Table I. Bond Distances and Angles in *anti*-α-Bromoacetophenone Oxime

Bond	Distance, Å	Esd	Angle	Deg	Esd
Br–C(1)	1.968	0.008	Br–C(1)–C(2)	109.0	0.5
C(1)–C(2)	1.509	0.010	C(1)–C(2)–C(3)	120.3	0.7
C(2)–C(3)	1.474	0.011	C(1)–C(2)–N	112.5	0.7
C(2)–N	1.291	0.010	N–C(2)–C(3)	127.2	0.6
N–O	1.409	0.008	C(2)–N–O	113.5	0.7
C(3)–C(4)	1.404	0.010	C(2)–C(3)–C(4)	119.3	0.7
C(4)–C(5)	1.366	0.015	C(2)–C(3)–C(8)	122.1	0.6
C(5)–C(6)	1.358	0.015	C(4)–C(3)–C(8)	118.6	0.7
C(6)–C(7)	1.389	0.015	C(3)–C(4)–C(5)	120.5	0.8
C(7)–C(8)	1.385	0.014	C(4)–C(5)–C(6)	121.0	0.9
C(8)–C(3)	1.402	0.011	C(5)–C(6)–C(7)	120.0	0.9
			C(6)–C(7)–C(8)	120.3	0.9
			C(3)–C(8)–C(7)	119.6	0.8

Table II. Final Atomic Positions for *anti*-α-Bromoacetophenone Oxime

Atom	*x/a*	*y/a*	*z/c*
Br	0.4587 (1)	1.2989 (0)	0.5470 (1)
C(2)	0.3219 (7)	1.2315 (6)	0.6050 (8)
C(3)	0.3228 (6)	1.1089 (6)	0.5798 (7)
N	0.3599 (5)	1.0505 (5)	0.6611 (6)
O	0.3604 (6)	0.9356 (5)	0.6400 (6)
C(6)	0.2800 (6)	1.0677 (5)	0.4734 (6)
C(7)	0.1792 (6)	1.1092 (6)	0.4327 (9)
C(8)	0.1365 (8)	1.0707 (9)	0.3355 (10)
C(9)	0.1907 (10)	0.9922 (8)	0.2757 (8)
C(10)	0.2919 (9)	0.9511 (8)	0.3123 (8)
C(11)	0.3358 (7)	0.9864 (7)	0.4120 (8)

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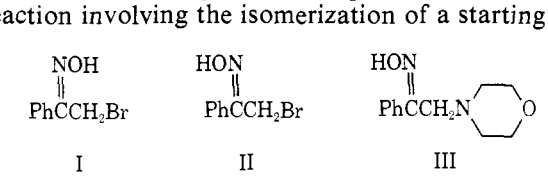
Kinetics and Stereochemistry of Nucleophilic Reactions of Phenacyl Halide Oximes

Sir:

In the preceding communication[1] the synthesis of *anti*-α-bromoacetophenone oxime[2] (II) and the determination of its structure by an X-ray diffraction study were reported. The first step in the reaction sequence leading to II is the conversion of *syn*-α-bromoacetophenone oxime (I) *via* solvolysis in aqueous morpholine buffer to *anti*-α-morpholinoacetophenone oxime (III), a reaction involving the isomerization of a starting material having a thermally favored geometry to a product with a thermally unfavored geometry. While several reports have appeared in the literature[3-7] concerning the reactions of α-halooximes with nucleophiles, the stereochemical consequences, with respect to the oxime function, of these reactions have not been analyzed. In the present communication, we report a kinetic and stereochemical investigation of the mechanism of the solvolysis of α-haloacetophenone oximes in aqueous media.



I II III

At pH values significantly below the pK_a values for the ionization of the oxime functions, the rates of solvolysis of three *syn*-α-haloacetophenone oximes and *anti*-α-bromoacetophenone oxime (II), determined spectrophotometrically, have been found to obey the rate law shown in eq 1.[8] The second-order rate constants

$$v = k[\alpha\text{-halooxime}][OH^-] \quad (1)$$

obtained are in the following ratio: syn fluoro, 1.0; syn chloro, 2.9×10^3; syn bromo, 1.0×10^5; and anti bromo, 4.8×10^6.[9] The pH–rate profile for the solvolysis of the *syn*-fluorooxime is sigmoidal at high pH (9–13) with a dependency on a group ionizing with $pK_a = 10.5$, which we postulate to be the oxime function.[10] These findings indicate that ionization of the oxime function as well as loss of halide ion occur in steps which crucially affect the rate of reaction.

As described already for the reaction of I with morpholine buffer, the solvolyses of the *syn*-α-haloacetophenone oximes, as well as that of the anti species II, in various buffered aqueous solutions gave products of anti configuration, corresponding to replacement of the halogen with the buffer compound.[11] However, the rates of reaction are independent of the concentration of the buffer species.[12]

Addition of excess Br^- (0.5 *M*) decreases the rate of solvolysis of 8.4×10^{-5} *M* *syn*-α-bromooxime (I) 16-fold in 0.01 *M* acetate buffer at pH 5. The behavior of the anti isomer (II) in the presence of Br^- is quite different. When II (1.9×10^{-4} *M*) is solvolyzed in the absence of Br^- in pH 4, 0.01 *M* acetate buffer, for example, there is a first-order decrease in the absorbance at 260 nm ($t_{1/2}$ = 6 sec), corresponding to replacement of the bromide in the substrate by acetate. However, in the presence of 0.5 *M* Br^-, there is an increase in absorbance to a maximum value, reached after 3 min, followed by a slower decrease in absorbance. By carrying out this

(1) J. H. Smith, J. H. Heidema, E. T. Kaiser, J. B. Wetherington, and J. W. Moncrief, *J. Amer. Chem. Soc.*, **94**, 9274 (1972).
(2) Throughout this article, syn refers to the isomer having the alkyl group cis to the oxime oxygen; anti refers to the isomer having the alkyl group trans to the oxime oxygen.
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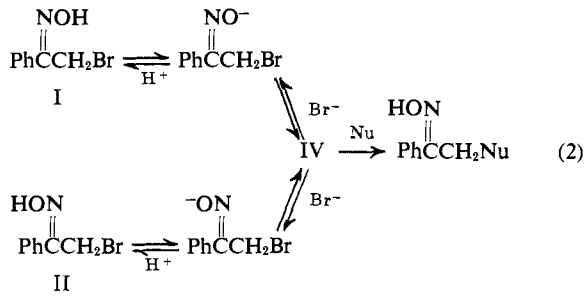
(4) W. Pritzkow, H. Schaefer, P. Papst, A. Ebenroth, and J. Beger, *J. Prakt. Chem.*, **29**, 123 (1965).
(5) H. P. Fischer and C. A. Grob, *Helv. Chim. Acta*, **45**, 2528 (1962).
(6) M. Masaki, K. Fukui, and M. Ohta, *J. Org. Chem.*, **32**, 3564 (1967).
(7) M. Ohno, S. Torimitsu, N. Naruse, M. Okamoto, and I. Sakai, *Bull. Chem. Soc. Jap.*, **39**, 1129 (1966), and earlier references therein.
(8) Below pH 2, the acid-catalyzed hydrolysis of the oxime function, resulting in α-halo ketone formation, becomes the primary reaction. The *syn*-α-halooximes were prepared from the corresponding α-haloacetophenones by reaction with hydroxylamine sulfate in methanol.
(9) These rate constants were determined from measurements in 0.1 *M* morpholine buffers containing 0.5 *M* KCl in the case of the syn fluoro compound, 0.05 *M* Tris buffers containing 0.5 *M* NaCl for the syn chloro, and 0.1 *M* acetate buffers for the syn and anti bromo compounds.
(10) The pK_a for the ionization of acetophenone oxime is 11.48 (R. P. Bell and W. C. E. Higginson, *Proc. Roy. Soc.*, **197**, 141 (1949)); a decrease of one unit in the pK_a due to the presence of the electron-withdrawing fluoro group would not be unreasonable.
(11) When unbuffered solutions are used (pH maintained with a pH-stat), the oxime function acts as a nucleophile to give a dimeric product.
(12) For example, a 40-fold increase in the concentration of morpholine at pH 9.0 resulted in an increase of only 10% in the observed rate constant for the solvolysis of I.

reaction on a preparative scale and performing a $CHCl_3$ extraction, the product responsible for the initial rise in absorbance was identified as *syn*-α-bromoacetophenone oxime (I).

The simplest mechanistic scheme consistent with our observations is illustrated for the α-bromooximes in eq 2 where Nu represents the nucleophilic buffer component. The reactions of both syn and anti isomers proceed through the oxime anions. In the absence of added excess halide ion, the rate-determining step for the solvolysis of both isomers is the loss of halide to form a common intermediate, IV, which we suggest to be α-nitrosostyrene.[13] This intermediate is rapidly trapped by the nucleophile Nu to give a substituted oxime of anti stereochemistry. Apparently, reaction of the intermediate in the s-trans conformation with nucleophiles like morpholine is more rapid than the reaction of the s-cis form,[14] and the anti α-substituted oxime is formed, therefore. In the case of added bromide ion, the intermediate IV is trapped in both the s-cis and s-trans conformations to give both isomers of the α-bromooxime. However, because the *syn*-α-bromooxime I undergoes elimination slower than the anti species II (*vide ante*), the solvolysis of II in the presence of excess Br^- proceeds by way of the initial accumulation of I.



(2)

Attempts to detect directly and positively identify the intermediate IV and related species in the nucleophilic reactions of α-haloalkyl aryl ketooximes in aqueous media are in progress in our laboratory.

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(13) Ample precedent for this hypothesis exists.[3,4,7] α,β-Unsaturated nitroso compounds, for example, have been isolated by the treatment of appropriately sterically hindered α-halooximes with triethylamine in ether. By reaction with piperidine, α-piperidinooximes are produced from these nitroso species (W. Höbold, U. Prietz, and W. Pritzkow, *J. Prakt. Chem.*, **311**, 260 (1969)).

(14) Similarly, *anti*-α-aminoacetophenone oxime esters and ethers undergo the abnormal Beckmann rearrangement about 2×10^3 times faster than the corresponding syn isomers (H. P. Fischer, C. A. Grob, and E. Renk, *Helv. Chim. Acta*, **45**, 2539 (1962)).

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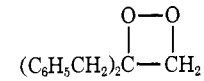
Excited State Carbonyl Species from the Thermal Decomposition of 3,3-Dibenzyl-1,2-dioxetane

Sir:

1,2-Dioxetanes undergo thermal decomposition to produce excited state carbonyl species as evidenced by chemiluminescence[1] and reactions sensitized by the excited state carbonyl species.[1e,2] We now report a type I reaction of an excited state carbonyl moiety produced from the thermal decomposition of a 1,2-dioxetane. Thermal decomposition of $1.04 \times 10^{-3} M$ 3,3-dibenzyl-1,2-dioxetane (**1**) in degassed benzene at 60° produces



1

bibenzyl and dibenzyl ketone in 2.2 and 88% yield, respectively. Bibenzyl is indicative of triplet dibenzyl ketone, which yields bibenzyl by a type I process.[3] Benzyl chloride is detected in the reaction mixture when **1** is decomposed at 60° in degassed carbon tetrachloride, which indicates that bibenzyl is produced from free benzyl radicals as proposed in the type I process.[3]

Further evidence for excited state carbonyl species from the thermal decomposition of **1** is shown by the production of chemiluminescence when 9,10-diphenylanthracene is incorporated in the reaction mixture. To show that chemiluminescence with 9,10-diphenylanthracene is intimately related to the excited state carbonyl species generated from **1**, quenching of bibenzyl formation with 9,10-diphenylanthracene was measured. An acceptable Stern–Volmer plot (Figure 1) was obtained and from the slope of the plot $k_q\tau$[4] is 20 M^{-1}. Assuming k_q is diffusion controlled (2×10^{10} M^{-1} sec^{-1} in benzene),[5] the lifetime (τ) of triplet dibenzyl ketone is 10^{-9} sec. This is in reasonable agreement with photochemical studies,[3] which indicate that triplet dibenzyl ketone is extremely short-lived. To ensure that stable anomalous quenchers were not present during the decomposition of **1**, which would lower the yield of bibenzyl, the following control experiment was conducted. The amount of bibenzyl produced from **1** in degassed benzene at 60° was determined. Now this reaction mixture, which contained dibenzyl ketone produced from **1**, and an authentic sample of dibenzyl ketone in benzene were irradiated on a merry-go-round[8] in degassed solutions. In both instances, about the same amount of bibenzyl was produced from irradiation.

Previously we have shown that a two-step mechanism, involving biradical intermediates, adequately accounts for the activation parameters of certain 1,2-dioxetanes.[9]

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(3) (a) P. S. Engel, *J. Amer. Chem. Soc.*, **92**, 6074 (1970); (b) W. K. Robbins and R. H. Eastman, *ibid.*, **92**, 6076 (1970).

(4) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 93.

(5) Calculated from the Debye equation[6] with 3.877×10^{-3} P as the viscosity of benzene at 60°.[7]

(6) Reference 4, p 95.

(7) "Annual Tables of Constants and Numerical Data Chemical, Physical, and Technological," Vol. 5, Interscience, New York, N. Y., 1971–1972, p 51.

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(9) (a) H. E. O'Neal and W. H. Richardson, *ibid.*, **92**, 6553 (1970); (b) W. H. Richardson, M. B. Yelvington, and H. E. O'Neal, *ibid.*, **94**, 1619 (1972).