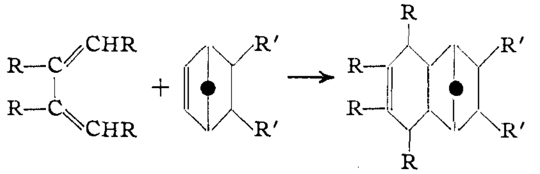
[CONTRIBUTION FROM THE BUREAU OF ANIMAL INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Synthesis of Condensed Ring Compounds. VII. The Successful Use of Ethylene in the Diels–Alder Reaction[1]

BY LLOYD M. JOSHEL AND LEWIS W. BUTZ

It has become increasingly evident during the last few years that the ability of the olefinic linkage to undergo 1,4-addition to conjugated dienes is more general than was originally supposed. It has been known for ten years that bicyclo[2,2,1]-2-heptene derivatives (I) react with 1,3-dienes to form the corresponding tricyclic derivatives (II).[2,3]

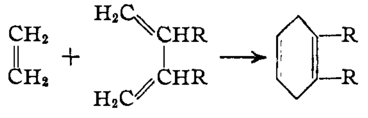


I II

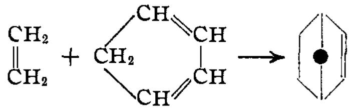
However, this was considered a special case attributable to exceptional reactivity of the double bond due to strain in the ring system; and, in general, some special structural feature, such as activation by an unsaturated group in the alpha position, was thought necessary to render a double bond capable of entering into the diene synthesis.

The formation of a hydrobiphenyl, in about 5% yield, by the addition of butadiene to the ostensibly isolated double bond in the vinyl group of 4-vinylcyclohexene[4] led Alder to investigate the reaction of dienes with olefinic bonds that were under little or no influence from activating groups. He and his co-workers found that a variety of allyl[5] and vinyl[6] derivatives readily reacted with 1,3-dienes in the usual manner. In addition, Alder and Windemuth[5] mentioned in a footnote that they had been successful in using propylene and also 1,5-hexadiene in the diene synthesis but gave no details and did not say what diene was employed.

We have found that the simplest possible olefin, namely, ethylene, readily reacts with 1,3-dienes at 200° and 200–400 atmospheres. Thus, butadiene (III) and ethylene combine to form cyclohexene (IV), and dimethylbutadiene (V) and ethylene yield the corresponding dimethylcyclohexene (VI). In a similar manner cyclopentadiene and ethylene react with the formation of bicyclo[2,2,1]-2-heptene (VII).



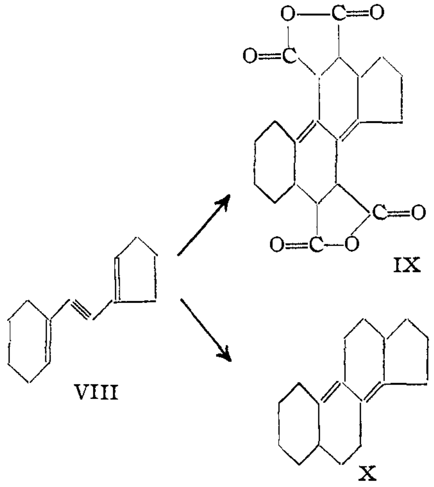
III, R = H IV, R = H
V, R = CH_3 VI, R = CH_3



VII

The yield of cyclohexene is rather low (18%) but no attempts have been made to find optimum conditions of time, temperature, and pressure. The use of an anti-polymerization agent such as acetylenedicarboxylic acid[4,7] or hydroquinone may also be useful in promoting higher yields by retarding undesirable side reactions. The yield of 1,2-dimethylcyclohexene is better (50%), and in the case of cyclopentadiene the conversion appears to be almost quantitative although only 74% was actually isolated, presumably because of the high volatility of the solid hydrocarbon product.

The application of the diene synthesis to ethylene affords a method of obtaining hydroaromatic



IX

VIII

X

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[2] Alder, Stein and Finzenhagen, *Ann.*, **485**, 223 (1931).

[3] Alder, Stein, Reese and Grassman, *ibid.*, **496**, 204 (1932).

[4] Alder and Rickert, *Ber.*, **71**, 373 (1938).

[5] Alder and Windemuth, *ibid.*, **71**, 1939 (1938).

[6] Alder and Rickert, *Ann.*, **543**, 1 (1939).

[7] Alder and Rickert, *Ber.*, **71**, 379 (1938).

compounds which are not burdened with the often unwanted activating groups. Since the dienyne VIII combines with maleic anhydride to form the steradienetetracarboxylic dianhydride IX,[8] the same dienyne may react with ethylene to give the steradiene X directly. This and other obvious extensions to the synthesis of steroids are being investigated.

Experimental

Apparatus and Technique.—An "Aminco" rocking autoclave with a 300-ml. bomb fitted with a glass liner was used. The bomb and liner were swept out with ethylene before introducing the diene. With the quantities of dienes mentioned below, there was a pressure drop of about 700 pounds per square inch after a few minutes of shaking at room temperature. The "initial" pressures given are the readings after this drop, presumably due to simple solution of ethylene in the diene.

Cyclohexene.—Forty grams of commercial butadiene was distilled from a cylinder directly into the liner. The initial pressure of ethylene was 900 lb. which rose to 4500 lb. on increasing the temperature to 200°. The pressure dropped slowly for fifteen hours and then remained constant for two hours at which point the shaking and heating were interrupted. The product was first distilled in a modified Claisen flask, collecting 18.7 g., b. p. 80–120° and 10.0 g., b. p. 120–135°. The second portion, which distilled mostly at 125–130°, is probably dimeric butadiene. The first portion was fractionated through a two foot Podbielniak column at a reflux ratio of ten to one, collecting 10.7 g. at 82.6–83.6° (758 mm.), $n^{20}\text{D}$ 1.4461, d^{20}_4 0.8097. Weighted mean literature values of these constants for cyclohexene are[9]: b. p. 83° (760 mm.), $n^{20}\text{D}$ 1.4465, d^{20}_4 0.8098. The 10.7 g. represents an 18% yield. However, this must be considered only a minimum value as an appreciable amount of butadiene was lost by evaporation while the bomb was being sealed. Another loss is encountered when the ethylene pressure is released at the end of the experiment. Some cyclohexene is undoubtedly carried off during this operation.

The nitrosochloride was prepared by dropping 0.8 ml. hydrochloric acid into a solution of 1 ml. cyclohexene, 2 ml. acetic acid, and 1.5 ml. isoamyl nitrite cooled in an ice-bath. On recrystallization from acetone, the compound formed colorless prisms, m. p. 154–155° dec., greatly dependent upon the temperature of immersion and rate of heating (lit.[10] 152–153° dec.). The m. p. was not depressed by mixing with a sample of nitrosochloride prepared in the same way from authentic cyclohexene.

1,2-Dimethylcyclohexene.—2,3-Dimethyl-1,3-butadiene was prepared by the improved procedure of Newton and Coburn[11] and the fraction b. p. 69–70° used. The diene (39 g.) was shaken with ethylene under an initial presure of 1200 lb., which rose to 6200 lb. at 200°. After shaking twenty-one hours at 190–200° the pressure ceased to drop and the treatment was stopped. The product was fractionated through a two-foot Podbielniak column at a ten to one reflux ratio and the dimethylcyclohexene (26.1 g., 50%) collected at 137.6–138.8° (760 mm.) (23.8 g. at 137.6–138.2°); $n^{20}\text{D}$ 1.4612, d^{20}_4 0.8235. The accepted literature values for these constants are[12]: b. p. 136° (760 mm.), $n^{20}\text{D}$ 1.4564–1.460, d^{20}_4 0.8232.

A solution of 149 mg. of the hydrocarbon in 10 ml. of acetic acid rapidly absorbed 1.31 millimoles of hydrogen when reduced in the presence of 50 mg. of Adams catalyst. This corresponds to an equivalent weight of 114; calcd. for C_8H_{14}, 110.

Bicyclo[2,2,1]-2-heptene.—Technical dicyclopentadiene was cracked by slow distillation through a column, the cyclopentadiene redistilled and the fraction b. p. 40–42° used immediately. Thirty-three grams of diene was shaken with ethylene at 190–200° for twenty-three hours. The initial pressure of 1300 lb. had risen to 5800 lb. and then slowly dropped, the pressure becoming constant several hours before the time mentioned. After cooling, the bomb was opened and the solid crystalline mass melted and distilled. The product distilled at 94–97°, over 90% at 95–96°, with no forerun and very little residue; yield 35 g., 74%. The hydrocarbon immediately crystallized in the receiver and the middle fraction melted at 44–46°, unchanged after vacuum sublimation. Since the m. p. of this hydrocarbon has been variously reported as 52–54°,[13] 51–53°,[13] and 50–52°,[6] the material was analyzed.

Anal. Calcd. for C_7H_{10}: C, 89.3; H, 10.7. Found: C, 89.1; H, 10.7.

Summary

Under suitable temperatures and pressures, ethylene reacts with 1,3-dienes in the usual Diels–Alder manner. In this way cyclohexene, 1,2-dimethylcyclohexene, and bicyclo[2,2,1]-2-heptene have been synthesized from 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, and cyclopentadiene, respectively.

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[8] Butz and Joshel, THIS JOURNAL, **63**, 3344 (1941).

[9] Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corporation, New York, N. Y., 1940, Vol. II, p. 324.

[10] Baeyer, *Ann.*, **278**, 108 (1894).

[11] Fieser, "Experiments in Organic Chemistry," 2nd ed. D. C. Heath and Company, Boston, Mass., 1941, p. 383.

[12] Ref. 9, p. 330.

[13] Komppa and Beckmann, *Ann.*, **512**, 184 (1934).