quenched by addition of 6 *N* hydrochloric acid and 50 ml of water. Extraction with three portions of ether gave 0.70 g of alcohol 3-*d* on evaporation of the extracts. The nmr spectrum displayed no appreciable absorption near $\delta$ 3.8. This material was converted into the corresponding *p*-toluenesulfonate ester and solvolyzed in a mixture of 12 ml of water and 18 ml of acetone (3 hr at 140°). The product displayed two peaks on gc analysis. The minor product showed the same retention time as the starting alcohol 3-*d* and is believed to have been carried over due to incomplete tosylation. The major product (>80%) was assigned structure **20**, nmr $\delta$ 3.64 (s, 1 H), 2.79–1.1 (m, 10 H). The location of the deuterium atom could not be unambiguously established, but mass spectral analysis was consistent with the assigned structure. Thus, both deuterated and undeuterated **3** showed a base peak at *m/e* 67 which corresponds to the loss of carbons C$_2$, C$_3$, and C$_4$. No isotopic shift was observed for this fragmentation. On the other hand the ions formed *via* related cleavage of C$_4$, C$_5$, and C$_8$ did show an isotopic shift from *m/e* 83 to 84, a result which is consistent with deuteration at C$_3$.[37]

**Kinetic Experiments.**—A solution of sodium acetate in acetic acid (0.1 *N*) was prepared by refluxing purified[38] reagent grade acetic acid (500 ml) with 2.65 g (0.0251 mol) of anhydrous sodium carbonate and 2.56 g (0.0251 mol) of acetic anhydride for 5 hr. Perchloric acid (0.05 *N*) was prepared from 2.1 ml of 70% perchloric acid, 2.2 ml of acetic anhydride, and enough acetic acid to bring the total volume to 500 ml. The exact normality was determined before each run by titration with standard potassium hydrogen phthalate solution in acetic acid using *p*-bromophenol as an indicator. The solvolyses were carried out in sealed ampoules into which were placed 2.5-ml samples of a *ca.* 0.1 *M* solution of brosylate **15** in the acetic acid–sodium acetate solution. At the appropriate time intervals ampoules were withdrawn from the oil bath and cooled before opening. A 2.00-ml aliquot was removed and quenched in 5 ml of purified dioxane.[39] The samples were then titrated with standardized perchloric acid. Infinity titers were obtained after warming samples to 120–130° for 2 hr and values obtained agreed to within 5% of the expected values. The first-order rate consant for production of acid drifted downward with time and remained constant for 4–5 half-lines. The values for the rate of solvolysis of the rearranged brosylate were determined at four temperatures and are recorded as follows: 47.68° (0.96 × 10$^{-5}$ sec$^{-1}$); 53.08° (1.30 × 10$^{-5}$ sec$^{-1}$); 61.37° (4.77 × 10$^{-5}$ sec$^{-1}$); 83.90° (53.0 × 10$^{-5}$ sec$^{-1}$). The rate constant for this reaction ($k_3$) at 25° was obtained by extrapolation: 3.79 × 10$^{-7}$ sec$^{-1}$.

The rate constants at 53.08° for direct acetolysis ($k_1$) and for rearrangement ($k_2$) were obtained by the method of Young, Winstein, and Goering,[18] and found to be $k_1$, 1.71 × 10$^{-4}$ sec$^{-1}$; $k_2$, 8.51 × 10$^{-4}$ sec$^{-1}$. These rate constants were used to calculate the instantaneous brosylate ion concentrations and were found to yield values within ±4% of those determined experimentally.

**Registry No.**—**3** *p*-nitrobenzoate, 32980-15-7; **3** brosylate, 27011-51-4; **3** acetate, 32980-17-9; **7**, 26955-51-1; **8**, 32980-18-0; **10**, 32980-19-1; **12**, 32980-20-4; **22**, 32980-21-5; **23**, 32980-22-6; **24**, 32980-23-7; **25**, 32980-24-8.

**Acknowledgments.**—We wish to acknowledge useful discussions with P. K. Freeman. Financial aid (to K. W. K.) from Merck and Company, the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We also wish to thank the Rutgers University Research Council for partial financial support. Funds toward the purchase of the mass spectrometer were obtained from the National Science Foundation.

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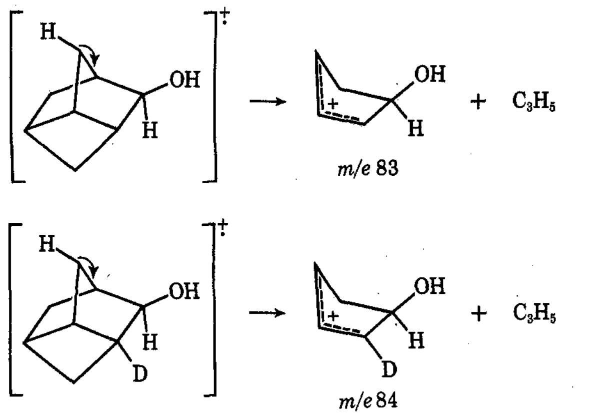
[37] Schematically, these cleavages may be symbolized as follows.



[38] H. Tanida, T. Tsuji, and J. Ishitobi, *J. Amer. Chem. Soc.*, **86**, 4901 (1964).

[39] Commercial dioxane was passed over a column of neutral alumina.

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# Addition of Nitrosyl Chloride to Some Strained Bicyclic Olefins

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*Received June 9, 1971*

Norbornene, norbornadiene, 5-methylene-2-norbornene (**1**), and 5-ethylidene-2-norbornene (**5**) add nitrosyl chloride to give exo-cis nitrosochlorides which dimerize to azodioxy compounds. In the latter two cases, addition does not occur at the exocyclic double bond, but 1,2 addition of nitrosyl chloride to the ring double bond occurs in two directions to give, after hydrolysis, a mixture of isomeric chloro ketones. In all cases, no rearrangement products were observed. 1,2,3,4,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-diene (**13**) does not add nitrosyl chloride in solution, but 1,2,3,4,7,7-hexachloro-5-methylenebicyclo[2.2.1]hept-2-ene (**14**) reacts very slowly under pressure to give addition to the exocyclic double bond. Addition to norbornene in a two-step process involving addition of nitrosonium tetrafluoroborate followed by addition of a chloride salt leads to small yields of chloro oximes instead of an azodioxy compound.

The reaction of nitrosyl chloride with alkenes to give nitrosochlorides, which dimerize if unhindered, has been known since 1875[2a] and has been adequately reviewed.[2b,c] Addition of the chloride to the carbon which can best support a positive charge is generally observed[3] and unstrained cyclic olefins give the products of trans addition.[4,5] A mechanism involving initial attack by NO$^+$ to form a strong olefin–electrophile

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[1] NDEA Fellow, 1965–1968; University of Alabama Fellow, 1969.

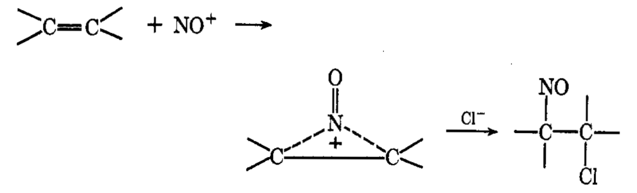
[2] (a) W. A. Tilden, *J. Chem. Soc.*, **28**, 514 (1875); (b) L. J. Beckham, W. A. Fessler, and M. A. Kise, *Chem. Rev.*, **48**, 319 (1951); (c) M. Plungian and F. E. DeVry, "Nitrosyl Chloride," An Annotated Bibliography, Hercules Technical Information Center, 1970, p 39.

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 669.

[4] J. Meinwald, Y. E. Meinwald, and T. N. Baker, *J. Amer. Chem. Soc.*, **86**, 4074 (1964).

[5] B. W. Ponder, T. E. Walton, and W. J. Pollock, *J. Org. Chem.*, **33**, 3957 (1968).

complex followed by attack by Cl⁻ has generally been assumed.[6]

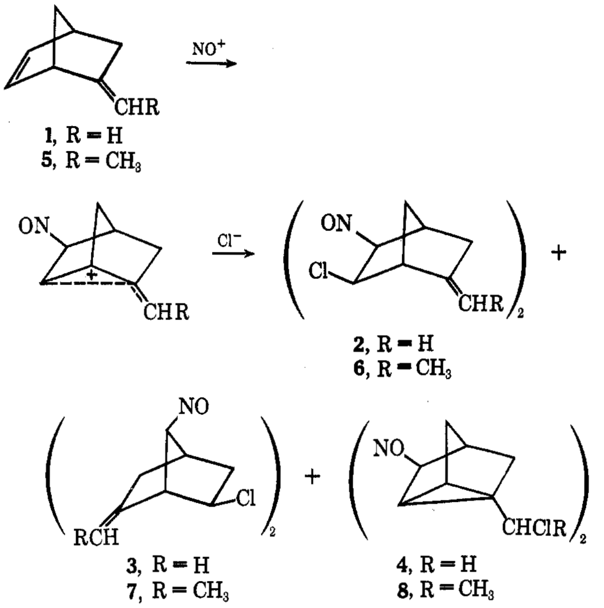


The observation that norbornene and norbornadiene react with nitrosyl chloride by cis,exo addition prompted the proposal of alternate mechanisms[4] and also initiated searches for the underlying reasons for the steric course of the reaction in these strained bicyclic systems.[7] We wish to report the results of our investigation into the generality of the cis,exo addition pathway of nitrosyl chloride with strained bicyclic olefins, and to comment upon the mechanism of this reaction.

## Results

Initially, norbornene, norbornadiene, 5-methylene-2-norbornene (**1**), and 5-ethylidene-2-norbornene (**5**) were chosen for study. The addition of nitrosyl chloride to the first two, norbornene and norbornadiene, had previously been reported by Meinwald[4] and Miller,[8] but, since their reported work dealt only with the solid dimers formed, the possibility existed that any rearrangement products in the supernatant liquid might have gone undetected. Because of the plethora of literature reports on the Wagner–Meerwein type rearrangements in the [2.2.1]bicyclic system when positive charge is generated at C-2,[7] it seemed reasonable that addition of strong electrophiles such as nitrosyl chloride would lead to appreciable rearrangement. Although no examples of rearrangement during this specific reaction have been reported, Hamann and Swern[9] reported a 13% yield of a rearranged product in the mechanistically similar reaction of nitrosyl formate with norbornadiene. We therefore carried out a detailed investigation on the total reaction mixtures resulting from nitrosyl chloride addition to norbornene and norbornadiene. Fractional crystallization of the solid dimeric products and glpc analysis of the concentrated supernatant liquids revealed the presence of only nitrosochloride dimers from 1,2 addition and a small quantity of yellow oils whose infrared spectra suggested a mixture of chloro oximes.

5-Methylene-2-norbornene (**1**) was chosen as a substrate because of the possible homoallylic stabilization of an intermediate positive charge with concomitant formation of a tricyclic structure **4**, in addition to products **2** and **3**.



Nitrosyl chloride adds to 5-methylene-2-norbornene (**1**) to give a 58% yield of solid dimeric nitrosochloride adduct, mp 161–167°. The supernatant liquid from the reaction was carefully concentrated and analyzed to reveal only unreacted olefin and a small quantity of chloro oximes. The dimeric solid was subjected to fractional crystallization procedures to ensure that it was homogeneous. The nmr proton spectrum of this solid is shown in Figure 1,[10] along with the spectrum of the starting olefin, **1**. The ring vinylic hydrogens of **1** absorb at $\tau$ 4.05, and the two exocyclic vinylic hydrogens absorb at $\tau$ 5.12 and 5.41. Inspection of the nmr spectrum of the nitrosyl chloride adduct reveals that addition takes place on the ring. This is reasonable in view of the fact that two sp$^2$ hybridized carbons are transformed to sp$^3$ carbons, which relieves a considerable amount of strain in the rigid bicyclic system. This is much more energetically favorable than the alternate path of converting only one ring sp$^2$ carbon to sp$^3$ if addition had occurred at the exocyclic double bond. It is also clear from the spectrum that one of the exocyclic vinylic hydrogens has been shifted downfield to an overlapping position with the -CHNO hydrogen. The doublet at $\tau$ 5.54 (-CHCl) is coupled by 7 Hz to the hydrogen absorbing at $\tau$ 4.84 (-CHNO). This AB pattern with $J = 7$ Hz is a good indication of cis,endo stereochemistry for the hydrogens at C-2 and C-3.[4] Thus, nitrosyl chloride adds to 5-methylene-2-norbornene to give only cis,exo addition, with no detectable rearrangement products **3** and **4**.

The reaction of 5-ethylidene-2-norbornene (**5**) with nitrosyl chloride, which should be mechanistically similar to **1**, proceeds rapidly in chloroform solution to yield 67% of the solid dimeric nitrosochloride, mp 135–139°. A careful analysis of the mother liquor revealed only starting olefin and a small quantity of a viscous yellow oil which was shown to be a mixture of chloro oximes. Fractional crystallization attempts on the solid dimer failed to reveal any isomeric products. The nmr spectrum of this dimer, as well as that of the starting olefin, 5, are shown in Figure 2. The two ring vinylic hydrogens absorb at $\tau$ 4.08 and the exocyclic vinylic hydrogen absorption is centered at $\tau$ 4.7. This absorption shows the starting olefin to be a mixture of the two geometric isomers, as can be seen from the small quartet of the least abundant isomer over-

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(6) L. Kaplan, H. Kwart, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **82**, 234 (1960).

(7) T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).

(8) J. B. Miller, *J. Org. Chem.*, **26**, 4904 (1961).

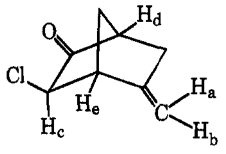
(9) H. C. Hamann and D. Swern, *J. Amer. Chem. Soc.*, **90**, 6481 (1968).

(10) The figures (1–5) showing the nmr spectra will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

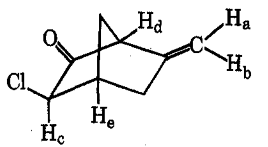
lapping the upfield side of the quartet of the major isomer. The spectrum of the nitrosyl chloride adduct (Figure 2) reveals that again addition has occurred to the endocyclic double bond, and two doublets at $\tau$ 5.21 (–CHNO) and 5.75 (–CHCl) with $J = 7$ Hz indicate that cis,exo addition has taken place.

Considerable difficulty was encountered during the analyses of the dimeric products resulting from nitrosyl chloride addition due to the limited solubility of most of the adducts. Several methods of modifying these dimers to make them more amenable to analysis, but without altering the original addition stereochemistry, were explored. Attempts to reduce the azodioxy linkage to the corresponding amine under a variety of conditions[11] led also to the removal of the chlorine atom from the molecule. The dimers could be converted into their corresponding chloro oximes,[12] but these were not as easily analyzed as had been hoped. These viscous oils were irreversibly absorbed on both alumina and silica gel chromatographic columns, and could not be successfully recrystallized nor distilled under vacuum.

Levulinic acid hydrolysis[13] of the methylenenorbornene adduct, (2), followed by vacuum distillation yielded a mixture of two chloro ketones, **9** and **10**, in a ratio of 5:1. Glpc separation and collection of these two chloro ketones gave analytical samples whose nmr spectra are shown in Figure 3. For **9**, absorptions at $\tau$ 4.79 and 5.05 are assigned to the exocyclic vinylic hydrogens, $H_a$ and $H_b$. A doublet at $\tau$ 6.43 ($J = 3$ Hz) is assigned to $H_c$. A multiplet at $\tau$ 7.24 is assigned to $H_d$ and the absorption at $\tau$ 6.90 is assigned to $H_e$. For **10**, absorptions at $\tau$ 4.88 and 5.02 are assigned to the exocyclic vinylic hydrogens $H_a$ and $H_b$. A doublet at $\tau$ 6.28 ($J = 3$ Hz) is assigned to $H_c$ and a multiplet at $\tau$ 7.12 is assigned to $H_e$. An absorption at $\tau$ 6.81 is assigned to the other bridgehead hydrogen, $H_d$. It is thus apparent that the methylenenorbornene adduct (2), which was originally thought to be homogeneous *via* recrystallization experiments, was in fact a mixture of positional isomers from cis,exo addition of nitrosyl chloride. The possibility of epimerization of the chlorine atom upon hydrolysis to give a mixture of exo and endo chloro ketones was considered, but then ruled out on the basis of infrared and nmr data.[4]

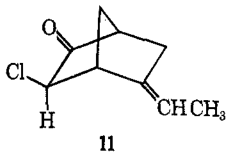


**9**

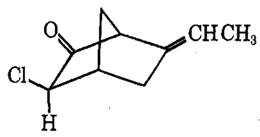


**10**

Hydrolysis of the nitrosyl chloride adduct from 5-ethylidene-2-norbornene (5) gave the chloro ketones **11** and **12** in a ratio of 4:1. Glpc separation and collection of the two isomers on a 15% Carbowax 20M column afforded analytical samples whose nmr spectra were very similar to those of **9** and **10**.

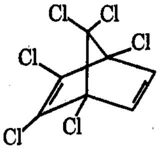


**11**

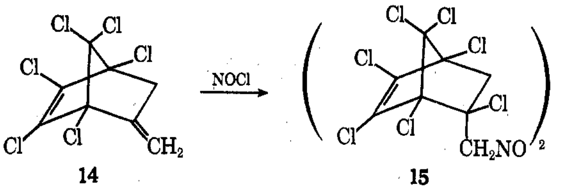


**12**

1,2,3,4,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-diene (**13**) was next chosen for study, since it should provide a convenient system for following the course of the addition of nitrosyl chloride by nmr. The spectrum of the diene consists of a singlet at $\tau$ 3.42, and the addition of NOCl should produce an AB pattern upfield from the vinyl singlet. Any rearrangement products would consequently be easily detectable. However, attempted addition to the hexachloronorbornadiene in solution produced no reaction under a variety of conditions. Traylor[7] also reports that hexachloronorbornadiene fails to undergo the oxymercuration reaction. We did observe that neat addition of nitrosyl chloride to hexachloronorbornadiene at room temperature in a pressure bottle and over a reaction time of 1 month produced a small yield of a complex mixture of products. The nmr spectrum of this mixture revealed as the most prominent feature a pair of doublets at $\tau$ 4.77 and 5.25 ($J = 4$ Hz) which is indicative of a trans addition of nitrosyl chloride.



**13**



**14** **15**

1,2,3,4,7,7-Hexachloro-5-methylene-2-norbornene (**14**) should also yield useful information upon its reaction with nitrosyl chloride. It was, first of all, of interest to determine if addition occurs at the deactivated ring double bond or at the exocyclic double bond. Addition at this latter site would give useful nmr data for comparison to the nmr data of ring double bond additions. Also, the fewer number of hydrogens in this chlorinated system should make the detection of any rearrangement products much easier by nmr. Hexachloro-5-methylene-2-norbornene (**14**) was easily prepared through the Diels–Alder condensation of hexachlorocyclopentadiene and allyl bromide,[14] followed by dehydrohalogenation.[15] The nmr spectrum of **14** is shown in Figure 4. The absorptions for the two C-6 hydrogens, which form the XY portion of an ABXY system, appear at $\tau$ 6.92 and 7.29 as a doublet of triplets ($J_{XY} = 15$ Hz, $J_{AX} = 1.5$ Hz). The exocyclic vinylic hydrogens absorb at $\tau$ 4.48 and 4.82, with the allylic coupling constant of 1.5 Hz readily apparent.

Reaction of nitrosyl chloride with **14** in solution failed to occur under a variety of conditions. The neat reaction of the diene did yield some product, **15**, however, and the nmr spectrum is shown in Figure 4. Prominent patterns of the C-6 hydrogens are located at

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[11] H. Greenfield and F. Dovell, *J. Org. Chem.*, **32**, 3670 (1967).

[12] L. K. Payne, U. S. Patent 3,328,457 (1967).

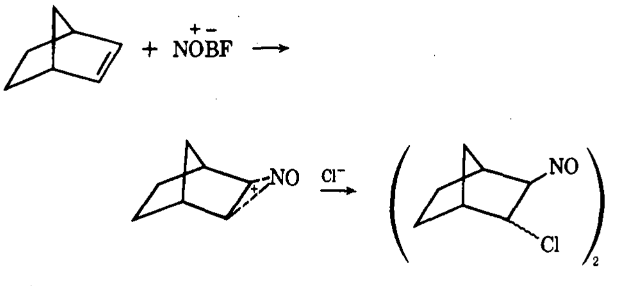
[13] (a) C. H. DePuy and B. W. Ponder, *J. Amer. Chem. Soc.*, **81**, 4629 (1959); (b) B. W. Ponder and D. R. Walker, *J. Org. Chem.*, **32**, 4136 (1967).

[14] E. K. Fields, *J. Amer. Chem. Soc.*, **78**, 5821 (1956).

[15] W. Johnson and V. Mark, *J. Org. Chem.*, **26**, 4105 (1961).

$\tau$ 6.27 and 7.10 ($J$ = 15 Hz). Lower field absorption of two doublets at $\tau$ 4.42 and 5.03 ($J$ = 13 Hz) are assigned to the two hydrogens of the 5-nitrosomethyl group. These two hydrogens provide a striking example of nonequivalence in diasteromeric hydrogens in an nmr spectrum. Thus, from the nmr, it is readily concluded that nitrosyl chloride adds to **14** at the exocyclic double bond, with no rearrangement.

It was of interest to determine if the addition of the elements of nitrosyl chloride could be accomplished in a two-step process as shown below. Addition of nitrosyl tetrafluoroborate to norbornene could be expected to produce a nitrosonium ion which could then undergo nucleophilic attack by chloride ion to yield the dimeric nitrosyl chloride adduct. Forcing the addition to occur in two steps should allow the maximum opportunity for rearrangement reactions to occur. The reaction was carried out in a number of solvents such as $CCl_4$, $CHCl_3$, DMSO, and acetone, and the appearance of a green color suggested the initial formation of a nitroso complex, but no dimeric nitrosochloride could be isolated upon addition of chloride ion. The use of iodide ion as the nucleophile resulted in its oxidation to molecular iodine by the reaction mixture. The small amount of organic product obtained was a viscous, uncharacterizable oil which had spectral properties of oximes.

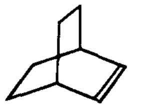


At about the same time as our work was in progress, Hamann and Swern[9] reported the addition of nitrosyl tetrafluoroborate to 2,3-dimethyl-2-butene in the presence of sodium acetate. The isolation of 2,3-dimethyl-2-acetoxy-3-nitrosobutane was attributed to the intermediate formation of a nitrosonium–olefin ion pair which then reacted with the nucleophilic acetate ion. It was of interest to determine whether norbornene would undergo a similar set of reactions, since observation of an exo,cis two-step addition of nitrosyl acetate to norbornene would establish the same point intended in the previous nitrosonium tetrafluoroborate–sodium chloride experiment. Addition of isoamyl nitrite and acetic acid to norbornene in the presence of a catalytic quantity of 70% perchloric acid yielded a white solid, which was identified as the dimeric 2-nitroso-3-nitronorbornane.[16] The addition of the elements of dinitrogen trioxide is not a new reaction, since several workers[5,17] have reported this product from nitrosyl chloride additions, and Swern[9] reported that generation of nitrosyl formate from sodium nitrite and formic acid yielded dinitrogen trioxide adducts with cyclohexene and styrene. It thus appears that the two-step addition of nitrosyl halides or acetates to norbornene is a very slow process, which allows isomerization of the nitrosonium complex to an oxime, or oxidation of the nitrosonium ion to dinitrogen trioxide, to become the predominant reaction pathway.

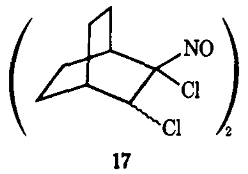
## Discussion

There are several theories that have been proposed to account for the fact that cis additions of a number of electrophilic reagents occur only in rigid olefins, and these have been reviewed.[7] A combination of the twist–strain theory of Traylor[7] and the torsional effects explanation of Schleyer[18] seem particularly attractive to us.

Bicyclo[2.2.2]octene-2, (**16**) should be an excellent choice to provide an evaluation of the influence of twist–strain on the addition of nitrosyl chloride to bicyclic olefins. It falls naturally between norbornene and cyclohexene in a series of decreasing strain in six-membered rings. It is also symmetrical about the double bond, so that steric hindrance should not lead to stereospecificity and torsional effects for cis or trans addition would be identical.



**16**



**17**

Nitrosyl chloride addition to bicyclo[2.2.2]octene-2 (**16**) occurs very slowly in comparison to norbornene, and the product, a white solid, has been identified as dimeric 2-nitroso-2,3-dichlorotricyclo[2.2.2]octane (**17**). The nmr of the alkene and the dichloronitroso product is shown in Figure 5. The product spectrum contains a doublet at $\tau$ 5.28 ($J$ = 3 Hz) which is assigned to the C-3 hydrogen, and multiplets at $\tau$ 7.42 and 7.59 are assigned to the bridgehead protons. A second small doublet at $\tau$ 5.39 is due to a C-3 epimer of the main product, and the ratio of major to minor isomer is 5:1. Although products with chlorine cis and trans to the nitroso group were obtained in this experiment, this provided little information as to the stereochemistry of the initial addition reaction. One may visualize the initial nitrosochloride adduct of bicyclo[2.2.2]octene-2 to be sterically hindered from dimerizing to form the azodioxy product, which then allows tautomerization to the oxime to occur. This intermediate chlorooxime then adds a second chlorine atom at C-2 to yield the observed mixture of *cis*- and *trans*-2-nitroso-2,3-dichlorobicyclo[2.2.2]octane.

With the evidence available in the literature on the addition of nitrosyl halides to olefins, one could legitimately consider either a molecular addition, a polar, nonconcerted addition, or a free radical addition. Preliminary experiments,[19] in which 5-ethylidene-2-norbornene adds nitrosyl chloride at the same rate whether or not a free radical inhibitor is present, seems to rule out the latter possibility in bicyclic systems. Our attempts at the trapping of any positively charged intermediate with iodide or chloride ion were frustrated due to redox reactions involving nitrosyl chloride and the halide ions. However, attempts in other laboratories to trap any such species with nucleophilic solvents

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

(17) A. Hassner and C. Heathcock, *ibid.*, **29**, 1350 (1964).

(18) P. V. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967).

(19) P. W. Wheat, unpublished studies of this laboratory.

have also met with failure.[4] It is difficult to propose meaningful experiments whose results will give definitive answers to the question of existence or nonexistence of polar characteristics in these reactions. A study of the sensitivity of the reaction to electron-withdrawing and electron-releasing substituents should give some indication of the degree of positive charge buildup during the reaction, and these experiments are presently underway.

We feel that the exo,cis addition of nitrosyl chloride to the [2.2.1]bicyclic olefins can be best explained by a combination of factors. The torsional strain introduced in the transition state for initial endo attack and the partial blocking of the endo side of the double bond in this system would dictate an initial exo attack whether by a nitrosonium ion or molecular nitrosyl chloride. If an intermediate ion is formed in the bicyclic system similar to the intermediate formed from unstrained cases, then certain things must be true of this ion. It must have the positive charge delocalized on the nitrosonium group, since generation of positive charge at C-2 would almost certainly lead to rearrangement. Any intermediate ion must also be capable of adding the nucleophile, chloride ion, in a cis manner, since twist-strain would make trans addition implausible. A skewed ion such as that proposed by Rolston and Yates[20] in the case of bromine addition to styrene would perhaps meet this requirement. The intermediate ion would also be required to have the chloride in close association with it so that the chloride ion could add before any solvent molecule in the surrounding cage could add. As we place more and more limits on this hypothetical intermediate ion, we move closer toward a mechanism involving molecular cis addition. The real crux of the problem then is one of trying to determine if there is an intermediate or only a transition state in the addition reaction. We feel that a molecular, cis addition of nitrosyl chloride to strained bicyclic systems can be best supported with the available experimental evidence.

## Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were taken with a Perkin-Elmer Model 337 instrument, and a CEC 21-104 moderate resolution mass spectrometer system was used. Nuclear magnetic resonance spectra were taken on a Varian Associates HA-100 instrument using TMS as internal standard and either $CDCl_3$ or $CF_3COOD$ as solvent. The general procedure used for the addition of nitrosyl chloride to olefins has been described previously.[5]

**Addition of Nitrosyl Chloride to Norbornene.**—A 5.8-ml (0.13 mol) sample of nitrosyl chloride was added to 12.0 g (0.13 mol) of norbornene in 150 ml of chloroform solvent by the general addition procedure at −50°. Stirring was continued for 30 min after addition was complete, and cold hexane (100 ml) was added. Suction filtration, followed by washing with cold hexane and air drying, yielded 14.8 g (75%) of *cis,exo*-3,3′-dichloro-*anti*-2,2′-azodioxynorbornane, mp 158–162° (lit.[4,8] mp 155.5–156.6°). The supernatant liquid was evaporated to a small volume and analyzed by glpc (20% SE-30 column) to reveal only chloroform, hexane, and unreacted norbornene. The yellow slurry obtained from continued evaporation of this supernatant liquid was shown by infrared analysis to have all the absorption peaks of the cis,exo nitrosyl chloride adduct, plus other peaks characteristic of oximes, particularly at 3450 ($\nu_{OH}$) and 1635 cm$^{-1}$ ($\nu_{C=N}$).

**Addition of Nitrosyl Chloride to Norbornadiene.**—A 5.8-ml (0.13 mol) sample of nitrosyl chloride was added to 11.75 g (0.13 mol) of norbornadiene in 150 ml of chloroform by the general addition method over a period of 1 hr. Work-up of the reaction as described above gave 12.3 g (63%) of *cis,exo*-6,6′-dichloro-*anti*-5,5′-azodioxy-2-norbornene as a white solid, mp 154–157° (lit.[4,8] mp 150–156°). Examination of the supernatant liquid in the manner previously described revealed the presence of only chloroform, hexane, some unreacted norbornadiene, and a small quantity of chloro oxime.

**Addition of Nitrosyl Chloride to 5-Methylene-2-norbornene (1).**—A 11.55-ml (0.25 mol) sample of nitrosyl chloride was added to 26.5 g (0.25 mol) of 5-methylene-2-norbornene (1) in 300 ml of chloroform at −50° by the general addition procedure. After an addition time of 50 min, 600 ml of cold hexane was added and stirring at −50° was continued for 12 hr. The yield of white solid (2), after collection by suction filtration and drying, was 30.0 g (70%), mp 157–163°. The mass spectrum of the solid showed a high mass cutoff of 171. The nmr spectrum is shown in Figure 1.

*Anal.* Calcd for $C_8H_{10}NOCl$: C, 56.10; H, 5.83; N, 8.18; Cl, 20.70. Found: C, 56.24; H, 5.67; N, 8.05; Cl, 20.46.

Work-up of the supernatant liquid in the manner described previously and analysis by glpc and infrared revealed a small amount of chloro oxime as the only additional product.

**Addition of Nitrosyl Chloride to 5-Ethylidene-2-norbornene[21] (5).**—Nitrosyl chloride (11.55 ml, 0.25 mol) was added to 30 g (0.25 mol) of 5-ethylidene-2-norbornene in 300 ml of chloroform below −50° over a period of 1 hr. After addition of 600 ml of hexane, stirring was continued for 5 hr. Work-up of the solution in the normal manner yielded 31 g (67%) of *cis,exo*-3,3′-dichloro-*anti*-2,2′-azodioxy-5-ethylidenenorbornane (6), mp 135–139°. The mass spectrum showed a high mass cutoff at 185. The nmr spectrum is shown in Figure 2.

*Anal.* Calcd for $C_9H_{12}NOCl$: C, 58.22; H, 6.49; N, 7.55; Cl, 19.14. Found: C, 58.45; H, 6.44; N, 7.60; Cl, 19.20.

Glpc analysis of the concentrated supernatant liquid on a 20% SE-30 column indicated only $CHCl_3$, hexane, and a trace of the starting olefin. The infrared spectrum of the final yellow residue from the evaporation of the mother liquor indicated the presence of an oxime.

**Levulinic Acid Hydrolysis of the 5-Methylene-2-norbornene Nitrosochloride Dimer (2).**—A 17.2-g (0.05 mol) sample of 2 in 339 ml of levulinic acid and 25 ml of 2 *N* HCl was heated with stirring at 85° for 1.5 hr. After the solution became clear, the mixture was stirred at 60° for an additional 21 hr. The mixture was diluted with 1 l. of water and extracted twice with 300-ml portions of ether. The combined ether extracts were washed with saturated sodium bicarbonate and dried over magnesium sulfate, and the ether was removed by rotary evaporation. Vacuum distillation of the remaining product gave a fraction, bp 135–138° (1 mm) whose infrared spectrum revealed it to be a mixture of two ketones, 9 and 10, in a ratio of 5:1, with an intense absorption at 1760 cm$^{-1}$. Glpc separation and collection of these two chloro ketones afforded analytical samples whose nmr spectra are shown in Figure 3. Satisfactory elemental analyses were obtained on each isomer.

**Levulinic Acid Hydrolysis of the 5-Ethylidene-2-norbornene Nitrosochloride Dimer.**—This hydrolysis was carried out in a manner identical to the preceding hydrolysis. Analysis of the product residue by glpc on a 15% Carbowax 20M column revealed two products in a ratio of 4:1. Infrared analysis of analytical samples of these two products identified them as the chloroketones 11 ($\nu_{max}$ 1760, 1665, 1660 cm$^{-1}$) and 12 ($\nu_{max}$ 1760, 1669 cm$^{-1}$) with 11 being the major isomer. Satisfactory elemental analysis were obtained on each isomer.

**Addition of Nitrosyl Chloride to 1,2,3,4,7,7-Hexachloro-5-methylene-2-norbornene[14,15] (14).**—This olefin failed to add nitrosyl chloride in solution under a variety of reaction conditions. However, neat addition of 0.04 mol of nitrosyl chloride to 0.02 mol of the olefin in a pressure bottle at room temperature for 1 month led to addition at the exocyclic double bond, as shown in Figure 4.

**Attempted Addition of Nitrosyl Acetate to Norbornene.**—Dry glacial acetic acid (200 ml) and 5 drops of 70% perchloric acid were cooled to 15° while 28.2 g (0.3 mol) of norbornene and 70.2 g (0.6 mol) of isoamyl nitrite were added over a 1-hr period.

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[20] J. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1477 (1969).

[21] A generous complimentary sample of this material was supplied by Union Carbide Corp., Olefins Division, New York, N. Y.

A light green color developed and the temperature dropped to 5° during the course of the addition. Water (200 ml) was added, and the solution was extracted several times with ether. Overnight storage of the ether extract in the refrigerator led to precipitation of a white solid, which was recrystallized from chloroform to give 30 g (30%) of white needles, mp 146–148° (lit.[16] mp 135°). This was identified as 3,3′-dinitro-2,2′-azodioxynorbornane from its melting point and infrared spectrum: ir (KBr) 1540, 1355 ($-NO_2$), 1193, 1223, and 1216 cm$^{-1}$ (azodioxy).

*Anal.* Calcd for $C_7H_{10}N_2O_3$: C, 49.31; H, 5.88; N, 16.47. Found: C, 49.50; H, 5.95; N, 16.34.

**Addition of Nitrosyl Chloride to Bicyclo[2.2.2]octene-2[22] (16).**—Nitrosyl chloride (2.3 ml, 0.05 mol) was added to 5.4 g (0.05 mol) of bicyclo[2.2.2]octene-2 in 25 ml of carbon tetrachloride by the general addition method at 10°. The color of the solution turned from red to blue in 4 hr, and a small amount (0.44 g) of white solid was isolated by filtration. Washing with acetone gave a purer material, mp 94.5–97.5°. This was identified as the dimer of a mixture of *cis-* and *trans*-2,3-dichloro-2-nitrosobicyclo[2.2.2]octane (17). The nmr spectrum is shown in Figure 5.

*Anal.* Calcd for $C_8H_{11}Cl_2NO$: C, 46.15; H, 5.29; Cl, 34.13; N, 6.73. Found: C, 45.96; H, 6.27; Cl, 33.87; N, 6.62.

The supernatant liquid was evaporated and the residue was shown to be a mixture of starting olefin and product 17.

**Registry No.**—**1,** 694-91-7; **2,** 32846-86-9; **5,** 16219-75-3; **6,** 32846-87-0; **9,** 32846-82-5; **10,** 32846-83-6; **11,** 32846-84-7; **14,** 4659-42-1; **15,** 32839-07-9; **16,** 931-64-6; **17,** 32839-08-0; nitrosyl chloride, 2696-92-6; 3,3′-dinitro-2,2′-azodioxynorbornane, 32861-60-2.

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[22] Chemical Samples Co., Columbus, Ohio.

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# *trans,trans,cis*-2,8,12-*trans*-Bicyclo[8.4.0]tetradecatriene[1,2]

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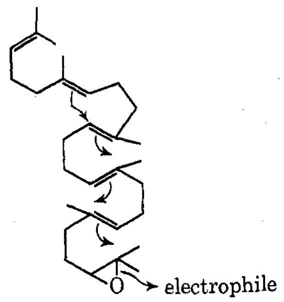
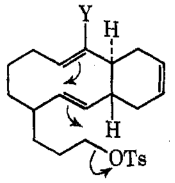
The synthesis is described of a *trans,trans*-1,5-cyclodecadiene **4a** which is thermally stable but not degenerate with respect to the Cope rearrangement.

One postulate for the enzymatically controlled cyclization of squalene oxide (**1**) involves epoxide cleavage with conformational holding and nucleophilic participation of remote double bonds, acting through intermediate double bonds. Attractive as such a postulate might appear, it is virtually without experimental test; and appropriate models are not easily conceived or synthesized.[3] Our experience with the *trans,trans*-2,8-*trans*-bicyclo[8.4.0]tetradecadiene system (**3a,b**)[4,5] suggested that a study of compounds like **2** should be informative with respect to the extent of participation of the remote bond in solvolysis of the tosylate, with Y appropriately substituted. This article details preliminary work leading to the synthesis of the corresponding unsubstituted system **4a**, *trans,trans,cis*-2,8,12-*trans*-bicyclo[8.4.0]tetradecatriene; **4a** possesses one more double bond than the system **3a,b**. This additional double bond should have the effect of heavily weighting the Cope-related equilibrium **4a,b** in favor of **4a** (**4b** is highly strained), thus avoiding the problem of constitutional isomers which arises upon substituting the **3b** system at C-4.



**1**



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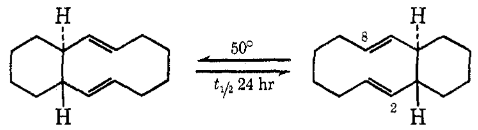
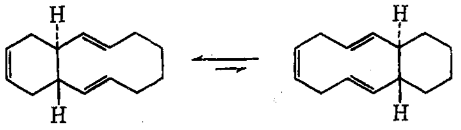


**3a** **3b**



**4a** **4b**

On the basis of the established synthetic route to **3a,b** (**5** → **6a** → **6c** → **3a,b** in Scheme I),[4] preparation of **4a,b** simply involved making and fragmenting the appropriately substituted *trans,syn,trans*-dodecahydroanthracene **7**. This appeared to be particularly straightforward because the synthesis of **3a,b** proceeded from **5** (formed by isomerizing the bis adduct of butadiene and benzoquinone[6]), a compound already functionalized with two identical double bonds, correctly positioned; and the simplest solution was therefore to reduce one of them. However, no conditions of catalytic hydrogenation could be found which resulted in any selectivity in the absorption of the first and second moles of hydrogen; or in any mixture which could be separated into its unreduced, partially reduced, and fully reduced components.

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[1] The investigation was supported by Public Health Service Research Grant GM 16338 from the Division of General Medical Sciences, U. S. Public Health Service.

[2] The article is abstracted from the Ph.D. Thesis of G. O. S., Wesleyan University, 1971.

[3] For a review of polyolefin cyclizations see W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968). For comments, additional references, and one example of a double bond participating in an S$_N$2′ displacement see G. D. Sargent, J. A. Hall, M. J. Harrison, W. H. Demisch, and M. D. Schwartz, *J. Amer. Chem. Soc.*, **91**, 2379 (1969).

[4] P. S. Wharton, Y. Sumi, and R. A. Kretchmer, *J. Org. Chem.*, **30**, 234 (1965).

[5] P. S. Wharton and R. A. Kretchmer, *ibid.*, **33**, 4258 (1968).

[6] K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **501**, 247 (1933).