into the extent to which the interesting properties of the [2.2]metacyclophanes are reflected in their larger homologs.

Experimental Section

Melting points were determined with a Fisher-Johns melting point apparatus and are corrected. Ultraviolet spectra were recorded with a Cary spectrophotometer, Model 11M. Infrared spectra were obtained with a Perkin-Elmer grating spectrophotometer, Model 237. Nmr spectra were recorded with a Varian A-60 nmr spectrometer.

Nitration of [3.2]Metacyclophane-2-carboxylic Acid (1).—A solution of [3.2]metacyclophane-2-carboxylic acid (100 mg, 0.375 mmole), glacial acetic acid (30 ml), and 70% nitric acid (10 ml) was maintained at 30–35° for 72 hr. The solution was poured on to crushed ice (100 g) and stirred. Water (100 ml) was added and the solution was extracted with five 20-ml portions of ether. The combined ether extract was washed with distilled water and with saturated salt solution, and then dried over anhydrous magnesium sulfate. Evaporation of the ether gave 104 mg of orange oil to which an ethereal solution of diazomethane (0.4 mmole) was added. The solvent was evaporated and the resulting oil taken up in carbon tetrachloride (0.25 ml) and placed on a column of 3 g of alumina (Woelm, neutral, activity grade I). Elution with benzene gave an early fraction containing 35 mg of colorless oil identified as methyl [3.2]metacyclophane-2-carboxylate by comparison of its nmr and infrared spectra with those of an authentic sample.[7]

A latter fraction, eluted with benzene, contained 37 mg (31% yield) of 2-nitro-4,5-(2′-carbomethoxypropano)-9,10-dihydrophenanthrene as a pale yellow oil. Repeated recrystallization from methanol gave 15 mg of yellow plates, mp 134–136°. The composition was determined by a high resolution mass spectrometric measurement. An exact mass measurement of the C^{13}-containing molecular ion was found to be *m/e* 324.1193. This agrees well with the molecular ion $C_{19}H_{17}NO_4^+$ containing one atom of C^{13} calculated[18] to exhibit *m/e* 324.1190.

A final fraction eluted from the column with ether contained 20 mg of orange oil. Thin layer chromatography (Woelm alumina plate developed in methylene chloride) of this material gave one red and two yellow spots, demonstrating the presence of at least three colored products. None of the components was isolated in sufficient quantity for identification.

2,3-Dimethyl[4.2]metacyclophan-1-ene.—A solution of dimethyl-2-[3.2]metacyclophanylmethanol[7] (200 mg, 0.714 mmole), glacial acetic acid (3 ml), and acetic anhydride (1 ml) was refluxed for 6 hr. The solvent was removed under reduced pressure and the residue taken up in ether (5 ml). This ether solution was washed with distilled water, 10% sodium bicarbonate solution, and saturated salt solution, dried over anhydrous magnesium sulfate, and evaporated. The infrared spectrum of the resulting oil exhibited no absorption at 2.83 and 5.79 μ (indicative of starting alcohol and its acetate ester) which had been observed when shorter reaction periods were employed. Although the oil showed two spots on thin layer chromatography (Woelm alumina plate developed in petroleum ether (bp 30–60°)), elution column chromatography on a column of 3 g of alumina (Woelm, neutral, activity grade I) failed to give a separation. Vapor phase chromatography using an Apiezon L column likewise gave only a broad unresolved band.

The nmr spectrum of the product taken in carbon tetrachloride contains a singlet at 5.35 ppm assigned to the 9,17 protons of 2-isopropylidene[3.2]metacyclophane, while a more complex multiplet at 4.8 ppm is assigned to the terminal olefinic and 9,17 protons of 2-isopropenyl[3.2]metacyclophane. Integration of these signals indicates a composition of *ca.* 1:3, respectively. This composition is supported by integration of the methyl protons signal (1.76 ppm) which indicates 3.8 protons (25% of six protons plus 75% of three protons). Strong absorption at 6.10 and 11.3 μ in the infrared taken as a neat liquid is indicative of a terminal olefin.

A solution of the olefinic mixture (169 mg), *p*-toluenesulfonic acid (50 mg), and glacial acetic acid (5 ml) was refluxed for 12 hr. The solvent was removed under reduced pressure and the residue taken up in ether (5 ml). The ether solution was washed with 10% sodium bicarbonate solution, distilled water, and saturated salt solution and dried over anhydrous magnesium sulfate. Evaporation of the ether gave 160 mg of semisolid residue which was taken up in petroleum ether and chromatographed on 2.5 g of alumina (Woelm). Elution with petroleum ether gave 73 mg (43% yield) of 2,3-dimethyl[4.2]metacyclophan-1-ene as white crystals, mp 101–102.5°.

Anal. Calcd for $C_{20}H_{22}$: C, 91.54; H, 8.46. Found: C, 91.63; H, 8.57.

Absorption at 11.9 μ (observable in chloroform solution) can be assigned to a vinyl hydrogen out-of-plane deformation. The ultraviolet absorption spectrum contains a broad maximum at 208 mμ (log ϵ 4.75) with a sharp shoulder at 265.5 mμ (log ϵ 2.62).

Registry No.—2, 14698-41-0; 2-isopropylidene[3.2]metacyclophane, 14633-62-6; 2-isopropenyl[3.2]metacyclophane, 14633-63-7; 2,3-dimethyl[4.2]metacyclophan-1-ene, 14698-42-1.

---

[18] J. H. Beynon and A. E. Williams, "Mass and Abundance Tables for Use in Mass Spectrometry," American Elsevier Publishing Co., Inc., New York, N. Y., 1963.

The Reactions of *exo*- and *endo*-5-Chloromethylnorbornene with Sodium[1]

PETER K. FREEMAN, V. N. MALLIKARJUNA RAO, DANIEL E. GEORGE,[2] AND GARY L. FENWICK

Department of Physical Sciences, University of Idaho, Moscow, Idaho

Received November 28, 1966

The reaction of either *exo*- or *endo*-5-chloromethylnorbornene with sodium in *n*-decane generates 3- and 4-allycyclopentene, *cis*-bicyclo[3.3.0]octene-2, and bicyclo[3.2.1]octene-2. Mechanistic routes for these ring-cleavage and ring-cleavage rearrangement reactions are proposed.

While norbornyl and norbornenyl systems are known to undergo a variety of carbonium ion rearrangements, as a result of the intensive study which these rearrangements have provoked over approximately a twenty-year period,[3] very few investigations, by comparison, have focused attention on other intermediates in these ring systems. Recently we have reported[4] that the reaction of either nortricyclyl or dehydronorbornyl chloride with sodium in *n*-decane results in rearrangement and ring cleavage, yielding a nearly identical mixture of hydrocarbon products: nortricyclene, norbornene, and 3- and 4-vinylcyclopentene (eq 1). The possibility that a similar mechanistic pathway might be uncovered for the reactions of *endo*

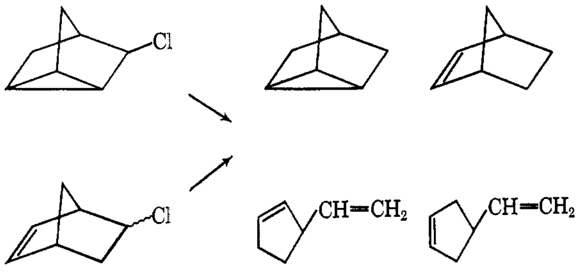
---

[1] Abstracts, Northwest Regional Meeting of the American Chemical Society, Bellingham, Wash., June 1960, p 25.

[2] National Defense Education Act Fellow, 1959–1962.

[3] J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, part I., Chapter 2; G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966); G. E. Gream, *Rev. Pure Appl. Chem.*, **16**, 25 (1966); H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

[4] P. K. Freeman, D. E. George, and V. N. Mallikarjuna Rao, *J. Org. Chem.*, **28**, 3234 (1963); **29**, 1682 (1964).



(1)

and *exo*-5-chloromethylnorbornene (I and II) with sodium aroused our curiosity and stimulated the present study. At the outset there appeared to be at least one complication. Since I and II are primary halides, the generation of a bivalent carbon intermediate as a consequence of α elimination induced by alkylsodium[5] seemed to be a likely alternative to a carbanionic or free-radical rearrangement pathway.

Results and Discussion

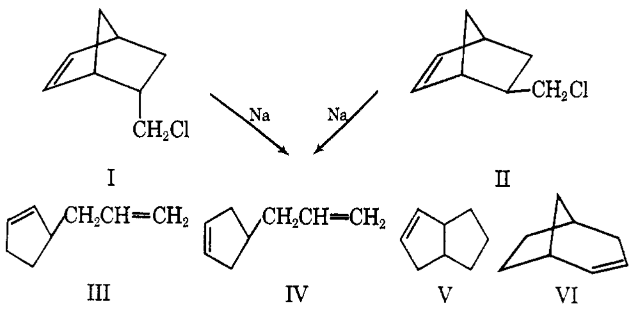
Treatment of either I or II with sodium in *n*-decane at 85–90° produced a 23–25% yield of C_8 hydrocarbons, isolated by direct distillation from the reaction mixture.[6] Vapor phase chromatographic analysis on a silicone oil column indicated the presence of two components in a 60:40 ratio. The 40% component was easily resolved into three peaks, which appeared in a ratio of 97:2:1, using a silver nitrate–ethylene glycol column. There were small variations in this ratio; nevertheless, the results appear to be nearly independent of the *exo* or *endo* nature of the reactant halide (Table I). Upon catalytic hydrogenation, the 97% component absorbed 1 molar equiv of hydrogen and gave a compound which had an infrared spectrum identical with that of *cis*-bicyclo[3.3.0]octane.[7] The nmr spectrum of the parent olefin exhibited absorptions centered at τ 4.5 (two olefinic protons), 6.9 (one tertiary proton α to a double bond), 7.4 (two methylene protons α to a double bond), 7.9 (one proton β to a double bond), and 8.5 (six methylene protons); and, thus, the structure of this olefin must be that of *cis*-bicyclo[3.3.0]octene-2 (V). The nmr spectrum of the 2% component seemed to be consistent with that expected of bicyclo[3.2.1.]octene-2 (VI), since it exhibited absorptions for three protons located α to a double bond (τ 7.7) and two olefinic protons (τ 4.2 and 4.7). Confirmation of this structural assignment was achieved by comparison of the spectral properties of the 2% component with those of bicyclo[3.2.1]octene-2, prepared by the method of Alder, Krieger, and Weiss,[8] and by hydrogenation to bicyclo[3.2.1.]octane.[9] Since it was difficult to obtain sufficient quantities of the 1% peak, separated on the silver nitrate column, it was not characterized further.

The 60% component, separated and collected using the silicone oil column, was partially resolved on the silver nitrate–ethylene glycol column into two peaks in approximately a 60:40 ratio. The infrared spectrum of the 60% peak had ν_{max} 3100, 1650, 1620, 1420, 995, 915 cm^{-1}, suggesting a vinylic double bond[10] and a cyclopentene double bond;[11] the infrared spectrum of the 40% peak was quite similar exhibiting absorptions at 3100, 1650, 1615, 1420 995 and 915 cm^{-1}. The nmr spectrum of an unresolved mixture of the 60% and 40% peaks was consistent with that expected for a mixture of 3- and 4-allylcyclopentene (III and IV): τ 3.82–4.67 (3 H, =CH—), 4.82–5.31 (2 H, $=CH_2$), and 6.98–9.11 (7 H).[12] Hydrogenation of this mixture resulted in the absorption of approximately 2 molar equiv of hydrogen and the production of a single compound whose spectral properties were identical with those of an authentic sample of *n*-propylcyclopentane.[13]

The allylcyclopentenes III and IV may be pictured as arising by an ionic ring cleavage of alkylsodium VII or VIII to yield the resonance stabilized allylic carbanion X. The resonance energy so gained seems to dictate the reaction pathway since the alternative mode of ring cleavage leading to a primary carbanion and to 3-methyl-5-vinylcyclopentene was not observed. The formation of V must involve a ring cleavage and subsequent reclosure. Thus, this product may arise by ring closure of X followed by proton abstraction. Bicyclo[3.2.1.]octene-2 could conceivably arise through the intermediate formation of tricyclic alkylsodium IX, which may then rearrange to VI[14] (Chart I).

Table I

Reactions of I and II with Sodium in *n*-Decane at 85–90°



I II

III IV V VI

Run	Sample	Allycyclopentene fraction III and IV, %	Bicyclo octene fraction V, %	VI, %	Unknown, %	C_8 yield, %
1	I:II (60:40)	60	35	3	2	24
2	I	61	37	1	1	25
3	I	61	38	1	<1	25
4	II	56	39	3	2	23
5	II	56	41	2	1	24

---

(5) H. G. Richey, Jr., and E. A. Hill, *J. Org. Chem.*, **29**, 421 (1964); W. Kirmse and W. von Doering, *Tetrahedron*, **11**, 266 (1960); L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **83**, 492 (1961); **83**, 500 (1961); P. S. Skell and A. P. Krapcho, *ibid.*, **83**, 754 (1961).

(6) The Wurtz hydrocarbon products were not investigated.

(7) J. D. Roberts and W. F. Gorham, *ibid.*, **74**, 2281 (1952).

(8) K. Alder, H. Krieger, and H. Weiss, *Chem. Ber.*, **88**, 144 (1955).

(9) C. Cupas, W. E. Watts and P. von R. Schleyer, *Tetrahedron Letters*, No. 36, 2503 (1964).

(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

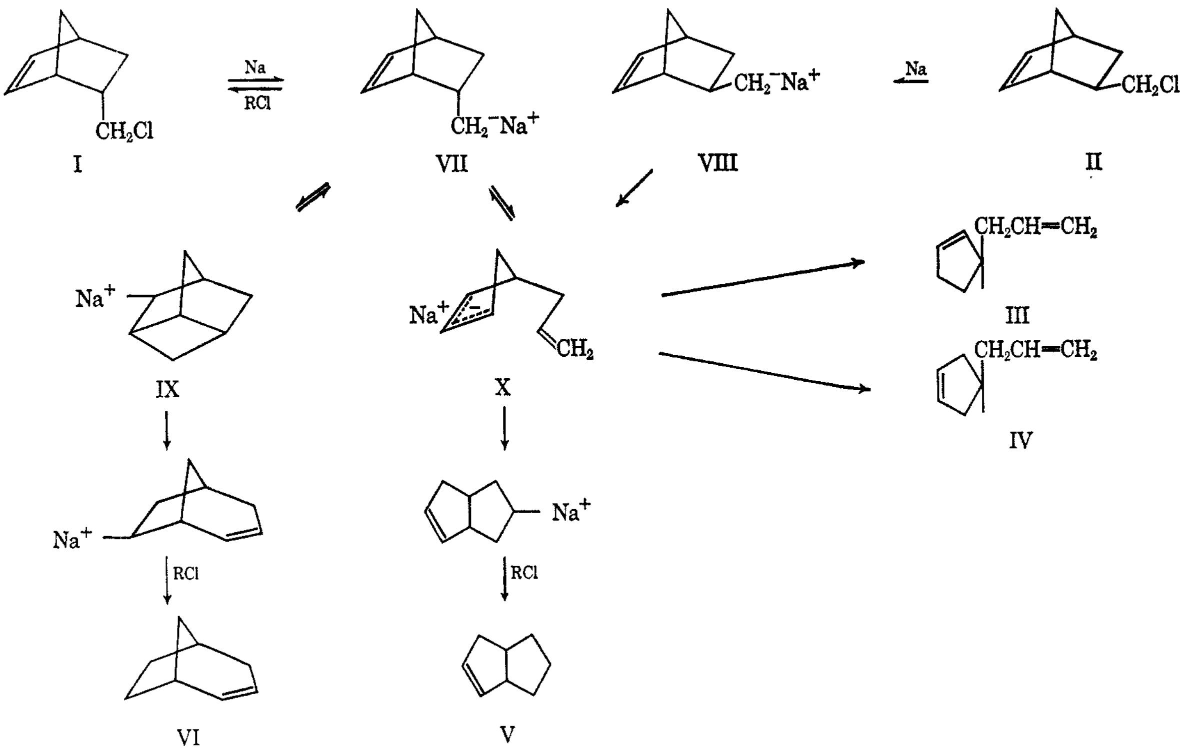
(11) R. M. Jones and C. Sandorfy, "Technique of Organic Chemistry, Vol. IX, Chemical Applications of Spectroscopy," W. West, Ed., Interscience Publishers, Inc., New York, N.Y., 1956, p. 371

(12) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, pp 51–62.

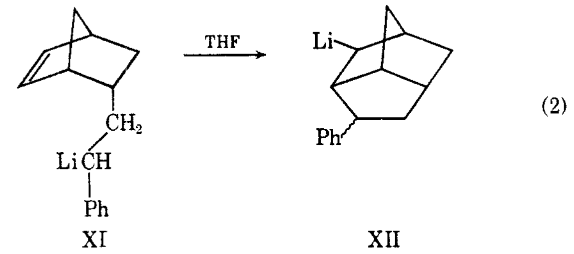
(13) G. Chavanne and P. Becker, *Bull. Soc. Chim. Belges*, **36**, 591 (1927)

(14) The ring cleavage and rearrangement reactions of I and II are represented as carbanionic processes partly as a matter of convenience, since it is possible that the reactions of I and II under discussion are free-radical rearrangements and cleavage reactions induced by one-electron transfer reactions of alkyl chloride and sodium. It seems more logical to represent the cleavage reaction as carbanionic, however, since the closely analogous cleavage reaction observed in the reactions of dehydronorbornyl chloride with sodium and magnesium depends upon the ionic character of the carbon–metal bond and has no precedent in previous studies of the dehydronorbornyl-free radical.[4]

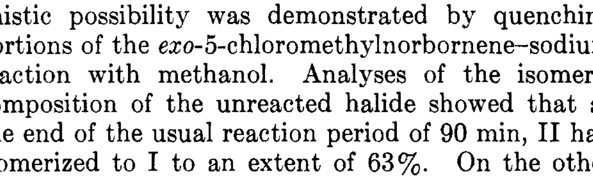
CHART I



Accordingly, we have found that treatment of *exo*-2-chlorotricyclo[3.2.1.0^{3,6}]octane with sodium in *n*-decane furnished predominantly hydrocarbon VI.[15] Additional support for the first step of the transformation of VII to VI is found in the analogous intramolecular addition of 5-norbornenylsodium and 5-norbornenylmagnesium chloride to give nortricyclene organometallics,[4] in the intramolecular addition of benzyllithium derivative XI to form a mixture of brendane isomers XII (eq 2), as reported by Lansbury, Sidler, and Caridi,[16,17] and in the intramolecular nucleophilic displacement reactions which occur as a result of treatment of *endo*-6-halomethyl-*exo*-3-oxatricyclo-[3.2.1.0^{2,4}]octane (XIII) with lithium or sodium to produce tricyclo[3.2.1.0^{3,6}]octan-2-ol (XIV), after hydrolysis.[18]



(2)



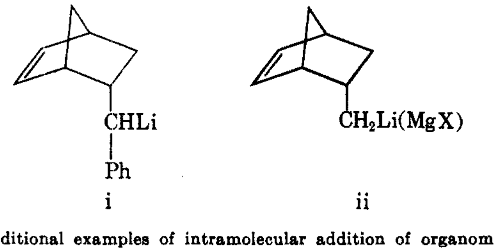
Since direct rearrangement of *exo*-chloride II to tricyclic IX is stereochemically impossible it seemed likely that VIII isomerized to the *endo* epimer VII *via* monocyclic X. That this is indeed a reasonable mechanistic possibility was demonstrated by quenching portions of the *exo*-5-chloromethylnorbornene–sodium reaction with methanol. Analyses of the isomeric composition of the unreacted halide showed that at the end of the usual reaction period of 90 min, II had isomerized to I to an extent of 63%. On the other hand a similar experiment with *endo*-5-chloromethylnorbornene revealed that no isomerization to II occurs during the reaction period.[19]

Alternatives to the mechanistic routes postulated in Chart I for the generation of bicyclo[3.2.1]octene-2 and *cis*-bicyclo[3.3.0]octene-2 immediately come to mind. Abstraction of an allylic proton from the side

---

[15] V. N. M. Rao, Ph.D. Thesis, University of Idaho, 1965; complete details will be reported at a later date. Professor E. A. Hill informs us that he has uncovered a similar rearrangement. The Grignard reagent analogous to IX rearranges at 130° in tetrahydrofuran to yield hydrocarbon VI, after hydrolysis.

[16] (a) P. T. Lansbury, J. D. Sidler, and F. J. Caridi, Abstracts, 152nd Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p 40U. (b) The picture is not completely clear, however, since intramolecular methano bridging was not observed with benzyllithium derivative i nor with the norbornenylmethyllithium or Grignard reagent ii.



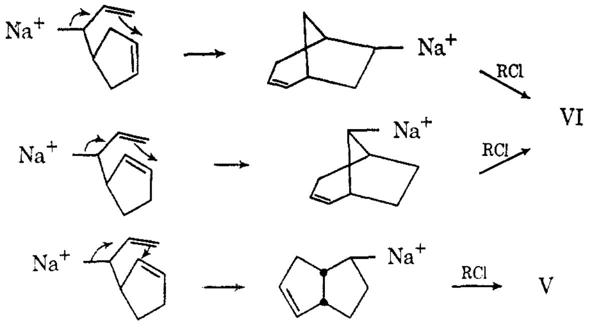
[17] Additional examples of intramolecular addition of organometallics to carbon–carbon double bonds have recently been reported: H. G. Richey, Jr., and T. C. Rees, *Tetrahedron Letters*, No. 36, 4297 (1966); E. A. Hill and J. A. Davidson, *J. Am. Chem. Soc.*, **86**, 4663 (1964); E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963); M. E. H. Howden, A. Maercker, J. Burdon, and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 1732 (1966); A. Maercker and J. D. Roberts, *ibid.*, **88**, 1742 (1966); D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965); M. S. Silver, P. A. Shafer, J. E. Nordlander, C. Ruchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960).

[18] R. R. Sauers, R. A. Parent, and S. B. Damle, *ibid.*, **88**, 2257 (1966); R. R. Sauers and R. A. Parent, *J. Org. Chem.*, **28**, 605 (1963).

[19] The factors controlling the isomerization of II to I and lack of rearrangement of I to II during the reaction conditions are presently under investigation.

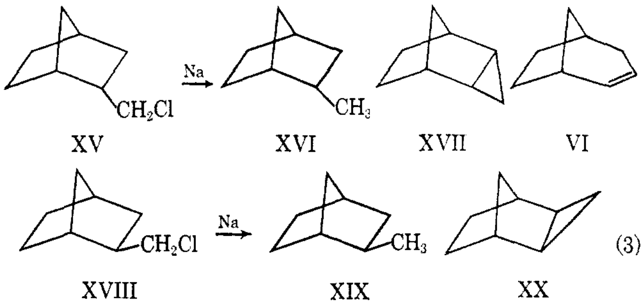
chain of 4-allylcyclopentene might very well result in intramolecular addition producing VI, after proton abstraction, while analogous reactions of 3-allylcyclopentene could conceivably generate both hydrocarbons V and VI (Chart II). These alternatives were tested by heating a mixture of III and IV and *n*-butylsodium in *n*-decane at 85–90° for 1.5 hr. After acidification with methanol, vpc and infrared analysis demonstrated that neither bicyclo[3.2.1]octene-2 nor *cis*-bicyclo[3.3.0]octene-2 had been formed, and thus the reaction pathways of Chart II may be ruled out.[20]

Chart II



The reactions of I and II with sodium are especially interesting since they parallel the reactions of nortricyclyl and dehydronorbornyl chloride with sodium.[4] In the dehydronorbornyl chloride–sodium and nortricyclyl chloride–sodium reactions, the first-formed alkylsodium intermediate undergoes at least some rearrangement and ring cleavage before proton abstraction. The ring cleavage occurs exclusively in the direction which produces a resonance stabilized carbanion. Only in the case of the dehydronorbornyl chloride–sodium reaction is there a small percentage of product formed (norbornadiene) which could possibly be ascribed to a bivalent carbon intermediate. In the reactions of I and II with sodium, the rearrangement of the first formed intermediate is so facile that no 5-methylnorbornene is formed from either starting chloride. Ring cleavage is the predominant rearrangement route and once again occurs exclusively in the direction necessary to produce a resonance stabilized carbanion. As in the reaction of nortricyclyl chloride with sodium, products resulting from a carbenoid precursor are completely absent in the volatile hydrocarbon fraction. By analogy to earlier studies,[5] one would anticipate that an α-elimination route for I or II would generate *endo*- or *exo*-5-methylnorbornene, the products normally expected as a result of proton abstraction by alkylsodium, and one or more C_8H_{10} products generated from carbenoid precursors.

The logic of this expectation for I and II was demonstrated by two experiments using the saturated relatives of I and II (XV and XVIII) (eq 3) and identical reaction conditions. *endo*-2-Methylnorbornane (XVI), *endo*-tricyclo[3.2.1.0^{2,4}]octane (XVII), and bicyclo[3.2.1]octene-2 (VI) were formed in a ratio of 65:11:24 from XV, and *exo*-5-methylnorbornane (XIX) and *exo*-tricyclo[3.2.1.0^{2,4}]octane (XX) in a 68:32 ratio from XVIII.[21] The role of the double bond in the reactions of I and II is thus clearly the same as that of the double bond in the reaction of dehydronorbornyl chloride with sodium. Ring cleavage in the norbornenyl systems provides a greater relief of strain[22] and produces a resonance stabilized carbanion. Consequently, intramolecular ring cleavage competes much more effectively with intermolecular proton abstraction for the first-formed alkylsodium intermediate. So much so, in fact, that the proton-abstraction reaction is not detectable. The reason for the apparent lack of products resulting from carbenoid precursors in the reactions of I and II is not clear. It may tentatively be suggested that the norbornenyl carbenoid intermediates may exhibit greater selectivity in making a choice between an intermolecular reaction with alkylsodium and intramolecular insertion or rearrangement. It is hoped that further experimentation will shed light on this point.



(3)

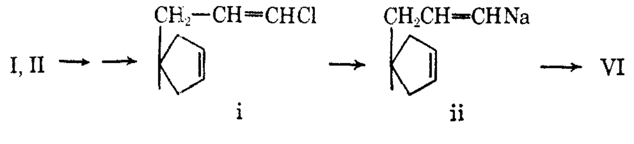
Experimental Section

All melting and boiling points are uncorrected. The microanalyses were carried out by Galbraith Microanalytical laboratories, Knoxville, Tenn., or Alfred Bernhardt, Max-Planck Institute fur Kohlenforshung, Mülheim, Ruhr, Germany. Infrared spectra were determined on Perkin-Elmer Model 137 and 237 spectrophotometers, and the nmr spectra were determined on a Varian Associates A-60 nmr spectrometer, using carbon tetrachloride as the solvent and tetramethylsilane as the internal standard. The gas phase chromatographic analyses and preparative separations were carried out using three columns. Column A was 0.25 in. × 3 m packed with 25% by weight of Dow Corning silicone oil 550 on 40–60 mesh Chromosorb P. Column B was of aluminum, 0.25 in. × 3 m, filled with 40–60 mesh Chromosorb P, which was coated with 25% by weight of Carbowax 1500. Column C was 0.25 in. × 1 m, packed with 20% by weight of a saturated solution of silver nitrate in ethylene glycol on 60–80 mesh HMDS-treated Chromosorb W.

***endo*-5-Chloromethylnorbornene (I).**—In a 300-ml, three-necked flask, provided with a nitrogen inlet, magnetic stirrer,

---

[20] A referee has suggested an additional possibility for formation of VI: abstraction of a proton from the α position of either I or II might produce a ring cleavage product analogous to X, which after proton abstraction (i) could undergo halogen–metal exchange to ii, which, in turn, could ring close to VI. The Δ^2 isomer related to i might upon ring closure produce either or both bicyclooctenes V and VI.



We believe that these additional possibilities are unlikely, since, according to the recent research of C. D. Broadus, T. J. Logan, and T. J. Flautt [*ibid.*, **28**, 1174 (1963)], one would expect vinyl sodium intermediate ii (as well as the Δ^2 isomer) to be formed directly in the reaction of III and IV with *n*-butylsodium along with the allylic intermediates pictured in Chart II. In addition, an analysis of recovered I and II from a reaction of I and II with sodium revealed no isomeric chloride formation.

[21] K. B. Desai, Ph.D. Thesis, University of Idaho, Moscow, Idaho, 1965.

[22] R. B. Turner, W. R. Meador, and R. E. Winkler [*J. Am. Chem. Soc.*, **79**, 4116 (1957)] have found that the heat of hydrogenation of norbornene is 6 kcal greater than that for cyclohexene, and 7.4 kcal greater than that for cyclopentene.

condenser, and pressure-equalizing funnel, was placed 145.0 g (1.22 moles) of redistilled thionyl chloride. To the stirred thionyl chloride at room temperature was added over a 2-hr period, 124.0 g (1.0 mole) of *endo*-5-hydroxymethylnorbornene[23] containing a few drops of piperidine. After addition of the alcohol, the mixture was heated at 85–90° for 3 hr. After the excess thionyl chloride was removed at reduced pressure, the residue was distilled, yielding 80.2 g of I, bp 60–61° at 12 mm, (56.3% yield).

Anal. Calcd for $C_8H_{11}Cl$: C, 67.36; H, 7.77. Found: C, 67.34; H, 7.68.

Hydrogenation of *endo*-5-chloromethylnorbornene over palladium on carbon gave a single saturated chloride, which proved to be identical in infrared spectral properties and vapor phase chromatographic retention times, on 25-ft DC-200 and Carbowax 20M columns, with an authentic sample of *endo*-2-chloromethylnorbornane.[21] *endo*-5-Chloromethylnorbornene (I) can be distinguished from *exo*-5-chloromethylnorbornene (II) by vapor phase chromatographic analysis on column B. There is a sufficient difference in the retention times of the two isomers to detect even 1% cross contamination. A sample of I prepared as described above was found to contain no detectable *exo* isomer II.

A mixture of I and II in the ratio 60:40 was prepared by the Diels–Alder reaction of allyl chloride and cyclopentadiene.[24] It was found that yields as high as 70% could be obtained if cyclopentadiene was used instead of dicyclopentadiene.

Reaction of *endo*-5-Chloromethylnorbornene (I) with Sodium.—In a 100-ml, three-necked flask provided with a nitrogen inlet, a TruBore stirrer, a condenser, and a pressure-equalizing funnel, was placed 4.6 g (0.20 g-atom) of thin slices of freshly cut sodium and 15 ml of redistilled *n*-decane. The flask was thoroughly swept with nitrogen and the contents were heated, to 70° with stirring. To the stirred mixture was added during a 30-min period 14.3 g (0.100 mole) of I in 15 ml of redistilled *n*-decane. After addition, the mixture was heated at 85–90° for an additional 90 min. The mixture was then distilled directly at 40 mm through a simple claisen head into a receiver, which was cooled in a Dry Ice–acetone bath. Careful fractionation of the distillate on an 18-in. semimicro spinning-band column at 90–91 mm gave 2.7 g (25%) of a mixture of C_8 hydrocarbons, bp 51–69°, free from any decane or unreacted starting material.

This hydrocarbon mixture was easily separated into two components (A and B) in a 61:39 ratio by vpc on column A at 122°. The 61% component (component A) was partially resolved on column C at 40° into two additional peaks in about a 60:40 ratio. Reinjection and heart-cut collection furnished the pure isomers without mutual contamination. The infrared spectrum of the 60% component had ν_{max} 3100, 1650, 1620, 1420, 995, 915 cm^{-1}, suggesting a vinylic double bond[10] and a cyclopentene double bond.[11] The over-all similarity of the spectrum, especially in the 1600–1650 cm^{-1} and 720–725 cm^{-1} regions, to that of 4-vinylcyclopentene[25] suggests that the 60% peak is 4-allylcyclopentene.

Anal. Calcd for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.75; H, 11.09.

The 40% peak (from partial resolution of component A) had ν_{max} 3100, 1650, 1615, 1420, 995, and 915 cm^{-1}. The spectrum resembled that of 3-vinylcyclopentene,[25] especially in the 1600–1650- and 720–725-cm^{-1} regions.

Anal. Calcd for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.86; H, 11.19.

The nmr spectrum of an unresolved mixture of the two allylcyclopentenes (III and IV) exhibited absorption bands at τ 3.82–4.67 (3 H, =CH—), 4.82–5.31 (2 H, =CH$_2$), and 6.98–9.11 (7 H). A 0.36-g mixture of III and IV was hydrogenated in ether over 10% palladium-on-carbon catalyst. Approximately 2 molar equiv of hydrogen was absorbed. The only product, separated for analysis by vpc, had an infrared spectrum identical with that of an authentic sample of *n*-propylcyclopentane, prepared by an independent method.[13]

The 39% component (component B) was easily resolved into three peaks in the ratio 97:2:1 on column C. The 97% component had an infrared spectrum similar, but not identical with that of a sample of a mixture of *cis*- and *trans*-bicyclo[3.3.0]-octene-2.[26] The nmr spectrum contained two olefinic protons at τ 4.5, one tertiary proton α to a double bond at 6.9, two methylene protons α to a double bond at 7.4, one proton β to a double bond at 7.9, and a six-proton multiplet centered at 8.5. A 0.56-g sample of this component was hydrogenated in methanol over palladium-on-charcoal catalyst. One molar equivalent of hydrogen was absorbed resulting in the formation of a single product. The spectral properties of this component were identical with those reported in the literature[7] for *cis*-bicyclo[3.3.0]octane. Thus the structure of the unsaturated parent must be *cis*-bicyclo[3.3.0]-octene-2 (V).

Anal. Calcd for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.99; H, 11.23.

The 2% component exhibited an unstrained double bond in the infrared at 1645 cm^{-1}. The nmr spectrum showed three protons α to a double bond centered at τ 7.7, two olefinic protons at 4.2 and 4.7, and a broad absorption between 7.8–8.8 encompassing seven protons, consistent with that expected for bicyclo[3.2.1]octene-2.

Anal. Calcd for C_8H_{12}: C, 88.81; H, 11.19. Found: C, 88.94; H, 11.11.

Final confirmation of the structural assignment was achieved by hydrogenation to bicyclo[3.2.1]octane[9] and also by comparison of the spectral properties of the 2% component with those of bicyclo[3.2.1]octene-2, prepared by an independent method.[8]

The 1% peak obtained by resolution of component B on column C was not identified.

***exo*-5-Chloromethylnorbornene (II).**—The procedure followed was similar to the one used for the preparation of I. A 52.3% yield of the *exo* isomer, bp 67–68° (20 mm), was obtained. Analysis on column B indicated less than 1% contamination with the *endo* isomer.

Anal. Calcd for $C_8H_{11}Cl$: C, 67.36; H, 7.77. Found: C, 67.37; H, 7.69.

Hydrogenation of a sample of *exo*-5-chloromethylnorbornene gave a single saturated product, which proved to be identical in infrared spectral properties and vpc retention times, using 25-ft DC-200 and Carbowax 20M columns, with an authentic sample of *exo*-2-chloromethylnorbornane.[21]

Reaction of *exo*-5-Chloromethylnorbornene (II) with Sodium.—The procedure was similar to that followed with the *endo* isomer. A 23–24% yield of C_8 hydrocarbons was obtained. The composition of the reaction mixtures obtained is listed in Table I.

Isomerization of *exo*- and *endo*-5-Chloromethylnorbornene During the Reaction Conditions.—The extent of isomerization of *exo*-5-chloromethylnorbornene during the reaction with sodium was determined in the following manner. The reaction mixture was neutralized with methanol. After the unreacted sodium had decomposed, the mixture was diluted with water and the decane layer was separated and was dried over magnesium sulfate. The unreacted chlorides were separated and collected using column A. Analysis of the chloride mixture using column B indicated the *exo* isomer II had rearranged to the *endo* isomer I to the extent of 63% during the reaction period of 90 min. A similar experiment was carried out with *endo*-5-chloromethylnorbornene. In this second case no evidence for isomerization to *exo* isomer was found.

Reaction of 3- and 4-Allylcyclopentene (III and IV) with *n*-Butylsodium.—The method of Morton and co-workers[27] was adapted for the preparation of *n*-butylsodium. A three-necked, 500-ml flask was fitted with a condenser, dropping funnel, mechanical stirrer, and a nitrogen inlet. Sodium metal (7.3 g, 0.32 g-atom) was cut into small pieces and placed under 65 ml of decane. The mixture was cooled with stirring in an ice bath. To this mixture was added, over a 60-min period, 10.6 g (0.11 mole) of *n*-butyl chloride in 5 ml of decane. The mixture was stirred at room temperature for 30 min and heated to 70°, at which temperature 5.4 g (0.05 mole) of a mixture of 3- and 4-allylcyclopentene in 15 ml of decane was added dropwise over a 30-min period. After addition, the mixture was heated

---

[23] J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Am. Chem. Soc.*, **83**, 3986 (1961).

[24] K. Alder and G. Stein, *Ann.*, **514**, 197 (1934).

[25] D. E. George, Ph.D. Thesis, University of Idaho, Moscow, Idaho, 1962.

[26] A. C. Cope and W. R. Schmitz, *J. Am. Chem. Soc.*, **72**, 3061 (1950).

[27] A. A. Morton, G. M. Richardson, and A. T. Hallowell, *ibid.*, **63**, 327 (1941).

at 85–90° for 90 min. The mixture was cooled in an ice bath and methanol was added. After the excess sodium and alkylsodium had been destroyed, the mixture was decanted into a 250-ml separatory funnel containing 50 ml of water. The organic layer was separated, washed once with 50 ml of water, and dried over anhydrous magnesium sulfate. Vapor phase chromatographic analysis of the dried organic phase on column A revealed only one product peak, and this peak had a retention time identical to that of a mixture of the allylcyclopentenes. The infrared spectrum indicated some methyl absorption near 1380 cm^{-1}, suggesting some isomerization. There was no evidence of any bicyclic isomers and a 33% recovery of unreacted allylcyclopentenes was obtained.

Registry No.—I, 14564-95-5; II, 14564-96-6; III, 14564-97-7; IV, 765-99-1; V, 930-99-4; VI, 823-02-9.

Acknowledgment.—The authors gratefully acknowledge the generous support of this research by the National Science Foundation (NSF-G13511) and the Air Force Office of Scientific Research (AF-34-65).

Bicyclo[3.3.1]nonanes. III. Preparation and Reactions of Bicyclo[3.2.2]nonanes

JOHN P. SCHAEFER, LELAND S. ENDRES,[1] AND MICHELLE D. MORAN

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Received June 28, 1967

The reaction of bicyclo[2.2.2]oct-2-ylcarbinylamine with nitrous acid gave a mixture of alcohols which consisted of bicyclo[3.2.2]nonan-2-ol (62%), bicyclo[3.2.2]nonan-3-ol (22%), and bicyclo[3.3.1]nonan-2-ol (16%). Dehydration of bicyclo[2.2.2]oct-2-ylmethanol at 165° with phosphoric acid produced only bicyclo[3.3.1]non-2-ene. Mechanisms for these transformations are suggested. The reaction of bicyclo[3.2.1]oct-2-en-8-one with diazomethane gave a 3:2 mixture of bicyclo[3.2.2]non-3-en-6-one and bicyclo[3.2.2]non-2-en-6-one which could be hydrogenated to bicyclo[3.2.2]nonan-6-one; the latter ketone could also be obtained from the reaction of bicyclo[3.2.1]octan-8-one with diazomethane. Reduction of bicyclo[3.2.2]nonan-6-one with lithium aluminum hydride gave an 87:13 mixture of *endo*-bicyclo[3.2.2]nonan-6-ol and *exo*-bicyclo[3.2.2]nonan-6-ol. Solvolysis of the *p*-nitrobenzenesulfonates of these alcohols produced bicyclo[3.3.1]nonan-2-ol and what is believed to be *exo*-bicyclo[4.2.1]nonan-2-ol. Solvolysis of the tosylate of bicyclo[3.2.2]nonan-2-ol yielded the unrearranged alcohol (52%), bicyclo[3.2.2]nonan-3-ol (16%), and bicyclo[3.3.1]nonan-2-ol (32%). Stereoelectronic influences governing the reactions of these bridged bicyclic compounds are discussed.

In a recent paper we described the synthesis of a series of bicyclo[3.3.1]nonane derivatives.[2] To compare the chemistry and the solvolytic reactivity of compounds in this series to those in the bicyclo[3.2.2]nonane system, we undertook to prepare the four possible secondary alcohols of the latter bicyclic framework. Although a number of diverse approaches for the preparation of the bicyclo[3.2.2]nonane system have been reported,[3–13] we decided that the method outlined by Alder[6–8] and his co-workers was the most promising, since the starting materials were easy to obtain and the conversions have been reported to be efficient.

Bromination of cyclohexene at low temperatures followed by dehydrohalogenation with potassium hydroxide in triglyme gave cyclohexa-1,3-diene of excellent purity in about 40% over-all yield. Reaction of the diene with acrylonitrile yielded 5-cyanobicyclo[2.2.2]oct-2-ene which was readily reduced to bicyclo[2.2.2]oct-2-ylcarbinylamine (**1**). Reaction of **1** with nitrous acid using Alder's conditions[7] gave a complex mixture of products from which three alcohols could be separated chromatographically. The components of the alcohol fractions were present in relative yields of 62, 22, and 16% as ascertained by integration of the vapor phase chromatograms of the mixture. To identify the components of this mixture, both bicyclo[3.2.2]nonan-2-ol (**2**) and bicyclo[3.2.2]nonan-3-ol (**3**) were synthesized by unambiguous routes for purposes of comparison.

Acylation of ethyl hydrocinnamate produced ethyl 3-(4-acetylphenyl)propionate in 75% yield, and oxidation and saponification of the latter gave 3-(4-carboxyphenyl)propionic acid (78% yield). Catalytic hydrogenation using Raney nickel followed by the addition of cerous chloride resulted in the formation of the cerous salt of 3-(4-carboxycyclohexyl)propionic acid (**4**) which upon pyrolysis produced bicyclo[3.2.2]nonan-2-one (**5**) in 22% yield (isolated as its semicarbazone). Reduction of **5** with lithium aluminum hydride yielded **2**, and a comparison of physical properties indicated that this compound corresponded to the major product formed in the Demjanov reaction of **1**.

Acylation of ethylbenzene followed by cautious oxidation of the product with potassium permanganate produced *p*-diacetylbenzene in 63% over-all yield. A Willgerodt reaction converted the diketone to *p*-benzenediacetic acid (69%). Catalytic hydrogenation of the diacid (using 50% rhodium on alumina as the catalyst) gave a mixture of the *cis* and *trans* isomers of 1,4-cyclohexane diacetic acid (**6**) in quantitative yield,

---

(1) Abstracted from the Ph.D. Thesis of L. S. Endres, University of Arizona, Tucson, Ariz., 1967.

(2) J. P. Schaefer, J. C. Lark, C. A. Flegal, and L. M. Honig, *J. Org. Chem.*, **32**, 1372 (1967).

(3) E. M. Mil'Vitskaya and A. F. Platte, *Zh. Obshch. Khim.*, **32**, 2566 (1962); *Chem. Abstr.*, **58**, 8927*e* (1963).

(4) T. Nozoe and Y. Toyooka, *Bull. Chem. Soc. Japan*, **34**, 623 (1962).

(5) O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **81**, 3696 (1959).

(6) K. Alder, S. Hartung, and G. Hausmann, *Ber.*, **89**, 1972 (1956).

(7) K. Alder, H. Krieger, and H. Weiss, *ibid.*, **88**, 144 (1955).

(8) K. Alder and R. Reubke, *ibid.*, **91**, 1525 (1958).

(9) J. A. Berson and M. Jones, *J. Am. Chem. Soc.*, **86**, 5019 (1964).

(10) G. A. Grob, M. Onta, E. Renk, and A. Weiss, *Helv. Chem. Acta*, **41**, 1191 (1953).

(11) L. T. Mann, Ph.D. Dissertation, Columbia University, New York, N. Y., 1951. (Doctoral Dissertation Series, Publication No. 9528, University Microfilms, Ann Arbor, Mich.)

(12) V. Ioan, M. Popovici, E. Mosanu, M. Eliean, and C. D. Nenitescu, *Rev. Roumaine Chim.*, **10**, 185 (1965).

(13) C. W. Jefford, S. Mahajan, J. Waslyn, and B. Waegell, *J. Am. Chem. Soc.*, **87**, 2183 (1965).