A study has also been made of the alkali lignin of the same straw. Cold alkali treatment removed less lignin than hot alkali. The sum total of the lignin extracted by cold alkali and that left in the residue was practically the same as the lignin obtained by acid treatment alone; the same was true of the methoxyl recovery. Hot alkali treatment reduced both the recovery of the lignin as a whole and of the methoxyl as well.

Preliminary treatment of the straw with dilute acid reduced the lignin yield. This was possibly due to the destruction of some hemicelluloses which would otherwise remain with the acid lignin residue. This interfering effect of hemicelluloses upon the yield of acid lignin has long been recognized, and pretreatment with dilute acid in the determination of lignin in plant materials has been utilized in the standard methods of analysis.

These results lead to the conclusion that the hypothesis proposed by Hilpert, that lignin does not exist in plant materials but is a result of the action of the acid upon certain carbohydrates, has no foundation. One cannot, of course, deny the fact, long recognized, however, by every investigator of lignin, that the present methods of lignin extraction and lignin determination modify considerably its chemical nature.

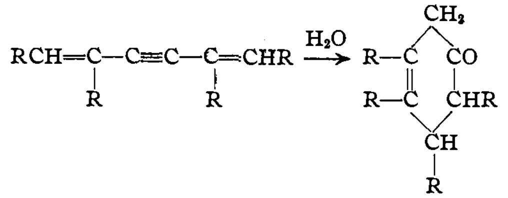
New Brunswick, N. J. Received March 21, 1936

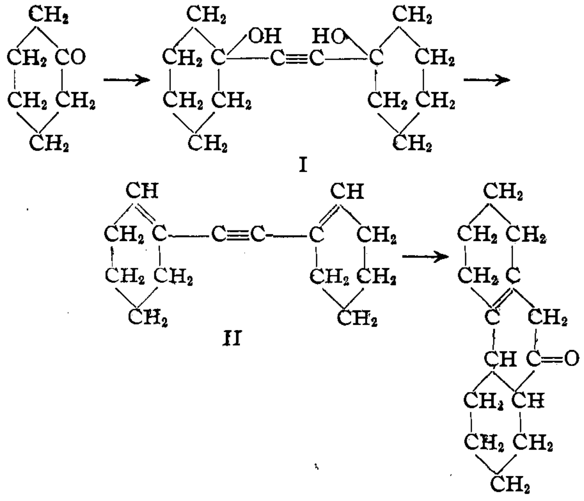
[Contribution from the Chemical Laboratory of the University of Illinois]

Hydrophenanthrenes and Related Ring Systems from Dieneynes[1]

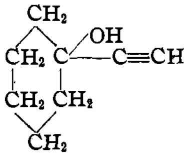
By P. S. Pinkney,[2] G. A. Nesty,[2] R. H. Wiley and C. S. Marvel

Previous work in this Laboratory has shown that a tetrasubstituted open-chain dieneyne can be hydrated and cyclized by the action of sulfuric acid in acetic acid. This reaction seemed to offer a novel method for the production of Δ^{11}-dodecahydrophenanthrone-9 (III) from cyclohexanone and acetylene through the preceding series of reactions.

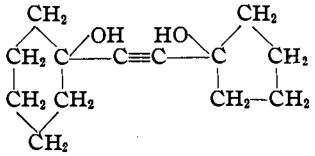




The acetylenic glycol has been prepared by DuPont[3] by treating the dimagnesium halide of acetylene with cyclohexanone. The yields by this procedure are only about 35–37%, and a better method of preparation was sought. Gould and Thompson[4] found that potassium tertiary butylate was a good catalyst for condensing acetylene with β-ionone, and this method was tried on cyclohexanone. This gave an excellent yield (81%) of 1-ethynylcyclohexanol (IV), but the method could not be adapted to making the glycol in one operation. By treating this acetylenic alcohol with an excess of ethylmagnesium bromide, and then with cyclohexanone, the glycol could be obtained in 48% yields, but this is not a practical procedure, as the over-all yield is lower than can be obtained by the DuPont method.[3] A mixed acetylenic glycol (V) having one cyclohexane and one cyclopentane ring was prepared by condensing 1-ethynylcyclohexanol with cyclopentanone.



IV



V

---

[1] This is the third paper on cyclization of dieneynes. For previous papers, see This Journal, **55**, 1655, 4276 (1933).

[2] Chemical Foundation Fellow in Organic Chemistry.

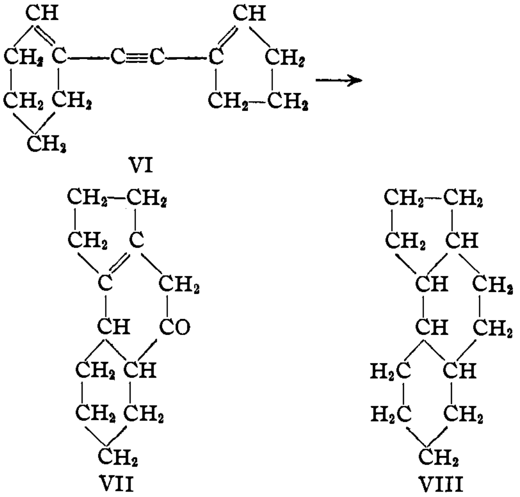
[3] DuPont, *Ann. chim.*, [8] **30**, 485 (1913).

[4] Gould and Thompson, This Journal, **57**, 340 (1935).

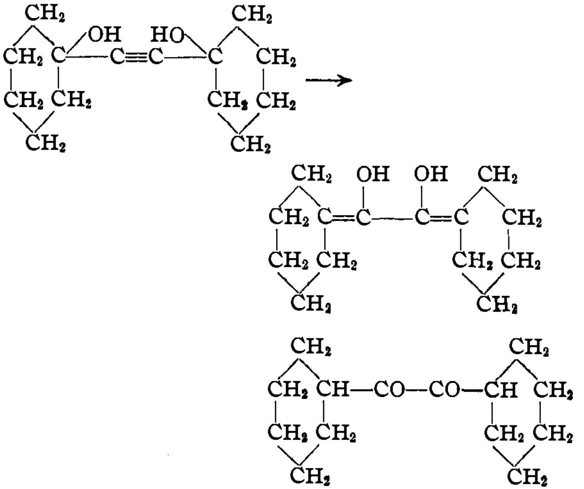
The dieneyne (II) was prepared by dehydrating the glycol (I) with 40% sulfuric acid, a reagent which DuPont[3] has used successfully on other acetylenic glycols. Cyclization of the dieneyne (II) was first accomplished by the method used in previous work in this Laboratory.[1] However, a better yield was obtained by using 85% formic acid in place of the sulfuric–acetic acid mixtures which had been used in earlier work. The Δ^{11}-dodecahydrophenanthrone-9 (III) thus obtained was a liquid. It was reduced by the Clemmensen method[5] to dodecahydrophenanthrene which agreed closely in properties with those reported by Schmidt[6] for a dodecahydrophenanthrene obtained by the reduction of phenanthrene with phosphorus and iodine. Moreover, our dodecahydrophenanthrene could be reduced with hydrogen over Raney nickel catalyst[7] to give a perhydrophenanthrene which agreed in properties with those reported for perhydrophenanthrene by Ipatiew, Jakowlew and Rakitin[8] and also with a sample which we prepared by the reduction of phenanthrene with hydrogen over Raney nickel. For comparison, the dieneyne was reduced to dicyclohexylethane. This hydrocarbon had quite different properties. From the highest boiling fraction of our cyclized ketone a small amount of crystalline substance was isolated. Its composition showed it to be isomeric with the Δ^{11}-dodecahydrophenanthrone-9. Its melting point was close to that reported for Δ^{10}-dodecahydrophenanthrone-9 by Rapeson and Robinson.[9] However, our product depressed the melting point of a sample of ketone prepared by this method. The 2,4-dinitrophenylhydrazones also failed to agree in properties. As yet the structure of our solid ketone has not been definitely determined.

The mixed glycol (V) was also dehydrated to the corresponding dieneyne (VI) and cyclized to the unsaturated ketone (VII).

The exact structure of this ketone was not established; the ketone group may be adjacent to the cyclopentane ring with the double bond in the cyclohexane ring. The dieneyne (VI) was reduced to cyclohexylcyclopentylethane and the ketone was also reduced stepwise to the perhydrocyclopentanonaphthalene (VIII).


VI
VII
VIII

Since the acetylenic glycols were dehydrated with sulfuric acid and the dieneynes were then hydrated with the same reagent, it occurred to us that these two reactions might be combined into one operation. The desired cyclic ketones can thus be obtained, but there are more side reactions, and it is necessary to spend more time in purifying the products than if the two operations of dehydration and hydration are carried out separately. When the acetylenic glycol from cyclohexanone was dehydrated and hydrated in one operation, there was produced not only the desired dodecahydrophenanthrone, but also dodecahydrobenzil (IX). It is interesting to note that this product is one that would be expected if a double Meyer and Schuster[10] rearrangement of the glycol occurred.


IX

When formic acid was used to dehydrate and hydrate the glycol in one operation, the expected ketone was found, and along with it the ketodi-

---

(5) Clemmensen, *Ber.*, **46**, 1837 (1913).
(6) Schmidt, *ibid.*, **40**, 4240 (1907).
(7) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).
(8) Ipatiew, Jakowlew and Rakitin, *Ber.*, **41**, 996 (1908).
(9) Rapeson and Robinson, *J. Chem. Soc.*, 1285 (1935).
(10) Meyer and Schuster, *Ber.*, **55**, 819 (1922).

hydrofuran derivative which DuPont[3] obtained by the action of mercuric sulfate solution on the glycol.

The reactions reported here seem to offer a new approach to phenanthrene derivatives, and extensions of these experiments are under way.

Experimental Part

1-Ethynylcyclohexanol.—A solution of 49 g. of cyclohexanone in 200 cc. of anhydrous ether and a solution of 20 g. of potassium in 240 cc. of anhydrous *t*-amyl alcohol were added to a saturated solution of acetylene in 200 cc. of ether at −15° over a period of two hours. The reaction mixture was decomposed with ammonium chloride solution, and the ether layer was separated and distilled. The yield of 1-ethynylcyclohexanol boiling at 83–84° (25 mm.) was 50 g. (81%); n^{20}_{D} 1.4812 (on supercooled liquid); m. p. 31–32° after crystallization from low-boiling petroleum ether.

Anal. Calcd. for $C_8H_{12}O$: C, 77.36; H, 9.75. Found: C, 77.34; H, 9.85.

The mercury derivative of this acetylenic carbinol was prepared by the method of Johnson and McEwen.[11] After recrystallization from alcohol, this product melted at 175.5–176.5°.

Anal. Calcd. for $C_{16}H_{20}O_2Hg$: Hg, 44.84. Found: Hg, 43.20.

1,1′-Ethynylene-bis-cyclohexanol (I).—The method of DuPont[3] was used for this preparation. It was found advisable to use hydrochloric acid rather than sulfuric acid in decomposing the Grignard reaction mixture, and also to steam distil the mixture to remove unchanged cyclohexanone and 1-ethynylcyclohexanol from the glycol. The glycol was crystallized either from carbon tetrachloride or high-boiling petroleum ether, and melted at 109–110°. Rupe, Messner and Kambli[12] report this same melting point, whereas Carothers and Coffman[13] report 106–107°, and DuPont[3] and Iotsitch[14] report 102° as the melting point. Our yields of crystallized glycol were 35–37% of the theoretical.

This glycol was also obtained from 1-ethynylcyclohexanol. A solution of 6.2 g. of the acetylenic alcohol in 20 cc. of dry ether was added to a solution of 0.1 mol of ethylmagnesium bromide in 70 cc. of dry ether. The mixture was kept cold during the addition, and then later warmed for a few hours. Then 4.8 g. of cyclohexanone in 20 cc. of ether was added, and the mixture was heated for about six hours. The product was isolated as in the previous preparation. The yield was 5.2 g. (48% of the theoretical).

1,1′-Ethynylenecyclohexanolcyclopentanol (V).—This mixed glycol was prepared by treating 6.2 g. of 1-ethynylcyclohexanol with 0.1 mol of ethylmagnesium bromide in ether and then adding 4.2 g. of cyclopentanone. The reaction mixture was worked up as in the preceding experiments. The yield was 5.5–6.5 g. (53–62% of the theoretical) of a product of m. p. 93–94°.

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 75.00; H, 9.62. Found: C, 74.40; H, 9.80.

Dehydration of the Acetylenic Glycols to the Dieneynes.—The glycols were dehydrated by refluxing for two to three hours with 40% sulfuric acid.[1,3] The dieneynes were obtained in 80–90% yields as colorless liquids which soon became yellow on exposure to air.

The symmetrical product (II) had the following properties: b. p. 126–128° (3 mm.); n^{20}_{D} 1.5520; d^{20}_{4} 0.9934.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.36; H, 9.64. Found: C, 89.80; H, 9.18.

The unsymmetrical product (VI) had the following properties: b. p. 103–104° (2.5 mm.); n^{20}_{D} 1.5582; d^{20}_{4} 0.9610.

Anal. Calcd. for $C_{13}H_{16}$: C, 90.70; H, 9.30. Found: C, 88.60, 88.69; H, 9.32, 9.30.

DuPont[3] observed that carbon values were usually low in the analysis of related dieneynes.

1,2-Dicyclohexylethane.—A solution of 10 g. of the symmetrical dieneyne in 60 cc. of methylcyclohexane[15] was heated, with shaking, with 15 g. of Raney nickel catalyst[7] in a steel bomb at 250° for eight hours under a hydrogen pressure of 1500–2000 pounds per square inch. The solution was filtered and distilled. After removal of the solvent, the remaining hydrocarbon was fractionated twice, boiled with sodium, and again distilled. The yield of final product was 6 g. of 1,2-dicyclohexylethane, b. p. 93–94° (2 mm.); n^{20}_{D} 1.4765; d^{20}_{4} 0.8795. These physical constants check well with those reported by Sabatier and Murat.[16]

Anal. Calcd. for $C_{14}H_{26}$: C, 86.51; H, 13.49. Found: C, 86.47; H, 13.48.

1-Cyclohexyl-2-cyclopentylethane.—This was obtained in 4 g. yield by reducing 5.5 g. of the unsymmetrical dieneyne with hydrogen, as described in the preceding experiment, b. p. 74–76° (2 mm.); n^{20}_{D} 1.4723; d^{20}_{4} 0.8746.

Anal. Calcd. for $C_{13}H_{24}$: C, 86.63; H, 13.37. Found: C, 86.65; H, 13.62.

Δ^{11}-Dodecahydrophenanthrone-9.—1,2-Dicyclohexenylacetylene was cyclized by treating 60 g. with 125 cc. of concentrated sulfuric acid in 250 cc. of glacial acetic acid for a period of three to four hours, according to the general procedure previously used for this type of reaction.[1] The yield of cyclic ketone was 33–40 g. (50–60% of the theoretical). An alternate method used was to heat the dieneyne with ten times its weight of 85% formic acid for two to three hours. The yields by this procedure were 65% of the theoretical. The product boiled at 130–132° (2 mm.); n^{20}_{D} 1.5315; d^{20}_{4} 1.041.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.29; H, 9.87. Found: C, 82.10; H, 10.05.

The 2,4-dinitrophenylhydrazone was prepared by the method of Allen,[17] and after crystallization from ethyl acetate, was obtained as bright red crystals, melting at 227–228°.

---

(11) Johnson and McEwen, This Journal, **48**, 469 (1926).

(12) Rupe, Messner and Kambli, *Helv. Chim. Acta*, **11**, 449 (1928).

(13) Carothers and Coffman, This Journal, **54**, 4071 (1932).

(14) Iotsitch, *J. Russ. Phys.-Chem. Soc.*, **38**, 656 (1906).

(15) Most of the methylcyclohexane used in this work was furnished to us by the Hooker Electrochemical Company. The authors take this opportunity to express their thanks to this Company for their aid in this problem.

(16) Sabatier and Murat, *Compt. rend.*, **154**, 1771 (1912).

(17) Allen, This Journal, **52**, 2955 (1930).

Anal. Calcd. for $C_{20}H_{26}O_4N_4$: N, 14.51. Found: N, 14.57.

From one sample of the cyclic ketone by careful fractional distillation, followed by crystallization of the highest boiling fraction from methyl alcohol at dry ice–acetone temperatures, a small amount of a solid ketone, m. p. 93–94°, was obtained.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.29; H, 9.87. Found: C, 82.22; H, 9.80.

This product gave a red 2,4-dinitrophenylhydrazone which melted at 186–187° after recrystallization from alcohol.

Anal. Calcd. for $C_{20}H_{28}O_4N_4$: N, 14.51. Found: N, 13.68.

Δ^{10}-Dodecahydrophenanthrone-9.—A sample of this ketone prepared in 17% yield by the method of Rapeson and Robinson[9] melted at 88.5–90°. A mixture of this ketone and our solid ketone melted at 65–77°.

Robinson's ketone gave a red 2,4-dinitrophenylhydrazone which, after crystallization from ethyl acetate, melted at 226–227°.

Anal. Calcd. for $C_{20}H_{26}O_4N_4$: N, 14.51. Found: N, 14.60.

The melting point of a mixture of this derivative with the 2,4-dinitrophenylhydrazone of Δ^{11}-dodecahydrophenanthrone-9 was found to be 193–213°, showing that these were isomeric and not identical products.

3-Keto-1,2,3,4,5,6,7,8-octahydro-1,2-cyclopentanonaphthalene.—This ketone was prepared from 1-cyclohexenyl-2-cyclopentenylacetylene in yields of 20–30% by the same procedure used above. It is a colorless liquid, b. p. 114–116° (2.5 mm.); n^{20}_D 1.5315; d^{20}_4 1.055.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.99; H, 9.52.

The 2,4-dinitrophenylhydrazone was prepared, and after recrystallization from ethyl acetate was obtained in dark red crystals, m. p. 221–222°.

Anal. Calcd. for $C_{19}H_{24}O_4N_4$: N, 15.13. Found: N, 15.22.

Considerable tar formation occurred in the cyclization of this unsymmetrical dieneyne.

Ozonization of the Ketooctahydrocyclopentanonaphthalene.—A solution of 5 g. of the above ketone in 85 cc. of glacial acetic acid was treated with a current of ozonized oxygen for about eleven hours. The reaction mixture was decomposed with water, and the acetic acid and water were removed under reduced pressure. The residual oil was distilled under reduced pressure. About 3 g. of the ketone was recovered unchanged. From the fraction boiling at 160–190° (2 mm.), 0.25 g. of adipic acid, m. p. 149.5–150.5°, was obtained. Neut. equiv. Calcd. for adipic acid: 73.0. Found: 72.6. No other oxidation products could be isolated.

Direct Conversion of 1,1'-Ethynylene-bis-cyclohexanol to the Cyclic Ketone.—A mixture of 55.5 g. of the symmetrical acetylenic glycol with 40 cc. of glacial acetic acid was added to a cooled solution of 85 cc. of concentrated sulfuric acid in 160 cc. of glacial acetic acid over a period of twenty minutes. Stirring was continued at room temperature for about twenty-four hours. The black reaction mixture was poured into cracked ice and extracted with benzene. The benzene solution was washed thoroughly with water, sodium carbonate solution, and then water again. After distillation of the benzene, the residue was carefully fractionated. There was about 2 g. of low-boiling material which was identified as dodecahydrobenzil, b. p. 117–119° (2 mm.); n^{20}_D 1.4795 (on supercooled liquid), m. p. 38–39° after crystallization from alcohol.[18]

The mono-3,4-dinitrophenylhydrazone, after crystallization from alcohol, was obtained as bright yellow crystals, melting at 120–121°.

Anal. Calcd. for $C_{20}H_{26}O_5N_4$: N, 13.92. Found: N, 13.50.

The main fraction obtained in the distillation was the desired cyclic ketone. The yield was 20 g. (39% of the theoretical).

In a second attempt to go directly from the acetylenic glycol to the cyclic ketone, 20 g. of the glycol was refluxed for two hours in 200 cc. of 85% formic acid solution. Then most of the solvent was removed under reduced pressure, the residue was taken up in benzene and all the formic acid was removed by washing with water and sodium carbonate solution. Distillation gave 2 g. of a low-boiling product and 5 g. (27% of the theoretical) of the desired cyclic ketone.

The low-boiling product distilled at 110–120° (2 mm.). It gave a 2,4-dinitrophenylhydrazone which, after crystallization from alcohol, was obtained as beautiful orange-yellow needles, m. p. 162–162.5°.

Anal. Calcd. for $C_{20}H_{26}O_5N_4$: N, 13.92. Found: N, 13.48.

This product was shown to be identical with the 2,4-dinitrophenylhydrazone of 2,5-dicyclopentamethylene-3-ketohydrofuran prepared by the method of DuPont.[3]

The unsymmetrical glycol (V) was treated with sulfuric and acetic acid and with formic acid by the procedures described above. Ketooctahydrocyclopentanonaphthalene was obtained in 20% yield in each case. No isomeric ketones were isolated.

Δ^{11}-Dodecahydrophenanthrene.—A mixture of 20 g. of Δ^{11}-dodecahydrophenanthrone-9, 130 g. of zinc amalgam and 50 cc. of hydrochloric acid (1 part water and 1 part hydrochloric acid, sp. gr. 1.19) was refluxed for about thirty-four hours. Concentrated hydrochloric acid was added from time to time to maintain a steady evolution of hydrogen. After cooling the reaction mixture, the organic material was collected in ether and washed with water and sodium carbonate solution. On distillation, there was obtained 15 g. of Δ^{11}-dodecahydrophenanthrene boiling at 81–82° (1.5 mm.); n^{20}_D 1.5102; d^{20}_4 0.9674.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.34; H, 11.66. Found: C, 88.68; H, 11.22.

Schmidt[6] reports a dodecahydrophenanthrene which has the following properties: b. p. 268–269° (737 mm.); n^{20}_D 1.5119; d^{20}_4 0.964.

1,2,3,4,5,6,7,8-Octahydro-1,2-cyclopentanonaphthalene.—In a manner similar to that described above, 8 g. of ketooctahydrocyclopentanonaphthalene was reduced to the

---

(18) This compound is reported as melting at 38° by Fischer and Stoffers, *Ann.*, **500**, 253 (1933).

corresponding hydrocarbon. The yield was 4 g. of a product, b. p. 74–76° (3 mm.); n^{20}_D 1.5074; d^{20}_4 0.9513.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.55; H, 11.45. Found: C, 88.46; H, 11.45.

Perhydrophenanthrene.—A solution of 4.5 g. of Δ^{11}-dodecahydrophenanthrene in 60 cc. of methylcyclohexane was reduced with hydrogen over Raney nickel catalyst at 250° and 1500–2000 lb. pressure for eight hours. From this reaction mixture, 2 g. of perhydrophenanthrene purified by boiling with metallic sodium was obtained. It boiled at 86–89° (2 mm.); n^{20}_D 1.5011; d^{20}_4 0.9447.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.41; H, 12.59. Found: C, 87.38; H, 12.56.

In a similar manner, 10 g. of phenanthrene was reduced.[19] In order to obtain complete reduction, it was necessary to isolate the product from the reduction mixture and reduce a second and third time with fresh catalyst each time. Two products were obtained on fractionation of the reduced hydrocarbon. These appeared to be identical with perhydrophenanthrene reported previously.[9] The first fraction (about 1 g.) boiled at 90–93° (2.5 mm.); n^{20}_D 1.4994; d^{20}_4 0.9385.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.41; H, 12.59. Found: C, 87.30; H, 12.66.

The second fraction (2 g.) boiled at 93–96° (2.5 mm.); n^{20}_D 1.5019; d^{20}_4 0.9437.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.41; H, 12.59. Found: C, 87.53; H, 12.46.

Attempts were made to dehydrogenate the perhydrophenanthrene obtained from our synthetic experiments, and also that obtained by the direct hydrogenation of phenanthrene by heating samples with selenium at 300–320° for twenty-five hours. These attempts were unsuccessful.

Decahydro-1,2-cyclopentanonaphthalene.—The octahyhydro-1,2-cyclopentanonaphthalene was reduced with hydrogen and Raney nickel catalyst in the same manner as described for the other hydrocarbons. From 1.5 g. of the unsaturated compound, about 0.5 g. of a colorless liquid boiling at 71–72° (2.5 mm.) was obtained: n^{20}_D 1.4895; d^{20}_4 0.9241.

Anal. Calcd. for $C_{13}H_{22}$: C, 87.55; H, 12.45. Found: C, 87.40; H, 12.66.

Summary

The reaction for converting dieneynes to cyclohexenone derivatives has been extended to produce derivatives of dodecahydrophenanthrene and octahydro-1,2-cyclopentanonaphthalene.

URBANA, ILLINOIS RECEIVED APRIL 23, 1936

---

[19] We are indebted to Professor Homer Adkins for his aid with this experiment.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Suggestion for an Empirical Method for Predicting the Configuration of Optically Active Carbon Compounds

BY RUSSELL E. MARKER

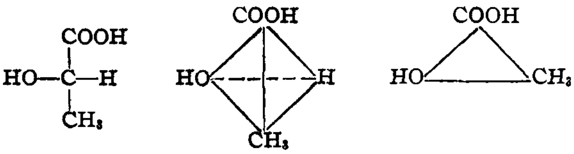
A knowledge of configurational relationships is necessary in any study of the Walden inversion.

As has been shown by Levene and his co-workers[1] all rules for determining these relationships have only limited application. Only the most difficult and painstaking experimental methods have given these relationships.

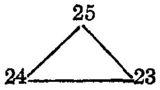
After many attempts at arranging the mass of available data, the table given was constructed largely from measurements by Levene and his co-workers, and to a lesser extent from those by Pickard and Kenyon[2] and their collaborators. The lower portion of the table contains the six more highly polar groups arranged in order of *increasing* levorotation instead of the *decreasing* order used in the upper part of the table. It should be noted carefully that this table and its applications are based only on the rotations of pure liquids at about 25° for the sodium D line.

From the first four columns in the table is obtained the *numerical order* of the groups listed in the R column. Sufficient data are not now available to place conclusively other groups in this series.

Since lactic acid is the standard reference substance for the determination of configurations, the application to it of the ordinal numbers in the last column is appropriate.



Levorotatory lactic acid



The two triangles represent the face of the tetrahedron if the H corner is placed to the back. The

---

[1] Levene and co-workers, *J. Biol. Chem.*, 1925 to date.

[2] Pickard and Kenyon, *J. Chem. Soc.*, 1912 to date.