratio of 42:12:46 and the combined yield was 60% again based on the perester used. No other product was detected.

Discussion

Nature of Hydrogen Abstracting Species. The present photoacetylation (product formation) was completely quenched by the addition of pyrene in an irradiating solution as shown in Table II. This finding indicates that the reaction proceeds via the triplet state of biacetyl since pyrene was reported to quench biacetyl phosphorescence in a nearly diffusion controlled rate through triplet energy transfer.[18] Thus, the mechanism shown in Scheme III was proposed.

In an interesting contrast to the pyrene quenching, oxygen *accelerated* the product formation of the present photoacetylation as shown in Table II. Oxygen is known to quench biacetyl phosphorescence again in a nearly diffusion-controlled rate[19] to give acetic acid.[20] A presented mechanism for acetic acid formation (eq 5) alone, however, does not interpret

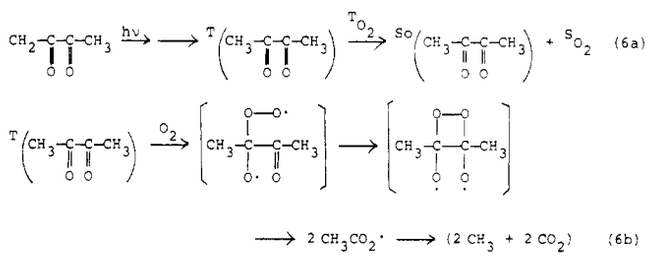


the observation of the efficient phosphorescence quenching. To interpret both of the reported facts, either the direct energy transfer from biacetyl triplet to ground oxygen leading to the formation of ground biacetyl and singlet oxygen, or some interaction between these in such a way as shown in Scheme IV (eq 6b), should be operative. The present finding of somewhat unusual acceleration of the product formation can be understood by accepting the above mechanism (eq 6b), where concentration of acetoxyl and/or methyl radical increases, resulting in the observed acceleration of the photoacetylation as well as induced autoxidation. The formation of a considerable amount of 2-acetyladamantane is consistent with the expected low regioselectivity of acetoxyl and/or methyl radicals. Generation of adamantanol under oxygen also supports the mechanism.

Table II. Effect of Pyrene or Oxygen on the Photoacetylation of Adamantane (2.0 g of Adamantane, 10.0 g of Biacetyl in 70 mL of Methylene Chloride)

Condition	1-Acetyladamantane, %	2-Acetyladamantane, %	1-Adamantanol, %
N_2, 2.0 h	13.8		
N_2, 235 mg of pyrene added, 2.0 h	0.0		
O_2, 1.5 h	28.6	12.3	8.3

Scheme IV



Hydrogen Abstraction and Acetyl Transfer. The second step of the reaction is the hydrogen abstraction from adamantane by triplet biacetyl (reaction 2 in Scheme III), which abstracts hydrogen from 2-propanol or ethanol.[21-23] Another product obtained was III (in approximately equimolar amount to acetyladamantane) as expected from the coupling of considerably stable acetoin radicals thus formed (reaction 3 in Scheme III). III was often produced in the solution photochemistry of biacetyl.[21-23] Adamantyl radical thus formed seems to give acetyladamantane by the transfer reaction with ground biacetyl not via the coupling with acetyl radical. The facile formation of 1-acetyladamantane (85% of total products) from 1-adamantyl radical generated by the thermolysis of the corresponding perester in biacetyl as shown in Scheme II supports the acetyl transfer mechanism (eq 4a) as the major path of the acetylation. A considerable amount (15% of total products) of adamantane was also detected, indicating the concurrent hydrogen abstraction (eq 4b). Similarly, 2-adamantyl radical gave 2-acetyladamantane (46%) as one of the major products, but 1-acetyladamantane (12%) was also formed together with adamantane (42%). Formation of the latter two compounds from 2-adamantyl radical is best interpreted by the mechanism of eq 9–12 via formation of adamantane. A ratio of transfer rate constant to abstraction rate constant was thus estimated for 1- or 2-adamantyl radical from the corresponding product ratio (see Scheme V). Relatively low value of k_{tr}/k_{ab} for 2-adamantyl radical may arise from larger steric hindrance in a transition state of 2-adamantyl transfer step (eq 9), since the steric effect is known to be a controlling factor in the atom transfer step of 2-adamantyl radical[1] (vide infra).

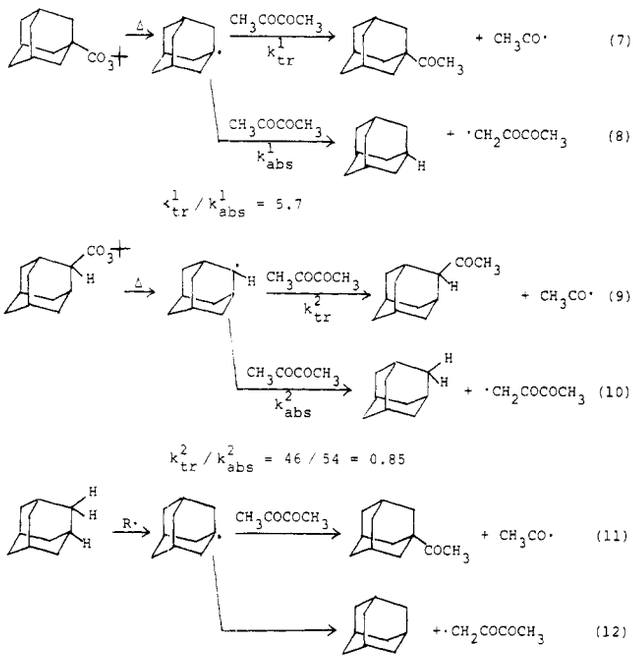
The quantum yield of the formation of acetyladamantane was ca. 0.03 and that of the disappearance of biacetyl was ca. 1. These values indicate that the major reaction for biacetyl[24] was its photodecomposition investigated earlier.[25] Acetyl radical from reaction 4 or methyl radical from the decarbonylation of acetyl may be a chain carrier of the decomposition of biacetyl. The low yield of acetylated compound in the case

Table III. BH/BR Reactivity Ratios

Attacking radical	BH/BR	Ref	ρ^*
·Cl	1.9–6.3	32	
·Br	9.0	1	−0.59[a]
·CH_2Br	9.0	1	
·CCl_3	24.3	1	−0.40[b]
T (biacetyl)	∞	This work	−0.71

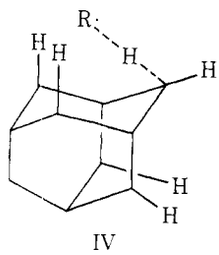
[a] Reference 27. [b] Reference 2.

Scheme V



of radical reaction utilizing initiator[26] may also be explained on the same grounds.

Exclusive Bridgehead Substitution. Although a radical in nature, biacetyl triplet in the present photoacetylation has a characteristic of exclusive bridgehead substitution. Reasonable assumptions to interpret this characteristic are: (i) Nearly exclusive hydrogen abstraction at bridgehead by triplet biacetyl, or (ii) much less facile acetyl transfer to adamantyl bridge than bridgehead radical from biacetyl. Among these, assumption (ii) is not the major product determining factor because adamantyl-2 radical, once formed, should give 2-acetyladamantane in ca. 30% yield (loc. cit.) in the presence of biacetyl (see Scheme V). Thus the conclusion may be drawn that the bridge hydrogen is not appreciably abstracted by triplet biacetyl. This very low reactivity of the bridge hydrogen toward radical abstraction may be due to the significant nonbonded repulsion between the attacking radical and β-axial hydrogens in the transition state IV. In Table III,



IV

bridgehead/bridge reactivity ratios were listed for a series of radical species. Comparing with other abstracting species, biacetyl should be very bulky in a sense that remote nonbonded repulsion is important. As is apparent from the table, *polar* effect (magnitude of ρ^*) is not reflected by the observed reactivity ratio (vide infra).

Large ρ^* Value. From a series of competitive experiments on substituted adamantanes, the ρ^* value of the photoacetylation was estimated to be −0.71. For comparison, several ρ values are shown in Table IV. Reported ρ^+ values for the benzylic hydrogen abstraction from substituted toluenes are multiplied by 0.4/1.46 in order to draw direct comparison with ρ^* for adamantanes, taking trichloromethyl radical as a standard. The present photoacetylation gives the largest ρ^* value among the radical substitutions investigated and it is considerably larger than that for benzophenone which is estimated to be −0.32 or −0.49. It is suggested[2] that the ρ^* value was a direct indicator of positive charge developed in the transition state of hydrogen abstraction. Oxygen atom in the ($n\pi^*$) state is formally half electron deficient and thought to be highly electrophilic.[28] The highly electrophilic character of the oxygen of triplet biacetyl (much stronger than triplet benzophenone on the basis of ρ^* values observed) may be due to electron withdrawal of the neighboring acetyl group.

Experimental Section

Materials. Commercially available adamantane and biacetyl were used with purification. 1-Bromoadamantane,[5] 1-adamantanecarboxylic acid,[6] 1-carbomethoxyadamantane,[6] and 1-methoxyadamantane[2] were prepared according to the literature.

***tert*-Butyl 1-Peroxyadamantanecarboxylate.** A dry pentane solution (5 mL) of 1-adamantanecarbonyl chloride, prepared from 1-adamantanecarboxylic acid (900 mg; 5 mmol) and thionyl chloride (6 mL), was kept at −6 to −7 °C. Into the solution was added a pentane solution (20 mL) of *tert*-butyl hydroperoxide (460 mg; 5.1 mmol) and pyridine (410 mg) dropwise and with stirring for 30 min. After the addition was over, the solution was further stirred below 0 °C for a few hours and allowed to warm up to room temperature and then kept overnight. The white precipitate was filtered and the filtrate was washed with dilute aqueous $NaHCO_3$ and then with water. The pentane solution was dried over $MgSO_4$ and evaporated. The residual oil was purified on a silica gel column using benzene as an eluent. Thus 420 mg (33%) of the perester was obtained. Spectral data were consistent with the literature.[29]

***tert*-Butyl 2-Peroxyadamantanecarboxylate.** 2-Adamantanecarboxylic acid was prepared by the free-radical chlorocarbonylation[12] of adamantane followed by esterification, fractional distillation, and hydrolysis.[12] *tert*-Butyl 2-peroxyadamantanecarboxylate was prepared in 49% yield from 2-adamantanecarboxylic acid by a similar procedure used for *tert*-butyl 1-peroxyadamantanecarboxylate: mp 61.0–62.0 °C; IR (neat) 2930, 1770, 1190, and 1165 cm^{-1}; NMR ($CDCl_3$) δ 1.37 (9 H, *tert*-butyl, singlet), 1.7–2.1 (12 H, multiplet), 2.1–2.5 (2 H, multiplet), 2.73 (1 H, α-H of the perester, multiplet).

Thermolysis of *tert*-Butyl 1-Peroxyadamantanecarboxylate. A solution of *tert*-butyl 1-adamantaneperoxycarboxylate (540 mg, 2.14 mmol) and biacetyl (7.544 g, 87.5 mmol) was kept at 80 °C for 2 h in a sealed tube. Products obtained were adamantane and acetyladamantane and any other product was not detected. Yields of adamantane and 1-acetyladamantane were found to be 8.5 and 48%, respectively. 2-Acetyladamantane was not detected at all by GLC or NMR which was investigated for acetyladamantane collected by preparative GLC.

Thermolysis of *tert*-Butyl 2-Adamantaneperoxycarboxylate. A solution of *tert*-butyl 2-adamantaneperoxycarboxylate (540 mg, 2.14 mmol) and biacetyl (7.544 g, 87.5 mmol) was kept at 80 °C for 70 h[30] in a sealed tube. Yields of adamantane and acetyladamantanes were found to be 25 and 35%, respectively, from the GLC analysis. Separation of 1- and 2-acetyladamantane by GLC was very poor. For the determination of the ratio of 1- to 2-acetyladamantane, a mixture of acetyladamantanes collected by preparative GLC was analyzed by NMR spectrum on the methyl protons of 1- and 2-acetyl groups which appeared as sharp singlets at δ 2.04 and 2.09, respectively. The NMR methyl signal was further ascertained by acetyladamantanes in relevant syntheses (vide infra). Thus, the ratio of 1- to 2-acetyladamantane in the photoacetylation was determined as 21/79.

Preparation of 2-Acetyladamantane. 2-Acetyladamantane was prepared from 2-adamantanecarboxylic acid by a similar procedure as that reported for the preparation of 1-acetyladamantane[31] in 48% yield: bp 103–105 °C (15 mmHg); $\mu_{C=O}$ 1710 cm^{-1}; NMR (CCl_4) δ 2.09 (singlet, $COCH_3$) and 2.0–1.6 (multiplet, 15 H).

Table IV

Substrate	Abstracting species	Kind of σ employed	ρ	Ref
p-X-C_6H_4-CH_3	$\cdot CCl_3$	σ^+	−1.46	*e*
p-X-C_6H_4-CH_3	·Br	σ^+	−1.39	*f*
p-X-C_6H_4-CH_3	$(C_6H_5)_2\dot{C}$-$\dot{O}$	σ^+	−1.16	*g*
p-X-C_6H_4-CH_3	·Cl	σ^+	−0.66	*h*
p-X-C_6H_4-CH_3	$(CH_3)_3C$-O·	σ and σ^+	−0.599[a], −0.35[b]	
1-X-$C_{10}H_{14}$-3-H[c]	·Br	σ^*	−0.59	27
1-X-$C_{10}H_{14}$-3-H	$\cdot CCl_3$	σ^*	−0.40	2
1-X-$C_{10}H_{14}$-3-H	$CH_3(CH_3CO)\dot{C}$-$\dot{O}$	σ^*	−0.71	This work
1-X-$C_{10}H_{14}$-3-H	$(C_6H_5)_2\dot{C}$-$\dot{O}$	σ^*	−0.32, −0.49[d]	

[a] In benzene (footnote *i*). [b] In 1,1,2-trichlorotrifluorethane (footnote *j*). [c] 1-Substituted adamantanes. [d] Extrapolated from ρ values for trichloromethyl radical-substituted toluene reactions by use of k_X/k_H and σ^* in Table I. [e] E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960). [f] R. E. Pearson and J. C. Martin, *ibid.*, **85**, 354 (1963). [g] C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965). [h] G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1964). [i] R. D. Gillion and B. F. Ward, Jr., *J. Am. Chem. Soc.*, **87**, 3944 (1965). [j] H. Sakurai and A. Hosomi, *ibid.*, **89**, 458 (1967).

Table V. NMR Spectra of Acetyladamantanes (CCl_4 or $CDCl_3$*, Me_4Si, δ)

Compd	Registry no.	NMR Spectra[a]
IIb*	42825-01-4	2.5–1.84 (m, 5 H) [2.09 (s, 3 H)], 1.80–1.30 (m, 12 H), 0.84 (s, 3 H)
IIc	42825-02-5	3.17 (s, 3 H), 2.40–2.10 (m, 2 H), 2.03 (s, 3 H), 1.77–1.47 (m, 12 H)
IV	42824-40-8	3.80 (s, 2 H), 2.16 (s, 3 H)
IId	42825-03-6	3.64 (s, 3 H), 2.25–2.10 (m, 2 H), 2.05 (s, 3 H), 1.95–1.65 (m, 12 H)
IIe	39917-43-6	2.40–2.20 (m, 6 H), 2.2–2.06 (m, 2 H), 2.04 (s, 3 H), 1.83–1.47 (m, 6 H)
IIf	40430-57-7	2.14 (m, 1 H), 2.00 (s, 3 H), 1.77–1.53 (m, 2 H), 1.53–1.27 (m, 8 H), 1.27–1.10 (m, 2 H), 0.87 (s, 6 H)

[a] m, multiplet; s, singlet.

Determination of Quantum Yield. Quantum yields of the formation of acetyladamantane and disappearance of biacetyl were determined by the standard method[15] with a potassium ferroxalate actinometer.[16] A three-compartment quarz cell of optical paths of 5, 5, and 10 cm was used. In the front cell $CoSO_4$ solution (8.4 g/100 cm^3),[15] in the central cell methylene chloride solution (35 mL) of adamantane (400 mg) and biacetyl (5 g), and in the rear cell $K_3Fe(C_2O_4)_3$ solutions (0.006 M)[15] were placed. The amounts of acetyladamantane that formed and biacetyl that disappeared were determined by GPC. Thus quantum yield was estimated to be ca. 0.03 for the formation of 1-acetyladamantane and ca. 1.0 for the disappearance of biacetyl.

Competitive Reactions. 1-Methoxyadamantane was used as a reference compound to investigate the relative reactivity of a 1-substituted adamantane. Thus, 2 g of 1-methoxyadamantane and an appropriate amount of a 1-substituted adamantane (the amount of the latter was calculated on the basis of the preliminary results of the competitive reaction so as to give roughly the equimolar amount of acetylated products from 1-methoxy and from the other adamantane in order to maximize the precision on GPC analyses) were irradiated in a Pyrex vessel with a 100-W high-pressure mercury lamp in methylene chloride solution (90 mL) of biacetyl (20 mL) under nitrogen. The relative rate of the formation of 1-bridgehead-substituted 3-acetyladamantane was followed by GPC. Based on the observed product ratio, k_X/k_{OCH_3} (methoxyadamantane is taken as a standard) was calculated in a similar way as in the literature,[2] where K_X is rate constant for 1-X-substituted adamantane (see Table I) and k_X/k_{OCH_3} was converted into k_X/k_H. The mean value from several runs was shown in Table I.

Preparative Photoacetylation. As a typical example, photoacetylation of adamantane is described. The procedure is practically the same for any other substituted adamantane. A solution of adamantane (5.0 g) and biacetyl (30 mL) in methylene chloride (80 mL) was irradiated in a Pyrex vessel by a high-pressure 100-W mercury lamp with water cooling under nitrogen for 8.5 h. Methylene chloride was distilled off and the adamantane that precipitated was collected and washed with methanol. The filtrate was further condensed to gain an additional crop of unreacted adamantane which was washed with methanol. Thus, from the precipitate was recovered 3.9 g of practically pure adamantane. The filtrate was distilled and the distillate at 72–82 °C (5 mmHg) was collected, dissolved in methylene chloride, and washed with 0.1 N NaOH solution. The organic layer was dried over $CaCl_2$ and methylene chloride was distilled off. From the residue practically pure 1-acetyladamantane was obtained (1.33 g, 92%) through a silica gel column eluted with petroleum ether, mp 53–54 °C (MeOH–H_2O) (lit.[31] mp 53–54 °C). Yields of isolated acetyladamantanes based on adamantanes consumed are described below in parentheses. NMR spectra are shown in Table V.

1-Acetyl-3,5-dimethyladamantane (IIf): 89%; $n^{25}D$ 1.4900; IR (neat) 1700 (C=O), 1230, 1170 cm^{-1}; mass spectrum *m/e* (fragment assigned, rel intensity) 206 (M^+ 3.66), 165, 164, and 163 ($Ad(Me)_2^+$, 21.5, 93.2, 98.5), 107 (100).

1-Acetyl-3-carbomethoxyadamantane (IId): 75%; $n^{25}D$ 1.4967; IR (neat) 1730 and 1700 (C=O), 1260, 1210, 1090 cm^{-1}; mass spectrum *m/e* (fragment assigned, rel intensity) 236 (M^+, 8.1), 194 and 193 ($AdCO_2CH_3^+$, 20.8, 100), 177 ($AdCOCH_3^+$, 13.6), 161 (35.0), 137, 136 and 135 (Ad^+, 11.0, 16.2, 79.2).

1-Acetyl-3-bromoadamantane (IIe): 22%; $n^{25}D$ 1.5395; IR (neat 1700 (C=O), 1220 cm^{-1}; mass spectrum *m/e* (fragment assigned, rel intensity) 258, 257, and 256 (M^+, 0.15, 0.075, 0.17), 213, 214, 215, and 216 ($AdBr^+$, 3.84, 37.0, 4.34, 37.8).

1-Acetyl-3-methoxyadamantane (IIc): 58%; $n^{25}D$ 1.4971; IR (neat) 1700 (C=O), 1120, 1100, 1060 cm^{-1}; mass spectrum *m/e* (fragment assigned, rel intensity) 209 and 208 (M^+, 1.9, 15.5), 177 ($AdCOCH_3^+$, 2.07), 166 and 165 ($AdOMe^+$, 26.8, 100).

1-Adamantyloxyacetone (IV): 5.2%; IR (neat) 1720 (C=O), 1360, 1120, 1100 cm^{-1}; mass spectrum (fragment assigned, rel intensity) 208 (M^+, 0.9), 198 (2.8), 178 (10.2), 166 and 165 ($AdOCH_2^+$, 1.33, 12.0), 136 and 135 (Ad^+, 33.0, 100).

1-Acetyl-3-methyladamantane (IIb): 86%; $n^{25}D$ 1.4901; IR (neat) 1700 (C=O), 1230, 1140 cm^{-1}; mass spectrum *m/e* (fragment assigned, rel intensity) 193 and 192 (M^+, 0.66, 4.25), 177 ($AdCOCH_3^+$, 0.72), 150 and 149 ($AdMe^+$, 13.5, 100).

Registry No.—IIa, 1660-04-4; *tert*-butyl 1-peroxyadamantanecarboxylate, 21245-43-2; 1-adamantanecarbonyl chloride, 2094-72-6; *tert*-butyl 2-peroxyadamantanecarboxylate, 53561-90-3; 2-adamantanecarboxylic acid, 15897-81-1; 2-acetyladamantane, 22635-58-1; biacetyl, 431-03-8.

References and Notes

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Correlation of Rate–Solvent Effects in Ionogenic Reactions

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There is ample evidence that a relation of log k with some commonly employed solvent parameter at a given temperature is not always a reliable index of the polarity of the activated complex. Through study of the temperature dependence of log k as a function of an empirical solvent property, viz. $\Delta G^{\ddagger}$ vs. (say) E_T, some perception of the ionogenic character of a reaction can be gained. The principal objective of this report is to show in some instances that the same rate data may be correlated with a universal and directly measurable property of matter, namely the dielectric, to permit a more quantitative and informative comparison of reaction transition states with respect to their polarities. For ionogenic reactions, where the activated complex possesses a significant dipole moment, a simple electrostatic argument based on the model developed by Kirkwood[9] is used to derive relationships between the activation parameters and readily accessible functions of the solvent dielectric (eq 9 → 13). These relationships have been tested by data gathered for two well known cases, the thermolysis of α-chlorobenzyl alkyl ethers[1] and the cycloaddition of TCNE to enol ethers,[8,10] both in aprotic solvents. In both cases the linear relationship involving activation free energy is found to be relatively insensitive to the occurrence of "chemical" interactions between the solvent and zwitterionic activated complex. However, though this treatment predicts an inverse linear correlation of negative activation entropy and solvent polarity, it is shown that "chemical" contributions of this nature can destroy the linearity and steeply invert the relationship so that the most polar solvents appear to be associated with the most negative entropies of activation. But, for a transition state of sufficiently high dipole moment, the "chemical" contribution term tends to predominate over the solvent dielectric term and to influence the $\Delta S^{\circ\ddagger}$ in such a way as to restore the appearance of linearity for all cases except those in which the solvent has nearly zero polarizability.

The use of empirical solvent parameters as a means of correlating solvent effects on rate has developed greatly since the introduction of the Winstein–Grunwald Y-value scale.[1a] Others such as the Kosower Z values[1b] and the Reichardt E_T values[1c] have gained widespread application in probing the polarity of the activated complex. Such applications rely on the occurrence of a simple linear plot of log k vs. (say) E_T at a given temperature, the steepness of the slope of the resulting line being accepted as a proportional measure of transition state polarity. But the information to be realized from this exercise is frequently of limited value; such factors in a polar transition state as charge separation and dipole moment do not emerge from the empirical solvent parameter relationship with rate.

Moreover, it is by no means unusual for an ionogenic reaction to display an inverse relationship between rate and an empirical measure of solvent polarity at a single temperature. Under circumstances where this is close to the isokinetic temperature,[2,3a] a frequently undetected occurrence, plots of log k vs.(say) E_T can be illusory. Two recent examples come to mind in which, at the given temperature, the observed inverse relationship of rate and solvent polarity suggested a non-ionogenic or a concerted process with an unpolarized transition state, namely, the thermolysis of trimethylsilylacetophenones to siloxyalkenes[2] and the corresponding rearrangement of aryl allyl sulfides[4] in aprotic solvents. Unequivocal evidence has subsequently been found to demonstrate the intervention of zwitterionic activated complexes in both of these cases.[3,4]

In a previous article[5] reporting on the thermolysis of α-chloro ethers in aprotic solvents, it was noted that the activation parameters E_a, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ for the reaction in seven solvents showed a decreasing trend with increasing ionizing character of the solvent. These results in conjunction with

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