talline solvate which melted at 153–157° with frothing. An analytical sample, dried over phosphorus pentoxide and paraffin at 78° and 20 mm., melted at 189–191°.

The trihydroxy compound was converted to tris-(*p*-propionoxyphenyl)-ethylene (compound 32) by reaction with propionic anhydride in pyridine solution as described above for the triacetoxy derivative.

Bromotris-(*p*-acetoxyphenyl)-ethylene (Compound 30).—To a stirred solution of 5 g. (0.012 mole) of tris-(*p*-acetoxyphenyl)-ethylene in 60 ml. of chloroform was added 2.1 g. (0.012 mole) of N-bromosuccinimide. After 15 minutes, the solution was heated to reflux for 20 hours, cooled and shaken with 250 ml. of cold water. The chloroform layer was separated, washed with cold water and evaporated. Three recrystallizations of the residue from methanol (charcoal decolorization) gave 1 g. (17%), m.p. 151–153°.

1,1,2-Tris-(*p*-methoxyphenyl)-ethane (Compound 37).—A mixture of 17.3 g. (0.05 mole) of tris-(*p*-methoxyphenyl)-ethylene and 1 g. of 10% palladium on charcoal in 200 ml. of ethyl acetate was hydrogenated at room temperature at an initial pressure of 30 p.s.i. Hydrogen absorption ceased in one hour. After the catalyst was removed and the solvent evaporated, the residue was recrystallized from absolute ethanol to give 15.2 g. (88%) of pure product, m.p. 86–87°.

Tris-(*p*-methoxyphenyl)-acrylic Acid (Compound 17).—A Grignard solution was prepared from 10 g. (0.0257 mole) of bromotris-(*p*-methoxyphenyl)-ethylene in the manner described above for the preparation of compound 20. The solution was decanted from the excess magnesium onto 25 g. of powdered, solid carbon dioxide. The complex was decomposed with 10% sulfuric acid, and the ether layer was separated and evaporated. The residue was chilled, and the solid material which separated was removed by filtration and dissolved in dilute, aqueous sodium hydroxide solution. The alkaline solution was extracted with ether, then poured onto a mixture of ice and concentrated hydrochloric acid. Recrystallization of the precipitated solid from dilute acetic acid gave a 34% yield of pure product, m.p. 202–203°.

1,1-Bis-(*p*-dimethylaminophenyl)-2-(*p*-methoxyphenyl)-ethylene (Compound 33).—To a stirred, hot solution of 20 g. (0.0766 mole) of Michler ketone in dry benzene was added, over a 20-minute period, a solution of 0.294 mole of *p*-methoxybenzylmagnesium chloride in 350 ml. of anhydrous ether. After the addition was complete, the mixture was heated to reflux for 16 hours, then decomposed with a solution of 30 g. of ammonium chloride in 150 ml. of water. The mixture was filtered, and the ether layer was evaporated.

The filter cake and the residue from the ether layer were combined and recrystallized from methanol containing a trace of ammonium hydroxide to give the carbinol, m.p. 150–151°. The carbinol was dehydrated by mixing with one-tenth its weight of thymolsulfonic acid and heating under vacuum in an oil-bath until effervescence ceased. The mixture was cooled, dissolved in chloroform and washed with 5% sodium hydroxide solution. The chloroform solution was evaporated and the residue was recrystallized from ether to give 10 g. (35%) of the pure ethylene, m.p. 106–108°.

***p*-Benzyloxybenzyl Alcohol.**[24]—A mixture of 600 ml. of dry isopropyl alcohol, 42.4 g. (0.2 mole) of *p*-benzyloxybenzaldehyde[25] and 10 g. (0.48 mole) of aluminum isopropoxide was heated at a rate such that the acetone distilled as it was formed. When no more acetone distilled,[26] most of the solvent was removed and the residue was poured onto a mixture of 300 g. of ice and 30 ml. of concentrated hydrochloric acid. The solid product retained water tenaciously. It was therefore extracted with 1300 ml. of boiling petroleum ether (75–90°). The solid which separated upon cooling was recrystallized from petroleum ether (75–90°) to give 31 g. (72%) of pure product, m.p. 86–87°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.58. Found: C, 78.70; H, 6.56.

***p*-Benzyloxybenzyl Chloride.**—A solution of 21.4 g. (0.1 mole) of *p*-benzyloxybenzyl alcohol in 300 ml. of anhydrous ether was chilled to 5°, saturated with dry hydrogen chloride, and the mixture was maintained at 5° for 16 hours. An equal volume of an ice–water mixture was added. The ether layer was separated, and the aqueous layer was extracted three times with ether. The combined ether solutions were washed with water, then with a saturated sodium carbonate solution, and dried over anhydrous sodium carbonate. After removal of the solvent, the residue was recrystallized from petroleum ether to give 20 g. (86%) of white plates, m.p. 79–80°.

Anal. Calcd. for $C_{14}H_{13}OCl$: C, 72.28; H, 5.63; Cl, 15.25. Found: C, 72.54; H, 5.88; Cl, 15.06.

Acknowledgments.—The authors are indebted to Dr. H. W. Werner and Mr. C. R. Thompson for the pharmacological evaluation of these compounds and to Dr. G. L. Krueger for technical assistance.

(24) The synthesis of this compound was mentioned by W. Tadros and L. Ekladius, *Nature*, **166**, 525 (1950), but no physical constants were reported.

(25) E. D. Bergmann and M. Sulzbacher, *J. Org. Chem.*, **16**, 84 (1951).

(26) The distillate was checked for acetone with 2,4-dinitrophenylhydrazine solution.

CINCINNATI 15, OHIO

[CONTRIBUTION NO. 1821 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY[1]]

On the Catalytic Hydrogenation of 3,4-Benzpyrene

BY W. LIJINSKY AND L. ZECHMEISTER

RECEIVED JUNE 2, 1953

Total catalytic hydrogenation of purified 3,4-benzpyrene yields the perhydro derivative. By partial hydrogenation 1′,2′,3′,4′-tetrahydro-3,4-benzpyrene was isolated; yield 40%. A by-product was tentatively identified as 6,7-dihydro-3,4-benzpyrene.

Although some partially reduced benzpyrenes have been prepared by indirect synthesis, no direct catalytic hydrogenation of 3,4-benzpyrene seems to have been carried out. We became interested in this process because of the occurrence of hydrogenated polycyclic hydrocarbons in some natural tars, a report on which will appear elsewhere.[1a]

At room temperature and in the presence of platinum oxide the complete saturation of 3,4-benzpyrene with 10 mols of hydrogen takes place without difficulty. The resulting perhydro compound, probably a mixture of stereoisomers, formed a colorless oil most of which crystallized after long standing.

When the reduction process had been interrupted after the uptake of 2 mols of hydrogen and the resulting mixture resolved chromatographically in ultraviolet light, a well-crystallized tetrahydro derivative was isolated. It was found to be identical with a colorless sample of 1′,2′,3′,4′-

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(1) The authors wish to thank the Damon Runyon Memorial Fund for a grant.

tetrahydro-3,4-benzpyrene (obtained by Fieser and Fieser[2] from γ-1-pyrenylbutyric acid *via* the corresponding ketotetrahydrobenzpyrene), for which we are indebted to Professor L. F. Fieser. The identification was based, besides analytical data and mixed-chromatogram tests, on the coincidence of the spectral curves as shown in Fig. 1 (*cf.* also ref. 3). Since the pure tetrahydro compound can be obtained from commercial 3,4-benzpyrene in about 40% yield, the reduction process described below constitutes a practical route for its preparation.

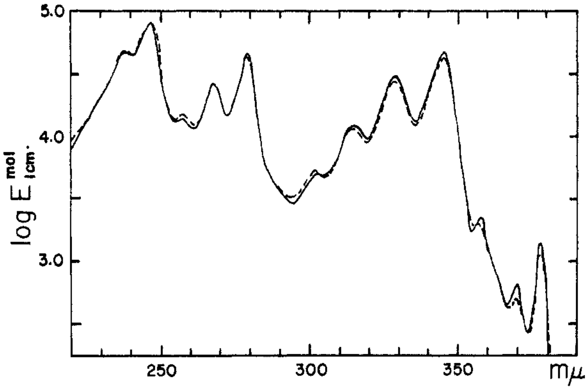


Fig. 1.—Molecular extinction curves of 1′,2′,3′,4′-tetrahydro-3,4-benzpyrene in hexane: full line, sample obtained by Fieser and Fieser from 4′-keto-1′,2′,3′,4′-tetrahydro-3,4-benzpyrene; and dashed line, prepared by direct hydrogenation. (The dashed line is given only where it does not coincide with the full line.)

A minor crystalline product of the partial hydrogenation was a dihydrobenzpyrene located between benzpyrene and the tetrahydro compound on the chromatographic column.

Twelve years ago Bachmann and Carmack[3] obtained, by elimination of hydrogen chloride from the 4′-chloro-1′,2′,3′,4′-tetrahydro-3,4-benzpyrene, a crystalline compound termed 1′,2′-dihydro-3,4-benzpyrene. Later the substance was interpreted by Kon and Roe,[4] on the basis of spectroscopic considerations and "in the absence of other evidence" as 6,7-dihydro-3,4-benzpyrene. These authors commented that Bachmann's compound showed a chrysene-type rather than a pyrene-type extinction curve. However, our dihydrobenzpyrene is spectroscopically more closely related to 5-ethylchrysene[5] than is Kon and Roe's substance (Fig. 2). Although no final structural assignments can be made at the present time, we suggest that the 1′,2′-dihydro structure as proposed by Bachmann for his compound may be correct. The structure of 6,7-dihydro-3,4-benzpyrene may be tentatively assigned to the minor hydrogenation product described below.

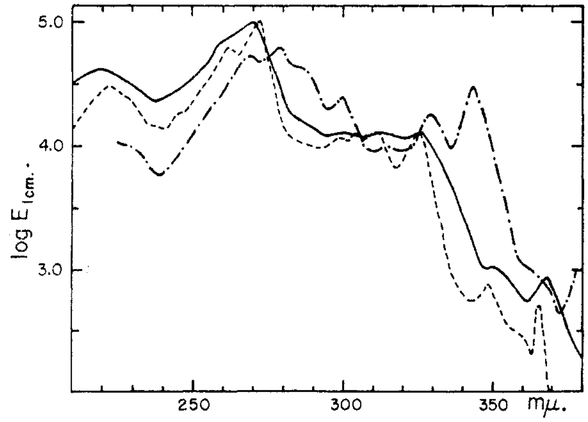
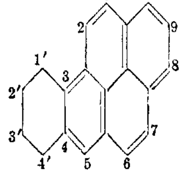
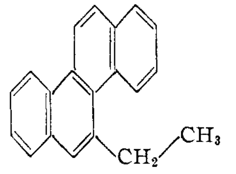


Fig. 2.—Molecular extinction curves in hexane: full line, 5-ethylchrysene (Newman[5]); dashed line, dihydro-3,4-benzpyrene obtained by hydrogenation; and dashed-dot-line, dihydro compound described by Bachmann, *et al.*,[3] and Kon and Roe.[4] (Although Newman's curve was taken in ethanol, we find that spectra in ethanol and hexane are practically identical in this series.)



1′,2′,3′,4′-Tetrahydro-3,4-benzpyrene



5-Ethylchrysene

Experimental

Materials and Procedures.—The PtO_2 catalyst was prepared according to Voorhees and Adams.[6] As adsorbent a 3:1:1 mixture of the following materials was used: Alumina Alorco, Grade F, reground to −200 mesh; Sierra Hydrated Lime, U. S. Lime Corp.; and Celite No. 545, Johns-Manville Co. Eluent: acetone–ethanol 3:1. The fluorescence was observed in the light of a General Electric photoflood no. 1 bulb, using a Corning light filter no. 5840. Spectral curves were taken in the Beckman instrument. The melting points (cor.) were determined in an electrically heated Berl block.

In order to purify commercial 3,4-benzpyrene (m.p. 177°) 250 mg. of the material (Hofmann–LaRoche) was dissolved in 100 ml. of benzene and diluted with 1 vol. of hexane. The material was adsorbed on a 28 × 8 cm. column and developed with a 2:3 benzene–hexane mixture. Above the intensely purple fluorescent benzpyrene zone minor fluorescent zones appeared. The eluate of the main zone was transferred by the addition of water into benzene–hexane 1:1, washed, dried with sodium sulfate, evaporated and crystallized from benzene by the addition of methanol; yield 94%, m.p. 177.5–178°. An old sample obtained from Eastman Kodak showed larger quantities of impurities on the column and yielded a pure product corresponding to only $^2/_5$ of the starting material, while a fresh sample gave 90% yield.

Hydrogenations were carried out at about 24° in a 1:1 mixture of cyclohexane and glacial acetic acid which had been saturated in the presence of the catalyst.

Perhydro-3,4-benzpyrene.—Using 110 mg. of substance, 40 mg. of the catalyst, 50 ml. of cyclohexane and 50 ml. of glacial acetic acid, the addition of 10.3 H_2 required 40 hr. The resulting, filtered solution was washed acid-free, dried, evaporated, dissolved in some hexane and washed with the same solvent through a 24 × 4.5 cm. column. Only traces of fluorescent materials were retained. The chromatographic filtrate (about 1 liter) did not fluoresce. The evaporated residue was dried under 1 mm. pressure at 55° for several hours: colorless oil, yield 79 mg.

Anal. Calcd. for $C_{20}H_{32}$: C, 88.14; H, 11.86; mol. wt., 272. Found: C, 88.40; H, 11.88; mol. wt. (in exaltone), 258.

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[2] L. F. Fieser and M. Fieser, This Journal, **57**, 782 (1935); *cf.* ref. 3.

[3] W. E. Bachmann and M. Carmack, *ibid.*, **63**, 1685 (1941).

[4] G. A. R. Kon and E. M. F. Roe, *J. Chem. Soc.*, 143 (1945).

[5] M. S. Newman; *cf.* R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," No. 452, John Wiley and Sons, Inc., New York, N. Y., 1951.

[6] V. Voorhees and R. Adams, This Journal, **44**, 1397 (1922).

After standing at 4° most of the material crystallized and formed, upon repeated recrystallization from hexane-ethanol, colorless prisms, m.p. 113–114°.

1′,2′,3′,4′-Tetrahydro-3,4-benzpyrene.—One hundred ninety mg. of substance, 180 mg. of catalyst and 100 ml. of solvent mixture were used. After about 2 hr. of shaking, 2 mols of hydrogen were taken up. The fluorescent solute was then transferred as described into 100 ml. of hexane, adsorbed on the upper 4–5-cm. section of a 28 × 8 cm. column and developed with benzene–hexane 1:3 (the figures on left designate thickness of zones in mm.; "fl." = fluorescence in ultraviolet light):

15 empty section
30 greenish color and fl.: unidentified
15 colorless, blue fl.: mainly unchanged benzpyrene
60 green, purplish fl.: dihydrobenzpyrene, etc.
10 interzone
55 colorless, purplish-blue fl.: tetrahydrobenzpyrene
100 empty section
Filtrate: pale-blue fl.: perhydrobenzpyrene, etc.

The 55-mm. zone was eluted, transferred into hexane, evaporated, dissolved at 60° in the minimum amount of hexane in a conical centrifuge tube, and cooled in ice-water. The crystals were centrifuged, washed with a little cold hexane, centrifuged again and dried *in vacuo;* yield 85 mg. of almost colorless crystals (m.p. 107.5–109.5°) which became colorless upon recrystallization; yield 67 mg. of pure substance, m.p. 111–111.5°. Fieser's synthetic preparation melted at 113–113.5°, and a mixture of the two at 111–112°. Two parallel experiments yielded, respectively, 88 mg. and 88 mg. of end-product and, after recrystallization, 71 and 77 mg. of pure crystals: thin plates with slightly concave sides showing complicated twinning; some four-sided, star-like structures also appeared. The compound is more soluble than 3,4-benzpyrene. Its adsorbates show purplish fluorescence which is markedly less brilliant than that of benzpyrene. For analysis the samples were dried under 1 mm. pressure at 50° for 3 hr.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.96; H, 6.02.

The orange-red trinitrobenzene complex was prepared by combining hot benzene solutions; m.p. 196–197° (after recrystallization from benzene–methanol); under the microscope: short, broad, quadrangular prisms and plates; the color is brownish-yellow, markedly darker than that of the corresponding dihydro derivative; thick individuals are reddish.

Anal. Calcd. for $C_{20}H_{16} + C_6H_3(NO_2)_3$: N, 8.94. Found: N, 9.03.

6,7-Dihydro-3,4-benzpyrene (?).—The 30-, 15- and 60-mm. zones were cut out together, eluted, and transferred into benzene–hexane 1:1. This solution was combined with a similar one obtained in a parallel experiment, and rechromatographed on a 28 × 8 cm. column (developer, benzene–hexane 2:3):

5 green; green fl.: unidentified
40 interzone
45 purple fl.: unchanged 3,4-benzpyrene (34 mg.)
10 interzone
50 dull blue fl.: dihydro-3,4-benzpyrene
15 interzone
65 faint bluish fl.: tetrahydrobenzpyrene (traces)

The dihydro zone was rechromatographed on a 21 × 3.5 cm. column, the main zone eluted, transferred into benzene–hexane 1:1 and evaporated to dryness. The residue was dissolved at 60° in the minimum amount of benzene and crystallized by dropwise addition of cold methanol; yield 32 mg. and, after recrystallization, 22 mg., m.p. 148.5–149°; colorless, long plates with some parallel twinning; the ends of individual crystals are oblique or roof-like. In contrast to benzpyrene, this compound does not show fluorescence in dilutions fit for Beckman readings; at higher concentrations a rather weak bluish fluorescence appears.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.22; H, 5.81.

The spectral curve of the hexane solution showed maxima at 222, 262, 272, 299, 305, 311, 325, 348, 365 mμ and minima at 241, 265, 293, 302, 307, 318, 343, 362 mμ.

When hydrogenated in the presence of PtO_2 the compound added within 24 hr. 9.7 H_2 (calcd. 9.0 H_2).

The 1,3,5-trinitrobenzene complex, obtained by mixing hot benzene solutions, melted sharply at 180–180.5°. Under the microscope thin yellow prisms were observed.

Anal. Calcd. for $C_{20}H_{14} + C_6H_3(NO_2)_3$: N, 8.99. Found: N, 9.29.

Acknowledgment.—The authors wish to thank Prof. A. J. Haagen-Smit, Mr. G. Swinehart and Dr. A. Elek for analyses.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Acetylenic Ethers. VI.[1] Phenylalkoxyacetylenes[2]

BY THOMAS L. JACOBS AND WILLARD R. SCOTT, JR.

RECEIVED JULY 31, 1953

Phenylmethoxyacetylene, $C_6H_5C{\equiv}COCH_3$, was synthesized by dehydrohalogenation of bromomethoxystyrene. This acetylenic ether polymerized readily, was easily hydrated in aqueous acid and reacted with methanolic potassium hydroxide yielding phenylacetic acid. Preliminary attempts were made to prepare the corresponding butyl and ethyl acetylenic ethers.

Several acetylenic ethers of the type $HC{\equiv}COR$ have been synthesized by dehydrohalogenation of alkoxyhaloethylenes, $HXC{=}CHOR$[3-9] and in a number of cases the acetylenic hydrogen in the ether has been replaced by an alkyl radical or some other group through the intermediate Grignard reagent, $ROC{\equiv}CMgBr$. No method has been devised for replacing an acetylenic hydrogen by an aryl group, and arylalkoxyacetylenes $ROC{\equiv}CAryl$ cannot be prepared in this way. The only such compound reported in the literature is phenylethoxyacetylene[10] which was believed to result from the action of sodamide in benzene on phenylketene diethyl acetal. This acetylenic ether was not

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[1] For paper V see T. L. Jacobs and W. P. Tuttle, Jr., THIS JOURNAL, **71**, 1313 (1949).

[2] Taken in part from a dissertation presented by Willard R. Scott, Jr., in partial satisfaction of the requirements for the degree Doctor of Philosophy, July, 1950. This work was supported in part by a research contract with the Office of Naval Research.

[3] M. Slimmer, *Ber.*, **36**, 289 (1903).

[4] T. L. Jacobs, R. Cramer and F. T. Weiss, THIS JOURNAL, **62**, 1849 (1940).

[5] T. L. Jacobs, R. Cramer and J. E. Hanson, *ibid.*, **64**, 223 (1942).

[6] A. E. Favorskiĭ and M. N. Shchukina, *Zhur. Obshcheĭ Khim.*, **15**, 385, 394 (1945); *C. A.*, **40**, 4347, 4657 (1946).

[7] D. A. van Dorp, J. F. Arens and O. Stephenson, *Rec. trav. chim.*, **70**, 289 (1951).

[8] M. F. Shostakovskii and F. P. Sidel'kovskaya, *Isvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 394, 641 (1950); *C. A.*, **45**, 2851, 8443 (1951).

[9] J. Queck, *Abhandl. brauschweig. wiss. Ges.*, **4**, 37 (1952).

[10] H. Scheibler, E. Marhenkel and R. Nikolic, *Ann.*, **458**, 21 (1927).