pattern. An increase in abundancy of lower masses [M − 19] and [M − 20] accompanied by a simultaneous decrease in higher masses [M − 17] and [M − 18] gives then the extent of HOD loss. A loss of HOD (*m/e* 19) was found with III-7,7-d_2, IV-*endo*-5,6-d_2, IV-7,7-d_2, and V-*exo*-5,6-d_2. All other deuterated compounds lost only H_2O (*m/e* 18). Deuterium randomization would require a ratio of ions [M − HOD]/[M − H_2O] of about 1:10 for monodeuterated and of about 1:5 for the dideuterated compounds, respectively, regardless of the position of deuteration. The fact that I-3,3-d_2, II-2-*d*, and II-3,3-d_2 do not lose HOD at all rules out a 1,1 and 1,2 elimination process. However, a 1,2 elimination including H from position 1 cannot be excluded on the basis of these results, but it seems unlikely to occur for steric reasons (Bredt's rule). The difference in HOD elimination from IV-*endo*-5,6-d_2 and V-*exo*-5,6-d_2 (which can be 1,3 as well as 1,4 elimination) confirms the stereospecificity of the dehydration. A similar result was obtained in the 1,4 elimination of cyclohexane-1,4-diol-1,4-d_2 where the loss of HOD from the molecular ion was due to 1,4 elimination, the proportion of ion yield associated with the [M − HOD] peak in the spectrum of trans compound being eight times greater than the corresponding peak from the spectrum of cis compound.[4] The loss of HOD in IV-*endo*-5,6-d_2 of 25% indicates that hydrogens from other positions are also contributing to the elimination. No evidence is available whether one or both hydrogens in positions 5 and 6 are involved in dehydration.

A substantial loss of HOD (>5%) was observed in the case of III-7,7-d_2 and IV-7,7-d_2. These compounds were 50% deuterated but these results are good indications that hydrogens from position 7 are involved in dehydration. On the other hand, it is interesting that in these compounds no difference between exo and endo position of the hydroxyl group was found.

The lack of contribution from hydrogens in position 3 in the case of I-3,3-d_2 and II-3,3-d_2 compared with substantial contribution from hydrogens in position 7 is an additional proof that positions 3 and 7 are not equivalent as one would expect in the case of involvement of nonclassical carbonium ion in the process of dehydration.

Experimental Section

Technique.—All spectra weie recorded under identical operating conditions with a CEC 21-110C mass spectrometer at about 100° with 70 eV, using a direct inlet (rod).

Origin of Samples.—The samples III, IV, V, III-7,7-d_2, IV-7,7-d_2, IV-*endo*-5,6-d_2, and V-*exo*-5,6-d_2 were prepared in the Physical Organic Chemistry Laboratory, Institute "Rudjer Bošković," by Dr. J. Jerkunica, whereas I, II, I-3,3-d_2, and II-3,3-d_2 were prepared as described earlier.[5]

Registry No.—I, 497-37-0; I-3,3-d_2, 10503-35-2; II, 497-36-9; II-2-*d*, 24867-16-1; II-3,3-d_2, 10503-34-1; III, 766-25-6; III-7,7-d_2, 30469-68-2; IV, 3588-21-4; IV-7,7-d_2, 30469-70-6; IV-*endo*-5,6-d_2, 30469-71-7; V, 3212-16-6; V-*exo*-5,6-d_2, 30469-72-8.

[4] C. G. Macdonald, J. S. Shannon, and G. Sugowdz, *Tetrahedron Lett.*, **13**, 807 (1963).

[5] J. P. Shaefer, M. J. Dagani, and D. S. Weinberg, *J. Amer. Chem. Soc.*, **89**, 6938 (1967).

Condensation Cyclization Reactions of Electron-Deficient Aromatics. III. N-Bromosuccinimide Oxidation of Bicyclic Dinitropropenides to Isoxazoline N-Oxides

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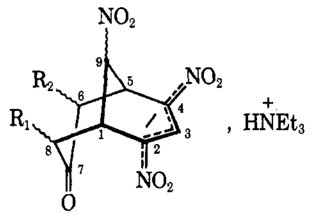
We have previously reported the preparation of a new class of stable bicyclic anions **1** which form spontaneously from appropriately structured Meisenheimer complexes.[1–5] We report here the unusual NBS oxidation of these anions to isoxazoline *N*-oxides and a detailed pmr analysis which provides evidence for the proposed structures.



1a, $R_1 = R_2 = C_6H_5$ (cis)
b, $R_1 = EtO_2C$; $R_2 = H$

Reaction of 2 equiv of NBS with 1 equiv of **1a**[3] or **1b**[3] in methanol solution at 25° results in immediate disappearance of the intense dinitropropenide absorption at 500 nm.[1] Two equivalents of NBS are required, as the first reacts with $HNEt_3^+$ (*vide infra*).[6] Quenching the yellow methanolic solution in a large excess of distilled water yields a voluminous white precipitate, which when filtered and recrystallized from ethanol gives colorless crystals of the oxidation product (*ca.* 50% yield).

The oxidation product obtained from NBS treatment of **1a** melts at 211–213° and analyzes correctly for $C_{21}H_{15}N_3O_7$. This corresponds to a formal loss of hydrogen and triethylamine from **1a**, and is consistent with the parent peak of 421 in the mass spectrum. The product readily forms a dinitrophenylhydrazone, mp 184–185°, rapidly decolorizes permanganate, but does not add bromine. It shows a broad band from 235 to to 290 nm (ϵ 6 × 10^3) in the uv and strong carbonyl and weak olefinic absorption at 1721 and 1653 cm^{-1} in the ir. Base treatment with alcoholic hydroxide or methoxide yields a solution with an intense absorption at 500 nm, indicating that the dinitropropenide function has probably been regenerated. These chemical and spectral properties, coupled with the observed disappearance of one of the benzylic proton resonances and induced nonequivalence of the phenyl groups in the pmr

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[1] Previous papers: M. J. Strauss, T. C. Jensen, H. Schran, and K. O'Conner, *J. Org. Chem.*, **35**, 383 (1970); H. Schran and M. J. Strauss, *ibid.*, **36**, 856 (1971).

[2] M. J. Strauss and H. Schran, *J. Amer. Chem. Soc.*, **91**, 3974 (1969).

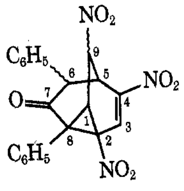
[3] M. I. Foreman, R. Foster, and M. J. Strauss, *J. Chem. Soc. C*, 2112 (1969).

[4] R. Foster, M. I. Foreman, and M. J. Strauss, *Tetrahedron Lett.*, 4949 (1968).

[5] M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).

[6] This was established by pmr analysis of the reaction of $HNEt_3^+$, Br^-, and NBS.

spectrum on conversion of **1a** to the oxidation product (*vide infra*), lead to the conclusion that a bond has formed between one of the benzylic centers, C-6 (C-8), and a constituent atom of the propenide function. The structures **2**, **3**, and **4a** reflect such possibilities, as each could result from initial NBS bromination at C-6 (C-8) of **1a**, followed by intramolecular displacement of bromide by the formal negative charge on C-2 (C-4) or a propenide NO_2 group.



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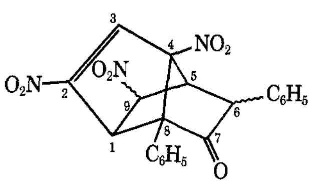

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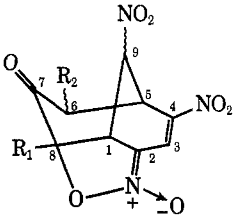


4a, $R_1 = R_2 = C_6H_5$
b, $R_1 = CO_2Et; R_2 = H$
c, $R_1 = H; R_2 = CO_2Et$

The carbonyl stretching frequency of the product is more consistent with **2** or **4a** than **3**, but the cyclopropyl C–H absorption near 3000 cm^{-1} anticipated for **2** could not be detected in the presence of the aromatic absorption. The 100-MHz pmr spectrum (Table I) provides substantive evidence for **4a**, however. The similarity of the H-5 and H-1 chemical shifts might be expected for **3** and **4a**, but not **2**. A cyclopropyl proton, even on a nitrocyclopropane, should resonate at higher field.[7] Since H-3 and H-6 are both strongly coupled to H-5, structure **3** seems unlikely. In addition, the triplet observed for H-9 requires that $J_{1,9} = J_{5,9}$. This would be expected if the dihedral angle between H-1 and H-9 is approximately equal to that between H-5 and H-9, a requirement which is met by **4a** and **2** but clearly not by **3**, regardless of the configuration at C-9. On the basis of the decoupling experiments, the following coupling constants have been determined: $J_{5,6} \cong 3.5$, $J_{1,9} \cong J_{5,9} \cong 2.5$, $J_{3,5} = 2.0$, and $J_{1,5} \cong 2.6$ cps. These values are accurate to about 0.15 cps. Using these coupling constants and the chemical shifts noted above, the calculated spectrum agrees well with that determined experimentally. Three recrystallizations from CH_3OD results in H-9 and H-6 resonances of diminished intensity owing to partial deuterium exchange. Thus, both these protons are relatively acidic, as expected.

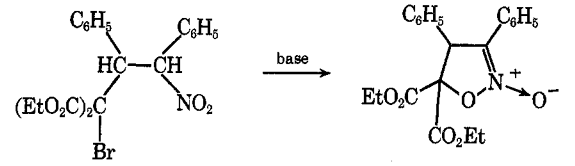
TABLE I

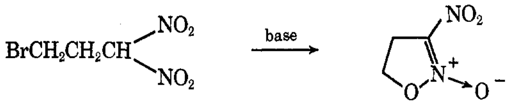
CHEMICAL SHIFTS (δ VALUES) AND SPLITTING[a] OF PROTONS IN THE ISOXAZOLINE *N*-OXIDES **4a** AND **4b** (IN ACETONE-d_6)

	Protons				
Compd	H-1	H-3	H-5	H-6	H-9
4a[e]	4.88 (m)	8.62 (d)	4.96 (m)	4.72 (d)	6.48 (t)
	irr[b]	d	*c*	d	d
	t[d]	irr[b]	*c*	d	t
	m	s	irr[b]	s	d
	m	d	*c*	irr[b]	t
	d[d]	d	*c*	d	irr[b]
	irr[b]	s	irr[b]	s	s
4b[f]	4.41 (m)	8.38 (d)	4.65 (br)	3.12 (dd)	6.09 (t)
	irr[b]	s	irr[b]	q	s
	t[d]	irr[b]	m	dd	t
	s, br	d	br	dd	irr[b]

[a] s = singlet; t = triplet; q = quartet or two droplets; m = multiplet; br = broad; dd = doublet of doublets. [b] Irradiated. [c] Simplified multiplet. [d] Poorly resolved. R_1, δ 7.56 (m, 2 H), 7.38 (m, 3 H); R_2, [a] 7.24 (br, 5 H); spectrum measured at 100 MHz. [f] R_1, δ 1.2 (t, 3 H), 4.2 (q, 2 H); spectrum measured at 60 MHz.

The pmr evidence for **4a** is supported by the ir and uv spectra, which are characteristic of isoxazoline *N*-oxides [uv, 280–290 nm (ε 6000); ir, 1610–1660 cm^{-1} ($C{=}N^+$)][8] and by analogous internal displacement reactions proposed to occur through nitronate intermediates.[8,9]





The bicyclic anion **1b** was treated with NBS in order to confirm the generality of the reaction. In this case, the two isomeric products **4b** and/or **4c** could form, since C-6 and C-8 are no longer equivalent as in **1a**. As expected on the basis of a bromination–internal displacement mechanism for the formation of these isoxazolines, only **4b** was obtained, corresponding to initial bromination of the most reactive site, C-8. The compound melts at 170–173° and analyzes correctly for $C_{12}H_{11}N_3O_9$. The pmr (Table I) and ir spectra of the material are consistent only with **4b**.

Both **4a** and **4b** could suffer base attack at C-8 with concomitant cleavage of the C-8–O bond to regenerate the dinitropropenide function. This is a reasonable explanation for the strong maximum at 500 nm observed in basic solutions of **4**. Attempts to isolate dinitropropenide products have been unsuccessful, as a complex isomeric mixture is formed.

The oxidation of compounds like **1** with NBS occurs generally, and does not require electron delocalizing or withdrawing substituents on C-6 and/or C-8. The instantaneous decolorization of other anions **1** ($R_1 = R_2 = CH_3$; $R_1 = R_2 = H$; $R_1 = CH_3CO$, $R_2 = H$; $R_1 = R_2 = CH_3O_2C$) readily occurs on treatment with NBS.

Experimental Section

The isoxazoline *N*-oxides, **4**, were prepared by adding 2 equiv of NBS to 1 equiv of the appropriate salt, **1**, in a minimum amount of dry methanol. The intense orange color of **1** immediately disappeared and the resulting yellow solution was stirred

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[7] J. Smidt and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **79**, 1235 (1960).

[8] A. Nielsen in "The Chemistry of the Nitro and Nitroso Groups," H. Feuer, Ed., Wiley, New York, N. Y., 1969.

[9] V. A. Tartakovskii, B. G. Gribov, I. A. Savost'yanova, and S. S. Novikov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1644 (1965); *Chem. Abstr.*, **64**, 2080 (1966).

for 5 min and poured into ten times its volume of distilled water. The resulting white precipitate was filtered, dried, and recrystallized twice from dry ethanol to yield pure **4** (~30–50% yield). *Anal.* Calcd for $C_{21}H_{15}N_3O_7$ (**4a**): C, 59.86; H, 3.59; N, 9.97. Found: C, 59.78; H, 3.69; N, 9.81. Calcd for $C_{12}H_{11}N_3O_9$ (**4b**): C, 42.24; H, 3.25; N, 12.31. Found: C, 42.20; H, 3.22; N, 12.17.

Registry No.—NBS, 128-08-5; **4a,** 30388-22-8; **4a** 2,4-DNP, 30388-23-9; **4b,** 30338-24-0.

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Pyrolysis of Phenylalkenylidenecyclopropanes[1]

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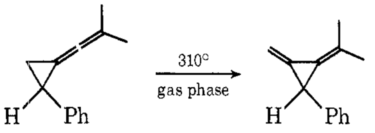
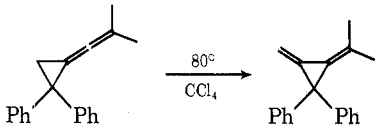
Dimethylenecyclopropanes have been found to be the products of the thermal rearrangement of alkenylidenecyclopropanes in both the parent[3] and methylated[4] systems. Because of the nature of the substitution of these compounds, little or no choice exists in the substitution pattern of the products. To probe this question, we have heated the mono- and diphenylalkenylidenecyclopropanes **1** and **2** and find that the phenyl groups always remain on the cyclopropane ring and do not migrate to the double bonds.[5]



1 **3**

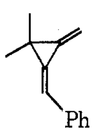


2 **4**

Pyrolysis of **1**[6] in a flow system at 310° under vacuum gives only **3** and starting material in the ratio 2.6:1. Compound **3** was identified by its elemental analysis and nmr spectrum in CCl_4: multiplets at δ 1.82 (3 H, methyl), 1.94 (3 H, methyl), 2.85 (1 H, benzyl cyclopropyl), 5.11 (1 H, vinyl), 5.34 (1 H, vinyl), and 6.9–7.2 (5 H, aryl). The chemical shift of the methyl signals leaves no doubt that it is the double bond and not the three-membered ring that bears the methyl groups. A broad band in the infrared spectrum at 1795 cm^{-1} confirms the methylenecyclopropane structure.[7,8]

Compound **2** is less volatile than **1** and was therefore rearranged to **4** in CCl_4 solution at 80°. **2** was made by an adaptation of the method of Hartzler[6] and was identified by its mass spectrum and nmr spectrum in CCl_4: singlets at δ 1.82 (6 H, methyls) and 2.13 (2 H, cyclopropyls) and a multiplet at 7.1–7.5 (10 H, aryl). A band in the infrared spectrum at 2005 cm^{-1} is appropriate for an allene.[9] Compound **4** was similarly identified by its mass spectrum and nmr spectrum in CCl_4: broad singlets at δ 2.09 (6 H, methyls), 5.50 (1 H, vinyl), and 5.64 (1 H, vinyl) and a multiplet at 7.2–7.7 (10 H, aryl). Again, a band in the infrared spectrum at 1795 cm^{-1} is typical of methylene cyclopropanes.[7,8]

The potential products **5–8** are not formed in significant amounts, as appropriate signals do not appear in the nmr spectra of the crude products. At first glance this may seem strange, but, if the mechanism of these changes involves perpendicular diradicals, as is generally thought,[10,11] it is understandable. The diradicals **9** and **10** should be the most stable ones available, and they must lead to **3** and **4**, and cannot give the others. At higher temperatures many other compounds are formed, and we hope to report on these at a later time.



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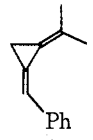

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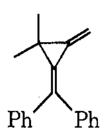

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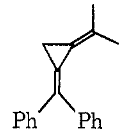

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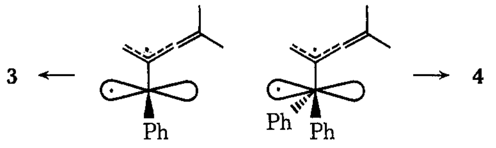

9 **10**

Experimental Section

General.—Nmr and infrared spectra were recorded on Varian Associates A-60A and Perkin-Elmer 237B instruments, respectively. Mass spectra were measured on an AEI MS-9 mass spectrometer.[12] Gas chromatographic analyses were performed on a Varian Aerograph A-90P instrument using a 5-ft 10% Dow-Corning 550 silicone oil on 60–80 mesh Chromosorb P column operated at 150° with a He flow rate of 100 ml/min.

Pyrolysis of 1.—Compound 1, 1-(2-methylpropenylidene)-2-phenylcyclopropane, was prepared by the method of Hartzler[6] and purified by bulb-to-bulb distillation immediately before use. The pyrolysis apparatus consisted of a 20-cm length of 14-mm quartz tube heated by chromel wire. Temperatures in the tube varied by a maximum of 6° over its length. The temperature reported is the maximum in the tube. In a typical run

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[1] We thank the National Science Foundation for support of this work through Grant GP-12759.

[2] National Science Foundation Predoctoral Fellow, 1967–1971.

[3] R. Bloch, P. LePerchec, and J.-M. Conia, *Angew. Chem.*, **82**, 910 (1970).

[4] D. R. Paulson, J. K. Crandall, and C. A. Bunnell, *J. Org. Chem.*, **35**, 3708 (1970).

[5] The rearrangement of **1** to **3** at 130° in solution has been noted by T. B. Patrick, E. C. Haynie, and W. J. Probst, *Tetrahedron Letters*, 423 (1971), and, in passing, by I. H. Sadler and J. A. G. Stewart, *Chem. Commun.*, 1588 (1970).

[6] H. D. Hartzler, *J. Amer. Chem. Soc.*, **83**, 4990 (1961).

[7] J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **75**, 3344 (1953).

[8] R. F. Bleiholder and H. Shechter, *ibid.*, **86**, 5032 (1964).

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958.

[10] W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970).

[11] J. J. Gajewski, *J. Amer. Chem. Soc.*, **90**, 7178 (1968).

[12] We thank the National Science Foundation for providing the funds for the purchase of this instrument through Grant GP-5200.