(s, acetate methyl proton), 8.49 (s, C-2-*endo* methyl proton), 8.0–9.0 (m, C-3, C-4, C-5, C-7 protons); mass spectrum parent mass peak 168, principal peaks 111, 110, 108, 80, and 43.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 70.2; H, 9.3.

Ketone **8** (relative retention time 19.8 min) was isolated as a colorless liquid, the infrared and nmr spectra of which were identical with those of the authentic specimen of 3-ketonorcamphene (**8**) prepared from N,N-dimethylammoniummethyl-2-norcamphor hydrochloride above.

The gas chromatography retention times and infrared and nmr spectra of acetate **3** (relative retention time 21.6 min) were identical with those of acetate **3** isolated from the lead tetraacetate oxidation of norcamphene.

Registry No.—**1,** 497-35-8; **2,** 694-92-8; lead tetraacetate, 546-67-8; **3,** 7593-21-7; **4,** 7593-22-8; **5,** 7593-23-9; **6,** 7593-24-0; **7,** 7593-25-1; **8,** 5597-27-3; semicarbazone of **8,** 7593-27-3; **30,** 695-05-6; **29,** 770-92-3; **12,** 7593-29-5; **11,** 7593-30-8; **13,** 7435-66-7.

Acknowledgments.—The author acknowledges the able technical work of Mr. Logan Stone and valuable discussions with Professor Ernest Wenkert. Pertinent discussions with Dr. C. D. Broaddus, particularly with regard to the synthesis of 2-methylnorbornene, are especially acknowledged.

The Structure of α-Keto Hydroperoxides

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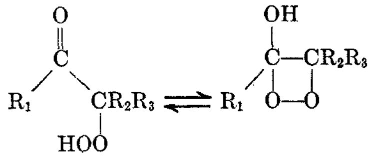
Received July 19, 1966

The structure of α-keto hydroperoxides was investigated in carbon tetrachloride and chloroform solution. Intra- as well as intermolecular hydrogen bonding was observed for 2,4-dimethyl-2-hydroperoxy-3-pentanone in carbon tetrachloride solution. The equilibrium constant for intermolecular hydrogen bonding at 33.1, 50.3, and 70.2° is given along with the corresponding enthalpy, free-energy, and entropy values. In addition, the enthalpy of intramolecular hydrogen bonding is reported. These values are discussed with relationship to intermolecular hydrogen bonding of *t*-butyl hydroperoxide. Both aryl- and alkyl-α-keto hydroperoxides exist solely in the hydroperoxide form. No cyclic peroxide tautomer could be detected by infrared or ultraviolet spectral analysis.

Only a limited amount of quantitative data is available for hydrogen bonding of hydroperoxides.[1] Quantitative data are invaluable for the interpretation of the kinetics of hydroperoxide decomposition. Our interest in the mechanism of α-keto hydroperoxide decomposition and the role of perepoxides in certain reactions[2] led us to study the structure of α-keto hydroperoxides. Particular attention is given to the importance of intra- *vs.* intermolecular hydrogen bonding. Although previous work[3] suggests that equilibrium (eq 1) is far or completely to the left when R_1 is aryl,

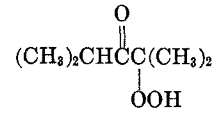


I II (1)

we desired to test this proposal. In addition, we wanted to determine if equilibrium (eq 1) was established with R_1 = alkyl. Here addition to the carbonyl group to give II would be more favorable than with R_1 = aryl.[4]

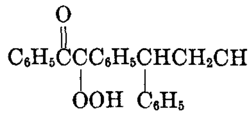
Results and Discussion

Both infrared and nmr spectra of 2,4-dimethyl-2-hydroperoxy-3-pentanone (III) show that it is mainly in the hydroperoxide form (I) rather than the cyclic peroxide form (II). A strong carbonyl absorption is observed in the infrared spectrum at 1717 cm^{-1} and the oxygen-bound proton is found far downfield (9.39 ppm) in the nmr spectrum. Hydroperoxy protons characteristically show low-field nmr absorption.[5] Further examination of the infrared spectrum of III



$$(CH_3)_2CH\overset{O}{\overset{\|}{C}}\underset{OOH}{C}(CH_3)_2$$

III



$$C_6H_5\overset{O}{\overset{\|}{C}}\underset{OOH}{C}C_6H_5\underset{C_6H_5}{C}HCH_2CH_3$$

IV

at low concentrations (down to 6.35 × 10^{-3} *M*) reveals no evidence for the cyclic form II. At low concentrations where monomeric peroxide is favored, the opportunity to detect cyclic form II is maximized. Yet only two oxygen–hydrogen stretching bands are seen in the infrared spectrum. A broad band at 3450 cm^{-1} is assigned to hydrogen-bonded species, while a reasonably sharp band at 3546 cm^{-1} is assigned to the free oxygen–hydrogen stretching mode of the hydroperoxy group. The frequency of the latter band is low for free hydroxyl groups as required by the cyclic peroxide form (II), but is consistent with the free hydroperoxy group of *t*-butyl hydroperoxide (3554 cm^{-1}).[1] A free hydroxyl oxygen–hydrogen stretching band that would give support to the cyclic form (II) is not observed in the infrared spectrum of III. The ultraviolet spectrum of 2,3-diphenyl-2-hydroperoxyvalerophenone (IV) should show a change in the molar extinction coefficient (ϵ) with changing peroxide concentration if equilibrium (eq 1) is valid. This also assumes that some dimeric hydroperoxide species are present over this concentration range. When the concentration of IV was varied from 0.150 × 10^{-2} to 1.50 × 10^{-2} *M* in chloroform solution, the ϵ value was constant at the wavelength

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(1) C. Walling and L. Heaton, *J. Am. Chem. Soc.*, **87**, 48 (1965).

(2) W. H. Richardson, J. W. Peters, and W. P. Konopka, *Tetrahedron Letters*, 5531 (1966).

(3) (a) J. Rigandy, *Compt. Rend.*, **226**, 1993 (1948); (b) R. C. Fuson and H. L. Jackson, *J. Am. Chem. Soc.*, **72**, 1637 (1950).

(4) For example, the equilibrium constant for cyanohydrin formation is 4.4 × 10^{-3} at 20° in ethanol solvent for benzaldehyde [J. W. Baker, G. F. C. Barrett, and W. T. Tweed, *J. Chem. Soc.*, 2831 (1952)] and about 1.4 × 10^{6} for acetaldehyde in water at 25° [W. F. Yates and R. L. Heider, *J. Am. Chem. Soc.*, **74**, 4153 (1952)].

(5) S. Fujiwara, M. Katayama, and S. Kamio, *Bull. Chem. Soc. Japan*, **32**, 657 (1959).

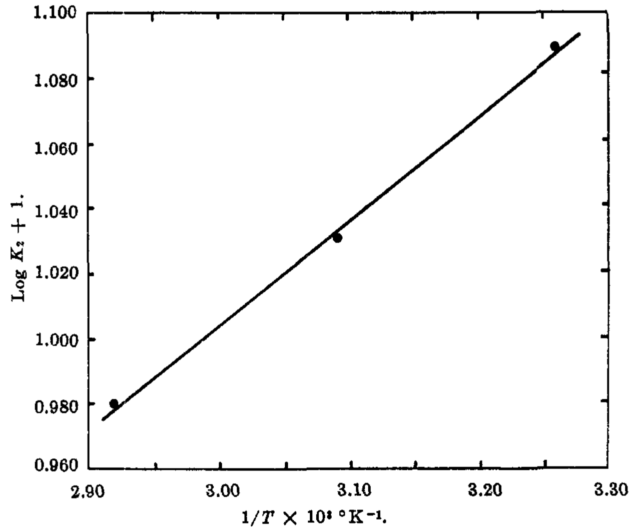
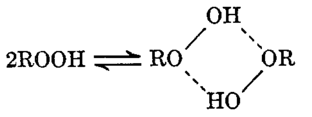


Figure 1.—The monomer–dimer equilibrium constant as a function of temperature in carbon tetrachloride solution for (III).

maximum. Neither α-keto hydroperoxide III nor IV give evidence for the cyclic form (II).

Since α-keto hydroperoxides do not appear to be in the form of cyclic peroxides (II), it was desired to determine their state in solution. For this reason an infrared analysis of peroxide III was made at various concentrations and at three different temperatures. Low solubility precluded a similar study of IV. The monomer–dimer equilibrium constant (eq 2) was calculated from the free hydroperoxy oxygen–hydrogen stretching band at 3546 cm⁻¹. A six-membered ring hydrogen bonded species was previously suggested for the dimer.[1] The structure of the monomer will be



(2)

pursued later. The equilibrium constant for eq 2 was calculated at three different temperatures by the method of Liddel and Becker.[6,7] The observed molar extinction coefficient (ϵ_F) for the free hydroperoxy O–H stretching band is given by eq 3, where K_2 and

$$\epsilon_F = \epsilon_{0F}(1 - 2K_2[\mathrm{ROOH}]_T - 3K_3[\mathrm{ROOH}]_T^2 - \cdots) \quad (3)$$

K_3 are the monomer–dimer and monomer–trimer equilibrium constants. The dimer, trimer, and more highly associated species are assumed to be in low enough concentration so that ϵ_F is a function of the stoichiometric hydroperoxide concentration, $[\mathrm{ROOH}]_T$. The molar extinction coefficient for the monomer is given by ϵ_{0F}. A plot of ϵ_F *vs.* $[\mathrm{ROOH}]_T$ gives ϵ_{0F} as the intercept and K_2 is calculated from the slope at infinite dilution ($-2K_2\epsilon_{0F}$). Table I presents the pertinent data. The enthalpy for the monomer–dimer equilibrium (eq 2) is calculated to be −1.45 kcal/mole from the slope of the plot given in Figure 1. From the equilibrium constant at 33.1°, the free energy is calculated to be −0.123 kcal/mole. The entropy is then calculated as −4.3 eu.

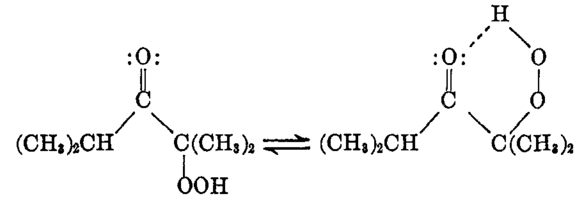
TABLE I

EFFECT OF CONCENTRATION AND TEMPERATURE ON THE 3546-CM⁻¹ BAND OF 2,4-DIMETHYL-2-HYDROPEROXY-3-PENTANONE (III) IN CARBON TETRACHLORIDE SOLUTION

Temp, °C	A_F[a]	Cell path, mm	ϵ_F	$[\mathrm{ROOH}]_T \times 10^2$, M
32.8	0.098	2.66	58	0.635
33.4	0.120	1.22	56.7	1.59
32.6	0.283	1.33	53.4	3.98
32.6	0.060	0.133	46	9.93
33.1	0.101	0.133	38.2	19.9
33.8	0.141	0.133	26.8	39.6
Av 33.1 ± 0.4				
50.6	0.097	2.66	58	0.635
50.2	0.118	1.33	55.8	1.59
50.2	0.282	1.33	53.2	3.98
50.2	0.095	0.133	36	19.9
50.1	0.141	0.133	26.8	39.6
Av 50.3 ± 0.2				
70.0	0.094	2.66	56	0.635
71.4	0.115	1.33	54.4	1.59
69.9	0.275	1.33	52.0	3.98
70.2	0.077	0.133	29	19.9
69.6	0.141	0.133	26.8	39.6
Av 70.2 ± 0.5				

[a] A_F is the observed optical density at 3546 cm⁻¹.

The possibility of intramolecular hydrogen bonding according to eq 4 is considered next. The first clue to intramolecular hydrogen bonding is found in the unusually low value for the enthalpy of monomer–dimer equilibrium. Walling and Heaton[1] report a monomer–dimer enthalpy value of −5.95 kcal/mole for *t*-butyl hydroperoxide compared to our value of −1.45 kcal/mole for III. The low enthalpy value for III is reasonable if the monomer is stabilized by hydrogen bonding. Further evidence for intramolecular hydrogen bonding is found by considering a plot of A_B/A_F *vs.* concentration, where A_B and A_F are the optical densities of the hydrogen bonded (3450 cm⁻¹) and free (3546 cm⁻¹) oxygen–hydrogen stretching bands. Upon extrapolation to infinite dilution, the ratio A_B/A_F does not proceed to 0. If A_B originated entirely from intermolecular hydrogen bonding, then A_B/A_F should approach 0 at low hydroperoxide concentration. The data for these plots are given in Table II.



(4)

The enthalpy of intramolecular hydrogen bonding (ΔH_{IB}) is calculated from a plot of log A_{0B}/A_{0F} *vs.* $1/T$ as shown in Figure 2. According to eq 5[8] ΔH_{IB}

$$\frac{\partial(\log A_{0B}/A_{0F})}{\partial(1/T)} = -\frac{\Delta H_{IB}}{2.303R} \quad (5)$$

is calculated from the slope of Figure 2 and is found to be −1.86 kcal/mole. Extrapolation to infinite dilution to give A_{0B}/A_{0F} ensures that only intramolecular hydrogen bonding is included in this calculation. The

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[6] U. Liddel and E. D. Becker, *Spectrochim. Acta*, **10**, 70 (1957).

[7] See ref 1 for the application of this method to the *t*-butyl hydroperoxide monomer–dimer equilibrium.

[8] See A. W. Baker, A. T. Shulgin, *Spectrochim. Acta*, **19**, 1611 (1963).

TABLE II

EFFECT OF CONCENTRATION AND TEMPERATURE ON A_B/A_F FOR 2,4-DIMETHYL-2-HYDROPEROXY-3-PENTANONE (III) IN CARBON TETRACHLORIDE SOLUTION

Temp, °C	A_B[a]	A_B/A_F[a]	[ROOH]$_T$ × 10^2, M
32.8	0.0094	0.254	0.635
33.4	0.0278	0.308	1.59
32.6	0.0872	0.409	3.98
32.6	0.301	0.667	13.4
33.1	0.767	1.01	19.9
33.8	1.69	1.60	39.6
Av 33.1 ± 0.4			
50.6	0.0079	0.215	0.635
50.2	0.0248	0.280	1.59
50.2	0.0790	0.372	3.98
50.2	0.639	0.895	19.9
50.1	1.55	1.47	39.6
Av 50.3 ± 0.2			
70.0	0.00715	0.202	0.635
71.4	0.0218	0.252	1.59
69.6	0.0707	0.342	3.98
70.2	0.421	0.726	19.9
69.6	1.35	1.27	39.6
Av 70.2 ± 0.5			

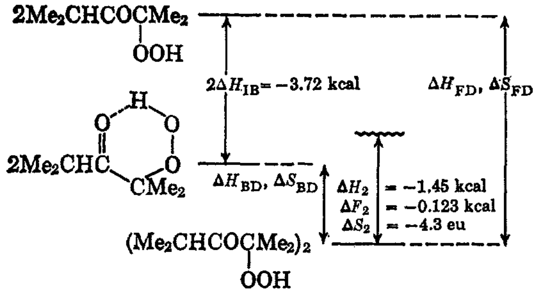
[a] Corrected to a 1-mm cell path length.

method of calculation assumes that the ratio of molar extinction coefficients is temperature independent.[9]

Scheme I summarizes the known thermodynamic quantities for the inter- and intramolecular hydrogen bonding of III. Since ΔH_2, ΔS_2, and ΔF_2 are differences between the dimer and the monomer, they cannot be related to a specific monomer species. If equilibrium constants could be calculated for intramolecular hydrogen bonding, then ΔH_{FD} and ΔS_{FD} as well as ΔH_{BD} and ΔS_{BD} could be calculated. Without the molar extinction coefficient for one of the monomeric species this is not possible.[10] Unfortunately, neither ϵ_F or ϵ_B can be obtained for hydroperoxide III. Our data do set a maximum negative value of -5.17 kcal ($= 2\Delta H_{IB} + \Delta H_2$) for ΔH_{FD}. This may be compared to a value of $\Delta H_{FD} = -5.95$ kcal for *t*-butyl hydroperoxide.[1] A lower value of $-\Delta H_{FD}$ for III as compared to *t*-butyl hydroperoxide does not seem unreasonable. The inductive effect of the α-keto group in III should lower the basicity of carbon-bonded hydroperoxide oxygen, but have a lesser effect on the acidity of the farther removed hydroperoxide hydrogen atom. This should lower $-\Delta H_{FD}$ of III for the six-membered ring species (eq 2).

SCHEME I

THERMODYNAMIC QUANTITIES FOR 2,4-DIMETHYL-2-HYDROPEROXY-3-PENTANONE (III) IN CARBON TETRACHLORIDE SOLUTION



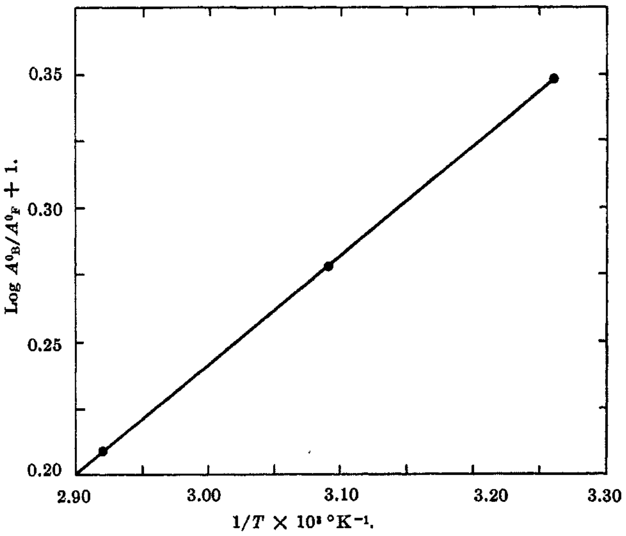


Figure 2.—A plot of log A_{0B}/A_{0F} *vs.* $1/T$ for 2,4-dimethyl-2-hydroxyperoxy-3-pentanone (III) in carbon tetrachloride solution. The slope equals $-\Delta H_{IB}/2.303R$.

Experimental Section

β-Chlorobenzyldeoxybenzoin.—This compound was prepared from benzaldehyde, deoxybenzoin (Matheson Coleman and Bell, mp 54–56°), and hydrogen chloride according to the procedure of Kohler and Nygaard.[11] The crude product was obtained in 66.5% yield, mp 153–157°.

Benzaldeoxybenzoin.—Following the procedure of Kohler and Nygaard[11] a 61.4% yield of benzaldeoxybenzoin, mp 101–102° (lit.[11] 101°), was obtained.

2,3-Diphenyl-2-hydroperoxyvalerophenone (IV).—Hydroperoxide IV was prepared according to the general procedure of Kholer.[12] Ethylmagnesium bromide (22.3 mmoles) in 10 ml of ether was added to 5.00 g (15.6 mmoles) of benzaldeoxybenzoin which was dissolved in 20 ml of 50% (v/v) ether-benzene solvent. After the addition was completed, the mixture was boiled under reflux for 4 hr under a nitrogen atmosphere. The mixture was poured into a saturated ammonium chloride solution (15 ml) and the organic phase was separated and washed with water. Air was bubbled through the organic phase for 24 hr. The solvent was removed on a rotary evaporator to give 6.05 g of a white solid, mp 128–132° dec. After repeated recrystallizations from ether 0.96 g [18% yield based on benzal deoxybenzoin, mp 152–153° dec (lit.[13] 149–149.5° dec)] of hydroperoxide IV was obtained.

2,4-Dimethyl-2-hydroperoxy-3-pentanone (III).—Hydroperoxide III was prepared by autoxidation of diisopropyl ketone according to the procedure of Sharp and co-workers.[14] After a 57-hr autoxidation period at 97–100°, the reaction mixture was found to contain 5.94 wt % hydroperoxide by an iodometric titration.[15] The reaction mixture was worked up according to the prescribed method[14] to give 0.868 g (1.60% yield based on the initial amount of diisopropyl ketone) of III, bp 41–43° (0.11 mm) [lit.[14] 62–69° (0.8 mm)]. Both the infrared and nmr spectra were consistent with the structure of III. The following absorptions were measured on a Varian A-60 nmr spectrometer relative to tetramethylsilane: 9.39 (singlet), 3.40 (multiplet), 1.38 (singlet), 1.13 ppm (doublet, J = 7 cps). The following

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[9] This approximation is evident from the equation for the equilibrium constant $K_{\text{intra}} = C_B/C_F = A_{0B}/\epsilon_B/A_{0F}/\epsilon_F$ and eq 5. Here C_B and C_F are the concentrations of the hydrogen-bonded and free hydroperoxide species. Accounting for the temperature dependence of ϵ_F/ϵ_B, a 5% correction in the enthalpy is required for *o*-chlorophenol; see A. W. Baker, H. O. Kerlinger, and A. T. Shulgin, *Spectrochim. Acta*, **20**, 1467 (1964); A. W. Baker, and A. T. Shulgin, *Can. J. Chem.*, **43**, 650 (1965).

[10] See ref 9.

[11] E. P. Kohler and E. M. Nygaard, *J. Am. Chem. Soc.*, **52**, 4128 (1930).

[12] E. P. Kohler, *Am. Chem. J.*, **36**, 177, 529 (1906).

[13] W. von E. Doering and R. M. Haines, *J. Am. Chem. Soc.*, **76**, 482 (1954).

[14] D. B. Sharp, L. W. Patton, and S. F. Whitcomb, *ibid.*, **73**, 5600 (1951).

[15] W. H. Richardson, *ibid.*, **87**, 247 (1965).

assignments were made with the observed relative areas: oxygen-bonded proton (1.0), tertiary CH (1.0), $(CH_3)_2$ adjacent to the hydroperoxy group (6.1) and $(CH_3)_2$ of the isopropyl group (6.0), respectively. A solution of 11% (w/v) of III in carbon tetrachloride was used.

Anal. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.72; H, 9.37.

Infrared Spectra.—A Perkin-Elmer Model 621 grating spectrophotometer was employed, using 0.133-mm or variable-space sodium chloride cells. The variable-space cells were set at 2.66 and 1.33 mm. A thermostated compartment was fabricated from $^1/_8$ in. aluminum sheet metal and was made to fit the sample compartment of the spectrophotometer. Both the sample and the reference cells were contained in the thermostated compartment. A 250-w heater was activated for rapid heating and two 50-w heaters were connected in parallel to a thermostating device. The power to the 50-w heaters was controlled by a rheostat. The thermostating device employed a relay and a sensor that was obtained from the National Appliance Co. Temperature was determined with a thermometer which was calibrated against a National Bureau of Standards platinum resistance thermometer.[16] The temperature could be controlled by this device to ±0.4° at room temperature and to ±0.5° at 70°. The sample solution and reference solvent were allowed to thermally equilibrate in the cells for 35 min before the spectrum was measured. No change in the spectrum was noticed upon remeasuring after a 55-min period. Spectro Grade carbon tetrachloride was used as the solvent.

Ultraviolet Spectra.—Measurements were made on a Cary 14 ultraviolet recording spectrophotometer. Spectra were measured at 22° using 1.0- and 0.1-cm cells and Spectro Grade chloroform.

Registry No.—III, 3944-52-3; β-chlorobenzyl deoxybenzoin, 7492-75-3; IV, 7492-76-4; III dimer, 7649-81-2; benzal deoxybenzoin, 4023-77-2.

Acknowledgment.—This investigation was supported by the U. S. Army Research Office (Durham).

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[16] Calibration was kindly performed by Mr. J. H. Table, Standards Laboratory, General Dynamics/Astronautics, San Diego, Calif.

The Mechanism of Solvolysis of Phenacyl Halides in Various Solvents[1]

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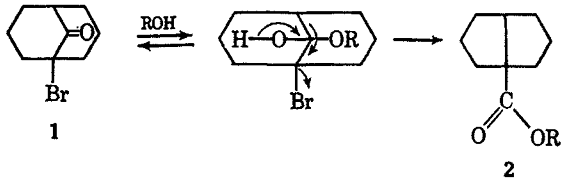
Received October 25, 1966

The kinetics of the solvolysis of phenacyl chloride and bromide in 50, 80, and 95% ethanol, 80% *t*-butyl alcohol, and formic acid have been measured at several temperatures. The Grunwald-Winstein *m* value, determined for phenacyl bromide in the aqueous ethanol solvent systems, is 0.20 ± 0.01 over the temperature range of 55 to 80°. The Hammett ρ values for the solvolysis of substituted phenacyl bromides in 80% aqueous ethanol and formic acid were found to be +0.35 and −0.04, respectively. Analysis of the products of the solvolysis reactions indicated that no rearrangement (phenyl migration) reactions had occurred thus precluding carbonyl oxygen and phenyl participation in the transition state of the solvolysis. The mechanism of the solvolysis of the phenacyl halides is best described as proceeding *via* a highly nucleophilic displacement of halide by the solvent molecules.

In a recent study in our laboratories on the role of the ketone carbonyl group in neighboring group participation in the solvolysis of ω-chloro ketones[2] it was observed that phenacyl chloride underwent silver ion assisted solvolysis 1.3 times as fast as *n*-butyl chloride in the presence of silver ion in 80% aqueous ethanol at 56°. The solvolytic reactivity of phenacyl chloride was unexpected in view of the strong electron-withdrawing power of the benzoyl group on the site of substitution. The enthalpy and entropy of activation for the silver ion assisted solvolysis of phenacyl chloride differed substantially from what might have been expected in comparison with the values obtained for the higher, homologous ω-chloro ketones which involve participation by the ketone carbonyl oxygen atom in the rate-determining step.

Several mechanistic pathways are potentially available in the solvolysis of the phenacyl halides. Cope and Synerholm observed that the bicyclic bromo ketone (1) reacted immediately with silver ion[3] in aqueous ethanol to produce the bicyclic acid or ester (2).[4] The mechanism proposed by Cope for this reaction involved the addition of water or ethanol to the carbonyl group followed by rearrangement and expulsion of bromide as illustrated. Addition of solvent to phenacyl halide results in formation of **3** (Scheme I) which may undergo solvolysis (with participation) in any of three directions: participation and migration involving OR or OH to generate an unrearranged phenacyl derivative, or by phenyl participation resulting in the formation of intermediate ion **4** which may give rise



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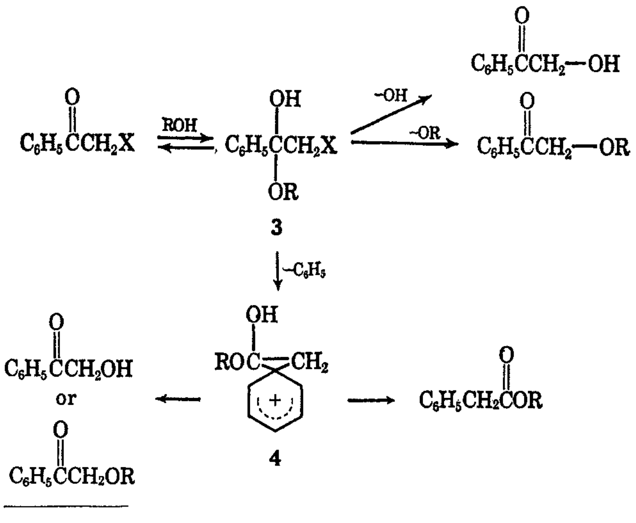
SCHEME I



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[1] Research supported by the National Science Foundation, Grant GP-4497. Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 12, 1966.

[2] D. J. Pasto and M. P. Serve, *J. Am. Chem. Soc.*, **87**, 1515 (1965).

[3] A. C. Cope and M. E. Synerholm, *ibid.*, **72**, 5228 (1950).

[4] A. C. Cope and E. S. Graham, *ibid.*, **73**, 4702 (1951).