The Synthesis of *syn*-8-Bromobicyclo[3.2.1]-2-octene

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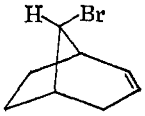
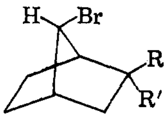
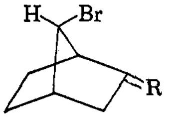
Bicyclo[2.2.2]-2-octene has been recently shown to react with N-bromosuccinimide in the presence of benzoyl peroxide in carbon tetrachloride to yield the rearranged product *syn*-8-bromobicyclo[3.2.1]-2-octene (I).[2] The skeleton of I was readily arrived at by chemical means, but the position of the bromine atom in I was determined indirectly by n.m.r. and dipole moment studies.[2] We now wish to record the synthesis of I.



I



III, R = OH; R′ = H
Va, R = OH; R′ = CH_3
b, R = CH_3; R′ = OH
VIIa, R = H; R′ = CH_2OH
b, R = CH_2OH; R′ = H



IV, R = O
VI, R = CH_2

Treatment of norbornylene (II) with hypobromous acid gave *syn*-7-bromobicyclo[2.2.1]heptan-2-*exo*-ol (III) as the major product. Roberts, Johnson, and Carboni[3] had previously shown that hypochlorous acids adds to norbornylene to give the corresponding chloro isomer of III. Jones[4] oxidation of III gave ketone IV which on treatment with methylmagnesium iodide gave a mixture of *syn*-7-bromo-2-*endo*-methylbicyclo[2.2.1]heptan-2-*exo*-ol (Va) and its C-2 isomer Vb. The C-2 methyl group in Va gave a signal at δ 1.23 whereas the C-2 methyl group in Vb gave a signal at δ 1.55 in their n.m.r. spectra. The mixture of alcohols V was distilled in the presence of iodine to give the bromo olefin VI which on hydroboration[5] gave a mixture of 7-*syn*-bromobicyclo[2.2.1]heptane-2-methanols (VII). Heating of mixture VII in the presence of phosphorous acid gave I, identical in all respects with that previously reported.[2]

Experimental[6]

Preparation of *syn*-7-Bromobicyclo[2.2.1]heptan-2-*exo*-ol. III.—N-Bromosuccinimide (140 g.) was added to norbornylene (60 g.) dissolved in 1.2 l. of 1 *N* sulfuric acid and 800 ml. of *t*-butyl alcohol. After stirring at room temperature overnight, the solution was diluted with 5 l. of water and exhaustively extracted with petroleum ether (b.p. 35–40°). The extract was washed with sodium carbonate solution, dried over magnesium sulfate, and concentrated. Fractionation of the residue gave 18.1 g. of nortricyclene bromide (b.p. 55° at 0.70 mm.) and 55.8 g. of the bromonorborneol fraction which solidified on standing. Gas chromatographic analysis of the latter fraction (10 ft. × 0.25 in. 10% silicone 550-on-firebrick column at 190° with a flow rate of 55 cc./min.) showed that it contained two components in a ratio of 3:1. The component in larger amount was identified as *syn*-7-bromobicyclo[2.2.1]heptan-2-*exo*-ol, and the minor component was identified as 3-bromobicyclo[2.2.1]heptan-2-ol by n.m.r. The bromonorborneol fraction gave m.p. 40–43° after two sublimations and was used without further separation for the next step.

Preparation of *syn*-7-Bromobicyclo[2.2.1]heptan-2-one (IV).[7]—The above-mentioned bromonorborneol fraction was oxidized in dry acetone using a molar equivalent of Jones reagent.[4] The reaction mixture was diluted with water, then extracted with *n*-hexane. The hexane extract, after washing with sodium carbonate solution, was dried and concentrated. The residue was fractionally distilled to yield *syn*-7-bromobicyclo[2.2.1]heptan-2-one (72%), b.p. 68–70° at 0.4 mm., ν_{max}^{film} 1750 cm.$^{-1}$, n.m.r. (CS_2) δ 4.4 (C-7 proton, quartet, J = 1 c.p.s.). The gas chromatogram (same conditions as above) showed <5% impurities. The 2,4-dinitrophenylhydrazone was prepared by the addition of an acidic, methanolic 2,4-dinitrophenylhydrazine solution and, after chromatography on alumina and recrystallization from petroleum ether (b.p. 50–70°), gave m.p. 201.5–202.5°.

Anal. Calcd. for $C_{13}H_{13}BrN_4O_4$: C, 42.29; H, 3.55. Found: C, 42.36; H, 3.80.

Preparation of *syn*-7-Bromo-2-methylbicyclo[2.2.1]heptan-2-ol (V).—A solution of ketone IV (0.185 mole) in ether was slowly added to 0.190 mole of methylmagnesium iodide in 250 ml. of dry ether. After stirring for 3 hr., aqueous ammonium sulfate was added, and the solution was extracted with ether. The ether extract was dried and evaporated to yield a residue (37 g.) whose n.m.r. spectrum indicated the presence of ~30% of unreacted IV, ~50% of *syn*-7-bromo-2-*endo*-methylbicyclo[2.2.1]heptan-2-*exo*-ol (Va), and ~20% of *syn*-7-bromo-2-*exo*-methylbicyclo[2.2.1]heptan-2-*endo*-ol (Vb). A pure sample of Vb was obtained after chromatography on Merck acid-washed alumina and had m.p. 74–75° after three recrystallizations from petroleum ether (b.p. 40–45°); ν_{max}^{KBr} 3320, 1188, and 930 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{13}BrO$: C, 46.85; H, 6.39. Found: C, 47.07; H, 6.62.

Preparation of 7-*syn*-Bromo-2-methylenebicyclo[2.2.1]heptane (VI).—The crude product (24 g.) from the above-mentioned Grignard reaction was slowly distilled at 85–110° (20–55 mm.) in the presence of a few crystals of iodine. The distillate was fractionally distilled to give 11.4 g. of 7-*syn*-bromo-2-methylenebicyclo[2.2.1]heptane (VI), slightly contaminated (<15%) with 7-*syn*-bromo-2-methylbicyclo[2.2.1]hept-2-ene (detected by n.m.r.), and 9.23 g. of a fraction containing ketone IV (unchanged from Grignard reaction) and olefin VI. The latter fraction was separated into 2.8 g. of VI and 4.8 g. of IV by use of Girard T reagent. The analytical sample of VI was obtained by preparative gas chromatography on a 20 ft. × $^1/_8$ in. silicone nitrile column; ν_{max}^{film} 3090, 1630, and 882 cm.$^{-1}$; n.m.r. (CS_2) δ 3.87 (doublet, J = 1.5 c.p.s., C-7 proton) and 4.85 (doublet, J = 10 c.p.s., vinylic protons).

Anal. Calcd. for $C_8H_{11}Br$: C, 51.36; H, 5.93. Found: C, 51.29; H, 5.96.

Conversion of VI into *syn*-8-Bromobicyclo[3.2.1]oct-2-ene (VIII).—A solution of sodium borohydride (0.37 g.) and boron trifluoride etherate (2.5 ml.) in 10 ml. of tetrahydrofuran was added to 2.3 g. of VI in 20 ml. of dry tetrahydrofuran and the solution was stirred at 60° for 3.5 hr.[5] After destroying the excess borohydride, 1.3 ml. of 3 *N* sodium hydroxide and 1.3 ml. of 30% hydrogen peroxide were cautiously added and after stirring at 50° for 1 hr. the solution was diluted with 150 ml. of water. Extraction with ether and removal of the ether gave an oily residue which on distillation gave 1.3 g. of the isomeric *syn*-7-bromobicyclo[2.2.1]heptane-2-methanols in a ratio of 3:1 (g.l.c. on silicone 550 column). The isomeric mixture (1.3 g.) was heated at 160° with 85% phosphoric acid[8] (0.5 g.) for 30 min. at 50 mm. during which period water and a dark-colored organic liquid distilled from the reaction mixture. The residue and distillate were combined, diluted with water, and extracted with petroleum ether (b.p. 40–45°). After washing and drying, the extract was concentrated to give 352 mg. of residue. Gas chromatographic

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[1] National Defense Education Act Fellow, 1962–1965.

[2] N. A. LeBel, J. E. Huber, and L. H. Zalkow, *J. Am. Chem. Soc.*, **84**, 2226 (1962).

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

[4] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[5] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

[6] Melting points are uncorrected. Infrared spectra were recorded with a Beckman IR-5 spectrophotometer; n.m.r. spectra were obtained with a Varian A-60 n.m.r. spectrometer, using tetramethylsilane as an internal standard (δ 0). Carbon and hydrogen analyses were performed by Midwest Microlabs, Inc., Indianapolis, Ind.

[7] The synthesis of IV was reported by Sauers and Beisler [*J. Org. Chem.*, **29**, 210 (1964)] after the submission of this paper.

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

analysis (silicone 550 column) indicated that this residue contained ~25% of the desired bromo olefin VIII. A sample of VIII was obtained by preparative gas chromatography (silicone 550 column) and the sample so obtained was identical in infrared and nuclear magnetic resonance spectra with a sample of VIII prepared as previously described.[2]

New Butadiene Dimers

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It is known that treatment of butadiene with a Ziegler type catalyst (combination catalyst of organoaluminum compounds and transition metal compounds) has given stereospecific polybutadiene.[1]

During our examination of the effect of various Ziegler catalysts on butadiene, a new reaction was found which produced linear dimers in good yield.

Treatment of butadiene in a hydrocarbon solution with the combined catalyst of trialkyl aluminum and cobalt(II) chloride resulted in a good yield of the butadiene dimer. These results are summarized in Table I.

TABLE I

DIMERIZATION OF BUTADIENE

Catalyst[a]	AlR_3–$CoCl_2$ molar ratio	Solvent	Product yield (%) Dimer	Product yield (%) Higher polymer
$Al(C_2H_5)_3$–$CoCl_2$	3.5	Benzene	90	Trace
$Al(C_2H_5)_3$–$CoCl_2$	3.5	Pentane	85	Trace
$Al(C_2H_5)_3$–$CoCl_2$	3.6	Hexane	82	Trace
$Al(C_2H_5)_3$–$CoCl_2$	3.6	Nonane	Trace	Trace
$Al(iso\text{-}C_4H_9)_3$–$CoCl_2$	3.5	Benzene	80	Trace

[a] The aluminum compound that produced the dimer was limited to trialkyl aluminum.

In comparing alkyl groups, ethyl had a higher rate of reaction than isobutyl. The dimers were not formed when nickel or iron was used as the transition metal in place of cobalt.

The product, a colorless liquid of b.p. 117–118°, slowly polymerized when left standing for a long time. Hydrogenation and bromination indicated that this product was a dimer of butadiene which had the formula C_8H_{12} with three double bonds.

Gas chromatography indicated that this dimer was a mixture of about 85% of A and about 15% of B, both of which were found to have the formula C_8H_{12}. It was assumed that the two components A and B were different, not only in the position of the double bonds but also in the skeleton, because the hydrogenated product was also composed of two components, the per cents of which were the same as the mixture dimers.

The basic skeletons of A and B were established by the fact that the hydrogenated product of A was identified as 3-methylheptane (III), and B as octane (IV).

The position of the double bonds in A and B was indicated by ultraviolet, infrared, and nuclear magnetic resonance spectra.

These spectra showed that only two of the three double bonds were conjugated, since A and B, respectively, had ultraviolet absorption at 226 and 225 mμ.

Infrared spectra of A and B showed the presence of a terminal double bond (900, 1000 $cm.^{-1}$), a conjugated double bond (1605, 1636, 1650 $cm.^{-1}$), and a methyl group (1372 $cm.^{-1}$). Further, strong absorptions at 900 and 915 $cm.^{-1}$ (CH_2 out-of-plane deformation) in A showed the presence of two terminal double bonds, one of which was conjugated.

The n.m.r. spectrum showed that compound A had a secondary methyl group from the presence of a symmetrical doublet at $\tau = 8.88$ p.p.m. and also had the following partial structure, $=CH-\overset{\overset{\textstyle CH_3}{|}}{C}H-CH=$, because of the presence of six lines at $\tau = 7.12$ p.p.m.

Further proof for the formula (III) was obtained by the fact that the n.m.r. spectrum showed that the hydrogenated product of A had three methyl groups.

The n.m.r. spectrum of B confirmed the presence of one methyl and methylene group, both of which were not coupled since there was a symmetrical doublet at $\tau = 8.38$ p.p.m. and a symmetrical triplet at $\tau = 7.19$ p.p.m.

Among the possible structures for A and B, only I and II could be proposed for dimers A and B, respectively, since the structures completely satisfied all the observations. (See Scheme I.)

It is evident that dimers like I and II are produced by 1,2-addition and 1,4-addition of butadiene monomers, respectively.

It is well-known that in the case of butadiene polymerization by Ziegler catalysts, fine differences of combined components have a great effect on the structure of the product.

Experimental

Materials.—1,3-Butadiene monomer was dried over sodium hydroxide and activated alumina. Triethylaluminum and triisobutylaluminum (Ethyl Corp., U. S. A.) were vacuum distilled. Cobalt(II) chloride (Wako Pure Chemical Industries, Ltd., Japan) was dried over thionyl chloride. All the solvents were purified or dried from commercial products by conventional procedures.

Dimerization of Butadiene by Triethylaluminum–Cobalt(II) Chloride.—Experiments were carried out in 500-ml. autoclave equipped with an inlet tube and thermometer. Additions of solvents and catalyst were performed in a dry nitrogen atmosphere. The autoclave was first purged with nitrogen, then evacuated. Liquid butadiene (200 ml.) was added to the autoclave which had been charged with 60 ml. of a benzene solution containing 3.6 ml. of triethylaluminum and 1 g. of cobalt(II) chloride. The autoclave was heated at 60° and stirred for 2 hr. After addition of 100 ml. of methanol, the reaction mixture was washed with dilute sulfuric acid and then filtered. The filtrate, dried over calcium chloride and distilled, yielded 40 g. of dimer, b.p. 117–118° (760 mm.). Chromatographic analysis showed the composition of the distillate to be 83% I and 11% II.

Dimer I had b.p. 117–118° (760 mm.), $n^{20}D$ 1.4670, $d^{18}{}_4$ 0.7724.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.78; H, 11.20.

(For the mixture of I and II: *Anal.* Found: C, 88.54; H, 11.29.)

Isolation of I and II.—Dimers I and II were isolated by gas-liquid chromatography by using a 4-m. Apiezon-M column. The conditions were column temperature, 110°; column pressure,

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(1) G. Natta, *Makromol. Chem.*, **16**, 213 (1955); G. Natta and P. Corradini, *J. Polymer. Sci.*, **20**, 251 (1956); G. Natta, *Rubber Plastics Age*, **38**, 493 (1959); N. G. Gaylord, T.-K. Kwei, and H. F. Mark, *J. Polymer. Sci.*, **42**, 417 (1960).