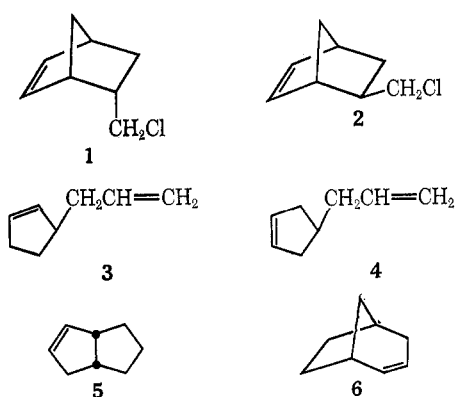# 5-Norbornenyl- and 2-Norbornylcarbene Intermediates

PETER K. FREEMAN*[1] AND KANTILAL B. DESAI

*Department of Chemistry, University of Idaho, Moscow, Idaho 83843*

Carbenoid decomposition of *endo*-5-norbornenecarboxaldehyde tosylhydrazone produces a mixture of 5-methylenenorbornene and *endo*-tricyclo[3.2.1.0$^{2,4}$]octene-6 in a ratio of 57:42. Decomposition of epimeric *exo*-5-norbornenecarboxaldehyde tosylhydrazone gives 5-methylenenorbornene and *exo*-tricyclo[3.2.1.0$^{2,4}$]octene-6 in a ratio of 23:76. In contrast, the reaction of *endo*-2-norbornylmethyl chloride with sodium in *n*-decane produces a mixture of *endo*-2-methylnorbornane, bicyclo[3.2.1]octene-2, and *endo*-tricyclo[3.2.1.0$^{2,4}$]octane in the ratio of 65:24:11. The exo epimer, *exo*-2-norbornylmethyl chloride, reacts with sodium under identical conditions to generate a hydrocarbon mixture of *exo*-2-methylnorbornane and *exo*-tricyclo[3.2.1.0$^{2,4}$]octane in a 68:32 ratio. Carbenoid decomposition of *endo*-2-norbornanecarboxaldehyde tosylhydrazone yields a hydrocarbon mixture of 2-methylenenorbornane, bicyclo[3.2.1]octene-2, and *endo*-tricyclo[3.2.1.0$^{2,4}$]octane in a ratio of 41:4:55. The epimeric *exo*-2-norbornanecarboxaldehyde tosylhydrazone decomposes under the same conditions to generate a mixture of methylenenorbornane and *exo*-tricyclo[3.2.1.0$^{2,4}$]octane in a ratio of 11:89. The mechanistic implications of these results are discussed.

The present study of 5-norbornenyl- and 2-norbornylcarbenes and carbenoids was initiated for several reasons. Previously we have reported that treatment of either *exo*- or *endo*-5-norbornenylmethyl chloride (**1** or **2**) with sodium in *n*-decane at 85–90° leads to a mixture of $C_8H_{12}$ hydrocarbons composed of allylcyclopentenes (**3** and **4**) and bicyclooctenes (**5** and **6**).[2] Thus the formation of products appears to be most reasonably explained on the basis of cleavage of the initially formed alkylsodium intermediates. The major products (**3**, **4**, and **5**) are formed by cleavage to a resonance-stabilized allylcyclopentenyl carbanion, which may generate either **3** or **4**, or undergo ring reclosure, which leads to *cis*-bicyclo[3.3.0]octene-2. The formation of bicyclo[3.2.1]octene-2 may be rationalized by suggesting that an intramolecular addition of *endo*-5-norbornenylmethylsodium generates 2-tricyclo[3.2.-1.0$^{3,6}$]octylsodium, which produces **6** by a ring cleavage route. Thus, all volatile hydrocarbon products are formed directly from alkylsodium intermediates; no carbenoid products ($C_8H_{10}$) were detected in the volatile hydrocarbon fraction investigated.



Therefore, we were interested in the reaction routes which would be utilized by both *endo*- and *exo*-5-norbornenylcarbene intermediates. The *endo*-5-norbornenylcarbene intermediate appears to be especially interesting, since intramolecular interaction with the double bond seems to be a likely possibility and should provide some distortion (geometry intermediate between **7** and **8**) and stabilization. Such intramolecular

interaction should lead to intramolecular addition generating symmetrical ($C_s$) tetracyclooctane (**8**), previously synthesized *via* a carbene insertion path of 2-carbenatricyclo[3.2.1.0$^{3,6}$]octane,[3] or, if the increase in strain energy for intramolecular reaction is prohibitive, intramolecular addition may be prevented, but the interaction with the double bond may confer nonclassical character upon the carbene intermediate (a "foiled reaction" methylene).[4]
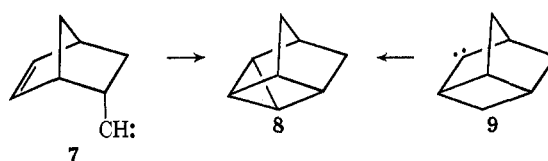


## Results

The tosylhydrazone of *endo*-5-norbornenecarboxaldehyde was prepared and then converted to the sodium salt using excess sodium methoxide (3.26 equiv) in bis(2-ethoxyethyl) ether. Decomposition of the sodium salt of **10** was effected by heating the bis(2-ethoxyethyl) ether solution at 180°; a 13% yield of volatile hydrocarbons was isolated, which consisted of 57% 5-methylenenorbornene (**11**) and 42% *endo*-tricyclo[3.2.1.0$^{2,4}$]octene-6 (**12**), which were readily identified by spectral comparison with spectra of authentic standards, and a 1% component, which was not identified, but was determined not to be bicyclo[3.2.1]octa-2,6-
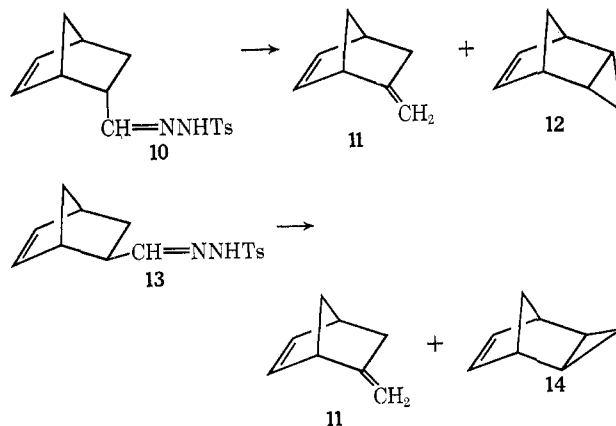


(1) Address all correspondence to this author at the Department of Chemistry, Oregon State University, Corvallis, Oreg. 97331.

(2) P. K. Freeman, V. N. M. Rao, D. E. George, and G. L. Fenwick, *J. Org. Chem.*, **32**, 3958 (1967).

(3) P. K. Freeman, V. N. M. Rao, and G. E. Bigam, *Chem. Commun.*, 511 (1965).

(4) R. Gleiter and R. Hoffman, *J. Amer. Chem. Soc.*, **90**, 5457 (1968).

diene. The epimeric tosylhydrazone (13) was prepared and decomposed in an identical manner yielding a 9% yield of hydrocarbons, which consisted of 23% 5-methylenenorbornene (11) and 76% exo-tricyclo-[3.2.1.0$^{2,4}$]octene-6 (14), which was identified by infrared and nmr spectral comparison with the spectra of an authentic sample of 14.

Thus the exo- and endo-5-norbornenylcarbene intermediates generate different ratios of hydrogen shift and C–H insertion products. In order to focus attention on the role of the double bond, we chose to investigate the related exo- and endo-2-norbornylcarbene intermediates. Treatment of endo-2-norbornylmethyl chloride with sodium in n-decane, under the same conditions used in the investigation of the cleavage reactions of exo and endo-5-norbornenylmethyl chloride with sodium, resulted in a 28% yield of a volatile hydrocarbon fraction which was composed of 65% endo-2-methylnorbornane (16), 24% bicyclo[3.2.1]octene-2 (17), and 11% endo-tricyclo[3.2.1.0$^{2,4}$]octane (18). The analogous reaction of exo-2-norbornylmethyl chloride with sodium in n-decane at 85–90° produced a 47% yield of hydrocarbons, which consisted of 68% exo-2-methylnorbornane (20) and 32% exo-tricyclo[3.2.1.0$^{2,4}$]octane (21). Tricyclo[3.2.1]octene-2, formed in the reaction of 15, was identified by spectral comparison with the corresponding data of an authentic sample, while 18, formed from 15, and 21, from 19, were identified by comparison of infrared and nmr data with those of standards prepared by reduction of olefins 12 and 14.



15



16          17          18



19          20          21
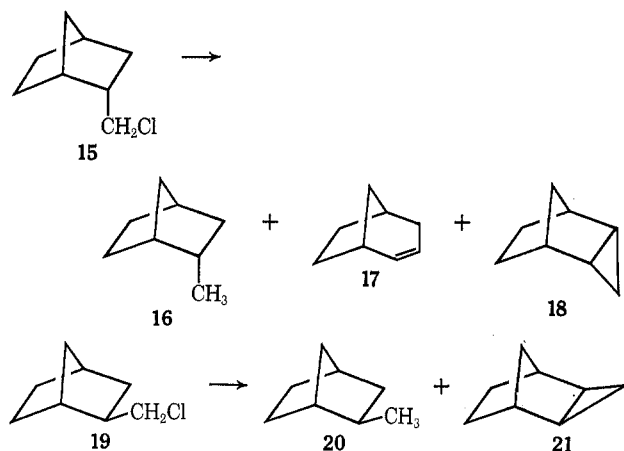
Since the reaction of primary chlorides 15 and 19 with sodium should generate carbenoids, rather than carbenes, additional reaction pathways, as illustrated by the formation of ring expansion product 17, might be the result of the complexed nature of the bivalent intermediate. We chose, therefore, to consider the exo- and endo-2-norbornylcarbene intermediates generated by decomposition of the corresponding tosylhydrazone percursors in excess sodium methoxide in bis(2-ethoxyethyl) ether. Decomposition of tosylhydrazone 22 under conditions similar to those used for decomposition of 10 and 13 resulted in a 43% yield of a hydrocarbon fraction which was composed of 41% 2-methylenenorbornane, 4% bicyclic 17, and 55% insertion product 18. In contrast, decomposition of tosylhydrazone 24, under identical conditions, generated a mixture of volatile hydrocarbons in 14% yield, which was composed of 11% 23 and 89% 21.



22          23



24          → 23 + 21
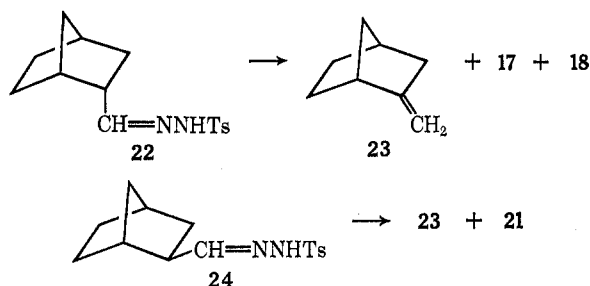
## Discussion

Since in the thermal decomposition of the sodium salt of tosylhydrazone 10 no tetracyclic 8 was detected, and since the reaction conditions used were similar to those employed for the generation of 8 via 2-carbenatricyclo[3.2.1.0$^{3,6}$]octane (9), it seems reasonably certain that if tetracyclic 8 were formed in the carbenoid decomposition of tosylhydrazone 10 it would have survived. Thus the alternatives available for intermediate 7 are that it might exhibit characteristics of a foiled carbene addition process or that the interaction might be chemically insignificant. If one assumes that the bivalent intermediates formed in the base-induced decompositions of hydrazones 10 and 13 are singlet-state intermediates, interaction of the empty p orbital on the carbene carbon ($C_\alpha$) with the $\pi$ cloud of the double bond might effect the relative rates of insertion and hydrogen migration. Thus in the intermediate formed from decomposition of 10, overlap of the p orbital with the $\pi$ bond should bend the carbene carbon toward the double bond and reduce the eclipsing interaction between $C_\alpha$ and the endo C-6 hydrogen. Since the favored transition state geometry is believed to be syn periplanar,[5] the insertion rate should be retarded relative to that for the exo epimer. On the other hand, inspection of models indicates that overlap of the p orbital with the $\pi$ system should align the p orbital in a syn periplanar fashion with the exo C-5 hydrogen and thus facilitate hydrogen migration. Since Kirmse found that base-induced decomposition of cyclopentanecarboxaldehyde tosylhydrazone produces methylenecyclopentane and bicyclo[3.1.0]hexane in a 27.5:72.5 ratio,[5a] the ratio of 23:76 for hydrogen migration/insertion in the case of exo-5-norbornenylcarbene appears normal and the corresponding ratio of 57:42 for endo-5-norbornylcarbene appears to be altered as anticipated for a delocalized carbene intermediate.

However, if the double bond and its geometric relationship to the carbenoid carbon were the most important factors, one would expect this to be reflected in the product ratios produced in the decompositions of 10 and 13 as contrasted with those of tosylhydrazones 22 and 24. Since, instead, we find that the ratios of hydrogen migration to insertion are quite similar for norbornenyl- and norbornylcarbene intermediates of similar geometry, a rationalization of the dependence of product composition upon the exo or endo positioning of the carbene carbon ($C_\alpha$) must lie with other steric factors. Although torsional steric effects tend to cancel in the formation or destruction of exocyclic double bonds at C-2 on the norbornane skeleton,[6] if there is

(5) (a) W. Kirmse and G. Wächtershäuser, *Tetrahedron*, **22**, 63 (1966); (b) W. Kirmse and G. Münscher, *Justus Liebigs Ann. Chem.*, **726**, 42 (1969).
(6) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967).

more single- than double-bond character in C-2–$C_\alpha$ in the transition state for hydrogen migration, one would expect the eclipsing of C-1–H and C-2–$C_\alpha$ in the case of the exo carbene intermediates to inhibit formation of 2-methylenenorbornane or 5-methylenenorbornene.

The product compositions formed as a result of generation of *exo*- and *endo*-2-norbornyl carbenoids by α elimination on primary chlorides **15** and **19** are more difficult to place in perspective. An overall similarity to the reactions of the carbenes generated in the decompositions of **22** and **24** is evident, and it is of interest to note that a ring expansion occurs for both *endo*-2-norbornylcarbene and for the analogous carbenoid. The fact that *endo*-2-norbornylcarbene undergoes ring expansion, while *endo*-5-norbornenylcarbene does not, is perhaps a hint that intermediate **7** does possess some nonclassical carbene character. Inspection of models reveals that alignment of the p orbital in intermediate **7** for maximum overlap with the π bond system provides an alignment which should inhibit ring expansion. Thus, while evidence supporting a foiled carbene addition reaction for intermediate **7** is not revealed by the ratio of hydrogen migration to insertion, the ring expansion reaction found for **22** suggests that nonclassical interaction may be of some importance in the *endo*-5-norbornenylcarbene system, and that **7** may be similar in this respect to the 9-carbenabicyclo[3.3.1]non-2-ene intermediate studied by Fisch.[7] We have underway at the present time additional experimentation directed toward revealing intramolecular interactions in similar carbene and carbenoid intermediates.

## Experimental Section[8]

**Separation of *exo*- and *endo*-Bicyclo[2.2.1]hept-2-ene-5-carboxaldehyde.**—A 183-g mixture of *exo*- and *endo*-bicyclo[2.2.1]hept-2-ene-5-carboxaldehyde[9] was distilled in an 18-in. semimicrospinning-band column at a reflux ratio of 15:1. Three fractions were collected. The first 50 g distilled at 62–63° (17 mm). This fraction, on a 20-ft DC-200 column, was found to be enriched in exo isomer. The second fraction (62.3 g) distilled at 63–65° (17 mm). This was found to be a mixture of both the isomers on the same column. The last fraction (70.7 g) distilled at 65–66° (17 mm) and gave 52.5 g of 99% pure endo isomer. The first fraction on careful redistillation gave 26.2 g of 99% pure exo isomer. Infrared spectra of both the isomers indicated $\nu_{max}$ at 3010 (HC=C), 1700 (C=O), 720 (cis olefinic hydrogens), and 1570 cm$^{-1}$ (norbornene C=C). The endo isomer showed a characteristic band at 930 cm$^{-1}$, while the exo isomer had a characteristic band at 880 cm$^{-1}$. The structure of exo isomer was further confirmed by elemental analysis.

*Anal.* Calcd for $C_8H_{10}O$: C, 78.68; H, 8.19. Found: C, 78.56; H, 8.19.

***endo*-Bicyclo[2.2.1]hept-2-ene-5-carboxaldehyde *p*-Toluenesulfonylhydrazone (10).**—In a three-necked round-bottom flask equipped with a mechanical stirrer, 37.2 g (0.200 mol) of *p*-toluenesulfonylhydrazine was dissolved in 200 ml of 60% aqueous methanol by warming to about 60°. To this warm solution was added a solution of 24.4 g (0.200 mol) of *endo*-bicyclo[2.2.1]hept-2-ene-5-carboxaldehyde in 60 ml of methanol, with stirring. Stirring was continued while allowing the mixture to cool to room temperature. The white, solid product was filtered, washed with ether, and recrystallized from methanol. White crystalline tosylhydrazone, 47.4 g (82%), mp 133–134°, was obtained.

*Anal.* Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.07; H, 6.21. Found: C, 62.24; H, 6.37.

**Decomposition of *endo*-Bicyclo[2.2.1]hept-2-ene-5-carboxaldehyde *p*-Toluenesulfonylhydrazone (10).**—The procedure was based on that reported by Friedman and Shechter.[10] A three-necked round-bottom flask was fitted with a nitrogen inlet, dropping funnel, stirrer, and a 12-cm Vigreux column heated to 70° with heating tape. The Vigreux column was connected to two receiving traps arranged in series and cooled with a Dry Ice–isopropyl alcohol bath. Dry reagent grade sodium methoxide (8.77 g, 0.163 mol) was added to the nitrogen-purged flask along with 300 ml of bis(2-ethoxyethyl) ether, which previously had been distilled from lithium aluminum hydride. The stirred suspension was raised to 180° in an oil bath. A slurry of *p*-toluenesulfonylhydrazone 10 (14.5 g, 0.050 mol) in 150 ml of bis(2-ethoxyethyl) ether was then added during 2 hr, under the nitrogen flow in order to sweep out volatile products as they formed. The reaction was continued at this temperature for an additional hour, sweeping the system with nitrogen. The material in the cold traps was diluted 5:1 with water and extracted with pentane. The pentane solution was dried and the solvent removed by careful distillation, which gave 0.695 g (13.1%) of $C_8$ hydrocarbons consisting of 57% of 5-methylenebicyclo[2.2.1]hept-2-ene, 42% of *endo*-tricyclo[3.2.1.0$^{2,4}$]oct-6-ene, and 1% of a component which was not characterized. The products were isolated by vapor phase chromatography using a 25-ft DC-200 column at 130°. The structure of 5-methylenebicyclo[2.2.1]hept-2-ene was confirmed by comparing its infrared and nuclear magnetic resonance spectra with those of an authentic sample (Dow Chemical Co.), while *endo*-tricyclo[3.2.1.0$^{2,4}$]oct-6-ene was confirmed by carbon and hydrogen analyses and by comparison of infrared and nuclear magnetic resonance spectra with published data.[11]

*Anal.* Calcd for $C_8H_{10}$: C, 90.56; H, 9.43. Found: C, 90.41; H, 9.55.

***exo*-Bicyclo[2.2.1]hept-2-ene-5-carboxaldehyde *p*-Toluenesulfonylhydrazone (13).**—A solution of *exo*-bicyclo[2.2.1]hept-2-ene-5-carboxaldehyde (12.2 g, 0.100 mol) in 30 ml of methanol was added to 18.6 g (0.10 mol) of *p*-toluenesulfonylhydrazine in 100 ml of 60% aqueous methanol at 60°, with stirring. The reaction mixture was allowed to cool; the solid was filtered, washed with pentane, and crystallized from methanol, giving 19.7 g (68%) of crystalline tosylhydrazone, mp 118–119°.

*Anal.* Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.07; H, 6.21. Found: C, 62.22; H, 6.39.

**Decomposition of *exo*-Bicyclo[2.2.1]hept-2-ene-5-carboxaldehyde *p*-Toluenesulfonylhydrazone (13).**—As described in the case of endo isomer, the slurry of tosylhydrazone of *exo*-bicyclo[2.2.1]-hept-2-ene-5-carboxaldehyde (10.73 g, 0.0370 mol) in 100 ml of bis(2-ethoxyethyl) ether was decomposed at 180° in the presence of sodium methoxide (6.5 g, 0.12 mol) and bis(2-ethoxyethyl) ether (150 ml) under a nitrogen atmosphere. The material in the cold traps was worked up as above, which gave 0.35 g (9.0%) of $C_8$ hydrocarbons. The product mixture was separated by vapor phase chromatography on a 25-ft DC-200 column and consisted of 23.0% 5-methylenebicyclo[2.2.1]hept-2-ene, 76.0% *exo*-tricyclo[3.2.1.0$^{2,4}$]oct-6-ene, and 1% of an unidentified product. The isomers were characterized by their infrared and nuclear magnetic resonance spectra. Each structure was ultimately confirmed by direct comparison of its infrared and nuclear magnetic resonance spectra with an authentic sample.

***exo*-2-Hydroxymethylbicyclo[2.2.1]heptane.**—The procedure of Berson and his coworkers[12] was adapted to fit the requirements of this laboratory. A solution of 50 g (0.4 mol) of 5-*exo*-hydroxymethylbicyclo[2.2.1]hept-2-ene in 200 ml of methanol was hydrogenated over 1 g of a 10% palladium-on-charcoal catalyst in a Parr apparatus. The theoretical quantity of hydrogen was absorbed within 0.5 hr. The reaction was continued for an additional 2 hr. After removal of the catalyst by filtration and the solvent by distillation, 48 g (92%) of *exo*-5-hydroxymethylbicyclo[2.2.1]heptane, bp 98–99° (15 mm), was collected by distillation through an 18-in. semimicrospinning-band column. The infrared spectrum of the product indicated complete disappearance of the bands due to double bond in the starting olefin.

***endo*-2-Hydroxymethylbicyclo[2.2.1]heptane.**—Application of the procedure described above for the reduction of 5-*exo*-hydroxymethylbicyclo[2.2.1]hept-2-ene to reduction of 45 g (0.36 mol) of

(7) M. H. Fisch and H. D. Pierce, Jr., *Chem. Commun.*, 503 (1970).

(8) Elemental analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany.

(9) O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **460**, 98 (1928).

(10) L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, **81**, 5512 (1959).

(11) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).

(12) J. A. Berson, J. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *ibid.*, **83**, 3986 (1961).

the endo epimer gave 40 g (88%) of 5-*endo*-hydroxymethylbicyclo[2.2.1]heptane, bp 94–96° (15 mm).

*exo*-5-Chloromethylbicyclo[2.2.1]heptane (19).—*exo*-5-Hydroxymethylbicyclo[2.2.1]heptane, 44.1 g (0.350 mol), together with a few drops of piperidine, was placed in a three-necked flask equipped with a condenser, stirrer, dropping funnel, and nitrogen inlet. The flask was heated to 85–90° (oil bath) and 62.5 g (0.525 mol) of thionyl chloride was added during a 1-hr period under a nitrogen atmosphere. The reaction mixture was heated at reflux at the same temperature for an additional 2 hr. Excess thionyl chloride was removed by distillation using a rotary evaporator. Distillation of the residue through a spinning-band column yielded 43 g (85%) of *exo*-5-chloromethylbicyclo[2.2.1]heptane, bp 64–65° (13 mm). The infrared spectrum of the product indicated complete disappearance of OH frequency and showed a characteristic frequency at 715 cm$^{-1}$ due to the CCl linkage.

This compound was also prepared by reducing catalytically *exo*-5-chloromethylbicyclo[2.2.1]hept-2-ene,[2] using 10% palladium-on-carbon as a catalyst. The infrared spectra of the two samples were identical and vpc analysis on a 25-ft DC-200 column and a 25-ft Carbowax 20M column showed only one peak in each case.

*Anal.* Calcd for C$_8$H$_{13}$Cl: C, 66.43; H, 8.99. Found: C, 66.31; H, 9.09.

*endo*-2-Chloromethylbicyclo[2.2.1]heptane (15).—Similarly, as in the case of *exo*-5-chloromethylbicyclo[2.2.1]heptane, the reaction of 37.8 g (0.300 mol) of *endo*-5-hydroxymethylbicyclo[2.2.1]heptane with 53.5 g (0.45 mol) of thionyl chloride gave 34 g (80%) of *endo*-5-chloromethylbicyclo[2.2.1]heptane. *endo*-5-Chloromethylbicyclo[2.2.1]hept-2-ene was reduced, with 10% palladium on carbon, to the saturated compound. The infrared spectra of samples prepared by these two different routes were identical. Vpc analysis of these samples provided evidence for identity by demonstrating identical retention times on a 25-ft DC-200 and a 25-ft Carbowax 20M column. The retention time on each column differed from that exhibited by the exo epimer.

*Anal.* Calcd for C$_8$H$_{13}$Cl: C, 66.43; H, 8.99. Found: C, 66.30; H, 9.02.

**Reaction of *exo*-2-Chloromethylbicyclo[2.2.1]heptane with Sodium (19).**—A 100-ml three-necked flask was fitted with a pressure-equalized dropping funnel, condenser, and ground-glass stirrer shaft and bearing. The dropping funnel was fitted with a nitrogen inlet tube; the condenser was connected to a calcium chloride drying tube; and the stirrer shaft was fitted with a Teflon stirrer blade. Under 15 ml of redistilled *n*-decane (bp 168–169°), 2.3 g (0.10 g-atom) of freshly pulled sodium ribbon was weighed out and cut into very small pieces. The sodium and decane were transferred to the reaction flask, the system was flushed out with nitrogen, and the flask was heated to 85–90° in an oil bath. A solution of 7.23 g (0.050 mol) of *exo*-5-chloromethylbicyclo[2.2.1]heptane in 10 ml of redistilled decane was added dropwise during 0.5 hr with mechanical stirring. The resulting reaction mixture was stirred for an additional 1.5 hr at the same temperature to complete the reaction.

When the reaction flask had cooled to room temperature, a vacuum pump was attached through a Dry Ice trap and a distillation head to the top of the condenser. The reaction mixture was subjected to a pressure of 20 mm; the reaction flask was heated until decane (bp 70°, 20 mm) reached the thermometer in the distillation head. The C$_8$ products collected in the Dry Ice trap.

Methanol was added to the remaining decane mixture to destroy the alkylsodium and unreacted sodium. The mixture was then washed with water. Upon standing, a solid precipitated from the decane solution. This material was probably the C$_{16}$ (Wurtz) hydrocarbons, but was not investigated further. The Dry Ice trap contained 2.57 g (46.8%) of C$_8$ hydrocarbons which by vapor phase chromatographic analysis on a 30-ft 25% Carbowax 1500 on Chromosorb column consisted of 68% 5-*exo*-methylbicyclo[2.2.1]heptane and 32.0% *exo*-tricyclo[3.2.1.0$^{2,4}$]octane. The products were identified by comparing infrared and nuclear magnetic resonance spectra with authentic samples synthesized as described below.

Similarly, the reaction of 3.610 g (0.025 mol) of 5-*exo*-chloromethylbicyclo[2.2.1]heptane with 0.575 g (0.025 g-atom) of sodium gave 0.59 g (31.1%) of C$_8$ hydrocarbons consisting of 68% 5-*exo*-methylbicyclo[2.2.1]heptane and 32% *exo*-tricyclo[3.2.1.0$^{2,4}$]octane.

**Reaction of *endo*-2-Chloromethylbicyclo[2.2.1]heptane (15) with Sodium.**—The reaction of 7.23 g (0.050 mol) of *endo*-

5-chloromethylbicyclo[2.2.1]heptane with 2.3 g (0.10 g-atom) of freshly pulled, finely cut sodium ribbon, was carried out in the same manner as described for the exo isomer.

The Dry Ice trap contained 1.53 g (28.4%) of C$_8$ hydrocarbons, which by vapor phase chromatography on a 30-ft 25% Carbowax 1500 on Chromosorb column consisted of 65% *endo*-5-methylbicyclo[2.2.1]heptane, 24% bicyclo[3.2.1]oct-2-ene, and 11% *endo*-tricyclo[3.2.1.0$^{2,4}$]octane. The products were characterized by comparison of their infrared and nuclear magnetic resonance spectra with those of authentic samples.

Similarly, the reaction of 3.620 g (0.025 mol) of 5-*endo*-chloromethylbicyclo[2.2.1]heptane with 0.575 g (0.025 g-atom) of sodium gave 0.64 g (23.7%) of C$_8$ hydrocarbons consisting of 72% 5-*endo*-methylbicyclo[2.2.1]heptane, 21% bicyclo[3.2.1]oct-2-ene, and 7.0% *endo*-tricyclo[3.2.1.0$^{2,4}$]octane.

*exo*-2-Methylbicyclo[2.2.1]heptane (20).—In a three-necked flask equipped with a dropping funnel, stirrer, and condenser attached with a calcium chloride tube, a solution of 1.0 g (0.026 mol) of lithium aluminum hydride in 15 ml of diglyme (previously distilled over sodium) was placed. The flask was heated to 125° and to it a solution of 3.62 g (0.025 mol) of *exo*-5-chloromethylbicyclo[2.2.1]heptane in 10 ml of diglyme was added. The reaction mixture was stirred and kept at 125° for 48 hr, after which it was cooled and treated successively with water and 20% hydrochloric acid. It was then extracted with pentane, washed with water, and dried over anhydrous sodium sulfate. Evaporation and distillation gave 1.32 g (48%) of 5-*exo*-methylbicyclo[2.2.1]-heptane, bp 66–67° (115 mm).

*Anal.* Calcd for C$_8$H$_{14}$: C, 87.27; H, 12.73. Found: C, 87.17; H, 12.83.

*endo*-2-Methylbicyclo[2.2.1]heptane (16).—Similarly, as described above in the case of the exo isomer, the reaction of 3.62 g (0.025 mol) of *endo*-5-chloromethylbicyclo[2.2.1]heptane with 1.0 g (0.026 mol) of lithium aluminum hydride in diglyme at 125° for 48 hr, gave 1.37 g (50%) of 5-*endo*-methylbicyclo[2.2.1]-heptane, bp 67–68° (115 mm).

*Anal.* Calcd for C$_8$H$_{14}$: C, 87.27; H, 12.73. Found: C, 87.11; H, 12.62.

*exo*-Tricyclo[3.2.1.0$^{2,4}$]octane (21).—A solution of 1.06 g (0.01 mol) of *exo*-tricyclo[3.2.1.0$^{2,4}$]oct-6-ene[18] in 10 ml of methanol was hydrogenated over 0.05 g of a 10% palladium-on-charcoal catalyst in a low-pressure hydrogenation apparatus. The hydrogenation was stopped when the uptake of hydrogen ceased. The catalyst was removed by filtration and the methanol by careful distillation. The product fraction was collected by vapor phase chromatography on 10-ft 25% Carbowax 1500 on Chromosorb column. *exo*-Tricyclo[3.2.1.0$^{2,4}$]octane, 0.54 g (50%), was obtained. The absorption at 1560 cm$^{-1}$ in the infrared spectrum of the unsaturated compound was no longer present in the spectrum of the product.

*endo*-Tricyclo[3.2.1.0$^{2,4}$]octane (18).—In a fashion similar to that described above for the case of the exo isomer, 0.10 g (0.001 mol) of *endo*-tricyclo[3.2.1.0$^{2,4}$]oct-6-ene (obtained from decomposition of the *p*-tosylhydrazone of *endo*-bicyclo[2.2.1]hept-2-ene-5-carboxaldehyde) was hydrogenated in 2.0 ml of methanol over 10% palladium-on-charcoal catalyst. The product, *endo*-tricyclo[3.2.1.0$^{2,4}$]octane, 0.065 g (70%), was collected by vapor phase chromatography using a 10-ft 25% Carbowax 1500 on Chromosorb column.

*Anal.* Calcd for C$_8$H$_{12}$: C, 88.88; H, 11.12. Found: C, 88.75; H, 11.31.

*endo*-Bicyclo[2.2.1]heptane-2-carboxaldehyde.—A solution of 18.3 g (0.15 mol) of *endo*-bicyclo[2.2.1]hept-2-ene-5-carboxaldehyde in 200 ml of methanol with 1 g of a 10% palladium-on-charcoal catalyst was hydrogenated in a Parr apparatus. The theoretical quantity of hydrogen was absorbed within 1 hr. The catalyst was removed by filtration, and then on distillation through the spinning-band column, after removal of solvent, 15 g (80%) of *endo*-bicyclo[2.2.1]heptane-2-carboxaldehyde, bp 62–64° (12 mm), was obtained.

*endo*-Bicyclo[2.2.1]heptane-2-carboxaldehyde *p*-Toluenesulfonylhydrazone (22).—*p*-Toluenesulfonylhydrazine (18.6 g, 0.10 mol) was dissolved in 100 ml of 60% aqueous methanol by warming to about 60°. To this warm solution was added a solution of 12.2 g (0.1 mol) of *endo*-bicyclo[2.2.1]heptane-2-carboxaldehyde in 30 ml of methanol, while stirring. The reaction mixture was allowed to cool to room temperature slowly, and the white solid product obtained was filtered, washed with ether, and re-

(13) H. E. Simons and R. D. Smith, *J. Amer. Chem. Soc,* **81**, 4256 (1959).

crystallized from methanol. White crystalline tosylhydrazone, 21.2 g (72.4%), mp 114–115°, was obtained.

*Anal.* Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.64; H, 6.84. Found: C, 61.81; H, 6.96.

**Decomposition of** *endo-***Bicyclo[2.2.1]heptane-2-carboxaldehyde** *p-***Toluenesulfonylhydrazone (22).**—As described earlier in this section, dry reagent grade sodium methoxide (7.16 g, 0.133 mol) was added to the nitrogen-purged flask along with 200 ml of bis(2-ethoxyethyl) ether (previously distilled over lithium aluminum hydride). The stirred suspension was raised to a temperature of 180° in an oil bath. The slurry of the tosylhydrazone of *endo*-bicyclo[2.2.1]heptane-2-carboxaldehyde (11.1 g, 0.0375 mol) in 100 ml of bis(2-ethoxyethyl) ether was then added during 1.5 hr, under nitrogen flow to sweep away the volatile products formed. The reaction was continued at this temperature for an additional hour, sweeping the system with nitrogen to remove all the products formed. The material in the cold traps was worked up as usual, giving 1.45 g (43.2%) of $C_8$ hydrocarbons. The products were separated by vapor phase chromatography on a 25-ft DC-200 column and consisted of 41% 5-methylenebicyclo[2.2.1]heptane, 4% bicyclo[3.2.1]oct-2-ene, and 55% *endo*-tricyclo[3.2.1.0²,⁴]octane. 5-Methylenebicyclo[2.2.1]heptane was characterized by infrared and nuclear magnetic resonance data and confirmed by comparing its infrared data with a published infrared spectrum.[14] Bicyclo[3.2.1]oct-2-ene and *endo*-tricyclo[3.2.1.0²,⁴]octane were identified by infrared and nmr spectral comparisons with the corresponding data of authentic samples.

*exo-***Bicyclo[2.2.1]heptane-2-carboxaldehyde.**—In a manner similar to that described above for the endo epimer, 12.2 g (0.10 mol) of *exo*-bicyclo[2.2.1]hept-2-ene-5-carboxaldehyde, on hydrogenation in methyl alcohol over 10% palladium-on-charcoal catalyst gave 9.3 g (75%) of *exo*-bicyclo[2.2.1]heptane-2-carboxaldehyde, bp 66–68° (12 mm).

*exo-***Bicyclo[2.2.1]heptane-2-carboxaldehyde** *p-***Toluenesulfonylhydrazone (24).**—*p*-Toluenesulfonylhydrazine (14.0 g, 0.075 mol) was dissolved in 75 ml of 60% aqueous methanol at 60°. To this 9.3 g (0.075 mol) of *exo*-bicyclo[2.2.1]heptane-2-carbox-

aldehyde in 23 ml of methanol was added. The reaction mixture was allowed to cool slowly to room temperature and the product was filtered, washed with pentane, and recrystallized from methanol. White tosylhydrazone (14.3 g, 65%), mp 94–95°, was obtained.

*Anal.* Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.64; H, 6.84. Found: C, 61.83; H, 6.89.

**Decomposition of** *exo-***Bicyclo[2.2.1]heptane-2-carboxaldehyde** *p-***Toluenesulfonylhydrazone (24).**—Tosylhydrazone **24** was decomposed in a manner similar to that employed for the endo epimer **22**. A mixture of dry reagent grade sodium methoxide (6.05 g, 0.112 mol) and 150 ml of bis(2-ethoxyethyl) ether (previously dried by distillation over lithium aluminum hydride) was placed in a nitrogen-purged flask. This mixture was heated to 180° in an oil bath, and a suspension of the *p*-toluenesulfonylhydrazone of *exo*-bicyclo[2.2.1]heptane-2-carboxaldehyde (10.2 g, 0.350 mol) in 100 ml of bis(2-ethoxyethyl) ether was added during 1 hr, under the nitrogen flow. The reaction was continued for an additional 2 hr at this temperature, sweeping the system with nitrogen to remove all the products formed. The material in the cold traps was worked up as described above for the endo isomer, which gave 0.83 g (13.7%) of $C_8$ hydrocarbons, consisting of 11% 5-methylenebicyclo[2.2.1]heptane and 83% *exo*-tricyclo[3.2.1.0²,⁴]octane. These products were isolated by vapor phase chromatography using a 25-ft DC-200 column. Comparison of infrared and nuclear magnetic resonance spectra of the *exo*-tricyclo[3.2.1.0² ⁴]octane component with corresponding data of an authentic sample established its identity.

**Registry No.**—**10**, 28455-84-7; **13**, 28455-85-8; **16**, 765-90-2; **18**, 22389-16-8; **19**, 6518-44-1; **20**, 872-78-6; **22**, 28455-92-7; **24**, 28455-93-8; *exo*-bicyclo[2.2.1]hept-2-ene-5-carboxaldehyde, 19926-88-6; *endo*-bicyclo[2.2.1]hept-2-ene-5-carboxaldehyde, 19926-90-0; *exo*-5-hydroxymethylbicyclo[2.2.1]heptane, 13118-79-1; 5-*endo*-hydroxymethylbicyclo[2.2.1]heptane, 13137-31-0; *exo*-bicyclo[2.2.1]heptane-2-carboxaldehyde, 3574-55-8.

(14) R. R. Sauers, *J. Amer. Chem. Soc.*, **81**, 4873 (1959).