of sodium ethoxide at 130° for six hours. During this time, only 3.2 g. of alcohol distilled from the reaction. On working up the reaction mixture in the manner described for the other dimalonic esters nothing could be distilled from the reaction product even at 230° and under 0.4 mm. pressure. This product, which was much more viscous than the starting material, was probably an intermolecular condensation product, and was not investigated further.

### Summary

A study of the behavior of methylmalonic ester, isopropylmalonic ester, methylene dimalonic ester, pentamethylene dimalonic ester and decamethylene dimalonic ester with sodium ethoxide has been made. The main reaction product in the cases of the monosubstituted malonic esters was the dialkylmalonic ester resulting from self-alkylation of the starting esters. There was no evidence of an intermolecular condensation product in either case.

With the methylene dimalonic esters no intramolecular condensation could be effected. When the reaction products could be identified they were found to be decomposition products, resulting from retrograde Michael reactions and decarboxylation, of the starting esters.

MADISON, WISCONSIN RECEIVED OCTOBER 20, 1936

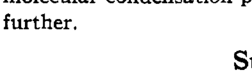
---

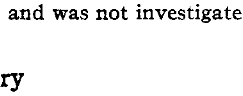
[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

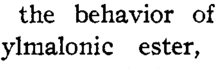
# Hydrogenation of Phenanthrene

BY JOHN R. DURLAND AND HOMER ADKINS

Three substances, 9,10-dihydrophenanthrene[1,3] (I), 1,2,3,4,5,6,7,8-octahydrophenanthrene[2,3,4] (II), and tetradecahydrophenanthrene[5] (III), have been made by the catalytic hydrogenation of phenanthrene. Incidental to an investigation of the relation of structure to the hydrogenation of certain phenanthrene derivatives we have developed procedures for the preparation of these compounds which may be of immediate value to others.


I


II


III

Burger and Mosettig took advantage of the greater activity of copper–chromium oxide[6] toward olefinic double bonds as compared with benzenoid nuclei[7] and selectively hydrogenated phenanthrene at 220°, obtaining 9,10-dihydrophenanthrene in yields of about 80%. We have duplicated their results. However, with a purer sample of phenanthrene we have obtained no dihydrophenanthrene at 220°. With this purer sample of phenanthrene we have been able to hydrogenate in the 9,10-position with copper–chromium oxide at 130° within four hours, as compared with the eight to ten hours at 220° reported by Burger and Mosettig. The best temperature for the production of 9,10-dihydrophenanthrene with copper–chromium oxide appears to be about 150°, the yield being 87%. At 180° a little octahydrophenanthrene was produced, while at 220° the latter is produced to the exclusion of the dihydro compound.

The fact that phenanthrene may be hydrogenated in the 9,10-position over copper–chromium oxide at 130° is rather striking evidence of the olefinic character of the double bond in that position. Copper–chromium oxide is not usually active toward any type of unsaturation at temperatures much below 130°.

With pure phenanthrene, Raney nickel may also be used for the preparation of dihydrophenanthrene. When the reaction was carried out at 96°, a 61% yield was obtained after five hours. However, nickel is not so satisfactory as copper–chromium oxide for this selective hydrogenation. With copper–chromium oxide there is a difference of about 50° between the temperature at which hydrogenation begins in the 9,10-position and the temperature required for further hydrogenation. With Raney nickel the temperature differential for these two types of reaction is no more than 10°. These facts are indicated by a com-

---

[1] Burger and Mosettig, THIS JOURNAL, **57**, 2731 (1935); **58**, 1857 (1936).

[2] Van de Kamp and Mosettig, *ibid.*, **57**, 1107 (1935).

[3] Schroeter, *Ber.*, **57**, 2025 (1924); Schroeter, Müller and Huang, *ibid.*, **62**, 645 (1929).

[4] Ipatieff, *ibid.*, **41**, 999 (1908).

[5] Pinkney and Marvel, THIS JOURNAL, **58**, 976 (1936).

[6] Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

[7] Adkins and Connor, *ibid.*, **53**, 1091 (1931).

parison of the data for experiments 1 and 5 (Ni) and 2, 4 and 8 (CuCrO).

Either Raney nickel or copper–chromium oxide may be used for the preparation of octa- or tetradecahydrophenanthrene, but nickel is to be preferred. Octahydrophenanthrene is best made at 120°, the time for pure phenanthrene with Raney nickel being only four or five hours instead of two to eight days at 120 to 140° as with less pure material.[2] Tetradecahydrophenanthrene is best made at about 200° with Raney nickel, the time required being three or four hours.

The copper–chromium oxide catalyst usually has been found to be inactive toward phenyl groups. However, as Folkers has pointed out,[8] this inactivity is merely relative and under certain drastic conditions even phenyl groups may be hydrogenated. In this Laboratory cyclohexyl derivatives have been produced over copper–chromium oxide from ethyl salcylate,[9] N-substituted phthalimides[10] and N-phenyl pyrrole.[11] The conversion of 9,10-dihydrophenanthrene to 1,2,3,4,5,6,7,8-octahydrophenanthrene is not a clear cut indication of the activity of copper–chromium oxide for the hydrogenation of a benzoid nucleus since this transformation apparently involves intramolecular rearrangement. However, the conversion of the octahydrophenanthrene to tetradecahydrophenanthrene at 300° is fairly clear evidence for the activity of copper–chromium oxide in catalyzing the hydrogenation of a benzenoid nucleus in a hydrocarbon.

## Experimental Part

Crude phenanthrene was purified by a combination and modification of the procedures used by Bachmann[12] and by Schroeter.[3] The former used an oxidizing agent but no sodium, the latter sodium but no oxidizing agent. One kilogram of "70% phenanthrene" (Eastman) was heated with six liters of 95% alcohol and the hot solution decanted from the insoluble portion (discarded) and cooled. The crystallized phenanthrene was dissolved in 2400 ml. of glacial acetic acid. To the boiling solution was added gradually a solution of 100 g. of sodium dichromate dihydrate in 20 ml. of sulfuric acid and 150 ml. of 50% acetic acid. Thirty ml. of sulfuric acid was then added slowly and the solution refluxed for fifteen minutes. After pouring the hot solution into an equal volume of cracked ice and water, the mixture was filtered and the phenanthrene washed with water until a colorless filtrate was obtained. After drying at 80° the product was fractionated carefully through a Widmer column, b. p. 181–183° (15 mm.). (The yield but not the purity of the final product was increased about 20 g. by one crystallization of this distillate from ethyl alcohol.) The distillate was heated for four hours at 200° with 10% of its weight of metallic sodium, the mixture being *stirred vigorously during the entire period*. The phenanthrene was distilled with care in a Claisen flask with a thin plug of glass wool in the side neck. The colorless product was fractionated over 5 to 10 g. of metallic sodium through a Widmer column, the low boiling fractions (diphenyl) being discarded. The pure product weighed 480–530 g., melted at 97–98°, and was perfectly colorless even in the liquid state. An additional 70–80 g. of impure phenanthrene was recovered by subliming all residues from the sodium treatment.

The reaction mixtures after hydrogenation were fractionated through a Widmer column having a glass spiral 15 cm. in length. The fractions considered to be dihydrophenanthrene were taken at 176–178° (20 mm.) or 140–142° (6 mm.). The octahydrophenanthrene fractions were taken at 172–173° (20 mm.) or 135–136° (6 mm.). Tetradecahydrophenanthrene was taken at 147–149° (20 mm.) or 142–144° (15 mm.). The best indication of the purity of the hydrogenated phenanthrenes so obtained is given by a comparison of the refractive indices of the products as given in Table I with those of more thoroughly purified products, and with those previously reported. Dihydrophenanthrene after one crystallization from methanol melted 33.8 to 34.4° and the supercooled material showed a $n^{25}_D$ of 1.6406. Octahydrophenanthrene was purified through the sulfonic acid as described by Schroeter. The pure compound so obtained, b. p. 134–135° (5 mm.), m. p. 16.6°, showed a $n^{25}_D$ of 1.5640, a figure almost identical with that of material purified only by a careful frac-

Table I

Hydrogenation of Phenanthrene

Reaction in a steel vessel under 150 to 200 atm. pressure of hydrogen in (a) 50 ml. methylcyclohexane or (b) 100 ml. ethanol as a solvent. (c) 32% and (d) 9% phenanthrene recovered. (c) 2% yield of octahydrophenanthrene. (f) 28 to 31% yield of a mixture having a refractive index averaging about 1.54. (g) 11% yield of octahydrophenanthrene.

| | $C_{14}H_{10}$, g. | Catalyst, g. | °C. | Hrs. | % yield | $n^{25}_D$ |
|---|---|---|---|---|---|---|
| | | | 9,10-Dihydrophenanthrene | | | |
| 1 | 50(a) | 5 Ni | 96 | 5.0 | 61(c) | 1.6295 |
| 2 | 40(b) | 4CuCrO | 130 | 4.0 | 79(d) | 1.6343 |
| 3 | 40(b) | 4 CuCrO | 150 | 3.0 | 87 | 1.6334 |
| 4 | 40(b) | 4 CuCrO | 180 | 1.5 | 88(e) | 1.6253 |
| | | | 1,2,3,4,5,6,7,8-Octahydrophenanthrene | | | |
| 5 | 50(a) | 5 Ni | 110 | 5.2 | 79 | 1.5640 |
| 6 | 50(a) | 10 Ni | 120 | 4.0 | 94 | 1.5611 |
| 7 | 100(a) | 5 Ni | 120 | 5.0 | 82 | 1.5630 |
| 8 | 40(b) | 4 CuCrO | 200 | 11.0 | 63(f) | 1.5650 |
| 9 | 40(b) | 4 CuCrO | 220 | 6.0 | 64(f) | 1.5631 |
| | | | Tetradecahydrophenanthrene | | | |
| 10 | 40(a) | 5 Ni | (150–200) | 9.0 | 89 | 1.5050 |
| 11 | 20(a) | 3 Ni | 200 | 3.1 | 82 | 1.5050 |
| 12 | 30(a) | 3 CuCrO | 300 | 9.0 | 50(f) (g) | 1.5035 |

---

(8) Folkers, This Journal, **58**, 1559 (1936).

(9) Connor and Adkins, *ibid.*, **54**, 4658 (1932).

(10) Wojcik and Adkins, *ibid.*, **56**, 2419 (1934).

(11) Signaigo and Adkins, *ibid.*, **58**, 709 (1936).

(12) Bachmann, *ibid.*, **57**, 555 (1935).

tionation. Rehydrogenation and refractionation of the tetradecahydrophenanthrene gave a product, b. p. 155–157° (27 mm.), having $n^{25}D$ of 1.5003 which agrees with the value given by Pinkney and Marvel.[5]

In the fractionation of the reaction mixtures there were intermediate fractions which are not reported in the table. Their amounts in most cases represented only a few per cent. of the weight of phenanthrene originally used. However, with copper–chromium oxide at temperatures of 200–300° these unidentified products amounted to about 30% of the weight of phenanthrene submitted to hydrogenation.

## Summary

Methods have been given for the preparation of 9,10-dihydrophenanthrene, 1,2,3,4,5,6,7,8-octahydrophenanthrene, and tetradecahydrophenanthrene from "70% phenanthrene."

MADISON, WIS. RECEIVED NOVEMBER 23, 1936

---

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

# Molecular Rearrangements in the Sterols. I. The Action of Anhydrous Potassium Acetate on Cholesteryl *p*-Toluenesulfonate in Acetic Anhydride Solution

BY EVERETT S. WALLIS, E. FERNHOLZ AND F. T. GEPHART

The epimerization of the hydroxyl group of cholesterol and other unsaturated sterols has become of great interest since Ruzicka[1] showed that the male hormone, androsterone, is a derivative of *epi*-dihydrocholesterol, and that its physiological activity is much greater than the corresponding epimer.

This difference in the activity of the two isomers stimulated our interest in the preparation of the epimer of dehydroandrosterone. In order to find a satisfactory method for the preparation of this latter compound we first thought it advisable to study possible methods for the epimerization of cholesterol, since the previous attempts of Stoll[2] to prepare *epi*-cholesterol had failed.

During the course of this investigation three papers have appeared which have an important bearing on this problem. Evans and Schoenheimer[3] have reported the preparation of *epi*-allocholesterol, which differs from *epi*-cholesterol only in the position of the double bond. Marker, Oakwood and Crooks[4] have described the preparation of *epi*-cholesterol by the action of oxygen on the Grignard reagent obtained from cholesteryl chloride. Beynon, Heilbron and Spring[5] have published experimental results obtained in an investigation of some reactions of the isomeric ethers of cholesterol.

These publications make it advisable to report certain experiments we have carried out on the problem of obtaining *epi*-cholesterol in good yields, and which also have interest regarding the constitution of the two series of isomeric ethers of cholesterol, discovered by Stoll.[2]

Stoll[2] found that when cholesteryl *p*-toluene sulfonate is boiled with an alcohol it reacts easily to form a normal levorotatory ether, but that an isomeric dextrorotatory ether is formed when the reaction is carried out in the presence of potassium acetate. Stoll[2] expressed the opinion that this new ether was a derivative of *epi*-cholesterol or of *epi*-allocholesterol.

In the same year Wagner-Jauregg and Werner[6] reported that cholesteryl chloride and bromide behaved in a similar manner, that is, when heated alone with alcohols the normal levorotatory ether is formed, but in the presence of potassium acetate the isomeric dextrorotatory ether is produced. They further observed that the isomeric methyl ether is converted into the normal ether when heated with hydrogen chloride in methyl alcohol at 130°. From this fact they concluded that in the formation of ethers from either cholesteryl halides or the *p*-toluene sulfonate the isomeric ethers are first formed, but that the acid produced in the reaction converts them into the so-called "normal" form. These investigators also attempted to hydrogenate the isomeric ether. Although they found that this reaction did not proceed smoothly, it is important to note in view of certain of our experiments about to be described that a small amount of the normal dihydrocholesteryl methyl ether was isolated.

In this connection the observations of Beynon, Heilbron and Spring[5] are also of special interest.

---

[1] Ruzicka and co-workers, *Helv. Chim. Acta*, **17**, 1395 (1934).

[2] Stoll, *Z. physiol. Chem.*, **207**, 147 (1932).

[3] Evans and Schoenheimer, THIS JOURNAL, **58**, 182 (1936).

[4] Marker, Oakwood and Crooks, *ibid.*, **58**, 481 (1936); see also, Marker, Kamm, Oakwood and Laucius, *ibid.*, **58**, 1948 (1936).

[5] Beynon, Heilbron and Spring, *J. Chem. Soc.*, 907 (1936).

[6] Wagner-Jauregg and Werner, *J. physiol. Chem.*, **213**, 119 (1932).