Reaction of Di-*t*-butyl Nitroxide (III) with Hydrogen Chloride and Chlorine.—A solution of 0.1 g of di-*t*-butyl nitroxide in 2.5 ml of chloroform was treated with gaseous hydrogen chloride at −65,° after which the reaction mixture was taken out of the cooling bath. The color of the reaction mixture turned from red to green to blue. A qualitative glpc determination of products, as described for the ozonation experiments, showed isobutene, *t*-butyl chloride, and 2-methyl-2-nitrosopropane. Evaporation of the solution left a solid which was identified as di-*t*-butyl-hydroxylammonium chloride by its ir spectrum. Similar results were obtained upon similar treatment of di-*t*-butyl nitroxide with chlorine.

Addition of Dinitrogen Trioxide to Nonconjugated Dienes
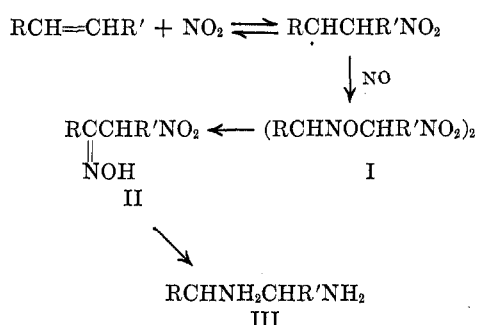
M. L. Scheinbaum[1]

Corporate Research Laboratories, Esso Research and Engineering Company, Linden, New Jersey 07036

The addition of dinitrogen trioxide is shown to proceed selectively at the bicyclic double bond of dicyclopentadiene. Simple adduct formation without transannular reaction occurs with 1,5-cyclooctadiene; however, norbornadiene undergoes considerable transannular addition to give nortricyclene derivatives. Reduction of the adducts leads to hydroxylamino oxime derivatives and diamines. The course of addition of nitrogen oxides is interpreted by a free-radical pathway.

The reaction of olefins with dinitrogen trioxide or with a mixture of nitrogen oxides to form 1:1 adducts is a classical technique of introducing two vicinal carbon–nitrogen bonds into an olefinic system.[2a] The adducts, known as pseudonitrosites, are usually 2-nitronitroso dimers I which can be thermally rearranged to the more soluble α-nitroximes II, and subsequently reduced to vicinal diamines III. The addition of dinitrogen trioxide is believed to involve reversible attack of nitrogen dioxide on olefin with the formation of a free-radical intermediate containing a carbon–nitrogen bond which can combine with nitric oxide and dimerize, resulting in the adduct 1.[2b,c]

$$RCH{=}CHR' + NO_2 \rightleftharpoons RCHCHR'NO_2$$

$$\downarrow NO$$

$$RCCHR'NO_2 \longleftarrow (RCHNOCHR'NO_2)_2$$
$$\underset{II}{\overset{\|}{N}OH} \qquad\qquad I$$

$$\searrow$$

$$\underset{III}{RCHNH_2CHR'NH_2}$$

It was of interest to determine whether the formation of these adducts from cyclic, nonconjugated dienes occurs selectively and whether transannular reactions take place. Dicyclopentadiene, 4-vinylcyclohexene-1, 1,5-cyclooctadiene, and norbornadiene were selected as cases for study. The results are in no disagreement with a free-radical mechanism and are interpreted accordingly.

Dicyclopentadiene–N₂O₃.—Dicyclopentadiene was reported to form a pseudonitrosite in 1908;[3] however, the structure of dicyclopentadiene was unknown at

that time, and consequently the structure proposed for the adduct was incorrect. Examination of the nmr spectrum reveals that one double bond manifested as a singlet at δ 5.0 ppm (in CDCl₃) is present. Cyclopentene exhibits a singlet at δ 5.7 ppm, whereas the bicyclic double bond in norbornene and in dicyclopentadiene is observed as an unsymmetrical triplet at δ 6.0 ppm. The singlet character and relative upfield position of the olefinic signal would suggest a cyclopentenyl rather than a norbornenyl double bond. Furthermore, the presence of a bicyclic double bond affects the chemical shift of the bridge protons; the 7s and 7a protons in norbornene and dicyclopentadiene show absorption patterns in the area of δ 1–1.5 ppm, whereas the spectrum of the pseudonitrosite possesses no signals in this region. A competition experiment involving a mixture of norbornene and cyclopentene with a limited quantity of nitrogen oxides results in almost exclusive consumption of the norbornene and formation of norbornene pseudonitrosite[4] rather than the cyclopentene derivative, indicating that a norbornenyl bicyclic double bond is intrinsically more reactive toward nitrogen oxides than is a cyclopentene system.

It is likely that the products are derived chiefly from *exo-cis* addition as in the case of norbornene,[4] but in this case there is less certainty. There are two *exo-cis* addition products for dicyclopentadiene IV and IVa, differing in the position of the double bond, and at least three types of dimers possible: dimers of IV and IVa, and the mixed dimer of IV and IVa, as well as *cis*- and *trans*-nitroso dimer forms, *i.e.*, geometric isomers *cis* and *trans* with respect to the nitrogen–nitrogen bond. Isomerization to the nitroxime affords a product whose nmr spectrum reveals a doublet of area 1 at δ 4.8 ppm, attributable to the highly shielded proton attached to the carbon atom bearing the nitro group. The 2-cps coupling reflected also in the signal assigned to the 7-*anti* bridge hydrogen at δ 1.8 ppm suggests that the 3 proton lies in an *endo* position, as in the case of norbornene nitroxime.[4] The nitroxime most likely

(1) Department of Chemistry, East Tennessee State University, Johnson City, Tenn.

(2) (a) H. Wieland, *Justus Liebigs Ann. Chem.*, **424**, 71 (1920); (b) H. Schechter, *Rec. Chem. Progr.*, **25**, 55 (1964); (c) M. L. Scheinbaum, *Amer. Chem. Soc. Petrol. Chem., Prepr.*, **13**, 193 (1968).

(3) (a) H. Wieland and H. Stenzel, *Justus Liebigs Ann. Chem.*, **360**, 299 (1908); (b) A. Rule, *J. Chem. Soc.*, **93**, 1508 (1908).

(4) M. L. Scheinbaum, *J. Org. Chem.*, **33**, 2586 (1968).

consists of a mixture of V and Va with the nitro group predominately in the *exo* position. Hydrogenation in the presence of palladium–carbon catalyst affords a single product, the hydroxylamino oxime VI. Attempts to effect catalytic reduction to the diamine were unsuccessful, probably owing to steric hindrance to the approach of hydrogen.
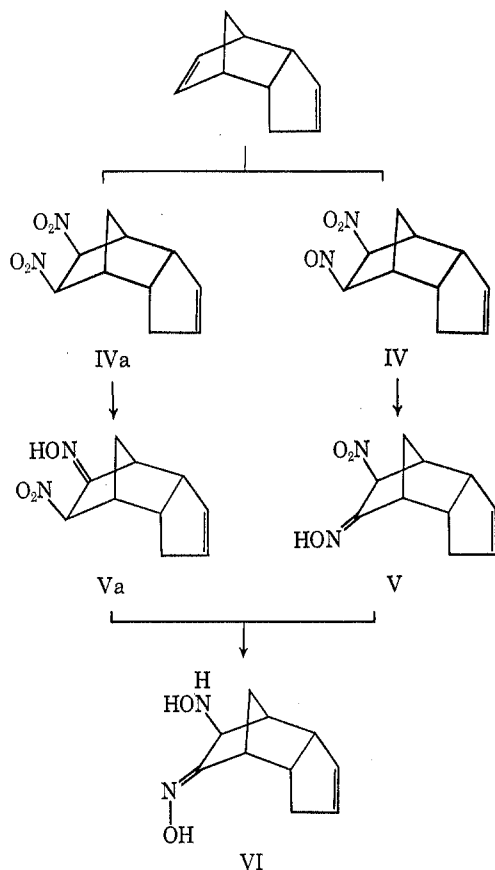
The selectivity of addition of nitrogen oxides to the bicyclic double bond of dicyclopentadiene is not particularly remarkable in that preference for this site is observed in the reactions of dicyclopentadiene with a variety of reagents.[5] What is significant is that dicyclopentadiene–dinitrogen trioxide monoadduct is readily obtained in high yield. Pseudonitrosites and other types of nitroso dimers are ordinarily poorly soluble species, so that monoadducts rapidly crystallize out of solution and are probably less prone to react at the free double bond to form diadducts in their crystalline form than is an olefin in solution.

4-Vinylcyclohexene–N₂O₃.—Addition of dinitrogen trioxide to 4-vinylcyclohexene results in a low yield of adduct that readily rearranges to the nitroxime. The nmr spectrum of the latter possesses signals corresponding to two olefinic protons and two nitromethylene protons; vinyl absorption is absent. The spectrum is in accord with structure VII derived from addition to the
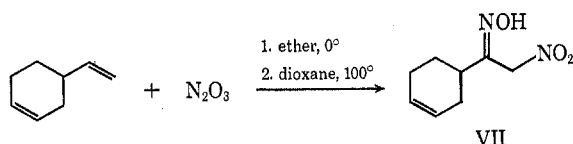

(5) P. Wilder Jr., C. F. Culberson, and G. T. Youngblood, *J. Amer. Chem. Soc.*, **81**, 655 (1959).

vinyl double bond. Since there is no change in the nature of unreacted starting material during the course of reaction, there is little reason to anticipate alteration in the position of the ring double bond.

The dinitrogen trioxide adduct of vinylcyclohexane (VIII) was prepared and characterized. The nmr spectrum resembles that of propylene pseudonitrosite[2b] with an ABC portion of an ABCX pattern for protons attached to nitrogen bearing carbon atoms. Reduction of this derivative with lithium aluminum hydride results in loss of nitrogen to give the same amine, 2-cyclohexylethylamine (IX), as obtained by high pressure, Raney nickel catalyzed hydrogenation of VII at
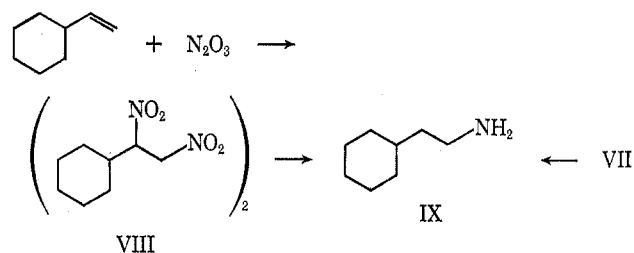
75°. The pseudonitrosite VIII is isomerized to the nitroxime X on treatment with refluxing dioxane. Hydrogenation of X with palladium-on-carbon catalyst affords the same hydroxyamino oxime XI as obtained from similar catalytic reduction of VII. Lithium aluminum hydride reduction or Raney nickel catalyzed, high-pressure hydrogenation of either X or XI affords the vicinal diamine XII. Since the reaction of N₂O₃ with vinylcyclohexane is straightforward, the matching of reduction products confirms the structure of VII as stemming from addition to the vinyl double bond.
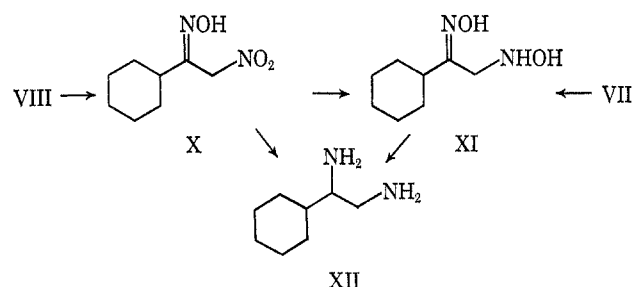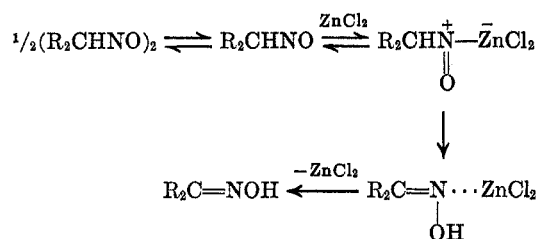

Selectivity of free-radical reactions toward the vinyl double bond of 4-vinylcyclohexene has been reported for a variety of reagents;[6] however, polar reagents often attack preferentially at the cyclohexene bond.[7] That the selective isolation of VII in the case of nitrogen oxide addition is not attributable to any special intrinsic reactivity of vinyl groups as opposed to cyclohexene double bonds is borne out by competition experiments. Cyclohexene is consumed about three times more rapidly than vinylcyclohexane, and 4-vinylcyclohexene reacts at a rate intermediate between the two. Probably, mostly ring attack does occur with 4-vinylcyclohexene-1, but crystallization of the vinyl adduct is preferred. This is attributable either to slow rates of recrystallization of the ring derivatives or to their susceptibility to undergo secondary reactions leading to soluble products, such as nitro olefins, nitro ketones, nitro nitrites,

(6) R. H. Fish, H. G. Kuivila, and I. J. Tyminski, *ibid.*, **89**, 5861 (1967).
(7) R. H. Perry, Jr., and B. G. Cornan, *Amer. Chem. Soc. Div. Petrol. Chem., Prepr.*, **12**, D5 (1967).

or dinitro compounds. The dimer which actually does crystallize, that derived from addition to the vinyl group, is obtained in only 11% yield.

1,5-Cyclooctadiene-N_2O_3.—1,5-Cyclooctadiene is known to form a monoadduct with dinitrogen trioxide.[8] Nmr examination of the crude product indicates that one double bond is retained. No isomerization of unreacted diene is observed during the course of reaction, suggesting that the position of the double bond is unchanged in the adduct XIII. Isomerization of 1,5-cyclooctadiene pseudonitrosite does not occur readily; exposure of the pseudonitrosite to refluxing dioxane results in partial recovery of the starting material along with decomposition and tar formation. Isomerization is best carried out in alcoholic solution in the presence of catalytic quantities of a transition metal salt, such as zinc chloride. The zinc ion probably coordinates with the nitroso group, rendering the adjacent proton more activated toward rearrangement. The technique also works for rearranging other stubborn nitroso compounds, e.g., cyclohexene pseudonitrosite undergoes rearrangement to 2-nitrocyclohexanone oxime.

$$\frac{1}{2}(R_2CHNO)_2 \rightleftharpoons R_2CHNO \overset{ZnCl_2}{\rightleftharpoons} R_2CH\overset{+}{N}{\overset{-}{\underset{\|}{O}}}ZnCl_2$$

$$R_2C{=}NOH \xleftarrow{-ZnCl_2} R_2C{=}\overset{}{\underset{\overset{|}{OH}}{N}}\cdots ZnCl_2$$

The nitroxime derived from XIII exhibits nmr signals for two olefinic protons as well as nitromethine and oxime protons. The spectrum is in accord with structure XIV; no evidence of transannular reaction is observed.
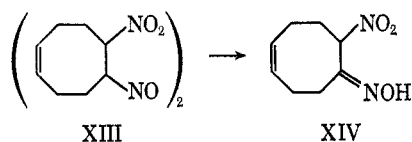
Lithium aluminum hydride reduction of XIII occurs with loss of a nitrogen functionality to give the unsaturated amine XV, which can be further reduced to cyclooctylamine.
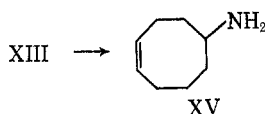
Hydrogenation of the nitroxime XIV with palladized carbon catalysis affords 2-hydroxylaminocyclooctanone oxime (XVI). The same derivative is formed by similar reduction of 2-nitrocyclooctanone oxime (XVII)[8] which is derived from cyclooctene through dinitrogen trioxide addition and isomerization. The preparation of XVI from either XV or XVII confirms the nmr assignment of XIII as a simple 1,2 adduct rather than a transannular product. The hydroxylamino oxime XVI

can be reduced by lithium aluminum hydride or catalytically to a mixture of *cis*- and *trans*-1,2-diaminocyclooctanes (XVIII).
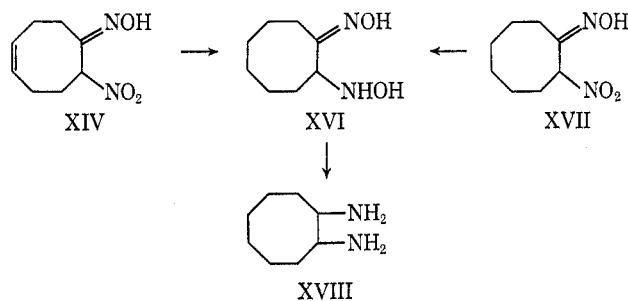
Although free-radical addition reactions of 1,5-cyclooctadiene leading to bicyclo[3.3.0]octane derivatives have been reported for a variety of reagents, only simple 1,2 adducts were observed in the addition of thiolacetic acid, thiolbenzoic acid, and benzenethiol to 1,5-cyclooctadiene.[9] The following explanation was used to rationalize the absence of transannular product in low-temperature addition of trimethyl tin hydride.[9] In the absence of a good radical donor, the intermediate radical XIX can undergo rearrangement to the bicyclic radical XX resulting in formation of transannular product. If a good B donor is present, such as a thiol, simple 1,2 addition to give XXI occurs more rapidly than formation of XX. This concept of
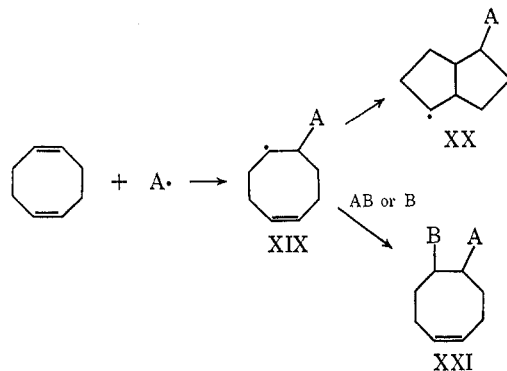
free-radical addition to 1,5-cyclooctadiene turns out to be applicable in the present case where AB is dinitrogen trioxide. The radical donor B is nitric oxide, a well-known free-radical trapping agent which is in relatively high concentration under the reaction conditions. Consequently, only the 1,2-addition product is obtained. The activation energy required to rearrange XIX to XX when A = NO_2 is evidently too high relative to the lifetime of XIX in the presence of nitric oxide. Transannular reaction has not been reported for free-radical additions to dicyclopentadiene or 4-vinylcyclohexene-1, and was not observed with dinitrogen trioxide.
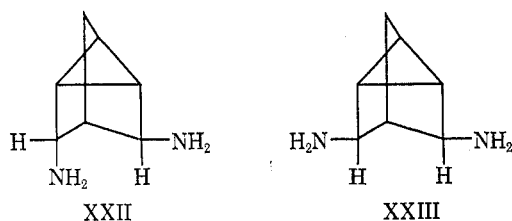
Norbornadiene-N_2O_3.—Norbornadiene reacts with nitrogen oxides to form a tan-colored N_2O_3 adduct which undergoes considerable decomposition to tarry products on attempted rearrangement or recrystallization in hot solvents. Nmr examination of the adduct indicates that olefinic absorption is only 30–40% as strong as expected for simple N_2O_3 addition to one double bond;

(8) D. Klamann, W. Koser, P. Weyerstahl, and M. Fligge, *Chem. Ber.*, **98**, 1831 (1965).

(9) J. M. Locke and E. W. Ducke, *Chem. Commun.*, 151 (1965).

apparently considerable transannular reaction to saturated products takes place.

High-pressure hydrogenation with Raney nickel converts the crude adduct to a tarry mixture which on distillation affords a mixture of diamines. Vpc inspection reveals two major components in a ratio of 3:2, and nmr examination of the crystalline dihydrochlorides indicates that these diamines are *trans*- and *exo-cis*-3,5-diaminonortricyclene (XXII and XXIII). Separation of the two isomers is achieved by conversion to the diacetamides. The diacetamide of the major isomer XXII is more soluble than that of XXIII so that the latter can be fractionally crystallized. Failure to form a cyclic urea on treatment of the diamine mixture with phosgene suggests that the *cis-endo* isomer is not present.

XXII   XXIII

Transannular reaction is more favored in the case of norbornadiene than in that of 1,5-cyclooctadiene. The formation of nortricyclene addition products is generally encountered in free-radical reactions of norbornadiene.[10] The radical intermediate XXIV formed by either *endo* or *exo* attack of nitrogen dioxide is geometrically well set up for conversion to a tricyclic radical XXV which combines with nitric oxide to form a 3,5-disubstituted nortricyclene.

XXIV   XXV
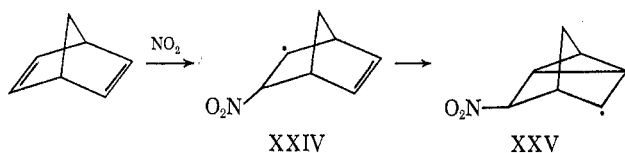
Experimental Section

Ir spectra were taken on a Beckman IR-5; nmr spectra with a Varian A-60, using TMS as internal reference. Melting points are uncorrected. Elemental analyses and molecular weight determinations were performed by Galbraith Laboratories.

Dicyclopentadiene Pseudonitrosite (IV and IVa).—A stirred solution of 132 g (1 mol) of dicyclopentadiene in 500 ml of 1:1 pentane-ether solution at 0° was treated with a stream of 2:1 nitric oxide-air until unabsorbed, brown nitrogen dioxide could be observed above the surface of the reaction mixture. The product was filtered, washed with ether, and dried to give 170 g (82% yield) of crude adduct. Two recrystallizations from methylene chloride-pentane afforded white crystals: mp 151–154°; nmr (CDCl₃) δ 5.8 (m, 2, J = Hz, fine splitting, CHN), 5.0 (m, 2, CH=CH), 2–3.5 (m, 7), and 1.7 ppm (m, 1, J = 2 Hz, fine splitting C₇ H). *Anal.* Calcd for C₁₀H₁₂N₂O₃: C, 57.68; H, 5.81; N, 13.46. Found: C, 57.65; H, 6.00; N, 13.36.

Dicyclopentadiene Nitroxime (V and Va).—A suspension of 20 g of recrystallized dicyclopentadiene pseudonitrosite in 250 ml of dioxane was refluxed several hours under nitrogen. The pseudonitrosite dissolved to form a blue solution which became yellow on completion of the isomerization. Removal of the solvent by evaporation and trituration with ether afforded a solid which was filtered and washed with 1:1 ether-pentane. The crude nitroxime (18 g, 90% yield) of recrystallization from methylene chloride-pentane gave pale yellow crystals, mp 129–132°. Recrystalliza-

(10) (a) T. V. VanAuken and E. A. Rick, *Tetrahedron Lett.*, **22**, 2709 (1968); (b) G. N. Sauser and A. L. Logothetis, *J. Org. Chem.*, **33**, 2330 (1968).

tion from methanol favored one particular isomer. Crystals with mp 171° were obtained: nmr (d₆-acetone) δ 5.7 (s, 2, CH=CH), 4.8 (d, 1, J = 2 Hz, *endo*-CHNO₂) 2–3.5 (m, 8) and 1.7 ppm (m, 1, J = 2 Hz, fine splitting, C₇ H; ir (CHCl₃), 3600 (OH), 1800 (C=N), and 1560 cm⁻¹ (NO₂). *Anal.* Calcd for C₁₀H₁₂N₂O₃: C, 57.68; H, 5.81; N, 13.46. Found: C, 57.48; H, 5.78; N, 13.74.

Norbornene vs. Cyclopentene.—The reaction of a mixture of 0.1 mol of norbornene and 0.1 mol of cyclopentene in 50 ml of ether with a 2:1 NO-air stream at 0° was followed by withdrawing samples of the reaction mixture at 25-min intervals and examining them on an Aerograph 1520B gas chromatogram with a DC-200 column at 100°. The ratios of norbornene/cyclopentene tabulated below indicate that norbornene was consumed at a much higher rate than cyclopentene.

Time, min	0	25	50	80	105
Ratio of norbornene/cyclopentene	1.0	0.95	0.75	0.3	0.05

After 1.75 hr the mixture was filtered; the product was washed with ether to give 5.2 g of product, mp 94–98°. A 1:1 mixture of the product with cyclopentene-pseudonitrosite[2c] showed a depressed melting point (88–91°); a similar mixture melting study with pure norbornene–pseudonitrosite revealed no depression. The infrared spectrum of the product was identical with that of the norbornene derivative[4] and different from the spectrum of cyclopentene-pseudonitrosite.

1,2-Dihydro-9-hydroximino-10-hydroxylaminodicyclopentadiene (VI).—A solution of 20.8 g (0.1 mol) of dicyclopentadiene nitroxime in 600 ml of absolute ethanol along with 1 g of 5% Pd-on-carbon catalyst was hydrogenated on a Parr apparatus, consuming 0.3 mol of H₂ after 8 hr. The catalyst was filtered and the solvent was evaporated to afford essentially quantitative yield (19 g) of hydroxylamino oxime (VI). Recrystallization from 95% ethanol afforded white crystals: mp 163°; nmr (CD₃-OD) δ 4.5 (s, 3, exchanged with D₂O), 3.2 (d, 2, J = 2 Hz, *endo*-C₁₀HN), and 1–3 ppm (m, 12). *Anal.* Calcd for C₁₀H₁₆N₂O₂: C, 61.20; H, 8.22; N, 14.28. Found: C, 61.46; H, 7.99; N, 14.34.

4-Vinylcyclohexene-1 Nitroxime (VII).—A stirred solution of 108 g (1 mol) of 4-vinylcyclohexene-1 dissolved in 600 ml of a 1:1 mixture of ether-pentane at −10° was treated with a mixed stream of 10:1 nitric oxide-air until brown nitrogen dioxide gas was observed above the surface of the reaction mixture. The precipitate was filtered, washed with ether, and dried to give 19.4 g (11% yield) of a mixture of pseudonitrosite and nitroxime. The crude product was refluxed 1 hr in dioxane solution under nitrogen and evaporated. The crude nitroxime was triturated with ether, filtered, and recrystallized from methylene chloride-pentane to obtain crystals: mp 121°; ir (CHCl₃) 3600 (OH), 1800 (C=N), and 1560 cm⁻¹ (NO₂); nmr (d₆-acetone) δ 5.2 (s, 2, CH=CH), 4.8 (s, 2, CH₂NO₂), 1.6 ppm (m, 7), and one exchangeable proton signal whose chemical shift varies with concentration. *Anal.* Calcd for C₈H₁₂N₂O₃: C, 52.16; H, 6.57; N, 15.21. Found: C, 52.65; H, 6.65; N, 14.85.

Vinylcyclohexane Pseudonitrosite (VIII).—The pseudonitrosite of vinylcyclohexane, prepared in the manner as described for 4-vinylcyclohexene-1, was obtained in 8% yield: mp 151° from methylene chloride-pentane; ir (CHCl₃) 1560 cm⁻¹ (NO₂) with no hydroxyl absorption; nmr (CDCl₃) δ 5.8 (m, 1, CHNO), 5.2 (q, 1, J = 15 Hz, J_AC = 11 Hz, CH_ANO₂), 4.5 (q, 1, J_AB = 15 Hz, J_BC = 3 Hz, CH_BNO₂), and 1–2 ppm (m, 11). *Anal.* Calcd for C₈H₁₄N₂O₃: C, 51.60; H, 7.58; N, 15.04. Found: C, 51.61; H. 7.56; N, 15.08.

Competition Studies with Vinylcyclohexane, 4-Vinylcyclohexene-1, and Cyclohexene.—Ethereal solutions containing vinylcyclohexane and 4-vinylcyclohexene-1, vinylcyclohexane, and cyclohexene and 4-vinylcyclohexene-1 and cyclohexene, each 0.2 M with respect to each olefin, were treated with 2:1 nitric oxide-air mixture at −15°. The change in concentration of olefin was followed by vpc examination, using an SE-30 column, an Aerograph 1520 instrument, and cyclohexane as internal reference. Response factors were determined empirically from the initial untreated solutions. The introduction of nitrogen oxides was carried out at a slow rate, so that the concentrations of nitrogen oxides are assumed to be constant and the rate first order with respect to olefin. The ratio of rate constants were calculated by the formula

$$\frac{K_c}{K_v} = \frac{\log (C_0/C_t)}{\log (V_0/V_t)}$$

where K_c = rate constant for cyclohexene, K_V = rate constant for vinylcyclohexane, C_0 = molarity of cyclohexene at t = 0, C_t = molarity of cyclohexene at t, V_0 = molarity of vinylcyclohexane at t = 0, V_t = molarity of vinylcyclohexane at t. On this basis cyclohexene was found to be consumed at a rate 2.9 ± 0.4 times as fast as vinylcyclohexane, and 1.4 ± 0.1 times as fast as 4-vinylcyclohexene-1. The latter was consumed at a rate 2.0 ± 0.2 times that of vinylcyclohexane.

1-Amino-2-cyclohexylethane (IX).—A solution of 25 g (0.135 mol) of nitroxime VII in 600 ml of absolute ethanol along with 2 g of Raney nickel was hydrogenated at 75° and 1500 psi for 3 days. The catalyst was filtered, solvent was evaporated, and residue was distilled providing 5 g (27% yield) of distillate boilng at 130–148° (0.5 mm), which was converted to a crystalline hydrochloride: mp 258° (from 95% ethanol); nmr (D₂O) δ 3.0 (t, 2, CH₂N) and 1–2 ppm (m, 13). *Anal.* Calcd for C₈H₈·NCl: C, 57.63; H, 10.80; N, 8.90; Cl, 22.52. Found: C, 58.58; H, 11.01; H, 8.56; Cl, 21.90. The same hydrochloride could be obtained from the reduction of vinylcyclohexane pseudonitrosite (VIII) with excess lithium aluminum hydride in ether.

Vinylcyclohexane Nitroxime (X).—Refluxing a solution of 4 g of vinylcyclohexane pseudonitrosite (VIII) in 50 ml of dioxane under nitrogen for 8 hr, followed by evaporation of solvent afforded a quantitative yield of the nitroxime X. Recrystallization from methylene chloride–pentane gave crystals: mp 133°; ir (CHCl₃ 3600 (OH), 1800 (C=N) and 1560 cm⁻¹ (NO₂); nmr (d₆-acetone) δ 5.2 (s, 2, CH₂NO₂), 1–2 ppm (m, 11) and one-proton absorption with concentration dependent chemical shift. *Anal.* Calcd for C₈H₁₄N₂O₃: C, 51.60; H, 7.58; N, 15.04. Found: C, 51.60; H, 7.63; N, 14.98.

1-Hydroxylamino-2-cyclohexyl-2-hydroximinoethane (XI).—A solution of either 9.3 g (0.05 mol) of nitroxime X or 9.2 g (0.05 mol) of nitroxime VII dissolved in 250 ml of absolute alcohol along with 1 g of 5% palladium-on-carbon catalyst was hydrogenated on a Parr apparatus at 1–2 atm and ambient temperature. Two equivalents of hydrogen were consumed with VIII and 3 equiv with VII. The catalyst was filtered, solvent was evaporated, and the product was triturated with ether to give 6 g (70%) of white crystals: mp 112° from methylene chloride–ether; ir 3600 (OH), 330 (broad, NH), and 1650 cm⁻¹ (C=N); nmr (CDCl₃) δ 6.8 (m, 3, exchanged with D₂O), 3.8 (s, 2, -CH₂N), and 1–2 ppm (m, 11). *Anal.* Calcd for C₈H₁₆N₂O₂: C, 55.79; H, 9.36; N, 16.27; mol wt, 172. Found: C, 55.79; H, 8.91; N, 16.25; mol wt, 153.

1-Cyclohexyl-1,2-diaminoethane (XII).—A solution of 6.0 g (0.035 mol) of hydroxylamino oxime XI dissolved in ether was added dropwise to a solution of 8 g of lithium aluminum hydride in 500 ml of anhydrous ether with stirring under a nitrogen stream at such rate as to maintain a gently reflux of ether. After 12 hr the reaction mixture was introduced dropwise to a stirred, icecooled suspension of 0.5 kg of sodium sulfate, 250 ml of distilled water, and 300 ml of ether under nitrogen. After the refluxing of ether ceased, the inorganic salt was filtered and washed with additional ether. The ethereal filtrate was dried (Na₂SO₄) and evaporated affording 3.7 g (74%) of colorless oil XII. Treatment with excess anhydrous hydrogen chloride in ether gave the crystalline dihydrochloride, mp 268° (from alcohol). The identical product was obtained by similar reduction of X with lithium aluminum hydride or by Raney nickel catalyzed hydrogenation of either X or XI in alcohol solution at 1500 psi and 75°: nmr (D₂O) δ 3.4 (m, 3, -CH-CH₂N) and 1–2 ppm (m, 11). *Anal.* Calcd for C₈H₂₀N₂Cl₂: C, 44.66; H, 9.37; N, 13.02; Cl, 32.88. Found: C, 45.20; H, 9.58; N, 12.64; Cl, 31.79.

1,5-Cyclooctadiene Nitroxime.—The pseudonitrosites of 1,5-cyclooctadiene (XIII) and cyclooctene, and cyclooctene nitroxime (XVII) were prepared according to Klamann, *et al.*[8] The following procedure proved successful to isomerize XIII to the corresponding nitroxime XIV. A mixture of 46 g (0.25 mol) of 1,5-cyclooctadiene pseudonitrosite (XIII) and 5 g of anhydrous zinc chloride dissolved in 1 l. of absolute ethanol was refluxed under nitrogen for 1 hr, cooled, treated with 2 l. of aqueous saturated ammonium chloride solution, and extracted with methylene chloride. The methylene chloride extract was diluted with an equal volume of ether, washed several times with ammonium chloride solution, dried over sodium sulfate, and evaporated to give an oil which on trituration with methylene chloride gave 33 g (70%) of white crystals: mp 138–140° (from 95% ethanol); ir (CHCl₃) 3550 (OH), 1790 (C=N), and 1550 cm⁻¹ (NO₂); nmr (d-₆-acetone) δ 5.7 (m, 2, CH=CH), 5.2 (m, 1, CHNO₂), 2.3 ppm (m, 8) and (s, 1, OH) of varying chemical shift. *Anal.*

Calcd for C₈H₁₂N₂O₃: C, 52.16; H, 6.57; N, 15.21; mol wt, 184.2. Found: C, 52.23; H, 6.38; N, 15.26; mol wt, 185.

5-Aminocyclooctene-1 (XV).—Finely powdered 1,5-cyclooctadiene pseudonitrosite (XIII) (18.4 g, 0.1 mol) was cautiously introduced to a stirred mixture of 600 ml of absolute ether and 15.1 g (0.4 mol) of lithium aluminum hydride under nitrogen nitrogen atmosphere at such rate as to maintain gentle reflux of ether. The reaction was stirred an additional 16 hr under nitrogen after introduction of the pseudonitrosite was complete. Excess hydride was decomposed by careful dropwise introduction of the mixture to a stirred slurry of 1 kg of sodium sulfate, 250 ml of water, and 200 ml of ether under nitrogen at such rate as to maintain mild reflux of ether. The ethereal layer was decanted and treated with hydrogen chloride to provide 6.8 g (42%) of crystalline hydrochloride: mp 218° (from ethanol–ether); nmr (D₂O) δ 5.8 (m, 2, CH=CH), 3.3 (m, 1, CHN) and 1–2.5 ppm (m, 10). *Anal.* Calcd for C₈H₁₆NCl: C, 59.43; H, 9.98; N, 8.67; Cl, 21.93. Found: C, 59.50; H, 9.85; N, 8.72; Cl, 21.77. Hydrogenation of an alcoholic solution of XV with 5% palladized carbon affords cyclooctylamine hydrochloride.

2-Hydroxylaminocyclooctanone Oxime (XVI).—A solution of 12.2 g (0.066 mol) of nitroxime XIV in 250 ml of absolute ethanol along with 0.5 g of 5% Pd–C catalyst was hydrogenated in a Parr apparatus at ambient temperature until 3 equiv of hydrogen (0.1 mol) was consumed. The catalyst was separated by filtration and the solvent was removed to give pink oil which on trituration with chloroform provided 7 g (65%) of white crystals, mp 148° (from 95% ethanol). The identical substance was ob-) tained in comparable yield by similar reduction of nitroxime (XVII) using 2 equiv of hydrogen: ir (KBr) 3500–2500 (OH and NH) and 1640 cm⁻¹ (C=N); nmr (d₆-DMSO) δ 3.3 (t, 1, CHN) and 1.12–2.5 ppm (m, 12). *Anal.* Calcd for C₈H₁₆N₂O₂: C, 55.79; H, 9.36; N, 16.27; mol wt, 172. Found: C, 55.72; H, 9.54; N, 16.27; mol wt, 167.

1,2-Diaminocyclooctane (XVIII).—A solution of 5.0 g (0.029 mol) of hydroxylaminooxime XVI in 200 ml of absolute ethanol along with 1 g of Raney nickel was placed in a high-pressure reactor and charged with hydrogen at 1500 psi. Th mixture was agitated 72 hr at 75°. The catalyst was removed by filtration and the solvent was evaporated. Distillation of the residue afforded 2.1 g (50%) of colorless oil, bp 65–75° (0.1 mm) which was converted to a hygroscopic dihydrochloride: mp 215° (from ethanol); nmr (D₂O) δ 3.7 (m, 2, CHN) and 1.5–2.3 ppm (m, 12). *Anal.* Calcd for C₈H₂₀N₂Cl₂: C, 44.67; H, 9.37; N, 13.03; Cl, 32.88. Found: C, 45.19; H, 9.59; N, 12.88; Cl, 31.64.

Conversion to the dibenzamide with benzoyl chloride and 2 *N* NaOH solution afforded a white solid, mp 286–288° (from ethyl acetate) *Anal.* Calcd for C₂₂H₂₆N₂O₂: C, 75.40; H, 7.48; N, 7.99. Found: C, 74.72; H, 7.60; N, 7.82.

Formation of the diacetamide afforded crystals: mp 160–170°; sublimed at 140° (0.05 mm); nmr (D₂O) δ 3.5–4 (m, 2, CHN), 1.7 (s, 6, CH₃), and 1.5 ppm [m, 12, (CH₂)₆]. *Anal.* Calcd for C₁₂H₂₂N₂O₂: C, 63.68; H, 10.54; N, 12.38. Found: C, 63.62; H, 10.23; N, 12.35.

3,5-Diaminonortricyclene (XXII and XXIII).—A solution of 9.2 g (0.1 mol) of freshly distilled norbornadiene in 500 ml of anhydrous ether was treated at −15° with a stream of 2:1 nitric oxide–air until the presence of brown nitrogen dioxide was observed above the surface of the reaction mixture. The light tan solid precipitate was filtered, washed with ether, and dried to give 13.4 g (81%) adduct, mp 117–121°; roughly 60–70% of the adduct consisted of saturated, presumably nortricyclene derivative, as indicated by nmr (d₆-acetone) δ 4–6 (m, 2.3) and 1.5–3 ppm (m, 5.3). *Anal.* Calcd for C₇H₈N₂O₃: C, 50.00; H, 4.80; N, 16.66, mol wt, 168.2. Found: C, 50.09; H, 4.76; N, 16.77; mol wt, 170. The substance was unstable affording resinous products when treated with hot solvents. Treatment of 10 g (0.06 mol) of the adduct with 300 ml of absolute ethanol, 1 g of Raney nickel, and hydrogen at 1500 psi and 75° for 24 hr afforded 8 g of oil on filtration and evaporation. Distillation gave 3 g (40%) of colorless oil, bp 75–85° (0.4 mm); vpc examination with a Carbowax 20M–KOH column at 150° showed two major components in a 3:2 ratio.

Conversion to the dihydrochloride provided white crystals: mp 300° (from 95% ethanol); nmr (D₂O) δ 3.85 (m, 0.67, *endo*-CHN), 3.6 (m, 1.33, *exo*-CHN), 2.5 (m, 1, C₄H), and 1.9 ppm (m, 5), corresponding to a 2:1 mixture of *trans-cis* isomers. *Anal.* Calcd for C₇H₁₄N₂Cl₂: C, 42.65; H, 7.16; N, 22; Cl, 35.99. Found: C, 42.61; H, 7.21; N, 14.06; Cl, 35.98.

Conversion to the dibenzamide gave crystals, mp 286° (from methylene chloride). *Anal.* Calcd for $C_{21}H_{10}N_2O_2$: C, 75.88; H, 6.07; N, 8.43. Found: C, 76.15; H, 6.38; N, 8.15.

Conversion to the diacetamide with acetic anhydride and triethylamine in ether afforded white precipitate: mp 220–225°; nmr in accord with 70% *trans*–30% *cis* mixture. *Anal.* Calcd for $C_{11}H_{18}N_2O_2$: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.47; H, 7.88; N, 13.34. Recrystallization from methanol afforded white crystals: mp 278–281°, the *cis-exo* isomer; nmr (2:1 D_2O–CD_3OD) δ 3.7 (m, 2, *endo*-CHN), 2.2 (m, 1, C_4-H), 2.0 (s, 6, CH_3), and 1.5 ppm (m, 5). Recrystallization of the second crop from methanol gave the *trans* isomer: mp 226–227°; nmr (D_2O) δ 4.0 (m, 1, *exo*-CHN), 3.7 (m, 1, *endo*-CHN), 2.1 (m, 1, C_4-H), 2.02 (s, 3, CH_3), 2.01 (s, 3, CH_3), and 1.5 ppm (m, 5).

1,2-Hydroxylamino Oximes and Pyrazine N,N-Dioxides
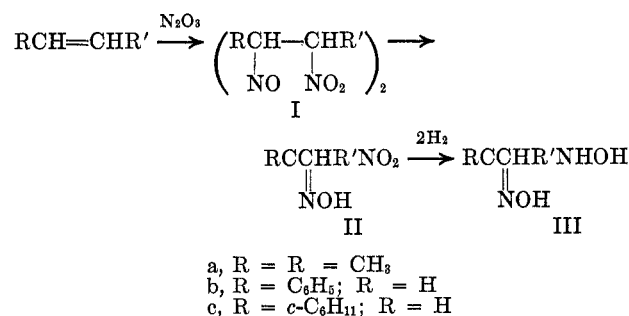
M. L. SCHEINBAUM[1]

Corporate Research Laboratories, Esso Research and Engineering Company, Linden, New Jersey 07036

1,2-Nitroximes obtained from the isomerization of olefin–dinitrogen trioxide adducts are selectively reduced with palladized carbon to afford 1,2-hydroxylamino oximes. The latter class of compounds can be reduced to vicinal diamines, oxidized to 1,2-dioximes, form stable chelates with mercuric salts, and undergo a novel acid-catalyzed autocondensation to pyrazine N,N-dioxides.

The reaction of dinitrogen trioxide with olefins affords 1,2-nitronitroso dimers, commonly referred to as pseudonitrosites I.[2] These adducts can be converted to the more soluble isomers, the corresponding 1,2-nitroximes II.[2,3] The latter undergo a general, selective hydrogenation to 1,2-hydroxylamino oximes III in the presence of a palladized carbon catalyst. The derivatives are readily isolated as the acetic acid salts which can be smoothly converted back to free hydroxylamino oximes. Thus, the nitroxime derived from N_2O_3 addition to *cis*- or *trans*-butene-2 is converted to IIIa, and α-nitroacetophenone oxime (IIIb) derived from styrene is converted to IIIb in over 90% yield.

from either the saturated nitroxime Vb, derived from cyclooctene, or the unsaturated derivative, 1,5-cyclooctadiene nitroxime, with the consumption of 2 or 3 mol of hydrogen, respectively. Similarly, IIIc can be obtained from either IIc or from the unsaturated nitroxime derived from 4-vinylcyclohexene-1.[3] The cyclohexene derivative IVa ($n = 4$) is identical with that prepared from the reaction of hydroxylamine with the nitrosyl chloride adduct of cyclohexene VIa ($n = 4$).[4] Owing to the mechanistic differences in orientation between nitrosyl chloride and dinitrogen trioxide additions to olefins, different hydroxylamino oximes would be expected, starting with unsymmetrical olefins from the two synthetic approaches.
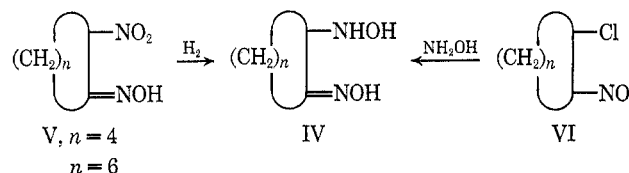
The 1,2-hydroxylamino oxime derivatives possess a pair of vicinal carbon–nitrogen bonds which can be reduced to diamines. Either lithium aluminum hydride or Raney nickel catalyzed hydrogenation converts IVb to the corresponding *vic*-diamine, namely 1,2-diaminocyclooctane. The hydroxylamino group is susceptible to oxidation, and in the case of the styrene derivative IIIb, treatment with ferric chloride affords the 1,2-dioxime of phenylglyoxal. Similarly, the butene-2 derivative VIIa is converted to dimethylglyoxime, but in other cases oxidation by ferric chloride pro-

Two equivalents of hydrogen are consumed to reduce the nitro group, and olefinic double bonds present in the nitroxime also undergo reduction. Thus, the same hydroxylamino oxime IVb ($n = 6$) is obtained

(1) Department of Chemistry, East Tennessee State University, Johnson City, Tenn.

(2) (a) H. Wieland, *Justus Liebigs Ann. Chem.*, **424**, 71 (1920); *Ber.*, **36**, 2558 (1903). (b) D. Klamann, W. Koser, P. Weyerstahl, and M. Fligge, *Chem. Ber.*, **98**, 1831 (1965). (c) M. L. Scheinbaum, *Amer. Chem. Soc. Div. Petrol. Chem., Prepr.*, **13**, 193 (1968).

(3) M. L. Scheinbaum, *J. Org. Chem.*, **35**, 2785 (1970).

(4) L. B. Volodarskii and Yu. G. Putsykin, *J. Org. Chem. USSR*, **3**, 1642 (1967).