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), 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).

ties of the dipyridinium salt cause a slight decrease in the yield of II. Reactions using benzene as the solvent have produced only tarry products.

The amination was carried out by three different methods; a) amination in methanol solution, b) amination in methanol suspension, and c) ammonolysis in liquid ammonia. Although both the homogeneous and heterogeneous reactions gave yields as high as 97%, the homogeneous method was considered to be impractical due to the volume of methanol required for the solution of II. Ammonolysis in liquid ammonia gave yields 10% lower.

EXPERIMENTAL[7]

Dipyridinium styphnate. Anhydrous pyridine (200 g., 2.53 moles) was added, with stirring, to 50 g. (0.20 mole) of dry styphnic acid. The resulting slurry was stirred for an additional 0.5 hr. The yellow product was collected by filtration and washed with approximately 100 ml. of ether. After drying at room temperature over phosphorus pentoxide for 5 hr., the yield of dipyridinium styphnate was 77 g. (94%), m.p.[8] 168–170°, lit. 173–176°.

1,3-Dichloro-2,4,6-trinitrobenzene. To 5 ml. (0.550 mole) of phosphorus oxytrichloride was added, with stirring, 29.8 g. (0.074 mole) of dipridinium styphnate in small portions. The reaction mixture was then heated on steam bath for 15 min. During this time all of the solid dissolved. The solution was then quenched in 500 g. of ice water. The light yellow precipitate was separated by filtration and washed with water until the wash water was neutral to litmus. The yield was 20.4 g. (98%), m.p. 130–131°., lit. 128°.

1,3-Diamino-2,4,6-trinitrobenzene. A suspension of 3 g. (0.010 mole) of 1,3-dichloro-2,4,6-trinitrobenzene in 9 ml. of absolute methyl alcohol was prepared. The slurry was cooled to 0° and ammonia was bubbled into the stirred suspension. After 20 min. the mixture was allowed to warm to room temperature, filtered by suction, and the solid was washed with methanol and ether until a negative Beilstein test for chloride was obtained. The yield was 2.5 g. (97%), m.p. 288–290°., lit. 285°.

EXPLOSIVES RESEARCH SECTION
PICATINNY ARSENAL
DOVER, N. J.

---

[7] All melting points are uncorrected.

[8] Melting points of dipyridinium styphnate were found to range from 168° to 176° in this laboratory.

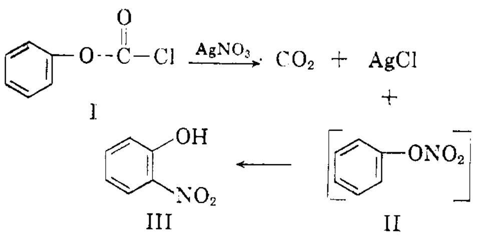
[9] Melting points for 1,3-diamino-2,4,6-trinitrobenzene reported in the literature range from 270° to 301°.

An Attempted Synthesis of Phenyl Nitrate[1]

ALAN CHANEY AND M. L. WOLFROM

Received January 12, 1961

The novel method for the synthesis of aliphatic nitrate esters, described by Boschan,[2] involving the treatment of alkyl chloroformates with silver nitrate, appeared to offer a route to the unknown phenyl nitrate. Thus, phenyl chloroformate (I) was added to silver nitrate dissolved in acetonitrile. Filtration of the resulting mixture afforded silver chloride (99% yield) and distillation of the filtrate afforded *o*-nitrophenol (III) in 64% yield.



Although phenyl nitrate (II) may have been produced originally by the sequence of rearrangements described by Boschan, this substance appears to be subject to further change to afford the more stable nitrophenol. Many similar rearrangements, usually acid-catalyzed, have been observed; the most closely related, that of phenylnitramine to *o*-nitroaniline, has been shown[3] to be an intramolecular process.

EXPERIMENTAL

Phenyl chloroformate (10 g.) was added dropwise to a solution of silver nitrate (15 g.) in 100 ml. of dry acetonitrile. After shaking the mixture at room temperature for 3 hr., filtration afforded 9.1 g. (99%) of slightly impure silver chloride. The filtrate and acetonitrile washings were evaporated under reduced pressure to about 30 ml. and this residue was distilled (b.p. 50–60°, 1.3 mm.) affording a yellow oil which crystallized; yield 5.8 g. (64%), m.p. 46–47°. On the basis of identical infrared spectra and the mixed melting point (45–46°) with an authentic specimen (m.p. 45–46°), the product was *o*-nitrophenol.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

---

[1] This work was carried out under contract between the Ordnance Corps (DA-33-019-ORD-2025) and The Ohio State University Research Foundation (Project 675).

[2] R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959).

[3] S. Brownstein, C. A. Bunton, and E. D. Hughes, *Chem. & Ind.* (London), 981 (1956).

The Sodium Borohydride Reduction of *N*-Substituted Phthalimides

FREDERICK C. UHLE

Received October 19, 1960

An attempt to reduce the 16-keto function of 3β-hydroxy-27-phthalimido-25α-5-cholesten-16,22-dione with sodium borohydride in isopropyl alcohol gave a complex product-mixture composed of both neutral and acidic molecules in a ratio of approximately 2:1.[1] The acidic fraction was presumed to derive from partial hydrolysis to the phthalamidic acid, a change known to be accomplished by the

---

[1] F. C. Uhle, *J. Am. Chem. Soc.*, **83**, 1460 (1961).