

[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

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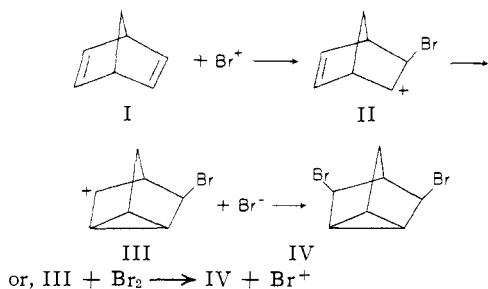
2,5-Norbornadiene (I) adds only one mole of bromine at -8 to -12° resulting in a 66% yield of dibromide which consists of about 80% 3,5-dibromonortricyclene (IV) and 20% dibromonorbornenes. Addition of hydrogen chloride or bromide to I yields monohalide which is chiefly 5-halo-2-norbornene (VIII) but 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-norbornadiene² (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-workers⁴ 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



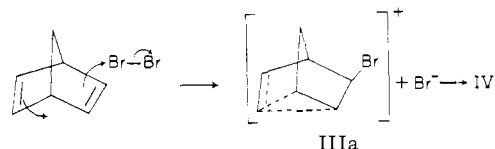
(1) Presented before the Division of Petroleum Chemistry of the American Chemical Society at the Minneapolis Meeting, September, 1955.

(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).

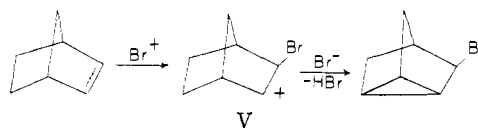
(4) J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner and M. Hine, *ibid.*, **77**, 594 (1955).

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



That the bromination product consisted largely of IV was suggested by a strong band at 12.3μ (indicative of the nortricyclene structure⁵) 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-norbornene⁶ 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-bromonortricyclene⁵ 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



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-

(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).

titative hydrogenation it absorbed 0.84 mole of hydrogen per mole of C_7H_8Cl ; under the same conditions VIII, prepared by the condensation of cyclopentadiene with vinyl chloride,⁶ 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. $64-68^\circ$ (19 mm.), $170-173^\circ$ (760 mm.),¹¹ n_D^{20} 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_D^{20} 1.4758, d_4^{20} 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 12.3μ indicative of the nortricyclene structure. Minor bands between 14.3 and 15.3μ showed the possibility of contamination of the sample with a minor amount of a com-

pound 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. $101-102^\circ$, the infrared spectrum of which was similar to that reported for 3-hydroxynortricyclene.⁵ Its phenylurethan melted at $143-144^\circ$.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 ($102-103^\circ$) 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. $76-77^\circ$ (20 mm.), n_D^{20} 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° .¹⁶

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

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

DES PLAINES, ILLINOIS

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

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

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

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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 Jacobs¹ and Craig, Jacobs and Lavin² 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. $160-165^\circ$, $116-118^\circ$, $185-188^\circ$, $108-110^\circ$, 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

(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).

The same type of compounds ($C_{20}H_{22}$, $C_{24}H_{30}$) is produced by the dehydrogenation of jervine (III) together with substances ($C_{20}H_{18}$, $C_{22}H_{20}$) 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-

(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).