

separately isolated, but did show the clean NMR spectrum characteristic of these reactions.

Preparation of 1- α - d_1 . The reduction of the mesylate was best accomplished with LiEt_3BH in THF (Aldrich "Superhydride"). Thus, 45 mL of 1 M LiEt_3BH in THF was added to 7.3 g of the mesylate of **5** (above). This mixture was refluxed overnight and then partitioned between pentane and water. Removal of pentane revealed substantial amounts of ethyl-containing impurities, presumably Et_3B , which were removed by treatment with NaOH solution (10%) for a short time. Repartitioning between pentane and water followed by distillation gave 2.1 g of propylbenzene, 99% pure by VPC analysis. NMR analysis showed clean monodeuteration, $0.97 \pm 0.05 d_1$ by multiple integration. The rotations were $[\alpha]^{20}_D -1.13$ (neat) and 1.40° (10% CCl_4 solution).

Reaction with Chromyl Chloride. In general, chromyl chloride was added by microliter syringe to a 5–10% solution of propylbenzene in CCl_4 containing hexachloroethane as an internal standard for VPC analysis. Slightly greater than molar ratios of CrO_2Cl_2 were employed in runs reported here. Higher amounts of CrO_2Cl_2 resulted in diminished yields of chlorinated product. Reactions were run for the times indicated in Table II at ice-bath temperatures. The data presented represent millimoles of material as measured by VPC. Rotations of the α -chlorinated product are also shown.

Determination of Optical Purity of Chloride. The resolution of 1-phenyl-1-propanol and its conversion to chloride followed the procedures of Kwart and Hoster.¹⁰ Chlorides of various optical rotations (see Table I) were then treated with a 5-fold excess of NaH_3 in DMF at room temperature. The half-life of this reaction was about 7 h, and complete reaction occurred in about 24 h. About half of these reaction mixtures were worked up after 5–6 h by pouring into water and extracting with ether.

This ether solution of azide and alcohol was then dried (MgSO_4) and treated with lithium aluminum hydride at room temperature for 2 h. Base workup (NaOH) gave an ether solution of amine and alcohol which was separated by normal acid wash/neutralization/ether extraction procedures. Preparation of the MTPA esters and amides allowed the optical purity to be determined.

MTPA esters and amides were prepared as described by Dale,

Dull, and Mosher.⁸ Analyses were accomplished by ^{19}F NMR using a Varian A56-60 spectrometer.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE-75-17816.

Registry No.—1- α - d_1 , 68408-59-3; 2, 10316-10-6; 4, 13595-05-6; 5, 68473-92-7; 5 mesylate, 68408-60-6; chromyl chloride, 14977-61-8.

References and Notes

- (1) C. N. Rentea, M. Rentea, I. Necsoiu, and C. D. Nenitzescu, *Tetrahedron*, **24**, 4667 (1968), and earlier papers.
- (2) H. O. House, "Modern Synthetic Reactions", 2nd ed., W. A. Benjamin, Menlo Park, Calif., 1972, p 289–291.
- (3) K. B. Wiberg, B. Marshall, and G. Foster, *Tetrahedron Lett.*, 345 (1962).
- (4) (a) R. H. Eastman and R. A. Quinn, *J. Am. Chem. Soc.*, **82**, 4249 (1960); (b) H. Kwart and G. D. Nall, *ibid.*, **82**, 2348 (1960); (c) K. B. Wiberg and A. S. Fox, *ibid.*, **85**, 3487 (1963); (d) J. I. Brauman and A. J. Pandell, *ibid.*, **92**, 329 (1970).
- (5) (a) K. B. Wiberg and R. J. Evans, *Tetrahedron*, **8**, 313 (1960); (b) K. B. Wiberg, Ed., "Oxidation in Organic Chemistry", Part A, Academic Press, New York, 1965, Chapter 2.
- (6) For previous work in this series, see L. M. Stephenson and D. E. McClure, *J. Am. Chem. Soc.*, **95**, 7888 (1973).
- (7) F. Fischer, *Chem. Ber.*, **94**, 893 (1961); *Chem. Abstr.*, **55**, 21082g (1961).
- (8) MTPA is α -methoxy- α -(trifluoromethyl)phenyl acetate. The use of the esters for determination of enantiomer excess in alcohols and amines was pioneered by J. A. Dale, D. L. Dall, and H. S. Mosher, *J. Org. Chem.*, **34**, 2543 (1969).
- (9) R. Pichard and J. Kenyon, *J. Chem. Soc.*, **105**, 1128 (1904).
- (10) H. Kwart and D. P. Hoster, *J. Org. Chem.*, **32**, 1867 (1967).
- (11) It is clearly established that both alcohol¹² and chloride¹³ are *R*(+). Thus, the conversion proceeds with net retention of configuration.
- (12) P. A. Levene and A. Mikeska, *J. Biol. Chem.*, **70**, 355 (1926).
- (13) P. A. Levene and R. Marker, *J. Biol. Chem.*, **97**, 379 (1932).
- (14) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).
- (15) U. Schollkopf and H. Schafer, *Justus Liebigs Ann. Chem.*, **683**, 42 (1965).
- (16) J. P. Lorand, R. W. Grant, P. A. Samuel, E. O'Connell, and J. Zaro, *Tetrahedron Lett.*, 4087 (1969).

Reductive Acetoxylation on α,α' -Dibromocycloalkanones by Ultrasonically Dispersed Mercury

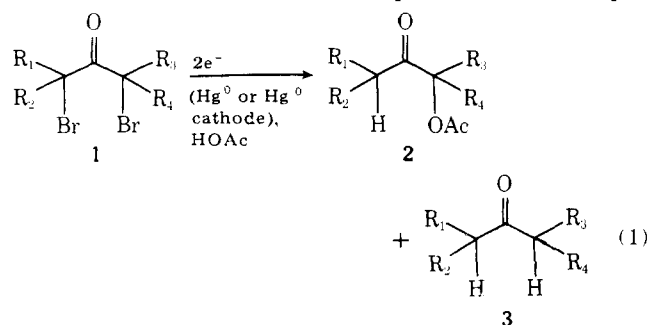
Albert J. Fry,* William A. Donaldson,¹ and Geoffrey S. Ginsburg¹

Hall-Atwater Laboratories of Chemistry, Wesleyan University, Middletown, Connecticut 06457

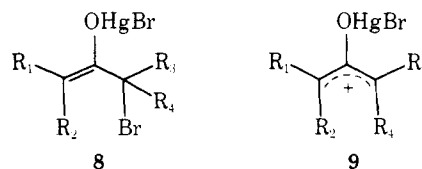
Received August 7, 1978

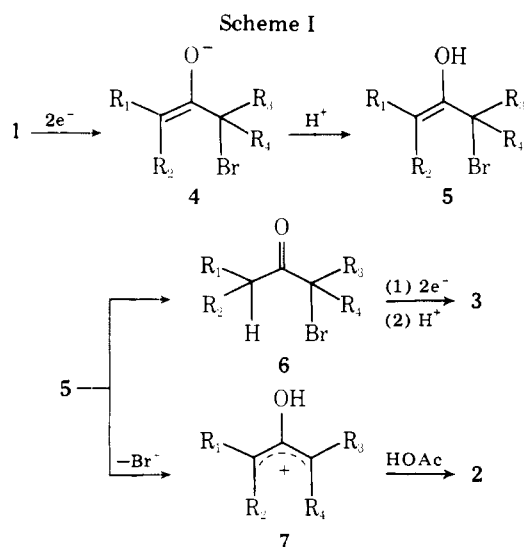
The α,α' -dibromocycloalkanones of ring size 5–12 were reduced by ultrasonically dispersed mercury in acetic acid. Products were the corresponding cycloalkanone and α -acetoxy cycloalkanone. The ratio of these two is quite sensitive to ring size, and this fact is used to support the intermediate formation of 2-hydroxyallyl cations as precursors of the keto acetates. Molecular mechanics calculations support the proposed mechanism.

We^{2,3} and others⁴ have reported the electrochemical reductive acetoxylation of α,α' -dibromo ketones (**1** \rightarrow **2**) in acetic acid. More recently, we discovered a similar conversion effected by ultrasonically dispersed metallic mercury.⁵ In both reactions the reductive substitution product (**2**) is accompa-



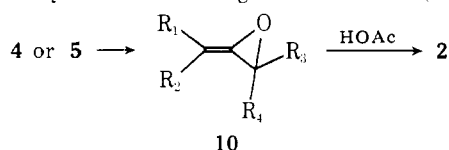
nied by the double reduction product **3** (or "parent" ketone, so-called because **1** is prepared from **3**) (eq 1). Small amounts of side products (most commonly α -bromo ketones or α,β -unsaturated ketones) often accompany **2** and **3**, but usually **2** and **3** constitute >90% of the reaction products, which are formed in high (85–94%) absolute yields in the electrochemical reaction but lower yields (30–75%) in the mercury reaction (the lower yields in the latter case possibly arising from partial conversion of **1** to insoluble organomercury byproducts).⁵ We have advanced^{2,3} the mechanism shown in Scheme I to ac-



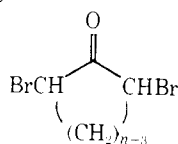


count for the formation of **2** and **3** in the electrochemical reaction and have advanced a similar mechanism, except involving oxymyrcic intermediates **8** and **9** instead of **5** and **7**, for the reactions effected by metallic mercury.⁵

While we believe that a fairly convincing case may be made for the mechanism shown in Scheme I, we appreciate that other mechanisms might be added to fit the experimental data. Specifically, we could not exclude the possibility that **2** is formed by a route involving an allene oxide (**10**), e.g.,



In fact, it is known that allene oxides do undergo ring opening to afford α -substituted ketones in hydroxylic solvents.⁶ The increasing proportion of α -acetoxy ketones as the degree of α - and α' -alkyl substitution is increased^{2,3,5} could then be rationalized in terms of the Thorpe-Ingold effect, i.e., the stabilization of small rings by alkyl, especially *gem*-dialkyl, substitution.⁷ We now wish to report the results of a study of the reduction of a series of α, α' -dibromocycloalkanones of ring size 5 through 12 (**11**–**18**) by mercury in acetic acid. The results are clearly in accord with expectations based upon the mechanism in Scheme I and, just as clearly, are inconsistent with the intermediacy of allene oxides (**10**) in the reaction.

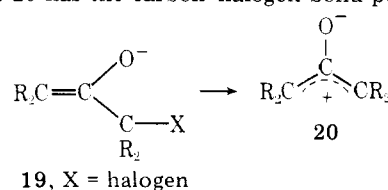


11 , $n = 5$	14 , $n = 8$	17 , $n = 11$
12 , $n = 6$	15 , $n = 9$	18 , $n = 12$
13 , $n = 7$	16 , $n = 10$	

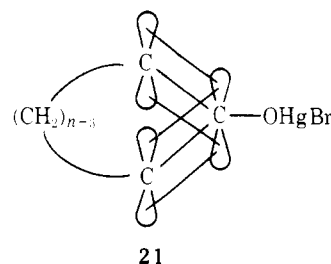
Reductions of the dibromo ketones by ultrasonically dispersed mercury at room temperature were carried out in acetic acid as solvent in most cases. However, **17** and **18** are insoluble in acetic acid and were therefore reduced in benzene-acetic acid and tetrahydrofuran-acetic acid mixtures; for this reason **11** and **13** were also reduced in these solvents for comparison. In general, the reductions proceeded in fair yield according to the overall reaction as presented in eq 1. The most striking feature of the results (Table I) is the very marked dependence on ring size of the "acetoxylation efficiency", i.e., the ratio of the yield of acetoxy ketone to that of the sum of parent ketone plus the [mechanistically equivalent] monobromo ketone.³ In acetic acid this ratio decreases steadily as one proceeds

through the series of dibromo ketones **11**–**15**; in fact, there is a total inversion of reactivity as one proceeds across this series from dibromocyclopentanone (**11**), which gives acetoxy ketone free of parent ketone, to dibromocyclooctanone and -nonanone (**14** and **15**), which afford little or no acetoxy ketone. The results are less clear in the larger rings (ten or more members) because of lower yields associated perhaps with the mixed solvent systems used, but it appears that formation of acetoxy ketones is reasonably efficient in the larger rings.

The results shown in Table I cannot be accommodated by a mechanism involving allene oxides (**10**) as precursors to acetoxy ketones **2**, since species **10** would be increasingly strained as the ring size decreases from nine to five in the sequence of dibromo ketones **14**–**11**, whereas the efficiency of acetoxy ketone formation *increases* with decreasing ring size in this series.⁸ The results are, however, nicely accommodated by the mechanism in Scheme I. As Bordwell has pointed out,⁹ the preferred geometry for ionization of α -haloenolates **19** to zwitterions **20** has the carbon-halogen bond perpendicular



to the plane of the enolate system, since in this geometry the incipient p orbital can best overlap with the enolate system as the halogen atom leaves. Similarly, ionization of bromine from **8** should be most efficient when the bromine atom can attain the same geometry and, correspondingly, when the planar allylic π -system geometry (**21**) can be most readily attained. Models indicate that geometry **21** is easily accom-



modated in the smaller (five- or six-membered) rings, which are already close to planarity, and also in the larger rings, which are flexible enough to accommodate the three-carbon planar allylic system. Models indicate, however, that formation of ion **21** should proceed with difficulty in the medium-ring series since the conjunction of three parallel p orbitals appears to generate considerable transannular nonbonded strain. Thus, the acetoxylation efficiency (Table I) exactly parallels the degree of strain expected in species **21** of various ring sizes and, therefore, is consistent with the hypothesis that **2** is formed via **21**.

Molecular Mechanics Calculations. We felt it desirable to support our impression from models that **21** should be strained in the medium ring systems and therefore decided to carry out molecular mechanics calculations¹⁰ on this point. The molecular mechanics, or empirical force-field, method has had some success in determination of the strain energies and geometries of cyclic species and has successfully been applied to carbonium ions.^{10b}

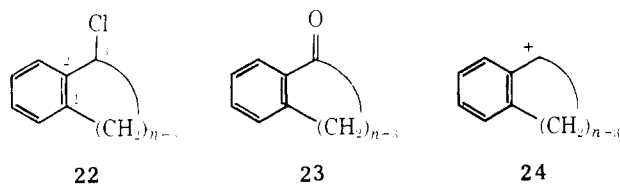
There are a number of force fields in current use, and each has both advantages and disadvantages, which depend upon the type of system one wishes to examine and the type of information one wishes to obtain.¹⁰ For our purpose we chose the so-called Allinger 1973 force field^{10a,11} which has the special advantage of having been parametrized for a variety of functional groups. Despite this fact, we found molecular

Table I. Reduction of Dibromocycloalkanones by Mercury

registry no.	dibromide	solvent	yields, % ^a					acetoxylation efficiency ^c
			α -acetoxy ketone ^b	registry no.	parent ketone ^b	registry no.	other	
53778-21-5	11	HOAc	36	52789-75-0	0	108-94-1	2	∞^d
	11	THF-HOAc ^e	16		0		3	∞^d
	11	benzene-HOAc ^e	19		0		2	∞^d
34006-70-7	12	HOAc	46	17472-04-7	11	502-42-1	2	4.2
	17346-17-7	13	HOAc		16		32	2
	13	THF-HOAc ^e	13		28		3	0.5
	13	benzene-HOAc ^e	14		35		2	0.4
	41597-11-9	14	HOAc		2		23438-71-3	61
68331-88-4	15	HOAc	0	10035-92-4	44	3350-30-9	22 ^{f,g}	0
68366-10-9	16	HOAc	15		58		1502-06-3	6
68331-89-5	17	THF-HOAc ^e	21	68297-82-5	9	878-13-7	5	2.3
	17	benzene-HOAc ^e	28		7		5	4.0
24459-40-3	18	THF-HOAc	9	26307-31-3	8	830-13-7	0	1.1
	18	benzene-HOAc	8		6		0	1.3

^a Analysis of VPC. ^b Identity proven by NMR and mass spectroscopy following isolation by preparative VPC. ^c % acetoxy ketone/(% parent ketone + % monobromide) (see ref 3). ^d No parent ketone detectable by VPC. ^e Aprotic solvent: HOAc = 9:1 (v/v). ^f Monobromide. ^g Registry no. 68297-83-6.

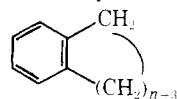
mechanics calculations on cyclic 2-hydroxyallyl cations **21** and their precursors to be considerably complicated by the large number of force constants involving oxygen which had to be more or less arbitrarily estimated. We, therefore, turned our attention to a related, but simpler, system involving many fewer approximations. It was found by Huisgen and co-workers¹² that S_N1 reactivity decreases with increasing ring size as one proceeds through the series of benzocycloalkenyl chlorides **22a-d** (relative rates of solvolysis in ethanol at 40 °C were found to be 1040:264:7.0:1). These workers advanced an explanation for this progression (and for progressive changes in the electronic spectra of benzocycloalkenes **23a-d**



a, n = 5; b, n = 6; c, n = 7; d, n = 8

with increasing size) which is identical to that advanced by us above for the decrease in acetoxylation ratio in proceeding through the series of dibromo ketones **11-15**. That is, they indicated that molecular models indicated that as ring size increases, it becomes increasingly difficult to attain a geometry in which the benzylic p orbital at C₃ is oriented parallel to those of the aromatic ring, as required for maximum overlap and resonance stabilization. (Parenthetically, it should be noted that the order of rates of ionization of **22a-d** and the enol allylic bromides **5** derived from **11-15** differs markedly from the rates of ionization of the saturated cycloalkyl tosylates, which do not decrease monotonically with increasing ring size).¹³

Since the Huisgen system lacks the oxygen atom present in **21**, we carried out molecular mechanics calculations on the ionization of **22** to **24** as a model system for formation of **21**. The procedure involved calculation of the enthalpies of formation of the chlorides **22** and carbonium ions **24**, and therefore the calculated $\Delta\Delta H_f^\circ$ for the conversion **22** \rightarrow **24**.



25

Calculation of this difference enabled us to cancel out the differences in ΔH_f° of the carbonium ions **24** due to differing

Table II. Molecular Mechanics Calculations on 3-Chloro-1,2-benzocycloalkenes and the Corresponding Benzyl Cations

ring size	species	registry no.	ϕ , deg ^a	steric energy, kcal/mol ^b	ΔH_f° , kcal/mol ^c	$\Delta\Delta H_f^\circ$, kcal/mol ^d
5	22a	35275-62-8	80	15.3	139.6	29.0
5	24a	68297-84-7	0	17.0	168.6	
6	22b	58485-68-0	72	12.7	130.1	40.3
6	24b	68297-85-8	2.8	13.7	170.4	
7	22c	35047-93-9	53	20.5	131.0	43.7
7	24c	68297-86-9	0.7	24.9	174.7	
8	22d	68297-87-0	42	23.0	126.6	47.0
8	24d	68297-88-1	3.3	30.8	173.6	

^a C₁-C₂-C₃-Cl dihedral angle in **22** or C₁-C₂-C₃-H dihedral angle in **24**. ^b $E_{steric} = E_{bend} + E_{stretch} + E_{torsion} + E_{van\ der\ Waals}$. ^c Computed heat of formation. For convention, see N. Allinger, *Adv. Phys. Org. Chem.*, **13**, 1 (1976). ^d $\Delta\Delta H_f^\circ = \Delta H_f^\circ(24) - \Delta H_f^\circ(22)$.

numbers of carbon and hydrogen atoms and, since we are interested only in how $\Delta\Delta H_f^\circ$ changes with ring size, also permitted cancellation of any systematic errors associated either with estimation of unknown force constants or with our method of treating carbonium ions within the framework of the Allinger force field (vide infra).

Starting geometries for each ring system were obtained by carrying out an initial geometry minimization on the series of benzocycloalkenes **25a-d**.¹⁴ One of the benzylic hydrogen atoms of **25** was then replaced by chlorine and a new minimization was carried out in order to obtain the geometry and energy of chloride **22**. Although the Allinger force field has previously been parametrized separately for arenes and alkyl chlorides, application to benzyl chlorides **22** required estimates of the force constants for rotation (torsion) about the central bond of an sp² carbon-sp² carbon-sp³ carbon-chlorine chain (the C₂-C₃ bond) and for sp² carbon-sp³ carbon-chlorine angle bending (the C₂-C₃-Cl angle). These estimates were made by reference to values previously assigned by Allinger for similar systems.¹⁵

Application of the molecular method to cations **24** did not involve explicit treatment of the positive charge on the species. Rather, it was assumed that bonds between any two of these carbons have character intermediate between double and single, and closer to the former, i.e., that all such bonds

Table III. Contributions to Steric Energy of Benzocycloalkenyl Cations

cation	ring size	E_{bend}^a	E_{stretch}^a	E_{torsion}^a	$E_{\text{van der Waals}}^a$
24a	5	5.9	0.5	7.0	3.6
24b	6	0.6	0.5	6.0	7.5
24c	7	3.8	0.9	9.0	11.0
24d	8	7.2	1.2	9.1	12.6

^a kcal/mol.

(especially the C₂-C₃ bond) are slightly shorter than the corresponding lengths in **22** because of contractions induced by the additional resonance and positive charge in **24**. Bond lengths and stretching constants were arbitrarily assigned to correspond to these assumptions.¹⁶ Torsional constants about such bonds were those for sp²-sp³ double bonds. The effect of the approximations is to render absolute values of the computed carbonium ion energies and of $\Delta\Delta H_f^\circ$ meaningless, but, as noted previously, the various errors should largely cancel when the homologous series **24a-d** is examined. The computed values of $\Delta\Delta H_f^\circ$ (Table II) support the impression from model building that cations **24** (and **21**) should form with difficulty in the medium ring systems. The molecular mechanics calculations show further that the largest single contributor to the increased $\Delta\Delta H_f^\circ$ in the seven- and eight-membered ring systems is, as expected, van der Waals' (non-bonded) repulsions (Table III).

Experimental Section

General. NMR spectra were recorded on a Varian A60-A spectrometer. Gas chromatographic analyses and preparative separations were carried out using a Varian 90-P chromatograph. Products were collected by preparative VPC for identification by NMR and mass spectroscopy. Most cycloalkanones were commercial samples, except for cyclodecanone, which was prepared from sebacoïn (obtained from P. S. Wharton) by the method of Reusch and Le Mahieu,¹⁷ and cycloundecanone, which was prepared by the method of Garbisch and Wohllebe.¹⁸ Dibromo ketones were prepared by literature procedures.¹⁹

Mercury reductions were carried out by a standard procedure.^{3,5} Analysis of mixtures was by integration of peak areas,²⁰ products were collected by preparative VPC and identified by NMR and mass spectroscopy. The α -acetoxy cycloalkanones obtained in this work are practically all known compounds²² whose spectral properties agreed with literature values where available or expectation where not.

Acknowledgment. Financial support was provided by the National Science Foundation and the Uniroyal Corp. The molecular mechanics program (MMI, 1973 version), modified for use on the Wesleyan DEC PDP-10 computer, was provided by Dr. David Pensak of the Dupont Corp.

References and Notes

- (1) This manuscript is taken in part from the Wesleyan University B.A. Theses of W.A.D. (1977) and G.S.G. (1978).
- (2) A. J. Fry and J. J. O'Dea, *J. Org. Chem.*, **40**, 3625 (1975).
- (3) (a) A. J. Fry and J. P. Bujanauskas, *J. Org. Chem.*, **43**, 3157 (1978); (b) monobromo ketones (**6**) are indeed slowly reduced to parent ketones **3** under these conditions (G. S. Ginsburg, unpublished observation).
- (4) J. P. Dirlam, L. Ebersson, and J. Casanova, *J. Am. Chem. Soc.*, **94**, 240 (1972).
- (5) A. J. Fry and D. Herr, *Tetrahedron Lett.*, 1721 (1978).
- (6) (a) T. H. Chan, B. S. Ong, and W. Mychajlowski, *Tetrahedron Lett.*, 3253 (1976); (b) B. S. Ong and T. H. Chan, *ibid.*, 3257 (1976).
- (7) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Wiley-Interscience, New York, 1965, p 191, and references therein.
- (8) Bordwell has argued against allene oxides as precursors of α -alkoxy ketones in the reaction of α -halo ketones with alkoxides on essentially similar grounds: F. G. Bordwell and M. W. Carlson, *J. Am. Chem. Soc.*, **92**, 3377 (1970).
- (9) (a) F. G. Bordwell, R. G. Scamehorn, and W. R. Springer, *J. Am. Chem. Soc.*, **91**, 2087 (1969); (b) F. G. Bordwell and R. G. Scamehorn, *ibid.*, **90**, 6751 (1968).
- (10) (a) N. L. Allinger, *Adv. Phys. Org. Chem.*, **13**, 1 (1976); (b) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973); (c) S. Fitzwater and L. S. Bartell, *ibid.*, **98**, 5107 (1976).
- (11) A version of this program (MMI)^{10a} adapted for operation on the DEC PDP-10 computer was supplied by Dr. D. Pensak, to whom we were referred by Professor Allinger.
- (12) R. Huisgen, W. Rapp, I. Ugi, H. Walz, and E. Mergenthaler, *Justus Liebigs Ann. Chem.*, **356**, 1 (1954).
- (13) In order of decreasing S_N1 reactivity of cycloalkyl tosylates one finds (n = ring size): 8 > 7 ~ 5 > 6: E. L. Eliel in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, 1956, p 123.
- (14) The starting geometry for the minimization had all carbon atoms of **25** in the same plane.
- (15) The values used were those for the C_{sp²}-C_{sp²}-C_{sp³}-S sulfur dihedral angle (thus simulating the electronegative chlorine atom) and the C_{sp³}-C_{sp³}-Cl angle. The results are not sensitive to the values chosen for these parameters.
- (16) A stretching force constant of 7.87 was selected (double and single bonds have values of 9.60 and 4.40, respectively); C_{sp²}-C_{sp²} natural (unstrained) bond lengths were all fixed at 1.39 Å.
- (17) W. Reusch and R. Le Mahieu, *J. Am. Chem. Soc.*, **86**, 3068 (1964).
- (18) E. W. Garbisch and J. Wohllebe, *J. Org. Chem.*, **33**, 2157 (1958).
- (19) H. M. R. Hoffmann and J. G. Vintner, *J. Org. Chem.*, **39**, 3921 (1974).
- (20) We have established²¹ that VPC response ratios for acetoxy ketones and parent ketones are generally very similar, hence no significant error is introduced by this procedure.³
- (21) A. J. Fry and A. T. Lefor, *J. Org. Chem.*, in press.
- (22) (a) T. Shono, M. Okawa, and I. Nishiguchi, *J. Am. Chem. Soc.*, **97**, 6144 (1975); (b) I. S.-Y. Wang, and E. W. Warnhoff, *Chem. Commun.*, 1158 (1969); (c) W. Treibs and P. Grossmann, *Chem. Ber.*, **90**, 103 (1957).

Kinetics of the Peroxymonophosphoric Acid Oxidation of Aromatic Amines¹

Yoshiro Ogata,* Kohtaro Tomizawa, and Takashi Morikawa

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

Received July 18, 1978

Oxidation of *N,N*-dimethylaniline (**1a**) and methyldiphenylamine (**1b**) with peroxymonophosphoric acid in aqueous acetonitrile at 30 °C gives the corresponding *N*-oxides. The oxidation obeys the rate equation: $v = k_2[\text{amine}]_t[\text{peracid}]_t$. The effect of the acidity of solution shows that neutral amine alone can react with peracid, the rate being determined by a nucleophilic attack of amine on peracid oxygen. The reactivity of H₃PO₅ to amine is ~100 times higher than that of H₂PO₅⁻, and the reactivity of **1a** to peracid is ~100 times higher than that of **1b**. These results are discussed on the basis of both a plot of rate constant vs. pH and acidity constants of H₃PO₅ and conjugate acids of amines.

As a promising substitute oxidant for percarboxylic acid, peroxymonophosphoric acid was successfully applied to aromatic hydroxylation² and Baeyer-Villiger reaction³ and they were kinetically studied. It has been reported that aniline is

oxidized by peroxymonophosphoric acid to *p*-aminophenol and *p*-aminophenyldihydrogen phosphate, and 2-naphthylamine is oxidized to 2-amino-1-naphthol, etc., while *N,N*-dimethyl-2-naphthylamine is oxidized to its *N*-oxide.⁴