3-one (7-$d_2$). 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (7) (1.5 g, 0.0055 mol) and sodium hydride (0.01 g, 0.0006 mol) in 100 ml of dioxane and 20 ml of deuterium oxide was stirred for 72 hr at room temperature. The reaction mixture was then extracted with chloroform and dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. There was obtained 1.2 g of dideuterated ketone 7-$d_2$: nmr (CDCl$_3$) $\delta$ 7.23 (m, 10 H, aromatic), 6.23 (t, 2 H, vinylic hydrogens H$_{6,7}$), 2.98 (m, 2 H, bridgehead hydrogens H$_{1,5}$) and 2.18 (m, 2 H, hydrogens H$_8'$, H$_8''$).

Formation of 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one Monoanions 8a,b and 12a,b. (a) Formation of Monoanions 8a,b in THF. This reaction, as well as each of the subsequently described monoanion formations, was carried out in a 15-ml, three-necked, round-bottom flask equipped with a magnetic stirrer, a septum, and a condenser connected to a gas collection apparatus consisting of an inverted 250-ml graduated cylinder filled with water. The flask was charged with 0.09 g (0.0037 mol) of sodium hydride, flushed with nitrogen, and closed to the atmosphere. A solution of 0.5 g (0.0018 mol) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (7) in 3 ml of THF was introduced into the reaction flask through the septum by means of a syringe. Reaction occurred quite readily as shown by the immediate evolution of hydrogen and was completed within 1 hr. The reaction mixture was then quenched with 4 ml of water. The organic layer was dried over magnesium sulfate and evaporated under reduced pressure to give 0.455 g (91 % yield) of the starting ketone 7, as shown by ir and nmr analysis of the crude reaction product.

In another experiment, a solution of 0.5 g (0.0018 mol) of ketone 7 in 2 ml of THF-$d_8$ was added to 0.09 g (0.0037 mol) of sodium hydride and the reaction mixture was stirred until 1 equiv of hydrogen gas had been evolved. Stirring was then discontinued, the excess sodium hydride was allowed to settle to the bottom of the flask, the supernatant brown liquid was transferred by means of a syringe into an nmr tube equipped with a septum, and the nmr tube was flushed with nitrogen. The nmr tube was centrifuged for 3–4 min at 1500 rpm, the liquid was transferred into a second nmr tube, and the spectrum of the solution was recorded on a Varian A-60 and an HA-100 instrument. The 100-MHz spectrum of the solution is shown in Figure 2. Integration of the peaks corresponding to protons H$_{6a}$ and H$_{6b}$ in the 60-MHz spectrum showed that isomeric enolates 8a and 8b were present in a ratio of 2:1.

(b) Formation of Monoanions 8a,b in DMSO and HMPA. 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (7) (0.5 g, 0.0018 mol) in 2 ml of DMSO or HMPA was treated with 0.09 g (0.0037 mol) of sodium hydride as described above, and the nmr spectrum of the resulting monoanions was recorded on a Varian A-60 instrument. The resonances observed were the same as those found for monoanions 8a,b in THF-$d_8$, except that the signals below $\delta$ 4.5 were obscured by the solvents. The ratio of the peaks corresponding to protons H$_{6a}$ and H$_{6b}$ was 2:1. Subsequent quenching of the solutions with water produced the starting ketone 7.

(c) Formation of Monoanions 12a,b in THF. 2,4-Dideuterated ketone 7-$d_2$ (0.5 g, 0.0018 mol) was treated with 0.09 g (0.0037 mol) of sodium hydride as described above and was subsequently quenched with deuterium oxide to give 0.40 g (80 % yield) of starting ketone 7-$d_2$, as shown by ir and nmr analysis of the crude reaction mixture.

In another experiment, monoanions 12a,b were formed from 0.5 g (0.0018 mol) of ketone 7-$d_2$ and 0.09 g (0.0037 mol) of sodium hydride in 2 ml of THF-$d_8$, and the spectrum of the solution was recorded on a Varian HA-100 instrument. The spectrum was practically identical with that of enolates 8a,b (Figure 2), except that the former had only residual peaks at $\delta$ 3.18 and 3.75.

Formation of 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one Dianion 9 in THF and Subsequent Deuteration with Deuterium Oxide. 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (7) (0.5 g, 0.0018 mol) was treated with 0.09 g (0.0037 mol) of sodium hydride in 2 ml of THF as described earlier to produce the monoanions 8a,b. The reaction was then treated with 2 ml (0.00316 mol) of 1.58 $M$ solution of $n$-butyllithium in hexane and was stirred for 4 hr. The brick-red solution was then cooled to $-5°$ and quenched with 4 ml of deuterium oxide, to give 0.37 g (74%) of dideuterated ketone 7-$d_2$, as shown by gas chromatographic analysis and nmr of the crude reaction mixture.

In another experiment dianion 9 was formed in THF-$d_8$ as described above and the brick-red solution was then transferred into an nmr tube containing a sealed capillary tube with TMS, and the nmr spectrum was recorded on a Varian XL-100 instrument. The spectrum is displayed in Figure 1.

# Reactions of 1,1-Dimethyldiazenium Bromide with Bicyclic Olefins. N-(Dimethylamino)aziridines

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Abstract: Norbornadiene (3) reacts with 1,1-dimethyldiazenium bromide (1) in 1.5 $M$ hydrobromic acid to give 52% of the endo-N-dimethylaminoaziridine (6), 4% of the other endo product 7, and 39% of 8, 9, 10, and 11, nortricyclene products of exo attack. The relative yields of 7–11 are greater with increasing hydrobromic acid concentrations, and that of 6 diminishes. Endo addition to such an extent is attributed to preliminary 2,6 cycloaddition of 1 to 3, and it has been shown to be reversible. Norbornene 2 also gives the aziridine 4 (here the exo isomer) and 5. The reaction of 4 with hydrobromic acid has been shown to give 5. endo-5-Norbornene-2-methanol gives 13, and benzonorbornadiene gives 14, products expected from their prior electrophilic additions.

I n hydrobromic acid 1,1-dimethyldiazenium bromide (1) adds like a dienophile to 1,3-alkadienes[1] and like an electrophile with some styrenes,[1b] but it does not react with ordinary olefins. However, such reactions occur with the more reactive bicyclic olefins.

With norbornene (2) or norbornadiene (3), the exo or endoaziridines (4 or 6) are important products. Both are remarkably stable in the aqueous acidic reaction mixtures. endo-5-Norbornene-2-methanol and benzonorbornadiene give expected products.[2,3]

(1) (a) W. H. Urry, H. W. Kruse, and W. R. McBride, *J. Amer. Chem. Soc.*, 79, 6568 (1957); (b) W. H. Urry, P. Szecsi, C. Ikoku, and D. W. Moore, *ibid.*, 86, 2224 (1964); (c) K. N. Zelenin and T. P. Bezhan, *Zh. Org. Khim.*, 6, 2206 (1970); (d) H. Böhme, K. Hartke, and A. Müller, *Chem. Ber.*, 96, 607 (1963), diene addition of (C$_5$H$_5$)$_2$N= CH$_2$$^-$Cl$^-$.

(2) (a) H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 221, 227 (1959); (b) R. Moriarty, *Tetrahedron Lett.*, 1165 (1964); (c) K. C. Ramey, *et al.*, *J. Amer. Chem. Soc.*, 89, 2401 (1967).

(3) (a) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, 32, 3727, 3838 (1967); (b) K. Tori, *et al.*, *Tetrahedron Lett.*, 9, 2921 (1966).

Typically in reaction 1, **2** with a 10% excess of 1.0 *M* **1** in 3.1 *M* hydrobromic acid was stirred at −5–0° for 9 hr. The oil that separated when the reaction mixture was made basic was distilled to give a 59% yield of **4** and a residual product mixture with **5** as its main component. The latter probably is formed from **4** since a 92% yield of the hydrobromide of **5** precipitated when **4** was added to 8.8 *M* hydrobromic acid at −15°.



$$(1)$$
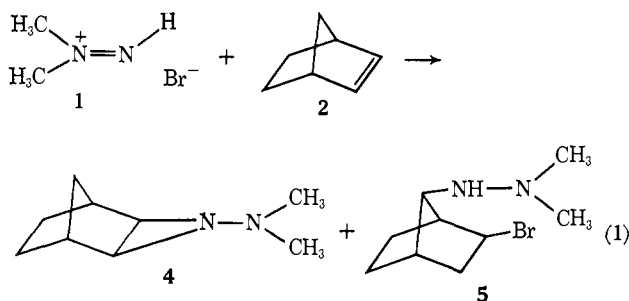
Higher hydrobromic acid concentrations in the reactions of **1** with **3** decrease the yields of **6** and the ratios of endo and exo attack ([**6** + **7**]/[**8** + **9** + **11**]: reactions 2a, 1.43; 2b, 0.47; and 2c, 0.31) and of hydroxy- to bromonortricyclenes ([**8** + **9**]/[**10** + **11**]: reactions 2a, 1.8; 2b, 0.74; and 2c, 0.17) (Scheme I).

**Scheme I**
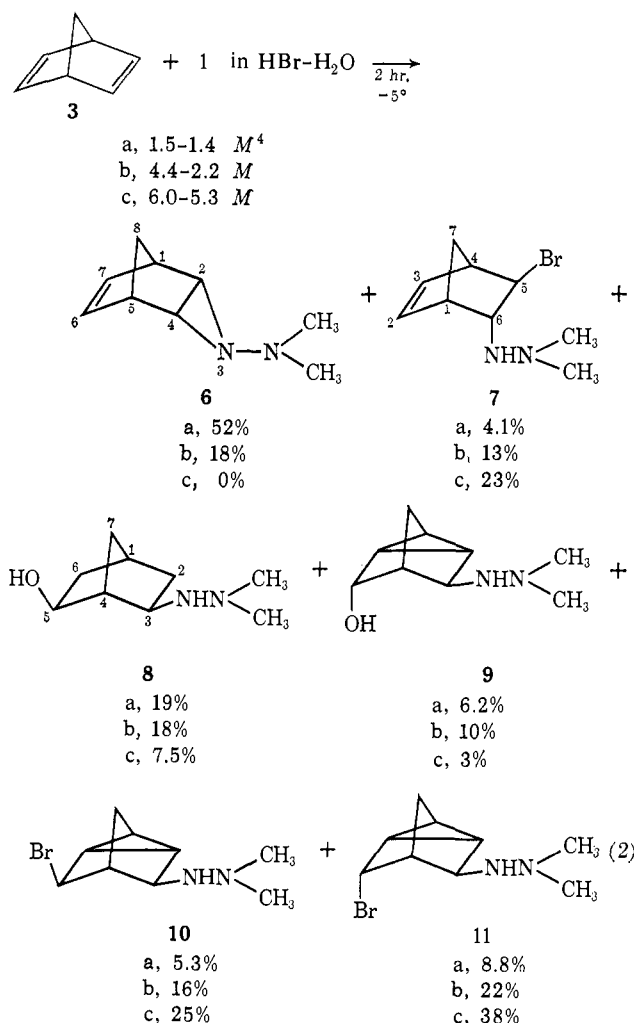


(4) Initial and final hydrobromic acid concentrations. The decline is due to consumption of the acid as **7**, **10**, and **11** are converted to their hydrobromides since none results from their formation.

Conventional separation of these product mixtures was not possible since they decomposed during distillation, and vapor phase or dry column chromatography. Hence, products were isolated in the various ways described below. Their nmr spectra were determined and provided the basis for the nmr analyses that gave the above yields.

Reaction mixture 2a was made basic and extracted with ether. Evaporation gave a mixture of **6, 7, 10** and **11** with 6% of unreacted **3** and some tetramethyltetrazene. Most of the **6** was recovered by bulb-to-bulb distillation at high vacuum and 25°. Redistillation of this fraction gave pure **6**. The symmetry of **6** is apparent from the simplicity of its nmr spectrum: (benzene, HA-100) δ 5.73 (t, 2, $J_{7,1} + J_{7,5} = J_{6,5} + J_{6,1} = 4.0$ Hz, 6 and 7 HC=CH), 2.62 (m, 2, 1 and 5 bridgehead CH), 2.31 (4 line m, 2, $J_{2x,1} + J_{2x,5} = J_{4x,5} + J_{4x,1} = 4.1$ Hz, 2 and 4 HCN), 2.21 (s, 6, NCH₃), and 1.50 ppm (t, 2, $J_{8,1} = J_{8,5} = 1.5$ Hz, 8 CH₂). With irradiation at δ 2.62, all other absorptions became singlets to establish **6** as the endo aziridine. The multiplet at δ 2.31 must be due to virtual coupling in the four-proton system comprised of the exo hydrogen atoms attached to the aziridine ring and the bridgehead ones (bridgehead and endo hydrogen atoms do not couple in norbornenes[5]). Also, the shielding of the olefinic hydrogen atoms known[6] for such substances with endo three-membered rings is apparent while shielding of one of the hydrogen atoms of the methylene bridge found with such exo compounds is absent (see below). As further structural evidence, hydrogenation of **6** gave **12**, the endo isomer of **4**. Their nmr spectra confirm this isomerism. That of **4** shows the known[7] shielding by exo aziridine rings of its 8-anti hydrogen atom (δ 0.51, dm) compared with its 8-syn one (δ 1.47). This AB absorption of **12** is at δ 1.54 and 1.49.

The remaining aqueous reaction mixture 2a was saturated with potassium carbonate, and then continuously extracted with ether for 7 days. Evaporation of this extract gave a mixture of 75% **8** and 25% **9**. Three recrystallizations from 90% ethanol gave pure **9**. Product recovered from filtrates was recrystallized from anhydrous ethanol to give **8**.

Most of the product crystallized as reaction mixture 2c was stored at −20° for 15 hr. Its filtration gave 87% of a solid containing 36% **7**, 27% **10**, and 37% **11** hydrobromides. Two recrystallizations from ethanol gave the hydrobromide of **10**. Fractional recrystallization of filtrate-derived material from ethanol gave a mixture of 95% **11** and 5% **10** hydrobromides that could not be further purified.

Nmr evidence supports the structures assigned to **8, 9, 10,** and **11**. Their spectra resembled other 3,5-disubstituted nortricyclenes with high-field multiplets (δ 1.01–1.6) due to their cyclopropyl hydrogens[9] but no olefinic absorption. The triplets giving maximal downfield shifts (except for NCH₃ singlets) in their nmr spectra in trifluoroacetic acid were assigned to hydrogen atoms attached to the hydrazino-bearing
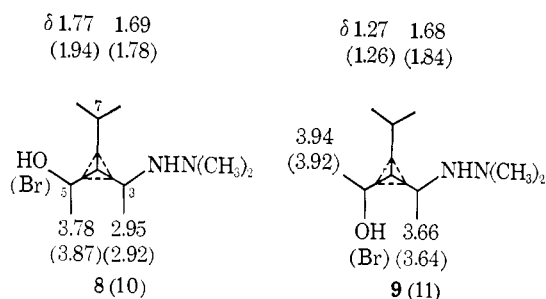
(5) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

(6) S. C. Clarke, J. J. Frayne, and B. L. Johnson, *Tetrahedron*, **25**, 1265 (1969).

(7) K. Tori, *et al.*, *Tetrahedron Lett.*, 869 (1965); 2921 (1966).

(8) R. S. Neale and E. B. Whipple, *J. Amer. Chem. Soc.*, **86**, 3130 (1964).

C-3. Then, the comparison shown in the molecular perspectives below (nmr, CDCl$_3$, A-60) reveals their stereochemistry. Substances **9** and **11** with those triplets due to hydrogens at C-3 so far downfield, and one of those of the methylene bridge similarly upfield, must have endo substituents (OH or Br) at C-5. Deshielding by functional groups so contiguous is well documented.[8,9]



δ 1.77   1.69
(1.94)  (1.78)

HO
(Br) 5     NHN(CH$_3$)$_2$
        3
3.78   2.95
(3.87)(2.92)
**8 (10)**

δ 1.27   1.68
(1.26)  (1.84)

3.94
(3.92)      NHN(CH$_3$)$_2$

OH  3.66
(Br) (3.64)
**9 (11)**

Attempts to isolate **7** from reaction mixture 2 became unnecessary. When **6** was added dropwise to excess 8.8 *M* hydrobromic acid at 0°, and the reaction mixture then was held at −20° for 8 hr, a quantitative yield of the hydrobromide of **7** precipitated. Its treatment with aqueous base gave 100% of **7**. Its chloro **7**$_{Cl}$ and iodo **7**$_I$ analogs were similarly prepared from **6** using concentrated hydrochloric and hydriodic acids. The stabilities of **7**, **7**$_{Cl}$, and **7**$_I$ were remarkable since they remained unchanged for weeks when stored at 0°. This accords with the small conversion to the exo aziridine observed[10] when *exo*-2-amino-*endo*-3-chlorobicyclo[2.2.1]heptane with aqueous potassium hydroxide solution was held at reflux for 70 hr. These molecules cannot attain the trans-coplanar transition state that usually gives aziridines so readily. More remarkably, attack by the dimethylamino part of the hydrazino function upon the vicinal halogen-bearing carbon to give the diazetidinium salts previously observed[1b] is also slow.

Its nmr spectrum suggests that **7** is a 5-exo-6-endo-disubstituted norbornene (also **7**$_{Cl}$ and **7**$_I$). Its triplet at δ 3.14 (CCl$_4$, HA-100) is due to an endo hydrogen atom at C-5 since it was shown to be coupled (both *J* = 2.5 Hz) with the 7-syn (δ 1.64, dq) and 6-exo- (δ 3.68, dd) hydrogens while the latter is coupled (*J* = 3.2 Hz) to the 1-bridgehead hydrogen (δ 2.87, m). A comparison of the nmr spectra of **7**, **7**$_{Cl}$, and **7**$_I$ was necessary since, unfortunately, both exo and endo multiplets gave about the same downfield shift in trifluoroacetic acid. However, the endo hydrogen atoms are attached to the halogen-bearing carbons since their triplets moved to higher field with the higher halogens (**7**$_{Cl}$, δ 3.18; **7**, 3.14; and **7**$_I$, 3.01) while their exo multiplets showed the inverse effect of the halogens on β hydrogens (**7**$_{Cl}$, δ 3.51; **7**, 3.68; and **7**$_I$, 3.85[11]).
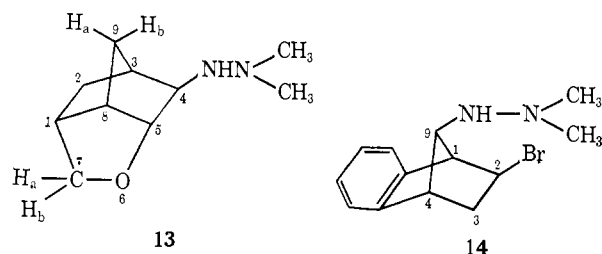
The reaction of **1** in hydrobromic acid with *endo*-5-norbornene-2-methanol gave **13**. Its methiodide, oxalate, and hydrochloride salts were prepared. The nmr and mass spectra confirm the assigned structure,

and the former closely resembles those of other 4-exo-substituted 6-oxatricyclo[3.2.1.1$^{3,8}$]nonanes.[2c] Rearrangement common to the additions of electrophilic reagents to benzonorbornadiene occurs in its reaction with **1** to give **14**. Again, its nmr spectrum supports



**13**



**14**

this structure (see Experimental Section), and it is like those of other such substances.[3]

The endo attack of **1** upon norbornadiene **3** as a major reaction is contrary to previous studies of such electrophilic additions wherein only products of exo attack have been observed.[3,12,13] However, peracetamidic acid with **3** gave 3.5% of its endo epoxide[14] and 21% of bicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehyde shown[15] to be from the reaction of acid with exo epoxide. Carbenoids also give some endo product. Our repeat of the reaction of **3** with methylene iodide and zinc–copper couple[16] gave *exo*- and *endo*-tricyclo[3.2.1.0$^{2,4}$]octanes in a 7:1 ratio. A similar ratio of their 3,3-dibromo derivatives results from **3** with bromoform and potassium *tert*-butoxide.[17]

Partial endo addition also occurs with some catalytic[18] and free radical[3a,19] reactions. Examples of the former are hydrosilations in the presence of platinum or chloroplatinic acid,[18a,b] but the high endo attack claimed in such reactions of **3** is based in part upon the assumption that it gives the nortricyclene products (here both endo and exo additions would give the same nortricyclenes). Also, the addition of hydrogen cyanide to **3** in the presence of Pd[P(OC$_6$H$_5$)$_3$]$_4$ gives 86% *exo*- and 14% *endo*-2-cyanobicyclo[2.2.1]hept-5-enes.[18c] Free radical addition of trimethylsilane to **3** gave 53% nortricyclene, 28% exo, and 7% endo norbornenes.[18a]

The dominant endo addition may involve initial cycloaddition to give **15** since **1** reacts like a dienophile with 1,3 dienes[1] and **3** gives 2,6 adducts with such reactants.[20] The indicated rearrangement of **15** would give **16**. Nearly all of the **7** formed in reaction 2a (**6** is quite stable in 1.5 *M* HBr, see below) must result from attack by bromide ion upon **16** before it can reach equilibrium with **17**. The stability of **6** in acid may be attributed to **17** being the dominant cation in the equilibrium since aziridine nitrogen is of reduced basicity (p$K_b$ of aziridine is 6.0 and that of dimethylamine is

(9) (a) S. J. Cristol, J. K. Harrington, and M. S. Singer, *ibid.*, **88**, 1529 (1966); (b) A. Ferretti and G. Tesi, *J. Chem. Soc.*, 5203 (1965); J. Passavirta, *Suom. Kemistilehti B*, **42**, 37 (1969).

(10) K. Schrage, *Tetrahedron*, **23**, 3033 (1967).

(11) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1969, p 164.

(12) S. Winstein, *J. Amer. Chem. Soc.*, **83**, 1516 (1961).

(13) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2719 (1966).

(14) J. T. Lumb and G. H. Whitham, *J. Chem. Soc.*, 1189 (1964).

(15) J. Meinwald, *et al.*, *Tetrahedron Lett.*, 1789 (1965).

(16) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959); *cf.* K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6374 (1960).

(17) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963).

(18) (a) H. G. Kuivila and C. R. Warner, *ibid.*, **29**, 2845 (1964); (b) M. M. Martin and R. A. Koster, *ibid.*, **33**, 3428 (1968); (c) E. S. Brown and E. A. Rick, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14**(2), B29 (1969).

(19) H. Kwart and J. T. Nyce, *J. Amer. Chem. Soc.*, **86**, 2601 (1964).

(20) Bibliography: S. J. Cristol, E. L. Allred, and D. L. Wetzel, *J. Org. Chem.*, **27**, 4058 (1962).

3.28 in water at 25°). Similar reasons account for the slow reaction of 4 with acids (Scheme II). Another

**Scheme II**

17

⇵

15 ⇌ 16 $\xrightarrow{Br^-}$ 7

1 + 3

18 → 19

$H_2O \mid Br^-$

8–11     (3)

reason for the stability of 6 in acid is that 16 does not have the favorable juxtaposition of the olefinic π electrons that permits the rapid rearrangement of 18. The latter must be concerted since it gives no bicyclic products. No 5-exo-bromo-7-anti-(2,2-dimethylhydrazino)-bicyclo[2.2.1]hept-2-ene was observed to correspond to the 5-exo-,7-anti-dibromonorbornene found as a minor product in the bromination of 3,[21] and no dimethylhydrazone of bicyclo[3.1.0]hex-2-ene-endo-6-carboxaldehyde via a rearrangement like that of the exo epoxide from 3.[15]

Presumably, an aziridinium ion like 18 derived from norbornene slowly rearranges to give 5, but rapidly reaches equilibrium with its stable N,N-dimethylhydrazinium cation. Rearrangement occurs more readily with the analogous aziridinium ion from benzonorbornadiene; and, with that from the endo-5-norbornene-2-methanol, intramolecular attack by its hydroxyl function occurs.

Since 6 reacts rapidly with 8.8 M hydrobromic acid to give only the other endo product 7, it was surprising that, with more dilute acid, reactions were remarkably slow and products of exo attack 8–11 were dominant. That of 6 with excess 1.7 M hydrobromic acid gave 7% of 7, 12.8% of 8, 4.2% of 9, 3.9% of 10, 5.4% of 11, and 62% of 6 remained unreacted after 28 hr at 0°. After 23 hr at 0° with 3.2 M hydrobromic acid, the product contained 36% of 7, 8% of 8, 3% of 9, 7% of 10, 10% of 11, and 36% of unreacted 6.

Acid-catalyzed rearrangement of 6 to exo aziridine might have been the first step in these reactions. However, a cyclic process probably occurs in which 6 dissociates via 16 and 15 to 1 and 3 that then recombine with the endo:exo ratio characteristic of the acidity. In both parts of the cycle, reaction of 16 with bromide

(21) S. Winstein and M. Shatavsky, *Chem. Ind. (London)*, 56 (1956).

ion to give 7 competes. The dissociation of 6 was proved by its reaction with an excess of the reagent used in the iodometric analysis of 1 (0.17 M KI in 1.5 M HCl) to give 1,1-dimethylhydrazine, iodine, 3,5-diiodonortricyclenes, and 3. Two other experiments gave results in accord with this explanation. The reaction of 6 with 3.1 M hydriodic acid was almost complete after 45 min at 25°, and it gave 60% $7_I$, 1,1-dimethylhydrazinium iodide, and iodine. Here the more reactive nucleophile, iodide ion, more effectively intercepted 16. To the extent that dissociation to 1 and 3 occurred, 1 was immediately reduced by the hydriodic acid to the hydrazine and no recombination was possible. In contrast, the poorer nucleophiles in the reaction of 6 with 4.0 M trifluoroacetic acid in water attack 16 only to a minor extent, and the cycle continued until all of the 6 was consumed to give the exo products, 50% 8 and 40% 9. The rate of this reaction was followed by nmr analysis. It followed pseudo-first-order kinetics and was very slow ($k_{0°} = 0.04$ hr$^{-1}$).

Reaction 2 is much faster and gives more exo attack, at higher acidity. The above dissociation–recombination cycle seems too slow to account for this exo trend. As an alternative, evidence has accumulated for the following equilibria.

20 + $H_3O^+$ ⇌ 1     (4)

1 + $H_3O^+$ ⇌ 21 + $H_2O$ ⇌

22 + $H_3O^+$     (5)

Probably then, 1 and 21 compete in reaction 2. The concentration of 21 would increase with that of acid, and possibly 21 is much more reactive than 1 and favors exo attack. Reaction 2 does not involve dimethylaminonitrene 20. When the usual acidic solution of 1 was dropped into a stirred mixture of excess 3 with 40% sodium hydroxide in water at 0°, 3 was recovered and tetramethyltetrazene was the only product.[22]

The equilibria 4 and 5 are supported by other studies of 1 to be reported elsewhere.[23] Its rate of disappearance from its solutions in hydrobromic acid ($-d[1]/dt = k[1]^2/H_0$) and the products suggest that two competing reaction sequences occur.

20 + 1 → 23     (6)

20 + 22 → 23     (7)

(22) (a) W. R. McBride and H. W. Kruze, *J. Amer. Chem. Soc.*, 79, 572 (1957); (b) W. R. McBride and E. M. Bens, *ibid.*, 81, 5546 (1959).
(23) W. H. Urry and Z. L. F. Gaibel, unpublished work.

Tetramethyltetrazene, detected as an intermediate (nmr), probably results from the interaction of **1** and **20**, and it then reacts further with the acid. Alternatively, **20** reacts with **22** to give **23** that hydrolyzes to give formic acid, methylhydrazine, and 1,1-dimethylhydrazine in equimolar amounts, or reacts further to give 1-methyl-1,2,4-triazole and dimethylamine. Further, the methyl groups of **1** undergo isotopic exchange in deuteriotrifluoroacetic acid or hydrobromic acid in deuterium oxide,[24] and reaction 5 is a likely mechanism.

The above evidence suggests that repeated failures of **1** to react with many olefins might have been due to unfavorable equilibria at high acidities used. Hence, it was interesting that 1,1-diphenyldiazenium ion, prepared by the electrochemical oxidation of the hydrazine in acetonitrile 0.1 $M$ in lithium perchlorate and perchloric acid, adds to *cis*-2-butene to give *cis*-1-diphenylamino-2,3-dimethylaziridine, and to *trans*-2-butene to give the *trans*-aziridine.[25] Hopefully, **1** may so add to such olefins under appropriate conditions.

## Experimental Section

**Reactions of 1 with Bicyclic Olefins. Norbornadiene (3).** A solution of 0.75 $M$ **1** in 1.5 $M$ hydrobromic acid was prepared by the dropwise addition of 60 g (0.375 mol) of bromine over 30 min to a stirred solution of 22.5 g (0.375 mol) of 1,1-dimethylhydrazine and 43 ml of 48% hydrobromic acid in 100 ml of water held at $-5°$, and then water was added until the volume was 500 ml. The reaction mixture was stirred at $-5°$ while 32.3 g (0.35 mol) of **3** was added to it over 20 min, and a total reaction time of 1.75 hr was reached. Its nmr spectra were taken to follow the reaction. After 1.5 hr, **1** (singlet at $\delta$ 4.61 with DSS) had nearly disappeared, and the hydrobromides of **6** (singlet at 3.02, $NCH_3$) and **7–11** (multiple singlets 3.14–3.20) were present.

A solution of 36 g (0.90 mol) of sodium hydroxide in 60 ml of water was added dropwise to the reaction mixture at 0°. It was extracted with ether (6 × 500 ml), and the extract was dried ($Na_2SO_4$). The remaining reaction mixture was saturated with potassium carbonate, and then it was continuously extracted with ether for 168 hr (see below for further work-up of this extract). The first ether extract was evaporated to give 45.6 g of a mixture that contained 5.5 g (0.059 mol) of unreacted **3**, 22.6 g (0.150 mol, 51.5%) of **6**, 2.8 g (0.012 mol, 4.1%) of **7**, 3.6 g (0.015 mol, 5.3%) of **10**, 5.9 g (0.26 mol, 8.8%) of **11**, and 5.2 g (0.045 mol) of tetramethyltetrazene (details of nmr analysis below). With vacuum line distillation at 25°, 21 g of **6** (also **3** and tetramethyltetrazene) was condensed in the $-80°$ bulb. Its redistillation gave pure **6**: bp 39–42° (2.1 mm), $n^{24}D$ 1.4940, tlc $R_f$ 0.47 with Eastman silica gel sheet and an eluent mixture of 30 vol % benzene, 50% hexane, 10% ether, and 10% methanol; nmr ($CCl_4$, HA-100) $\delta$ 5.58 (t, 2, $J_{6,5} + J_{6,1} = J_{7,1} + J_{7,5} = 4.0$ Hz, 6 and 7 CH=CH), 2.74 (m, 2, bridgehead 1 and 5 CH), 2.27 ($A_2X_2$ m, 2, $J_{2x,1} + J_{2x,5} = J_{4x,5} + J_{4x,1} = 4.1$ Hz, 2-exo and 4-exo CHN), 2.13 (s, 6, $NCH_3$), 1.60 (m A of $ABX_2$, 1, $J_{8s,8a} = 7.2$ Hz, $J_{8s,1} = J_{8s,5} = 1.8$ Hz, 8-syn HC*H*), and 1.49 ppm (m B of $ABX_2$, $J_{8,a8s} = 7.2$ Hz, $J_{8a,1} = J_{8a,5} = 1.2$ Hz, 8-anti HC*H*); decoupling with irradiation of 2.74, the absorptions at 2.27, 5.58 and the four peaks of the AB system became singlets; mass spectrum (40 eV) $m/e$ (rel intensity) 150 (10), 106 (9), 92 (40), 91 (100), 79 (14), 78 (17), 66 (70), 65 (31), 63 (13), 51 (15), 45(11), 44 (20), 43 (16), 42 (16), 40 (12), 39 (41).

*Anal.* Calcd for $C_9H_{14}N_2$: C, 72.0; H, 9.4; N, 18.6; precise mass, 150.1157. Found: C, 72.2; H, 9.3; N, 18.5; precise mass, 150.1162.

When **6** was treated with excess methyl iodide in ether, its methiodide precipitated: mp 163–165° from ethanol; nmr ($D_2O$ with DSS) $\delta$ 5.87 (t, 2, $J_{6,5} + J_{6,1} = J_{7,1} + J_{7,5} = 4.0$ Hz, 6 and 7 CH=CH), 3.56 ($A_2X_2$ m, 2, $J_{2x,1} + J_{2x,5} = J_{4x,5} + J_{4x,1} = 3.9$ Hz, 2-exo and 4-exo CHN), 3.18 (s over m, 11, $NCH_3$, 1 and 5 CH), 1.70 (m A of $ABX_2$, 1, $J_{8s,8a} = 8.0$ Hz, $J_{8s,1} = J_{8s,5} = 1.8$ Hz, 8-syn HC*H*), and 1.51 ppm (m B of $ABX_2$, 1, $J_{8a,8s} = 8.0$ Hz, $J_{8a,1} = J_{8a,5} = 1.3$ Hz, 8-anti HC*H*).

(24) W. H. Urry and C. Ikoku, unpublished work.
(25) G. Cauquis and M. Genies, *Tetrahedron Lett.,* 3959 (1971).

*Anal.* Calcd for $C_{10}H_{17}N_2I$: C, 40.5; H, 6.0; N, 9.6; I, 43.4. Found: C, 40.6; H, 5.8; N, 9.3; I, 43.1.

Hydrogenation (dioxane, Raney nickel, 40°, 70 psi) of 14 g (0.093 mol) of **6** gave, after filtration and solvent evaporation (Rinco), 10.8 g of crude product; tlc as with **6**, single spot $R_f$ 0.66. Its distillation gave 6.5 g (0.043 mol, 46%) of **12**: bp 51–51.5° (5.1 mm): $n^{25}D$ 1.4736; ir 2970 (s), 2860 (s), 2775 (m), 1458, 1440, 1425 (m), 1330 (w), 1300 (m), 1235 (w), 1195 (m), 1150 (m), 1113 (w), 1084 (w), 1058 (w), 1017 (m), 962 (w), 871 (s), 803 (s) cm⁻¹; nmr ($CCl_4$) $\delta$ 2.20 (s with broad base, 10, $NCH_3$, 1 and 5 CH and 2-exo and 4-exo CHN), 1.54 (m A of $ABX_2Y_2$, 1, $J_{8s,8a} = 10.2$ Hz, $J_{8s,1 \text{ and } 5} = J_{8s,6n \text{ and } 7n} = 1.8$ Hz, 8-syn HC*H*), 1.49 (m B of $ABX_2Y_2$, 1, 8-anti HC*H*), 1.21 (m A of AB, 2, $J_{6x,6n} = J_{7x,7n} = 8.2$ Hz, 6-exo and 7-exo HC*H*), and 1.12 ppm (m B of AB, 2, $J_{AB}$ 8.2 Hz, 6-endo and 7-endo HC*H*); mass spectrum (70 eV) $m/e$ (rel intensity) 152 (27), 137 (5), 123 (18), 98 (18), 83 (12), 80 (12), 79 (14), 66 (55), 58 (30), 44 (18), 43 (100), 42 (16), 41 (12), 39 (23).

*Anal.* Calcd for $C_9H_{16}N_2$: C, 71.0; H, 10.6; N, 8.4. Found: C, 71.1; H, 10.7; N, 8.7.

No hydrogenolysis of the aziridine ring, or of the nitrogen–nitrogen bond, occurred when **6** was hydrogenated under other conditions (in methanol or ethanol, with Pd or Pt catalysts); and **12** was recovered unchanged after its treatment with lithium aluminum hydride in tetrahydrofuran or with hydrazine hydrate in methanol under reflux over Raney nickel.

Substance **12** also gave a crystalline methiodide, mp 190.5–191°, from 2-propanol and ether.

*Anal.* Calcd for $C_{10}H_{19}N_2I$: C, 40.8; H, 6.5; N, 9.5; I, 43.1. Found: C, 40.6; H, 6.1; N, 9.9; I, 43.1.

The continuous ether extract was evaporated to give 12.2 g of a mixture containing 75% **8** and 25% **9**. It was recrystallized twice from 90% ethanol and sublimed at high vacuum to give pure **9**: mp 98–99°; nmr ($CDCl_3$, A-60) $\delta$ 3.94 (m, 1, 5-exo C*H*OH), 3.66 (d, 1, $J$ = 1.4 Hz, 3-endo CHN), 3.17 (bs, 2, NH and OH), 2.45 (s, 6, $NCH_3$), 1.92 (bm, 1, $W_H$ = 5 Hz, 4 CH), 1.68 (m A of AB, 1, $J$ = 11.5 Hz, 7-syn, to hydrazino, *H*CH), 1.27 (m B of AB, 1, 7-anti HC*H*), and 1.17 ppm (m, 3, cyclopropyl CH); mass spectrum (70 eV) $m/e$ (rel intensity) 168 (30), 105 (8), 91 (8), 80 (8), 79 (27), 78 (9), 77 (11), 60 (18), 59 (100), 54 (11), 50 (10), 44 (17), 43 (19), 42 (13), 41 (20), 40 (16).

*Anal.* Calcd for $C_9H_{16}N_2O$: C, 64.25; H, 9.59; N, 16.65; precise mass, 168.1262. Found: C, 63.98; H, 9.81; N, 16.53; precise mass, 168.1263.

The residual solid from the evaporation of the recrystallization filtrate was recrystallized twice from anhydrous ethanol to give **8**: mp 88–89°; nmr ($CDCl_3$, A-60) $\delta$ 3.78 (t, 1, $J_{5n,6} + J_{5n,4} = 3.0$ Hz, 5-endo C*H*OH), 2.95 (t, 1, $J_{3n,4} + J_{3n,2} = 2.6$ Hz, C*H*NH), 2.65 (bs, 2, NH and OH), 2.42 (s, 6, $NCH_3$), 1.98 (bm, 1, $W_H$ = 6 Hz, 4 CH), 1.77 (m A of AB, $J_{7a,7s} = 10.8$ Hz, *H*CH), 1.69 (m B of AB, 1, HC*H*), and 1.27 ppm (m, 3, cyclopropyl CH); mass spectrum (70 eV) $m/e$ (rel intensity) 168 (4), 106 (3), 80 (4), 79 (3), 78 (4), 70 (4), 61 (7), 60 (13), 59 (43), 45 (7), 44 (100), 43 (9), 42 (7), 40 (7).

*Anal.* Calcd for $C_9H_{16}N_2O$: C, 64.25; H, 9.59; N, 16.65; precise mass, 168.1262. Found: C, 64.61; H, 9.66; N, 16.62; precise mass, 168.1267.

A stirred solution of 2.1 $M$ **1** (1 mol) in 4.4 $M$ hydrobromic acid was held at 0° while 92.2 g (1.0 mol) of **3** was added. Then the reaction mixture was stirred at 0° for 2 hr. A cold solution of 110 g of sodium hydroxide in 200 ml of water was added dropwise over 30 min. The two-phase alkaline mixture was extracted with ether (6 × 470 ml), and the residual reaction mixture was continuously extracted with ether for 24 hr. The combined extracts were dried ($Na_2SO_4$) and then evaporated to give 168.2 g of a product mixture. Nmr analysis showed that it contained 26 g (0.17 mol) of **6**, 29 g (0.13 mol) of **7**, 15 g (0.09 mol) of **8**, 9.9 g (0.06 mol) of **9**, 37 g (0.16 mol) of **10**, 48 g (0.21 mol) of **11**, and 3.5 g of unreacted **3**. Continuous extraction of the reaction mixture for 12 days gave 20.1 g of a mixture of 70% **8** and 30% **9**.

While the reaction mixture was stirred at $-5°$, 36.9 g (0.40 mol) of **3** was added dropwise over 10 min to 500 ml of 0.88 $M$ **1** in 6.0 $M$ hydrobromic acid, and then reaction was continued for 1.5 hr. The initial oil suspension changed until, after 30 min, solid product began to precipitate. The mixture then was stored at $-20°$ for 15 hr, and the white solid was recovered on a filter. It weighed 80.6 g (64.5%), and its nmr analysis showed that it contained 36% **7**, 27% **10**, and 37% **11** hydrobromides.

The filtrate was evaporated at high vacuum to give 41.3 g of dark solid. It was dissolved in 100 ml of water, and the solution was saturated with potassium carbonate. Then its continuous extraction with ether for 20 hr gave, after evaporation of the solvent, 26.6

g of solid product that contained 5.0 g (0.030 mol) of **8**, 2.1 g (0.012 mol) of **9**, 6.5 g (0.028 mol) of **10**, and 13.1 g (0.057 mol) of **11**.

Two recrystallizations of the mixture of hydrobromides from absolute ethanol gave 19.1 g of **10** hydrobromide: mp 196–198°; mass spectrum (70 eV) $m/e$ (rel intensity) 232 (1.2), 230 (1.2), 151 (10.3), 108 (2.5), 107 (6.2), 106 (8.8), 91 (3.7), 85 (4.9), 82 (5.4), 80 (5.4), 79 (4.7), 77 (2.1), 59 (19.5), 53 (4.5), and 41 (2.5).

*Anal.* Calcd for $C_9H_{16}N_2Br_2$: C, 34.6; H, 5.2; N, 9.0; Br, 51.2. Found: C, 34.4; H, 5.4; N, 8.8; Br, 50.9.

Treatment of this salt with saturated sodium carbonate solution gave **10**: nmr $(CCl_4, \text{HA-100}), \delta$ 4.51 (s, 1, NH), 3.87 (t, 1, $J_{5n.6} + J_{5n.4} = 3.0$ Hz, 5-endo CHBr), 2.92 (t, 1, $J_{3n.2} + J_{3n.4} = 3.4$ Hz, 3-endo C$H$NH), 2.33 (s, 6, NCH$_3$), 2.15 (m, 1, $W_H = 5$ Hz, 4 CH), 1.85 (m AB, 2, $J_{AB} = 10.8$ Hz, 7 CH$_2$), 1.54 (m, 1, $J_{6.2} = J_{6.1} = 5.0$ Hz, $J_{6.5n} = 1.5$ Hz, 6 CH), 1.37 (m, 1, $J_{1.2} = J_{1.6} = 5.0$ Hz, $J_{1.7} = 1.2$ Hz, 1 CH), and 1.05 ppm (m, 1, $J_{2.6} = J_{2.1} = 5.0$ Hz, $J_{2.3n} = 1.2$ Hz, 2 CH); decoupling: irradiation at 2.15 gives d at 3.87 and 2.93, and sharpens peaks of m at 1.05, 1.37, and 1.54; at 3.87 modifies m at 1.54; at 1.54 gives d at 3.87; at 2.93 sharpens lines of m at 1.06;. at 1.06 gives d at 2.93; and at 1.37, the two m at 3.87 and 2.93 unchanged; nmr $(CF_3COOH, \text{HA-100}), \delta$ 4.02 (t, 1, $J_{5n} + J_{3n.4} = 3.0$ Hz, 5-endo HCBr), 3.45 (t, 1, $J_{3n.2} + J_{3n.4} = 3.0$ Hz, 3-endo $H$CNH), 3.21 (s, 6, NCH$_3$), 2.41 (m, 1, $W_H = 7$ Hz, 4 CH), 2.17 (m A of AB, 1, $J_{7s.7a} = 12.0$ Hz, 7-syn, to hydrazino, H$CH$), 1.88 (m B of AB, 1, 7-anti $H$CH), 1.81 (m, 1, $J_{6.1} = J_{6.2} = 5.0$ Hz, 6 CH), 1.64 (m, 1, $J = 5.0$ Hz, 1 CH), and 1.48 ppm (m, 1, $J = 5.0$ Hz, 2 CH).

The filtrate from the recrystallization was evaporated under nitrogen, and the recovered solid was recrystallized. This was repeated seven times. Crystals from the sixth and seventh such recrystallizations contained 95% **11** and 5% **10** hydrobromides (nmr). Other attempts to purify **11** were no better. However, it was possible to deduce the nmr spectra of **11**: nmr $(CCl_4, \text{HA-100}) \delta$ 3.92 (t, 1, $J_{5x.6} + J_{5x.4} = 3.0$ Hz, 5-*exo* CHBr), 3.64 (t, 1, $J_{3n.4} + J_{3n.2} = 3.5$ Hz, 3-endo C$H$NH), 2.36 (s, 6, NCH$_3$), 2.04 (m, 1, $W_H = 4.5$ Hz, 4 CH), 1.84 (m A of ABXY, 1, $J_{7s.7a} = 10.7$ Hz, $J_{7s.1} + J_{7s.4} = 3.3$ Hz, 7-syn to hydrazino HC$H$), 1.50 (m, 1, $J_{6.1} = J_{6.2} = 5.0$ Hz, $J_{6.4} + J_{6.5x} = 2.9$ Hz, 6 CH), 1.26 (m B of ABXY, 1, $J_{7a.7s} = 10.7$ Hz, $J_{7a.1} + J_{7a.4} = 3.0$ Hz), and 1.20 ppm (m, 2, 1 and 2 CH); decoupling: irradiation of $\delta$ 2.04 gives d at 3.92 and 3.64, dd at 1.84 and 1.26 and td at 1.50; at 1.50 d at 3.92; and at 1.20, d at 3.64; nmr $(CF_3COOH, \text{A-60}) \delta$ 4.14 (m, 1, 5-exo CHBr), 4.03 (t, 1, $J_{3n.4} + J_{3n.2} = 3.2$ Hz, 3-endo C$H$NH), 3.25 (s, 6, NCH$_3$), 2.37 (m, 1, 4 CH), and an unresolved part 2.05–1.40 ppm (1, 2, 6, 7-syn and 7-anti).

Nmr analyses of mixtures of **6–11** depended upon the relative heights of their *N*-methyl peaks in scans at 100 sweep width. Figures so obtained were always the same as those determined from integrated areas of the triplets due to the olefinic hydrogen atoms of **6** and **7**, and to hydrogens at C-5 (OH or Br bearing) for **8–11**.

A mixture of 120 g of sodium hydroxide in 180 ml of water and 104.5 g (1.134 mol) of **3** was stirred (Trubore) at $-5°$ while 405 ml of a solution of 1.086 $M$ **1** in 5.43 $M$ hydrobromic acid was added to it dropwise over 1.5 hr. Then the reaction mixture was extracted with ether (7 × 430 ml), and the extract was dried (Na$_2$SO$_4$). The ether was removed by distillation through a Podbielniak column. The 119.4 g of material that remained contained (nmr) 95.7 g of unreacted **3** and 23.6 g (0.203 mol, 92%) of tetramethyltetrazene.

**Norbornene (2).** A reaction mixture containing **1** (0.25 mol, 1.0 $M$) in 3.1 $M$ hydrobromic acid with 23 g (0.24 mol) of **2** in 70 ml of ether was stirred for 9 hr while it was cooled in a methanol–ice bath ($-15$ to 5°). Then sodium hydroxide pellets were added until the aqueous phase was strongly basic. The organic layer was separated and the aqueous solution was extracted with ether (3 × 100 ml). The ether extract was washed with saturated brine and dried (Na$_2$SO$_4$). Evaporation (Rinco) gave 21.5 g (59%) of crude **4**. It was distilled to give 20 g of pure **4**: bp 41–43° (2.2 mm); $n^{26}$D 1.4790; tlc Eastman silica gel plate, $R_f$ 0.51, with benzene–ethanol, 4:1 v/v, eluent, nmr $(CCl_4) \delta$ 2.26 (m, 2, $W_H = 5.5$ Hz, 1,5-bridgehead), 2.16 (s, 6, NCH$_3$), 1.69 (m, 2, $W_H = 2.3$ Hz, 2- and 4-endo), 1.47 (m A of ABX$_4$, 1, $J_{8s.8a} = 9.2$ Hz, $J = 1.8$ Hz, 8-syn), 1.22 (m ABX$_2$, 4, $J_{6x.6n} = J_{7x.7n} = 9.0$ Hz, $J = 1.7$ Hz, 6- and 7-exo and 6- and 7-endo), and 0.51 ppm (m B of ABX$_4$, 1, $J_{8a.8s} = 9.2$ Hz, $J_{8a.2n}$ and $_{4n} = J_{8a.1}$ and $_5 = 1.2$ Hz, 8-anti); mass spectrum (70 eV) $m/e$ (rel intensity) 152 (23), 123 (7), 108 (5), 98 (20), 94 (14), 91 (7), 79 (16), 77 (11), 66 (87), 59 (10), 58 (44), 44 (16), 43 (100).

*Anal.* Calcd for $C_9H_{16}N_2$: C, 71.0; H, 10.6; N, 18.4. Found: C, 71.1; H, 10.5; N, 18.6.

When a solution of **4** and methyl iodide in benzene was allowed to stand overnight, its methiodide (white needles, mp 145° from 2-propanol–acetone) precipitated.

*Anal.* Calcd for $C_{10}H_{19}N_2I$: C, 40.8; H, 6.5; N, 9.5; I, 43.1. Found: C, 40.9; H, 6.6; N, 9.6; I, 43.1.

A brown precipitate formed when **4** was treated with alcoholic silver nitrate. No hydrogen was absorbed, and **4** was recovered unchanged, when its hydrogenation (Pt in ethanol, 60 psi at 40°) was attempted.

At higher acidity and temperature, 23 g (0.24 mol) of **2** in 50 ml of ether was stirred with a solution of **1** (0.2 mol, 0.57 $M$) in 3.75 $M$ hydrobromic acid held at 0° for 15 hr. The reaction mixture then was made basic by the addition of sodium carbonate. The organic layer was separated, and the aqueous one was extracted with ether (4 × 100 ml). Combined ether extracts were washed with saturated brine and then were dried (MgSO$_4$). Distillation gave 10 g (0.066 mol, 33%) of **4** and 21.7 g (0.102 mol, (51% based upon its analysis below)) of a colorless oil. Redistillation of the latter gave, after a first yellow fraction that contained a small amount of **4** (0.92 g, bp 97.5–98° (3.5 mm), $n^{25}$D 1.5040), three fractions of uniform composition (19.84 g, bp 98–100° (3.5 mm), $n^{27}$D 1.5052). Each of the latter fractions contained two substances (tlc, Eastman silica gel sheet, $R_f$ 0.45 and 0.65, with benzene, cyclohexane, ether, and methanol, 4:4:1:1 v/v eluent). Their nmr spectra also suggest two main components (nmr, $CCl_4$, 2s, $\delta$ 2.37 and 2.40 ppm, NCH$_3$). Their analyses suggest that they are mixtures of 66% hydrazino bromide and 34% hydrazino alcohol.

*Anal.* Calcd for $C_9H_{17.34}N_2Br_{0.66}O_{0.34}$: C, 51.0; H, 8.3; N, 13.2; Br, 24.9. Found: C, 51.4; H, 8.4; N, 12.7; Br, 24.9.

The hydrobromide of the dominant product of this mixture precipitated when 5 g (0.033 mol) of **4** was added to 35 ml of 8.8 $M$ hydrobromic acid at $-15°$. Filtration of the cold reaction mixture gave 9.5 g (0.030 mol (92%)) of the hydrobromide of **5**: mp 171–173° from ethanol; mass spectrum (composite of **5** and HBr) (70 eV) $m/e$ (rel intensity) 234 (6), 232 (7), 153 (88), 82 (19), 80 (19), 59 (100), 40 (20).

*Anal.* Calcd for $C_9H_{18}N_2Br_2$: C, 34.4; H, 5.8; N, 8.9; Br, 50.9. Found: C, 34.2; H, 5.7; N, 9.0; Br, 51.1.

The hydrobromide of **5** was treated with sodium carbonate solution to give **5**: nmr (benzene, HA-100) $\delta$ 3.68 (m, 1, $J_{2n.3n} = 8.0$ Hz, $J_{2n.3x} = 4.5$ Hz, $J_{2n.7a} = 1.3$ Hz, 2-endo CHBr), 2.96 (m, 1, 7-anti C$H$NH), 2.68 (m A of ABXYZ, 1, $J_{3x.3n} = 13.5$ Hz, $J_{3x.2n} = 4.5$ Hz, $J_{3x.4} = 4.5$ Hz, 3-exo HC$H$), 2.33 (s, 6, NCH$_3$), 2.28 (m, 1, partly obscured by 2.33, 1 CH), 2.06 (m, 1, 4 CH), 1.77 (m B of ABXYZ, 1, $J_{3n.3x} = 13.5$ Hz, $J_{3n.2n} = 8.0$ Hz, 3-endo HCH), 1.27 (m A of AB, 2, 5- and 6-exo HC$H$), and 0.73 ppm (m B of AB, 2, 5- and 6-endo HC$H$). Decoupling: irradiation of $\delta$ 3 68 simplifies 2.96 (fine structure) and makes 1.77 a doublet; of 2.96 makes 3.68 four peak AXY and simplifies 2.06; of 2.68 makes 1.77 a doublet, $J = 8.0$ Hz; of 1.77 makes 3.68 a pair of doublets, $J = 4.5$ Hz and 1.3 Hz; and 0.73 modifies 1.27; nmr $(CF_3COOH, \text{HA-100})$ $\delta$ 4.13 (m AXY, 1, $J_{2n.3n} = 8.0$ Hz, $J_{2n.3x} = 4.2$ Hz, 2-endo CHBr), 3.61 (s, 1, C$H$NH), 3.33 (s, 6, NCH$_3$), 2.88 (m, 1, $J = 3.0$ Hz, 1 CH), 2.55 (m, 1, 3-exo HC$H$), 2.45 (m, 1, 4 CH), 2.31 (m, 1, $J_{3n.3x} = 13.5$ Hz, $J_{3n.2n} = 8.0$ Hz, 3-endo HC$H$), 1.81 (m AB, 2, 5- and 6-exo HC$H$), and 1.35 ppm (m, 2, 5- and 6-endo HC$H$).

**5-Norbornene-2 methanol (24).** The **24** used (Matheson Coleman and Bell, technical grade, bp 95–97° (15 mm), probably prepared by the reaction of cyclopentadiene with allyl alcohol at 180°, claimed[26] and subsequently regarded[27] as the pure endo isomer) is apparently a mixture of 70 mol % *endo*-**24** and 30 mol % *exo*-**24**. Its nmr spectrum (in $CCl_4$ with TMS) supports this conclusion. The upfield part of an ABXY absorption ($\delta$ 0.48, $J_{AB} = 11.5$ Hz, $J_{AX} = 4.0$ Hz, $J_{AY} = 2.5$ Hz) is clearly due to the 3-endo hydrogen atom of the *endo*-**24**, and its integration indicates 0.7 hydrogen atom. Two ABX absorptions ($\delta$ 3.0–3.8) must be due to the methylenes of the hydroxymethylene groups. That of *endo*-**24** ($\delta$ 3.21, $J_{AB} = 7.0$ Hz, $J_{AX} = 4.5$ Hz, $J_{BX} = 3.5$ Hz) and that of *exo*-**24** ($\delta$ 3.51, $J_{AB} = 10.5$ Hz, $J_{AX} = 4.0$ Hz, $J_{BX} = 6.5$ Hz) have integrated areas indicating 75% *endo*-**24** and 25% *exo*-**24**.

These conclusions were confirmed when a similar mixture was prepared by the sodium borohydride reduction of the mixture of *endo*- and *exo*-5- norbornene-2-carboxaldehydes from the cycloaddition of acrolein to cyclopentadiene. A reaction mixture of 56 g (0.85 mol) of cyclopentadiene, 8 ml of ether, and 40 g (0.71 mol) of acrolein was stirred at 0° for 2 hr and at 25° for 15 hr. Distillation gave a mixture of 80% 5-norbornene-2-*endo*-carbox-

(26) K. Alder and E. Windemuth, *Ber.*, **71**, 1939 (1938).

(27) J. A. Berson, *et al.*, *J. Amer. Chem. Soc.*, **83**, 3995 (1961).

aldehyde and 20% of its exo isomer: bp 60° (18 mm), 60 g (0.49 mol, 70%); nmr (CCl₄) δ 9.33 (d, $J$ = 2.2 Hz, endo CHO) and 9.71 ppm (d, $J$ = 2.0 Hz, exo-CHO), ratio of areas 4.

Preparative vapor phase chromatography (20 $M$, 130°) separated the two isomers: 5-norbornene-2-*exo*-carboxaldehyde [nmr (CCl₄, A-60) δ 9.71 (d, 1, $J$ = 2.0 Hz, CHO), 6.11 (m, 2, HC=), 3.10 (m, 1, bridgehead 1 CH), 2.93 (m, 1, bridgehead 4 CH), 2.22 (m, 1, 2-endo CH), 1.97 (m, 1, 3-exo CH), and 1.60–0.97 with peak 1.31 ppm (m, 3, 7a, 7b and 3-endo CH)] and the endo isomer [nmr (CCl₄, A-60), δ 9.33 (d, 1, $J$ = 2.2 Hz, CHO), 6.12 (m A of ABX, 1, $J_{6,5}$ = 5.6 Hz, $J_{6,1}$ = 2.8 Hz, 6-CH), 5.92 (m B of ABX, 1, $J_{5,6}$ = 5.6 Hz, $J_{5,4}$ = 2.5 Hz, 5-CH), 3.20 (m, 1, bridgehead 4-CH), 2.91 (m, 1, bridgehead 1 CH), 2.83 (AX₂Y m, 1, $J_{2x,3x}$ = 8.7 Hz, $J_{2x,1}$ = $J_{2x,3n}$ = 3.5 Hz, $J_{2x,formyl}$ = 2.5 Hz, 2-exo), 1.88 (m A of AB, 1, $J_{3x,3n}$ = 12.0 Hz, $J_{3x,2x}$ = 8.7 Hz, $J_{3x,4}$ = 3.5 Hz, 3-exo), 1.47 (m A of AB, $J_{7s,7a}$ = 8.0 Hz, 7s or 7a), 1.32 (m B of AB, 1, 7a or 7s), and 1.30 ppm (m B of AB, 1, $J_{AB}$ = 12.0 Hz, 3-endo)].

A solution of 12.2 g (0.1 mol) of this mixture of aldehydes in 50 ml of methanol was stirred at 0° while a solution of 1.32 g (0.035 mol) of sodium borohydride in 30 ml of methanol was added to it slowly. After an extra hour of stirring at 0°, the solvent was evaporated, and product was taken up in ether. The ether solution was washed with brine and dried (Na₂SO₄). Evaporation gave a mixture of *endo*- and *exo*-24 that gave an nmr spectrum identical with the 24 sample above.

A stirred solution (580 ml) of 0.86 $M$ −1 in 3.9 $M$ hydrobromic acid was held at 0° while 62 g (0.35 mol endo) of the 24 was added dropwise. Stirring at 0° was continued for 5.5 hr when nmr analysis showed that over 90% of the initial 1 had been consumed. The acidic reaction mixture was extracted with ether (3 × 100 ml), and evaporation of the extract gave 7 g of neutral products (the weak olefinic absorption in its nmr spectrum suggests some unreacted *exo*-24).

Sodium hydroxide solution was added to the remaining reaction mixture until it was basic (pH 11), and the resulting two-phase mixture was extracted with ether (5 × 200 ml). This extract was dried (KOH pellets), and then its evaporation gave 77 g of a yellow oil. Its distillation gave 13: bp 54.5–57° (0.045 mm), $n^{22}$D 1.4952, 48.0 g (0.263 mol, 75%).

*Anal.* Calcd for C₁₀H₁₈N₂O: C, 65.9; H, 10.0; N, 15.4. Found: C, 66.2; H, 10.0; N, 15.9.

Treatment of 13 with a saturated solution of oxalic acid in ether gave its oxalate: mp 126–128° after two recrystallizations from ethanol–isopropyl ether.

*Anal.* Calcd for C₁₂H₂₀N₂O₅: C, 52.9; H, 7.4; N, 10.3. Found: C, 53.1; H, 7.6; N, 10.1.

When a solution of 13 and methyl iodide in benzene was allowed to stand overnight its methiodide precipitated, mp 208–209° from ethanol–ether.

*Anal.* Calcd for C₁₁H₂₁N₂OI: C, 40.8; H, 6.5; N, 8.6; I, 39.1. Found: C, 41.0; H, 6.7; N, 8.5; I, 39.3.

The spectra of 13 confirmed the assigned structure. A previous comprehensive study of nmr spectra of related substances[2c] assisted analysis of that of 13: nmr (benzene, A-60) δ 3.94 (d, 1, $J_{5x,8}$ = 4.8 Hz, 5-exo HCO), 3.74 (m A of ABX, 1, $J_{7a,7b}$ = 7.8 Hz, $J_{7a,1x}$ = 3.6 Hz, HCHO), 3.58 (m B of ABX, 1, $J_{7,b7a}$ = 7.8 Hz, $J_{7b,1x}$ ~ 0, HCHO), 2.62 (d, 1, $J_{4n,9a}$ = 1.2 Hz, 4-endo HCN), 2.42 (m, 1, $J_{8,5x}$ = 4.8 Hz, $J_{8,1x}$ = 4.2 Hz, $J_{8,3}$ = $J_{8,9a}$ = $J_{8,9b}$ ~ 1.5 Hz, bridgehead 8), 2.29 (m, 1, partly concealed (placed by decoupling), 1-exo), 2.25 (s, 6, NCH₃), 2.00 (m, 1, 3 CH), 1.84 (m AB, 9b), 1.73 (m A of ABXY, 1, $J_{2x,2n}$ = 11.0 Hz, $J_{2x,3}$ = 4.6 Hz, 2-exo), 1.31 (m, 1, $J_{9a,9b}$ = 10.0 Hz, $J_{9a,3}$ = $J_{9a,8}$ = 2.2 Hz, $J_{9a,4n}$ = 1.2 Hz, 9a) and 0.95 ppm (m B of ABX₂, 1, $J_{2n,2x}$ = 11.0 Hz, $J_{2n,1x}$ = $J_{2n,9b}$ = 2.0 Hz, 2-endo); decoupled with double irradiation scan +87 difference frequency decoupled 7a at 3.74 and 1x at 2.29, and 5x at 3.92 and bridgehead 8 at 2.42 while +80 difference frequency decoupled 4n at 2.62 and 9a at 1.31; nmr spectrum of 13 in trifluoroacetic acid gave downfield shifts of 0.23–0.30 ppm for all absorptions except 4-endo, 0.50, and NCH₃ 1.00 ppm; mass spectrum (70 eV) m/e (rel intensity) 182 (9.2), 180 (7.8), 167 (2.7), 138 (3.1), 136 (2.8), 81 (9.1), 79 (3.5), 69 (6.2), 59 (11.2), 45 (4.9), 44 (8.9), 43 (3), 42 (4.4), 41 (39); metastables: 153.3, 182 → 167, 104.7, 182 → 138; 76.7, 108 → 91, and 60.9, 136 → 91.

**Benzonorbornadiene.** A solution of 12.5 g (0.088 mol) of this olefin[28] in 25 ml of ether was stirred with 200 ml of 1 with 0.5 $M$ 1 in 2.5 $M$ hydrobromic acid for 25 hr at 0°. The product that had precipitated was collected on a filter and was washed with ether–

(28) G. Wittig and E. Knauss, *Chem. Ber.*, 91, 895 (1958).

methanol (9:1 vol) to give white crystalline 14 hydrobromide, 7.1 g (0.0196 mol), mp 218–220° from 2-propanol containing HBr, 219–220° from ethanol.

*Anal.* Calcd for C₁₃H₁₈N₂Br₂: C, 43.1; H, 5.0; N, 7.7; Br, 44.1. Found: C, 43.1; H, 5.2; N, 7.7; Br, 43.8.

This hydrobromide was treated with 50% sodium hydroxide solution, and the mixture was extracted with carbon tetrachloride. Evaporation then gave 14. Its nmr spectra in trifluoroacetic acid and carbon tetrachloride were complementary, and they resembled those of such 9-anti-2-exo derivatives previously studied:[3a] nmr (trifluoroacetic acid, A-60) δ 7.18 (s, 4, aromatic), 3.96 (m, 1, 9-syn), 3.82 (m, 1, partially obscured, 2-endo), 3.75 (m, 1, 1 bridgehead), 3.52 (m, 1, 4 bridgehead), 3.32 (s, 6, N-CH₃), 2.58 (m A of ABXY, 1, $J_{3x,3n}$ = 13.5 Hz, $J_{3x,4}$ = $J_{3x,2n}$ = 3.8 Hz, 3-exo), and 2.19 ppm (m B of ABXY, 1, $J_{3n,3x}$ = 13.5 Hz, $J_{3n,3n}$ = 8.0 Hz, 3-endo); nmr (CCl₄, A-60) δ 7.03 (s, 4, aromatic), 3.64 (AXY m, 1, $J_{2n,3n}$ = 8.0 Hz, $J_{2n,3x}$ = 3.8 Hz, 2-endo), 3.37 (m, 1, 1 bridgehead), 3.22 (m, 2, 4 bridgehead and 9-syn), 2.40 (s, 6, NCH₃), 2.54 (m A of ABXY, 1, $J_{3x,3n}$ = 13.5 Hz, $J_{3x,4}$ = $J_{3x,3n}$ = 3.8 Hz, 3-exo), and 1.93 ppm (m B of ABXY, 1, $J_{3n,3x}$ = 13.5 Hz, $J_{3n,2n}$ = 8.0 Hz, 3-endo).

The filtrate of the original reaction mixture was worked up with base as usual. A yellow oil recovered weighed only 0.7 g, and it had the same nmr spectra above.

**Reactions of 6 with Acids. Hydrochloric Acid.** Reaction was immediate (nmr) as 1.9 g (0.013 mol) of 6 was added dropwise to 25 ml of 12.2 $M$ hydrochloric acid held at −5° under nitrogen and stirred. After an added 30 min of stirring at −5°, the reaction mixture was stored for 8 hr at −20°. Since no solid had precipitated, it was evaporated under vacuum in a flow of nitrogen to give 2.8 g of a dark crystalline product. It was recrystallized twice from acetonitrile and sublimed under high vacuum to give pure 7$_{C1}$·HCl: mp 170–171°, 85%; nmr (10 vol % pyridine in D₂O, A-60) δ 6.36 (t, 2, $J + J$ = 3.8 Hz, HC=), 3.87 (m AXY, 1, $J_{6x,5n}$ = 2.4 Hz, $J_{6x,1}$ = 3.4 Hz, HCN), 3.63 (t, 1, $J_{5n,6x}$ + $J_{5n,7s}$ = 4.3 Hz, HCCl), 3.13 (m, 1, 4 CH), 3.02 (s, 6, NCH₃ with m, 1, 1 CH under it), 1.98 (m A of ABXYZ, 1, $J_{7n,7s}$ = 9.5 Hz, 7-anti HCH), and 1.75 ppm (m B of ABXYZ, 1, $J_{7s,7a}$ = 9.5 Hz, $J_{7s,1}$ + $J_{7s,5n}$ = 5.8 Hz, 7-syn HCH); mass spectrum (70 eV) m/e (rel intensity) 188 (2), 186 (5), 122 (36), 120 (100), 107 (10), 105 (31), 91 (8), 77 (9), 59 (36), 44 (25), 43 (39), 42 (27), 38 (18), 36 (47) (salt dissociates with mass spectrometry: calcd precise mass, 186.0924; found, 186.0931).

*Anal.* Calcd for C₉H₁₆N₂Cl₂: C, 48.44; H, 7.23; N, 12.55; Cl, 31.78. Found: C, 48.65; H, 7.27; N, 12.53; Cl, 31.87.

Treatment of this hydrochloride with aqueous sodium hydroxide solution gave 7$_{C1}$: nmr (CCl₄, A-60) δ 6.07 (t, 1, $J + J$ = 3.8 Hz, see above for designations), 3.51 (AXY m, 1, $J$ = 2.4 Hz, $J$ = 3.4 Hz), 3.18 (t, 1, $J + J$ = 4.8 Hz), 2.87 (m, 2, 1 and 4 CH), 2.35 (s, 6, NCH₃), 1.93 (m A of AB, 1, $J_{AB}$ = 9.5 Hz, 7-anti to olefin HCH), and 1.62 ppm (m B of AB 1, $J_{AB}$ = 9.5 Hz, $J + J$ = 6.0 Hz).

**Hydrobromic Acid.** In the reactions as above of 6 with 1.5 g of 6 with 25 ml of concentrated hydrobromic acid (8.8 $M$, −5°, N₂, stirring), a white solid precipitated. A nmr spectrum of the supernatant reaction mixture taken after 30 min showed that the reaction was complete, and 7 is its only product. After this reaction mixture was held at −20° for 8 hr, 2.83 g (90%) of the precipitated solid was recovered on a filter. Recrystallization from anhydrous ethanol gave pure 7 hydrobromide: mp 152–154°; mass spectrum (70 eV) m/e (rel intensity) 232 (6), 230 (6), 166 (100), 164 (100), 151.1230 (29), 150.9689 (22), 149 (22), 107 (13), 106 (20), 91 (14), 85 (31), 82 (37), 81 (14), 80 (40), 79 (17), 76 (13), 58 (63).

*Anal.* Calcd for C₉H₁₆N₂Br₂: C, 34.64; H, 5.17; N, 8.98; Br, 51.22. Found: C, 34.55; H, 5.25; N, 9.05; Br, 51.32.

When this salt was treated with 10% sodium hydroxide, an oil separated. It was extracted with ether, and the ether solution was dried (Na₂SO₄). Distillation gave 7: bp 70° (0.5 mm); nmr (CCl₄, HA-100) δ 6.02 (t, 2, $J_{2,1}$ + $J_{2,4}$ ~ $J_{3,4}$ + $J_{3,1}$ = 3.5 Hz, 2 and 3 CH=CH), 3.68 (m AXY, 1, $J_{6x,1}$ = 3.0 Hz, $J_{6x,5n}$ = 2.7 Hz, 6-exo CHNH), 3.14 (t, 1, $J_{5n,7s}$ + $J_{5n,6x}$ = 5.2 Hz, 5-endo CHBr), 2.94 (m, 1, 4 CH), 2.87 (m, 1, 1 CH), 2.33 (s, 6, NCH₃), 2.15 (bs, 1, NH), 1.96 (m A of ABXYZ, 1, $J_{7a,7s}$ = 9.0 Hz, $J_{7a,1}$ + $J_{7a,4}$ = 3.0 Hz, 7-anti to olefin HCH), and 1.64 ppm (m B of ABXYZ, 1, $J_{7s,7a}$ = 9.0 Hz, $J_{7s,1}$ ~ $J_{7s,4}$ ~ 1.7–1.8 Hz, $J_{7s,5n}$ = 2.5 Hz, 7-syn HCH); decoupling: irradiation at δ 1.64 gave d at 3.14, $J_{5n,6x}$ = 2.7 Hz; at 2.87, d at 3.68, $J_{6x,5n}$ = 2.4 Hz; at 3.14 d at 3.68, $J_{6x,1}$ = 3.0 Hz, and 1.64 became dt; at 3.68, d at 3.14, $J_{7s,5n}$ = 2.5 Hz; at 6.02, dt at 1.96; and at 2.92 gave s at 6.02 and d at 3.68; nrm (CF₃COOH, A-60) δ 6.29 (m, 2, 2 and 3 CH=CH), 4.14 (m, 1, 6-exo CHNH), 3.63 (t, 1, $J_{5n,7s}$ + $J_{5n,6x}$ = 5.1 Hz, CHBr), 3.23 (s, 6, NCH₃), 3.17 (m, 2, 1 and 4 CH), 2.17 (m A of ABXYZ, 1, $J_{7a,7s}$ =

9.4 Hz, 7-anti HC$H$), and 1.91 ppm (m B of ABXYZ, 1, $J_{7s,7a}$ = 9.4 Hz, $J_{7s,1}$ + $J_{7s,4}$ + $J_{7s,5n}$ = 5.0 Hz, 7-syn $H$CH).

At lower acidity, 1.17 g (0.0078 mol) of **6** in 25 ml of 2 $M$ hydrobromic acid (initial concentrations, 0.31 $M$ **6** hydrobromide and 1.69 $M$ hydrobromic acid) was held at 0° for 28 hr. The reaction was followed by nmr analysis, and it was so slow that it initially gave the spectrum of **6** hydrobromide: nmr (1.7 $M$ HBr, A-60) $\delta$ 5.85 (t, 2, HC=CH), 3.47 (t, 2, HCN), 3.18 (m, 2, 1 and 5 HC), 2.94 (s, 6, NCH₃), 1.79 (m A of AB, 1, $J$ = 9.0 Hz, $H$CH), and 1.62 ppm (m B of AB, 1, HC$H$). Work-up with base, extraction, and evaporation as before gave 0.91 g of a light yellow oil. Its nmr analysis showed that it contained 79 mol % of unreacted **6**, 9 mol % of **7**, 5 mol % of **10**, and 7 mol % of **11** (yield 0.0054 mol, 69%). The aqueous reaction mixture was saturated with potassium carbonate, and its continuous extraction with ether gave 0.22 g of a mixture containing 75 mol % **8** and 25 mol % **9** (nmr).

In an experiment at intermediate acidity, 1.17 g (0.0078 mol) of **6** was added to 25 ml of 3.5 $M$ hydrobromic acid (initial concentrations 0.31 $M$ in **6** and 3.2 $M$ in hydrobromic acid), and the reaction mixture was stored at 0°. After 23 hr at 0°, the reaction mixture was worked up as before. The 1.40 g (91%) of product from the first extract contained 40 mol % of unreacted **6**, 40 mol % of **7**, 8 mol % of **10**, and 11 mol % of **11**. That from the continuous extraction weighed 0.144 g, and contained 75 mol % **8** and 25 mol % **9**.

**Hydriodic Acid.** A yellow precipitate formed as 1.3 g of **6** was added dropwise to 30 ml of 5.5 $M$ hydriodic acid stirred under nitrogen at −10°. After this reaction mixture was stored at −10° for 8 hr, 2.92 g of solid was removed on a filter and washed twice with cold water. Evaporation of the filtrate gave 0.7 g of the same solid (100%). It was recrystallized three times from ethanol to give white crystalline **7**₁ hydriodide: mp 138–140° dec; nmr (15 vol % pyridine in D₂O, A-60) $\delta$ 6.31 (t, 1, $J$ + $J$ = 3.5 Hz, HC=CH), 4.14 (m AXY, 1, $J_{6x,5n}$ = 2.9 Hz, $J_{6x,1}$ = 3.8 Hz, CHN), 3.36 (t, 1, $J_{5n,6x}$ + $J_{5n,7s}$ = 5.6 Hz, CHI), 3.11 (bm, 2, 1 and 4 CH), 2.97 (s, 6, NCH₃), 2.05 (m A of AB, 1, $J_{7,5,7s}$ = 9.0 Hz, $H$CH), and 1.74 ppm (m B of AB 1, HC$H$): mass spectrum (70 eV) $m/e$ (rel intensity) 278 (3), 254 (43), 152 (19), 151 (99), 128 (100), 127 (73), 108 (18), 107 (49), 106 (95), 91 (40), 85 (29), 80 (26), 79 (48), 77 (26) (decomposes to C₉H₁₃N₂I and HI: calcd precise masses 278.0281 and 127.9124: found, 278.0311 and 127.914.

*Anal.* Calcd for C₉H₁₆N₂I₂: C, 26.62; H, 3.97; N, 6.90; I, 62 51. Found: C, 26.37; H, 3.95; N, 6.94; I, 62.74.

This salt was treated with a saturated solution of sodium carbonate in water, and the resulting suspension was extracted to give a carbon tetrachloride solution of **7**₁: nmr (CCl₄, HA-100) $\delta$ 6.03 (m, 2, HC=CH), 3.85 (t, 1, $J_{6x,5n}$ + $J_{6x,1}$ = 6.3 Hz, HCN), 3.02 (t, 1, $J_{5n,6x}$ + $J_{5n,7s}$ = 5.5 Hz, CHI, over m, 1, 4 CH), 2.84 (m, 1, 1 CH), 2.32 (s, 6, NCH₃), 2.11 (m A of ABXYZ, 1, $J_{7n,7s}$ = 9.0 Hz, $H$CH), 1.98 (s, 1, NH), and 1.67 ppm (m B of ABXYZ, $J_{7s,7a}$ = 9.0 Hz, $J_{7s,1}$ + $J_{7s,4}$ + $J_{7s,5n}$ = 6.6 Hz, HC$H$); decoupling: irradiation at $\delta$ 3.02 gave dd at 1.67, d at 3.85, $J$ = 3.0 Hz, and m at 6.03 became sharper; and of 3.85 gave d at 3.02, $J$ = 2.3 Hz.

Again in an experiment at lower acidity, 1.15 g (0.0077 mol) of **6** was added to 3.4 $M$ hydriodic acid (initial concentrations 0.31 $M$ **6** hydriodide and 3.1 $M$ in hydriodic acid) at 25° with stirring. The reaction mixture developed a yellow color at once, and it gave a positive test for iodine with starch–iodide paper (the hydriodic acid used did not). A brown oil separated and became a yellow solid. A nmr spectrum of the supernatant reaction mixture showed that **6** hydriodide (NCH₃ singlet at $\delta$ 2.91) had almost disappeared after 45 min, and the dominant products were **7**₁ and 1,1-dimethylhydrazinium iodide (NCH₃ singlet at 3.10, enhanced by authentic hydrazine). With subsequent nmr scans at 4.5 and 31 hr, the spectrum of **7**₁·HI decreased as it crystallized while ⎯⎯ of the 1,1-dimethylhydrazinium iodide remained unchanged. The solid was

recovered on a filter, and the filtrate was made basic and extracted. These recoveries gave **7**₁ and its hydriodide in 60% yield.

**Trifluoroacetic Acid.** Over 25 min, 48.8 g (0.325 mol) of **6** was added dropwise to a stirred solution of 286.4 g (2.51 mol) of trifluoroacetic acid in water to make 500 ml that was held at 0° under nitrogen. The $N$-methyl singlets of **6** ($\delta$ 2.93) and the major products ($\delta$ 3.07 and 3.11) were integrated to follow the reaction. It was slow at 0° (77% complete in 20 hr; 86%, 43 hr; and 94% after 67 hr); pseudo first order, $k$ = 4 × 10⁻² hr⁻¹ at 0°.

After the reaction mixture had been allowed to stand for 188 hr, one-half of it was evaporated under high vacuum, and the remainder was saturated with potassium carbonate. Evaporation of the ether solution from 72 hr of continuous extraction gave 52.2 g (95%) of a product mixture containing (nmr) 50% of **8**, 40% of **9**, and 10% of presumed 5-*endo*-(2,2-dimethylhydrazine)-6-*exo*-hydroxybicyclo[2.2.1]hept-2-ene (**25**). Recrystallization of 44.6 g of of it from 50 ml of 90% ethanol gave 7.3 g of nearly pure **9**. Another recrystallization from anhydrous ethanol, and sublimation at high vacuum, gave pure **9**: mp 98–99°; nmr and mass spectra identical with those of **9** previously described.

The recrystallization filtrate was evaporated under vacuum in a stream of nitrogen, and the 37.2 g of product mixture obtained was recrystallized from 40 ml of anhydrous ethanol. The 13.0 g of crystals that separated at −20° contained 80% of **8** and 20% of **9**. Another such recrystallization and high-vacuum sublimation gave pure **8**, mp 88–89°, nmr and mass spectra identical with those of **8** described earlier.

The residue from evaporation of recrystallization filtrates was distilled on the vacuum line to give 1.2 g of a mixture containing 60% of **25**, 20% of **8**, and 20% of **9**. From the nmr spectrum of this mixture it was possible to deduce that of **25**: nmr (CDCl₃, A-60) $\delta$ 6.02 (AB m, 2, $J_{AB}$ = 6.0 Hz, $J$ = 2.8 Hz, $J$ = 1.2 Hz, HC=), 3.70 (m, 1, CHN), 3.55 (w, 2, NH and OH), 3.25 (m, 1, $J$ = 1.8 Hz, $J$ = 3.0 Hz, C$H$OH), 2.78 (bm, 2, $W_{H}$ = 6 Hz, bridgehead CH), 2.45 (s, 6, NCH₃), and 1.77 ppm (AB m, 2, CH₂).

**Dilute Hydriodic and Hydrochloric Acids.** An 800-ml solution prepared with 22.73 g of potassium iodide and 103 ml of 12.2 $M$ hydrochloric acid in water (0.171 $M$- iodide and 1.57 $M$ acid) was held at 0° while 9.84 g (0.0665 mol) of **6** was dropped in over 10 min. The reaction mixture immediately became an opaque yellow.

After 4.5 hr at 0°, a nmr spectrum of this reaction mixture showed 84% of 1,1-dimethylhydrazinium ion (singlet at $\delta$ 3.08) and 16% of unreacted **6** (singlet at $\delta$ 2.96). After 20 hr at 0°, it was extracted continuously with ether for 18 hr. The brown extract was titrated with standard sodium thiosulfate and was found to contain 0.0111 mol (17%) of iodine. The remaining ether solution was washed twice with water and then it was dried (Na₂SO₄). Its distillation left a residue that contained (nmr) 0.34 g (0.0036 mol) of **3**, 10.5 g (0.030 mol) of *cis*-3,5-diiodonortricyclene, and 3.5 g (0.010 mol) of *trans*-3,5-diiodonortricyclene.[29]

The acidic reaction mixture following its continuous extraction was made basic by the addition of 50% sodium hydroxide solution. Then this alkaline solution was distilled through a Podbielniak Heligrid column. Fractions with a total volume of 750 ml and boiling from 70 to 100° were titrated with 1 $N$ hydrochloric acid. They contained 0.054 mol (82%) of base shown to be 1,1-dimethylhydrazine. The solution was evaporated to give 5.16 g (0.054 mol, 82%) of 1,1-dimethylhydrazinium chloride: vacuum mp 87–88° from anhydrous ethanol, melting point of mixture with authentic hydrochloride 87–88°. This substance is so hygroscopic that previously recorded melting points are low (81–82°).[30]

(29) H. W. Johnson, Jr., and P. N. Landerman, *J. Org. Chem.*, **27**, 303 (1962).

(30) H. H. Hatt, "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 211.