16526-78-6; X, 16526-79-7; XI, 16526-80-0; XII·barium salt, 16526-81-1.

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The Addition of Dinitrogen Trioxide to Norbornene[1]

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Schechter, *et al.*[2] have shown that the reaction of dinitrogen tetroxide with norbornene proceeds without skeletal rearrangement of the norbornyl system affording 22% *exo,cis*-2,3-dinitronorbornane, 12% of the *trans*-dinitro compound, and 60% of a mixture of nitronitrites. *exo* attack on the norbornyl system is favored for steric reasons; similar *exo,cis* additions have been observed in radical reactions of *p*-toluenethiol,[3] ethyl bromoacetate,[4] and hydrogen bromide[5] with norbornene. The addition of dinitrogen trioxide to olefins is generally believed to involve an extension of the free-radical mechanism applied to N_2O_4 additions,[6] so it was of interest to examine the course of adduction of norbornene with N_2O_3.

The addition of dinitrogen trioxide to norbornene can be visualized as proceeding through either 2,3, 2,7, or 2,6 addition. The 2,7 addition would be the result of Wagner–Meerwein-type rearrangement of the intermediate radical species. Hydrogen radical transfer in the intermediate would lead to 2,6 product. The course of addition was determined by employing *exo,exo*-5,6-dideuterionorbornene[7] as a substrate for N_2O_3 addition. Were the reaction to proceed without rearrangement to the 2,3 product, the 5,6-methylene protons would remain in *endo* positions in the pseudonitrosite I and nitroxime II (path A, Skeletal rearrangement to a 2,7 product would be accompanied by transformation of the 5,6-methylene hydrogens to *exo* protons in III and IV (path B, Scheme I). Hydrogen transfer in 2,6 addition would result in a deuterium attached to the nitrosated carbon atom in the pseudonitrosite V and oxime deuterium in the nitroxime VI. The results indicate that both the pseudonitrosite and nitroxime possess only *endo* hydrogens at the 5,6 positions. No rearrangement to 2,7 or 2,6 products has taken place; therefore, the reaction must have occurred *via* path A.

The nmr spectrum of the recrystallized nitroxime in deuterioacetone is in accord with structure I, that of *exo,exo*-5,6-dideuterio-3-nitro-2-norbornanone oxime. The oxime proton gives a sharp singlet whose chemical shift varies with concentration. The two bridgehead protons are observed as multiplets at δ 3.0 ppm. The three-proton is highly deshielded, being surrounded by the nitro and oximino groups, and is seen as a doublet at δ 4.8 ppm, with $J = 2$ cps. This proton is in an *endo* position coupling with the 7-*anti* bridge proton.[8] The bridge protons lie in different magnetic environments; their chemical shifts differ and so do their coupling patterns. A singlet peak at δ 1.4 ppm is attributable to the 5,6-*endo* protons; had they been *exo* in nature, larger coupling would be expected.

The deuterated pseudonitrosite has a high-field spectrum similar to that of the nitroxime. An unrecrystallized, but ether-washed sample of the pseudonitrosite shows a peak (area 2) at δ 5.0 ppm. This is the signal for the protons attached to the carbons bearing nitrogen atoms. This product appears to consist predominantly of the *exo,cis*-nitroso dimer II, since a *trans* configuration would result in *endo* and *exo* protons of different chemical shifts and larger coupling constants. Furthermore, *exo* protons should experience a coupling of 4–5 cps with the bridgehead protons.[8] A two-proton peak at δ 3.0 ppm is assigned to the bridgehead hydrogens and a doublet (area 2, $J = 2$ cps) at 1.2 ppm is assigned to the 5,6-*endo* protons. The bridge protons are manifested as signals centered at δ 1.5 and 2.3 ppm.

Catalytic reduction of the nitroxime gives a mixture of 2,3-diaminonorboranes. Conversion of the crude diamine product into the dihydrochloride followed by several recrystallizations of this salt affords *trans*-2,3-diaminonorborane dihydrochloride. This substance is identical with the salt prepared by Inglessis.[9] The signals for protons attached to nitrogen-bearing carbon atoms experience different chemical shifts as would be expected for *endo* and *exo* protons. A *cis* configuration would be more symmetrical, leading to the same chemical shift for either proton.

The N_2O_3 addition reaction probably involves initial *exo* attack by nitrogen dioxide. The steric demands of the norbornyl system then direct the combination of the intermediate radical with nitric oxide to favor the *exo,cis* product as in path A.

Experimental Section

Nmr spectra were taken in deuteriochloroform solution with a Varian A-60. Vapor phase chromatography was carried out on an FM-500. Melting points are uncorrected.

Preparation of Norbornene Pseudonitrosite.—A well-stirred solution of 1 mol of norbornene in 500 ml of a 1:1 solution of pentane–ether at −10 to 5° is treated with a mixed stream of nitric oxide at a flow rate of 80 cc/min and air at a flow rate of 40 cc/min. Completion of the reaction is evidenced by the appearance of brown gas above the surface of the reaction mixture, indicating that oxides of nitrogen are no longer being absorbed.

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[1] Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[2] H. Schechter, J. J. Gardikes, T. S. Cantrell, and G. V. D. Tiers, *J. Amer. Chem. Soc.*, **89**, 3005 (1967).

[3] S. J. Cristol and G. D. Brindel, *ibid.*, **76**, 5699 (1954).

[4] J. Weinstock, Abstracts, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept 1955, p 19-Org.

[5] H. Kwart and J. L. Nyce, *J. Amer. Chem. Soc.*, **86**, 2601 (1964).

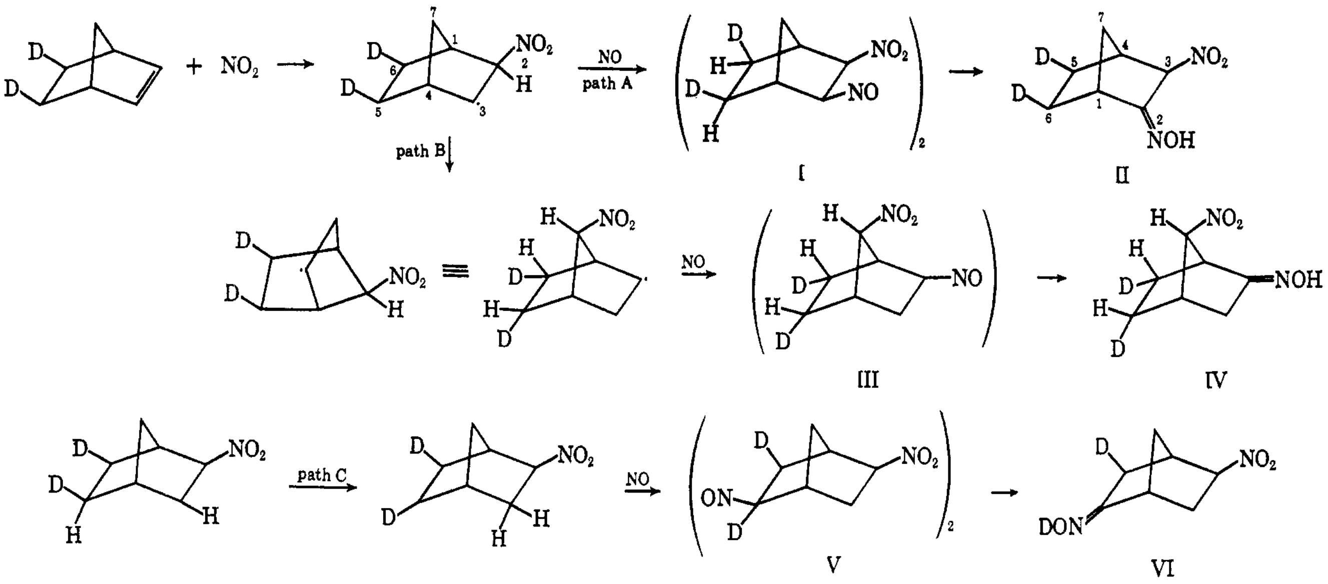
[6] H. Schechter, *Rec. Chem. Progr.*, **25**, 55 (1964).

[7] (a) B. Franzus, W. C. Baird, Jr., and J. H. Surridge, *J. Org. Chem.*, **33**, 1288 (1968); (b) W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *J. Amer. Chem. Soc.*, **89**, 410 (1967).

[8] J. Meinwald, Y. C. Meinwald, and T. N. Baker III, *ibid.*, **86**, 4074 (1964).

[9] C. S. Inglessis, Ph.D. Thesis, Clark University, 1959.

Scheme I



The crystalline product is separated by filtration, washed with ether, air dried, and recrystallized from methylene chloride-pentane. A 60% yield of white crystals, mp 135°, is obtained.

Anal. Calcd for $C_7H_{10}N_2O_3$: C, 49.42; H, 5.92; N, 16.47; O, 28.21. Found: C, 49.42; H, 6.13; N, 16.21; O, 28.07.

Norbornene Nitroxime.—A solution of norbornene pseudonitrosite in dioxane is refluxed under nitrogen until the green color of the nitroso monomer has completely disappeared (1-2 hr). The dioxane is evaporated leaving crude solid residue. Recrystallization from methylene chloride-pentane affords pure (75% yield) nitroxime, mp 167°.

Anal. Calcd for $C_7H_{10}N_2O_3$: C, 49.42; H, 5.95; N, 16.47; O, 28.21. Found: C, 49.42; H, 5.90; N, 16.14; O, 28.54.

2,3-Diaminonorborane.—Treatment of 17 g (0.1 mol) of norbornene nitroxime in absolute ethanol with 1 g of Raney nickel at 75° and 1500 psi hydrogen for 2-3 days followed by filtration of the catalyst, evaporation of the solvent, and vacuum distillation of the crude oil affords 10 g of colorless, liquid distillate, bp 100-135° (0.2 mm). Gc studies reveal that a mixture of products is present. Treatment of an ethereal solution of the crude diamine with dry hydrogen chloride affords a salt which after recrystallization from ethanol fails to melt below 300°. *Anal.* Calcd for $C_7H_{14}N_2Cl_2$: C, 42.44; H, 8.13; N, 14.15; Cl, 35.79. Found: C, 42.02; H, 8.03; N, 13.87; Cl, 35.83. The nmr spectrum in D_2O reveals absorption patterns of area 6 at δ 1.7, area 2 at 2.7 (bridgehead protons), one-proton signals at 3.3 (quartet) and 3.7 ppm (triplet) as well as exchangeable proton absorption.

The infrared and nmr spectra of the dihydrochloride and retention time of the free diamine on a Carbowax 20M-KOH column at 150° are identical with the substance prepared according to the procedure of Inglessis.[9]

***exo,exo*-5,6-Dideuterionorbornene.**—The deuterated olefin is prepared according to the procedure of Baird, Franzus, and Surridge.[7] Reaction with nitrogen oxides and subsequent conversion into nitroxime are carried out in the manner described above.

Registry No.—Dinitrogen trioxide, 16529-92-3; norbornene, 498-66-8; norbornene pseudonitrosite, 16526-91-3; norbornene nitroxime, 16526-92-4; 2,3-diaminonorbornane dihydrochloride, 16526-93-5.

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Nuclear Magnetic Resonance Chemical Shifts of Cyclopropane HCH in Unsubstituted Bicyclo[x.1.0]alkanes as a Function of Ring Size[1]

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In connection with product identifications in another study,[2] we required samples of several bicyclo[x.1.0]-alkanes (Figure 1). These compounds were prepared by methyleneation of the appropriate cycloalkene with methylene iodide and zinc-copper couple.[2-4] When we examined the nuclear magnetic resonance (nmr) spectra of these bicycloalkanes, we were impressed with the continuing upfield shift of the signal from one of the cyclopropane CH_2 protons as the size of the larger ring increased from five to ten members (Table I). The signal associated with the proton geminal to the first apparently is shifted downfield by the same change that brings about the upfield shift of the first proton in the cyclopropane CH_2 group. We cannot be certain about the regularity of the shift, however, be-

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[1] (a) Presented in part at the Southeast-Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 1965, paper no. 97, and at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstracts, p S125. (b) We gratefully acknowledge partial support of this research by grants from the Petroleum Research Fund administered by the American Chemical Society (Grant No. 1817-A4) and the National Science Foundation (Grant No. GP 5749). (c) Based in part on a portion of the Ph.D. Dissertation of J. S. D., Louisiana State University, 1966. The financial assistance from the Charles E. Coates Memorial Fund, donated by George H. Coates, for preparation of the Ph.D. Dissertation of J. S. D. is gratefully acknowledged.

[2] J. G. Traynham and J. S. Dehn, *J. Amer. Chem. Soc.*, **89**, 2139 (1967).

[3] H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

[4] A commercial mixture of *cis*- and *trans*-cyclododecene was used for the preparation of bicyclo[10.1.0]tridecane. The sample of bicyclotridecane used in this study was shown by gas chromatographic analysis to be approximately 50% *cis*, 50% *trans*; only one of the isomers (presumably *cis*) gave the upfield nmr signal reported.