pected to approximate more nearly the rate of hydrolysis of *p,p'*-dibromobenzophenone oxime. An examination of the data in Table I shows that the rate of hydrolysis of α-*p*-bromobenzophenone oxime more nearly approximates the rate for benzophenone oxime than it does that for *p,p'*-dibromobenzophenone oxime. Thus this criterion of configuration would assign the *syn*-phenyl configuration to the α-*p*-bromobenzophenone oxime. Similarly, the closer relationship between the rates of hydrolysis of the β-*p*-bromobenzophenone oxime and *p,p'*-dibromobenzophenone oxime would assign the *syn*-*p*-bromophenyl configuration to the β-*p*-bromobenzophenone oxime. These configurations agree with those assigned to the α- and β-forms of this oxime by the method of Hantzsch, based on the products of the Beckmann rearrangement of the individual oximes. However, if *trans* addition of water occurs, the interpretation of the above data would reverse the assigned configurations. Thus no claim can be made for the validity of this method until further investigations have been made on other pairs of oximes. In particular data on the rates of hydrolysis of oximes whose configurations have been determined by other means are needed. This work will be done in this Laboratory.

Summary

1. The velocities of hydrolysis of benzophenone oxime, *p,p'*-dibromobenzophenone oxime and the stereoisomeric α- and β-*p*-bromobenzophenone oximes were determined under identical conditions.

2. A possible tentative method for the assignment of configurations to stereoisomeric oximes, based on a comparison of velocity of hydrolysis constants, is discussed.

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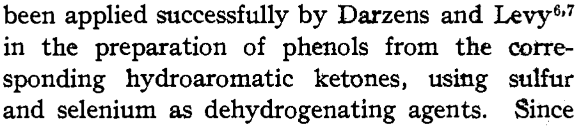
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Studies in the Phenanthrene Series. XIV. The Preparation of 1- and 4-Phenanthrol

BY ERICH MOSETTIG AND HARRY M. DUVALL[1]

As starting material for the synthesis of new compounds which might possess oestrogenic activity, we were in need of several of the phenanthrols. While all five of the possible monohydroxyphenanthrenes are known, heretofore there has been no satisfactory method of preparing the 1- and 4-isomers. The total synthesis of 1- and 4-methoxyphenanthrene by Pschorr's method[2] can hardly be considered for large scale preparation. The synthesis of the 1-hydroxy- and in particular of the 4-hydroxyphenanthrene by the pyrolysis of α- and β-naphthylparaconic acid,[3] respectively, appears quite impracticable. The more recent preparations of 1-phenanthrol by potassium hydroxide fusion of the rare 1-sulfonic acid[4] and by diazotization of 1-aminophenanthrene[5] do not appear feasible.

In a previous communication of this series[6] we stated that 1-phenanthrol can be obtained from 1-keto-2-bromo-1,2,3,4-tetrahydrophenanthrene in a yield of about 50% by elimination of hydrogen bromide, while 4-phenanthrol is obtained only in small amounts by an analogous reaction. A more direct way, however, appeared to be dehydrogenation of the 1- and 4-ketotetrahydrophenanthrenes themselves, according to the scheme



The principle of this method is not new and has been applied successfully by Darzens and Levy[6,7] in the preparation of phenols from the corresponding hydroaromatic ketones, using sulfur and selenium as dehydrogenating agents. Since we found the application of these agents to the ketotetrahydrophenanthrenes not very successful,

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[1] E. R. Squibb and Sons Research Fellow.

[2] (a) Pschorr, Wolfes and Buckow, *Ber.*, **33**, 162 (1900); (b) Pschorr and Jäckel, *ibid.*, **33**, 1826 (1900).

[3] (a) Shoesmith and Guthrie, *J. Chem. Soc.*, 2332 (1928); (b) Behrend and Ludewig, *Ann.*, **379**, 351 (1911).

[4] Fieser, THIS JOURNAL, **51**, 2460 (1929).

[5] Bachmann and Boatner, *ibid.*, **58**, 2194 (1936).

[6] Mosettig and Burger, *ibid.*, **57**, 2189 (1935).

[7] Darzens and Levy, *Compt. rend.*, **194**, 181 (1932); Levy, *ibid.*, **194**, 1749, 1952 (1932). See also Ruzicka, *Helv. Chim. Acta*, **19**, 419 (1936); Fieser, Hershberg and Newman, THIS JOURNAL, **57**, 1509 (1935).

a systematic investigation on catalytic dehydrogenation was carried out with respect to solvent, time of reaction, catalyst and amount of catalyst, which finally enabled us to prepare 1- and 4-phenanthrol in yields of 68–86% and 56–63%, respectively. As the ketotetrahydrophenanthrenes are relatively accessible,[8] this method appears to be a convenient approach to the hitherto rare 1- and 4-phenanthrol. Furthermore, we found that, with the exception of the few cases noted in Table I, the ketotetrahydrophenanthrene which was not converted to phenanthrol can be recovered nearly quantitatively.

TABLE I

DEHYDROGENATION OF 1-KETO-1,2,3,4,-TETRAHYDROPHENANTHRENE[a]

Dehydrogenating agent	Solvent[i]	Time of refluxing, hrs.	Yield of Phenanthrol,[o] %
0.10 g. Pd[b]	Tetralin[j]	24	38
0.10 g. Pd	Xylene	3	10
0.10 g. Pd	Xylene	24	38
0.10 g. Pd	Xylene	48	53
0.10 g. Pd	Xylene	96	70
0.20 g. Pd	Xylene	24	63
0.10 g. Pd	Naphthalene	24	86[p]
0.10 g. Pd	Naphthalene[k]	48	68
ca. 2 g. Ni[c]	Xylene	8	8
ca. 4 g. Ni	Xylene	24	38
ca. 6 g. Ni	Naphthalene	24	27
0.20 g. PtO_2[d]	Tetralin[j]	24	41
0.20 g. PtO_2	Xylene	24	40
0.12 g. PtO_2	Naphthalene	24	73
0.10 g. PdO[e]	Xylene	24	0
1.00 g. Pd charcoal[f]	Xylene	24	0
0.10 g. Pd + 5.0 g. safrole[g]	Xylene	24	0
0.54 g. S	Naphthalene[l]	3	35
1.34 g. Se[h]	Naphthalene[l]	3	0
DEHYDROGENATION OF 4-KETO-1,2,3,4,-TETRAHYDROPHENANTHRENE			
0.10 g. Pd	Tetralin[j]	0.5	Negligible
0.10 g. Pd	Xylene	3	5
0.30 g. Pd	Xylene	24	57[p]
0.20 g. Pd	Xylene	120	47
0.10 g. Pd	Naphthalene[m]	24	18
0.10 g. Pd	Phenanthrene[m,n]	24	0
0.10 g. Pd	Benzene	72	Negligible
ca. 6 g. Ni	Xylene	24	2
0.10 g. PdO	Xylene	24	0
0.20 g. PtO_2	Xylene	24	0
0.54 g. S	Naphthalene[l]	3	17

[a] All runs listed in the table were made on 3.00-g. batches of ketotetrahydrophenanthrene. [b] Willstätter and Waldschmidt-Leitz, *Ber.*, **54**, 123 (1921). [c] Raney catalyst, Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932). [d] Adams, Vorhees and Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 452. [e] Shriner and Adams, THIS JOURNAL, **46**, 1683 (1924). [f] In the proportion 0.14 g. palladium on 0.86 g. charcoal. Ott and Schröter, *Ber.*, **60**, 633 (1927). [g] Compare Akabori and Suzuki, and Akabori and Saito, *Proc. Imp. Acad.* (Japan), **5**, 255 (1929); **6**, 236 (1930); *C. A.*, **23**, 4671 (1929); **24**, 5037 (1930). [h] See experiment without solvent, Mosettig and Burger, ref. 6. [i] All solvents were dried and purified by refluxing and distilling over sodium. [j] This solvent was chosen in view of the dehydrogenation experiments of Kindler and Peschke, *Arch. Pharm.*, **272**, 236 (1934). It is noteworthy that when platinum oxide catalyst was used, all of the ketotetrahydrophenanthrene which had not been dehydrogenated to phenanthrol could be recovered, but when palladium black catalyst was used, only about half of the expected ketotetrahydrophenanthrene could be recovered, indicating that with the latter catalyst side reactions had taken place (possibly hydrogenation by means of the fixed hydrogen of the tetralin). [k] An unidentified by-product (0.4 g.), insoluble in ether and in alkali, and sparingly soluble in benzene, melting with decomposition at about 340°, was obtained. [l] No attempt was made to work up the non-phenolic part of the reaction products. [m] No ketotetrahydrophenanthrene could be recovered. The formation of water was observed in both cases. It is very likely that phenanthrene was formed; see Cook and Hewett, *J. Chem. Soc.*, 403 (1933), who obtained phenanthrene on selenium dehydrogenation of 4-ketotetrahydrophenanthrene. [n] A by-product (1.5 g.) insoluble in ether and in alkali, but moderately soluble in benzene, melting without decomposition at 306–309°, was obtained. It is probably identical with the compound, m. p. 312°, which Cook and Hewett[m] obtained as a by-product from the selenium dehydrogenation of 4-ketotetrahydrophenanthrene. [o] The figures in this column represent the yield of about 90–95% pure phenanthrol. [p] These conditions were adopted as most satisfactory for the preparation of the phenanthrols in larger quantities. Thus, in two runs on 10.0-g. batches of 1-ketotetrahydrophenanthrene, using 0.33 g. of palladium black catalyst, we obtained yields of 82 and 84%. These yields were obtained using portions of the same catalyst. With another catalyst, prepared from the same stock of palladium chloride, the yield dropped to 68%, apparently because of uncontrollable factors in the preparation of the catalyst. 4-ketotetrahydrophenanthrene was dehydrogenated in two 25.0-g. batches, using 3.30 g. of palladium black catalyst, whereby yields of 56 and 63% were obtained.

We plan to subject the phenanthrols, in part continuing previous work,[9] to the Friedel and Crafts reaction, using various acid chlorides and anhydrides, which should give us a variety of hydroxy carbonyl compounds, including those containing a fourth ring.

Experimental Part

Dehydrogenation Experiments.—The ketotetrahydrophenanthrene was refluxed with the catalyst in ten parts

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(8) Haworth, *J. Chem. Soc.*, 1125 (1932); Fieser and Peters, THIS JOURNAL, **54**, 4354 (1932); Martin, *ibid.*, **58**, 1438 (1936).

(9) Mosettig and Burger, THIS JOURNAL, **55**, 2981 (1933); Burger and Mosettig, *ibid.*, **56**, 1745 (1934).

by weight of solvent. The catalyst was recovered from the reaction mixture, either by filtration of the latter, if liquid at room temperature, or by filtration of an ethereal solution of the reaction mixture. The reaction solvent was removed either by distillation under reduced pressure or by steam distillation, after removal of the ether. The residue from these distillations was then warmed for about fifteen minutes with an excess of 5% potassium hydroxide solution, and the undissolved material taken up in ether. Four or five extractions of the ethereal solution with alkali removed practically all of the phenanthrol. The alkaline extracts were combined with the first alkaline solution and acidified with concentrated hydrochloric acid, whereupon the phenanthrol separated in a crystalline state. From the residue of the ethereal solution the unreacted ketotetrahydrophenanthrene may be recovered as its semicarbazone. The results of some of the experiments are summarized in Table I.

1-Phenanthrol.—Pure 1-phenanthrol was obtained from the dehydrogenation product by one distillation at 1 mm., followed by sublimation; m. p. 153–154°.

Anal. Calcd. for $C_{14}H_{10}O$: C, 86.56; H, 5.19. Found: C, 86.21; H, 5.16.

The acetate and the methyl ether melted at 134–135° and 103–104°, respectively. The melting points agree with the corresponding values given in the literature.[2a,3a,4,6]

4-Phenanthrol.—4-Phenanthrol was purified in the same manner as the 1-isomer, and melted at 113–115°, in agreement with the value given by Mosettig and Burger.[6]

Anal. Calcd. for $C_{14}H_{10}O$: C, 86.56; H, 5.19. Found: C, 86.44; H, 5.55.

The acetate and methyl ether melted at 58–59.5° and 67–68°, respectively, in agreement with the values given in the literature.[2b,3b]

Summary

1- and 4-phenanthrol have been prepared in yields of 68–86% and 56–63%, respectively, by the catalytic dehydrogenation of 1- and 4-keto-1,2,3,4-tetrahydrophenanthrene.

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[CONTRIBUTION NO. 48 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Chemical Constitution of a Bituminous Coal as Revealed by its Hydrogenation Products

BY BURNARD S. BIGGS[1] AND J. F. WEILER

In earlier contributions from this Laboratory[2] it was shown that both the extract and the residue from the extraction of a Pittsburgh seam coal with benzene at 260°, yielded, upon high pressure hydrogenation at 350° with a copper-calcium chromite catalyst, 80% of their carbon as petroleum ether soluble oils essentially hydrocarbon in nature. Boiling points, refractive indices and hydrogen–carbon ratios indicated that these hydrocarbons were partially hydrogenated polycyclic aromatic compounds. Because of (1) the nature of the catalyst employed, which is particularly effective in breaking cyclic and linear ether oxygen linkages, (2) the moderate temperatures used, which preclude appreciable degradation of hydrocarbon structures and (3) the large fraction of the carbon of the original coal converted, it appears that these oils properly may be regarded as fundamental units of the coal in the sense that the coal structure may be considered as built of such units combined through peripheral functional groups.

In this paper are presented the results so far obtained in the characterization of these oils. The oils recovered from the preliminary hydrogenation with copper–calcium chromite were completely saturated by hydrogenation over Raney nickel catalyst, then fractionally distilled and the fractions characterized through their boiling points, refractive indices, molecular weights and hydrogen–carbon ratios.

Experimental.—Both the residue and the extract from the extraction of Edenborn[3] coal with benzene at 260° were hydrogenated over Adkins catalyst by the stepwise procedure described by Biggs[2b] in which hydrogenation, followed by removal of petroleum ether soluble oils, was repeated until there was practically complete conversion to oils. From 200 g. of residue there was obtained in seven steps 24.5, 21.7, 18.6, 20.4, 26.5, 12.6 and 9.2 g., or a total of 133.5 g. of petroleum ether soluble oils containing 79.7% of the carbon of the starting materials. From 100 g. of extract there was obtained in five steps 21.5, 26.7, 19.5, 12.8 and 4.7 g., or a total of 85.2 g. of petroleum ether soluble oils representing 87% of the carbon of the original extract. The accumulated products in each case were then dissolved in benzene and subjected to a final hydrogenation over Adkins catalyst at 280° for twenty-four hours. After removal of benzene the product was dissolved in cyclohexane and subjected to hydrogenation over 10% of Raney nickel catalyst at 220° and 1800 pounds (120 atm.) initial hydrogen pressure until the absorption of hydrogen had ceased. This necessitated cooling the bomb

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[1] Now located at Summit, N. J., Bell Telephone Laboratories.

[2] Biggs, THIS JOURNAL, (a) 58, 484 (1936); (b) 58, 1020 (1936).

[3] U. S. Bureau of Mines Tech. Paper No. 525 (1932).