

b.p. 145.5–146.5°/9.2 mm.; $n_D^{25} = 1.4471$. Infrared spectrum: 3800 (NH), 2925 (—CH₂—), 1665 (—CONH—). The infrared spectrum in the finger-print region was distinctly different from that of *N*-*sec*-octylacetamide.

Hydrolysis of fraction IV. One gram of Fraction IV was heated with 80% sulfuric acid for 4 hr. at 100° and was then allowed to stand over the week end at room temperature. The solution was made alkaline with 30% sodium hydroxide, extracted with ether, dried with magnesium sulfate, and distilled. *sec*-Octylamine was isolated in ~20% conversion, b.p. 76–80°/20 mm. $[\alpha]_D^{25} = (+) 6.6$ (5.95% solution in benzene). Purity is thus ~76%.¹⁴

Displacement of sec-octyl isonitrile from complex. Complex I residue 2.9 g., 5 ml. of hydrogen cyanide, 5 ml. of methyl alcohol, and 100 ml. of acetonitrile were heated in an auto-

clave for 8 hr. at 120°. The acetonitrile was distilled, the residue was hydrolyzed with 1*N* hydrochloric acid, and was processed as described above. Only 20 mg. of the *sec*-octylamine was isolated. The 1.1% solution of the *sec*-octylamine in benzene had a rotation of $[\alpha]_D^{25} = (+) 3.05$. This experiment is not very conclusive because of the small amount of *sec*-octylamine isolated, but it appears that the alkylation proceeds with a concerted displacement.

Acknowledgment. The author wishes to thank Dr. G. R. Coraor for many helpful discussions and suggestions.

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The Catalytic Hydrogenation of Dibenz[*a,h*]anthracene¹

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Received December 12, 1960

Catalytic hydrogenation of dibenz[*a,h*]anthracene with platinum at atmospheric pressure proceeds as far as 1,2,3,4,1a,4a,5,6,8a,11a,12,13,8,9,10,11-hexadecahydrodibenz[*a,h*]anthracene. Seven intermediate hydrogenated products were isolated, three of them in more than one stereoisomeric form. They were 5,6-dihydro-, 1,2,3,4-tetrahydro-, 5,6,12,13-tetrahydro-, 1,2,3,4,12,13-hexahydro-, 1,2,3,4,8,9,10,11-octahydro-, 1,2,3,4,1a,4a,5,6-octahydro-, and 1,2,3,4,1a,4a,5,6,8,9,10,11-dodecahydrodibenz[*a,h*]anthracene. The yields ranged from 3% to 25% of the reacted dibenz[*a,h*]anthracene.

Following the study of the catalytic hydrogenation of benzo[*a*]pyrene,² with the object of investigating the carcinogenic and anti-carcinogenic properties of the products, a similar investigation of the catalytic hydrogenation of dibenz[*a,h*]anthracene was undertaken, with the same objective. A preliminary report of the biological activity of some of the hydrogenation products of dibenz[*a,h*]anthracene has been published.³

Some partially hydrogenated derivatives of dibenz[*a,h*]anthracene have been described, although none were prepared under the conditions of this investigation. The 7,14-dihydro compound has been prepared through the corresponding disodio compound⁴ and by hydrogenation with nickel under pressure.⁵ Cook reported the preparation of an octahydrodibenz[*a,h*]anthracene⁶ by reduction with sodium and amyl alcohol, although the structure of the compound was not determined at that time.

An octahydro derivative has also been prepared synthetically by reduction of bistetramethylene-anthraquinone (obtained by cyclization of vinylcyclohexane with 1,4-benzoquinone).⁷ This com-

pound, 1,2,3,4,8,9,10,11-octahydrodibenz[*a,h*]anthracene, had a melting point (196–197°) higher than that of Cook's compound (188–190°). One of the octahydrodibenz[*a,h*]anthracenes (IVa) prepared by catalytic hydrogenation (as described below) had a melting point very close to that of the octahydro compound prepared by synthesis,⁷ which would be expected to have an absorption spectrum similar to that of anthracene.

The hydrogenations of dibenz[*a,h*]anthracene to be described were carried out under the same conditions as were used for benzopyrene,² the catalyst being platinum. Several hydrogenations of dibenz[*a,h*]anthracene were carried out to various stages. Under these conditions, hydrogen was taken up until a hexadecahydro compound was formed, after which no further addition of hydrogen occurred, even after prolonged exposure to the gas. No perhydrodibenz[*a,h*]anthracene could be isolated and, apparently, reduction of the last aromatic ring was very difficult under these conditions. At all intermediate stages in the hydrogenation of dibenz[*a,h*]anthracene a mixture of several partially hydrogenated derivatives was present in the reaction mixture. Unchanged dibenz[*a,h*]anthracene was present after addition of four moles of hydrogen, but not after five moles of hydrogen had been taken up.

A tentative mechanism of addition of hydrogen to dibenz[*a,h*]anthracene (I) is shown in Fig. 1. The hydrogenated compounds were identified from

(1) This investigation was supported by Grant C-4249 of the National Institutes of Health, U. S. Public Health Service.

(2) W. Lijinsky and L. Zechmeister, *J. Am. Chem. Soc.*, **75**, 5495 (1953).

(3) P. Kotin, H. L. Falk, W. Lijinsky, and L. Zechmeister, *Science*, **123**, 102 (1956).

(4) W. E. Bachmann, *J. Org. Chem.*, **1**, 347 (1936).

(5) J. W. Cook, *J. Chem. Soc.*, 1592 (1933).

(6) J. W. Cook, *J. Chem. Soc.*, 489 (1931).

(7) H. J. Baeker and J. R. Van der Bij, *Rec. Trav. Chim.*, **62**, 561 (1943).

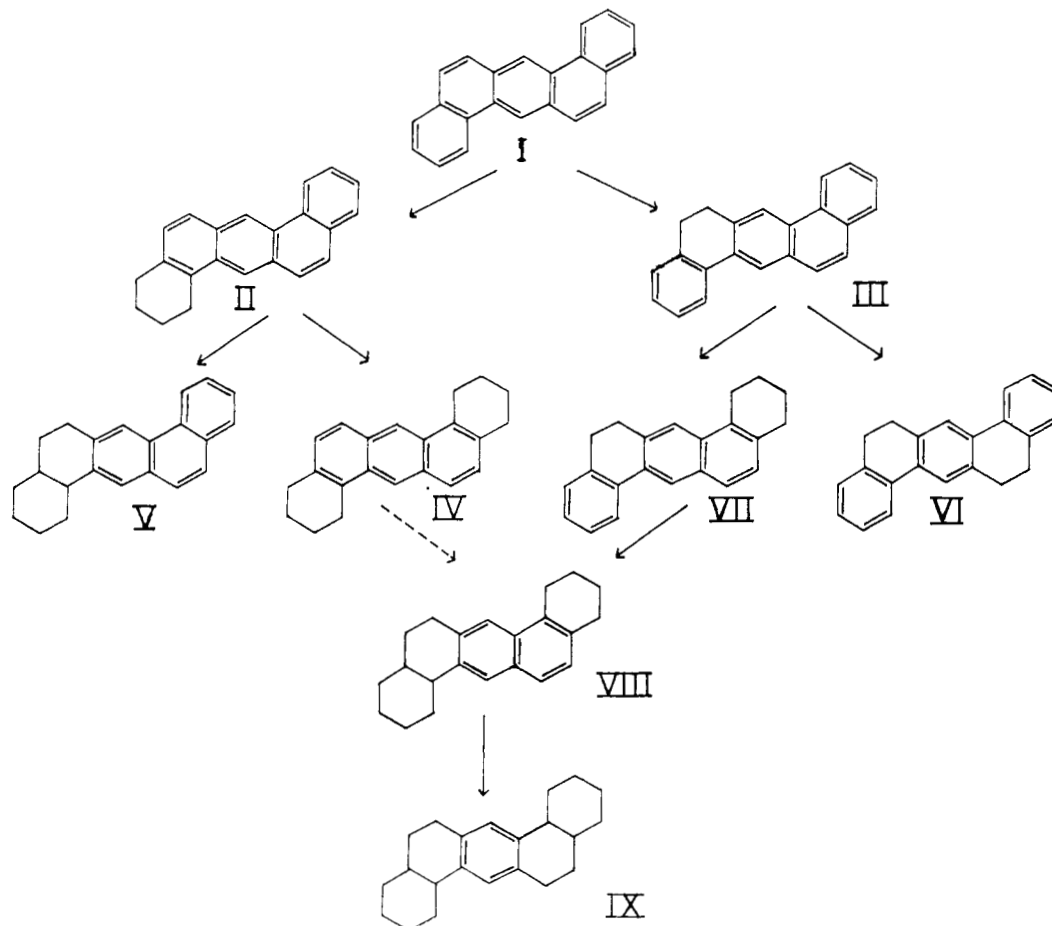


Fig. 1. Schematic presentation of catalytic hydrogenation of dibenz[*a,h*]anthracene

their absorption spectra, by analogy with those of known compounds.

7,14-Dihydrodibenz[*a,h*]anthracene was prepared by a modification of Bachmann's procedure.⁴ After chromatography the melting point (222.5–223.5°) was somewhat higher than that reported by Bachmann (218.5–219.5°), which, in turn, was considerably higher than that reported by Cook⁵ (196–198°). No product with the absorption spectrum of this compound (Fig. 2) was detected in any of the hydrogenated mixtures. Under the conditions described, addition of hydrogen in the 7,14-positions of dibenz[*a,h*]anthracene apparently did not occur. This fact made structural determinations of the hydrogenated derivatives somewhat easier, by reducing the number of possibilities.

It appeared that the 1,2,3,4-tetrahydro compound (II) was reduced almost as readily as dibenz[*a,h*]anthracene since, after addition of four moles of hydrogen, II could not be detected in the reaction mixture. Reasonable quantities of II could be prepared only by hydrogenating a large amount of dibenz[*a,h*]anthracene in small batches, until about two moles of hydrogen had been taken up and combining the products (which, at this stage, contained a large proportion of unchanged dibenz-

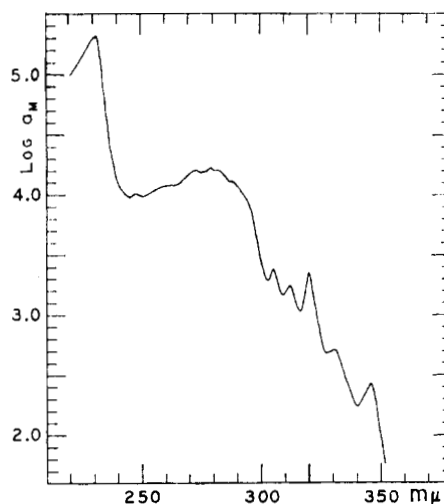


Fig. 2. Molar absorptivity spectrum of 7,14-dihydrodibenz[*a,h*]anthracene in isoctane

[*a,h*]anthracene). Compound II was identified as 1,2,3,4-tetrahydrodibenz[*a,h*]anthracene from the similarity of its absorption spectrum (Fig. 3) to that of benz[*a*]anthracene^{8a} and more closely to that of 8,9-cyclopentenobenz[*a*]anthracene.^{8b} A small quantity of a compound with an absorption

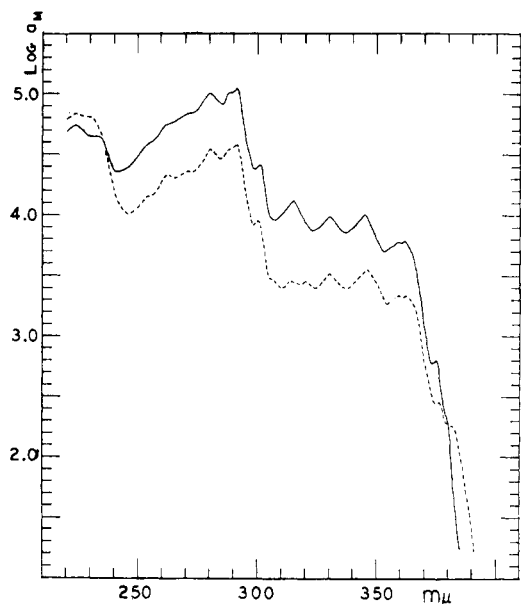


Fig. 3. Molar absorptivity spectra of 1,2,3,4-tetrahydrodibenz[*a,h*]anthracene in isoctane: ——— m.p. 211-212.5°, - - - - m.p. 208-209°

spectrum qualitatively identical to that of compound II was isolated from a fraction much less strongly adsorbed than the latter, by fractional crystallization followed by purification through the 2,4,7-trinitrofluorenone complex. This compound melted 3° below II and a mixture of the two exhibited depression of melting point. The melting points of the respective trinitrofluorenone complexes differed by 6° and the two complexes appeared different under the microscope. The molar absorptivity of the lower melting hydrocarbon was only one third that of the higher melting one. It seemed likely, therefore, that the two compounds were stereoisomers, produced through different intermediate complexes of dibenz[*a,h*]anthracene, hydrogen, and catalyst. This phenomenon has been discussed by Hadler⁹ in the case of hydrogenation of cholestene-4 and cholestene-5. The infrared spectra of the two compounds showed small but significant differences in the region of CH stretching frequencies (2800-3000 cm^{-1}) which is consistent with their being stereoisomers.¹⁰

In the early stages of the hydrogenation (two moles of hydrogen) a dihydrodibenz[*a,h*]anthracene was the major product, four to five times as much of this compound as of II being present. It was adsorbed on magnesia/Celite immediately below II (which was, in turn, immediately below dibenz[*a,h*]anthracene). The absorption spectrum

(8) R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley & Sons, Inc., New York, N. Y., 1951, (a) No. 499, (b) No. 514, (c) No. 382, (d) No. 538, (e) No. 388, (f) No. 362, (g) No. 171, (h) No. 195, (i) No. 216, and (j) No. 14.

(9) H. I. Hadler, *Experientia*, 11, 175 (1955).

(10) K. Lunde and L. Zechmeister, *Acta Chem. Scand.*, 8, 1421 (1954).

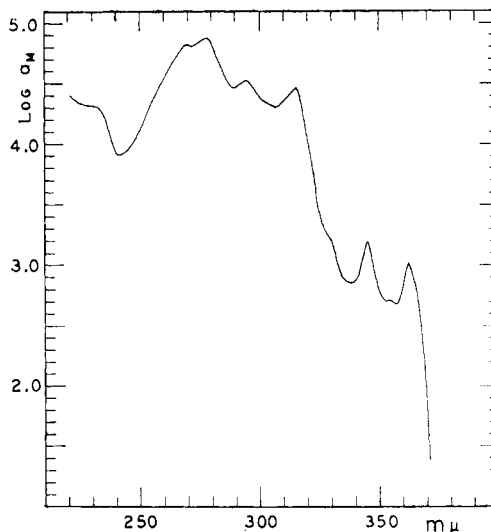


Fig. 4. Molar absorptivity spectrum of 5,6-dihydrodibenz[*a,h*]anthracene in isoctane

of this compound (Fig. 4) showed some resemblance to that of 2-phenylphenanthrene^{8c} and an even closer similarity to that of 2',1'-naphtho-1,2-fluorene,^{8d} and was quite different from the spectrum of 7,14-dihydrodibenz[*a,h*]anthracene. This compound (III) was assigned the structure 5,6-dihydrodibenz[*a,h*]anthracene.

When the products of hydrogenation (two to five moles of hydrogen) of dibenz[*a,h*]anthracene were adsorbed on magnesia/Celite, a blue fluorescent zone was observed below the 5,6-dihydro compound (III). This zone, on development with acetone-benzene-hexane, passed rapidly into the filtrate. The absorption spectrum of this fraction indicated that it was a mixture of compounds. This was confirmed by further chromatography on magnesia/Celite, which produced changes in the relative intensities of the absorption maxima, but could not resolve the mixture into its components. Such resolution was obtained by chromatography on silica gel/Celite, using benzene-hexane (1:19) as developer. A blue fluorescent band passed into the filtrate. The compound crystallized from the filtrate had an absorption spectrum (Fig. 5) very similar to that of anthracene^{8c} and qualitatively almost identical with that of a compound prepared by reduction of dibenz[*a,h*]anthracene with sodium in boiling amyl alcohol following the procedure of Cook.⁶ (This reduction also produced in addition to octahydrodibenz[*a,h*]anthracene a small quantity of 7,14-dihydrodibenz[*a,h*]anthracene, which was isolated through its trinitrofluorenone complex.) This compound (IVa) was, therefore, assigned the structure 1,2,3,4,8,9,10,11-octahydrodibenz[*a,h*]anthracene. Although the octahydro compound (IVa) prepared by catalytic hydrogenation had almost the same melting point as that prepared by sodium reduction, the melting point of a mixture of the two was considerably depressed. The molar

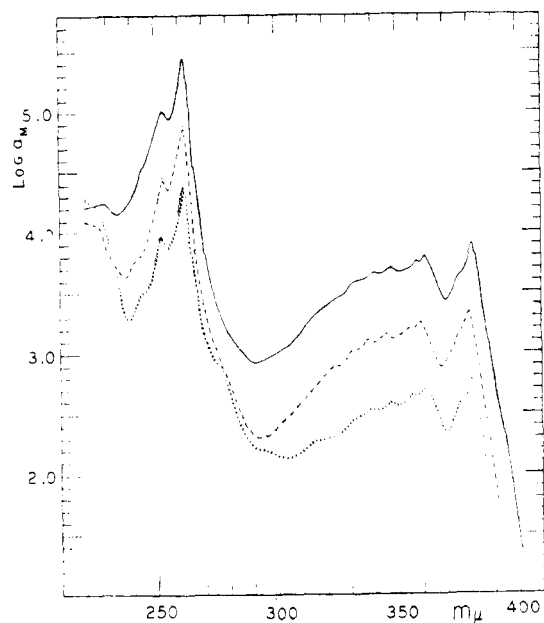


Fig. 5. Molar absorptivity spectra of 1,2,3,4,8,9,10,11-octahydrodibenz[*a,h*]anthracene in isoctane: ——— m.p. 196–197°, - - - - from olive green trinitrofluorenone complex, ····· from yellow trinitrofluorenone complex

absorptivity of the former compound (IVa) was about ten times that of the latter. The two compounds had different crystalline forms. The respective trinitrofluorenone complexes differed in color and melting point. As in the case of 1,2,3,4-tetrahydrodibenz[*a,h*]anthracene, the infrared spectra of the two octahydro compounds showed small differences. Therefore, these, too, are probably stereoisomers.

The material retained on the silica gel column after elution of compound IVa was itself eluted and rechromatographed on a small column of silica gel/Celite. Upon development with benzene-hexane (1:9) a blue fluorescent zone again passed into the filtrate; the material retained on the column was nonfluorescent. The crystalline material obtained from this filtrate had an absorption spectrum qualitatively identical with that of compound IVa. The melting point, however, was 20° below that of IVa. Although the sharpness of the melting point suggested that it was a pure compound, preparation of the trinitrofluorenone complex showed this to be untrue. Fractional crystallization of the complex from benzene-ethanol gave an olive-green first crop. From the yellow mother liquor a crop of much more soluble yellow crystals was obtained. The melting points of these two complexes were not markedly different, nor did they differ in crystal structure. The hydrocarbon was regenerated from each of the two complexes and crystallized. The two compounds had absorption spectra (Fig. 5) which differed only quantitatively, the molar absorptivity of that from the green trinitrofluorenone complex (IVb) being 3.5 times that from

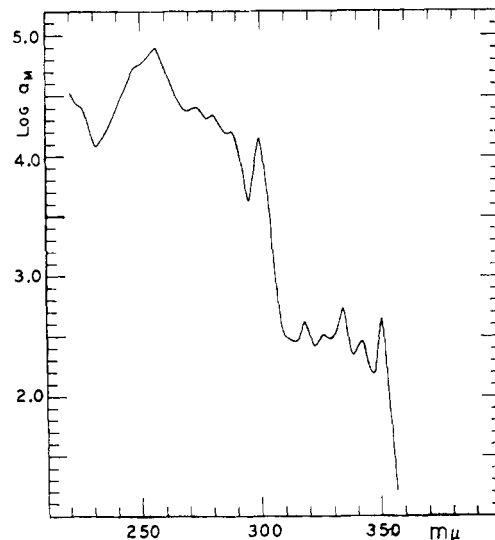


Fig. 6. Molar absorptivity spectrum of 1,2,3,4,1a,4a,5,6-octahydrodibenz[*a,h*]anthracene in isoctane

the yellow complex (IVc). The crystalline forms of the two hydrocarbons were very similar, as were their melting points. The infrared spectra, however, did show significant differences in the 2800 to 3000 cm^{-1} region, indicating that they were stereoisomers of 1,2,3,4,8,9,10,11-octahydrodibenz[*a,h*]anthracene (IV). It appeared, therefore, that three isomeric compounds of the above structure were produced by catalytic hydrogenation and a fourth by sodium/amyl alcohol reduction of dibenz[*a,h*]anthracene. They were all thermostable (subliming *in vacuo* unchanged). IVa and IVb could not be converted one into another by crystallization with seeding.

The mother liquor of the crystallization of IVa gave a yellow compound on addition of trinitrofluorenone. After recrystallization, this complex was decomposed by filtration through magnesia/Celite and the filtrate gave colorless crystals with an absorption spectrum (Fig. 6) reminiscent of that of phenanthrene and very similar to that of 1,2-cyclopentenophenanthrene.^{8f} The structure 1,2,3,4,1a,4a,5,6-octahydrodibenz[*a,h*]anthracene (V) was, therefore, assigned to this compound.

The material retained on the silica column after elution of the octahydro compounds was eluted with benzene and crystallized from benzene-hexane. The first crop of crystals had an absorption spectrum (Fig. 7) which could not be identified with that of any known polycyclic aromatic hydrocarbon. It was at first thought to be a peroxide, analogous to the peroxide obtained by filtration of 7,12-dimethylbenz[*a*]anthracene through alumina,¹¹ but analysis showed it to contain only carbon and hydrogen and to be a tetrahydrodibenz[*a,h*]anthracene. Since it could be prepared by catalytic hy-

(11) R. Sandin and L. F. Fieser, *J. Am. Chem. Soc.*, **62**, 3098 (1940).

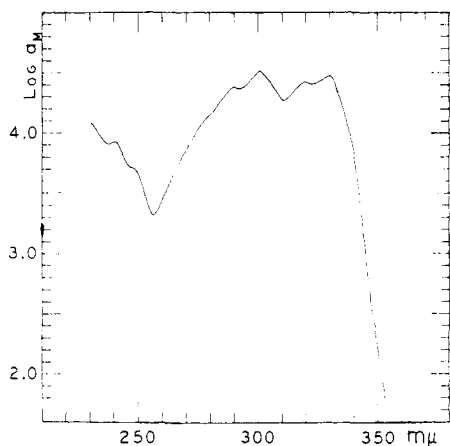


Fig. 7. Molar absorptivity spectrum of 5,6,12,13-tetrahydrodibenz[*a,h*]anthracene in isoctane

drogenation of the 5,6-dihydro compound (III), the structure 5,6,12,13-tetrahydrodibenz[*a,h*]anthracene (VI) was assigned to this compound. Although such a structure is very similar to that of *p*-terphenyl, the spectrum of the latter^{8g} was quite different from that of VI. This is probably a consequence of the restricted rotation of the three benzene rings in VI as compared with terphenyl.¹²

The mother liquor of the crystallization of compound VI was evaporated to a small volume and crystallized from benzene-ethanol. These crystals had a much lower melting point than VI and a spectrum (Fig. 8) very similar to that of 5,6-dihydroxy-5,6-dihydrobenz[*a*]anthracene¹³ prepared

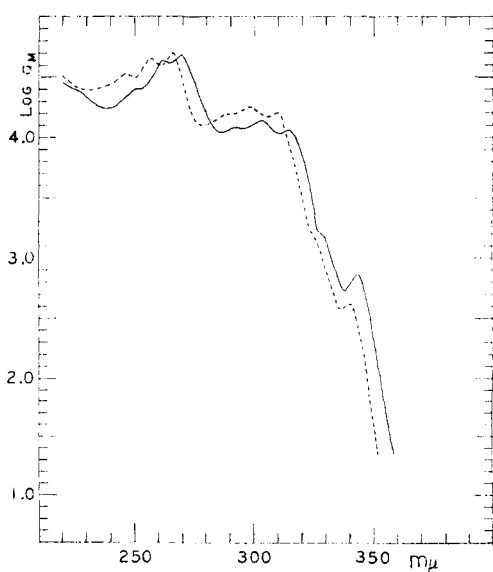


Fig. 8. Molar absorptivity spectra: — 1,2,3,4,12,13-hexahydrodibenz[*a,h*]anthracene in isoctane, - - - 5,6-dihydroxy-5,6-dihydrobenz[*a*]anthracene in ethanol

(12) M. T. O'Shaughnessy and W. H. Rodebush, *J. Am. Chem. Soc.*, **62**, 2906 (1940).

(13) Kindly supplied by Dr. E. Kaufmann of this department.

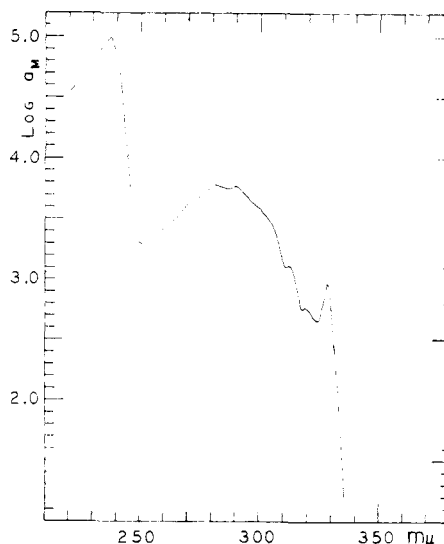


Fig. 9. Molar absorptivity spectrum of 1,2,3,4,1a,4a,5,6,8,9,10,11-dodecahydrodibenz[*a,h*]anthracene in isoctane

by oxidation of benz[*a*]anthracene with osmium tetroxide.¹⁴ The hydrogenated derivative of dibenz[*a,h*]anthracene was, therefore, assigned the structure 1,2,3,4,12,13-hexahydrodibenz[*a,h*]anthracene (VII). This compound, like VI, was produced by catalytic hydrogenation of 5,6-dihydrodibenz[*a,h*]anthracene.

Although some more saturated compounds than the above (II-VII) were present in the preparation described, their quantity was rather small and larger quantities for characterization were prepared by hydrogenation of dibenz[*a,h*]anthracene to a considerably further stage (6.5 moles of hydrogen).

After addition of five moles of hydrogen, the principal hydrogenated product was a low melting point compound which was best purified (after removal of the less saturated compounds IV and VI on magnesia) through the trinitrofluorenone complex. Trinitrofluorenone was added to the oily product dissolved in a small volume of benzene, ethanol added to the solution and the red solid was recrystallized from benzene-ethanol. The hydrocarbon was regenerated by passing the complex in benzene solution through a small column of magnesia/Celite. The compound which crystallized from the filtrate melted sharply and had an absorption spectrum (Fig. 9) reminiscent of that of naphthalene^{8h} and 1,2,3,4-tetrahydroanthracene.⁸ⁱ The same compound was produced by catalytic hydrogenation of VII and, therefore, the structure 1,2,3,4,1a,4a,5,6,8,9,10,11-dodecahydrodibenz[*a,h*]anthracene (VIII) was assigned to it. It is obvious that further hydrogenation of IV also gives rise to VIII.

Addition of 6.5 moles of hydrogen to dibenz[*a,h*]anthracene gave a product containing very little of

(14) J. W. Cook and R. Schoental, *J. Chem. Soc.*, 170 (1948).

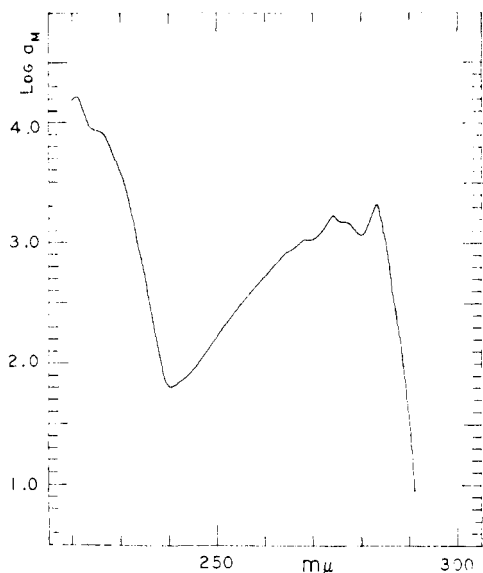


Fig. 10. Molar absorptivity spectrum of 1,2,3,4,1a,4a,5,6,8a,11a,12,13,8,9,10,11-hexadecahydrodibenz[*a,h*]anthracene in isoctane

compounds II to VII. These were removed by passage through magnesia/Celite. The filtrate was collected in two portions, the first after hexane washing and the second after washing with benzene-hexane (1:19). The latter fraction consisted mainly of compound VIII. The solid obtained by evaporation of the hexane eluate had a much higher melting point than that of VIII and was also purified through the trinitrofluorenone complex. This complex was a bright yellow substance, less soluble than the trinitrofluorenone complex of VIII and with a higher melting point. The hydrocarbon was regenerated and the absorption spectrum (Fig. 10) of this compound (IX) was very similar to that of 1,2,3,4,5,6,7,8-octahydroanthracene.^{8j} It seemed likely that the structure was that of 1,2,3,4,1a,4a,5,6,8a,11a,12,13,8,9,10,11-hexadecahydrodibenz[*a,h*]anthracene. This structure was supported by the further hydrogenation of VI which gave IX as the sole product. Compound IX, together with VI and VII, was produced by hydrogenation of 5,6-dihydrodibenz[*a,h*]anthracene (III) and these were the only compounds isolated from the reaction mixture.

Exhaustive catalytic hydrogenation of dibenz[*a,h*]anthracene (until no further uptake of hydrogen occurred) produced a crystalline material with a wide melting point range (115–150°). Addition of trinitrofluorenone to this product gave a yellow complex which, after recrystallization, melted sharply. Decomposition of the complex gave a hydrocarbon with an absorption spectrum identical with that of IX, but of considerably lower melting point. The infrared spectra of the two compounds showed small differences. It was concluded that these were stereoisomers of the hexadecahydro compound (IX).

EXPERIMENTAL

Materials and procedure. The platinum oxide catalyst was prepared according to the method of Voorhees and Adams.¹⁵ The adsorbents were a 2:1 mixture of magnesium oxide (Seasorb No. 43 magnesia; Food, Machinery and Chemical Corp.) with Celite (No. 545; Johns-Manville Co.) and a 2:1 mixture of silica gel (grade 922, through 200 mesh, Davison Chemical Co.) with Celite. Columns were packed with dry adsorbent and run under reduced pressure. Fractions were cut from the extruded adsorbent, eluted with acetone-ethanol (5:1) and the eluted material transferred to benzene according to LeRosen.¹⁶ Evaporations were carried out under nitrogen. Fluorescence was observed using a Mineralight Model SL 3660, long wave (Ultra Violet Products, Inc., San Gabriel, Calif.). Melting points were taken in an electrically heated block and are corrected. Ultraviolet absorption spectra were taken in 2,2,4-trimethylpentane (isooctane) in a Beckman DK-1 instrument. Infrared spectra were taken in carbon tetrachloride in a Beckman IR-7 instrument.

Dibenz[*a,h*]anthracene (white, puriss) m.p. 267–268° was obtained from L. Light and Co., England, and was sufficiently pure for use without further treatment; 2,4,7-trinitrofluorenone was from Eastman Kodak Co.

Hydrogenations were conducted at room temperature and atmospheric pressure in 100 ml. of a 1:1 mixture of 2,2,4-trimethylpentane and glacial acetic acid. The ratio of dibenz[*a,h*]anthracene to catalyst was 5:1. The catalyst was reduced to platinum *in situ* before addition of the hydrocarbon, which was contained in a platinum crucible suspended within the hydrogenation flask.

Trinitrofluorenone complexes were prepared by mixing hot concentrated solutions of 2,4,7-trinitrofluorenone and the hydrocarbon in benzene and allowing to cool. If crystallization did not occur, ethanol was added. The complexes were recrystallized from benzene-ethanol, except where otherwise indicated. The hydrocarbon was recovered from the complex by filtration of the latter in benzene-hexane solution through a small column of magnesia/Celite, trinitrofluorenone being retained on the adsorbent.

Crystallizations were made from a single solvent (benzene or hexane) or by dissolving the compound in a minimum of hot benzene and adding ethanol dropwise until crystals appeared.

Samples for analysis¹⁷ and absorptivity determinations were sublimed *in vacuo* at 250°.

Preparation of hydrogenation products. Eight grams of dibenz[*a,h*]anthracene were hydrogenated in 400 mg. portions for approximately 48 hr., by which time an average 2 moles of hydrogen were taken up. The resulting hydrogenation products were combined, the isoctane solution washed free of acid with water and, after drying, evaporated under nitrogen to dryness. The residue was dissolved in 500 ml. of hot benzene. On cooling, a large crop of crystals was obtained. These were filtered off and again crystallized from hot benzene. The crystalline material (4.6 g.) was unchanged dibenz[*a,h*]anthracene.

The combined mother liquors were dissolved in 200 ml. of benzene-hexane (1:1) and chromatographed on a 28 × 8 cm. column of magnesia/Celite, the developer being acetone-benzene-hexane (1:1:3). The lower of four fluorescent zones passed into the filtrate with 1.5 l. of developer. Fractions were cut from the column as follows (first figure on left designates thickness of zone in mm.; figure on right shows sequence of fractions; "fl." = fluorescent in ultraviolet

(15) V. Voorhees and R. Adams, *J. Am. Chem. Soc.*, **44**, 1397 (1922).

(16) A. L. LeRosen, *Ind. Eng. Chem., Anal. Ed.*, **14**, 165 (1942).

(17) Analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

light): 80 blue fl., 1; 10 interzone; 50 intense blue fl., 2; 10 interzone; 70 blue fl., 3; 20 nonfluorescent.

Fraction 1 was unchanged dibenzanthracene—350 mg.

The fluorescent filtrate was evaporated to dryness, the residue (2.7 g.) dissolved in 100 ml. of benzene-hexane (1:9) and rechromatographed on a 28 × 8 cm. column of silica gel/Celite. Hexane (1.5 l.) eluted negligible material. Using benzene-hexane (1:10; 4 l.) as developer, the appearance of the chromatogram was as follows: 20 empty zone; 20 blue fl., 4; 130 non fl., 5; 60 blue fl., 6; 20 non-fl.; Filtrate: 2 l. blue fl., 7; 2 l. nonfl., 8.

Fraction 4 was spectroscopically identical with 3. The two were combined. Fraction 6 was rechromatographed on a 26 × 6 cm. column of silica gel/Celite. 1 liter of benzene-hexane (1:9) produced the following: 120 empty zone; 125 non-fl., 9; filtrate: 1 l. blue fl., 10.

1,2,3,4-Tetrahydrodibenz[a,h]anthracene (II). (a) Fraction 2 was rechromatographed on a 26 × 6 cm. column of magnesia/Celite and developed with 1 l. of acetone-benzene-hexane (1:1:3). The major blue fluorescent zone was cut out, eluted, and crystallized from benzene-ethanol. Yield of crude material—202 mg. After recrystallization twice from benzene-ethanol, colorless crystals, m.p. 210–212°. Final purification was achieved by decomposition of the trinitrofluorenone complex and crystallization of the fluorescent material in the filtrate from benzene-ethanol. Yield, 105 mg.; m.p. 211–212.5°; colorless flat plates.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.56; H, 6.44. Found: C, 93.27; H, 6.39.

μ_M at 291 $m\mu$ = 103,000. Infrared bands at 2840, 2862, 2939, 3050 cm^{-1} .

Recrystallization of the trinitrofluorenone complex was very difficult owing to its low solubility; m.p. 237.5–239°, clusters of brown hair-like crystals.

(b) From the mother liquor of fraction 5, after crystallization of hexahydrodibenz[a,h]anthracene VII (described later) a compound with a spectrum qualitatively the same as that of 1,2,3,4-tetrahydrodibenz[a,h]anthracene IIa (above) was isolated. A trinitrofluorenone complex was prepared and the hydrocarbon regenerated. The crystalline solid (28 mg.) was crystallized from benzene-ethanol. Yield, 16 mg.; m.p. 208–209°; colorless irregular flat plates. A mixture with compound IIa melted at 204–209°.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.56; H, 6.44. Found: C, 93.18; H, 6.77.

μ_M at 291 $m\mu$ = 37,700. Infrared bands at 2868, 2942, 3057 cm^{-1} . The trinitrofluorenone complex formed brownish yellow needles from benzene, m.p. 231.5–233°.

5,6-Dihydrodibenz[a,h]anthracene (III). Fraction 3 (combined with 4) was rechromatographed on a 26 × 6 cm. column of magnesia/Celite and developed with 800 ml. of acetone-benzene-hexane (1:1:8). The large blue fluorescent zone (15 cm.) was separated from the minor zones, eluted and evaporated to dryness. Yield of crude material—530 mg. After crystallization twice from benzene-ethanol, colorless crystals were obtained, m.p. 194–195°. Yield 380 mg.; colorless flat plates.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.22; H, 5.78. Found: C, 94.22; H, 5.71.

The trinitrofluorenone complex was recrystallized from benzene, m.p. 186–186.5°, orange-red needles.

1,2,3,4,8,9,10,11-Octahydrodibenz[a,h]anthracene (IV). (a) Filtrate 7 was evaporated to dryness (residue 390 mg.) and crystallized from benzene-ethanol, giving 177 mg. of colorless crystals, m.p. 189–193°. After recrystallization from the same solvent, 162 mg., m.p. 196–197°, colorless prisms.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.25; H, 7.75. Found: 92.64; H, 7.66.

μ_M at 262 $m\mu$ = 273,000. Infrared bands at 2845, 2872, 2889, 2945, 3060 cm^{-1} . The trinitrofluorenone complex was recrystallized from benzene; clusters of gray needles, m.p. 234–235°.

(b) Filtrate 10 was evaporated to dryness, leaving 320 mg. of crystalline solid. This was crystallized twice from

benzene-ethanol, yielding 126 mg. of colorless flat plates, m.p. 174.5–176°. Mixing of benzene solutions of this substance and of trinitrofluorenone gave olive-green needles, m.p. (after recrystallization) 218–219°. The mother liquor was yellow and deposited yellow crystals on cooling.

Decomposition of the trinitrofluorenone complex and crystallization of the hydrocarbon from benzene-ethanol, yielded 70 mg. of colorless crystals, m.p. 176.5–177.5°; flat plates.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.25; H, 7.75. Found: C, 91.75; H, 8.17.

μ_M at 262 $m\mu$ = 72,600. Infrared bands at 2850, 2872, 2890, 2945, 3040 cm^{-1} .

(c) The yellow trinitrofluorenone complex from IVb was recrystallized from benzene-ethanol; m.p. 208–209°, greenish yellow needles. The hydrocarbon was regenerated and crystallized from benzene-ethanol; yield, 40 mg., colorless flat plates, m.p. 176–177°.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.25; H, 7.75. Found: C, 91.64; H, 8.40.

μ_M at 262 $m\mu$ = 21,200. I.R. bands at 2818, 2840, 2861, 2939, 3017, 3036, 3068 cm^{-1} .

1,2,3,4,1a,4a,5,6-Octahydrodibenz[a,h]anthracene (V). The mother liquor of the crystallization of the octahydrodibenz[a,h]anthracene (IVa) m.p. 196–197°, was evaporated to dryness and mixed in benzene solution with trinitrofluorenone in benzene. An orange-yellow precipitate formed on addition of ethanol and melted at 181.5–183°. After recrystallization from benzene-ethanol, clusters of yellow needles were obtained, m.p. 184.5–186°. The complex was decomposed on magnesia/Celite, the filtrate evaporated to dryness and the solid (m.p. 99–102°) recrystallized from benzene-ethanol. Yield, 100 mg.; m.p. 106.5–107.5°; colorless long plates or prisms.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.25; H, 7.75. Found: C, 91.75; H, 8.01.

5,6,12,13-Tetrahydrodibenz[a,h]anthracene (VI). Fraction 5 was crystallized from benzene-hexane, giving 220 mg. of pale yellow crystals, m.p. 183.5–185.5°. After recrystallization from the same solvent, colorless crystals were obtained, m.p. 193.5–194.5°. Yield, 170 mg.; triangular flat plates.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.56; H, 6.44. Found: C, 93.10; H, 6.66. No trinitrofluorenone complex could be prepared.

1,2,3,4,12,13-Hexahydrodibenz[a,h]anthracene (VII). The mother liquor from the crystallization of 5,6,12,13-tetrahydrodibenz[a,h]anthracene (VI) was crystallized from benzene-ethanol (the final mother liquor contained IIb) and the crystals combined with fraction 9 and with the mother liquor of the crystallization of IVb from filtrate 10 (qualitatively all three were spectroscopically identical). The total crude material was 574 mg., m.p. 135–138°. This was recrystallized from benzene-hexane (first crop, m.p. 130–150° discarded) and then from benzene-ethanol. Yield, 340 mg.; m.p. 140–141°; irregular flat plates.

Anal. Calcd. for $C_{22}H_{22}$: C, 92.95; H, 7.05. Found: C, 92.49; H, 7.47. The trinitrofluorenone complex was recrystallized from benzene-ethanol. Red-brown needles, m.p. 188–189°.

1,2,3,4,1a,4a,5,6,8,9,10,11-Dodecahydrodibenz[a,h]anthracene (VIII). Dibenz[a,h]anthracene (1.3 g.) was hydrogenated in 100 ml. of isoctane-acetic acid until approximately 6.5 moles of hydrogen had been absorbed. The product was transferred to benzene as described, evaporated to a small volume and chromatographed on a 28 × 8 cm. column of magnesia/Celite. The column was developed with 1500 ml. of hexane, followed by 1500 ml. of hexane-benzene (19:1). The appearance of the chromatogram was as follows: 10 mm. nonfl., 60 mm. blue fl., 190 mm. nonfl., filtrate 1.5 l., 11, 1.5 l., 12. The hexane-benzene filtrate (11) was combined with the material eluted from the 190 mm. zone (the two were spectroscopically similar). The hexane filtrate (12) was collected separately. The material eluted from the 60 mm. zone was crystallized from benzene-ethanol

and yielded 163 mg. of octahydro compound, m.p. 196–197° (IVa). The mother liquor contained about 100 mg. of hexahydrodibenz[*a,h*]anthracene (VII).

Filtrate 11 was evaporated to dryness and cooled. The crystalline residue weighed 560 mg. This was crystallized from benzene-hexane-ethanol. Yield, after three crystallizations, 320 mg., m.p. 95.5–96.5°, colorless long thin prisms.

Anal. Calcd. for C₂₂H₂₈: C, 90.97, H, 9.03. Found: C, 90.60, H, 9.16.

A further crop of the same compound was prepared from the mother liquor by decomposition of the purified trinitrofluorenone complex. The trinitrofluorenone complex was recrystallized from benzene-ethanol, red needles, m.p. 126.5–127.5°.

*1,2,3,4,1a,4a,5,6,8a,11a,12,13,8,9,10,11-Hexadecahydrodibenz[*a,h*]-anthracene (IX).* (a) Hexane filtrate 12 (above) was evaporated to dryness. The solid residue weighed 450 mg. Fractional crystallization from a variety of solvents failed to produce material with a sharp melting point, 247 mg. from benzene-ethanol melted at 114–120°, after recrystallization, m.p. 114–150°.

A trinitrofluorenone complex was prepared. A bright yellow precipitate appeared on cooling the benzene solution. A further crop of yellow crystals was obtained by adding ethanol to the mother liquor. The combined crystals were recrystallized from benzene-ethanol, m.p. 170.5–172°, yellow prisms.

The yellow complex was decomposed on a 24 × 4.5 cm. column of magnesia/Celite and the colorless filtrate evaporated to dryness. After crystallization from benzene-ethanol, yield, 180 mg.; m.p. 178.5–180.5°, long rectangular plates.

Anal. Calcd. for C₂₂H₂₆: C, 89.80, H, 10.20. Found: C, 89.92, H, 10.30. Infrared bands at 2875, 2940, 3002, 3123 cm.⁻¹.

(b) Dibenz[*a,h*]anthracene (337 mg.) was hydrogenated until no further hydrogen was taken up (the product of 5 days hydrogenation was rehydrogenated with a fresh batch of catalyst). The product (expected to be the perhydro compound) was crystalline and melted at 110–130°. After recrystallization from hexane the melting point was 115–150°. Trinitrofluorenone complex, yellow triangular prisms, m.p. 171–172°. The trinitrofluorenone complex was decomposed and the hydrocarbon crystallized from benzene-ethanol, yield, 80 mg., m.p. 116–117°.

Anal. Calcd. for C₂₂H₂₆: C, 89.80, H, 10.20. Found: C, 89.64, H, 10.18. Infrared bands at 2866, 2935, 2997, 3118 cm.⁻¹.

*7,14-Dihydrodibenz[*a,h*]anthracene.* About 0.5 g. of sodium was melted under xylene in a stoppered flask and vigorously shaken to pulverize the metal. After cooling, the xylene was decanted and 100 ml. of ether added, together with 107 mg. of dibenz[*a,h*]anthracene in 20 ml. benzene. The solution was stirred magnetically for 12 hr., by which time the color had changed from yellow to dark blue-green. Methanol, 50 ml., was added to the solution, the color becoming light green. Benzene was added, the water-soluble materials washed out and the benzene solution evaporated to a small volume. This was chromatographed on a 20 × 3.5 cm. column of magnesia/Celite, with hexane-benzene-acetone (2:1:1) as developer. A small blue fluorescent zone appeared below the major blue fluorescent zone (which was unchanged dibenz[*a,h*]anthracene) and passed into the filtrate. The residue after evaporation of the filtrate—35 mg.—was crystallized from benzene-hexane-ethanol; yield, 26 mg.; m.p. 222.5–223.5°, colorless rectangular flat plates.

Anal. Calcd. for C₂₂H₁₆: C, 94.22, H, 5.78. Found: C, 93.53, H, 6.19.

The trinitrofluorenone complex was recrystallized from benzene, m.p. 257–259°, clusters of hair-like orange needles.

*Sodium-alcohol reduction of dibenz[*a,h*]anthracene.* Dibenz[*a,h*]anthracene (200 mg.) was dissolved in 100 ml. of *n*-amyl alcohol, heated in an oil bath. Approximately 10 g. of clean sodium were added slowly in small pieces. The solution became yellow and eventually boiled. After dissolution of all the sodium, the solution was cooled, benzene added, followed by water and the water-soluble materials washed out. The benzene solution was diluted with hexane and chromatographed on a 24 × 4.5 cm. column of magnesia/Celite, the developer being acetone-benzene-hexane (2:1:7). No fluorescent zone could be seen. The filtrate was evaporated to dryness leaving a yellow solid. Fractional crystallization gave two products (a) 55 mg. prisms, m.p. 201–207°, after purification through the orange trinitrofluorenone complex, 13 mg., m.p. 208–214°, colorless needles, with a spectrum identical with that of 7,14-dihydrodibenz[*a,h*]anthracene. (b) 66 mg., forming a brown trinitrofluorenone complex, which, after recrystallization, gave green needles and prisms, m.p. 214.5–216.5°. The hydrocarbon was regenerated, 28 mg., m.p. (after recrystallization) 192–194°, colorless flat plates. The absorption spectrum was qualitatively very similar to that of 1,2,3,4,8,9,10,11-octahydrodibenz[*a,h*]anthracene (IV) μ_M at 261 μ = 28,600. Infrared bands at 2840, 2862, 2888, 2933, 3035 cm.⁻¹

CHICAGO, ILL.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION OF G. D. SEARLE AND Co.]

The Use of Sodium Metal in the Birch Reduction of Aromatic Compounds¹

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Received February 23, 1961

Contrary to the reports of previous investigators, Birch reductions of estradiol derivatives and other high molecular weight, relatively insoluble phenolic ethers can be effected in good yields with sodium. Suitable experimental conditions are described. Iron salts have been found to catalyze strongly the reaction between sodium and alcohols in liquid ammonia; the corresponding reaction between lithium and alcohols is much less strongly catalyzed by iron. In view of the common occurrence of colloidal iron compounds in commercial ammonia, these findings probably account for the failures of previous investigators to effect Birch reductions efficiently with sodium in contrast to the successful use of lithium.

In 1937 Wooster² reported that aromatic compounds are reduced by sodium and a proton donor in liquid ammonia solution. A. J. Birch greatly extended Wooster's observations and, as a result, the so-called Birch reduction has found considerable utility in synthetic organic chemistry.³ Birch

established that the reduction proceeds predominantly by the addition of hydrogen to afford

(1) Presented at the 126th Meeting of the American Association for the Advancement of Science, Chicago, Ill., December 1959.