The Mechanism of Alkylation Reactions. Part 1. The Effect of Substituents on the Reaction of Phenacyl Bromide with Pyridine in Methanol

By **William Forster**, Department of Science, Sunderland Church High School, Mowbray Road, Sunderland SR2 7TS
Robert M. Laird,* Department of Chemistry, Newcastle upon Tyne Polytechnic, Ellison Place, Newcastle upon Tyne, Tyne and Wear NE1 8ST

Rate constants have been determined for the solvolysis of phenacyl bromide in 50—100% aqueous methanol, for the reactions in methanol of six *m*- and *p*-substituted phenacyl bromides with pyridine and for phenacyl bromide with five 3- and 4-substituted pyridines, aniline, imidazole, and benzimidazole. The results have been discussed in terms of linear free energy relationships. Evidence is presented for a reaction in which a special combination of field and conjugative effects contribute to the enhanced reactivity of phenacyl halides.

ALTHOUGH the high reactivity of phenacyl halides relative to alkyl halides has long attracted attention,[1,2] opinions still differ [3-10] as to the precise mechanism. To clarify the reaction mechanism, a study of substituent effects for the reaction of phenacyl bromide with pyridine was undertaken.

EXPERIMENTAL

Materials.—Phenacyl bromide [11] and the *p*-bromo,[12] *m*-nitro,[12,13] *p*-nitro,[14] *p*-methyl,[15] and *p*-methoxy [16] compounds were prepared according to the literature. 2,2-Dideuteriophenacyl bromide was prepared [11] from the product of Friedel–Crafts acylation of benzene with trideuterioacetyl chloride. The amines were purified by distillation or recrystallisation as appropriate.[17] Spectroscopic grade methanol was used as obtained and its water content, 0.02%, checked by Karl Fischer titration.

Kinetic Measurements.—The slow solvolyses were followed by potentiometric titrations of aliquot portions with standard alkali. The second-order reactions were followed by volumetric titrimetry using the Volhard method and in addition, where noted, conductimetrically using a Mullard conductance meter.

The solvolyses followed the first-order rate expression and for the reactions with aniline and the tertiary amines, in which two and one equivalents of nucleophile are respectively consumed, the appropriate second-order expressions [18] were used. Both equal and unequal initial concentrations of each reactant were used. Calibration curves were required to relate conductance to concentration for bromide molarities above 0.02 mol l^{-1}. Salt effects were negligible up to 0.05 mol l^{-1}. Reactions were normally followed for at least three half-lives and were reproducible. For the kinetic isotope effects, solutions 10^{-3} and 0.115 mol l^{-1} in phenacyl bromide and pyridine, respectively, gave apparent first-order rate constants which were determined conductimetrically using a Wayne-Kerr B641 autobalance bridge. Using resistance standards, the thermal stability during these measurements is estimated to be ±0.02 K or better over one week.

RESULTS

Arrhenius parameters and interpolated rate constants at 310 K for the reaction of phenacyl bromide with solvent and with pyridine in aqueous methanol are collected in Tables 1 and 2, respectively. Arrhenius parameters for the reactions of substituted phenacyl bromides with pyridine are contained in Table 3 and for the reaction of phenacyl bromide with amines in Table 4. Rate determinations were made between 298 and 328 K, excepting the slower solvolyses measured between 303 and 328 K.

TABLE 1

Arrhenius parameters and interpolated values for the rate constant at 310 K for the solvolysis of phenacyl bromide in aqueous methanol

v/v% Methanol	$10^7k/s^{-1}$	E_a/kJ mol^{-1}	log (A/s^{-1})
50	10.7	83.*9*	8.1*7*
60	9.33	82.*2*	7.8*1*
70	8.05	76.*9*	6.8*6*
80	5.71	79.*8*	7.2*0*

TABLE 2

Arrhenius parameters and interpolated values for the rate constant at 310 K for the reaction of phenacyl bromide and pyridine in aqueous methanol

v/v% Methanol	10^4k/ l mol^{-1} s^{-1}	E_a/kJ mol^{-1}	log (A/s^{-1})
50	40.4	56.1	7.06
65	23.7	56.7	6.96
75	14.9	57.7	6.90
90	7.89	62.1	7.36
100	6.15	62.0	7.25

TABLE 3

Arrhenius parameters and interpolated rate constants at 310 K for the reaction of aryl-substituted phenacyl bromides and pyridine in methanol

Substituent	10^4k/ l mol^{-1} s^{-1}	E_a/kJ mol^{-1}	log (A/s^{-1})
p-CH_3O	5.03	65.7	7.8
p-CH_3	5.42	61.6	7.12
H	6.15	62.0	7.25
p-Br	7.08	63.5	7.54
m-NO_2	9.06	67.6	8.35
p-NO_2	9.52	67.2	8.31

The rate constants for the reactions are estimated to be accurate to 3% or better, except for the slow solvolyses which are only accurate to 5%. Thus at 308.2 K for the reaction of phenacyl bromide with pyridine, five determinations of *k* by the conductimetric method gave a mean value of $(5.24 \pm 0.07) \times 10^{-4}$ l mol^{-1} s^{-1} and duplicate determinations by titrimetry gave $(5.43 \pm 0.14) \times 10^{-4}$ l mol^{-1} s^{-1} and at 318.1 K the corresponding values were $(1.145 \pm 0.014) \times 10^{-3}$ and $(1.14 \pm 0.003) \times 10^{-3}$ l mol^{-1} s^{-1}, respectively. These errors in *k* correspond to estimated errors of 3.3 and 6 kJ mol^{-1} in E_a and of 0.4 and 0.9 in log*A*, respectively. Rate constants for the reaction of phenacyl bromide and its deuteriated analogue with pyridine in methanol at 298.1 K were 2.870×10^{-5} and 2.738×10^{-5} s^{-1} with a standard deviation of $\pm 1 \times 10^{-8}$ s^{-1}. This corresponds to a H/D isotope effect of 1.048 ± 0.004 at the 95% certainty level [(2.4 ± 0.2)% per D].

TABLE 4

Arrhenius parameters and interpolated rate constants at 310 K for the reaction of phenacyl bromide with aniline, pyridine, and related compounds in methanol

Amine	10^4k/ l mol^{-1} s^{-1}	E_a/kJ mol^{-1}	log (A/s^{-1})
Aniline	9.77	59.7	7.06
Imidazole	10.4	64.9	7.95
Benzimidazole	2.25	65.3	7.35
Pyridine	6.15	62.0	7.25
Substituent			
m-CH_3	10.1	63.8	7.76
p-CH_3	11.7	61.8	7.48
m-CH_3CO	1.47	64.0	6.96
m-NH_2CO	1.53	67.9	7.63

DISCUSSION

Good agreement is obtained with the results of other workers [18-20] for the reaction of phenacyl bromide with aniline in methanol. For the solvolyses in aqueous methanol (Table 1) correlation of log$k$ with the Grunwald–Winstein Y parameters [21] gives an m value of 0.18 ± 0.1. This is close to the value of 0.20 ± 0.01 obtained by Pasto *et al.*[22] for the corresponding solvolysis in aqueous ethanol and is indicative of a bimolecular process. In contrast, the second-order reaction with pyridine in the same solvent range (Table 2) gives an m value of 0.32 suggesting a bimolecular reaction with greater charge separation in the transition state. At high methanol concentrations, a positive departure from the line of regression is found for correlations of log$k$ with dielectric constant [23] and other solvent parameters [21,24] with the exception of the Brownstein S relation [25] which gives a small negative deviation for 90% methanol alone.

As in addition previous workers have obtained evidence against neighbouring-group participation by either the phenyl [22] or the ketone [6] groups and the conditions under which the ketone group forms an acetal or related addition compound are well established,[26-28] a bimolecular nuclear-displacement need only be considered.

Many workers have not only commented on the activating influence of the carbonyl and cyano-groups on *some* bimolecular reactions, but have also attempted to explain the retarding effects of the electronically similar nitro, sulphinyl, sulphonyl, and trifluoromethyl groups.[29,30] In addition to the view that the reaction is a normal S_N2 mechanism,[3] Dewar,[4] Winstein,[5] and Pearson and his co-workers [6] have suggested additional stabilisation of the transition state through π-conjugation of the carbonyl group with the p-orbital containing the incoming and leaving groups, through σ-conjugation of the p-orbital of the carbonyl group with the incoming and leaving groups, and through a favourable electrostatic attraction between the incoming nucleophile and the adjacent carbon atom of the carbonyl groups, respectively.

The effect of specific acid catalysis by silver ions in reducing the Hammett ρ value *as bond-breaking is promoted relative to bond-forming* [22,31] seems to preclude mechanisms [30] based on electron donation by the carbonyl group.

The nucleophilicity sequence shown in Table 4, imidazole > aniline > pyridine, follows that for displacement at a ' soft ' carbon centre [32] and, not following the well established sequence [32] for carbonyl addition reactions, gives no support for reaction mechanisms with transition states involving partial addition at the carbonyl group.[5] For the reactions of substituted pyridines, the Hammett ρ value [33] remained constant at -1.87 ± 0.04 from 298 to 324 K and an isoenthalpic relation [34] cannot be ruled out (Table 5). Both the magnitude of ρ in comparison with the value of 6.01 obtained for the ionisation of pyridines in water [35] and activation volume studies [36] suggest that only a third of the positive charge carried by the pyridinium ion is developed in the transition state.

TABLE 5

Enthalpy-entropy relationships [34]

Reaction sets	m [a]	l [b]	s^{c}_{00}	s^{d}_{0}	$\beta^{e}$$K^{-1}$
Solvolysis (Table 1)	13	4	0.0395	0.0265	167—227 [f]
Solvent effect (Table 2)	43	4	0.0736	0.0734	0 [g]
Arene substituents (Table 3)	41	5	0.0619	0.0832	None [h]
Pyridine substituents (Table 4)	43	5	0.0298	0.0326	0 [i]

[a] Number of measurements. [b] Number of reactions. [c] Standard deviation from the unconstrained lines. [d] Standard deviation from the isokinetic lines. [e] Isokinetic temperature. [f] 95% confidence limits. [g] Isoenthalpic. [h] Isokinetic hypothesis must be rejected at 95% confidence limits. [i] Isoenthalpic relation cannot be rejected at the 95% probability level.

The secondary α-deuterium isotope effect falls clearly within the expected range [37] for simple bimolecular displacements. If intermediate formation [38] can be rejected,[39] and both solvent relaxation and vibrational couplings not considered in the original theoretical treatment can be neglected, then for isotopic exchange reactions, as a consequence of the principle of microscopic reversibility, the partial bonds formed by the entering and leaving groups must be identical in the transition state and hence a normal secondary α-deuterium isotope effect indicates [37] a ' loose ' transition state in which the total bond order at the atom undergoing substitution is less than one and bond breaking leads over bond forming. Conversely for such reactions abnormal α-deuterium isotope effects indicate [37] a ' tight ' transition state. Comparison of the small normal isotope-effect (2.4% per D) with those for iodide exchange with methyl iodide in the same solvent [38] and for the recent value for chloride exchange with phenacyl chloride in acetonitrile,[40] 1.6 and 2.0% per D respectively, suggests a reaction with bond order near one if the asymmetry introduced into the transition state by the different leaving and entering groups can be neglected.[39] Such a reaction with little charge development at the carbon atom undergoing substitution would indicate *a priori* a small ρ value for this phenacyl substitution, but the transmission of changes in charge at the reaction centre to the arene ring must be considered before the significance of the measured ρ values can be assessed.

By comparing the reactivities of 5,7-dinitrocoumaran-3-one and ω-(4-acetyl-2,6-dinitrophenoxy)acetophenone with iodide ion in acetone, Bartlett and Trachtenberg [9] confirmed that the stereochemistry of the transition state was that required for the conjugative mechanisms of Dewar [4] and Winstein [5] and the electrostatic mechanism of Pearson and his co-workers,[6] a transition state in which the carbonyl group lies in the nodal plane of the *p*-orbital containing the entering nucleophile and the leaving group. Both Bartlett and Trachtenberg [9] and Bordwell and Brannen [30] therefore assumed the initial state to be the *cis*-conformation of the phenacyl halide, with the halogen in close proximity to the carbonyl group. A high reactivity [1,2,6,30,41] is observed for α-methylene halides which possess conjugative groups such as carbonyl, carboxy, cyano, and nitroso, and which *in addition* exhibit rotational isomerism.[42] Any discussion of the reactions of phenacyl halides and related compounds must therefore take account of the *cis–gauche*-equilibria preceding the rate-determining substitution.

The mechanism of Pearson and his co-workers,[6] that through-space interactions between the entering nucleophile and the phenacyl carbonyl carbon atom facilitate the reaction, has been criticised [41] on the grounds that the effect remains when neutral nucleophiles react. The authors suggest that this objection is removed if the electrostatic interaction, which exists between the carbonyl group and the potential leaving-group for the phenacyl halide in the *cis*-conformation, is considered.

I.r. spectra [42] and *X*-ray crystallography [43] have shown that the carbonyl group in the *cis*-conformation has more double-bond character as a result of a through-space interaction with the adjacent halogen bearing a partial negative-charge and it is proposed that loss of this interaction in the transition state, leading to additional polarisation of the carbonyl bond, will result in additional stabilisation of the partial negative charge at the reacting carbon atom. Polarisation of the carbonyl group, suppressed by the through-space interaction in the initial state, occurs on entering the transition state as the distance between the carbonyl oxygen and the departing halogen increases as a result of (a) rotation of the carbonyl group into the 'spectator-group' plane (the nodal plane of the *p*-orbital containing the entering and leaving groups) and (b) extension of the carbon–halogen bond. For the less reactive benzenesulphinylmethylene halides [30] however, the distance between the sulphoxide group and the halogen is too great to allow through-space interactions, as shown by the absence of *cis–gauche*-isomerism.[44]

All recorded ρ values for S_N2 reactions of substituted phenacyl halides are lower than the value of 1.43 obtained for the ionisation of phenylglyoxylic acids in water,[45] as would be expected for reactions in which there is less charge development in the transition state. Recent studies on cross-conjugation [46] would predict that as the reaction centre becomes itself a better donor, so conjugative electron donation from the benzene ring to the carbonyl group will decrease, thus enabling the polarising carbonyl group to further stabilise the partial negative charge at the reaction centre. Sisti and Memeger [47] obtained a higher ρ value, 0.60, for the reaction of pyridine with substituted phenacyl chlorides in methanol at 293.2 K: the expected result of both a poorer leaving group, requiring additional bond formation in the transition state, and a longer carbonyl C–O distance [43] indicating less double-bond character than the bromide in the initial state, the reaction is more dependent on initial-state conjugation with electron-withdrawing substituents in the benzene ring.

The results collected in Table 4 show that, relative to the pyridines, aniline is more reactive and the imidazoles are less reactive than indicated by their basicities in water.[48] It is likely that, in the transition state for the primary amine, hydrogen bonding between an amino-hydrogen of the aniline and the phenacyl carbonyl oxygen stabilises the developing partial positive and partial negative charges, respectively. Such a concerted process is also possible for the hydroxylic nucleophiles, would lead to *substantial charge dispersion* in the transition state and could be the explanation for the *less polar transition states* indicated in the earlier mY [21,22] analysis for aqueous alcohol solvolyses relative to the reactions with pyridine.

The insensitivity of the ρ value for pyridine substitution to change in temperature is characteristic of an isoenthalpic relation and it is therefore interesting to note that Arnett and Reich [49] have reported an isoenthalpic relationship for the methylation of substituted pyridines by reagents covering a wide range of reactivities. Although statistical analysis [34] (Table 5) neither confirms nor rejects an isoenthalpic relation, it is clear that the selectivity is *mainly* determined by entropy changes associated with charge development in the nucleophile.[49] Moreover, charge development as measured by a ρ value of -1.87 is much greater for the activated phenacyl bromide than for an alkyl bromide reacting with substituted pyridines in the same solvent and having a ρ value of -0.847.[50] Phenacyl activation doubles the extent of bond-forming in the transition state. Solvent effects on the pyridine reaction give an isoenthalpic relation and the solvolyses obey an isokinetic relationship, but for substitution in the phenacyl bromide, with the substituents affecting *both* reaction rates *and* conformer equilibria,[42] no simple isokinetic relationship exists (Table 5).

In conclusion, because the α-carbonyl carbon atom has a smaller van der Waals radius than the radii of methyl and trifluoromethyl groups and of elements such as sulphur, absence of steric hindrance [29,30] contributes to the reactivity of phenacyl compounds. Phenacyl halides in the terminology of Ingold [51] have for the reaction studied wide, shallow basket-shaped energy surfaces and hence changes in the nucleophile affecting bond formation affect only enthalpy with no compensation in entropy (Table 5). Both favourable steric and electronic properties contribute to the reactivity of phenacyl halides.

Initial studies were done at the Science Department, South Shields Marine and Technical College, South Shields. The Royal Society is thanked for a chemicals grant (Research in Schools Scheme), and Mr. J. Watson for assistance, and Misses G. Softley and P. Taylor are thanked for experimental work.

[1/659 *Received, 24th April,* 1981]

REFERENCES

[1] H. T. Clarke, *J. Chem. Soc.*, 1910, 416.

[2] J. B. Conant and W. R. Kirner, *J. Am. Chem. Soc.*, 1925, **46**, 232.

[3] E. D. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603.

[4] M. J. S. Dewar, 'The Electronic Theory of Organic Chemistry,' Oxford University Press, Oxford, 1949, p. 73.

[5] S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, 1951, **73**, 2700; A. Streitwieser, ' Solvolytic Displacement Reactions,' McGraw-Hill, New York, 1962, p. 26.

[6] R. G. Pearson, S. H. Langer, F. V. Williams, and W. J. McGuire, *J. Am. Chem. Soc.*, 1952, **74**, 5130.

[7] J. Hine, ' Physical Organic Chemistry,' 1956, McGraw-Hill, London, 1956, p. 157.

[8] E. L. Eliel in ' Steric Effects in Organic Chemistry,' eds. M. S. Newman, Chapman and Hall, London, 1956, p. 103.

[9] P. D. Bartlett and E. N. Trachtenberg, *J. Am. Chem. Soc.*, 1958, **80**, 5807.

[10] C. A. Bunton, ' Nucleophilic Substitution at a Saturated Carbon Atom,' Elsevier, London, 1963, p. 35.

[11] R. M. Cowper and L. H. Davidson, *Org. Synth.*, 1943, Coll. Vol. II, 480.

[12] W. D. Langley, *Org. Synth.*, 1941, Coll. Vol. I, 127.

[13] E. G. Cobb, *Proc. South Dakota Acad. Sci.*, 1945, **25**, 64 (*Chem. Abstr.*, 1946, **40**, 7180); W. L. Evans and B. T. Brooks, *J. Am. Chem. Soc.*, 1908, **30**, 404.

[14] C. Engler and O. Zielker, *Ber.*, 1889, **22**, 203.

[15] P. K. Bose, *J. Indian Chem. Soc.*, 1926, **3**, 205.

[16] K. Kindler and L. Blaas, *Ber.*, 1944, **77**, 585.

[17] A. K. Covington and T. Dickenson in ' Physical Chemistry of Organic Solvent Systems,' Plenum Press, London, 1973, p. 13; R. M. Laird and M. J. Spence, *J. Chem. Soc. B*, 1971, 1435.

[18] J. F. Bunnett in ' Techniques of Organic Chemistry,' 2nd edn., eds. S. L. Friess, E. L. Lewis, and A. Weissberger, Interscience, London, 1961, vol. 8, p. 180.

[19] V. K. Seth and A. N. Bose, *J. Indian Chem. Soc.*, 1967, **44**, 955.

[20] R. Rath, G. B. Behara, and M. K. Rout, *Indian J. Chem.*, 1968, **6**, 202; R. K. Mohanty, G. Behara, and M. K. Rout, *ibid.*, 1967, **5**, 259.

[21] E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 1949, **71**, 846.

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

[23] J. G. Kirkwood, *J. Chem. Phys.*, 1934, **2**, 351; L. P. Hammett, *J. Am. Chem. Soc.*, 1937, **59**, 96; *Trans. Faraday Soc.*, 1938, **34**, 156.

[24] E. Kosower, *J. Am. Chem. Soc.*, 1958, **80**, 3253; K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Liebigs Ann. Chem.*, 1963, **661**, 1.

[25] S. Brownstein, *Can. J. Chem.*, 1968, **38**, 1590.

[26] R. P. Bell and A. O. McDougall, *Trans. Faraday Soc.*, 1960, **56**, 1281.

[27] T. I. Temnikova and V. A. Kropacheva, *Zh. Obshch. Khim.*, 1949, **19**, 1917; C. L. Stevens, W. Malik, and R. Pratt, *J. Am. Chem. Soc.*, 1950, **72**, 4758; M. O. Funk and E. T. Kaiser, *ibid.*, 1977, **99**, 5336.

[28] T. Suzuki, A. Yano, M. Okada, and Y. Ishii, *Nippon Kagaku Zasshi*, 1960, **81**, 301.

[29] W. Reeve, E. L. McCaffery, and E. T. Kaiser, *J. Am. Chem. Soc.*, 1954, **76**, 2280.

[30] F. G. Bordwell and W. T. Brannen, *J. Am. Chem. Soc.*, 1964, **86**, 4645.

[31] M. Murakami, S. Oae, and S. Takeuchi, *Bull. Chem. Soc. Jpn.*, 1951, **24**, 1; S. Oae, *J. Am. Chem. Soc.*, 1956, **78**, 4030.

[32] R. G. Pearson in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, p. 281.

[33] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 227.

[34] O. Exner, *Prog. Phys. Org. Chem.*, 1973, **10**, 411.

[35] A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 1964, 3591.

[36] H. Heydtmann, A. P. Schmidt, and H. Hartmann, *Ber. Bunsenges. Phys. Chem.*, 1966, **70**, 444; Y. Kondo, M. Ohnishi, and N. Tokara, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 3579.

[37] S. E. Scheppele, *Chem. Rev.*, 1972, **72**, 520; V. J. Shiner in ' Isotope Effects in Chemical Reactions,' Van Nostrand-Reinhold (A.C.S. Monograph 167, eds. C. J. Collins and N. S. Bowman), London, 1970, p. 116; A. V. Willi in ' Isotopes in Organic Chemistry,' eds. E. Buncel and C. C. Lee, Elsevier, London, 1977, pp. 237—280.

[38] S. Seltzer and A. A. Zavitas, *Can. J. Chem.*, 1967, **45**, 2023.

[39] W. J. Albery and M. M. Kreevoy, *Adv. Phys. Org. Chem.*, 1978, **16**, 87.

[40] J.-i. Hayami, T. Koyanagi, and A. Kaji, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1441.

[41] A. J. Sisti and S. Lowell, *Can. J. Chem.*, 1964, **42**, 1896.

[42] L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 1957, 4294; L. J. Bellamy, L. C. Thomas, and R. L. Williams, *ibid.*, 1956, 3704; R. N. Jones and E. Spinner, *Can. J. Chem.*, 1958, **36**, 1020; L. J. Bellamy, ' The Infrared Spectra of Complex Molecules,' 2nd edn., Methuen, London, 1958, p. 400; C. N. R. Rao and K. R. Bhaskar in ' The Chemistry of the Nitro and Nitroso Groups,' eds. H. Feuer and S. Patai, Interscience, London, 1969, p. 140; S. I. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa, and N. Shido, *J. Chem. Phys.*, 1953, **21**, 815.

[43] Y. Barrans and J.-J. Maisseu, *C.R. Acad. Sci., Sect. C*, 1966, **262**, 91; M. P. Gupta and S. M. Prasad, *Acta Crystallogr.*, 1971, *B***27**, 1649.

[44] L. J. Bellamy, 'Advances in Infra-red Group Frequencies,' Methuen, London, 1968, p. 195.

[45] M. S. Wheatley, *Experientia*, 1956, **12**, 339.

[46] C. Laurence and M. Berthelot, *J. Chem. Soc., Perkin Trans. 2*, 1979, 98.

[47] A. J. Sisti and W. Memeger, *J. Org. Chem.*, 1965, **30**, 2102.

[48] E. M. Arnett in ' Proton-Transfer Reactions,' eds. E. F. Caldin and V. Gold, Chapman and Hall, London, 1975, p. 79.

[49] E. M. Arnett and R. Reich, *J. Am. Chem. Soc.*, 1978, **100**, 2930.

[50] K. Murai, S. Takeuchi, and C. Kimura, *Nippon Kagaku Zasshi*, 1973, 95.

[51] C. K. Ingold, *Quart. Rev.*, 1957, **11**, 1.