The alkaloid yields a methiodide, m.p. 183°, which does not depress the melting point of that prepared by exhaustive methylation of 5-methoxytryptamine.[7] The methiodide samples are identical by infrared spectroscopy.

Bufotenine from Piptadenia colubrina. A 2.26-kg. sample of ground seeds of *Piptadenia colubrina*[13] was extracted continuously with ethanol until exhausted of alkaloids. The alcoholic extract was evaporated to dryness and partitioned between 500 ml. of 5% aqueous ammonia and 500 ml. of chloroform. The layers were separated and the ammoniacal solution was extracted six times with 300-ml. portions of chloroform. The chloroform solutions were combined, concentrated to 1 l. and extracted five times with 350 ml. portions of 5% hydrochloric acid. Emulsions formed which were broken by centrifugation. The combined acid solutions were made basic with concentrated aqueous ammonia and extracted eight times with 300-ml. portions of chloroform. Evaporation of the chloroform solutions to dryness left 74 g. of total bases in the form of a solid brown resin.

The crude bases were powdered and boiled thoroughly with ethyl acetate. Insoluble black material was removed by filtration. The ethyl acetate solution was poured onto a column of alumina and the alkaloids were eluted by repeated washing with ethyl acetate. Dark-colored materials remained adsorbed on the column. The ethyl acetate eluates were concentrated and yielded 47 g. (2.1% yield) of bufotenine, m.p. 146–147°. The alkaloid gave no depression of melting point upon admixture with an authentic specimen of bufotenine obtained from the Upjohn Co., Kalamazoo, Mich. The two samples were spectrally identical.

N,N-Dimethyltryptamine from Mimosa hostilis. A 2.7-kg. sample of ground roots of *Mimosa hostilis*[14] was extracted continuously with ethanol until the marc was exhausted of alkaloids. The alcohol was removed and the residue stirred with 500 ml. of 5% aqueous ammonia and 2 l. of chloroform. The layers were separated by centrifugation and an interphase was extracted several more times with aqueous ammonia and chloroform until it no longer contained alkaloids. The combined aqueous solutions were extracted three additional times with 1 l. portions of chloroform. The chloroform solutions were combined, concentrated, and extracted with 2% hydrochloric acid until the acid solutions no longer gave positive tests with Mayer's reagent. The combined acid solutions (3 l.) were adjusted to *p*H 9 with concentrated aqueous ammonia and extracted three times with 500-ml. portions of chloroform. Emulsions were separated by centrifugation. The chloroform solutions were dried over magnesium sulfate and evaporated to dryness to give 18.5 g. of crude brown alkaloid.

Paper chromatography of the crude material on Whatman 3MM paper using 10:1:10 *t*-amyl alcohol:formic acid:water showed a single alkaloid, R_f 0.78.

A 12.0 g. sample of the total alkaloid was dissolved as completely as possible in boiling ether and filtered to remove black resinous matter. The ethereal filtrate was evaporated to dryness and the residue dissolved in 30 ml. of methanol. A solution of 15 g. of picric acid in 75 ml. of methanol was added to the alkaloidal solution and a crystalline picrate separated. This was filtered and dried to give 21.9 g. of picrate, m.p. 168–170°. Three crystallizations from benzene gave 16.9 g. of first crop material, m.p. 171–172°, and 3.8 g. of second crop material, m.p. 169–171°.

A 10 g. sample of the picrate was converted to the free base, which crystallized from hexane containing a little ethyl acetate to give 3.3 g. of *N,N*-dimethyltryptamine, m.p. 48–49°.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found. C, 76.88; H, 8.83; N, 14.71.

Based on the formula $C_{12}H_{16}N_2$ for the alkaloid, the combined weight of first and second crops of the aforementioned picrate derived from 65% of the total bases corresponds to a yield of 0.57%.

When warmed with methyl iodide in ethereal solution, the alkaloid yielded a crystalline methiodide which, upon recrystallization from ethanol, melted at 215–216°.

PHILADELPHIA, PA.

[CONTRIBUTION FROM CENTRAL EXPERIMENT STATION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

Selective Hydrogenation of Polynuclear Aromatic Hydrocarbons

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It has been found that dicobalt octacarbonyl, in the presence of carbon monoxide and hydrogen, functions as a selective homogeneous hydrogenation catalyst for polynuclear aromatic hydrocarbons. Isolated benzene rings are stable in this system. Naphthalenes are slowly reduced to tetralins. Linearly condensed compounds, such as anthracene, are readily hydrogenated at the meso positions. Phenanthrene-type compounds are reduced very slowly at 200° to dihydro derivatives. More highly condensed systems are reduced to yield phenanthrene derivatives. In most cases, only one reduction product is obtained. The system provides a convenient synthetic method for preparing certain hydrogenated derivatives of polynuclear aromatic compounds.

Discovery of the hydroformylation reaction by Roelen[1] during World War II led to investigation of the reaction of various types of olefinic substances with carbon monoxide and hydrogen in the presence of a cobalt carbonyl. Since the 9,10-double bond in phenanthrene possesses considerable olefinic character, Adkins and Krsek[2] attempted to hydroformylate this compound at 125°, but no reaction was observed at this temperature. Wender, Levine, and Orchin[3] treated phenanthrene with carbon monoxide and hydrogen in the presence of a cobalt catalyst at a higher temperature and found that this compound was slowly hydrogenated. After 2 hr. at 180–185°, a 7% yield of 9,10-dihydrophenanthrene and a 1% yield of 1,2,3,4-tetrahydrophenanthrene were obtained; 81% of the starting compound was recovered unchanged.

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(1) O. Roelen, U.S. Patent **2,327,066**, Aug. 17, 1943.

(2) H. Adkins and G. Krsek, *J. Am. Chem. Soc.* **71**, 3051 (1949).

(3) I. Wender, R. Levine, and M. Orchin, *J. Am. Chem. Soc.*, **72**, 4375 (1950).

TABLE I

HYDROGENATION OF POLYCYCLIC AROMATIC HYDROCARBONS[a]

Compound	Moles	$Co_2(CO)_8$, G.	Temp.	Initial Pressure of 1:1 H_2/CO P.S.I.G.	Products[b]	Yield, %	Recovered starting material, %
Naphthalene[c]	0.195	2.5	200	3100	Tetralin	16[d]	84[d]
2-Methylnaphthalene[c]	.49	6.5	200	3500	Methyltetralins[e]	43[d]	42[d]
1,1-Dinaphthyl	.002	1.0	200	3500			95
Acenaphthene	.032	2.5	200	3500	2a,3,4,5-Tetrahydroacenaphthene[f]	45	45
Fluorene	.012	1.0	200	3600			96
Anthracene	.56	2.0	135	2900	9,10-Dihydroanthracene	99	1
Phenanthrene	.028	2.1	200	3500	Di- and Tetra-hydrophenanthrene	8	92
Naphthacene	.012	2.0	140	3000	5,12-Dihydronaphthacene[g]	70	30
Chrysene	.004	3.4	150	3500			98
Chrysene	.004	2.0	200	3000	5,6-Dihydrochrysene[h]	24	56
Fluoranthene	.005	1.4	200	3200	1,2,3,10b-Tetrahydrofluoranthene[i]	54	35
Triphenylene	.002	3.7	200	3200			98
Pyrene	.005	1.9	150	3600			94
Pyrene	.005	1.5	200	3000	4,5-Dihydropyrene	69	17
Perylene	.002	2.0	150	3000	1,2,3,10,11,12-Hexahydroperylene[j]	72	18
Coronene	.0007	1.3	200	2800			75

[a] Except where noted, 70–90 ml. of benzene was used as solvent. [b] Products identified by ultraviolet absorption spectra; except for the compounds indicated, the comparison spectra were those given by R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley & Sons, Inc., New York, N. Y., 1951. [c] No solvent used. [d] Yields based on mass spectral analysis. [e] No attempt made to distinguish whether one or both of the isomeric 2-methyltetralins formed. [f] Ultraviolet spectrum, W. S. Johnson and H. J. Glenn, *J. Am. Chem. Soc.* **71**, 1087 (1949). [g] Ultraviolet spectrum, E. Clar, *Ber.* **75**, 1271 (1942). [h] Ultraviolet spectrum, S. E. Hunt and A. S. Lindsey, *J. Chem. Soc.* **1958**, 2227. Also identified by chromic acid oxidation to chrysenequinone. [i] Ultraviolet spectrum, *Catalog of Ultraviolet Spectral Data of API Research Project 44*, Carnegie Institute of Technology, Pittsburgh, Pa., #548. [j] Ultraviolet spectrum, Hua-Chih and Conrad-Billroth, *Z. physik. Chem.* B **20**, 333 (1933).

Similarly, when 1-hydroxymethylnaphthalene was treated, small amounts of 1- and 5-methyltetralins were found.[4]

The present investigation started with the unexpected discovery that anthracene, the linear isomer of phenanthrene, is hydrogenated in the presence of synthesis gas at comparatively low temperatures (135°) to give 9,10-dihydroanthracene in quantitative yield. This encouraging result led to investigation of the reaction of other polynuclear hydrocarbons with carbon monoxide and hydrogen under hydroformylation conditions; the results are summarized in Table I.

EXPERIMENTAL

Reagents. Naphthacene was obtained from Organic Specialties, Inc.; perylene and triphenylene were from K. & K. Laboratories, Inc.; naphthalene, phenanthrene, anthracene, chrysene, and acenaphthene were Eastman Kodak White Label chemicals; coronene was from Badische-Anilin und Soda Fabrik.[5] Pyrene, fluorene, and fluoranthene were commercial-grade chemicals from Reilly Tar & Chemical Corp. and were purified before use. The 1,1-dinaphthyl was prepared in these laboratories.[6] Dicobalt octacarbonyl was prepared by the reaction of synthesis gas on cobalt carbonate in petroleum ether.[7] The equimolar mixture of carbon monoxide and hydrogen used in all the experiments was manufactured and compressed by the Bureau of Mines at Bruceton, Pa.

Apparatus. The reactions were carried out in a standard American Instrument Co. 200 ml. stainless-steel rocking autoclave with a free space of 185 ml.

Hydrogenation experiments. The procedure was essentially the same as described previously[4]; actual conditions and results for each experiment are shown in Table I. The hydrogenation of naphthacene will be described in detail to illustrate the procedure.

Hydrogenation of naphthacene. A solution of 2.8 g. (0.012 mole) of naphthacene and 2.0 g. of $Co_2(CO)_8$ in 85 ml. of benzene was placed in the autoclave. Synthesis gas ($1H_2$: 1CO) was added until the pressure reached 3000 p.s.i. The autoclave was heated with rocking to 140° within 90 min. and held at this temperature for 5 hr. The autoclave was allowed to cool overnight, and the gases were vented to the atmosphere.

The benzene was evaporated and replaced by toluene. The solution was refluxed for 24 hr., during which time the catalyst was completely decomposed. The solution was filtered and the toluene removed *in vacuo*. The residue was dissolved in petroleum ether (60–68° B.R.) and chromatographed on activated alumina (Alcoa F-40), using petroleum ether, benzene, chloroform, and ethanol as eluents.

Two principal fractions were isolated, one identified as unreacted naphthacene, the other as 5,12-dihydronaphthacene, m.p. 209–210°. All fractions were analyzed by ultraviolet spectral analysis, and from these analyses the yield of dihydronaphthacene was calculated as 70%. Recovered naphthacene amounted to 30% of the starting material.

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(4) I. Wender, H. Greenfield, and M. Orchin, *J. Am. Chem. Soc.* **73**, 2656 (1951).

(5) A gift from Dr. M. Neuworth of Consolidation Coal Co.

(6) M. Orchin and R. A. Friedel, *J. Am. Chem. Soc.* **68**, 573 (1946).

(7) I. Wender, H. W. Sternberg, S. Metlin, and M. Orchin, *Inorganic Synthesis*, Vol. V, McGraw-Hill Book Co., New York, N. Y., 1957, pp. 190–192.

Identification of products. The products, after chromatographic separation, were identified by ultraviolet absorption spectra in all cases, and by melting point when available in the literature. In the case of the naphthalene and methylnaphthalene reductions, mass spectral analysis was also used.

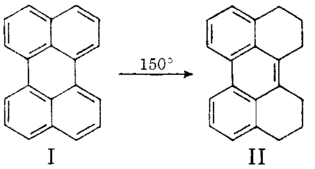
DISCUSSION OF RESULTS

Benzene and simple alkyl-substituted benzenes are not reduced to any significant extent and may be used as solvents for hydroformylation reactions. Naphthalene, on the other hand, is reduced slowly, as is shown in Table I. The specificity of this reducing system is demonstrated most strikingly by comparing the results for anthracene and phenanthrene. Anthracene is reduced rapidly to 9,10-dihydroanthracene at a temperature of about 135°; phenanthrene is very slowly reduced even at 200°.

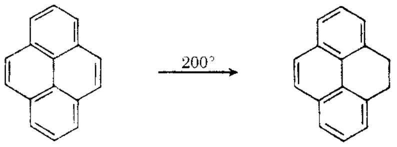
This behavior of aromatic systems extends to the larger molecules. Naphthacene, which is similar to anthracene in both structure and behavior, is readily reduced to 5,12-dihydronaphthacene under conditions similar to those used for reduction of anthracene. The product contains benzene and naphthalene systems, both of which are stable toward further reduction at this low temperature.

Chrysene, which is a benzphenanthrene, is slowly hydrogenated at 200° to the 5,6-dihydro compound.

Further proof of the stability of the phenanthrene system is shown by the reduction of perylene (I) to 1,2,3,10,11,12-hexahydroperylene (II) and of pyrene (III) to 4,5-dihydropyrene (IV):



I II



III IV

In both instances, the product is a phenanthrene derivative and so appears to be inert to further hydrogenation with this catalytic system.

1,1-Dinaphthyl, which resembles perylene except for one bond, cannot be converted to a phenanthrene derivative on reduction and is found to be resistant to reduction in contrast to perylene.

Triphenylene, which may be considered a benzphenanthrene or a compound containing three separate substituted benzene rings, is also inert to reduction with the dicobalt octacarbonyl catalyst.

Fluorene, which contains two isolated benzene rings, is resistant to hydrogenation, as expected. Fluoranthene picks up hydrogen readily to give 1,2,3,10b-tetrahydrofluoranthene, which may be regarded as a substituted fluorene.

Coronene, which can also be regarded as phenanthrenelike in nature, appears to be hydrogenated little, if at all.

A large number of polynuclear condensed aromatic hydrocarbons are available from tars prepared by carbonizing coal. Little is known concerning the properties of partly hydrogenated polycyclics owing to the fact that they have not been available in appreciable quantities. In the past, polynuclear aromatic hydrocarbons have always been hydrogenated using heterogeneous catalysts (Ni, Pt, WS_2, etc.),[8] but a mixture of partly hydrogenated polynuclears is generally obtained. With a heterogeneous catalyst, particular hydroaromatics may be prepared by careful control of temperature, pressure, and reaction time; even so, they are usually obtained in mixtures difficult to resolve. The use of the soluble dicobalt octacarbonyl as catalyst in the presence of carbon monoxide and hydrogen offers a new and simple route to the synthesis of various hydroaromatic compounds.

The following may be listed as advantages of this catalytic system: (1) The catalyst, $CO_2(CO)_8$, is easy to prepare; (2) the system is not poisoned by sulfur[2]; (3) careful control of reaction conditions is not essential, and (4) in most instances, the sole product of the hydrogenation is the di- or tetrahydro derivative and represents one of the difficultly isolatable intermediates postulated in hydrogenation of the same compound using heterogeneous catalysts.

We have treated coal itself with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl at 200°; both hydrogen and carbon monoxide are added to coal under these conditions.[9] This is the lowest temperature at which it has as yet been possible to add molecular hydrogen to coal.

Acknowledgments. We wish to thank Dr. Robert A. Friedel and Mr. John Queiser for spectral determinations and interpretations.

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(8) H. A. Smith, *Catalysis*, Vol. V, P. H. Emmett, ed., Reinhold Publishing Corp., New York, 1957, pp. 175–256.

(9) S. Friedman, H. F. Kauffman, and I. Wender, unpublished work.