Orientation Effects on the Rate and Equilibrium Constants for Formation and Decomposition of Tetrahedral Intermediates

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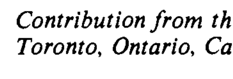
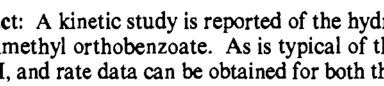
Abstract: A kinetic study is reported of the hydrolysis of the ortho ester **2** obtained by exchange of *exo,exo*-2,3-norbornanediol and trimethyl orthobenzoate. As is typical of this type of ortho ester, a change in slow step is observed between high pH and low pH, and rate data can be obtained for both the first stage, loss of the exocyclic methoxy group forming a 1,3-dioxolan-2-ylium ion, and the third stage, breakdown to ester products of the hemiorthoester derived by addition of water to this cation. This hemiorthoester is the tetrahedral intermediate of the degenerate transfer of the benzoyl group from one oxygen of the norbornanediol to the other. Rate constants for its formation in this reaction have been obtained from the rate of carbonyl oxygen exchange in norbornanediol monobenzoate. The equilibrium constant has also been calculated as the ratio of forward and reverse rate constants. The hemiorthoester in the norbornane system is a factor of 10^4 more stable relative to its ring-opened isomer than the corresponding hemiorthoester in the parent dioxolane. Kinetically, most of this effect is seen in the formation direction, cyclization in the norbornane system being more rapid by factors of 3000 (H^+-catalyzed reaction) and 3500 (pH-independent reaction). The norbornane hemiorthoester undergoes ring opening more slowly but the effect, factors of 4 and 3, is much smaller. It is concluded that variations in rates of intramolecular acyl-transfer reactions do reflect variations in thermodynamic stabilities of tetrahedral intermediates relative to their acyl precursors.

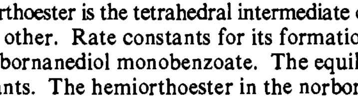
Ortho ester hydrolysis is now well established[1,2] to proceed via a three-stage reaction process: (1) acid-catalyzed generation of a dialkoxycarbocation, (2) hydration of this cation to form a hemiorthoester, and (3) decomposition of this intermediate to products. Until recently, kinetic studies of ortho ester hydrolysis were generally made under conditions where the first stage is rate determining.[1] In the last few years however, a number of ortho esters have been found for which a changeover occurs.[2,3] Stage 1 is rate determining at high pH, but at low pH stage 3 is the slow step. This occurs whenever acid catalysis of stage 3 is less effective than that of stage 1, so that under acid conditions stage 3 is slower. The very rapid base catalysis of stage 3, however, makes it the faster step at higher pH.



$$R-C(OR)_3 \longrightarrow R-C^+(OR)_2 + ROH \qquad (1)$$



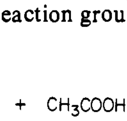
$$R-C^+(OR)_2 + H_2O \longrightarrow R-C(OH)(OR)_2 \qquad (2)$$



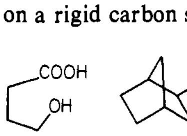
$$R-C(OH)(OR)_2 \longrightarrow RCOR\,(=O) + ROH \qquad (3)$$

A hemiorthoester intermediate is also the tetrahedral intermediate of an ester interchange reaction. Under conditions where stage 3 is rate limiting, rate constants based on product formation refer to decomposition of this intermediate. The observation of such changeovers has therefore presented the opportunity for directly measuring rates of tetrahedral intermediate breakdown.[2-4] These rates cannot be obtained in the acyl-transfer reactions themselves where the intermediates are generated only in small stationary-state amounts. Moreover by coupling rates of breakdown with rates of formation from appropriate acyl precursors, equilibrium constants for tetrahedral intermediate formation have also been measured.[3a,4d]

The ortho esters for which the changeover was first observed[2] are 2-aryl-2-alkoxy-1,3-dioxolanes (such as **1**). In this paper we report a study of the ortho ester **2** where the dioxolane ring has been fused to norbornane. This was chosen in order to investigate the effect of imposing rigidity in the dioxolane ring. We were particularly drawn to such a system by the work of Storm and Koshland,[5] who observed large rate enhancements on lactonization by fixing the reaction groups on a rigid carbon skeleton. This



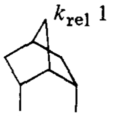
1



2

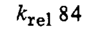
CH_3CH_2OH + CH_3COOH

k_{rel} 0.013



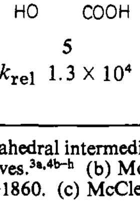
3

k_{rel} 1



4

k_{rel} 84



5

k_{rel} 1.3 × 10^4

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[1] Cordes, E. H.; Bull, H. G. *Chem. Rev.* **1974**, *74*, 581-603.

[2] Ahmad, M.; Bergstrom, R. G.; Cashen, M. J.; Chiang, Y.; Kresge, A. J.; McClelland, R. A.; Powell, M. F. *J. Am. Chem. Soc.* **1979**, *101*, 2669-2677.

[3] (a) McClelland, R. A.; Ahmad, M.; Bohonek, J.; Gedge, S. *Can. J. Chem.* **1979**, *57*, 1531-1540. (b) McClelland, R. A.; Gedge, S.; Bohonek, J. *J. Org. Chem.* **1981**, *46*, 886-891. (c) McClelland, R. A.; Alibhai, M. *Can. J. Chem.* **1981**, *59*, 1169-1176. (d) Burt, R. A.; Chiang, Y.; Kresge, A. J.; McKinney, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 3685-3687. (e) Burt, R. A.; Chiang, Y.; Hall, H. K.; Kresge, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 3687-3690.

[4] (a) Hemiorthoester tetrahedral intermediates have also been generated from other ortho acid derivatives.[3a,4b-h] (b) McClelland, R. A.; Ahmad, M. *J. Org. Chem.* **1979**, *44*, 1855-1860. (c) McClelland, R. A.; Patel, G. *J. Am. Chem. Soc.* **1981**, *103*, 6908-6911. (d) McClelland, R. A.; Patel, G. *J. Am. Chem. Soc.* **1981**, *103*, 6912-6915. (e) Capon, B.; Grieve, D. M. A. *J. Chem. Soc., Perkin Trans. 2* **1980**, 300-305. (f) Capon, B.; Ghosh, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 1765-1768. (g) Capon, B.; Sanchez, M. N. M. *J. Am. Chem. Soc.*, in press. (h) Capon, B.; Dosunmu, M. I. *J. Am. Chem. Soc.*, in press.

[5] Storm, D. R.; Koshland, D. E. *J. Am. Chem. Soc.* **1972**, *94*, 5805-5815, 5815-5825.

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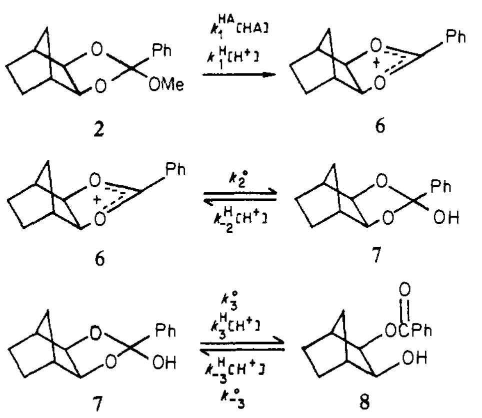
led to the controversial[6] proposal of "orbital steering", that enzymes achieve their catalytic efficiency by optimizing the orientation of reaction groups at their active sites.

Results

The ortho ester **2** was prepared by acid exchange of *exo,exo*-2,3-norbornanediol and trimethyl orthobenzoate. A 9:1 mixture of the two isomeric forms of **2** is formed, this probably being an equilibrium mixture because of the presence of the acid. We assign the major isomer to that structure drawn as **2** by analogy with benzaldehyde acetals of *exo,exo*-2,3-norbornanediol.[7] Under conditions where conversion of ortho ester to cation is rate determining, we observe excellent first-order kinetic plots. We interpret this to mean that the two isomers are undergoing hydrolysis at similar rates, so that the small amount of the second isomer has little effect.

The indication that an ortho ester undergoes a change in rate-determining step is the observation of different hydronium ion catalytic coefficients at high pH and low pH. Rates of hydrolysis of the ortho ester **2** were therefore measured in phosphate buffers of pH 6–7 (ionic strength (μ) = 0.1) and in HCl solutions (μ = 0.1) and $HClO_4$ solutions (μ = 1.0). These data are given in Tables S1 and S2. The behavior can be analyzed in the same manner as before,[2] with appropriate constants defined as in eq 4–6.



(4) 2 → 6

(5) 6 ⇌ 7

(6) 7 ⇌ 8

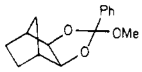
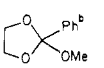
Rate constants in the phosphate buffers refer to the first stage in the ortho ester hydrolysis (eq 4).[2,3] These take the expected[2,8] form,

$$k_{obsd} = k_1^{H}[H^+] + k_1^{HA}[HA] \tag{7}$$

showing catalysis by the hydronium ion and the acid component of the buffer. Values of the catalytic coefficients are $k_1^{H} = 2.3 \times 10^4$ M^{-1} s^{-1}, $k_1^{H_2PO_4^-} = 0.015$. It can be noted that the first stage is written with exocyclic bond cleavage to produce the cyclic dioxolenium ion. This mode of breakdown was established in several ways with the parent dioxolane system[2,8a] and is supported in the present case by the observation of the hydroxyester **8** as the sole product of hydrolysis.

The rates observed in the strong acid solutions are significantly smaller than expected on the basis of $k_1^{H}[H^+]$, so that the change in slow step has occurred. Plots of k_{obsd} vs. $[H^+]$ are linear in the more dilute acid solutions, but some downward curvature is apparent in more concentrated acids. This behavior was observed previously.[2] It is associated with stage 3 (eq 6) being rate determining, with stage 2 (eq 5) being a rapid preequilibrium. The curvature in the more acidic solutions occurs as this equilibrium shifts toward the dioxolenium ion **6**, and indeed the cation can be observed as an transient intermediate with λ_{max} = 265 nm in the more concentrated acids. The rate equation for this system has the form

Table I. Rate and Equilibrium Constants[a] in the Hydrolysis of Dioxolane Ortho Esters **1** and **2**

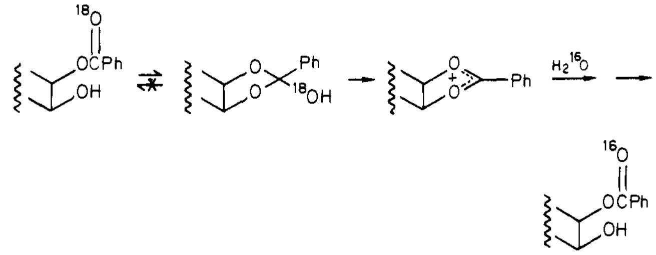
constant		
k_1^{H}, M^{-1} s^{-1}	2.3×10^4	5.4×10^3
pK_2^{R}	−0.15	−0.6
pK_2^{R} (μ = 1.0)	0.55	0.1
k_3^{H}, M^{-1} s^{-1}	7×10^1	3×10^2
k_3^{H} (μ = 1.0)	1.2×10^2	6.1×10^2
k_3°, s^{-1}	0.45	1.5
k_{-3}^{H}, M^{-1} s^{-1}	2.3×10^{-3}	8.1×10^{-7}
k_{-3}°, s^{-1}	3.2×10^4	3.7×10^8
k_{-3}°, s^{-1}	1.4×10^{-5}	4.1×10^{-9}
K_3	3.2×10^4	3.7×10^8

[a] T = 25 °C, μ = 0.1, unless otherwise noted. [b] References 2 and 3a.

$$k_{obsd} = \frac{k_3^{\circ} + k_3^{H}[H^+]}{1 + ([H^+]/K_2^{R})} \tag{8}$$

where $K_2^{R} = [7][H^+]/[6]$. Observed rates were fitted to this equation to provide the constants in Table I. For the data at μ = 0.1 M, it was difficult to precisely determine K_2^{R}, and the value in the table was calculated[2] as pK_2^{R} (μ = 0.1) = pK_2^{R} (μ = 1.0) − 0.7.

Rate constants for the formation of hemiorthoester **7** from the hydroxyester **8** were obtained from the rate of carbonyl ^{18}O exchange in acid solutions of the hydroxyester. This approach[3a] takes advantage of the fact that in acids equilibration of the hemiorthoester **7** and dioxolenium ion **6** is rapid compared to breakdown of **7** to hydroxyester. Therefore any cyclization of the hydroxyester **8** to the hemiorthoester **7** will result in loss of the carbonyl oxygen via the dioxolenium ion and its replacement with solvent oxygen. The overall result is carbonyl oxygen exchange of the hydroxyester. The rate of this exchange in acids is equal to the rate of cyclization, which, in acids, is $k_{-3}^{H}[H^+] + k_{-3}^{\circ}$. First-order rate constants for ^{18}O exchange were obtained in three acid solutions (Table S3). These are linear in H^+ concentration and give $k_{-3}^{H} = 2.3 \times 10^{-3}$ M^{-1} s^{-1} and $k_3^{\circ} = 1.4 \times 10^{-5}$ (at μ = 0.1). The equilibrium constant for interconversion of hemiorthoester and hydroxyester, $K_3 \equiv [8]/[7]$, can then be calculated as the ratio of the cyclization rate and the rate of hemiorthoester breakdown. The ratio of the acid-catalyzed rates, k_3^{H}/k_{-3}^{H}, is 3.05×10^4, and the ratio of the noncatalyzed rates, $k_3^{\circ}/k_{-3}^{\circ}$ is 3.2×10^4. These ratios are both equal to K_3. The excellent agreement shows the overall consistency of the analysis.



Discussion

Qualitatively, the behavior of the norbornane fused system is identical with that of the parent. The ortho ester does exhibit a change in slow step in its hydrolysis, and this allows for the

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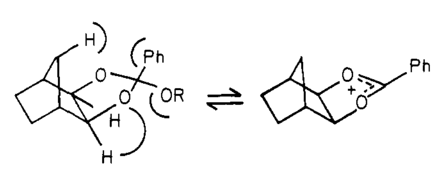
(6) Bruice, T. C.; Brown, A.; Harris, D. O. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 658–661. Page, M. I.; Jencks, W. P. *Ibid.* **1971**, *68*, 1678–1683. Page, M. I. *Chem. Soc. Rev.* **1973**, *2*, 295–323. Scheiner, S.; Lipscomb, W. N.; Kleier, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 4770–4777. Page, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 449–459. Danforth, C.; Nicholson, A. W.; James, J. C.; Loudon, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 4275–4281. Winnans, R.; Wilcox, C. F. *Ibid.* **1973**, *98*, 4281–4285. Menger, F. M.; Glass, L. E. *Ibid.* **1980**, *102*, 5404–5406.

(7) Bazbouz, A.; Christol, H.; Caste, J.; Plenat, F. *Bull. Soc. Chim. Fr.* **1978**, 305–311.

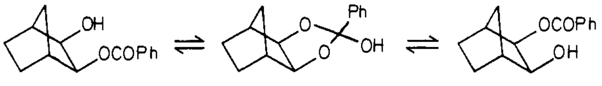
(8) (a) Chiang, Y.; Kresge, A. J.; Salomaa, P.; Young, C. I. *J. Am. Chem. Soc.* **1974**, *96*, 4494–4499. (b) Bergstrom, R. G.; Cashen, M. J.; Chiang, Y.; Kresge, A. J. *J. Org. Chem.* **1979**, *44*, 1639–1642.

determination of rate and equilibrium constants for all three reactions stages. A quantitative comparison of the two systems is given in Table I.

In the first two stages there is not a great difference to be seen. The norbornane system has a 4-fold faster rate in the first stage, the formation of the dioxolenium ion from the ortho ester. A 3-fold decrease is seen in the value of K_2^R for the second stage, the equilibration of the cation and hemiorthoester. These changes are in the same direction and imply that the dioxolenium ion fused to the norbornane ring is slightly more stable relative to the tetrahedral forms. This may arise through some steric interaction in the ortho ester or hemiorthoester that is absent in the cation.



It is the third stage that is the more interesting in the comparison. 2-Hydroxy-1,3-dioxolane hemiorthoesters are tetrahedral intermediates of degenerate intramolecular (O,O)-acyl-transfer reactions. For example, the hemiorthoester **7** is the tetrahedral intermediate of the transfer of a benzoyl group from one oxygen to the other in *exo,exo*-norbornanediol. There are two attractive features to our approach for the study of intramolecular acyl-transfer reactions. The first is that rates of tetrahedral intermediate formation are unambiguously measured. With other systems such as the lactonization reactions studied by Storm and Koshland,[5] there is the question as to whether intermediate formation or breakdown is rate determining.[9] The second advantage is that both the kinetics and thermodynamics of the ring-closure process are provided, since the intermediate is directly observed. It is then possible to see if an effect observed on a rate has a kinetic origin or a thermodynamic origin.



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The fusion of the norbornane ring does have a very pronounced effect on the thermodynamic stability of the tetrahedral intermediate relative to its hydroxyester isomer, a 10^4 smaller equilibrium constant being observed in the rigid system. This corresponds to a 5.6 kcal/mol increase in relative stability of the tetrahedral intermediate in the norbornyl system. This intermediate is in fact only 6 kcal/mol less stable than its ring-opened acyl isomer.

The origins of the effect of the norbornane ring have been much discussed.[5,6] There is probably a combination of an entropic factor that results in relative stabilization of the tetrahedral intermediate in the fused system with a steric factor that results in relative destabilization of the hydroxyester form in this system. The former has its origins in the free rotation of the carbon–carbon bond in 2-hydroxyethyl benzoate. The cyclization process therefore results in a considerable decrease in entropy associated with the freezing of this rotation. In the norbornane system the corresponding bond cannot rotate in the hydroxy ester, so that the same decrease in entropy does not occur. On the other hand the hydroxyester in the norbornane system has an eclipsing interaction between the hydroxy group and benzoyloxy group. This is not present in 2-hydroxyethyl benzoate, which can adopt gauche or anti staggered conformations.

What is also interesting is that almost all of the thermodynamic stabilization shows up kinetically in the cyclization direction, the rate constant k_{-3}^{H} for acid-catalyzed cyclization being 3000 times larger in the norbornane system, while the rate constant k_{-3}° for the pH-independent reaction is 3500 times greater. These increases parallel those seen by Storm and Koshland[5] in lactonization reactions, although they are more of the order of magnitude of the increase seen in the 2,6-endo,endo system **5** than in the more related 2,3-exo,exo compound **4**. The close similarity in the effects seen on ring-closing rates and the effect seen on the equilibrium constant implies that the rate accelerations associated with the rigid systems are thermodynamic in origin. That is there is no special factor stabilizing the transition state.

The rates of ring opening k_3^{H} and k_3° are smaller in the norbornane system, but the effect is very small, amounting only to factors of 4 and 3. In other words, the dioxolane ring in the norbornane system is opened just about easily as the ring in the parent system, despite being much more stable thermodynamically compared to the ring-opened product. This leads to the conclusion that from the point of view of the dynamics of the ring-opening–ring-closing processes the transition states in both the acid-catalyzed and noncatalyzed reactions lie close to the tetrahedral intermediate.

In conclusion it would appear from the present study that the considerable variations that are observed in the rates of intramolecular acyl-transfer reactions do reflect changes in thermodynamic stabilities of the cyclic tetrahedral intermediates relative to their ring-opened forms.

Experimental Section

exo,exo-2,3-Norbornanediol was prepared by the method of Sauers and Odorisio.[10] The ortho ester **2** was prepared by mixing equimolar quantities of this diol and trimethyl orthobenzoate in the presence of a small amount (one crystal) of *p*-toluenesulfonic acid. The methanol produced in the exchange was removed by applying a vacuum (1 mmHg). After 3 h a small amount of triethylamine was added to neutralize the acid, and the ortho ester (78% yield) was obtained by distillation (110 °C/0.1 mmHg).

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.26; H, 7.36. The presence of the two isomeric forms of the ortho ester was indicated in the ^1H NMR spectrum. The major isomer had peaks at δ 4.25 (broadened s, 2 H) and 3.15 (s, 3 H) corresponding to the two endo hydrogens at C_2 and C_3 and OCH_3, respectively. In the minor isomer (10%) the corresponding signals appeared at δ 3.75 and 3.50, respectively.

exo,exo-2,3-Norbornanediol monobenzoate was prepared by stirring the ortho ester with an excess of water. The resulting solid was recrystallized from ethanol/water and had a melting point of 67–68 °C.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 71.78; H, 6.88. Found: C, 72.01; H, 6.93.

Carbonyl-^{18}O *exo,exo*-2,3-norbornanediol monobenzoate was obtained in a similar manner, using 81.5% ^{18}O water. The position of the label was established from the mass spectrum of the sample (see later).

UV kinetic procedures have been described in detail previously.[2] Experiments in phosphate buffers were carried out on a Unicam SP1800 Spectrophotometer with jacketed cell block thermostated at 25.00 ± 0.01 °C, while experiments in HCl and $HClO_4$ solutions were carried out on a Durrum-Gibson stopped-flow spectrophotometer thermostated at 25.0 ± 0.1 °C. Kinetic measurements were in general made by following the appearance of the benzoate product at 232 nm. In the more concentrated acid solutions a short-lived transient with λ_{max} near 265 nm could also be observed. This corresponds to the 1,3-dioxolan-2-ylium ion[2,3a]. Rate constants based upon disappearance of this transient were found to be identical, within experimental error, to rate constants based upon product appearance.

Carbonyl oxygen experiments were performed by dissolving 0.05 g of the labeled monobenzoate in 5 mL of ethanol, followed by addition of this solution to 1 L of the appropriate aqueous acid solution thermostated at 25.0 °C. After an appropriate length of time a portion of this solution was removed and extracted with ether. The ether layer was washed with aqueous bicarbonate and dried over $MgSO_4$, and after filtration, the ether was removed. The remaining solid was analyzed directly on an AEI Model MS902 mass spectrometer. The monobenzoate exhibits reasonably intense peaks at m/e 232 and 234 corresponding to ^{16}O and ^{18}O molecular ions, respectively. Fragment peaks at m/e 123 and 125 corresponding to protonated benzoic acid are also present. The 234/232 and 125/123 ratios were measured in four–five scans for each sample and the excess ^{18}O calculated according to the formula 0.02 + 99.8 ($R - R_o$)/

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(9) De Tar, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 7205–7212.

(10) Sauers, R. R.; Odorisio, P. A. *J. Org. Chem.* **1979**, *44*, 2980.

(1.002 + $R - R_0$) where R is the ratio in the sample in question and R_0 is the ratio in unlabeled material. Good agreement was found between measurements of the two pairs of peaks. A fragment peak at m/e 127 is also observed, attributed to the loss of benzoyl group. The ratio 129/127 in all samples was within experimental error identical with that in unlabeled material. This establishes that the ^{18}O label is in the carbonyl oxygen. First-order rate constants for exchange were evaluated as the slopes of plots of ln (excess ^{18}O) vs. time.

Acknowledgment. Continued financial support of the Natural Sciences and Engineering Research Council is gratefully acknowledged.

Registry No. 2 (major isomer), 86239-10-3; 2 (minor isomer), 86287-25-4; 6, 86239-11-4; 7, 86239-12-5; O_2, 7782-44-7; *exo,exo*-2,3-norbornanediol, 16329-23-0; trimethyl orthobenzoate, 707-07-3; *exo,-exo*-2,3-norbornanediol monobenzoate, 77085-41-7.

Supplementary Material Available: Tables S1–S3 listing observed rate constants (1 page). Ordering information is given on any current masthead page.

Reluctant Azoalkanes: The Photochemical Behavior of Acyclic, Bridgehead-Centered Azoalkanes on 185- and 350-nm Irradiation

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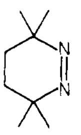
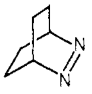
Abstract: Azo-1-adamantane (**1a**), azobicyclo[2.2.2]octanes (**1b** and **1c**), and azo-1-norbornane (**1d**) isomerize to the *cis*-azoalkanes but are reluctant to lose nitrogen directly upon long-wavelength irradiation. Use of 185-nm light is shown to enhance deazatization quantum yields considerably, though photoisomerization remains an important reaction. In the case of **1a** especially, thermolysis of the cis isomer is the dominant decomposition mechanism at long and probably at short wavelength; however, the cis isomer of **1d** is thermally stable. It follows that the second excited singlet state is responsible for deazatization of **1d**. The products of photolysis in pentane have been identified, and the amount of bridgehead radical hydrogen abstraction relative to recombination is found to increase under short-wavelength irradiation.

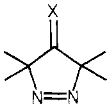
While azoalkanes have in general served an important role in the mechanistic elucidation of radical and diradical reactions[1] and as convenient precursors for unusual organic molecules,[2] a number of azoalkanes have recently received attention because of their low propensity toward conventional (λ >300 nm) photochemical deazatization. These "reluctant" azoalkanes include structure types A–D where the R groups in D are bridgehead-centered



A



B



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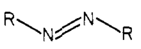

D

radicals. The long wavelength (λ >300 nm) photolysis of several reluctant azoalkanes could be significantly accelerated by employing elevated temperatures[3] and vapor-phase conditions[3a,b,g] or by introducing radical-stabilizing substituents[3d] and ring strain.[3d,g] Recently we reported that short wavelength (185 nm) radiation effectively promotes deazatization of structure types A[4], B,[4] and C.[5] In order to extend the generality of this wavelength dependence, it was of interest to determine whether azoalkanes of structure type D[6] were also photoreactive at 185 nm. Presently we confirm that photolysis of the bridgehead-centered, acyclic azoalkanes **1a–d** in solution is considerably more efficient at 185 nm than at long wavelengths.

Results

Synthesis of *trans*-Azoalkanes 1. The azoalkanes **1a–d** are all known[7] compounds, except **1c**, and were prepared by the usual sulfamide route.[8] The respective bridgehead amines were con-

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(1) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

(2) Adam, W.; De Lucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.

(3) (a) Turro, N. J.; Renner, C. A.; Waddell, W. H.; Katz, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 4320. (b) Turro, N. J.; Liu, K.-C.; Cherry, W.; Liu, J. M.; Jacobson, B. *Tetrahedron Lett.* **1978**, 555. (c) Mirbach, M. F.; Mirbach, M. J.; Liu, K.-C.; Turro, N. J. *J. Photochem.* **1978**, *8*, 299; (d) Engel, P. S.; Nalepa, C. J.; Leckonby, R. A.; Chae, W.-K. *J. Am. Chem. Soc.* **1979**, *101*, 6435. (e) Quast, H.; Fuss, A.; Heublein, A. *Angew. Chem.* **1980**, *92*, 55; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 49. (f) Quast, H.; Fuss, A. *Angew. Chem.* **1981**, *93*, 293; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 291. (g) Turro, N. J.; Liu, J. M.; Martin, H. D.; Kunze, M. *Tetrahedron Lett.* **1980**, 1299. (h) Engel, P. S.; Soltero, L. R.; Baughman, S. A.; Nalepa, C. J.; Cahill, P. A.; Weisman, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 1698.

(4) Adam, W.; Mazenod, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 7131.

(5) (a) Adam, W.; Fuss, A.; Mazenod, F. P.; Quast. H. *J. Am. Chem. Soc.* **1981**, *103*, 998. (b) Quast, H.; Seiferling, B. *Liebigs Ann. Chem.* **1982**, 1566.

(6) (a) Engel, P. S.; Melaugh, R. A.; Page, M. A.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 1971. (b) Chae, W. K.; Baughman, S. A.; Engel, P. S.; Bruch, M.; Ozmeral, C.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 4824.

(7) Golzke, V.; Groeger, F.; Oberlinner, A.; Rüchardt, C. *Nouv. J. Chim.* **1978**, *2*, 169.

(8) Stowell, J. C. *J. Org. Chem.* **1967**, *32*, 2360. Ohme, R.; Preuschof, H. *Liebigs. Ann. Chem.* **1968**, *713*, 74.

0002-7863/83/1505-6141$01.50/0