Acyl Migration in the Acid-Catalyzed Decomposition of α-Hydroperoxy Ketones

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Abstract: The CF_3CO_2H-catalyzed decomposition of α-hydroperoxy ketones ($R_1COC(OOH)R_2R_3$, **1**) in benzene proceeds in most cases via acyl migration affording carboxylic acids R_1CO_2H and ketones $R_2R_3C\!=\!O$. The decomposition obeys the rate equation $v = k_2[\text{acid}][\mathbf{1}]$ and is retarded by weak bases, e.g., benzophenone, MeCN, and dioxane. The effect of added amine suggests a general acid catalysis by the free acid. The substituent effect in the nonmigrating phenyl ring (R_3) gives $\rho = -0.82$ correlated with σ^+, while the effect in the migrating benzoyl ring ($R_1C\!=\!O$) affords $\rho = -2.23$ with σ. The relative migratory aptitude of acyl groups is in the order $PhC\!=\!O < MeC\!=\!O < i\text{-}PrC\!=\!O$. These results suggest that the order of acyl migration is determined by the electron-releasing power of R_1 and the facile migration of acyl groups is related to the resonance stabilization with lone pair electrons of carbonyl oxygen. Aryl (R_3) migration becomes competitive with benzoyl migration only when $R_3 = p$-anisyl and p-tolyl. The migration ratio of p-anisyl/benzoyl changes from 0.04 to 2.5, increasing with increasing acidity of the catalyst. This is explained by the difference of the extent of developing positive charge in the transition state of migration between the aryl and the benzoyl shifts.

Rearrangements involving nucleophilic 1,2 shifts of alkyl and aryl groups to a cationic center are extensively studied.[1] A similar migration of acyl groups has been noted in the Beckmann rearrangement[2] and the BF_3-catalyzed reaction of epoxides,[3] where the migratory aptitude is in the order Ph > PhC=O > H > Me.[3a-d] Recently, a pinacol-type rearrangement of acyl group was reported[4a] together with migrations of alkoxycarbonyl group.[4b-e] Acyl migration also occurs in the decomposition of peroxides,[5-7] where a migratory order tertiary alkyl > MeC=O > secondary alkyl is known.[7] However, the nature of acyl migration is not well understood because the quantitative data are poor.

Recently, we reported the alkoxide-catalyzed[8] and the thermal or redox decomposition[9a] and the photolysis[9b] of α-hydroperoxy ketones (**1**). Here, we wish to describe our quantitative data for the facile 1,2 shift of acyl group in the acid-catalyzed decomposition of α-hydroperoxy ketones (**1**).

Results

Acid-catalyzed decomposition of α-hydroperoxy ketones (**1**) in benzene at 25 °C afforded mostly ketones and carboxylic acid (eq 1). Here, HA is CF_3CO_2H in most runs and

$$R_1C\!\!-\!\!CR_2R_3 \xrightarrow{\text{HA}} R_1CO_2H + R_2R_3C\!=\!O \qquad (1)$$
$$\underset{O}{\|} \quad \underset{OOH}{|}$$
$$\mathbf{1}$$
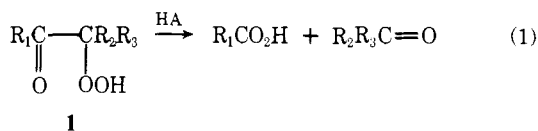
$ClCH_2CO_2H$ in some runs. The products were determined by GLC and the rate was followed iodometrically.

Effect of Acidity. The CF_3CO_2H-catalyzed decomposition of **1** fits pseudo-first-order kinetics with respect to the peroxide to give k_{obsd}, and the linearity of the plot of k_{obsd} vs. [HA] suggests the rate equation 2 (Table IA and Figure 1).

$$v = k_{\text{obsd}}[\text{ROOH}] = k_2[\text{HA}][\text{ROOH}] \qquad (2)$$

Here, ROOH is peroxide **1** and HA is trifluoroacetic acid. The straight line of the plot of k_{obsd} vs. [HA] does not intercept the origin, which is probably due to the hydrogen bonding of HA with reactants and products. The rates are decreased by the addition of benzophenone, dichloromethane, acetic acid, or acetonitrile (Table IB), and the reaction is practically stopped by adding dioxane or ethanol.

The retardation is more definite when N,N-dimethylaniline is added; the rate is lowered to 64 and 11% by adding 10 and

20 mol % of the amine (based on HA), respectively (Table II). The data in the last column in Table II show that 1 mol of the amine deactivates ca. 4.5 mol of HA.

Substituent Effect. The electron-releasing group on benzoyl group increases the rate of decomposition and the substituent effect affords $\rho = -2.23$ correlated with σ ($r = 0.999$) as shown in Table IIIA. On the other hand, the substituent effect in the nonmigrating phenyl (R_3) affords $\rho = -0.82$ with σ^+ ($r = 0.952$) as shown in Table IIIB.

The results for various types of **1** are summarized in Table IV. Although the decomposition rates of **1** do not differ so much from that of cumene hydroperoxide, the rates change significantly with the structure of **1**. Firstly, when $R_1 = R_2 = Ph$, the rate order for R_3 is $PhCH_2 < Et < Me < i$-Pr. Secondly, when $R_2 = Ph$ and $R_3 = PhCH_2$, the effect of $R_1C\!=\!O$ has the order of $PhC\!=\!O < MeC\!=\!O < i\text{-}PrC\!=\!O$, which is probably the order of electron-releasing power of R_1. Thirdly, the rate for $R_2 = R_3 = Me$ is extremely slow.

Products. The acid-catalyzed decomposition of **1** in benzene proceeds mostly via acyl ($R_1C\!=\!O$) migration to give high yields of ketone $R_2R_3C\!=\!O$ and carboxylic acid R_1CO_2H (eq 1). But, only for the case of **1f** ($R_3 = p$-anisyl) and **1g** ($R_3 = p$-tolyl), aryl (R_3) migration also occurs competitively to give phenol R_3OH and diketone R_1COCOR_2 (Table V).

Table VI lists the results of acid-catalyzed decomposition of **1f** ($R_3 = p$-anisyl), exhibiting the competitive migration of p-anisyl and benzoyl groups. The decomposition rate of **1f** increases with increasing $[CF_3CO_2H]$ and so the migration ratio of anisyl:benzoyl; e.g., the ratio is 8:2 with 0.01 M acid but 3:7 with 0.2 M acid. This tendency is also apparent from the predominant migration of benzoyl in the $ClCH_2CO_2H$-catalyzed reaction. The decomposition with acetic acid is too slow at 25 °C.

Discussion

Acid Catalysis. Acid-catalyzed decompositions of hydroperoxides proceed via specific acid catalysis, i.e., via protonation in aquoorganic solvents,[10] and general acid catalysis is noted only for the case of diacyl peroxides in organic solvents.[11] The acid-catalyzed decomposition of hydroperoxides is complex because of possible protonation at either one of two peroxidic oxygens,[10] and the benzenesulfinic acid catalysis in benzene has rates of second or third order with respect to the acid.[12]

Table I. Acid-Catalyzed Decomposition of PhCOC(OOH)Ph₂ (1a) in Benzene at 25.0 °C[a]

| [CF₃CO₂H], M	Conditions[b]	$10^3 k_{obsd}$, s⁻¹
A. Effect of [CF₃CO₂H]		
0.010		0.037
0.025		0.172
0.050		0.505
0.075		0.938
0.10		1.40
0.20		3.32
0.30		5.30
B. Effect of Additives		
0.10		1.40
0.10	0.01 M Ph₂C=O	1.19
0.10	0.10 M Ph₂C=O	0.458
0.10	20% CH₂Cl₂	0.972
0.10	20% AcOH	0.028
0.10	20% MeCN	0.0095
0.10	20% dioxane	<0.0001
0.10	20% EtOH	<0.0001

[a] Reaction with [1a] = 0.010 M. [b] Reaction in pure benzene unless otherwise noted (percent is expressed in volume percent).

Table II. Effect of the Addition of *N,N*-Dimethylaniline on the Rate of Acid-Catalyzed Decomposition of MeCOC(OOH)(Ph)-CH₂Ph (1n)[a]

[HA], M	[PhNMe₂], M	Amine/HA, mol %	$10^3 k_{obsd}$, s⁻¹	Rate decrease, %	% decrease/ (% amine/HA)[b]
0.167	0	0	0.310		
0.167	0.0042	2.5	0.261	15.8	~6.3
0.167	0.0084	5.0	0.241	21.3	4.3
0.167	0.0167	10.0	0.198	36.1	3.6
0.167	0.0250	15.0	0.100	67.7	4.5
0.167	0.0334	20.0	0.035	88.8	4.4

[a] Reaction with [1n] = 0.083 M in benzene at 25 °C. HA is CF₃CO₂H. [b] This ratio corresponds to the molar ratio of the deactivated HA vs. added amine.

But the rate of present decomposition of 1 in benzene is proportional to [CF₃CO₂H] as shown in Figure 1, indicating a general acid catalysis. This can be ascertained by the effect
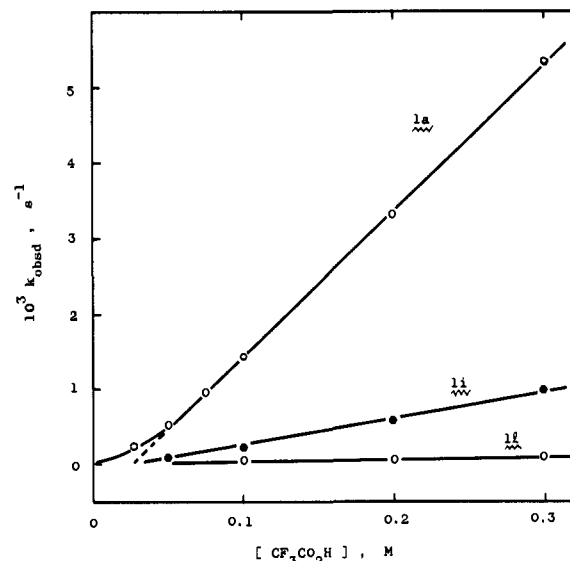
Figure 1. Effect of [CF₃CO₂H] on k_{obsd} in benzene at 25.0 °C (see Tables I and IV for the conditions and data).

of the added amine on the rate. That is, a linear plot of k_{obsd} vs. [amine] is obtained as shown in Figure 2, which indicates that 1 mol of amine deactivates ca. 4.5 mol of the acid (Table II). This mode of deactivation by tertiary amine R₃N implies the following scheme:

$$R_3N + HA \rightleftharpoons R_3NH^+ + A^- \qquad (3a)$$

$$A^- + 3.5HA \rightleftharpoons A^- \cdots \cdots (HA)_{3.5} \qquad (3b)$$

After consumption of 1 mol of HA, trifluoroacetic acid, by the amine R₃N (eq 3a), 3–4 mol of HA is associated with the produced carboxylate ion A⁻ via hydrogen bonding (eq 3b). This assumption is reasonable since the added amine is completely protonated under the conditions of Table II,[13] and CF₃CO₂⁻ has two basic oxygens, and since CF₃CO₂H is a strong acid,[14] i.e., a strong hydrogen donor. This is also supported by a similar fact that 3 mol of ROH is hydrogen bound to HO⁻ in benzene[15a] and in water (R = H).[15b]

The data in Table II and the linearity in Figure 2 together with the UV data[13] suggest that the equilibria of eq 3a and 3b

Table III. Effect of Ring Substituents on the Acid-Catalyzed Decomposition of 1 in Benzene at 25.0 °C[a]

	R₁COC(OOH)R₂R₃ R₁, R₂, R₃	$10^3 k_{obsd}$, s⁻¹ 0.05 M HA	0.10 M HA	$10^3 k_2$,[b] M⁻¹ s⁻¹
A. Substituent Effect for Migrating Benzoyl Group				
1b	*p*-MeOPh, Ph, Ph	2.40	6.22	76.5
1c	*p*-MePh, Ph, Ph	0.952	2.88	38.3
1a	Ph, Ph, Ph	0.505	1.40	19.3
1d	*p*-ClPh, Ph, Ph	0.133	0.413	5.60
1e	*m*-ClPh, Ph, Ph	0.052	0.184	2.64
	ρ (σ)			−2.23 (r = 0.999)
	ρ (σ⁺)			−1.28 (r = 0.948)
B. Substituent Effect for Nonmigrating Group				
1f	Ph, Ph, *p*-MeOPh	1.19[c]	4.70[c]	70.2
1g	Ph, Ph, *p*-MePh	0.425	1.42	19.8
1a	Ph, Ph, Ph	0.505	1.40	19.3
1h	Ph, Ph, *p*-ClPh	0.265	0.793	10.6
	ρ (σ)			−1.38 (r = 0.867)
	ρ (σ⁺)			−0.82 (r = 0.952)

[a] Reaction with [1] = 0.01 M. HA = CF₃CO₂H and Ph = C₆H₄ or C₆H₅. [b] The k_2 values were calculated from the slope of plot of k_{obsd} vs. [HA] (see eq 2). [c] The value is a rate constant for benzoyl migration, which was estimated from k_{obsd} and the selectivity for *p*-methoxydeoxybenzoin (see Table VI).

Table IV. Comparison of CF_3CO_2H-Catalyzed Decomposition of Various Types of α-Hydroperoxy Ketones[a]

	$R_1COC(OOH)R_2R_3$			10^3k_{obsd}, s^{-1}			10^3k_2,[b]
	R_1	R_2	R_3	0.1 M HA	0.2 M HA	0.3 M HA	M^{-1} s^{-1}
1a	Ph	Ph	Ph	1.40	3.32	5.30	19.3
1i	Ph	Ph	Me	0.194	0.553	0.924	4.53
1j	Ph	Ph	Et	0.234	0.502		2.7
1k	Ph	Ph	i-Pr	1.55	3.1		~16
1l	Ph	Me	Me	0.0175	0.0654	0.104	0.45
1m	Ph	Ph	PhCH$_2$	0.051	0.112	0.201	0.84
1n	Me	Ph	PhCH$_2$	0.152	0.375	0.623	2.35
1p	i-Pr	Ph	PhCH$_2$	3.48[c]			48[c]
PhCMe$_2$OOH[d]				0.226	0.914	1.88	8.5

[a] Reaction with [1] = 0.01 M in benzene at 25 °C. HA is CF_3CO_2H and Ph is C_6H_5 or C_6H_4. Migrating group is R_1CO except for the case of cumene hydroperoxide. [b] See footnote b, Table III. [c] The k_{obsd} value is 1.07×10^{-3} s^{-1} with [HA] = 0.05 M. [d] Cumene hydroperoxide, where migrating group is phenyl.

Table V. Products from the CF_3CO_2H-Catalyzed Decomposition of 1 in Benzene at 25 °C[a]

Peroxide (R_3)	Migrating group	Products, %[b]			
		R_1CO_2H	$R_2R_3C=O$	R_1COCOR_2	Others
1a (Ph)	$R_1C=O$	100	95	0	
1b–e,h (Ph)	$R_1C=O$	71–102	91–102	0	
1g (p-MePh)	$R_1C=O + R_3$	95	101	4	
1f (p-MeOPh)	$R_1C=O + R_3$	27	34	65	p-MeOPhOH (36%)
1i–m (Alkyls)	$R_1C=O$	50–99	80–94	0	
1n,p (PhCH$_2$)	$R_1C=O$	c	90–97	0	
PhCMe$_2$OOH[d]	Ph				PhOH (88%)

[a] Reaction with [peroxide] = 0.01 M and [CF_3CO_2H] = 0.1 M for 0.5–50 h. Ph is C_6H_5 or C_6H_4. [b] Yields were determined by GLC analysis in comparison to authentic samples. Benzoic acids were analyzed as esters after methylation with diazomethane. [c] Not determined. [d] Cumene hydroperoxide.

Table VI. Effect of Acidity on the Decomposition of $PhCOC(OOH)Ph(p\text{-MeOPh})$ (1f) in Benzene at 25.0 °C[a]

HA	[HA] M	10^3k_{obsd}, s^{-1}	PhC=O		p-MeOPh		PhC=O:p-MeOPh[b]
			PhCO$_2$H	p-MeOPhCOPh	p-MeOPhOH	PhCOCOPh	
CF_3CO_2H	0.01	0.078	53	81	11	20	80:20
	0.025	0.514	42	55	17	39	59:42
	0.05	2.49	34	50	30	55	48:52
	0.10	10.9	27	34	36	65	34:66
	0.20	c	17	28	37	69	29:71
$ClCH_2CO_2H$	0.10	0.0047	c	76	0	2.7	97:3
	0.20	0.0093	c	59	0	3.2	95:5
CH_3CO_2H	0.20	<0.0001[d]					

[a] Reaction with [1f] = 0.01 M. Products were determined as described in footnote b, Table V. [b] Ratio of PhC=O vs. p-MeOPh migration was calculated from the product ratio of p-methoxybenzophenone vs. benzil. [c] Not determined. [d] Too slow.
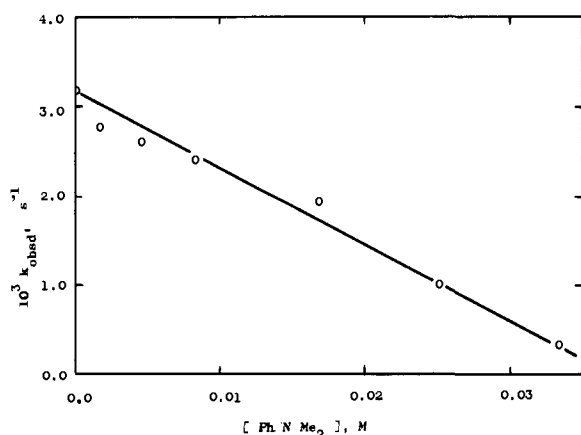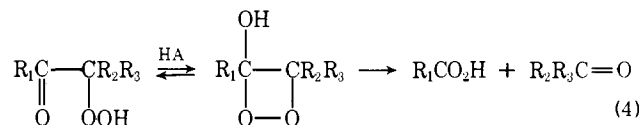

Figure 2. Effect of the addition of N,N-dimethylaniline on the rate of CF_3CO_2H-catalyzed decomposition of 1n in benzene at 25.0 °C. Initial concentrations: [1n] = 0.083 M; [CF_3CO_2H] = 0.167 M; [PhNMe$_2$] = 0–0.033 M.

shift much to the right and the catalysis is due to the free HA, i.e., general acid catalysis. The retardation by the basic solvent B such as dioxane is due to the deactivation of HA by the exclusive formation of B···HA because of the presence of excess B which is more basic than peroxide 1.[16]

Facile Acyl Shift. A conceivable scheme for the acid-catalyzed decomposition of 1 is a dioxetane mechanism (eq 4).

$$R_1C{\overset{\|}{\underset{O}{C}}}\overset{}{\underset{OOH}{C}}R_2R_3 \overset{HA}{\rightleftharpoons} R_1\overset{OH}{\underset{O-O}{C}}CR_2R_3 \longrightarrow R_1CO_2H + R_2R_3C=O \tag{4}$$

However, this is denied by the following examinations.

(1) The CF_3CO_2H-catalyzed decomposition occurs, though slowly, for the case of $PhCOC(OO\text{-}t\text{-Bu})Ph_2$ which is incapable of cyclizing to dioxetane.[17]
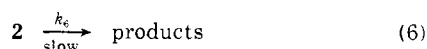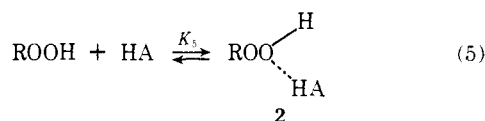
(2) α-Acylperoxy ketones, $R_1COC(OOCOR')R_2R_3$, decompose very fast by acyl shift.[5b] When α-hydroperoxy ketones

are treated with a mixture of acetic anhydride and pyridine, the hydroperoxides decompose easily to give ketone $R_2R_3C{=}O$ via the α-acylperoxy ketones.[17a]

(3) A chemiluminescent cyclic dioxetane mechanism has been shown to operate as a minor reaction for the case of base-catalyzed decomposition of 1.[8b] In contrast, no chemiluminescence was observed from the CF_3CO_2H-catalyzed decomposition of $1a$, $1m$, $1n$, and others in the presence of dibromo- or diphenylanthracene, denying the dioxetane mechanism (eq 4).

Thus, it may be concluded that the facile acid-catalyzed decomposition of 1 occurs via the facile shift of acyl group $R_1C{=}O$. The reported order of migratory aptitude is Ph > $PhC{=}O$ > H > Me for the BF_3-catalyzed decomposition of epoxides,[3a-d] and tertiary alkyl > $MeC{=}O$ > secondary alkyl for α-keto peroxides.[7] For the present decomposition of 1, the product study shows that the acyl migration is much faster than phenyl and that p-anisyl and p-tolyl shifts are barely competitive with benzoyl shift (see Table V). The relative migratory aptitudes with 0.1 M CF_3CO_2H in benzene are p-anisyl:p-tolyl:benzoyl = 1.9:0.04:1.0. Although the migration ratio of p-anisyl/benzoyl changes from 0.04 to 2.5 with the acidity (Table VI), it is apparent that migratory aptitude to peroxidic oxygen is in the order of $PhC{=}O \gg$ Ph. This is contrasted to the migration of benzoyl group to carbon (i.e., Ph > $PhC{=}O$) in the rearrangement of epoxides.[3a-d] But the migration to peroxidic oxygen seems to reflect an intrinsic nature of migrating groups[18] much more than the migration to carbon does, probably because the steric demand of oxygen as a migration terminus is much less than that of carbon.[19] These examinations lead to a conclusion that the intrinsic migratory aptitude is $PhC{=}O \gg$ Ph as is the present case.

Mechanism. Rate equation 2 and the general acid catalysis suggest a scheme of eq 5 and 6 (ROOH = 1). Here, k_2 in eq 2 equals K_5k_6, and hence the observed ρ value is the sum of ρ_5 for the hydrogen bonding equilibrium (i.e., K_5 in eq 5) and ρ_6

$$ROOH + HA \underset{}{\overset{K_5}{\rightleftharpoons}} ROO\diagup{\overset{H}{\underset{HA}{}}} \qquad (5)$$

$$2$$

$$2 \xrightarrow[slow]{k_6} products \qquad (6)$$

for the rearrangement of 2 (i.e., k_6 in eq 6). But the substituents are attached to a remote β- or γ-phenyl ring[20] and a leveling effect may be expected since trifluoroacetic acid is a strong acid. Hence, the observed ρ value is close to that of the migration step; i.e., $\rho = \rho_5 + \rho_6 \simeq \rho_6$. The transition state of the acyl migration from 2 can be written as 3. The substituent

$$R_1{-}C{=}O$$
$$R_2{\diagup}{\overset{\delta+}{C{=}O}}$$
$$R_3{\diagup}\quad\quad\underset{HO{\cdots}H{\cdots}A}{}$$
$$\underbrace{\qquad\qquad}_{\delta-}$$

$$3$$
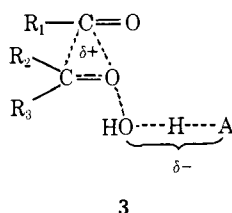
effect of nonmigrating group R_3 gives a ρ value of -0.81 correlated with σ^+, which suggests that the nonmigrating phenyl group delocalizes the developing positive charge at the migration origin.[22] A similar acceleration by phenyl was reported for the acid-catalyzed decomposition of hydroperoxide.[23] The very slow reaction of 10 ($R_2 = R_3 =$ Me) reflects a less effective delocalization with Me than that with Ph.

The migration ratio of p-anisyl:benzoyl changes with acidity and anisyl migration becomes predominant with increasing acidity[24] (Table VI). Similar results have been reported for the ratio of aryl:hydride shift in the decomposition of benz-

hydryl hydroperoxide,[18] the Baeyer-Villiger reaction of benzaldehydes,[17a] and also the pinacol rearrangements.[25] These seem to be due to the different dependence on acidity; i.e., the aryl shift is more sensitive to acidity than hydride or benzoyl shift. This difference is caused probably by the difference in the extent of charge separation of the transition state of migration; i.e., a demand of positive charge in the acyl and hydride shifts is less than that of the aryl shift.

Substituent Effect in the Migrating Acyl Group. In nucleophilic 1,2 rearrangements in peroxides, the effect of cationic stability of the migrating group is large ($\rho = -4$ to -5) and correlated with σ^+,[17] as is the case with other 1,2 shifts to cationic carbon.[26] But the present substituent effect on benzoyl migration is correlated with σ (Table IIIA). This σ correlation is not surprising since the reported substituent effects related to benzoyl cations are all correlated with σ; i.e., the BF_3-catalyzed rearrangement of epoxides ($\rho \sim -1$),[3d] the S_N1 solvolysis of benzoyl chloride in formic acid ($\rho = -4.6$),[27] and the heat of formation of benzoyl cations.[28] These effects are contrasted to the σ^+ correlation for benzyl groups,[26] and the migration ratio of p-MeO/H is large (i.e., 33) for the heterolysis of $XC_6H_4CH_2CMe_2OOC_6H_4$-p-NO_2.[29] For the case of benzyl groups, the σ^+ correlation is rational since benzyl cation $PhCH_2^+$ is stabilized by the charge delocalization to phenyl groups.

On the contrary, the σ correlation for benzoyl groups suggests the positive charge is not stabilized by the delocalization to phenyl groups. That is, the charge is mostly stabilized by the interaction with neighboring carbonyl oxygen; i.e., the contribution of $4b$ is predominant.

$$R_1C^+{=}O \leftrightarrow R_1C{\equiv}O^+ \leftrightarrow R_1^+{=}C{=}O$$
$$\quad 4a \qquad\qquad 4b \qquad\qquad 4c$$
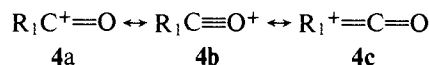
The order of $PhC{=}O < MeC{=}O < i$-$PrC{=}O$ for the present reaction is probably the order of electron-releasing ability of R_1 group and supports the above suggestion that the contribution of $4b$ is important, while a resonance stabilization with R_1 (i.e., $4c$) is not. The ^{13}C chemical shifts of benzoyl cation was explained by the ketenelike structure $4c$,[30] but a recent study[28] on benzoyl cations notes a doubt about the previous explanation. At any rate, σ correlation is always observed for the reaction of benzoyl groups and hence $4b$ is much more important than $4c$.

A similar explanation is applied to the case of acyl radical $R\dot{C}{=}O$. That is, benzoyl radical $Ph\dot{C}{=}O$ is a σ radical[31] which is not stabilized by the resonance with phenyl but with lone pair electrons of carbonyl oxygen.[32] The hydrogen abstraction of benzaldehydes to produce benzoyl radical gave a negative ρ value correlated with σ.[33] The relative β-scission of acyl radicals from α-acylalkoxy radicals produced by the radical decomposition of 1 is also in the order of $Ph\dot{C}{=}O < Me\dot{C}{=}O < i$-$PrC{=}O$,[9a] which can be explained similarly as described above.

Experimental Section

Materials. α-Hydroperoxy ketones (1) were synthesized by the ethoxide- or the *tert*-butoxide-catalyzed autoxidation of ketones.[8] Peroxides $1a$-j,l,m[8] and $1k$,n,p[9] were reported previously.

Decomposition Rates and Products. The rates were monitored by iodometry.[8] Products were determined by GLC in comparison with authentic samples as described previously.[8,9] Benzoic acids were analyzed by GLC directly and/or after esterification with diazomethane.

References and Notes

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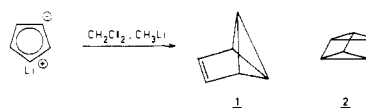(33) C. Walling and E. A. McElhill, *J. Am. Chem. Soc.*, **73**, 2927 (1951).

Diels–Alder Cycloadditions of a Bicyclobutane Bridged Diene. Acid and Thermal Stability of Benzvalene Derivatives as a Function of Substituents

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Abstract. Diels–Alder cycloadditions of 1,2,5,6-tetramethyl-3,4-dimethylenetricyclo[3.1.0.0^{2,6}]hexane (**5**) with a variety of dienophiles have been investigated. Depending on the dienophile used derivatives of benzvalene, of benzene, or of homofulvene are isolated. The benzene derivatives are formed from the corresponding benzvalenes via a thermal reaction, whereas the homofulvene derivatives result from an acid-catalyzed rearrangement. Benzene derivatives are the exclusive reaction products when the cycloadditions are carried out in the presence of silver perchlorate/sodium carbonate. The rates of cycloaddition are enhanced by Lewis acid catalysis of Ag thereby providing a useful synthetic approach for tetraline derivatives. The reaction of benzvalene derivatives with acid has been investigated in detail. The conclusion is reached that both the acid lability as well as the preferred pathways of the rearrangement depend on the nature of the substituents. The acid and thermal stability of benzvalene derivatives is enhanced by the presence of strongly electron-withdrawing groups at the C=C double bond of the benzvalene skeleton.

Among the multitude of interesting chemical structures derivable from the unit –CH– used n times, that of benzvalene (**1**), a (CH)$_6$ isomer, is one of the most fundamental and intriguing. Benzvalene is thus a valence bond isomer of benzene;[1] the molecule was first discussed by Hückel in 1937.[2] The parent benzvalene (**1**) was first synthesized[3,4] in the late 1960s by ultraviolet irradiation of liquid benzene. Through photochemical routes a few corresponding benzvalene derivatives have been prepared.[5,6] The yields from these photochemical methods are usually small and as a consequence the study of the chemical properties of benzvalene and its derivatives has not been extensive. In 1971 Katz and co-workers[7] reported an efficient synthesis of the parent benzvalene (**1**), which is de-

picted below. Since then, microwave studies[8] and calculations[9] of benzvalene have been performed and some interesting chemistry, culminating in the synthesis[10] of the parent prismane (**2**), have been reported.[11]

Benzvalenes are highly strained molecules. The heat of the reaction **1** → benzene has recently[12] been measured and found to be 67.54 kcal/mol.[13] At room temperature, benzvalene (**1**) reverts quantitatively to benzene with a half-life of about 10 days.[12,15] The strain energy of prismane (**2**) was calculated[14]