carbonyl bands at 1740 and 1760 cm^{-1}. The NMR spectrum ($CDCl_3$) in ppm: 1.33 (t, 3 H); 4.10 (d, 2 H); 4.30 (q, 2 H); 5.73 (broad, 1 H); 7.38 (d, 2 H); 8.30 (d, 2 H).

Anal. Calcd for $C_{11}H_{12}N_2O_6$: C, 49.25; H, 4.48, Found: C, 49.05; H, 4.54.

***tert*-Butyl 2,4,5-Trichlorophenyl Dicarbonate (13).** A suspension of 18.3 g (0.15 mol) of potassium *tert*-butoxide in 200 mL of THF was cooled with ice–salt. Carbon dioxide was passed into the suspension with vigorous stirring for 30 min. A solution of 39.0 g (0.15 mol) of 2,4,5-trichlorophenyl chloroformate in 120 mL of THF was added dropwise. The reaction mixture was stirred at 0 °C for 2 h and 5–10 °C for another 1–5 h. Insoluble materials were removed, and the filtrate was evaporated at reduced pressure. The crude product was recrystallized from 400 mL of pentane and then from 280 mL of pentane to give 21.1 g (41%) of *tert*-butyl 2,4,5-trichlorophenyl dicarbonate, mp 65.5–66.5 °C.

The IR spectrum (CCl_4) showed carbonyl bands at 1835 and 1770 cm^{-1}, and the NMR spectrum (CCl_4) showed peaks at 1.62 (s, 9), 7.66 (s, 1 H), and 7.81 (s, 1 H) ppm.

Anal. Calcd for $C_{12}H_{11}Cl_3O_5$: C, 42.17; H, 3.22. Found: C, 42.21; H, 3.28.

Registry No.—**1**, 22085-39-8; **2**, 24424-95-1; **3**, 22085-40-1; **4**, 24424-99-5; **5**, 65815-73-8; **6**, 65815-74-9; **7**, 65815-75-0; **12**, 60416-11-7; **13**, 60450-67-1; **14**, 65815-76-1; glycine ethyl ester HCl, 623-33-6; 1-adamantanol, 768-95-6; *tert*-butylthiol chlorocarbonate, 13889-95-7; di-*tert*-butyldithiol carbonate, 16118-32-4; *p*-nitrophenyl chloroformate, 7693-46-1; *p*-nitrophenol, 100-02-7; di-*p*-nitrophenyl carbonate, 5070-13-3; 2,4,5-trichlorophenyl chloroformate, 4511-19-7.

References and Notes

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(2) (a) Tennessee Eastman Company, Kingsport, Tenn.; (b) Chemistry Department, Soochow University, Taipei, Taiwan; (c) School of Pharmacy, Ferris State College, Big Rapids, Mich.; (d) Pharmaceutical Institute, Tohoka University, Sendai, Japan.
(3) A. W. Friederang and D. S. Tarbell, *Tetrahedron Lett.*, 5535 (1968).
(4) C. S. Dean and D. S. Tarbell, *Chem. Commun.*, 728 (1969).
(5) C. S. Dean, D. S. Tarbell, and A. W. Friederang, *J. Org. Chem.*, **35**, 3393 (1970).
(6) C. S. Dean and D. S. Tarbell, *J. Org. Chem.*, **36**, 1180 (1971).
(7) B. M. Pope, Y. Yamamoto, and D. S. Tarbell, *Org. Synth.*, **57**, 45 (1978).
(8) D. S. Tarbell, Y. Yamamoto, and B. M. Pope, *Proc. Natl. Acad. Sci., U.S.A.*, **69**, 730 (1972).
(9) V. F. Pozdnev and E. S. Chaman, *Khim. Prir. Soedin.*, **10** (2), 266 (1974); *Chem. Abstr.*, **81**, 49995*q* (1974); V. F. Pozdnev, *Khim. Prir. Soedin.*, **10** (6), 764 (1974); *Chem. Abstr.*, **82**, 156690*d* (1975); L. Moroder, A. Hallett, E. Wünsch, O. Keller, and G. Wersin, *Z. Physiol. Chem.*, **357**, 1651 (1976).
(10) From Fluka AG, Buchs, Switzerland.
(11) Unpublished results of Dr. Y. Yamamoto.
(12) T. Wieland, *Makromol. Chem.*, **92**, 277 (1966); *Chem. Abstr.*, **66**, 18854*d* (1967).
(13) R. L. Stanley and D. S. Tarbell, *J. Org. Chem.*, **42**, 3686 (1977).
(14) D. D. Perin, W. L. F. Amarego, and D. R. Perin, "Purification of Laboratory Chemicals", 1966, p 82.
(15) E. F. Degering, G. L. Jenkins, and B. E. Sanders, *J. Am. Pharm. Assoc.*, **39**, 624 (1950); *Chem. Abstr.*, **45**, 1949*h* (1951).
(16) Y. Yamamoto, D. S. Tarbell, J. R. Fehlner, and B. M. Pope, *J. Org. Chem.*, **38**, 2524 (1973).
(17) S. G. Cohen and A. Schneider, *J. Am. Chem. Soc.*, **63**, 3382 (1941).

Influence of the Steric Requirements of the Nucleophile on the Transition State Structure of E2 Reactions. A Kinetic Study of the Eliminations from 1-Bromo-2-arylethanes and 1-Chloro-1-phenyl-2-arylethanes Promoted by Sodium 2,6-Di-*tert*-Butylphenoxide

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The kinetics of the eliminations from 1-bromo-2-arylethanes and 1-chloro-1-phenyl-2-arylethanes promoted by sodium 2,6-di-*tert*-butylphenoxide in DMF–Me_2SO (9:1 v/v) have been investigated. With the first series of substrates values of ρ (+2.44), k_H/k_D (9.0), and Br/Cl leaving-group effect (146) have been evaluated which turn out to be quite similar to those (+2.64, 7.6, and 120, respectively) calculated for the corresponding reactions promoted by sodium phenoxide. The reaction of 1-chloro-2-arylethanes with sodium 2,6-di-*tert*-butyl phenoxide also exhibits a ρ value (+2.30) which is very similar to that (+ 2.40) of the same reaction with sodium phenoxide. From these results it is possible to conclude that with both series, the transition state structure of the E2 reaction is substantially unaffected by the steric requirements of the nucleophile. The influence of steric effects on the elimination rate is also not very large, sodium 2,6-di-*tert*-butylphenoxide being only 200-fold less reactive than sodium phenoxide.

The study of elimination reactions promoted by sodium phenoxides in a dipolar aprotic solvent provides a very useful tool for investigating the effect of the nature of the nucleophile on the mechanism of E2 reactions. Accordingly, unequivocal information on the effect of the nucleophile basicity upon the transition state structure of E2 reactions has been recently obtained by the study of eliminations from 2-arylethyl derivatives[1-3] induced by phenoxides of different basicity in DMF.

A continuation of this investigation with the purpose of acquiring information also on the effects of the steric requirements of the nucleophile appears worthwhile since it is recognized that these effects can be of importance in determining geometrical and positional orientation of E2 reactions.[4-9] Moreover it has been recently suggested[10] that the steric requirements of the base might play a significant role in producing the "anti-Thornton" behaviors observed in several reactions involving slow proton transfer.[11]

In this paper we report the results of a kinetic study of the eliminations from 1-bromo-2-arylethanes, 1-chloro-1-phenyl-2-arylethanes, and 1-chloro-2-phenylethane promoted by sodium 2,6-di-*tert*-butylphenoxide in DMF–Me_2SO mixed solvent. 2,6-Di-*tert*-butylphenoxide is a sterically very hindered base that has been found to produce a positional orientation much different from that anticipated by its basic strength in the reaction with 2-iodobutane.[6] In the case of

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Table I. Effect of the Base Concentration on the Rate Constants for the Elimination Reactions of 1-Chloro-1,2-diphenylethane Induced by Sodium 2,6-Di-*tert*-butylphenoxide in DMF–Me_2SO (9:1 v/v) at 30 °C

[Nucleophile], M	k_2, M^{-1} s^{-1}
0.023	6.22×10^{-3}
0.032	5.86×10^{-4}
0.045	5.06×10^{-4}
0.065	4.40×10^{-4}
0.055	5.81×10^{-5} [a]
0.065	7.55×10^{-4} [b]

[a] In the presence of $NaClO_4$ (0.85 M). [b] In the presence of 18-crown-6 ether (0.082 M).

1-chloro-1-phenyl-2-arylethanes and 1-chloro-2-phenylethane also the reactions with sodium phenoxide have been investigated.

Results

Sodium 2,6-di-*tert*-butylphenoxide has been prepared by the reaction of NaH with an excess (about 20%) of 2,6-di-*tert*-butylphenol in Me_2SO and its concentration was determined by acidimetric titration. In the kinetic runs a Me_2SO solution of sodium 2,6-di-*tert*-butylphenoxide has been mixed with a DMF solution of the substrate in order to obtain a DMF–Me_2SO (9:1 v/v) final mixture. The kinetic data obtained in this mixed solvent should be comparable with those previously obtained in pure DMF for the reaction of 1-bromo-2-arylethanes with sodium phenoxide.[1,2] Of course, the DMF–Me_2SO mixed solvent was used also for the reactions of sodium phenoxide with 1-chloro-1-phenyl-2-arylethanes and 1-chloro-2-phenylethane studied in the present work.

In the reactions of 1-bromo-2,2-dideuterio-2-phenylethane and 1-chloro-1,2-diphenylethane with sodium 2,6-di-*tert*-butylphenoxide the yield of olefin (styrene and *trans*-stilbene, respectively) was practically quantitative. Moreover, a quantitative yield of *p*-methyl-*trans*-stilbene was obtained in the reaction of 1-chloro-1-phenyl-2-*p*-tolylethane with sodium phenoxide. It is therefore fully justified to assume a quantitative yield of olefin also in the other reactions investigated.

Kinetics have been followed by potentiometric titration of the halide ions formed during the reaction. In all cases an excess of base (at least tenfold) was used.

When the base was sodium phenoxide the kinetic complications due to the not complete dissociation of this salt were overcome by carrying out the reaction in the presence of $NaClO_4$ (0,85 M).[2] In these conditions regular first-order kinetics were obtained and the second-order rate constant (k_2) does not change when the base concentration is changed. Ion pairing, however to a much smaller extent, is present also with sodium 2,6-di-*tert*-butylphenoxide. In the reactions promoted by this base the first-order plots exhibited an excellent linearity but a slight decrease of k_2 values with increasing the base concentration was observed. Moreoever the rate of elimination increases in the presence of a crown ether and decreases in the presence of $NaClO_4$. Some representative data for the reaction of 1-chloro-1,2-diphenylethane are reported in Table I. Thus, the structural effects in the reactions with sodium 2,6-di-*tert*-butylphenoxide were evaluated by comparing kinetic data obtained at the same base concentration.

The kinetic results for all reactions investigated are collected in Tables II and III.

Discussion

Since sodium phenoxide and sodium 2,6-di-*tert*-butylphenoxide are associated to a different extent, an approximate estimate of their reactivity ratio is only possible by comparing the kinetic data obtained, with 1-chloro-1,2-diphenylethane as the substrate, in the presence of 18-crown-6 ether which should convert most of the ion pairs into dissociated ions. From this comparison (Tables I and III) it turns out that sodium 2,6-di-*tert*-butylphenoxide is about 200-fold less reactive than sodium phenoxide. This is a quite significant factor but not very large. Clearly the rate of an E2 reaction appears to be much more sensitive to changes in the basicity of the nucleophile[12] than to changes in its steric requirements.

Another observation is that in going from 1-chloro-2-phenylethane to 1-chloro-1,2-diphenylethane the rate increases threefold with sodium phenoxide but only 1.2-fold with sodium 2,6-di-*tert*-butylphenoxide (see Tables II and III). Probably with the more hindered nucleophile the favorable electronic effect of the α-phenyl group is nearly completely counterbalanced by an adverse steric effect.

The data of Table II allow the calculation of the values of the Hammett reaction constant, ρ, the deuterium kinetic isotope effect (k_H/k_D), and the bromide/chloride leaving group effect (k_{Br}/k_{Cl}) for the reactions of 1-bromo-2-arylethanes with sodium 2,6-di-*tert*-butylphenoxide. These values are reported in Table IV and compared with the corresponding ones for the reaction with sodium phenoxide. We immediately see that the two reactions exhibit very similar

Table II. Rate Constants for the Elimination Reactions of 1-Bromo-2-arylethanes and 1-Chloro-2-phenylethane Induced by Sodium Phenoxide and Sodium 2,6-Di-*tert*-butylphenoxide in DMF–Me_2SO (9:1 v/v)

Nucleophile	Registry no.	Substrate	Registry no.	Temp, °C	k_2, M^{-1} s^{-1} [a]
Sodium phenoxide [b]	139-02-6	$C_6H_5CH_2CH_2Br$	103-63-9	30	4.29×10^{-2}
		$C_6H_5CH_2CH_2Cl$	622-24-2	30	3.58×10^{-4}
Sodium 2,6- di-*tert*-butylphenoxide [c]	7175-96-4	$C_6H_5CH_2CH_2Br$		0	5.98×10^{-3}
		$C_6H_5CD_2CH_2Br$	23088-37-1	0	5.67×10^{-4}
		p-$CH_3C_6H_4CH_2CH_2Br$	6529-51-7	0	3.25×10^{-3}
		p-$OCH_3C_6H_4CH_2CH_2Br$	14425-64-0	0	1.84×10^{-3}
		p-$BrC_6H_4CH_2CH_2Br$	1746-28-7	0	3.28×10^{-2}
		$C_6H_5CH_2CH_2Br$		10	1.36×10^{-2}
		$C_6H_5CD_2CH_2Br$		10	1.31×10^{-3}
		$C_6H_5CH_2CH_2Br$		20	3.49×10^{-2}
		$C_6H_5CD_2CH_2Br$		20	3.87×10^{-3}
		$C_6H_5CH_2CH_2Br$		30	7.31×10^{-2}
		$C_6H_5CD_2CH_2Br$		30	8.78×10^{-3}
		$C_6H_5CH_2CH_2Cl$		30	4.99×10^{-4}

[a] Average of at least two determinations. The average error is ±4%. [b] In the presence of $NaClO_4$ (0.85 M). [c] The base concentration was ca. 0.024 M.

Table III. Kinetic Data for the Elimination Reactions of 1-Chloro-1-phenyl-2-arylethanes with Sodium Phenoxide and Sodium 2,6-Di-*tert*-butylphenoxide in DMF–Me_2SO (9:1 v/v) at 30 °C

Nucleophile	Substrate[a]	Registry no.	k_2, M^{-1} s^{-1}[b]
Sodium phenoxide[c]	H	4714-14-1	1.08×10^{-3}
	H		1.56×10^{-1}[d]
	p-CH_3	4714-15-2	6.04×10^{-4}
	p-Cl	4714-17-4	5.05×10^{-3}
	p-NO_2	4781-42-4	1.52
Sodium 2,6-di-*tert*-butylphenoxide[e]	H		5.86×10^{-4}
	p-CH_3		4.30×10^{-4}
	p-Cl		2.65×10^{-3}
	p-NO_2		6.64×10^{-1}

[a] H refers to 1-chloro-1,2-diphenylethane. [b] Average of at least two determinations. The average error is ±2%. [c] In the presence of $NaClO_4$ (0.85 M). The base concentration was in the range 0.03–0.1 M. [d] In the presence of 18-crown-6 ether (0.081 M). [e] The base concentration was 0.03 M for p-H, p-CH_3, and p-Cl derivatives. For the p-NO_2 derivative the concentration was 0.015 M.

Table IV. Isotope Effects, Hammett Parameters, and Leaving Group Effects for Elimination Reactions of 1-Bromo-2-arylethanes with Sodium Phenoxide and Sodium 2,6-Di-*tert*-butylphenoxide in DMF–Me_2SO (9:1 v/v)

Nucleophile	Temp, °C	k_H/k_D[a]	ρ	k_{Br}/k_{Cl}[b]
Sodium phenoxide	0		+2.64[c,d]	
	21	7.6		
	30			120
Sodium 2,6-di-*tert*-butylphenoxide	0	10.5	+2.44[e]	
	10	10.4		
	20	9.0		
	30	8.3		146

[a] The probable error is ±8%. [b] Reactivity ratio between 2-phenylethyl bromide and 2-phenylethyl chloride. [c] Reference 2. The solvent in this case was DMF. [d] $r = 0.996$; $S = 0.059$. [e] $r = 0.989$; $S = 0.096$.

values of ρ and k_{Br}/k_{Cl}, which suggests that the structures of the transition state of the two eliminations closely resemble each other with respect to the carbanion character and the extent of carbon–leaving group bond breaking. At most a very small decrease of the carbanion character of the transition state for the reaction with sodium 2,6-di-*tert*-butylphenoxide could be suggested.

The k_H/k_D value is slightly larger in the reaction with sodium 2,6-di-*tert*-butylphenoxide than in that with sodium phenoxide. However, in the light of the very similar values of ρ and k_{Br}/k_{Cl} it seems unlikely that the transition states of the two reactions have a significantly different degree of C–H bond breaking. We feel that a larger tunneling contribution in the reaction with the more hindered base could be a more reasonable suggestion even though a study of the temperature dependence (between 0 and 30 °C) of k_H and k_D (Table II) was inconclusive in this respect, since the A_H/A_D value (1.20) turned out to be affected by too large an error (±3.76).

From the data of Table III values of +2.40 ($r = 0.999$, $S = 0.082$) and +2.30 ($r = 0.997$, $S = 0.128$) are calculated for the reactions of 1-chloro-1-phenyl-2-arylethanes with sodium phenoxide and sodium 2,6-di-*tert*-butylphenoxide, respectively. The similarity in the ρ values suggests that also in this system the two eliminations are characterized by transition states having a similar degree of carbanion character.

Thus the present work allows the conclusion that in spite of the effect on the reaction rate and on the positional and geometrical orientation, the steric requirements of the nucleophile do not significantly influence the transition state structure of the elimination reactions of β-phenyl activated alkyl halides. It seems therefore very unlikely that the repulsive interaction between the base and the substrate may play a significant role in determining the appearance of "anti-Thornton" patterns in E2 reactions.

Finally, the similar behavior of eliminations from 1-bromo-2-arylethanes and 1-chloro-1-phenyl-2-arylethanes with respect to changes in the steric requirements of the nucleophile is noteworthy since, in contrast, these two reaction series have been found to respond in a much different way when the nucleophile was changed from associated *t*-BuOK to crown ether complexed *t*-BuOK.[13] In the light of the present results this phenomenon cannot be due to a different response of the two series to the large difference in the steric requirements of complexed and uncomplexed *t*-BuOK.[7]

Experimental Section

Materials. 1-Bromo-2-phenylethane and 1-chloro-2-phenylethane were redistilled commercial samples (Fluka).

1-Bromo-2,2-dideuterio-2-phenylethane was prepared as described by Saunders and Edison;[14] the mass spectrum showed that the sample contained 1.92 atoms of D/molecule.

1-Bromo-2-arylethanes and 1-chloro-1-phenyl-2-arylethanes were available from previous studies.[13]

$NaClO_4$ (anhydrous, BDH) was used without further purification.

2,6-Di-*tert*-Butylphenol (Fluka) was recrystallized from *n*-hexane at −20 °C, mp 37–37.5 °C.

18-Crown-6 ether (Fluka) was purified by recrystallization from *n*-hexane, mp 38.5–39.5 °C.

Sodium phenoxide was prepared by treating phenol (C. Erba, RPE) with an equimolecular amount of NaOH in water. Water was removed at reduced pressure and the residue was recrystallized twice from dry acetone. Before use, sodium phenoxide was kept at 100 °C (0.1 mmHg) for 4 hr.

Base–Solvent Solutions. The solution of sodium 2,6-di-*tert*-butylphenoxide in Me_2SO was prepared as described by Bartsch, Weigers, and Guritz.[15] A portion of this solution (10 mL) was poured into a 100-mL volumetric flask and diluted to the calibration mark with DMF (C. Erba, RPE). The final concentration of sodium 2,6-di-*tert*-butylphenoxide was determined by titration with H_2SO_4 (0.01 N). Sodium phenoxide and $NaClO_4$ were weighed into a 100-mL volumetric flask. Me_2SO (10 mL) was added and the solution was diluted to the calibration mark with DMF.

Kinetic Study. The formation of bromide and chloride ions was followed by potentiometric analysis with $AgNO_3$. In the case of the very reactive 1-chloro-1-phenyl-2-*p*-nitrophenylethane the elimination was followed by a batchwise procedure.

Olefin Analysis. The yields of styrene in the reaction of 1-bromo-2-phenylethane with sodium 2,6-di-*tert*-butylphenoxide and of *trans*-stilbene in the reaction of 1-chloro-1,2-diphenylethane with the same base were determined by GPC analysis using a 20% LAC 728 (3 m) column in the former case and a 10% SE 30 (1 m) column in the second. The internal standards were isopropylbenzene and biphenyl, respectively.

The yield of *p*-methyl-*trans*-stilbene in the reaction of 1-chloro-1-phenyl-2-*p*-tolylethane with sodium phenoxide was determined spectrophotometrically. The olefin was extracted with *n*-heptane from the reaction mixture and the optical density of the *n*-heptane solution (after dilution to 25 mL) was determined at 297.5 nm.[16]

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References and Notes

(1) S. Alunni and E. Baciocchi, *Tetrahedron Lett.*, 4665 (1973).
(2) S. Alunni, E. Baciocchi, and V. Mancini, *J. Chem. Soc., Perkin Trans. 2*, 1866 (1974).
(3) S. Alunni, E. Baciocchi, and P. Perucci, *J. Org. Chem.*, **42**, 205 (1977).
(4) H. C. Brown, I. Moritani, and Y. Okamoto, *J. Am. Chem. Soc.*, **78**, 2193 (1956).
(5) H. C. Brown and M. Nakagawa, *J. Am. Chem. Soc.*, **78**, 2197 (1956).
(6) R. A. Bartsch, G. M. Pruss, B. A. Bushaw, and K. E. Wiegers, *J. Am. Chem. Soc.*, **95**, 3405 (1973).

(7) R. A. Bartsch, G. M. Pruss, D. M. Cook, R. L. Buswell, B. A. Bushaw, and K. E. Wiegers, *J. Am. Chem. Soc.*, **95**, 6745 (1973).
(8) S. Alunni, E. Baciocchi, R. Ruzziconi, and M. Tingoli, *J. Org. Chem.*, **39**, 3299 (1974).
(9) S. Alunni and E. Baciocchi, *J. Chem. Soc., Perkin Trans. 2*, 877 (1976).
(10) D. J. McLennan, *J. Chem. Soc., Faraday Trans. 1*, 1516 (1975).
(11) According to the Thornton model less proton transfer is expected in the transition state of the reaction with the stronger base. See E. R. Thornton, *J. Am. Chem. Soc.*, **89**, 2915 (1967), and L. J. Steffa and E. R. Thornton, *ibid.*, **89**, 6149 (1967). However, for further development of the theory, see D. A. Winey and E. R. Thornton, *ibid.*, **97**, 3102 (1975).
(12) The rate of elimination from 1-bromo-2-phenylethane increases by a factor of approximately 10^5 when the nucleophile is changed from sodium *p*-nitrophenoxide to sodium phenoxide.[1]
(13) The character of the transition state remains unchanged in the reactions of 1-bromo-2-arylethanes but becomes significantly more carbanionic in the reactions of 1-chloro-1-phenyl-2-arylethanes when the nucleophile is changed from *t*-BuOK to crown ether complexed *t*-BuOK. See S. Alunni, E. Baciocchi, and P. Perucci, *J. Org. Chem.*, **41**, 2636 (1976); **42**, 2170 (1977).
(14) W. H. Saunders, Jr., and D. H. Edison, *J. Am. Chem. Soc.*, **82**, 138 (1960).
(15) R. A. Bartsch, K. E. Wiegers, and D. M. Guritz, *J. Am. Chem. Soc.*, **96**, 430 (1974).
(16) E. Baciocchi, P. Perucci, and C. Rol, *J. Chem. Soc., Perkin Trans. 2*, 329 (1975).

Kinetics of the Baeyer–Villiger Reaction of Acetophenones with Permonophosphoric Acid[1]

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The Baeyer–Villiger reaction of acetophenones with permonophosphoric acid (H_3PO_5) has been studied kinetically in acetonitrile at 30 °C. The sole product, the corresponding aryl acetate, which is a product via aryl migration, is obtained almost quantitatively. The yields are much higher than those obtained by means of the other peroxycarboxylic acid oxidations. The rate equation is $v = k_2$[acetophenones][H_3PO_5]. The reaction is catalyzed by H_2SO_4, the rate being correlated with the acidity function (H_0). The rate-determining step is a migration step under these conditions. The apparent rate for ring-substituted acetophenones affords a Hammett ρ value of −2.55 (σ). The migration step seems to be a concerted process.

The preparation of permonophosphoric acid was discovered by Schmidlin and Massini in 1910.[2] Since then various techniques for its preparation,[3,4] decomposition mechanisms,[5] and dissociation constants[6,7] have been reported, but only a few reports have appeared on the oxidation of organic compounds, which were confined to oxidations of aromatic amines.[8] Recently, we have reported[9] on the oxidation of phenol, anisole, and toluene with permonophosphoric acid in acetonitrile; the oxidation rates for phenol and anisole (ArH) were expressed as $v = k$[ArH][H_3PO_5]$^2h_0$, where h_0 is Hammett's acidity function.

In the present paper, our study on the oxidations of organic compounds with H_3PO_5 was extended to the Baeyer–Villiger (B–V) reaction, in which we chose acetophenone and ring-substituted acetophenones as substrates. Ordinary B–V reactions using peroxycarboxylic acids were well studied,[10-12] where the rate equation is expressed as $v = k$[ketone][peracid]. The reaction is acid-catalyzed.[12,13] The rate-determining step may be either addition of peracid to carbonyl or migration from the adduct, depending on the substrate.[14]

This report summarizes our kinetic data on the B–V reaction of acetophenones with H_3PO_5. It was found that H_3PO_5 is a strong and excellent reagent for the B–V reaction, the rate being determined by a concerted migration which is catalyzed by strong acid.

Results and Discussion

The reaction of 0.2 molar equiv of acetophenones with H_3PO_5 was conducted in MeCN at 30 °C. The corresponding aryl acetates were obtained, and the yields were as follows: *p*-MeO, 70%; *p*-Me, 98%; H, 91%; *p*-Cl, 95%. But the corresponding methyl benzoates were not detected. Therefore, only

$$p\text{-}XC_6H_4\overset{O}{\overset{\|}{C}}Me + H_3PO_5 \xrightarrow[\text{in MeCN}]{30\ ^\circ C} pX\text{-}C_6H_4O\overset{O}{\overset{\|}{C}}Me + H_3PO_4 \quad (1)$$

the aryl group migrates, giving aryl acetate in agreement with the migratory apptitude observed with other peracid reactions.[10] No reaction occurred with *p*-nitroacetophenone, which has a strong electron-withdrawing group.

The rates for the H_2SO_4-catalyzed B–V reaction satisfied the second-order kinetics as shown in eq 2. But in the absence

$$v = k_2[C_6H_5COMe][H_3PO_5] \quad (2)$$

of H_2SO_4, the integral rate order was not observed because of the variation of the acidity of the system with the change of initial concentration of H_3PO_5, which is a fairly strong acid ($K_{1a} = 8 \times 10^{-2}$, $K_{2a} = 3 \times 10^{-6}$, and $K_{3a} = 2 \times 10^{-13}$ at 25 °C)[7] comparable to phosphoric acid.

A comparison of yields and rate constants with those by some other percarboxylic acids is shown in Table I. It is evident that H_3PO_5 is superior to peracetic acid and perbenzoic acid in yield and reaction rate.

Effect of Acidity. The correlation between rate constant k_2 and acidity constant H_0 of the solution was measured for the H_2SO_4-catalyzed reaction of acetophenone. A plot of log k_2 vs. $-H_0$ gave a straight line with a slope of 0.75 as shown

Table I. Comparison of the B–V Reactions of Acetophenone

Peracid	Yield, %	Rate constant
H_3PO_5[a]	91	2.9×10^{-3} M^{-1} s^{-1}
$PhCO_3H$	63[b]	1.47×10^{-5} M^{-1} s^{-1}[c]
CH_3CO_3H	33[d]	
CF_3CO_3H[e]	Quantitative	2.7×10^{-2} M^{-2} s^{-1}[f]

[a] In MeCN at 30 °C; $H_0 = -0.64$. [b] In $CHCl_3$ at 23–26 °C: S. L. Friess, *J. Am. Chem. Soc.*, **71**, 14 (1949). [c] In MeCN at 25 °C: S. L. Friess and N. Farnham, *J. Am. Chem. Soc.*, **72**, 5518 (1950). [d] In MeCN at 25 °C: W. von E. Doering and L. Speers, *J. Am. Chem. Soc.*, **72**, 5515 (1950). [e] In $ClCH_2CH_2Cl$ at 29.8 °C: M. F. Hawthorne and W. D. Emmons, *J. Am. Chem. Soc.*, **80**, 6398 (1958). [f] $v = k[CF_3CO_3H][CF_3CO_2H][R_1R_2CO]$.

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