Acknowledgment. The author is indebted to Dr. John Lancaster for the NMR spectra, to Mr. Robert Paylor for gas phase separation, and to Dr. Robert Rabinowitz for his helpful discussion of the work.

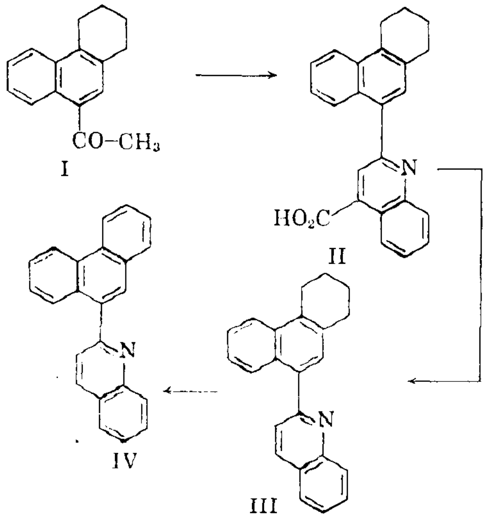
Chemical Research Department
American Cyanamid Co.
Stamford, Conn.

Some Derivatives of 1,2,3,4-Tetrahydrophenanthrene

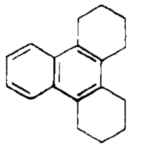
N. P. Buu-Hoï and G. Saint-Ruf

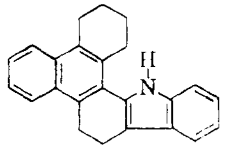
Received December 12, 1960

1,2,3,4-Tetrahydrophenanthrene displays a site of selective reactivity, *viz.* position 9, and is thus a convenient intermediate for the synthesis of phenanthrene derivatives substituted in *meso*-position, such as triphenylene,[1] and dibenz[a,c]anthracene and tribenz[a,c,h]anthracene.[2] We have now used 1,2,3,4-tetrahydrophenanthrene for preparing the hitherto unknown 2-(9-phenanthryl)quinoline (IV); the isomeric 2-(2-phenanthryl)- and 2-(3-phenanthryl)quinoline had previously been prepared by Buu-Hoï and Cagniant.[3] The synthesis of IV proceeded as shown in the flow sheet: 9-acetyl-1,2,3,4-tetrahydrophenanthrene underwent a Pfitzinger reaction with isatin to give 2-(1,2,3,4-tetrahydro-9-phenanthryl)cinchoninic acid (II); this was decarboxylated to 2-(1,2,3,4-tetrahydro-9-phenanthryl)quinoline (III), which in turn was dehydrogenated to IV. In the acetylation of 1,2,3,4-tetrahydrophenanthrene, a diketone was obtained along with the monoketone; in view of the known rules governing substitution in the naphthalene nucleus,[4] this compound might perhaps be 7,9-diacetyl-1,2,3,4-tetrahydrophenanthrene.



Another interesting aspect of the chemistry of 1,2,3,4-tetrahydrophenanthrene was its conversion, by the succinic anhydride method,[1] into 1,2,3,4-9,10,11,12-octahydrotriphenylene (V). Some discrepancies concerning the properties of this hydrocarbon have been noted in the literature: Bachmann and Struve,[1] who prepared it by Clemmensen reduction of 1-keto-1,2,3,4,9,10,11,12-octahydrotriphenylene, gave m.p. 120.5–122° (picrate, m.p. 193–195°), while Rapson,[5] who obtained it by cyclization of 1-phenyl-2-(Δ^1-cyclohexenyl)cyclohexanol, gave m.p. 129–130° (picrate, m.p. 185°). We found that hydrocarbon V, prepared by Wolff-Kishner reduction of the 1-keto derivative, melted at 144° and gave a picrate melting at 193°.


V



VI

Treatment of 1-keto-1,2,3,4,9,10,11,12-octahydrotriphenylene phenylhydrazone with indole yielded 1,2,3,4,9,10-hexahydrotriphenylene(11′,12′-3,2)indole (VI).

EXPERIMENTAL

Acetylation of 1,2,3,4-tetrahydrophenanthrene. 1,2,3,4-Tetraphenanthrene (m.p. 38°) was prepared by Haworth's method,[6] except that the keto acids from naphthalene and succinic anhydride and the 1-oxo-1,2,3,4-tetrahydrophenanthrene were reduced by Huang-Minlon's modification of the Wolff-Kishner reduction. To a solution of 20 g. of 1,2,3,4-tetrahydrophenanthrene and 11 g. of acetyl chloride in 150 ml. of anhydrous carbon disulfide, 20 g. of aluminum chloride was added in small portions at 0°, with stirring. The mixture was kept for 12 hr. at room temperature, then gently refluxed for 30 min. on the water-bath; it was then cooled, decomposed with ice and hydrochloric acid, and chloroform was added. The organic layer was washed first with dilute hydrochloric acid, then with water, and dried over sodium sulfate, the solvent was removed, and the residue vacuum-fractionated. The lower-boiling portion, b.p. 235–237°/15 mm., n_D^{25} 1.6523, which solidified on standing, was crystallized from petroleum ether (b.p. 45-60°), giving 9-acetyl-1,2,3,4-tetrahydrophenanthrene (11 g.), m.p. 58° lit.,[1] m.p. 56.5–58). The higher-boiling portion, b.p. 280–281°/15 mm., was a *diketone*, possibly 7,9-diacetyl-1,2,3,4-tetrahydrophenanthrene; it crystallized from ethanol in shiny colorless prisms (2 g.), m.p. 154°, giving a yellow coloration in sulfuric acid.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.7. Found: C, 81.2; H, 6.9.

γ-(1,2,3,4-Tetrahydro-9-phenanthryl)butyric acid. The following procedure gave higher yields than Bachmann and Struve's method: a solution of 12 g. of *β*-(1,2,3,4-tetrahydro-9-phenanthroyl)propionic acid[1] and 6.5 g. of 95% hydrazine

---

(1) W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, **4**, 472 (1939).

(2) N. P. Buu-Hoï and G. Saint-Ruf, *J. Chem. Soc.*, 2845 (1960).

(3) N. P. Buu-Hoï and P. Cagniant, *Rec. trav. chim.*, **62**, 519 (1943).

(4) See N. P. Buu-Hoï and R. Daudel, *Rec. trav. chim.*, **65**, 731 (1946).

(5) W. S. Rapson, *J. Chem. Soc.*, 15 (1941).

(6) R. D. Haworth, *J. Chem. Soc.*, 1125 (1932).

hydrate in 200 ml. of diethylene glycol was refluxed for 6 hr. with 7.5 g. of potassium hydroxide, with removal of water; after being cooled, diluted with water, and acidified with hydrochloric acid, a precipiate was obtained which crystallized from methanol in shiny colorless needles (9 g.), m.p. 134° (lit.,[1] m.p. 133–134°).

1,2,3,4,9,10,11,12-Octahydrotriphenylene (V). A solution of 1.5 g. of 1-keto-1,2,3,4,9,10,11,12-octahydrotriphenylene and 0.6 g. of hydrazine hydrate in 50 ml. of diethylene glycol was treated with 0.7 g. of potassium hydroxide as above, and worked up in the usual way. Crystallization from petroleum ether afforded shiny colorless needles (1 g,.) m.p. 144°, which gave no coloration in sulfuric acid.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.5; H, 8.5. Found: C, 91.4; H, 8.4.

The orange-red *picrate* melted at 193° (slight decomposition above 190°).

Anal. Calcd. for $C_{24}H_{23}N_3O_7$: N, 9.0. Found: N, 9.3.

Dehydrogenation of 0.2 g. of this hydrocarbon with 0.3 g. of selenium at 320–350° yielded triphenylene.

2-(1,2,3,4-Tetrahydro-9-phenanthryl)cinchoninic acid (II). A solution of 7 g. of 9-acetyl-1,2,3,4-tetrahydrophenanthrene, 5 g. of isatin, and 6 g. of potassium hydroxide in 50 ml. of ethanol was refluxed for 20 hr. on the water-bath; after evaporation of the solvent, the residue was treated with water, the neutral impurities removed by ether extraction, and the aqueous layer acidified with acetic acid. The precipitate was recrystallized from ethanol, giving yellowish prisms (10 g.), m.p. 284°.

Anal. Calcd. for $C_{24}H_{19}NO_2$: C, 81.6; H, 5.4. Found: C, 81.5; H, 5.4.

2-(1,2,3,4-Tetrahydro-8-phenanthryl)quinoline (III). The foregoing cinchoninic acid was heated above its melting point in a distillation flask, and the decarboxylation-product vacuum-fractionated. Recrystallization of the distillate from ethanol afforded shiny colorless prisms (80% yield), m.p. 113°.

Anal. Calcd. for $C_{23}H_{19}N$: C, 89.3; H, 6.2; N, 4.5. Found: C, 89.0; H, 6.5; N, 4.5.

2-(9-Phenanthryl)quinoline (IV). Dehydrogenation of the foregoing compound was effected by heating with 5% palladium charcoal, and the reaction-product was vacuum-distilled and recrystallized from ethanol, giving colorless needles (75% yield), m.p. 130°.

Anal. Calcd. for $C_{23}H_{15}N$: C, 90.5; H, 5.0; N, 4.6. Found: C, 90.2; H, 5.2; N, 4.8.

The *picrate* crystallized from ethanol in shiny yellow prisms, m.p. 229°.

Anal. Calcd. for $C_{29}H_{18}N_4O_7$: N, 10.5. Found: N, 10.5.

1,2,3,4,9,10-Hexahydrotriphenyleno(11′,12′-3,2)indole (VI). A mixture of 5 g. of 1-keto-1,2,3,4,9,10,11,12-octahydrotriphenylene and 5 g. of phenyl hydrazine was heated at 120° for a few minutes, and the crude phenylhydrazone was treated with a solution of hydrogen chloride in acetic acid, and the mixture then boiled for a few seconds. After being cooled and diluted with water, a precipitate was formed which was recrystallized twice from cyclohexane, giving cream-colored prisms (5 g.), m.p. 175°.

Anal. Calcd. for $C_{24}H_{21}N$: C, 89.1; H, 6.6; N, 4.3. Found: C, 88.9; H, 6.5; N, 4.3.

Acknowledgment. This work was supported in part by a research grant from the National Cancer Institute of the National Institutes of Health, U.S. Public Health Service; the authors thank the authorities concerned.

THE RADIUM INSTITUTE
UNIVERSITY OF PARIS
PARIS (V^e), FRANCE

Improved Procedure for the Preparation of 1,3-Diamino-2,4,6-trinitrobenzene

M. WARMAN AND V. I. SIELE

Received December 1, 1960

The preparation of 1,3-diamino-2,4,6-trinitrobenzene (I) by existing procedures has not been satisfactory in most instances. Several complicated procedures for the synthesis of I have been reported. The two most commonly used methods for the preparation of I are described as follows. In the first of these the synthesis is accomplished by vigorously nitrating *m*-dichlorobenzene at elevated temperatures.[1–3] The 1,3-dichloro-2,4,6-trinitrobenzene (II) thus obtained is aminated in methanol solution to yield I. The second synthesis described is the amination of 3-amino-2,4,6-trinitroanisole.[4] No yields were reported for the foregoing syntheses. However, in this laboratory the overall yield from the first method was found to be 46%.

Recently, Haas, Feuer, and Harban[5] described the preparation of II from styphnic acid with an overall yield of 64%. Their synthetic scheme involved the formation of dipyridinium styphnate, which, upon treatment with phosgene in acetone for nine hours, gave II.

Subsequently, Boyer, Spencer, and Wright[6] reported obtaining a 98% yield of picryl chloride by chlorination of pyridinium picrate with phosphorus oxytrichloride in benzene. It was thus considered entirely possible that phosphorus oxytrichloride could also be used to chlorinate dipyridinium styphnate.

Dipyridinium styphnate can be prepared from styphnic acid in 94% yield. II can be obtained in 98% yield by allowing phosphorus oxytrichloride and dipyridinium styphnate to react directly at steam-bath temperatures. The treatment of a suspension of II in methanol with gaseous ammonia leads to the formation of I in yields as high as 97%. The overall yield of I is therefore 89%, considerably better than the yield obtainable through existing procedures.

Theoretically 1.0 mole of dipyridinium styphnate will react with 0.7 mole of phosphorus oxytrichloride. However, the optimum molar ratio has been found to be 0.135 mole of dipyridinium salt to 1.0 mole of phosphorus oxytrichloride. Larger quanti-

---

(1) J. J. Sudborough and N. Picton, *J. Chem. Soc.*, **89**, 589 (1906).

(2) Nietzki and Schedler, *Ber.*, **30**, 1666 (1897).

(3) Beilstein, *Handbuch der Organischen Chemie*, Springer, Berlin, 4th Ed., Vol. 13, p. 60.

(4) C. F. Van Duin and B. C. Roeters Van Lennep, *Rec. Trav. Chem.*, **39**, 147 (1920).

(5) H. B. Haas, H. Feuer, and A. A. Harban, *J. Am. Chem. Soc.*, **72**, 2282 (1949).

(6) R. Boyer, E. Y. Spencer, and G. F. Wright, *Can. J. Res.*, **24**, 200 (1946).