[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Fused Ring Systems from Dieneynes. VI.[1] Some Limitations of the Cyclization Reaction

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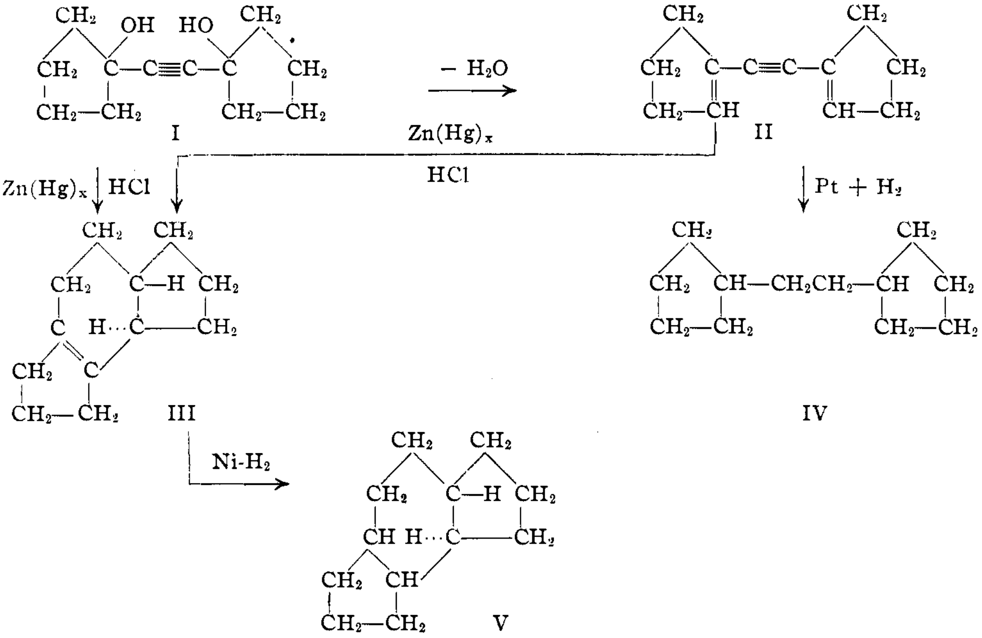
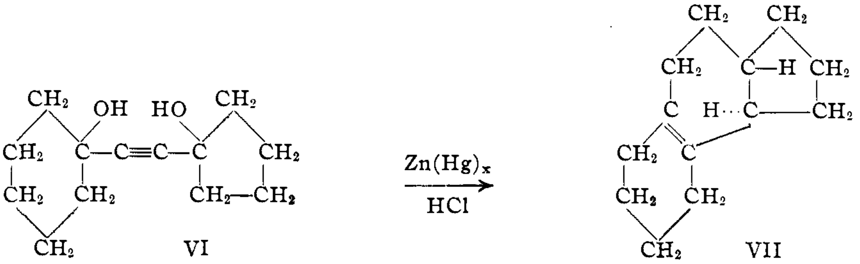
An attempt to synthesize reduced rings of the indacene, chrysene and picene types by cyclization of the appropriate dieneynes has shown that there are certain limitations to this reaction. Some of these limitations are due to difficulties in obtaining the necessary acetylenic glycols and others are due to the failure of certain dieneynes to cyclize.



It has been found possible to condense acetylenedimagnesium bromide with cyclopentanone to yield 1,1′-ethynylenebiscyclopentanol (I) and to dehydrate this glycol to di-Δ^1-cyclopentenylacetylene (II). Attempts to cyclize this dieneyne to a ketone with the usual acid reagents gave only tarry polymerization products. However, a product which seemed to be decahydroindacene (III) was obtained by treating either the glycol (I) or the dieneyne (II) with zinc amalgam and hydrochloric acid to effect reduction of the carbonyl group during the reaction. This direct method of going from the acetylenic glycol to the cyclic hydrocarbon also was applied successfully to the conversion of 1,1′-ethynylenecyclohexanolcyclopentanol (VI) to octahydro-α-naphthindan (VII) which had been accomplished previously through several intermediate steps.[3]



The octahydro-α-naphthindan (VII) prepared by the Clemmensen reduction of the glycol was identical with the product obtained in the previous work, and this established the fact that ring closure actually had occurred in this treatment of the acetylenic glycols. Also reduction of the

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(1) For the fifth paper in this series see Pinkney, Nesty, Pearson and Marvel, THIS JOURNAL, 59, 2666 (1937).

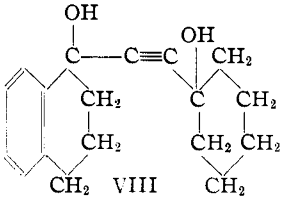
(2) Chemical Foundation Fellow in Organic Chemistry.

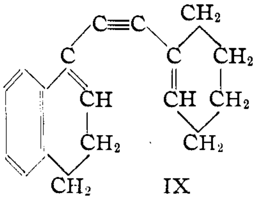
(3) Pinkney, Nesty, Wiley and Marvel, THIS JOURNAL, 58, 972 (1936).

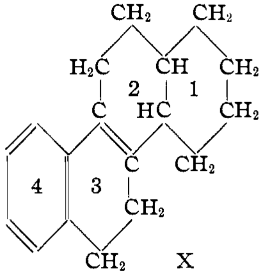
decahydroindacene (III) gave dodecahydroindacene (V) which was entirely different in properties from the 1,2-dicyclopentylethane (IV) which was prepared by reduction of di-Δ^1-cyclopentenylacetylene.

Attempts to produce 1-ethynylcyclopentanol from cyclopentanone and acetylene with various condensing agents did not give satisfactory results. A small amount of the acetylenic alcohol was obtained as a by-product in making the glycol (I) but not enough of the alcohol could be obtained to use it in other reactions.

α-Tetralone was condensed with 1-ethynylcyclohexanol-1 to give the unsymmetrical glycol (VIII) which in turn was successfully dehydrated to the dieneyne (IX). This product was cyclized but the yields were very low and the decahydrochrysene (X) was of doubtful purity.

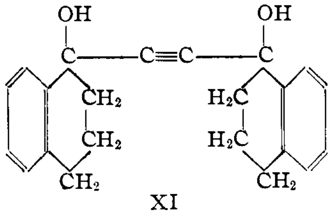

VIII

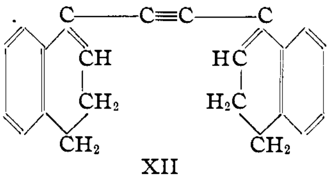

IX


X

The exact structure of the cyclized product is unknown as the double bond may be common to rings 1 and 2 or, as indicated, common to rings 2 and 3. Dehydrogenation of the cyclic hydrocarbon (X) did not give a crystalline product.

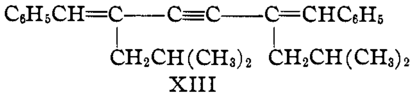
When an attempt was made to prepare the acetylenic glycol (XI) by the condensation of α-tetralone with acetylenedimagnesium bromide, the only product isolated was the dehydration product (XII) of the glycol.


XI


XII

Attempts to cyclize this hydrocarbon were unsuccessful and only amorphous powdery products resulted from such reactions.

Benzyl isobutyl ketone was converted to the corresponding acetylenic glycol which was dehydrated to the dieneyne (XIII).



$$C_6H_5CH{=}\underset{CH_2CH(CH_3)_2}{C}{-}C{\equiv}C{-}\underset{CH_2CH(CH_3)_2}{C}{=}CHC_6H_5$$

XIII

Attempts to cyclize this dieneyne were unsuccessful. In this case the unsaturated hydrocarbon was recovered almost unchanged. A small amount of a volatile bluish substance was formed in the reaction, but several redistillations of the recovered ketone removed this colored product. The blue color was probably due to the formation of a halochromic salt of the unsaturated ketone formed by hydration of the triple bond in a small portion of the dieneyne.[4]

The work which has been carried out thus far on the cyclization of various dieneynes makes it possible to set certain limitations on this method for preparing polynuclear compounds.

1. At least one of the carbon atoms at one end of the dieneyne system must carry a hydrogen atom.
2. The dieneyne must carry enough substituents so that polymerization does not become the principal reaction when cyclization is attempted. In this connection it is significant that the derivatives of cyclopentane described in this paper polymerize more readily than either the cyclohexane or the mixed cyclopentane–cyclohexane derivatives described previously.[3]
3. In order for the cyclization reaction to proceed to give a cyclic ketone, neither of the double bonds in the dieneyne system may be a part of an aromatic system of double bonds.
4. Cyclization can be accomplished when one of the double bonds is conjugated with an aromatic ring but apparently cannot be accomplished when both of the double bonds are so conjugated.

Experimental

1,1′-Ethynylenebiscyclopentanol.—A solution of 168 g. of cyclopentanone in 350 cc. of dry ether was added over a

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[4] Conant and Cutter, This Journal, **48**, 1016 (1926).

period of two hours to a cold, well-stirred solution of acetylenedimagnesium bromide prepared from 50 g. of magnesium, 218 g. of ethyl bromide, 1500 cc. of dry ether and acetylene. On working up the reaction mixture in the usual way,[3] 149 g. (77%) of the acetylenic glycol was obtained. A sample purified by treatment with decolorizing carbon in an alcohol solution and then recrystallization from petroleum ether melted at 107–108°.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.20; H, 9.34. Found: C, 74.43; H, 9.42.

The steam distillate obtained in purifying the glycol was extracted with ether and the ether solution was distilled. In this way there was obtained 3 g. of 1-ethynylcyclopentanol; b. p. 65–65.5° at 16 mm.; m. p. 20°; n^{20}_D 1.4741; d^{20}_4 0.9746.

Anal. Calcd. for $C_7H_{10}O$: C, 76.30; H, 9.15. Found: C, 76.32; H, 9.10.

In one experiment acetylenedimagnesium iodide was used in place of the bromide. In this case the yield of glycol dropped to 42% and a considerable amount of cyclopentylidenecyclopentanone was formed.

Di-Δ^1-cyclopentenylacetylene.—A mixture of 36 g. of the above glycol and 5 g. of potassium bisulfate was heated in a Claisen flask mounted in an oil-bath at 200–205° for ten minutes. The water was then distilled from the reaction mixture under 17 mm. pressure and the hydrocarbon under 2 mm. pressure. The hydrocarbon, b. p. 105–110° at 2 mm., crystallized in the receiver. The yield was 22 g. (71%). Recrystallization of the distillate from alcohol and acetone gave a white product melting at 58.5–60°. The crystals gradually turned yellow from standing in the air and eventually changed into a brownish tar.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.07; H, 8.93. Found: C, 89.75; H, 8.64.

1,2-Dicyclopentylethane.—To a solution of 8 g. of the dieneyne in 125 cc. of alcohol was added 0.15 g. of platinum oxide[5] and the solution was hydrogenated under a pressure of about 45 pounds (3 atm.). Reduction was complete in fifteen minutes. The product was isolated by distillation and purified by distilling from sodium. Its physical properties were: b. p. 109–110° at 17 mm.; n^{20}_D 1.4657; d^{20}_4 0.8633.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.72; H, 13.22.

1,2,3,3a,4,5,6,7,8,8b-Decahydro-*as*-indacene.—Treatment of either the acetylenic glycol or the dieneyne with sulfuric and acetic acids or formic acid did not produce a cyclic product but gave only polymeric tars.

A mixture of 30 g. of the acetylenic glycol and 75 g. of zinc amalgam with about 100 cc. of concentrated hydrochloric acid was heated under a reflux condenser for three days. More acid was added as needed to maintain a steady evolution of hydrogen. The reaction product was collected in ether, washed with sodium carbonate solution, dried and distilled. A considerable amount of dieneyne was obtained but in addition 0.7 g. of a new hydrocarbon was isolated. This product after boiling with sodium had the following physical properties: b. p. 107–108° at 17 mm.; n^{20}_D 1.4990; d^{20}_4 0.9397.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.84; H, 11.16. Found: C, 88.28; H, 10.57.

In a similar manner 22 g. of the dieneyne was treated with zinc amalgam and hydrochloric acid to give 1.1 g. of decahydro-*as*-indacene; b. p. 112–113° at 18 mm.

3a,4,4a,6,7,8,9,9b-Octahydro-α-naphthindan.—From 20 g. of 1,1′-ethynylcyclohexanolcyclopentanol, zinc amalgam, and hydrochloric acid there was isolated 0.5 g. of octahydro-α-naphthindan which was identical with the product previously prepared by the cyclization of the glycol to an unsaturated ketone followed by a Clemmensen reduction.[3]

Dodecahydro-*as*-indacene.—A solution of 1.5 g. of the decahydro-*as*-indacene in 60 cc. of methylcyclohexane[6] was shaken with hydrogen at 175° and 2200–2500 pounds (149–170 atm.) pressure for eight hours in the presence of 10 g. of Raney nickel catalyst.[7] On working up this reaction mixture there was obtained 0.6 g. of a product; b. p. 106–108° at 18 mm.; n^{20}_D 1.4840; d^{20}_4 0.9145.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.72; H, 12.28. Found: C, 87.04, 87.00; H, 12.80, 12.84.

1,1′-Ethynylenetetrahydronaphtholcyclohexanol.[8]—Using the general methods previously described,[3] 6.2 g. of 1-ethynylcyclohexanol and 7.4 g. of α-tetralone were converted into 3 g. of a crystalline glycol which melted at 85–95° when purified from petroleum ether. The crystals were not stable in air and gradually turned to tarry products.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 80.00; H, 8.15. Found: C, 79.67; H, 8.30.

Δ^1-Cyclohexenyl-α-3,4-dihydronaphthylacetylene.—Forty-five grams of crude glycol prepared by the general method indicated above was dehydrated by heating with 10 g. of potassium bisulfate at 200–205° for ten minutes. Water was distilled under 17 mm. and the hydrocarbon under 2 mm. The yield was 16 g. of product; b. p. 170–172° at 2 mm.; n^{20}_D 1.6186; d^{20}_4 1.0443.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.58; H, 7.42. Found: C, 91.12; H, 7.64.

1,2,2a,3,4,5,6,6a,7,8-Decahydrochrysene.—No method of converting the above dieneyne to a cyclic ketone proved successful and only tarry products resulted from the usual treatments with acidic reagents. Clemmensen reduction of 17 g. of the hydrocarbon for four days gave 0.5 g. of a clear yellow liquid boiling at 140–144° at 1.5 mm.; n^{20}_D 1.5672; d^{20}_4 1.0249.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.69; H, 9.31. Found: C, 88.99, 89.11; H, 9.49, 9.85.

Attempts to dehydrogenate this material by heating with selenium at 340–350° gave no crystalline products. Peak and Robinson[9] were successful in converting their mixed decahydrochrysenes to crystalline chrysene by such a treatment.

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(5) Adams, Voorhees and Shriner, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 452.

(6) The authors take this opportunity to express their thanks of the Hooker Electro-Chemical Company for a generous supply to methylcyclohexane.

(7) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

(8) This experiment was performed by Mr. R. H. Wiley.

(9) Peak and Robinson, *J. Chem. Soc.*, 759 (1936).

1,1′-Ethynylene-bis-3,4-dihydronaphthalene.—Treatment of the acetylenedimagnesium bromide prepared from 15.3 g. of magnesium, 65.5 g. of ethyl bromide and acetylene in 350 cc. of ether with 86 g. of α-tetralone in 150 cc. of ether gave 22 g. of a crude product which after crystallization from benzene melted at 120–121°. Analysis indicated that it was not the expected glycol but its dehydration product.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.58; H, 6.42. Found: C, 93.68; H, 6.53.

Attempts to cyclize this product with the usual reagents gave amorphous products.

1,6-Diphenyl-2,5-diisobutyl-1,5-hexadiene-3-yne.—Eighty-eight grams of benzyl isobutyl ketone was treated with acetylenedimagnesium bromide in the usual fashion to give 29 g. of a crude glycol which was not purified but was dehydrated directly by heating with potassium bisulfate. There was thus obtained 19 g. of the expected dieneyne; b. p. 160–190° at 2 mm. Redistillation gave a viscous product; b. p. 179–180° at 2 mm.; $n^{20}D$ 1.5872; $d^{20}{}_4$ 0.9951.

Anal. Calcd. for $C_{26}H_{30}$: C, 91.17; H, 8.83. Found: C, 90.28; H, 8.93.

Attempts to cyclize this dieneyne by treatment with sulfuric and acetic acids or formic acid were unsuccessful. Most of the dieneyne was recovered, but it was contaminated with a bluish, volatile product which was destroyed gradually by several distillations.

Summary

1. Di-Δ^1-cyclopentenylacetylene could not be cyclized directly to a decahydroketoindacene but by cyclization in a reducing mixture some of the corresponding cyclic hydrocarbon was obtained.

2. Attempts to obtain decahydrochrysene from the condensation product of α-tetralone and 1-ethynylcyclohexanol-1 led to compounds of doubtful structures.

3. Some limitations to this method of preparing polynuclear compounds have been described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

The Ionization Constant of Lactic Acid, 0–50°, from Conductance Measurements

BY A. W. MARTIN AND H. V. TARTAR

To test the results of a preliminary study made in this Laboratory on the ionization constant of lactic acid, it seemed advisable to determine this important constant from conductance measurements. Because of the importance of lactic acid in biochemical reactions an accurate knowledge of its physicochemical constants is of considerable significance. Before the completion of this investigation Nims and Smith[1] reported results on the ionization constant of lactic acid, 0–50°, from electromotive force measurements.

Results of the present investigation are from conductance measurements. The method used was, with certain minor changes, essentially the procedure used by MacInnes and Shedlovsky[2] in the determination of the ionization constant of acetic acid combined with the procedure of these same workers[3] in extending conductance measurements, in the determination of the ionization constant of carbonic acid, to a range of temperature.

Apparatus.—It was necessary in this investigation to use different conductance assemblies. Both a Leeds and Northrup conductivity bridge[4] and a conductivity bridge constructed according to specifications given by Jones and Josephs[5] were used. It was possible, however, by using the same conductance cell and a temperature of 25° to compare resistance measurements of the bridges. Comparison of the bridges was within the limits of accuracy with which measurements could be carried out using a single assembly. The conductance cell, used with nitrogen, was similar in design to a cell described by Shedlovsky.[6] Because of the magnified effects of adsorption at very dilute concentrations it was desirable to limit platinization to the minimum value allowed by polarization. For measurements included in this investigation the electrodes of the conductance cell were given a light gray coating of platinum using the procedure suggested by Jones and Bollinger.[7] The cell constant at 25° was of the order of 0.37252. The oscillators were similar to one described by Jones and Josephs.[5] A two-stage vacuum tube amplifier was used. The oil thermostat varied by not more than 0.005° from the temperature established by a thermometer certified by the Bureau of Standards.

Materials.—All solutions were made by weight using weights which had been calibrated and compared with a set certified by the Bureau of Standards. The hydrochloric acid used for standardization of sodium or potassium hydroxide was a carefully prepared constant boiling mixture using the data of Foulk and Hollingsworth.[8] Conductivity water, from a special still, not exceeding a specific conductance of 4.0×10^{-7} was used in the prepara-

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[1] Nims and Smith, *J. Biol. Chem.*, **113**, 145 (1936).

[2] MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932).

[3] Shedlovsky and MacInnes, *ibid.*, **57**, 1705 (1935).

[4] Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[5] Jones and Josephs, THIS JOURNAL, **50**, 1049 (1928).

[6] Shedlovsky, *ibid.*, **54**, 1411 (1932).

[7] Jones and Bollinger, *ibid.*, **53**, 411 (1931).

[8] Foulk and Hollingsworth, *ibid.*, **45**, 1220 (1923).