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°.

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(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]

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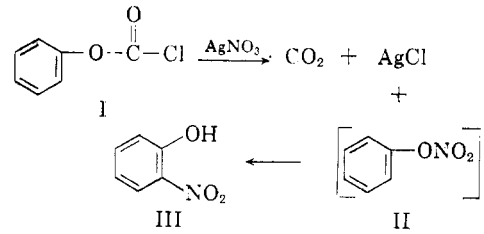
The novel method for the synthesis of aliphatic nitrate esters, described by Boschan,[2] involving the treatment of alkyl chloroformates with silver nitrate, appeared to offer a route to the unknown



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.

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

The Sodium Borohydride Reduction of *N*-Substituted Phthalimides

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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) 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).

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