**Oxidation of Benzoin.**—The oxidation of 1.04 g (4.9 mmol) of benzoin with 1.35 g (10.3 mmol) of sodium dichromate was effected in the presence of benzophenone as an internal standard. After work-up as described above, the amount of benzil was determined by comparison of its vpc trace area with that of benzophenone. No benzaldehyde was found using this excess of chromium(VI). The products were benzil (2.42 mmol, 48%) and benzoic acid (5.37 mmol, 52%).

**Registry No.**—Chromic acid, 7738-94-5; deoxybenzoin, 451-40-1; 3-trifluoromethyl deoxybenzoin, 30934-66-8.

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# Oxymercuration–Demercuration of 6-Methylenebicyclo[3.1.1]heptane and 5-Methylenebicyclo[2.1.1]hexane[1]

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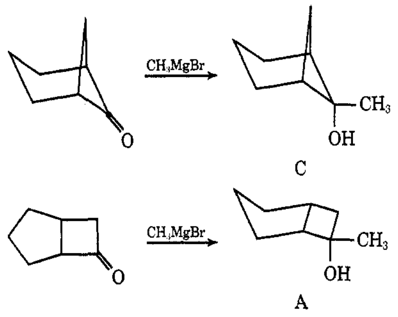
Oxymercuration followed by borohydride reduction has been applied to 6-methylenebicyclo[3.1.1]heptane (I) and 5-methylbicyclo[2.1.1]hexane (II). The reaction of I led to 22% of 6-methylbicyclo[3.1.1]heptan-6-ols, 67% of 6-methylbicyclo[3.2.0]heptan-6-ols, 4% of 2-methylnorbornan-2-ol, and 6% of 2-methylenecycloheptanol. The rearrangements are analogous to those found in the solvolytic reactions of 6-substituted bicyclo[3.1.1]heptanes. The reaction of II led to 44% 2-methylenecyclohexanol, 28% of 3-methylenecyclohexanol, and 28% of 3-methylcyclohex-3-en-1-ol. An examination of the nmr spectrum of the reaction solution as a function of time indicated that a cyclopropane derivative was first formed and that this rearranged further to olefinic compounds. Corresponding product studies showed that the cyclopropane derivative, on reduction, gave 4-methylenecyclohexanol, whereas the other products were derived from the olefinic intermediates.

The oxymercuration of bicyclic olefins followed by *in situ* borohydride reduction of the organomercurial intermediate has been found to be a useful route to alcohols.[3] The reaction leads in effect to Markovnikov hydration, and generally gives little or no rearrangement. Because the reaction might provide a convenient route to alcohols which are epimeric with those formed by Grignard reagent addition to the corresponding ketones, the reaction has been explored with the strained methylenecyclobutane type compounds, 6-methylenebicyclo[3.1.1]heptane (I) and 5-methylenebicyclo[2.1.1]hexane (II).

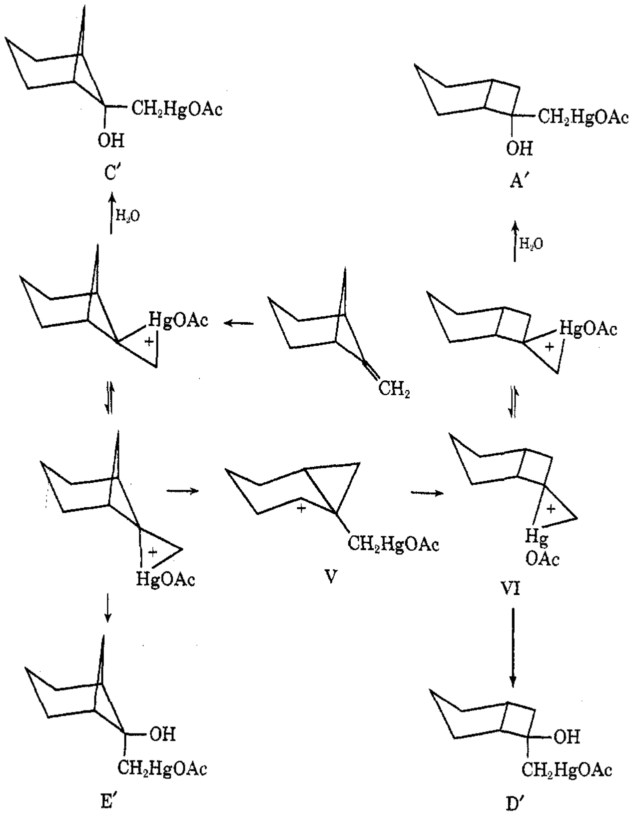
The reaction of I with mercuric acetate in aqueous tetrahydrofuran occurred readily and sodium borohydride reduction was essentially instantaneous. However, instead of producing only one alcohol, a mixture of six alcohols was obtained. They could be separated by gas chromatography, giving A (32%), B (4%), C (20%), D (36%), E (2%), and F (6%). The alcohols A–E all had methyl singlets in their nmr spectra at $\tau$ 8.6–8.8, indicating they were tertiary alcohols. The infrared spectrum of F showed bands at 1625 and 850 cm$^{-1}$, suggesting an exocyclic double bond.

The alcohol C was found to be *endo*-6-methylbicyclo[3.1.1]heptan-6-ol by comparison with the nmr spectrum of an authentic sample prepared by the addition of the methyl Grignard reagent to bicyclo[3.1.1]heptan-6-one. The assignment of configuration is based on analogy with the lithium aluminum hydride reduction of the ketone, which gives 98% of *endo*-bicyclo[3.1.1]heptan-6-ol.[4]

Mechanistic considerations suggested that one of the alcohols might be 6-methylbicyclo[3.2.0]heptan-6-ol. The endo isomer was prepared by the addition of the



SCHEME I



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[1] This investigation was supported by Public Health Service Grant GM12800 from the National Institute of General Medical Studies.

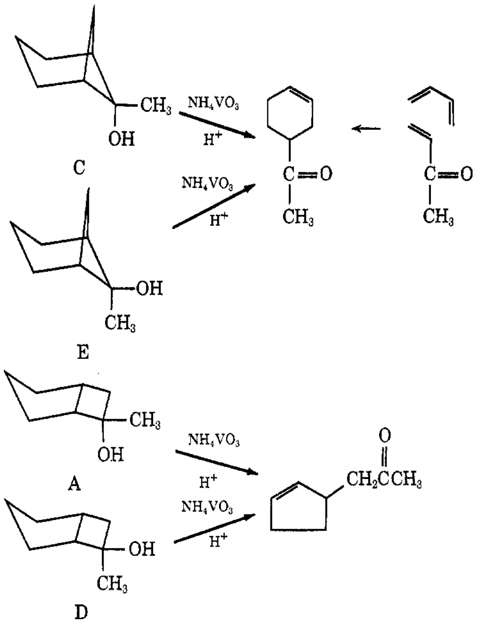
[2] Taken from part of the Ph.D. thesis of Wan-fang Chen, 1971.

[3] H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967); H. C. Brown and W. J. Hammer, *ibid.*, **89**, 1525 (1967); H. C. Brown, J. H. Kawakawi, and S. Ikegamin, *ibid.*, **89**, 1526 (1967).

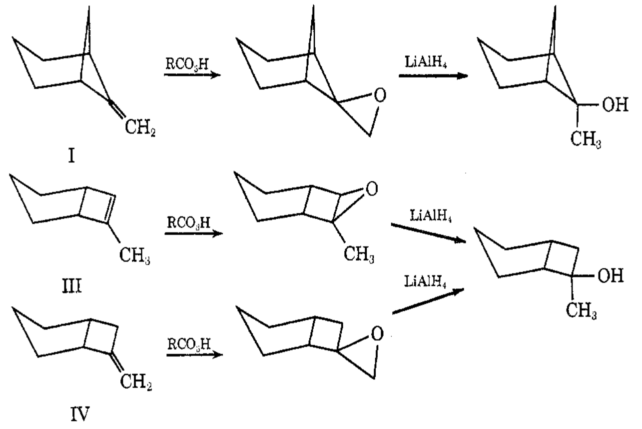
[4] K. B. Wiberg and B. A. Hess, Jr., *ibid.*, **89**, 3015 (1967).

methyl Grignard reagent to bicyclo[3.2.0]heptanone, and was found to be identical with A. Again, the assignment of configuration is based on analogy with the lithium hydride reduction of bicyclo[3.2.0]heptanone, which gives 90% of the endo isomer.[5]

The spectra of E and D were similar to those of C and A, respectively, suggesting that they might be the other members of the epimeric pairs. This was confirmed using vanadium(V) oxidation, which is known to lead to cleavage of tertiary alcohols.[6] The results are shown below.

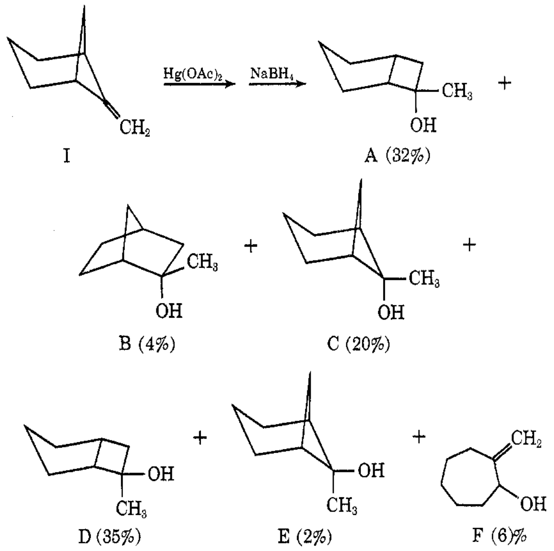


In each case, both isomers gave the same ketonic product, which was identified by comparison with an authentic sample. The alcohols E and D also were prepared by the following methods.



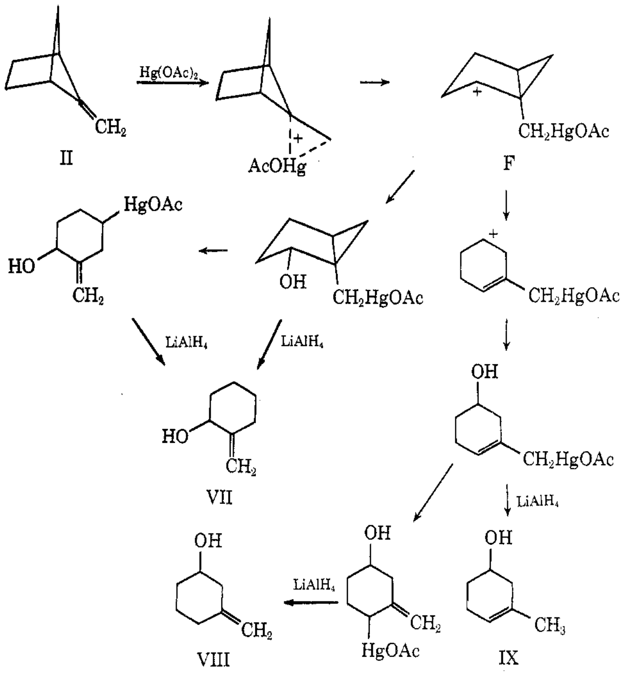
The preparations of the olefins III and IV are described in the Experimental Section.

The alcohol F had an nmr spectrum very similar to that of 2-methylenecyclohexanol except for two more protons in the $\tau$ 8.0–8.8 region. Thus, it appears to be 2-methylenecycloheptanol. The alcohol B had an nmr spectrum corresponding to that of 5-methyl-*endo*-bicyclo[2.1.1]heptan-5-ol, formed by the addition of the methyl Grignard reagent to norbornanone. The course of the oxymercuration–demercuration of I may then be described as



The addition of mercuric acetate to olefins appears to involve initially the addition of HgOAc$^+$ to give a bridged ion.[7] This may be attacked by water to give C′ and E′, from which C and E are derived. A rearrangement corresponding to that found in the solvolysis of *endo*-bicyclo[3.1.1]heptyl-6 tosylate[4] would then give a bicyclo[3.1.0]heptyl cation (V) which may further rearrange to the bicyclo[3.2.0]heptyl-6 cation (VI) from which A′ and D′ are formed (Scheme I).

In order to gain further information on the nature of the reaction, 5-methylenebicyclo[2.2.1]hexane (II) was used as the reactant. The products of the reaction were 2-methylenecyclohexanol (VII) (44%), 3-methylenecyclohexanol (VIII) (28%), and 3-methylcyclohex-3-en-1-ol (IX) (28%). These results may be accommodated as follows.



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(5) F. F. Nelson, Ph.D. Thesis, University of Wisconsin, 1960.

(6) J. R. Jones and W. A. Waters, *J. Chem. Soc.*, 2772 (1960).

(7) *Cf.* W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968); it should be noted that H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **93**, 7335 (1971), have presented evidence which they interpret as disfavoring this type of intermediate.

The results raise two questions. First, why are no unrearranged alcohols formed, whereas significant amounts of such products were found with 6-methylbicyclo[3.1.1]heptane? Second, why does the product have predominantly the less stable exocyclic double bond when its precursor presumably had an endocyclic double bond?

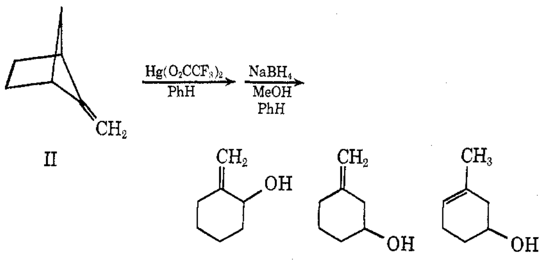
Additional information concerning the course of the reaction was obtained *via* an nmr study of the reaction of mercuric trifluoroacetate[8] with II in benzene solution. The signal from the original olefin protons disappeared completely by the time the first spectrum was taken (5 min). Cyclopropyl protons and olefinic protons were found at τ 9–10 and 4.5–6, respectively. As time went on, the cyclopropyl protons began to disappear and were replaced by olefinic protons (Table I).

TABLE I

CHANGE IN NMR SPECTRUM DURING THE REACTION OF MERCURIC TRIFLUOROACETATE WITH 5-METHYLENEBICYCLO[2.1.1]HEXANE

| Reaction time | Number of protons | | |
|---|---|---|---|
| | τ 4.5–6 | τ 7.5–9 | τ 9–10 |
| 5–75 min | 1.3 | 7.4 | 1.3 |
| 24 hr | 1.7 | 7.6 | 0.7 |
| 40 hr | 1.74 | 7.86 | 0.4 |
| 60 hr | 1.8 | 7.92 | 0.28 |
| 132 hr | 1.92 | 7.94 | 0.14 |

The products from the mercuric trifluoroacetate reaction were determined by adding the benzene solution to sodium borohydride in methanol. The results were



II

| | VII | VIII | IX |
|---|---|---|---|
| (a) 70° | 16% | 70% | 14% |
| (b) 0° | 71% | 29% | 0% |

When the reaction was carried out at 0° for a short time before quenching with sodium borohydride, 4-methylenecyclohexanol was the major product, and no 3-methylcyclohex-3-en-1-ol was formed. When the reaction was carried out at 70° (corresponding to the longer reaction times in Table I), 3-methylenecyclohexanol became the major product and some IX was also formed.

It is clear from these results that VII is formed from a precursor containing a cyclopropane ring and that VIII and IX are formed from further rearranged species. The lack of unrearranged alcohols probably results from the driving force for strain relief which leads to rapid rearrangement to the cyclopropylcarbinyl cation, F. The alcohols VIII and IX are not formed from the same intermediate, but rather appear to be formed from two separate intermediates, one of which is derived from the other.

## Experimental Section

**7-Formylbicyclo[3.2.1]octan-6-one.**—With ice-bath cooling, 62 g (0.5 mol) of bicyclo[3.2.1]octan-6-one[9] was dropped into a suspension of 54 g of sodium methoxide in 60 g of methyl formate and 100 ml of anhydrous ether. The mixture was stirred overnight at room temperature. It was then cooled and 20 ml of ice–water was added. The ether layer was separated and the aqueous layer was washed once with ether. The aqueous layer was acidified with 60 g of acetic acid and 100 ml of water and extracted with three 300-ml portions of ether. The combined extracts were dried over anhydrous magnesium sulfate. The solvent was removed using a rotary evaporator, and the residue was distilled giving 53 g (70%) of 7-formylbicyclo[3.2.1]octan-6-one, bp 80° (0.5 mm).

**7-Diazobicyclo[3.2.1]octan-6-one.**—To a solution of 53 g (0.35 mol) of 7-formylbicyclo[3.2.1]octan-6-one and 70 g of triethylamine in 345 ml of ethylene chloride was added dropwise 70 g of *p*-toluenesulfonyl azide. The reaction mixture was stirred at room temperature overnight. The yellow solution was washed with a solution of 21 g of potassium hydroxide and 200 ml of water. The aqueous solution was separated and washed with three 80-ml portions of methylene chloride. The methylene chloride solutions were combined, washed with saturated sodium chloride solution, and dried over magnesium sulfate. The solvent was removed using a rotary evaporator, giving 30 g (58%) of 7-diazobicyclo[3.2.1]octan-6-one, which was used without further purification. The diazoketone was converted to bicyclo[3.1.1]-heptane-6-carbonyl chloride as described previously.[9]

***N*,*N*-Dimethylbicyclo[3.1.1]heptane-6-carboxamide.**—To a stirred and cooled mixture of 55 g of 25% dimethylamine and 150 ml of ether was added 20.1 g (0.13 mol) of bicyclo[3.1.1]heptane-6-carbonyl chloride. The solution was stirred for 8 hr after the addition was completed. The mixture was then diluted with 150 ml of water and extracted with four 50-ml portions of ether. After drying the ether was removed by distillation. The residue was distilled, giving 18.8 g (89%) of the amide, bp 121–122° (15 mm).

**6-Dimethylaminomethylbicyclo[3.1.1]heptane.**—To a stirred slurry of 15 g of lithium aluminum hydride and 100 ml of anhydrous ether was added a solution of 18.8 g (0.11 mol) of *N*,*N*-dimethylbicyclo[3.1.1]heptane-6-carboxamide in 200 ml of anhydrous ether. After the addition, the mixture was stirred for 24 hr at room temperature. It was then cooled in an ice bath, 50 ml of cold water was added cautiously, and it was stirred vigorously for 2 hr. After filtering by suction the salt was washed with three 50-ml portions of ether. The ether fractions were combined and dried over magnesium sulfate. The ether was distilled using a 30 in. Helipack column and the residue was distilled to give 15.5 g (90%) of the amine, bp 69° (10 mm).

**6-Dimethylaminomethylbicyclo[3.1.1]heptane *N*-Oxide.**—To a cooled and stirred solution of 15.5 g (0.1 mol) of 6-dimethylaminomethylbicyclo[3.1.1]heptane in 120 ml of methanol was added dropwise 57 g of 30% hydrogen peroxide. After the reaction mixture was stirred for 24 hr, 10 g of 30% hydrogen peroxide was added. The reaction mixture was then stirred for another 20 hr. A small amount of platinum black in water was added and the solution was stirred for 4 hr until no further oxygen was involved. The solvent was removed under reduced pressure, giving a residue which solidified to a waxlike paste (17.8 g, 97%) of the crude *N*-oxide.

**6-Methylenebicyclo[3.1.1]heptane.**—6-Dimethylaminomethylbicyclo[3.1.1]heptane *N*-oxide (17.8 g, 0.11 mol) was heated to 190° in a 15-ml round-bottom flask fitted with two successive Dry Ice–acetone traps at a pressure of 5 mm. After 10 hr the reaction mixture was completely pyrolyzed. The collection traps contained two liquid phases. After an addition of 150 ml of olefin-free pentane, the reaction mixture was washed successively with 100-ml portions of 1 *N* hydrochloric acid, two 50-ml portions of saturated sodium carbonate solution, 50 ml of water, and 50 ml of saturated sodium chloride solution. After drying over anhydrous potassium carbonate, pentane was removed using a 30-in. Helipack column. The residue was distilled carefully to give 7.9 g (70%) of the olefin, bp 92° (150 mm). The infrared spectrum had a C=C band at 1670 $cm^{-1}$. The nmr spectrum had bands at τ 5.4 (2 H, s), 6.7–7.0 (2 H, broad singlet), 7.8–8.8 (8 H, multiplet).

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[8] H. C. Brown, M.-H. Rei, and K.-T. Liu, *J. Amer. Chem. Soc.*, **92**, 1760 (1970).

[9] K. B. Wiberg and B. A. Hess, Jr., *J. Org. Chem.*, **31**, 2250 (1966).

*Anal.* Calcd for $C_8H_{12}$: C, 88.8; H, 11.2. Found: C, 88.6; H, 11.1.

**Bicyclo[3.1.1]heptan-6-one.**—A mixture of 1.5 g (0.014 mol) of 6-methylenebicyclo[3.1.1]heptane and 2 ml of pyridine in 20 ml of methylene chloride was placed in the flask with an ozone inlet and the outlet attached to a 5% potassium iodide solution. The mixture was cooled at −80° in a Dry Ice–acetone bath. A stream of ozone was bubbled into the mixture until the potassium iodide solution turned from pale yellow to dark brown. The mixture was then allowed to warm to room temperature. The solvent was removed using a rotary evaporator and the residue was extracted with three 50-ml portions of ether. The combined ether solution was then washed successively with dilute acid, water, saturated sodium bicarbonate solution, and saturated sodium chloride solution. After drying over anhydrous potassium carbonate, the ether was removed using a 30-in. Helipack column to give 0.8 g (53%) of the ketone. Vpc analysis indicated only one component. The infrared spectrum showed a peak at 1780 $cm^{-1}$ (C=O) and the nmr spectrum had bands at $\tau$ 6.8–7.1 (2 H, broad singlet), 7.4–7.8 (4 H, multiplet), 7.9–8.5 (4 H, multiplet). The product was identical with that previously prepared *via* a different method.[4]

**6-Methyl-*endo*-bicyclo[3.1.1]heptan-6-ol.**—Methyl bromide was bubbled into a mixture of 0.5 g of magnesium turnings and 25 ml of anhydrous ether until the magnesium had dissolved. The reaction mixture was heated to reflux for 30 min to remove the excess methyl bromide. It was then cooled to 0° and 0.8 g (7 mmol) of bicyclo[3.1.1]heptan-6-one in 15 ml of anhydrous ether was added dropwise. After the addition, the solution was stirred overnight and then the magnesium salt was decomposed by adding 5 ml of ice–water and 15 ml of saturated ammonium chloride solution. The ether layer was separated, and the water layer was saturated with sodium chloride and extracted with two 20-ml portions of ether. The ether layers were combined and dried over magnesium sulfate and the solvent was removed using a rotary evaporator. The residue was distilled at 150° (0.3 mm), giving 0.8 g (87%) of the alcohol. The nmr spectrum had bands at $\tau$ 8.6 (3 H, s) and 7.67–8.9 (10 H, multiplet).

*Anal.* Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 75.9, 76.1; H, 11.3, 11.2.

The 3,5-dinitrobenzoate was prepared and after recrystallization from hexane it had mp 117–118.5°.

**6-Methyl-*exo*-bicyclo[3.1.1]heptan-6-ol.**—A mixture of 1.62 g (0.015 mol) of 6-methylenebicyclo[3.1.1]heptane and 1.5 g of sodium carbonate in 20 ml of methylene chloride was cooled in an ice–water bath and 4 g of *m*-chloroperbenzoic acid in 25 ml of methylene chloride was added dropwise. After stirring overnight, the solution was cooled to 0° and sodium sulfite was added to destroy the excess perbenzoic acid. The reaction mixture was diluted with 50 ml of water and the methylene chloride later was separated. The aqueous layer was washed with 20-ml portions of methylene chloride. The methylene chloride solutions were combined and washed with sodium bicarbonate solution, water, and saturated sodium chloride solution. After drying over anhydrous magnesium sulfate, the excess methylene chloride was removed, giving 1.7 g of crude epoxide. This was purified by vpc using a 10 ft × 0.375 in. Silicon oil column at 140°, giving 0.92 g (50%) of the pure epoxide, retention time 17 min. The nmr spectrum had bands at $\tau$ 7.49 (2 H, s) and 7.5–8.7 (10 H, multiplet).

*Anal.* Calcd for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.2, 77.2; H, 10.0, 9.8.

A solution of 0.92 g (7.4 mmol) of the epoxide and 20 ml of anhydrous ether was added to a stirred slurry of lithium aluminum hydride and 40 ml of anhydrous ether. The reaction mixture was worked up in the usual fashion, giving 0.75 g (81%) of the tertiary alcohol. The nmr spectrum had bands at $\tau$ 8.82 (3 H, s) and 7.73–8.84 (10 H, multiplet).

*Anal.* Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.1, 75.9; H, 11.0, 11.2.

The dinitrobenzoate was prepared and after recrystallization from hexane it had mp 165–166°.

**6-Methyl-*endo*-bicyclo[3.2.0]heptan-6-ol.**—The reaction of 1.1 g (0.01 mol) of bicyclo[3.2.0]heptan-6-one with methylmagnesium bromide was carried out as described above. Distillation at 150° (0.3 mm) gave 1.0 g (81%) of 6-methyl-*endo*-bicyclo-[3.2.0]heptan-6-ol. Its nmr spectrum had bands at $\tau$ 8.7 (3 H, s) and 7.33–9.07 (10 H, multiplet).

*Anal.* Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 75.9, 76.1; H, 11.3, 11.2.

The 3,5-dinitrobenzoate was prepared. After recrystallization from hexane it had mp 126–127°.

**6-Methylbicyclo[3.2.0]hept-6-ene.**—6-Bicyclo[3.1.0]hexyl methyl ketone (1.24 g, 0.01 mol) was converted to the tosylhydrazone with 1.86 g (0.01 mol) of *p*-toluenesulfonhydrazide in 10 ml of 60% aqueous methanol. After recrystallization from methanol, it had mp 123–125°. The tosylhydrazone was converted to the sodium salt using the procedure of Friedman and Schechter[10] and was pyrolyzed at 160°. The product was analyzed by vpc using a 10 ft × 0.375 in. silicon oil column at 100°. Besides the solvent, diglyme, only 0.4 g (28%) of a product with retention time 10 min was obtained. The nmr spectrum had bands at $\tau$ 4.58 (broad singlets), two bridgehead hydrogens at 7.01 and 7.12, and nine methylene hydrogens at 8.1–8.8.

**6-Methyl-*exo*-bicyclo[3.2.0]heptan-6-ol.**—6-Methylbicyclo-[3.2.0]heptene-6 (0.4 g, 3.7 mmol) was converted to the epoxide with 1.5 g of *m*-chloroperbenzoic acid as described above. Reduction was affected using 0.2 g of lithium aluminum hydride in 40 ml of ether, giving 0.2 g (88%) of the tertiary alcohol. The nmr spectrum had bands at $\tau$ 8.92 (3 H, singlet) and 6.92–8.85 (10 H, multiplet).

*Anal.* Calcd for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 76.0, 76.1; H, 11.3, 11.4.

**6-Methylenebicyclo[3.2.0]heptane.**—A solution of 0.05 mol of *n*-butyllithium in about 150 ml of ether was stirred under nitrogen, and 0.5 mol of crystalline methyltriphenylphosphonium bromide was added over a 5-min period. After the solution was stirred for 4 hr at room temperature, 5 g (0.045 mol) of bicyclo-[3.2.0]heptan-6-one was added dropwise. The solution became colorless and the white precipitate separated. The mixture was heated to reflux overnight and cooled, and the precipitate was removed by filtration. The ether solution was washed with water and then dried. The ether was distilled through a 30-in. Helipack column and the residue was purified by vpc using a 10 ft × 0.375 in. silicon oil column to give 0.8 g (16%) of 6-methylenebicyclo[3.2.0]heptane, retention time 11 min. The ir spectrum showed C=C absorption at 1640 and 880 $cm^{-1}$. The nmr spectrum had bands at $\tau$ 5.33 (2 H, m) and 6.62–8.7 (10 H, m).

**6-Methyl-*exo*-bicyclo[3.2.0]heptan-6-ol.**—6-Methylenebicyclo-[3.2.0]heptane (0.8 g, 0.074 mol) was converted to the epoxide with 3 g of *m*-chloroperbenzoic acid as was described above, giving 0.41 g (44%) of the epoxide. The lithium aluminum hydride reduction of 0.4 g of the epoxide gave 0.32 g (77%) of 6-methyl-*exo*-bicyclo[3.2.0]heptan-6-ol. The product was identical with that described above.

The alcohol was converted to the 3,5-dinitrobenzoate, which after recrystallization from hexane had mp 115–116°.

**Vanadium(V) Oxidation of 6-Methyl-*endo*-bicyclo[3.1.1]heptan-6-ol.**—A solution of 1 g of concentrated sulfuric acid in 10 ml of water was added dropwise to a mixture of 0.25 g (0.02 mol) of 6-methyl-*endo*-bicyclo[3.1.1]heptan-6-ol, 0.47 g (0.04 mol) of ammonium vanadate, and 30 ml of water. The reaction mixture was stirred overnight and then extracted with three 40-ml portions of ether. The solution was dried over magnesium sulfate, ether was removed, and the residue was analyzed by vpc using a 20 ft × 0.375 in. DEGS column at 150°. Only one product, retention time 22 min, was found. It was shown to be 3-cyclohexenyl methyl ketone by comparison with an authentic sample.

The reaction also was carried out using the exo isomer, and the same product was found.

**Vanadium(V) Oxidation of 6-Methyl-*endo*-bicyclo[3.2.0]heptan-6-ol.**—The oxidation of 6-methyl-*endo*-bicyclo[3.2.0]heptan-6-ol was effected using the above procedure. The only product, retention time 37 min, was identified as 2-cyclopentenyl-1-acetone by comparison with an authentic sample.

**5-Methylenebicyclo[2.1.1]hexane.**—To a stirred slurry of 3.2 g of lithium aluminum hydride in 100 ml of anhydrous ether was added a solution of 12.5 g (0.082 mol) of *N*,*N*-dimethylbicyclo-[2.1.1]hexane-6-carboxamide[11] in 150 ml of dry ether. After stirring for 24 hr, the mixture was cooled in an ice bath and treated with 50 ml of cold water. The ether solution was separated by filtration, dried over magnesium sulfate, and distilled, giving 10.5 g (93%) of 5-dimethylaminobicyclo[2.1.1]hexane, bp 46–47° (8 mm). To a cooled and stirred solution of the amine in 120 ml of methanol was added dropwise 52 g of 30% hydrogen

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(10) L. Friedman and H. Schechter, *J. Amer. Chem. Soc.*, **83**, 3159 (1961).

(11) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *ibid.*, **83**, 3998 (1961).

peroxide. After 24 hr, an additional 10 g of hydrogen peroxide was added. Twenty hours later it was treated with platinum black in water. Removal of the solvent gave 11 g (94%) of the *N*-oxide. The latter was heated in a 50-ml flask to 180° (5 mm) and the product was collected in two successive Dry Ice–acetone traps. It was taken up in 150 ml of olefin-free pentane, and the pentane solution was washed with 100 ml of 1 *N* hydrochloric acid, two 50-ml portions of sodium bicarbonate solution, and water. After drying over potassium carbonate, distillation gave 4 g (60%) of 5-methylenebicyclo[2.1.1]hexane, bp 70–72° (100 mm). The nmr spectrum had bands at $\tau$ 5.78 (2 H, s), 7.17 (2 H, s), 8.28–9.2 (6 H, m).

*Anal.* Calcd for $C_7H_{10}$: C, 89.3; H, 10.7. Found: C, 89.2; H, 10.6.

**Oxymercuration–Demercuration of 6-Methylenebicyclo[3.1.1]heptane.**—To a stirred mixture of 9.57 g (0.03 mol) of mercuric acetate, 30 ml of water, and 30 ml of tetrahydrofuran was added 3.24 g (0.03 mol) of 6-methylenebicyclo[3.1.1]heptane. The solution became colorless and clear in 28 sec. After the solution was stirred for an additional 5 min at room temperature, 30 ml of 3 *M* sodium hydroxide was added followed by 30 ml of 3 *M* sodium borohydride in 3 *M* sodium hydroxide. The reduction appeared to be instantaneous. The aqueous layer was saturated with sodium chloride, and the organic layer was separated. The aqueous solution was extracted with ether. The combined organic solution was dried over magnesium sulfate, concentrated using a rotary evaporator, and separated into its components by vpc using a 28 ft × 0.375 in. 20% Carbowax column at 140°. The products were 6-methyl-*endo*-bicyclo[3.2.0]heptan-6-ol (32%, 35 min); 2-methylbicyclo[2.2.1]heptan-2-ol (4%, 40 min); 6-methyl-*endo*-bicyclo[3.1.1]heptan-6-ol (20%, 45 min); 6-methyl-*exo*-bicyclo[3.2.0]heptan-6-ol (35%, 50 min); 6-methyl-*exo*-bicyclo[3.1.1]heptan-6-ol (2%, 58 min); and 2-methylenecycloheptanol (6%, 80 min).

**Oxymercuration–Demercuration of 5-Methylenebicyclo[2.1.1]hexane.**—To a mixture of 3.2 g (0.01 mol) of mercuric acetate, 10 ml of water, and 10 ml of tetrahydrofuran was added 0.94 g (0.01 mol) of 5-methylenebicyclo[2.2.1]hexane. The solution became clear and colorless in 32 sec. Reduction with sodium borohydride (10 ml of 0.5 *M*) and subsequent work was effected as described above giving 2-methylenecyclohexanol (44%, 17.7 min, 220-in. TCEP column at 110°), 3-methylenecyclohexanol (28%, 18.7 min), and 3-methyl-$\Delta^3$-cyclohexanol (28%, 21.5 min).

**Nmr Study of the Reaction of Mercuric Trifluoroacetate with 5-Methylenebicyclo[2.1.1]hexane in Benzene Solution.**—A 2 *M* solution of 5-methylenebicyclo[2.1.1]hexane in benzene (solution A) and a 2 *M* solution of mercuric trifluoroacetate in benzene (solution B) was prepared. Equal volumes of the two solutions were mixed in an nmr tube and spectra were taken 5 min, 20 min, 45 min, 75 min, 24 hr, 40 hr, 60 hr, and 132 hr after mixing. The signal of the original olefinic protons ($\tau$ 5.78) had completely disappeared in 5 min and cyclopropyl protons ($\tau$ 9–10), new olefinic protons and the proton $\alpha$ to the trifluoroacetyl group ($\tau$ 4.5–6) were found. As time went on the cyclopropyl proton bands diminished and were replaced with olefinic protons.

The reaction also was carried out on a preparative scale. To a solution of 0.94 g (0.01 mol) of 5-methylenebicyclo[2.1.1]hexane in 5 ml of benzene was added a solution of 4.35 g (0.01 mol) of mercuric trifluoroacetate in 5 ml of benzene. The reaction was quite exothermic and the temperature increased to 70°. After the solution had cooled to room temperature, a solution of 0.9 g of sodium borohydride in 10 ml of 1:1 benzene-methanol was added. The mixture was filtered, concentrated using a rotary evaporator, and analyzed by vpc using a 220-in. TCEP capillary column at 110°. The products were 2-methylenecyclohexanol (16%), 3-methylenecyclohexanol (70%), and 3-methyl-$\Delta^3$-cyclohexanol (14%). The reaction was repeated with the temperature controlled at 0° throughout. The products were 2-methylenecyclohexanol (71%) and 3-methylenecyclohexanol (29%).

**Registry No.**—I, 35324-39-1; II, 28366-41-8; 7-formylbicyclo[3.2.1]octan-6-one, 35324-41-5; *N*,*N*-dimethylbicyclo[3.1.1]heptane-6-carboxamide, 35324-42-6; 6-dimethylaminomethylbicyclo[3.1.1]heptane, 35378-27-9; 6-methyl-*endo*-bicyclo[3.1.1]heptan-6-ol, 35378-28-0; 6-methyl-*endo*-bicyclo[3.1.1]heptan-6-ol 3,5-dinitrobenzoate, 35378-29-1; 6,8-epoxybicyclo-[3.1.1]heptene-6, 35323-95-6; 6-methyl-*exo*-bicyclo-[3.1.1]heptan-6-ol, 35323-96-7; 6-methyl-*exo*-bicyclo-[3.1.1]heptan-6-ol 3,5-dinitrobenzoate, 35323-97-8; 6-methyl-*endo*-bicyclo[3.2.0]heptan-6-ol, 13837-37-1; 6-methyl-*endo*-bicyclo[3.2.0]heptan-6-ol 3,5-dinitrobenzoate, 35323-99-0; 6-methyl-*exo*-bicyclo[3.2.0]heptan-6-ol, 35324-00-6; 6-methyl-*exo*-bicyclo[3.2.0]heptan-6-ol 3,5-dinitrobenzoate, 35324-01-7.

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# Bridged Polycyclic Compounds. LXXIII. Nitrous Acid Deaminations of Some Isomeric Aminodibenzobicyclooctadienes[1]

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Reaction of 7-aminodibenzobicyclo[2.2.2]octadiene (**1a**) and *exo*- and *endo*-2-aminodibenzobicyclo[3.2.1]octadienes (**2a** and **3a**) with nitrous acid in glacial acetic acid leads primarily to dibenzobicyclo[3.2.1]octadien-*exo*-2-ol (**2c**) and the corresponding acetate (**2d**). Changes in product ratios with solvent composition suggest that the relatively large amount of alcohol product results partly from an intramolecular reaction pathway, involving the diazohydroxide intermediate.

Quantitative differences in product-forming pathways in amine deaminations, compared with halide or sulfonate solvolyses, have been described by many workers.[2] However, the inherent difficulty of using product-distribution studies to determine the roles of diazonium ions and carbonium ions with varying structures and under widely different conditions has led to proposals of a variety of intermediate species in the product-determining steps of the amine–nitrous acid and related reactions. Only recently has a comprehensive theory begun to emerge, which can account for the many "unusual" products in the amine–nitrous acid reaction.[2b–d]

The large body of data concerning solvolytic pathways in the dibenzobicyclooctadienyl system led us to a comparative study of the amine–nitrous acid reaction in this system. Cationic intermediates produced by solvolysis of dibenzobicyclo[2.2.2]octadienyl substrates

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[1] (a) Paper LXXII: S. J. Cristol, A. L. Noreen, and G. W. Nachtigall, *J. Amer. Chem. Soc.*, **94**, 0000 (1972). (b) This work was reported at the 18th National Organic Symposium of the American Chemical Society, Columbus, Ohio, June 1963.

[2] (a) H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1961, pp 123–136; (b) R. A. M. O'Ferrall, *Advan. Phys. Org. Chem.*, **5**, 362 (1967); (c) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, pp 440–483; (d) L. Friedman in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 655–713.