

[JOINT CONTRIBUTION FROM THE NAVAL ORDNANCE LABORATORY, THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE, AND THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

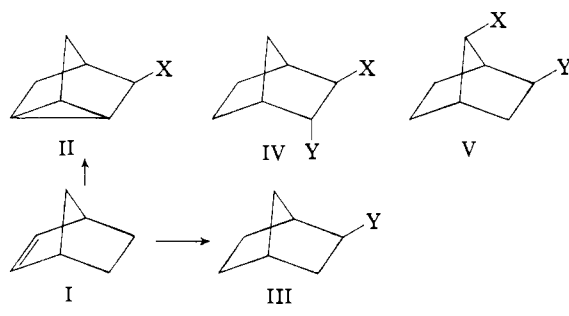
Addition Reactions of *exo*-Trimethylene-2-norbornene

BY L. KAPLAN,^{1a} H. KWART^{1b} AND P. VON R. SCHLEYER^{1c}

RECEIVED JULY 8, 1959

The reactions of *exo*-trimethylene-2-norbornene (VI) with a variety of addition reagents have been studied. By bromination in carbon tetrachloride solution, the 2,3-*trans* addition product has been identified as predominant. When this reaction is conducted in a pyridine medium small amounts of a 2,7-rearranged dibromide and a nortricyclic monobromide have been isolated and characterized alongside the 2,3-*trans* product. Hydroxylation by means of performic acid yields entirely a 2,7-rearranged diol structure. These are the first cases in the dicyclopentadiene series of *exo* to *endo* rearrangement of the substituent five-membered ring. The equilibrium between onium ion XXI and bridged ion XXII is postulated as a dominant factor in determining the structures of products of addition reactions of bicyclic olefins. This equilibrium in turn can be influenced by many factors including substituents on the bicyclic ring and the nature of the addition reagent.

A number of polar reagents, XY, have been added to norbornene (I) heterolytically, under a variety of experimental conditions. In those cases where neither fragment X nor Y is hydrogen, it has been possible to determine the structural and stereochemical disposition of both the groups in the product.² These reactions can be generalized in the following manner. If the attack of the electrophilic species X⁺ was followed by ejection of a proton, the nortricyclic derivative II formed as well as the protonic acid HY. In a competing side reaction, the latter could add to I in the usual manner to give a norbornyl derivative III. If, however, the attack of X⁺ was followed by reaction with Y⁻, either unrearranged product IV or rearranged material V resulted. Inspection of Table I, summarizing the course of the reported additions, indicates that a full spectrum of results has been obtained.



(1) (a) Naval Ordnance Laboratory, White Oak, Md. Present address: Convair Research Labs., San Diego, Calif. (b) Department of Chemistry, University of Delaware, Newark, Del. Paper VIII of a series on Addition Reactions in Bicyclic and Alicyclic Systems; paper VII, see reference 2j. (c) Department of Chemistry, Princeton University, Princeton, N. J. Paper II of a series on Bridged Ring Systems. Paper I, P. von R. Schleyer, *THIS JOURNAL*, **80**, 1700 (1958).

(2) (a) J. D. Roberts, E. R. Trumbull, W. Beunett and R. Armstrong, *ibid.*, **72**, 3116 (1950); (b) H. Kwart and L. Kaplan, *ibid.*, **76**, 4072 (1954); (c) L. Kaplan, Thesis, University of Delaware, 1955, and unpublished results of J. L. Nyce, Thesis, University of Delaware, 1959; (d) H. Kwart and R. K. Miller, *THIS JOURNAL*, **78**, 5678 (1956); (e) S. J. Cristol and G. D. Brindell, Abstracts, Am. Chem. Soc. Mtg., Cincinnati, Ohio, April, 1955, p. 35-N; S. J. Cristol, R. P. Arganbright, G. D. Brindell and R. M. Heitz, *THIS JOURNAL*, **79**, 6035 (1957); (f) J. D. Roberts, F. O. Johnson and R. A. Carboni, *ibid.*, **76**, 5692 (1954); (g) H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954); (h) H. M. Walborsky and D. F. Loncrini, *ibid.*, **76**, 5396 (1954); (i) L. Schmerling, U. S. Patent 2,500,385, March 14, 1950 (C. A., **44**, 5391 (1950)); (j) H. Kwart, R. K. Miller and J. L. Nyce, *THIS JOURNAL*, **80**, 887 (1958); (k) H. Krieger, *Suomen Kemistilehti*, **B31**, 340 (1958); (l) G. F. Wright, *et al.*, *Can. J. Chem.*, **37**, 1328 (1959); (m) R. L. Rowland, *THIS JOURNAL*, **73**, 2381 (1951).

TABLE I
SUMMARY OF THE COURSE OF ADDITION REACTIONS OF NORBORNENE

Reagent X-Y	Solvent	Temp., °C.	Product compositions, ^a %			Ref.
			II	IV	V	
AcOHg-OAc	HOAc	Room	..	100	..	21,m
ArS-Cl ^b	CCl ₄ or pyri- dine	20	..	100	..	2d,e
ArS-Cl ^c	C ₂ H ₄ Br ₂	25	..	100	..	2j
ArS-Cl ^d	C ₂ H ₄ Br ₂	50	V. small	100	..	2j
ArS-Br ^e	C ₂ H ₄ Cl ₂	15-20	7	93	..	2d
ArS-Cl ^f	C ₂ H ₄ Br ₂	50	13 ^g	87	..	2d
Br-Br	CCl ₄	-1	35 ^g	15	26	2a,b,c
Br-Br	CCl ₄ + 1 mole pyri- dine	0	27	16	57	2a,b,c
Cl-Cl	Pentane	-70	54-61	..	39-46	2f,i
Cl-OH	(H ₂ O)	10-20	37	..	63	2f
HO-OOC	HCOOH	40-45	100	2g,h,k

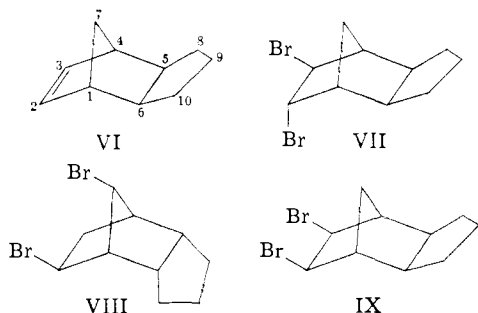
^a Approximate; based upon the reported relative amounts of products actually isolated. ^b *p*-Toluenesulfonyl-Ar. ^c 4-Nitrobenzenesulfonyl-Ar. ^d 2-Nitrobenzenesulfonyl-Ar. ^e 2,4-Dinitrobenzenesulfonyl-Ar. ^f The presence of moisture or the use of acetic acid as the solvent increased the amount of this material. ^g The product contained 24% of III.

In addition to variations in the nature of the reactant and in the experimental conditions, we would expect that structural modification of the olefin should influence the course of these addition reactions. With the exception of certain carboxylic acid derivatives of norbornene³ and certain structural analogs, such possibilities have not been thoroughly examined.^{3f}

We should like to report the effect that a substituent on the carbocyclic ring has upon the course of some of these addition reactions. The compound

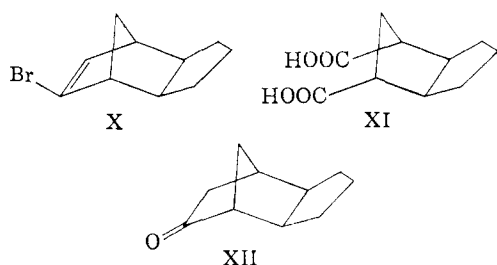
(3) (a) H. Kwart and L. Kaplan, *ibid.*, **75**, 3356 (1953); (b) **76**, 4078 (1954); (c) J. A. Berson and R. Swidler, *ibid.*, **76**, 4060 (1954); (d) J. A. Berson, *ibid.*, **76**, 4069 (1954); (e) **76**, 5748 (1954). Furthermore, the halogenation of norbornene carboxylate anions in basic solution gave rise to lactones and other products. Earlier work has been summarized, E. Josephy and F. Radt, Eds., "Elsevier's Encyclopaedia of Organic Chemistry," Vol. 12A, Elsevier Publ. Co., Inc., New York, N. Y., 1948. For more recent examples, see the following references: C. D. Ver Nooy and C. S. Rondstedt, *THIS JOURNAL*, **77**, 3583, 4878 (1955); E. T. McBee, C. G. Hsu and C. W. Roberts, *ibid.*, **78**, 3389 (1956); M. Mousseron, F. Winternitz and G. Rouzier, *Compt. rend.*, **238**, 1661 (1954); *Bull. soc. chim. France*, 170 (1955); J. S. Meek and W. B. Trapp, *THIS JOURNAL*, **79**, 3909 (1957); P. Wilder, Jr., and C. F. Culberson, *ibid.*, **81**, 2027 (1959); (f) M. Gates and S. P. Malchick, *ibid.*, **76**, 1378 (1954), have studied the reaction between performic acid and dicyclopentadiene. The product, after saponification, was not characterized, but was assigned the rearranged 2,7-diol structure on the basis of the failure to cleave with Pb(OAc)₄ or HIO₄. A similar result has been observed by E. L. Eliel and C. Pillar, *ibid.*, **77**, 3600 (1953), with a compound quite analogous in structure to dicyclopentadiene; cf. J. Meinwald and G. W. Wiley, *ibid.*, **80**, 3667 (1958).

chosen, *exo*-trimethylene-2-norbornene (VI),⁴ was of further interest since it was quite possible that polar addition might have occurred with formation of *cis* products, even though *trans* stereochemistry is the normal result with such reactions (*vide supra*).



Bromination in CCl₄.—The bromination of VI in the cold in carbon tetrachloride solution gave a dibromide product which appeared to consist very largely of one component. Mechanistic considerations suggest three possible structures for this product; the "normal" *trans* adduct VII, the rearranged compound VIII, and the *cis* product IX. Preliminary evidence in favor of VII was the fact that the observed dipole moment, 2.35 D., was compatible only with that structure.⁵ Results of chemical degradations confirmed the fact that this conclusion was correct.

Potassium *t*-butylate dehydrohalogenation^{2b,3a} of VII gave the vinyl bromide derivative X. The structure of X was established by oxidation to the known dicarboxylic acid XI as well as by hydrolysis to *exo*-trimethylene-2-norbornanone XII. These results, taken in conjunction with the dipole



moment data, the infrared spectrum and n.m.r. evidence, unequivocally establish the structure of the dibromide as VII. Thus the infrared spectrum of X displays an absorption in the C=C region at 6.35 μ . This is the unusually high wave length characteristic of a disubstituted norbornene-type structure (see ref. 9), but the trisubstituted nature of the olefin bond is revealed by the strong doublet at 12.25–12.40 μ and the lack of the band near 14 μ

(4) The reported bromination of this compound (P. Wilder, Jr., and G. T. Youngblood, *THIS JOURNAL*, **78**, 3795 (1956)) has been shown to have involved an isomeric hydrocarbon (P. Wilder, Jr., and G. T. Youngblood, *ibid.*, **78**, 5706 (1956); P. von R. Schleyer and M. M. Donaldson, *ibid.*, **78**, 5702 (1956)). The nomenclature employed in the present paper will follow a suggestion made in the latter reference.

(5) The calculated dipole moments for VII, VIII and IX are, respectively, 2.0, 3.9 and 3.8 D. The value previously found for *trans*-2,3-dibromonorbornane (IV, X = Y = Br), 2.3 D., is in excellent agreement with that found here. The observed value for 2-*exo*-7-*syn*-dibromonorbornane (V, X = Y = Br) was 3.5 D. (see ref. 2b, 3a) and H. Krieger, *Suomen Kemistiilehti*, **B31**, 348 (1958).

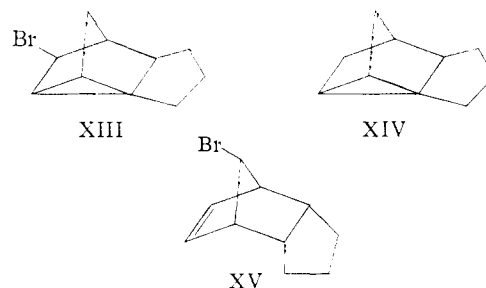
that has been attributed to a *cis*-disubstituted olefin.⁶

The n.m.r. data (see Table II) confirm that X possesses half as many vinylic as bridgehead proton resonances and no halomethyl proton peaks. The n.m.r. data on the analogous unsubstituted bromonorbornene Xa listed in Table II further strengthens this interpretation and assignment of the structure of X.

Bromination in Pyridine.—When pyridine was employed as the solvent, the bromine addition took a somewhat different course. The major product was still VII, but, in addition, a monobromide XIII and a higher boiling dibromide VIII formed in small amounts. The structural assignments of VIII and XIII were made on the following grounds.

The infrared spectrum of XIII indicated that the compound was not unsaturated, but suggested rather that the material was a nortricyclene derivative with an alkyl substituent upon the three-membered ring, as indicated by the characteristically strong absorption band at 11.73 μ .⁷

Hydrogenolysis with the aid of alkaline palladium-charcoal catalyst led to a bromine-free hydrocarbon which was tentatively assigned the structure XIV. Freedom from contamination was determined by a negative Beilstein halogen test and by the results of vapor phase chromatography. Furthermore, XIV was not identical with any of



the known olefins or saturated hydrocarbons in this series. It possessed the same infrared characteristics of the three-membered ring (3.305 μ and 11.82 μ) as its bromo progenitor XIII, as well as a complete lack of any 6 μ and 12–16 μ olefin bands. Elementary analysis also confirmed the assignment of XIII. However, several attempts at synthesis of XIV by mercuric oxide oxidation of the hydrazone of XII failed, although this is a recognized standard method of preparation of nortricyclene derivatives.⁸

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., Second Edition, 1958, p. 34. The comparable vinyl bromide derivative, 2-bromo-2-norbornene (Xa), has the same spectral features.^{2b} 2-Methyl-2-norbornene, on the other hand, displays the bands under discussion at 6.12 and 12.4 μ .

(7) It has been found (P. R. Schleyer, Ph.D. Thesis, Harvard University, 1956; P. R. Schleyer and R. E. O'Connor, Abstracts, 134th National Meeting, Am. Chem. Soc., Chicago, Ill., Sept., 1958) that nortricyclenes substituted upon the cyclopropane ring have a characteristic infrared band in the region centering around 11.7 μ (*cf.*, H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959)).

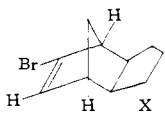
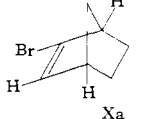
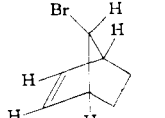
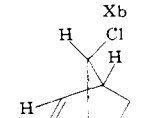
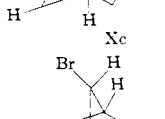
(8) For example, *cf.* Elsevier's Encyclopaedia (ref. 3), Vol. 13, 1946; K. Alder, *et al.*, *Ann.*, **593**, 23 (1955); R. L. Young, Ph.D. Thesis, Brown Univ., 1959; *Diss. Abstr.*, **20**, 1182 (1959).

The new dibromide was assigned the structure of VIII on the basis of several lines of evidence. Its dipole moment (3.7 D.) was in very satisfactory agreement with the moment computed for its structure.⁹ Upon dehydrohalogenation with potassium *t*-butylate^{2b,3a} a bromoolefin (XV) was obtained which was decidedly different from X in all its properties and yet almost identical in elementary analysis. Furthermore, XV possessed the bands at 6.35 μ and at 13.7 μ in the infrared which are highly characteristic of a norbornene-type structure.⁹ The n.m.r. data strongly support the structural assignment of the bromoolefin XV since they confirm that XV possesses the three peaks corresponding to vinylic, halomethinyl and bridgehead hydrogens in the ratio 2:1:2 just as do the known calibrating haloolefins Xb and Xc. Clearly, also, the *cis*, *vic*-dibromide structure IX, which is acceptably in accord with the dipole moment data, must be rejected as the structure of the new dibromide on the grounds delineated above. In view, also, of the very probable mechanism of its formation there can be little doubt concerning the correctness of the assigned structure VIII, but it must be noted here in passing (and will be discussed at some length in a later section of this article) that this represents conversion of a thermodynamically more stable *exo* substituted norbornane to a product in which the same substituent has the less stable *endo* configuration.

In summary, the products obtained in pyridine solution were, approximately, 1.5% XIII, 90% VII and 8.5% VIII. Bromination in CCl₄ led to VII as the only identifiable product. Recently, we have been advised that Cristol, Seifert and Soloway¹⁰ have brominated VI in acetic acid solution with N-bromosuccinimide and obtained predominantly the Wagner-Meerwein rearrangement product, *syn*-7-bromo-*exo*-2-acetoxy-*endo*-trimethylenenorbornane.

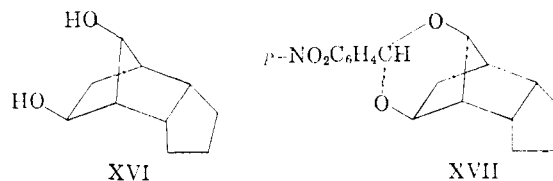
Reaction with Performic Acid.—The performic acid oxidation of VI gave rearranged product. After saponification, the resulting diol XVI, characterized as a bis-phenylurethan derivative, failed to reveal the presence of any *vic*-diol by quantitative periodic acid oxidation¹¹; XVI formed a *p*-nitrobenzylidene derivative XVII characteristic of 2,7-diols in this series.^{2b} Furthermore, the infrared spectrum showed the presence of intramolecular hydrogen bonding; the $\Delta\gamma$ value of the compound was 72 cm^{-1} in good agreement with that expected of a compound having the structure XVI.^{2g} Failure to enhance the conductivity of boric acid¹² further confirmed the 2-*exo*-7-*syn*-diol assignment. Although degradative studies were not made that would establish with even greater certainty the orientation of the trimethylene substituent, the evidence above when taken in conjunction with considerations regarding the mechanism of forma-

TABLE II
NUCLEAR MAGNETIC RESONANCE IDENTIFICATIONS
Proton resonances identified^a
Vinylic, (—C=C—H), A
Halomethinyl, (—C—H), B
Bridgehead, C

Compound	Peak frequency, cycles/sec.	Relative area (abundance)	Assigned structure
	+62	1	A
	-84	2	C
	+84	1	A
	-41	2	C
	+66	2	A
	-20	1	B
	-57	2	C
	+66	2	A
	-26	1	B
	-66	2	C
	+42	2	A
	-32	1	B
	-71	2	C

^a No attempt was made to resolve and identify proton resonances at fields beyond -84 c.p.s. corresponding to the remaining methylene and methinyl groups of the structures listed in this chart.

tion of rearranged diol appears to necessitate the rearranged *endo* orientation suggested for XVI.



Again, this must be noted as another example of the formation of an *endo* product of rearrangement *via* the reaction of VI, in which the trimethylene substituent has the more stable *exo* configuration.

The Factors that Determine Orientation in Addition Reaction of Bicyclo[2.2.1]heptanes. (a) Structure of the Olefin and the Nature of the Solvent.—Comparison of the results described above with the analogous reactions carried out with norbornene (Table I) emphasizes the considerable difference between the two. The presence of the trimethylene substituent reduces by a marked amount both the tendency toward rearrangement and the tendency toward nortricyclene formation. Even in the more polar solvent pyridine, VIII and XIII are formed only in minor amounts.

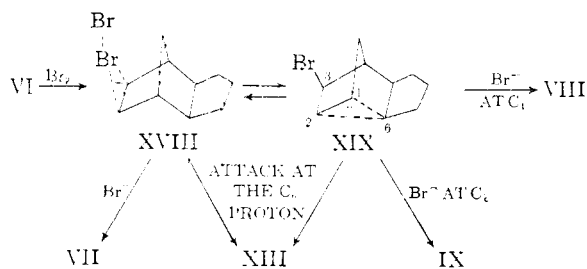
(9) The spectra of a very large number of norbornene derivatives all have a band very near 6.35 μ (unpublished observation of P.R.S.); cf. R. C. Lord and R. W. Walker, *THIS JOURNAL*, **76**, 2518 (1954), and refs. therein cited, and ref. 5 (P.R.S. and M.M.D.).

(10) S. J. Cristol, W. K. Seifert and S. B. Soloway, private communication, Sept. 23, 1959, and *ibid.*, **82**, 2351 (1960).

(11) S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 8-9.

(12) H. Kwart and G. C. Gatos, *THIS JOURNAL*, **80**, 881 (1958).

The following scheme provides a rationalization for the presently observed course of bromination. It also seems that the arguments adduced here can be extended to include the performic acid oxidation of XI and, even further, to suggest reasons for the behavior of other bicyclo[2.2.1]heptenes.



Bromination of VI would lead initially to an intermediate, formulated as the bromonium ion-pair XVIII. Nucleophilic attack in the usual manner would give VII. Competing with this reaction, however, would be participation of the electrons associated with the C₁₋₆-bond. Formation of the bridged-ion XIX could conceivably be followed by bromide ion attack at C₁ to give VIII or attack at C₂ to give IX. Attack at the proton attached to C₆, either in XVIII or in XIX, would lead to the tricyclene derivative XIII.

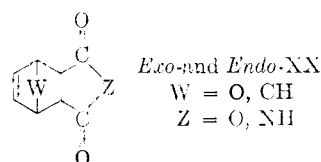
Since data have not been obtained which would allow distinction between the intimate mechanistic possibilities, speculation concerning the detailed pathways whereby the products arise would not be prudent. However, several known features of the chemistry of trimethylenenorbornanes help to reconcile the results with those noted previously for norbornene.

It has been established that anchimeric assistance is greatly diminished in the trimethylenenorbornane series relative to compounds lacking alkyl groups attached to the participating carbon (C₆).¹³ Thus, the rate of solvolysis of 2-*exo*-norbornyl derivatives is from 30 to 100 times faster than the corresponding *exo*-trimethylene-2-*exo*-norbornyl compounds. Therefore, the decreased proportion of VIII in comparison with V (X = Y = Br) is consistent with this factor.

The compounds XX, containing strongly electron-withdrawing carbonyl functions directly attached to the ring probably could not experience the participation of the neighboring carbon bonds under the conditions of bromination.³ The products actually observed did not involve rearrangement, but in several cases, *cis*, *vic* materials were obtained. A completely general explanation covering the few known instances³ of *cis*, *vic*-halogen addition to a norbornene double bond (which is unsubstituted by halogen or analogous groups) is not yet at hand, although Cristol and co-workers have suggested that such products can be correlated with a classical free radical mechanism.¹⁴

(13) R. S. Barnes, Thesis, Harvard University, 1950; P. D. Bartlett, Abstracts, 12th National Organic Symposium, Denver, Colo., June 21, 1951, pp. 4-7 (the data here have erroneously been recorded as sec.⁻¹ instead of min.⁻¹); see P. Schleyer, Thesis, Harvard University, 1956, and unpublished observations.

(14) See S. J. Cristol and R. P. Arganbright, *THIS JOURNAL*, **79**, 6039 (1957), and references 1-9 cited therein for a discussion of this question.



It is a reasonable assumption that VII is thermodynamically the most stable of all three of the possible dibromides. This follows from the known greater stability of *exo* ring over *endo* ring isomers in this series,¹⁵ as well as from the demonstrated isomerization of V into IV (X = Y = Br) in the presence of Lewis acids.^{2b,c} The formation of IX apparently is resisted since it involves eclipsing of bulky bromine atoms which would, moreover, give rise to unfavorable dipole-dipole interactions.¹⁶

Limited observations on the effect of solvent on the course of the bromination are consistent with the idea that the superior ion-solvating media pyridine and acetic acid¹² increase the proportion of rearranged product VIII due to an increased stability and/or promotion of the equilibrium formation of the bridged ion XIX.

Decision between the possible precursors XVIII or XIX of the nortricyclene derivative XIII is not possible from the present data, but it is clear that the base pyridine should favor its production by either path. Nevertheless, the quantity of XIII produced even under such conditions was quite small by comparison with what has been observed with norbornene.^{2a,b,c} This was probably in some measure a reflection of the relative stabilities of the nortricyclene (as II) and of the trimethylenenortricyclene (XIII) structures. Examination of the geometry of nortricyclene by means of models discloses that the incorporation of a trimethylene bridge between the 2- and 3-positions is attended by an increase of angle strain and this may account for the difficulties experienced in synthesizing XIII from the hydrazone of XII. Although nortricyclene derivatives are frequently discovered as by-products in reactions of bicycloheptane compounds,⁷ similar observations in the trimethylenenorbornane series have not been recorded previously in the literature.^{8,17,15}

(b) **Influence of the Nature of the Reagent:** Rearrangements in the trimethylenenorbornane series invariably have been observed to proceed from *endo*-ring to *exo*-ring derivatives.^{11,19} It was considered possible, therefore, that the performic acid oxidation would be constrained to yield *cis*, *vic* product analogous to IX and contrary to the usual stereochemical course of such additions.²⁰

(15) *exo*-Trimethylenenorbornanes are more stable than their *endo* counterparts to the extent of 2-3 kcal.; K. Alder and G. Stein, *Ber.*, **67**, 613 (1934); P. R. Schleyer and M. M. Donaldson, unpub. obsn.

(16) For a full discussion of this effect in vicinal dihalogenocyclohexanes see S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954, p. 77 *et seq.*; and O. Hassel, *Quart. Revs.*, **7**, 221 (1953).

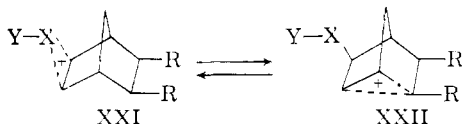
(17) Cf., in particular, G. T. Youngblood and P. Wilder, Jr., *J. Org. Chem.*, **21**, 1436 (1956).

(18) Contrast the behavior of norbornane derivatives (P. von R. Schleyer, *THIS JOURNAL*, **80**, 1700 (1958)).

(19) P. D. Bartlett and A. Schneider, *ibid.*, **68**, 5 (1945); H. A. Bruson and T. W. Riener, *ibid.*, **67**, 723 (1945), and subsequent papers in the same series.

(20) *cis*-Diols have been observed in the oxidation of certain styrene derivatives; D. Y. Curtin, A. Bradley and Y. G. Hendrickson, *THIS*

The *cis, vic*-diol, which could form from the bridged intermediate, would retain the substituent ring in the less strained *exo* configuration. The actual product XVI, which represents complete rearrangement, demonstrates once again²¹ the marked propensity toward rearrangement which appears to be a characteristic feature of this reaction, due perhaps in part to the excellent ion-solvating power of the medium coupled with the low nucleophilicity of formic acid.²² However, another factor determining the course of the addition is to be found in the instability of the oxonium ion (XXI, where X = O, Y = H) with respect to the bridged ion XXII.²³ The results summarized in Table I also point to this factor in determining the course of other additions to the norbornene double bond. The greater ease of formation and stability of



tertiary sulfonium ions²⁴ is thus reflected in the almost exclusive formation of *trans* addition product when aryl sulfonyl halides are added.^{2d,e,i} The formation of a mixture of *trans* addition and 2,7-rearranged products in bromination,^{2a,b,c} whereas the 2,7-rearranged product is the exclusive result in chlorination of norbornene^{2f,i} is consistent with the greater facility for neighboring group participation of the bromonium ion as compared to the chloronium ion.²⁵ A similar interpretation

JOURNAL, **78**, 4064 (1956); J. H. Brewster, *ibid.*, **78**, 4061 (1956); R. C. Cookson and J. Hudec, *Proc. Chem. Soc.*, 24 (1957).

(21) Cf. many transannular reactions with medium ring-size olefins and their oxides; A. C. Cope, *et al.*, THIS JOURNAL, **79**, 3905 (1957), and their previous papers in the same series; V. Prelog, *et al.*, *Helv. Chim. Acta*, **35**, 2044 (1952); **36**, 471 (1953); **38**, 1776, 1786 (1955).

(22) With regard to this point it is instructive to compare the present instance with the behavior of *cis*-cyclooctene. With bromine or with HBr upon the corresponding epoxide, both reactions conducted in CCl₄ solution, normal (*trans*-1,2) products were observed (A. C. Cope, *et al.*, THIS JOURNAL, **79**, 3885, 3889 (1957)). The action of performic acid upon the same olefin or the formolysis of its oxide gave a great variety of products, chiefly of rearrangement (*idem. ibid.*, **79**, 3900 (1957) and previous work therein cited). The similar behavior of a $\Delta^{9,11}$ -steroid epoxide may also be cited (N. L. Wendler, *et al.*, *ibid.*, **79**, 4476 (1957)). However, the action of HBr upon norbornene epoxide gave only rearranged (2,7) product (H. M. Walborsky and D. F. Loncrini, *J. Org. Chem.*, **22**, 1117 (1957); S. Winstein and E. T. Stafford, THIS JOURNAL, **79**, 505 (1957); H. Kwart and V. Roller, unpublished results). Cf. the effect of different reaction media upon the relative amounts of transannular vs. normal product from *cis*-cyclooctene oxide (A. C. Cope, J. M. Grisar and D. E. Peterson, *ibid.*, **81**, 1040 (1959)).

(23) This conclusion is inferred from the observations of S. Winstein, E. Greenwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948), and P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 405 (1950), on the reluctance of oxonium ions to participate in solvolytic reactions; the comments of Long and co-workers (see, for example, J. G. Pritchard and P. A. Long, *ibid.*, **80**, 4162 (1958), on the manner in which the conjugate acid of isobutylene oxide undergoes ionization, and, finally, the reports of S. Winstein and L. Goodman, *ibid.*, **76**, 4368 (1954), regarding the inability to identify oxonium ion participation in the addition reactions of allylic alcohols. Cf., A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956); S. Winstein, E. Alred, R. Heck and R. Glick, *Tetrahedron*, **3**, 1 (1958); D. S. Noyce, B. R. Thomas, and B. N. Bastian, THIS JOURNAL, **82**, 885 (1960).

(24) See, for example, P. D. Bartlett and C. G. Swain, *ibid.*, **71**, 1406 (1949) and H. Meerwein, G. Hinz, P. Hofmann, E. Kronig and E. Pfeil, *J. prakt. Chem., N.F.*, **147**, 257 (1937). For a review, see A. Streitwieser, Jr., ref. 23.

(25) For a more extensive discussion of this point see S. Winstein and R. E. Buckles, THIS JOURNAL, **64**, 2780 (1942); H. J. Lucas and

accounts for the results (exclusively IV) of mercuric acetate addition *via* an intermediate mercurinium ion^{21,26} (XXI, where X = Hg, Y = OAc).

Thus, it seems apparent that the relative amounts of rearranged (2,7) vs. unrearranged (2,3) products obtained with norbornene and its analogs is dependent not solely upon the conditions of reaction and the structural variations of the olefin but also upon the nature of the attacking reagent. The longer the lifetime and the greater the stability of the onium ion intermediates (like XXI), the smaller will be the chances for the formation of rearranged product *via* the bridged ion XXII. It must be admitted, however, that, where conditions obtain which prevent or slow the attainment of equilibrium, the actual product distribution observed will not reflect the relative stabilities of XXI and XXII.

A final example seems worthy of mention here, namely, the addition of nitrosyl chloride to olefins which is almost certainly an ionic process initiated by attack of nitrosonium ion²⁷ NO⁺. Despite the inclination of dicyclopentadiene,¹⁸ 2-pinene²⁸ and norbornadiene^{29a} toward rearrangement during ionic additions, reaction with NOCl gave products with unaltered carbon skeletons.²⁷⁻²⁹ Clearly the high stability of the presumed onium intermediates (XXI where X = N and Y = O) in such addition reactions is in accord with this idea.

Experimental

Bromination of *exo*-Trimethylene-2-norbornene (VI).—The conditions used were similar to those employed for the bromination of norbornene by Kwart and Kaplan.^{2b} A solution of 20.6 g. (0.154 mole) of VI⁵ in 35 ml. of CCl₄ was cooled in an ice-salt-bath. To this was added dropwise 24.0 g. (0.150 mole) of bromine in 25 ml. of CCl₄ at such a rate as to maintain the temperature below 0°. Uptake of bromine was rapid. After removal of the solvent at reduced pressure, the product was distilled; yield, crude, 41.2 g. (0.140 mole, 93%). Upon redistillation, the heart cut had b.p. 107–112° (0.59 mm.), *n*_D²⁵ 1.56528, *d*₄²⁵ 1.6709. The dipole moment of this fraction, *trans*-2,3-dibromo-*exo*-trimethylenenorbornene VII, was determined; μ 2.35 D.³⁰

The fractionation of a second preparation was carried out by means of a 6-inch Widmer column. The following fractions were obtained at 0.15 mm: (1) up to 83°, ca. 2 g.; (2) 84–97°, 8.9 g., *n*_D²⁷ 1.5638; (3) 98–102°, 14.4 g., *n*_D²⁷ 1.5645.

Anal. Calcd. for C₁₀H₁₄Br₂: C, 40.84; H, 4.80; Br, 54.36. Found: C, 41.11; H, 4.86; Br, 54.09.

Dehydrobromination of *trans*-2,3-Dibromo-*exo*-trimethylenenorbornane (VII).—Eight hundredths of a mole (23.3 g.) of the dibromide was added to a solution of 0.1 mole (3.9 g.) of potassium in 75 cc. of *t*-butyl alcohol distilled from

C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941), and S. Winstein and D. Seymour, *ibid.*, **68**, 119 (1946). Also, A. Streitwieser, Jr., ref. 23.

(26) H. J. Lucas, F. R. Hepner and J. Winstein, *ibid.*, **61**, 3102 (1939); H. B. Henbest and B. Nichols, *J. Chem. Soc.*, 227 (1959); H. B. Henbest and R. S. McElhinney, *ibid.*, 1834 (1959); and J. Chatt, *Chem. Revs.*, **48**, 7 (1951).

(27) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 669; L. J. Beckham, W. A. Fessler and M. A. Kise, *Chem. Revs.*, **48**, 319 (1951). (28) J. L. Simonsen, "The Terpenes," 2nd Ed., Vol. II, Cambridge University Press, Cambridge, England, 1949.

(29) (a) G. T. Youngblood and P. Wilder, Jr., *J. Org. Chem.*, **23**, 684 (1958), and refs. therein cited; (b) for a summary of the literature with regard to dicyclopentadiene, see "Elsevier's Encyclopaedia," Vol. 13, ref. 3.

(30) Very kindly carried out by Dr. A. J. Petro, Princeton University, by means of a heterodyne heat apparatus, employing the pure liquid material (cf. C. P. Smyth, in A. Weissberger, Ed., "Physical Methods of Organic Chemistry," Vol. I, Pt. II, Interscience Publishers, New York, N. Y., 2nd Ed., 1949, Chapt. XXIV, p. 1633).

calcium hydride. The resulting mixture was refluxed for 8 hours.

The reaction mixture was then poured into an equal volume of water and extracted with three 50-cc. portions of ether. The combined ether extracts were dried over magnesium sulfate, and the *t*-butyl alcohol and ether were removed by slow distillation through a 6-inch Widmer column. Fractionation of the residue *in vacuo* afforded the following fractions at 1.5 mm.: (1) up to 72°, ca. 0.5 g.; (2) 72–76°, 7.3 g., n_D^{20} 1.5366; (3) 74–78°, 7.35 g., n_D^{20} 1.5371.

Anal. Calcd. for $C_{10}H_{13}Br$: C, 56.35; H, 6.20; Br, 37.45. Found: C, 56.59; H, 6.23; Br, 37.55.

A second preparation of this compound, 2-bromo-*exo*-trimethylene-2-norbornene (X), gave a 92% yield of material, b.p. 102.5–103.5° (12 mm.), n_D^{20} 1.53686.

Oxidation of 2-Bromo-*exo*-trimethylene-2-norbornene (X).—Using the procedure of Birch, Oldham and Johnson,³¹ employing dilute aqueous sodium permanganate, the dibasic acid XI was obtained in 70–80% yield, m.p. 182.5–183.0° (lit.³² m.p. 182–184°). Mixed m.p. with an authentic sample of m.p. 182.4–182.9° was 182.4–182.9°.

Solvolysis of 2-Bromo-*exo*-trimethylene-2-norbornene (X).—Three hundredths of a mole (6.35 g.) of the olefin bromide X was refluxed with 0.75 mole (5.6 g.) of lithium carbonate in 100 cc. of water for 12.5 days. During this time the mixture was stirred continuously with a magnetic stirrer.

After cooling to room temperature, the slurry was diluted with 150 cc. of water and continuously extracted with ether for 24 hours. The ether extract was dried over magnesium sulfate and the ether removed by slow distillation through a 6-inch Widmer column. Distillation of the residue through the same assembly gave as the predominant fraction, b. 56–58.5° (0.5 mm.). This material showed a strong carbonyl absorption in the infrared. However, it also gave a strong, positive reaction with silver nitrate in the sodium fusion procedure.

In an attempt to separate the ketonic component, the crude material was treated with a solution of 2,4-dinitrophenylhydrazine in methanolic hydrochloric acid. Recrystallization of the derivative so obtained from ethanol yielded an orange product, m. 141–146°. An authentic sample of the 2,4-dinitrophenylhydrazone of 2-keto-*exo*-trimethylene norbornane (XII) had a melting point of 155.3–156.3° (*vide infra*).

The crude derivative from the solvolysis was chromatographed on a 35 × 300 mm. column of G. F. Smith silicic acid. The crude was absorbed from a benzene solution and developed with 15% chloroform in hexane. After developing, the column had separated into a large red-orange band residing about in the middle and a small brown-red band at the top. The column was extruded, and the red-orange band eluted with ethanol. Concentration of the ethanolic solution, followed by crystallization, yielded the 2,4-dinitrophenylhydrazone, m. 152.5–154.8°. On mixing with an authentic sample of this derivative, it melted from 154.5–156°. The infrared spectra of the two derivatives were identical.

2-Keto-*exo*-trimethylenenorbornane 2,4-Dinitrophenylhydrazone.—Two hundredths of a mole (0.29 g.) of the ketone³³ XII was added to a hot solution of excess 2,4-dinitrophenylhydrazine in methanolic hydrochloric acid. An orange solid separated almost immediately. Several recrystallizations from ethanol afforded the 2,4-dinitrophenylhydrazone as fine, orange needles, m. 155.3–156.3°.

Anal. Calcd. for $C_{16}H_{17}N_3O_4$: C, 58.18; H, 5.45; N, 16.97. Found: C, 58.21, 58.19; H, 5.39, 5.45; N, 17.05, 17.24.

Bromination of *exo*-Trimethylenenorbornene in Pyridine Solution.—Two and four-tenths moles (321 g.) of the olefin were dissolved in one liter of Karl Fisher pyridine in a three-necked flask fitted with a mechanical stirrer, dropping funnel, thermometer and condenser. The entire apparatus was

protected from moisture with drying tubes. With continuous stirring and cooling, 2.5 moles (400 g.) of bromine was added at such a rate that the temperature did not rise above –5° during the reaction period.

After the addition was completed, the mixture was filtered to separate the pyridinium bromide. The solid salt was washed with 500 cc. of carbon tetrachloride, and these washings added to the filtrate. The filtrate was in turn washed with 500 cc. of water containing about 25 g. of sodium bisulfite to remove excess bromine. These aqueous washings were extracted with 100 cc. of carbon tetrachloride and this was added to the organic phase. The organic phase was then washed with ice-cold 6 *N* sulfuric acid until the washings were strongly acidic. After washing out the excess acid with water, the carbon tetrachloride extracts were dried over calcium chloride.

The carbon tetrachloride was removed *in vacuo* at ambient temperatures and the residue fractionated under reduced pressure.

Fraction	Temp., °C.	Press., mm.	Wt., g.	n_D^{20}
1	Less 70	0.3–0.4	Trace	1.5105
2	70–76	.2–0.3	19.6	1.5515
3	80–92	.17	43.6	1.5629
4	92–99	.20	90.45	1.5647
5	95–100	.17	81.57	1.5651
6	95–98	.18	75.58	1.5655
7	98–105	.20	59.26	1.5662
8	100–120	.30	17.59	1.5682
9	120–125	.3–0.5	50.15	1.5771

Fractions 3 through 8 were refractionated through a 6-inch Widmer still. From this operation was obtained 317 g. of *trans*-2,3-dibromo-*exo*-trimethylenenorbornane (VII), 95–99° (0.2 mm.), n_D^{20} 1.5651.

Fractionation of cut 9 through a 6-inch Widmer still afforded 30 g. of a dibromide that crystallized on standing at room temperature, b. 115–125° (80 μ) (called "solid" dibromide) (VIII).

Anal. Calcd. for $C_{10}H_{14}Br_2$: C, 40.82; H, 4.76. Found: C, 40.89, 41.18; H, 4.99, 4.99.

Careful inspection of the infrared spectra of intermediate cuts between the boiling points of VII and VIII showed no evidence for the presence of a third dibromide.

Refractionation of cut 2 yielded 5.30 g. of a liquid bromide, b. 55–57° (0.35 mm.), having n_D^{20} 1.5453. From the boiling point and refractive index data, this product appeared to be a monobromide as judged from the analytical data and a negative unsaturation test. Furthermore, both the analytical data and infrared data support the assignment *exo*-2-bromo-*endo*-trimethylenenorbornane (XIII).

Anal. Calcd. for $C_{10}H_{13}Br$: C, 56.34; H, 6.10. Found: C, 56.50, 56.63; H, 6.24, 5.98.

Hydrogenolysis of XIII.—Employing a procedure using 0.8 g. of 10% palladium-on-charcoal catalyst (Baker), 2.50 g. of XIII in 100 ml. of 95% ethanol in which 1.25 g. of potassium hydroxide was dissolved, after the fashion of Fieser and Huang,³⁴ the uptake of hydrogen ceased in about 1.5 hours. The product was worked up by drowning in water, neutralizing with acid and extracting with pentane. The extracts were dried over potassium carbonate and distilled through a 16-inch Widmer column. The product (1.1 g.) was collected at atmospheric pressure at 151–159°. Vapor phase chromatographic analysis with a column containing an Apiezon on firebrick (80–100 mesh) packing showed four peaks. The principal component, trimethylenenorbornane (XIV), was computed to be present in 96% concentration and none of the remaining components was present to a greater extent than 3%. Compound XIV gave a negative Beilstein test indicating the absence of any halogen bonds and a negative permanganate test for unsaturation. The infrared data were used to complete the characterization of XIV.

Dipole Moment on the "Solid Dibromide" (VIII).—This was determined by the method given in references 2b and 3a to be 3.7 D.

(34) L. F. Fieser and W. Y. Huang, *THIS JOURNAL*, **75**, 4937 (1953).

(31) S. F. Birch, W. J. Oldham and E. A. Johnson, *J. Chem. Soc.*, **818** (1947).

(32) (a) H. A. Bruson and T. W. Riener, *THIS JOURNAL*, **67**, 723 (1945); (b) P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946); (c) P. R. Schleyer and M. M. Donaldson, *ibid.*, **78**, 5702 (1956); (d) P. Wilder, Jr., C. F. Culbertson and G. T. Youngblood, *ibid.*, **81**, 655 (1959).

(33) Prepared according to the method of H. A. Bruson and T. W. Riener, ref. 32a.

Dehydrobromination of the "Solid" Dibromide VIII.—Forty-two hundredths of a mole (1.64 g.) of potassium was dissolved in 50 cc. of *t*-butyl alcohol distilled from calcium hydride. To this solution was added 0.035 mole (10.3 g.) of the dibromide dissolved in 35 cc. of *t*-butyl alcohol. The mixture was refluxed for 18 hours.

At the end of this time, it was poured into an equal volume of water and extracted with three 75-cc. portions of ether. The combined ether extracts were dried over magnesium sulfate and the ether and *t*-butyl alcohol were removed by slow distillation at atmospheric pressure. On distilling the residue *in vacuo*, one fraction was obtained, b. 70–80° (0.3 mm.). This product was highly unsaturated to permanganate but on oxidation with aqueous sodium permanganate according to the procedure of Birch, Oldham and Johnson²⁷ the product obtained in only small yield possessed a long melting point range. None of the dibasic acid XI could be recovered which would have been expected from a vinyl bromide structure, (see above). Both the infrared data and the n.m.r. data support the structure of 7-bromo-*endo*-trimethylene-2-norbornene (XV) assigned to this product.

Anal. Calcd. for C₁₀H₁₃Br: C, 56.34, H, 6.10. Found: C, 56.64, 56.27; H, 6.32, 6.16.

anti-7-Chloronorbornene (Xc) was prepared according to the procedure of Kwart and Miller.^{2d}

2-Bromo-2-norbornene (Xa) and syn-7-bromo-2-norbornene (Xb) were prepared according to the procedures given by Kwart and Kaplan.^{2b}

Oxidation of VI to the Diol XVI.^{s,b}—To a stirred solution of 20 g. (0.149 mole) of VI in 200 ml. of ether and 60 ml. of 88% formic acid was added 42 ml. of 30% H₂O₂. After stirring overnight, the ether was removed *in vacuo* and the product saponified carefully with sodium hydroxide. Crude product (23.3 g., 0.139 mole, 93%) was isolated as a light yellow oil by extraction with ether, drying the solution with anhyd. Na₂SO₄, and evaporating the solvent at water-pump pressure. The vicinal diol content of the product, *vide infra*, was determined on this material.

Purification of 16 g. of the crude diol by distillation at 3.5 mm. pressure through a 10-cm. Vigreux column gave the following results: (1) 145–147°, 8.7 g.; (2) 147–153°, 3.5 g.; (3) 153°-up, 1.3 g.; (4) pot residue, 2.2 g. The greatest portion of the material had b.p. 146–147°, and was a highly viscous colorless oil. A small amount of fraction 2 solidified in the receiver, but initial attempts at characterization of this material were without success. The analytical sample, an oil, was obtained by redistillation, b.p. 132.5–133.5° (0.03–0.05 mm.). Chromatography of the crude diol on alumina did not give any separation into isomers detectable by differences in the infrared spectra of the various cuts.

Anal. Calcd. for C₁₀H₁₆O₂: C, 71.39; H, 9.59. Found: C, 71.62; H, 9.71.

Quantitative Determination of Vicinal Diol Content.—The procedure followed was that of Siggia.¹¹ The standard periodic acid-acetic acid solution containing a weighed portion of the crude diol was allowed to stand for 0.5 hour at room temperature before titration. The result was indistinguishable from that of a blank indicating no vicinal diol content. As a check on the procedure, a similar determination was carried out on pinacol; titration showed 99.6% vicinal diol content.

Bis-phenyl Urethan Derivative of XVI.—After several recrystallizations from benzene-hexane, the m.p. was 160.0–160.5°.

Anal. Calcd. for C₂₄H₂₆O₂N₂: C, 70.91; H, 6.45. Found: C, 71.05; H, 6.50.

***p*-Nitrobenzylidene Derivative XVII.**—Diol XIII (2.0 g.) was converted to the *p*-nitrobenzylidene acetal by the method

of Walborsky and Loncrini.^{2b} By successive concentrations of the mother liquors after filtration, a virtually quantitative yield of derivative was obtained. Recrystallization from 60–70° ligroin to constant m.p. 127.8–128.6° gave material of analytical purity.

Anal. Calcd. for C₁₇H₁₉O₄N: C, 67.76; H, 6.36. Found: C, 67.69; H, 6.30.

Infrared Spectrum.—The infrared absorption of the diol XVI in the OH stretching region was determined with a Perkin-Elmer model 21 spectrophotometer equipped with a LiF prism. An approximately 0.005 *M* solution of the compound in CCl₄ had peaks at 3617 (free) and 3545 cm.⁻¹ (intramolecularly hydrogen bonded). Dilution did not alter the positions or the relative intensities of these bands. The comparable values for *exo*-2-*syn*-7-dihydroxynorbornane (V, X = Y = OH) are 3621 and 3545 cm.⁻¹.^{2s,12}

Determination of Boric Acid Conductivity.—Compound XVI did not enhance the conductivity of a boric acid solution; hence, no boric acid complex formed.¹² This behavior was identical to that of *exo*-2-*syn*-7-dihydroxynorbornane (V, X = Y = OH) but contrary to that of both *endo* and *exo* isomers of *cis*-2,3-dihydroxynorbornane.¹²

Attempted Synthesis of Trimethylenenorbornene (XIV).—2-Keto-*exo*-trimethylenenorbornane²⁹ (65 g.) was converted to the hydrazone by refluxing overnight with a large excess (56 g.) of anhydrous hydrazine in ethanol (200 ml.). After evaporation of the solvent, water, and excess hydrazine at water-pump pressure and finally at oil-pump pressure there remained 73 g. of crude, solid hydrazone. Characterization of this material was not attempted.

To a rapidly stirred slurry of 108 g. (0.5 mole) of freshly prepared mercuric oxide in 200 ml. of diethylene glycol was added, dropwise, a solution of 71 g. of the above crude hydrazone in the same solvent. Although the reaction mixture turned dark almost immediately, no nitrogen was evolved initially. The temperature rose suddenly, nitrogen was evolved copiously and the resultant frothing was difficult to control. After the reaction subsided, addition was completed and the reaction mixture was heated with provision for take-off of the product. Even though heating was continued until the pot temperature was 240° no hydrocarbon fraction was obtained. A large amount of mercury had formed during the course of the reaction. The fate of the organic material was not determined.

The above procedure was modeled after that employed by Alder and co-workers⁸ for the preparation of norbornene from norbornanone hydrazone. A second attempt, employing trimethylene glycol as solvent and hydrazone purified by reduced pressure fractional distillation, was also unsuccessful. Very much azine formed during the distillation of the hydrazone. Although it is quite possible that proper conditions might be found for carrying out this transformation, further investigation was abandoned.

Nuclear Magnetic Resonance Measurements.—The data recorded in Table II were obtained by means of a Varian High Resolution nuclear magnetic resonance spectrometer and associated electromagnet at 40 Mc. and field of approximately 10,000 gauss. Spectra were calibrated in terms of displacements in cycles per second from the proton resonance of water at 25°.

Infrared Spectra.—The spectra were determined on thin liquid films with spectrometers equipped with NaCl and LiF prisms. The positions of many of the most significant bands have been mentioned in the text. Complete data are available from P. R. S.

WHITE OAK, MD.
NEWARK, DEL.
PRINCETON, N. J.