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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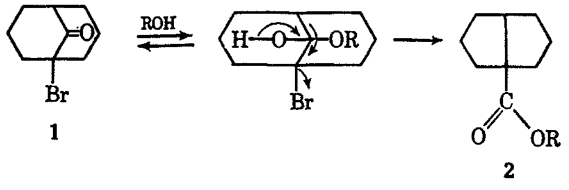
Received October 25, 1966

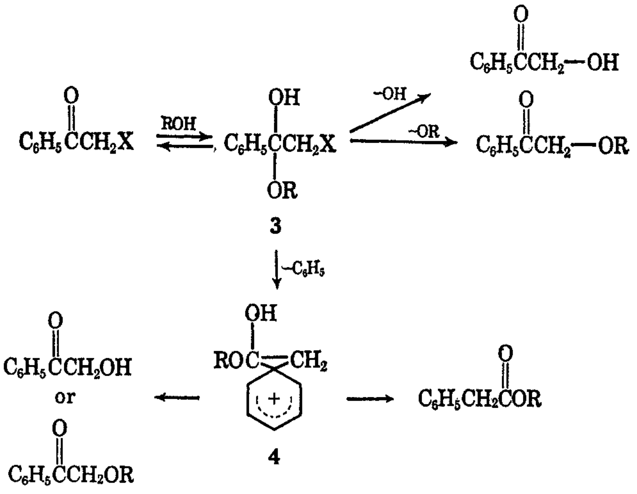
The kinetics of the solvolysis of phenacyl chloride and bromide in 50, 80, and 95% ethanol, 80% *t*-butyl alcohol, and formic acid have been measured at several temperatures. The Grunwald–Winstein *m* value, determined for phenacyl bromide in the aqueous ethanol solvent systems, is 0.20 ± 0.01 over the 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



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.

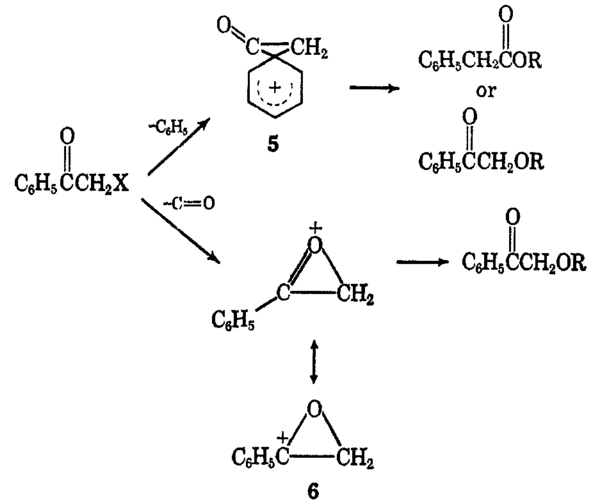
[2] D. J. Pasto and M. P. Serve, *J. Am. Chem. Soc.*, **87**, 1515 (1965).

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

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

to rearranged products, derivatives of phenylacetic acid, or unrearranged products. Alternate mechanisms for solvolysis involving neighboring group participation involve direct participation by phenyl to produce **5**, and hence rearranged products, or by carbonyl oxygen participation to produce **6** which may ultimately lead to unrearranged or rearranged products (Scheme II). Participation by aryl groups has been reported in solvolyses of many phenyl substituted systems.[5] The intermediacy of ions of similar structure to **6** have been proposed in one of the possible mechanisms for the rearrangement of α-chloro epoxides to α-chloro ketones.[6] A final mechanism for the solvolysis of phenacyl halides which must be considered is the simple nucleophilic displacement by solvent. The type of mechanism operating in any given instance may well depend on the structure of the phenacyl halide, substitution on phenyl and the β carbon, and the solvent, function of the nucleophilicity and solvation power, employed in the solvolysis. In view of our earlier findings we have investigated more extensively the kinetics of the solvolysis of phenacyl chloride and bromide in a variety of solvent systems.

SCHEME II



Tables I and II present the pseudo-first-order rate constants for phenacyl chloride, phenacyl bromide, and substituted phenacyl bromides in a variety of solvent systems at several temperatures. The rates of solvolysis were followed by titration of the hydrohalic acid formed during the solvolysis reaction. All solvolysis reactions provided excellent pseudo-first-order plots up to 70% reaction indicating that the hydrohalic acid formed in the solvolysis reaction does not affect the reaction mechanism. Duplicate runs in several of the systems indicated a reproducibility of 2% or better. Solvolysis of the phenacyl bromides in formic acid led to some decomposition (development of a yellow-brown color) and gas formation during the prolonged course of the reaction; however this decomposition did not appear to affect the kinetics of the reactions. This decomposition became more pronounced at temperatures above 85° and severely limited the temperature span accessible for the kinetic measurements. Attempted solvolysis of phenacyl bromide in acetic acid led to a very slow reaction, approximately one-tenth that in formic acid. Extensive decomposition occurred above 80° in acetic acid and no kinetic measurements could be made in this solvent.

TABLE I

PHENACYL HALIDE SOLVOLYSIS RATE CONSTANTS

Substrate	Solvent	$k \times 10^3$, min^{-1} at 55°	70°	80°
Phenacyl chloride	80% ethanol	0.0070	0.0232	0.062 (0.161)[a]
Phenacyl bromide	50% ethanol	0.292	1.22	2.71
Phenacyl bromide	80% ethanol	0.160	0.668	1.41
Phenacyl bromide	95% ethanol	0.077	0.331	0.64
Phenacyl bromide	80% *t*-butyl alcohol	0.079	0.243	0.58
Phenacyl bromide	Formic acid	...	0.00369	... (0.0148)[b]

[a] Rate constant at 90°. [b] Rate constant at 85°.

TABLE II

SUBSTITUTED PHENACYL BROMIDE SOLVOLYSIS RATE CONSTANTS AT 70°

Substrate	$k \times 10^3$, min^{-1} in 80% ethanol	Formic acid
p-NO_2-phenacyl bromide	1.25	0.0035
p-Cl-phenacyl bromide	0.79	...
p-Br-phenacyl bromide	...	0.0033
m-CH_3O-phenacyl bromide	0.63	0.0039
p-CH_3O-phenacyl bromide	0.53	0.0034

The rate data presented in Table I were used to calculated the enthalpies and entropies of activation. These values are presented in Table III.

TABLE III

ACTIVATION PARAMETERS FOR THE SOLVOLYSIS OF PHENACYL CHLORIDE AND BROMIDE IN VARIOUS SOLVENTS

Substrate	Solvent	$\Delta H^\ddagger$, kcal/mole	$\Delta S^\ddagger$, eu
Phenacyl chloride	80% ethanol	21.3	25.6
Phenacyl bromide	50% ethanol	19.7	22.7
Phenacyl bromide	80% ethanol	18.7	26.7
Phenacyl bromide	95% ethanol	18.9	27.7
Phenacyl bromide	80% *t*-butyl alcohol	17.8	31.3
Phenacyl bromide	Formic acid	20.6	

The rate of solvolysis of phenacyl bromide in 80% ethanol at 55° is compared in Table IV with the rates of solvolysis of methyl, ethyl, isopropyl, and *t*-butyl bromides[7] under identical conditions. It is interesting

TABLE IV

ALKYL BROMIDE SOLVOLYSIS RATE CONSTANTS IN 80% ETHANOL AT 55°

Compd	$k \times 10^5$, sec^{-1}
Methyl bromide[a]	0.35
Ethyl bromide[a]	0.14
Isopropyl bromide[a]	0.26
t-Butyl bromide[a]	1010
Phenacyl bromide[b]	0.27

[a] Taken from ref 7. [b] This investigation.

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[5] See A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 144–153.

[6] R. N. McDonald and P. A. Schwab, *J. Am. Chem. Soc.*, **85**, 4004 (1963).

[7] L. C. Bateman, K. A. Cooper, E. O. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 925 (1940).

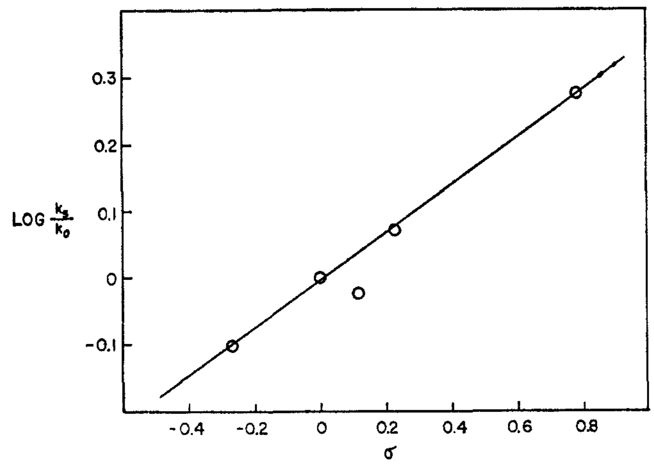


Figure 1.—Hammett plot for the solvolysis of substituted phenacyl bromides at 70° in 80% ethanol.

to note that phenacyl bromide solvolyzes two times as fast as ethyl bromide and at approximately the same rate as isopropyl bromide. This is in qualitative agreement with our earlier observations in the silver ion assisted reactions.

Application of the Grunwald–Winstein relationship[8] to the data for the solvolysis of phenacyl bromide in 50, 80, and 95% ethanol yields m values of 0.20, 0.19, and 0.21 at 55, 70, and 80°, respectively.[9] For comparison purposes the m values for a series of alkyl bromides are given in Table V. The Grunwald–Winstein m value is a measure of the sensitivity of the substrate to the ionizing power of the solvent and increases as the carbonium ion character of the transition state increases. The m values for phenacyl bromide indicate less carbonium ion character in the transition state for solvolysis than in the solvolysis of methyl bromide, a process which is characterized essentially as a SN2 process.

TABLE V

GRUNWALD–WINSTEIN m VALUES FOR ALKYL BROMIDES IN AQUEOUS ETHANOL

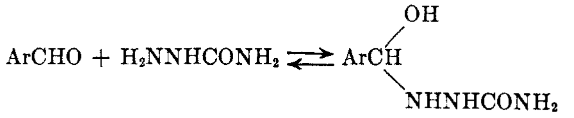
Substrate	Temp, °C	m
Phenacyl bromide[a]	55	0.20[b]
Phenacyl bromide[a]	70	0.19[b]
Phenacyl bromide[a]	80	0.21[b]
Methyl bromide[c]	50	0.258
Ethyl bromide[c]	50	0.343
n-Butyl bromide[d]	59.4	0.392
n-Butyl bromide[d]	75.1	0.331
Isopropyl bromide[c]	50	0.544
t-Butyl bromide[d]	25	0.917

[a] Present investigation. [b] These values are estimated to be reliable to ±0.01. [c] S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951). [d] Reference 8.

The products formed under the conditions of the kinetic experiments consist of only ethyl phenacyl ether and phenacyl alcohol. No rearrangement products, ethyl phenylacetate or phenylacetic acid, were detected by gas–liquid partition chromatography. The use of product ratios in determining the rates of attack by ethanol and water was prevented by the observation that ethyl phenacyl ether and phenacyl alcohol undergo an acid-catalyzed equilibration in aqueous ethanol in the presence of hydrohalic acid in the concentration ranges encountered in the kinetic runs. In all cases ethyl phenacyl ether was formed in greater quantities than phenacyl alcohol (generally in a ratio of between 70:30 and 80:20).

Application of the Hammett equation to the data for the substituted phenacyl bromides in 80% ethanol gives a ρ value of +0.35 (see Figure 1). The kinetic data correlate with δ and not δ^+. Comparison of the ρ value with ρ values for reactions of phenacyl systems in which a highly carbonium ion type process and SN2-type reactions occur provides a guide in defining the transition state in the solvolysis of phenacyl bromide. The ρ value for the reaction of diazoacetophenone in 99.85% acetic acid at 40° (the transition state probably possessing considerable carbonium ion character) is −0.914.[10] In contrast, the ρ value for the nucleophilic displacement of bromide in phenacyl bromide by pyridine in acetone at 20° is +0.558[11] and with 2,6-dimethyl-4-thiopyrone in benzene at 25.4° it is +0.984.[12] The ρ value of +0.35 for the solvolysis of phenacyl bromide in aqueous ethanol is indicative of a nucleophilic displacement involving a relatively poor nucleophile (ethanol or water).

The possible intermediacy of a solvent addition intermediate such as **3** may be ruled out on the basis of the observed ρ value. The experimentally observed ρ value would be the product of the ρf or the prerate-determining step equilibrium and the ρ value for the solvolysis step. The ρ value for the equilibrium addition of semicarbazide to substituted benzaldehydes is +1.81[13] and for cyanohydrin formation it is +1.49.[14] Although the ρ values for hydrate and hemiketal formation are not known, they would be expected to be in the same range as for the semicarbazide addition equilibrium if not larger. Such a ρ value for the formation of **3** would require a ρ value for the displacement ρ in the range of −1.2 to above −1.5 which would appear unreasonably large when considering the reacting system. Furthermore, the entropy of activation is not consistent with a mechanism involving the formation of intermediate **3** which then undergoes solvolysis.



$$\mathrm{ArCHO + H_2NNHCONH_2 \rightleftharpoons ArCH(OH)(NHNHCONH_2)}$$

Participation by the phenyl and carbonyl oxygen in the rate-determining step does not appear likely in view of the type of products formed and the activation parameters. Participation by phenyl should lead to the formation of rearranged products, phenylacetic acid or its ethyl ester. The complete lack of rear-

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(8) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

(9) The temperature dependence on m is given by the equation

$$2.303Y\frac{dm}{dT} = \frac{E\ddagger - E_0\ddagger}{RT^2}$$

in which $E_0\ddagger$ is the activation energy in 80% ethanol.[8] As the term ($E\ddagger - E_0\ddagger$) is nearly 0 (see Table II) the value of m is relatively insensitive to changes in temperature.

(10) J. F. Lane and R. L. Feller, *J. Am. Chem. Soc.*, **73**, 4230 (1951).

(11) J. W. Baker, *Trans. Faraday Soc.*, **37**, 632 (1941).

(12) F. J. Ozog, V. Comte, and L. C. King, *J. Am. Chem. Soc.*, **74**, 6225 (1952).

(13) B. M. Anderson and W. P. Jencks, *ibid.*, **82**, 1773 (1960).

(14) H. H. Jaffé, *Chem. Rev.*, **53**, 200 (1953).

ranged products indicates that participation by phenyl is not occurring. Participation by the carbonyl oxygen atom does not appear to occur in that the entropy of activation is too small in comparison with former data derived with higher homologous ω-chloro ketones.[2] The mechanism of the solvolysis of phenacyl bromide and chloride in aqueous ethanol therefore appears to proceed *via* a highly nucleophilic displacement of halide by solvent molecules, the surprisingly fast rate of solvolysis being related to the greater reactivity of phenacyl derivatives in nucleophilic displacements[15] and not to neighboring group participation in the rate-determining step.

In an attempt to force the phenacyl halides to react *via* one of the other possible mechanisms outlined earlier, we investigated the solvolysis of phenacyl bromide in solvents of lower nucleophilicity. The kinetics of the solvolysis of phenacyl bromide were successfully measured in 80% *t*-butyl alcohol and formic acid. Attempts were made to solvolyze phenacyl bromide in acetic acid; however the reaction was exceedingly slow and extensive decomposition of the system occurred. The rate data for the solvolysis of phenacyl bromide in 80% *t*-butyl alcohol and formic acid are presented in Tables I and II. The predominant product (~70%) formed in 80% *t*-butyl alcohol was surprisingly the *t*-butyl phenacyl ether along with phenacyl alcohol. No rearranged products could be detected. This compound was prepared independently by refluxing phenacyl bromide in pure *t*-butyl alcohol in the presence of silver nitrate. The reduction in the rate of solvolysis of phenacyl bromide in aqueous *t*-butyl alcohol relative to aqueous ethanol, of equal mole per cent, is primarily due to the entropy of activation contribution and probably represents a more highly crowded transition state. Again the mechanism must involve a highly nucleophilic displacement of halide by the solvent molecules.

Solvolysis of phenacyl bromide in formic acid produced only phenacyl formate. No rearrangement products could be detected. The rate of solvolysis of phenacyl bromide in formic acid is about 1/200 as fast as the solvolysis of phenacyl bromide in 80% ethanol. The Hammett ρ value for the formolysis of substituted phenacyl bromides is approximately -0.04. This value is distinctly more negative than the ρ value for the solvolysis of substituted phenacyl bromides in 80% aqueous ethanol ($+0.35$) and indicates that the transition state in formic acid involves greater S_N1 character. This is as expected as formic acid is a better solvating solvent and is less nucleophilic compared to water or ethanol. The exceedingly low ρ value of -0.04 does not suggest extensive carbonium ion formation and the mechanism of formolysis is still best described as highly concerted with formic acid displacing the halide ion.

Summary.—The present data clearly indicate that phenacyl chloride and bromide undergo solvolysis *via* a highly concerted nucleophilic attack by solvent with loss of halide ion even in solvents of high ionizing power. The effect of substituents on the β carbon is being investigated to see if it is possible to detect reaction *via* one of the other mechanisms discussed earlier.

Experimental Section

General.—Phenacyl chloride and bromide were recrystallized several times from hexane. The distilled water used to prepare the water–ethanol solvent systems was prepared by distillation from potassium permanganate. The water–ethanol and water–*t*-butyl alcohol solvent systems were standardized by density measurements.

Kinetic Procedure.—Standard solutions (0.01 to 0.033 *M*) of phenacyl chloride and bromide in the solvent systems were prepared. Aliquots of the solutions were sealed in ampoules, wrapped in aluminum foil, and placed in a constant-temperature bath. Ampoules were periodically removed and their contents were washed with water into a beaker containing 25 ml of benzene. The liberated acid (HCl or HBr) was titrated with standard sodium hydroxide employing a Beckman Research Model pH meter equipped with a Beckman 41263 glass electrode and standard calomel.

Product Analysis.—Solutions of 0.4 to 1.0 g of phenacyl chloride and bromide in 10 ml of the solvent systems were sealed in ampoules and placed in the constant-temperature bath at the same temperatures as the kinetic runs. After approximately 3 half-lives the contents of the ampoules were removed and dissolved in ether. The ethereal solutions were washed once with 5% sodium hydroxide and dried over magnesium sulfate. The solvent was removed under reduced pressure. The residues were analyzed by gas–liquid partition chromatography (glpc) on a 4-ft THEED on Chromosorb W column at 110° showing the presence of the phenacyl ether and phenacyl alcohol (approximately 70:30 ratio) and several very minor (unidentified) fractions.

The sodium hydroxide extract (from above) was acidified and extracted with ether. The ether extract was dried over magnesium sulfate. The ether was removed by evaporation giving approximately 5% by weight acidic material (total recoveries averaged 90–95%). The residues were dissolved in a few milliliters of ether and treated with ethereal diazoethane. Analysis of the resulting solution by glpc showed no ethyl phenylacetate present.

The above procedure was modified for the product analysis in the formolysis experiment. The formic acid was removed under reduced pressure leaving a dark residue. Analysis of the residue by glpc indicated the presence of only phenacyl formate (by retention time comparison). The residue was then hydrolyzed with sodium hydroxide in 50% ethanol. The solution was poured into water and extracted once with ether. The ether layer was discarded. The aqueous phase was strongly acidified with concentrated hydrochloric acid. The acidified solution was extracted twice with ether. The ether extract was washed once with water and was dried over anhydrous sodium sulfate. The ether was partially removed from the sample by distillation and ethereal diazoethane was added until an excess was present. The ether was removed under reduced pressure and the residue was analyzed by glpc. No ethyl phenylacetate was present.

Preparation of Authentic Samples for Glpc Retention Time Comparison.—Ethyl phenacyl ether and phenacyl alcohol were available from our earlier investigations.[2] *t*-Butyl phenacyl ether was prepared by refluxing for 4 days a mixture of 4.0 g (0.020 mole) of phenacyl bromide and 3.5 g (0.021 mole) of silver nitrate in 60 ml of *t*-butyl alcohol. The *t*-butyl alcohol was removed under reduced pressure. The residue was triturated with ether and the solids were removed by filtration. The ether solution was washed with dilute sodium bicarbonate solution and then dried over anhydrous sodium sulfate. The ether was removed under reduced pressure. Vacuum distillation of the residue gave 1.8 g (48%) of a viscous liquid, bp 88–90° (0.8 mm). The infrared spectrum (carbon tetrachloride solution) displayed a carbonyl peak at 1690 cm^{-1}. The nmr spectrum displayed singlets at 2.44 and 4.23 ppm (relative to tetramethylsilane) with an area ratio of 9:2 and a multiplet at 7.46 ppm with a relative area of 5.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.96; H, 9.93. Found: C, 75.91; H, 10.15.

Phenacyl formate was prepared by refluxing a mixture of 4.5 g (0.02 mole) of phenacyl bromide and 2 g (0.04 mole) of sodium formate in 60 ml of 95% ethanol for 12 hr. The reaction mixture was poured into 300 ml of water and was extracted with 150 ml of ether. The organic layer was removed and was washed with saturated sodium bicarbonate solution. The organic phase was

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(15) F. G. Bordwell and W. T. Brannen, Jr., *J. Am. Chem. Soc.*, **86**, 4645 (1964), and references cited therein.

dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave a liquid which was distilled at 63° (2.7 mm). The sample was induced to crystallize and was recrystallized from petroleum ether (bp 61–70°) giving mp 39–40° (lit.[16] mp 40°).

Registry No.—Phenacyl chloride, 532-27-4; phenacyl bromide, 70-11-1; p-NO$_2$-phenacyl bromide, 99-81-0; p-Cl-phenacyl bromide, 536-38-9; p-Br-phenacyl bromide, 99-73-0; m-CH$_3$O-phenacyl bromide, 5000-65-7; p-CH$_3$O-phenacyl bromide, 2632-13-5; t-butyl phenacyl ether, 7616-91-3; phenacyl formate, 614-20-0.

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[16] F. Stodola, *Microchem. J.*, **7**, 389 (1963).

The Silver Ion Assisted Solvolysis of Phenacyl Halides in Aqueous Ethanol[1]

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The kinetics of the silver ion assisted solvolyses of phenacyl chloride, bromide, and iodide, in 50, 80, and 95% aqueous ethanol have been measured at three temperatures. The Hammett ρ value determined for substituted phenacyl bromides in 80% aqueous ethanol at 70° was found to be approximately 0 compared to +0.35 for the unassisted solvolysis. The rate data for the silver ion assisted solvolyses are compared with the rate data reported for the silver ion assisted solvolyses of other alkyl halides and the rate data for the unassisted solvolyses. The mechanism of the silver ion assisted solvolysis of phenacyl bromide is best described as a highly concerted push–pull mechanism (electrophically assisted nucleophilic displacement). The carbon atom undergoing substitution possesses slightly greater carbonium ion character in the silver ion assisted solvolysis than in the unassisted solvolysis. The role of silver ion as the electrophilic catalyst in the transition state is discussed. A linear correlation is observed between the enthalpies of activation for the silver ion assisted solvolysis of phenacyl chloride, bromide, and iodide and the difference in silver–halogen and carbon–halogen bond energies. It is concluded that extensive silver–halogen and carbon–oxygen bond formation and carbon–halogen bond cleavage have occurred in going to the transition state.

In a recent investigation of the silver ion assisted solvolysis of a series of keto halides it was observed that phenacyl chloride underwent solvolysis 1.3 times as fast as n-butyl chloride in 80% aqueous ethanol at 56° and that the activation enthalpy and entropy for phenacyl chloride differed substantially from what might have been expected in comparison with the values obtained for the higher homologs.[2] In view of the mechanistic implications of this earlier finding we have investigated more extensively the unassisted solvolysis[3] and the silver ion assisted solvolysis of phenacyl halides.

The procedure used for following the kinetics of the silver ion assisted solvolyses is identical with the procedure used in our earlier investigation[2] utilizing silver perchlorate as the source of the silver ion. Under these conditions clean second-order kinetics are observed.[2] The products derived from the silver ion assisted solvolysis of the phenacyl halides are only ethyl phenacyl ether and phenacyl alcohol; no rearrangement products, ethyl phenylacetate or phenylacetic acid, were observed. In all cases the predominant product was the ethyl phenacyl ether (~70%).[4]

The second-order rate constants for the silver ion assisted solvolysis of phenacyl chloride, bromide, and iodide are presented in Table I. The activation enthalpies and entropies as determined from the rate data are presented in Table II.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE SILVER ION ASSISTED SOLVOLYSIS OF PHENACYL HALIDES[a]

Substrate	Solvent	$k_2 \times 10^3$, l. mole^{-1} min^{-1} at 40°	55°	70°
Phenacyl chloride	80% ethanol	0.060	0.319	1.16[b]
Phenacyl bromide	50% ethanol	10.8	43.2	121
Phenacyl bromide	80% ethanol	12.7	...	153
Phenacyl bromide	95% ethanol	16.7	61.4	200
Phenacyl iodide	80% ethanol	160	436	1230
p-NO$_2$-phenacyl bromide	80% ethanol	...	...	176
p-Cl-phenacyl bromide	80% ethanol	...	...	169
m-CH$_3$O-phenacyl bromide	80% ethanol	...	...	171
p-CH$_3$O-phenacyl bromide	80% ethanol	...	...	170

[a] Probable experimental uncertainty ±4%. [b] k_2 at 80°; 3.27 × 10^3 l. mole^{-1} min^{-1}.

TABLE II

ACTIVATION PARAMETERS FOR THE SILVER ION ASSISTED SOLVOLYSIS OF PHENACYL BROMIDES IN AQUEOUS ETHANOL

Substrate	Solvent	$\Delta H^{\ddagger}$, kcal/mole[a]	$\Delta S^{\ddagger}$, eu[b]
Phenacyl chloride	80% ethanol	21.2	18.1
Phenacyl bromide	50% ethanol	15.7	25.2
Phenacyl bromide	80% ethanol	17.1	20.9
Phenacyl bromide	95% ethanol	16.9	20.8
Phenacyl iodide	80% ethanol	14.1	25.2

[a] Estimated precision, ±0.8 kcal/mole. [b] Estimated precision, ±1.6 eu.

It is interesting to compare the trends in the rates of the unassisted and silver ion assisted solvolysis reactions. It was originally reported that phenacyl chloride undergoes silver ion assisted solvolysis at a rate 1.3 times that of n-butyl chloride in 80% ethanol at 56.2°.[2] Comparison of the calculated rate for the silver ion assisted solvolysis of phenacyl bromide in 70% ethanol at 64° (see Table III) reveals that phenacyl bromide solvolyzes somewhat slower in the presence of silver perchlorate than straight-chain alkyl

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[1] Research supported by the National Science Foundation, Grant GP-4497.

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

[3] D. J. Pasto, K. Garves, and M. P. Serve, *J. Org. Chem.*, **32**, 774 (1967).

[4] In the previous article[3] it was shown that ethyl phenacyl ether and phenacyl alcohol slowly equilibrate in aqueous ethanol under the conditions of the kinetic experiments.