[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS CO.]

Some Reactions of 2,5-Norbornadiene (Bicyclo[2.2.1]-2,5-heptadiene)[1]

BY LOUIS SCHMERLING, J. P. LUVISI AND ROBERT W. WELCH

RECEIVED DECEMBER 24, 1955

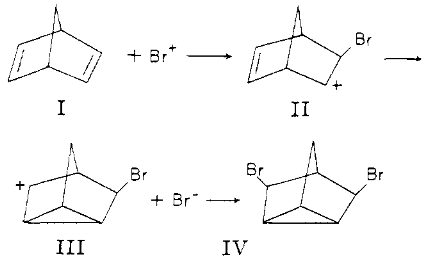
2,5-Norbornadiene (I) adds only one mole of bromine at −8 to −12° resulting in a 66% yield of dibromide which consists of about 80% 3,5-dibromonortricyclene (IV) and 20% dibromonorbornenes. Addition of hydrogen chloride or bromide to I yields monohalide which is chiefly 5-halo-2-norbornene (VIII) but which may contain 15–30% 3-halonortricyclene (VII). The reaction of I with formic acid gives formate consisting principally of 3-nortricyclyl formate. Saponification of the product yields 3-hydroxynortricyclene.

At the time the investigation described in this paper was carried out, the preparation of 2,5-norbornadiene[2] (bicyclo[2.2.1]-2,5-heptadiene, I) was described only in foreign patents, *e.g.*, Belgian Patent 498,176 (to Julius Hyman and Co., 1951) which claims the formation of the diene by the condensation of cyclopentadiene with acetylene. In the present study compound I was obtained by the dechlorination of 5,6-dichloro-2-norbornene with magnesium iodide in ether,[3] a method which has since been described by Hine and co-workers[4] who did not, however, discuss any reactions of the hydrocarbon.

Compound I boiled at 89.5–90.0° and melted at about −25°. Its infrared spectrum was consistent with that to be expected of a bicyclo[2.2.1]heptadiene. There was a very intense band in the region characteristic of a *cis* symmetrical disubstituted olefin. This band was approximately twice as intense in the bicycloheptadiene as the same band, at about the same wave length, in bicyclo-[2.2.1]-2-heptene (2-norbornene).

Hydrogenation of I at room temperature in the presence of platinum catalyst resulted in the absorption of 2.00 moles of hydrogen per mole of hydrocarbon yielding bicyclo[2.2.1]heptane (norbornane).

On the other hand, only one mole of bromine was absorbed per mole of the diene. Thus, the addition of bromine to I in carbon tetrachloride solution at −8 to −12° resulted in a 66% yield of dibromide believed to consist chiefly of 3,5-dibromonortricyclene (IV) formed by the following mechanism

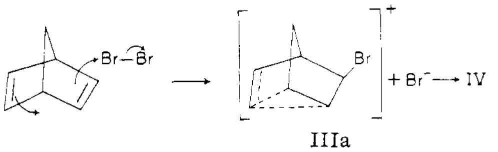


I II

III IV

or, III + Br_2 ⟶ IV + Br^+

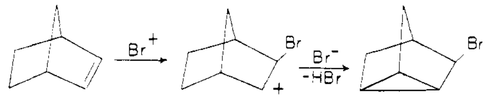
An alternative mechanism for the bromination emphasizes the driving force involved in the participation of the second double bond



IIIa

That the bromination product consisted largely of IV was suggested by a strong band at $12.3\ \mu$ (indicative of the nortricyclene structure[5]) in its infrared spectrum. The material absorbed 0.20 mole of hydrogen per mole, indicating admixture with 20% of dibromonorbornenes, *e.g.*, 5,7-dibromo-2-norbornene[6] formed by addition of bromide at C-4 of IIIa.

The ring closure to form the nortricyclene derivative differs from that which occurs in the bromination of 2-norbornene to yield 3-bromonortricyclene[5] in that the latter ring closure involves the abstraction of a proton from the 5-carbon atom of a bromobicycloheptyl ion by a bromide ion with the resulting formation of hydrogen bromide



V

II and V may probably be more nearly correctly written as bridged ions similar to IIIa.[5,7]

It is significant to compare the bromination of 2,5-norbornadiene with that of 1,4-cyclohexadiene. The latter reaction yields no 2,4-dibromobicyclo-[3.1.0]hexane (VI) formed in analogous manner to IV.[8]

Addition of hydrogen chloride to I at −78° resulted in a 70% yield of a monochloride which was chiefly 5-chloro-2-norbornene (VIII, X = Cl), but which may have contained up to about 20% of 3-chloronortricyclene (VII, X = Cl) as indicated by its infrared spectrum and by the fact that it absorbed only 84% of the theoretical amount of hydrogen. 5-Chloro-2-norbornene, prepared by the reaction of cyclopentadiene and vinyl chloride, ab-

---

[1] Presented before the Division of Petroleum Chemistry of the American Chemical Society at the Minneapolis Meeting, September, 1955.

[2] The name norbornane has been recommended as the preferred name for bicyclo[2.2.1]heptane. For a discussion of the nomenclature of its derivatives see, "System of Nomenclature for Terpene Hydrocarbons," Advances in Chemistry Series, No. 14, A. C. S., Washington, D. C., 1955, p. 57.

[3] R. K. Summerbell and R. R. Umhoefer, THIS JOURNAL, **61**, 3017 (1939).

[4] J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner and M. Hine, *ibid.*, **77**, 594 (1955).

[5] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

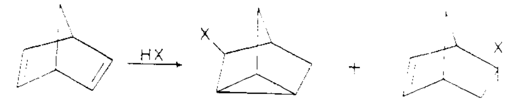
[6] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955), in a Communication to the Editor concerning 7-norbornenyl and 7-norbornyl ions mention that 5,7-dibromo-2-norbornene used as an intermediate in their work was one of the products of the addition of bromine to 2,5-norbornadiene.

[7] S. Winstein and D. S. Trifan, *ibid.*, **71**, 2953 (1949); **74**, 1147, 1154 (1952).

[8] E. E. van Tamelen, *ibid.*, **77**, 1704 (1955).

sorbed 105% of the theoretical amount of hydrogen.

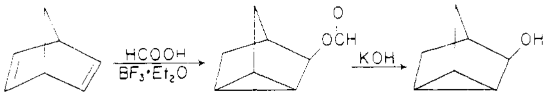
Similarly, product which contained about 30% of 3-bromonortricyclene (VII, X = Br) was obtained by the hybromination of I.



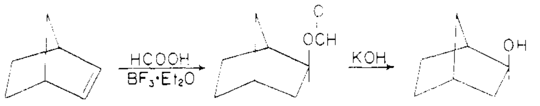
VII VIII

The reaction of I with 90% formic acid in the presence of boron fluoride etherate at room temperature resulted in a 63% yield of a formate consisting principally of 3-nortricyclyl formate (IX). The presence of about 10% of 5-norbornen-2-yl formate was indicated by the infrared spectrum of the product and its hydrogen absorption (0.11 mole per mole).

Saponification of the formate with alcoholic potassium hydroxide yielded 3-hydroxynortricyclene (X) having a melting point and infrared spectrum in good agreement with those previously reported.[5]



IX X



XI XII

For purposes of comparison, 2-norbornene was also converted to an alcohol by way of the formate. The alcohol XII was the same, namely, *exo*-norborneol (*exo*-bicyclo[2.2.1]-2-heptanol), as that obtained by the hydrolysis of *exo*-2-chloronorbornane formed by the addition of hydrogen chloride to 2-norbornene and by the hydrogen–chlorine exchange reaction between norbornane and *t*-butyl chloride.[9]

The addition of *p*-thiocresol to I has been described recently.[10] The product consisted of 40% *exo*-5-*p*-thiocresoxy-2-norbornene (1,2-addition) and 60% nortricyclyl-*p*-tolyl thioether (addition with ring closure).

Experimental

***trans*-5,6-Dichloro-2-norbornene (XIII)** was obtained in 30–34% yield (together with a large amount of higher boiling product) by heating 500 g. (5.2 moles) of *trans*-dichloroethylene and 250 g. (3.8 moles) of cyclopentadiene or 250 g. (1.9 moles) of dicyclopentadiene at 180–200° in glass liner in an Ipatieff-type rotating autoclave under 30 atm. initial nitrogen pressure during 4.5–5.0 hours; b.p. 83–85° (22 mm.), 188–191° (760 mm.).[11] Roberts, Johnson and Carboni[12] obtained the dichloride in 34% yield by heating 2.15 moles of *trans*-dichloroethylene and 1.35 moles of cyclopentadiene at 190–195° for 24 hr.

***endo-cis*-5,6-Dichloro-2-norbornene (XIV)** was similarly obtained in 18–20% yield by the reaction of 500 g. of *cis*-dichloroethylene and 250 g. of cyclopentadiene or dicyclopentadiene at 180–200° for 4.5 to 5.0 hours; b.p. 104–108° (18 mm.), 220–225° (760 mm.), m.p. 74–75°. Roberts, Johnson and Carboni[12] isolated an 8% yield of resublimed compound, m.p. 70–72°, from the product of the reaction of 4.2 moles of *cis*-dichloroethylene and 2.7 moles of cyclopentadiene at 190° for 17 hr.; the recrystallized product melted at 72–74° and an analytical sample which was boiled with water to remove more reactive chlorides and then recrystallized from hexane melted at 76–77°.

2,5-Norbornadiene (I).—5,6-Dichloro-2-norbornene was dechlorinated by a procedure analogous to that used by Summerbell and Umhoefer[8] for the dechlorination of 2,3-dichloro- and 2,3,5,6-tetrachlorodioxane. A solution of magnesium iodide in ether was formed by adding 0.06 mole of iodine to 1.5 gram atoms of magnesium turnings in excess anhydrous ethyl ether, after which 1.0 mole of the dichloronorbornene (XIII or XIV) was added dropwise at such a rate as to maintain a gentle reflux of the ether. The product was treated with ice-water, extracted with ether, washed, dried and distilled.

Five experiments were carried out using 1.0 mole of the *trans* isomer XIII in each. In three of these, the yield of I was 71–72%; in the remaining two, it was 57–59%. In a single experiment using 0.33 mole of the *cis* compound XIV the yield of I was 51%. Hine and co-workers[4] obtained a 25% yield of I from "2,3-dichlorobicyclo[2.2.1]-2-heptene" using butyl ether as solvent.

Compound I boiled at 89.5–90.0°, chiefly 90.0–90.0°, when redistilled through a 30-plate Oldershaw column; m.p. about −25°, $n^{20}{}_D$ 1.4699, $d^{20}{}_4$ 0.9056; mol. ref. calcd. for I 29.33, obsd. 28.35.

Anal. Calcd. for C_7H_8: C, 91.25; H, 8.75. Found: C, 91.24; H, 8.76.

The infrared spectrum had a very intense band at 13.7 μ, characteristic of a *cis* symmetrical disubstituted olefin. This band was approximately twice as intense in the norbornadiene as the corresponding *cis*-olefinic band in 2-norbornene which appears at 14.1 μ.

Hydrogenation of I in pentane solution in the presence of platinum oxide showed that the compound absorbed 0.0217 mole of hydrogen per gram, equivalent to 2.00 moles per mole of C_7H_8.

The bromine number[13] of I was only 175, which is one-half that (348) calculated for a diene having a molecular weight of 92. This was probably due to the formation of 3,5-dibromonortricyclene (IV). However, it should be pointed out that the bromine number of XIV, for example, was only 10 instead of the calculated value of 98. In other words, the dichloronorbornene absorbed little bromine under the standard bromine number reaction conditions (addition, with shaking, of a potassium bromate–potassium bromide solution to a mixture of a solution of the olefinic compound in carbon tetrachloride and an aqueous 10% solution of sulfuric acid at ice-bath temperature). On the other hand, on quantitative hydrogenation, XIV absorbed 1.05 moles of hydrogen per mole.

Bromination of I.—A solution of 40 g. (0.25 mole) of bromine in 50 cc. of carbon tetrachloride was added slowly to a stirred solution of 27 g. (0.29 mole) of I in 75 cc. of carbon tetrachloride at −8 to −12° during 50 minutes. Distillation of the product yielded 48 g. (66%) of dibromide, largely 3,5-dibromonortricyclene (IV), b.p. 99–102° (5 mm.), $n^{20}{}_D$ 1.5795, $d^{20}{}_4$ 1.8795; mol. ref. calcd. for $C_7H_8Br_2$ (no double bond) 43.77, obsd. 44.62.

Anal. Calcd. for $C_7H_8Br_2$: C, 33.37; H, 3.20; Br, 63.43. Found: C, 33.65; H, 3.35; Br, 63.13.

The dibromide absorbed 0.20 mole of hydrogen per mole when quantitatively hydrogenated in pentane solution in the presence of platinum oxide. Its infrared spectrum had a strong band at 12.3 μ indicative of the presence of the nortricyclene structure.

Addition of Hydrogen Chloride to I.—Hydrogen chloride was bubbled during 0.5 hour into a solution of 8 g. of I in 25 g. of *n*-pentane at −78°. Distillation of the washed product yielded 8.0 g. (72%) of monochloride, b.p. 66–68° (43 mm.), $n^{20}{}_D$ 1.4949.

The infrared spectrum of the product indicated that it probably consisted of *exo*-5-chloro-2-norbornene (VIII)[5] mixed with about 20% of 3-chloronortricyclene. On quan-

---

[9] L. Schmerling, This Journal, **68**, 195 (1946).

[10] S. J. Cristol and G. D. Brindell, paper presented before the Division of Organic Chemistry at the Cincinnati Meeting of the American Chemical Society, April 1, 1955.

[11] Calculated from boiling point under reduced pressure using Lippincott nomograph, *Ind. Eng. Chem.*, **38**, 320 (1946).

[12] J. D. Roberts, F. O. Johnson and R. A. Carboni, This Journal, **76**, 5692 (1954).

[13] A. W. Francis, *Ind. Eng. Chem.*, **18**, 821 (1926).

titative hydrogenation it absorbed 0.84 mole of hydrogen per mole of C_7H_9Cl; under the same conditions VIII, prepared by the condensation of cyclopentadiene with vinyl chloride,[5] absorbed 1.05 moles per mole.

It may be concluded that the hydrochlorination product consisted of 80–84% VIII (X = Cl) and 16–20% of VII (X = Cl).

Addition of Hydrogen Bromide to I.—Hydrogen bromide was bubbled into a solution of 8.5 g. (0.09 mole) of I in 26 g. of *n*-pentane at −78° for 10 minutes. The product which contained much excess hydrogen bromide was poured onto ice, washed with dilute alkali and water, dried and distilled. There was obtained 9 g. (56%) of monobromide, b.p. 64–68° (19 mm.), 170–173° (760 mm.),[11] $n^{20}\mathrm{D}$ 1.5282–1.5292. Its infrared spectrum indicated that it was a mixture, about one-third of which was 3-bromonortricyclene (VII, X = Br) as shown in comparison with the spectrum of product prepared by the reaction of 2-norbornene with bromine.[5]

3-Nortricyclyl formate (IX) was obtained by the acid-catalyzed reaction of I with formic acid.[14] A mixture of 17 g. (0.18 mole) of I, 76 g. (1.5 moles) of 90% formic acid and 2 g. of boron fluoride etherate was shaken at room temperature for 5 hr. during which the originally two-phase system became a single deep amber solution. The product was treated with water, extracted with ether and the extract was washed, dried and distilled. There was obtained 16 g. (63%) ester, chiefly 3-nortricyclyl formate, b.p. 79° (21 mm.), $n^{20}\mathrm{D}$ 1.4758, d^{20}_4 1.1103; mol. ref. calcd. for $C_8H_{10}O_2$ (IX) 34.45, obsd. 35.08.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.37; H, 7.52.

The compound absorbed 0.11 mole of hydrogen per mole in the presence of platinum oxide.

The infrared spectrum showed a major intensity band at 12.3 μ indicative of the nortricyclene structure. Minor bands between 14.3 and 15.3 μ showed the possibility of contamination of the sample with a minor amount of a compound containing a double bond in the ring, *e.g.*, 5-norbornen-2-yl formate.

3-Hydroxynortricyclene (X).—Addition of 5 g. of IX to a solution of 4 g. of potassium hydroxide in 10 g. of ethanol resulted in an exothermic reaction accompanied by the precipitation of a small amount of salt. On standing, the mixture separated into two layers, most of the salt going into solution. Water was added and the product was extracted with pentane. Evaporation of the pentane yielded 3 g. (75%) of crystalline compound, m.p. 101–102°, the infrared spectrum of which was similar to that reported for 3-hydroxynortricyclene.[5] Its phenylurethan melted at 143–144°.[5]

2-Norbornyl Formate (XI).—A mixture of 30 g. (0.32 mole) of 2-norbornene, 100 g. (1.9 moles) of 88% formic acid and 2 g. of boron fluoride etherate was heated under reflux (102–103°) for 1 hr., during the first half of which the originally two-phase system became homogeneous. Distillation of the extracted and washed product yielded 32 g. (71%) of XI, b.p. 76–77° (20 mm.), $n^{20}\mathrm{D}$ 1.4641; mol. ref. calcd. for $C_8H_{12}O_2$ 36.43, obsd. 36.72.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.59; H, 8.74.

The product absorbed no hydrogen under the usual hydrogenation conditions.

exo-**Norborneol (XII).**—When 13.5 g. of XI was added to a solution of 11 g. of potassium hydroxide in 30 g. of 95% ethyl alcohol, an exothermic reaction occurred and a white salt separated. The mixture was allowed to stand for an hour and water was then added. The oil which separated soon crystallized. Filtration yielded about 6 g. of crude XII, m.p. 126°.[15] Extraction of the aqueous solution with pentane yielded 2.4 g. (78% total yield) additional product, m.p. 125°. Its phenylurethan melted at 144°.[15]

It is of interest to note that both X and XII yielded phenylurethans melting in the range 143–144°. The melting point of a mixture of approximately equal amounts of the two derivatives was only slightly depressed to 140–140.5°.

---

[14] *Cf.* H. B. Knight, R. E. Koos and D. Swern, THIS JOURNAL, **75**, 6212 (1953).

[15] G. Komppa and S. Beckmann, *Ann.*, **512**, 172 (1934).

DES PLAINES, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY, JERUSALEM]

1,2-Cyclopentenofluorenes and Some Derivatives of 1,2,3,4-Tetrahydrofluorene

BY ERNST D. BERGMANN AND RAPHAEL IKAN

RECEIVED NOVEMBER 25, 1955

1,2-Cyclopentenofluorene, 3′-methyl-1,2-cyclopentadienofluorene and 3′-methyl-1,2-cyclopentenofluorene have been prepared from fluorene-1-aldehyde, by standard procedures. The spectra of the 1,2-cyclopentenofluorenes are identical with those of a series of hydrocarbons, obtained by Jacobs and co-workers in the dehydrogenation of cevine and jervine. A by-product of the reduction of fluorenone-1- to fluorene-1-carboxylic acid with sodium amalgam has been identified as 1,2,3,4-tetrahydrofluorene-1-carboxylic acid. 1,2,3,4-Tetrahydrofluorene behaves as a true indene derivative in condensing with *p*-chlorobenzaldehyde to a (substituted) benzofulvene.

Craig and Jacobs[1] and Craig, Jacobs and Lavin[2] have obtained by dehydrogenation of cevine (I) a number of polycyclic aromatic hydrocarbons of which the simplest one, $C_{13}H_{12}$, has been identified as the liquid 4,5-benzhydrindene. In addition, a homologous series of hydrocarbons $C_{17}H_{16}$, $C_{18}H_{18}$, $C_{19}H_{20}$ and $C_{24}H_{30}$ (m.p. 160–165°, 116–118°, 185–188°, 108–110°, respectively) has been isolated. They have been assumed to be derivatives of 1,2-cyclopentenofluorene (II) ($C_{16}H_{14}$). Their spectra are very similar and the presence of the fluorene system was indicated by their chemical behavior.[3] The same type of compounds ($C_{20}H_{22}$, $C_{24}H_{30}$) is produced by the dehydrogenation of jervine (III) together with substances ($C_{20}H_{16}$, $C_{22}H_{20}$) believed to be derivatives of 1,2-cyclopenteno-7,8-benzofluorene (IV).[3,4]

It appeared of interest to prepare the unknown 1,2-cyclopentenofluorene (II) and to compare it and its simple alkyl derivatives with the products obtained by the above dehydrogenation reactions.

Fluorenone-1-carboxylic acid (V) was obtained by oxidation of fluoranthene[5,6] and reduced to fluorene-1-carboxylic acid (VI, R = COOH). A by-product observed in this reduction was identi-

---

[1] (a) L. C. Craig and W. A. Jacobs, *J. Biol. Chem.*, **129**, 79 (1939); (b) **139**, 263 (1941).

[2] L. C. Craig, W. A. Jacobs and G. I. Lavin, *ibid.*, **139**, 277 (1941).

[3] *Cf.* W. A. Jacobs and S. W. Pelletier, *J. Org. Chem.*, **18**, 765 (1953).

[4] W. A. Jacobs, L. C. Craig and G. I. Lavin, *J. Biol. Chem.*, **141**, 51 (1941); *cf.* W. A. Jacobs and Y. Sato, *ibid.*, **181**, 55 (1949).

[5] R. Fittig and F. Gebhard, *Ann.*, **193**, 149 (1878).

[6] L. F. Fieser and A. Seligman, THIS JOURNAL, **57**, 2174 (1935).