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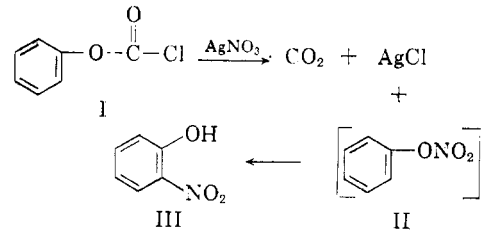
The novel method for the synthesis of aliphatic nitrate esters, described by Boschan,[2] involving the treatment of alkyl chloroformates with silver nitrate, appeared to offer a route to the unknown



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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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) 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).

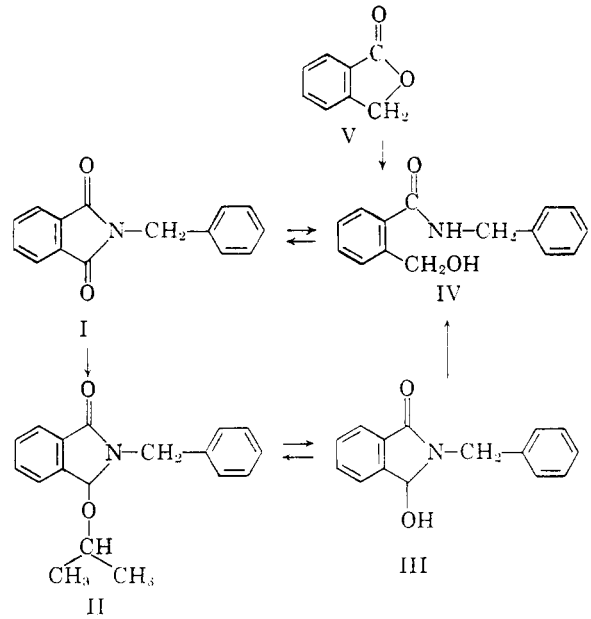
(1) F. C. Uhle, *J. Am. Chem. Soc.*, **83**, 1460 (1961).

most gentle basic intervention.[2] The resistance of the neutral portion to imposed hydrolytic action with potassium bicarbonate, however, signified an unexpected[3] reductive alteration of the imide moiety itself.

An examination of the behavior of simpler *N*-substituted phthalimides with sodium borohydride disclosed a pronounced vulnerability to the reagent. In isopropyl alcohol alone, under conditions of equivalence and dilution employed with the steroid derivative, hydrolysis to the phthalamidic acid occurred to the extent of 30–40%. The neutral products proved to be 2-substituted 3-hydroxy-1-isoindolinones and their 3-isopropyl "ethers," little known substances first prepared by zinc–sodium hydroxide,[4] and more recently by magnesium–aqueous methanolic ammonium chloride[5] reduction.

The proportion of 3-isopropoxy- to 3-hydroxy-1-isoindolinone isolated in any individual experiment appeared dependent on the manner of exposure to hydrochloric acid during the work-up routine, as both ether formation and ether hydrolysis are acid catalyzed under appropriate circumstances. Moderate aqueous acid treatment of the neutral fraction from sodium borohydride reduction of *N*-benzylphthalimide (I), for example, gave 2-benzyl-3-hydroxy-1-isoindolinone (III) in 42% yield. In another experiment, a comparable amount of 2-benzyl-3-isopropoxy-1-isoindolinone (II) was isolated directly; in a third run chromatography permitted recovery of both substances.

Reduction of *N*-benzylphthalimide (I) or of 2-benzyl-3-hydroxy-1-isoindolinone (III) in aqueous isopropyl alcohol, on the other hand, progressed one degree beyond to give 80% of *o*-hydroxymethyl-*N*-benzylbenzamide (IV), a compound alternatively available from phthalide (V) and aqueous benzylamine. Manganese dioxide, as well as chromic acid in acetic acid, caused reversion of the benzamide to *N*-benzylphthalimide.[6]



The results were substantiated with *N*-phenylphthalimide, with *N*-phenylethylphthalimide and with *N*-isopropylphthalimide. Phthalimide itself, in isopropyl alcohol alone, gave 35% of 3-isopropoxy-1-isoindolinone; in the presence of water, phthalide (V) was produced in 60% yield.[7]

EXPERIMENTAL[8]

2-Benzyl-3-isopropoxy-1-isoindolinone (II) and 2-benzyl-3-hydroxy-1-isoindolinone (III) from N-benzylphthalimide (I). To a solution of 948 mg. (0.004 mole) of *N*-benzylphthalimide (I)[9] in 400 ml. of isopropyl alcohol was added 624 mg. (0.016 mole) of sodium borohydride. After the mixture had been stirred for 18 hr. at 25°, 4 ml. of aqueous 6*N* hydrochloric acid was added dropwise. The solution was concentrated to give a residue which was diluted with water and extracted with ether. The organic phase was washed with dilute ammonia and with water and was concentrated. (Acidification of the ammoniacal solution gave 430 mg. (42%) of felt-like needles of *N*-benzylphthalamidic acid,

(2) *Cf., e.g.* the limitations of phthaloyl peptides as substrates in enzymatic studies because of imide hydrolysis at the weakly alkaline pH optimal for proteolytic activity: H. Hanson and R. Illhardt, *Z. Physiol. Chem.*, **298**, 210 (1954).

(3) N. C. Gaylord, *Reductions with Complex Metal Hydrides*, Interscience, New York, 1956, pp. 385, 629.

(4) A. Reissert, *Ber.*, **46**, 1484 (1913).

(5) A. Dunet and A. Willemant, *Compt. rend.*, **226**, 821 (1948); *Bull. soc. Chim.*, **887**, 1045 (1948).

(6) Manganese dioxide was expected to reform III, as benzyl alcohols have given good yields of benzaldehydes with properly prepared oxidant: M. Harfenist, A. Bavely, and W. A. Lazier, *J. Org. Chem.*, **19**, 1608 (1954). The present finding is not without precedent, however, in view of transformation of the aldehyde ammonia hydrastinine to the lactam oxyhydrastinine with the Attenburrow reagent: R. J. Highet and W. C. Wildman, *J. Am. Chem. Soc.*, **77**, 4399 (1955). Direct phthalimide isolation may be taken as evidence for hydroxyisoindolinone intermediacy, as the phthalamidic acid should not close under conditions of the experiment. Apparently the second oxidation stage proceeds more rapidly than the first.

(7) *Cf.* the preparation of phthalide (67–71%) by zinc-copper reduction of phthalimide in aqueous sodium hydroxide; J. R. Gardner and C. A. Naylor, Jr., *Org. Syntheses*, **Coll. Vol. II**, 526 (1943).

(8) Melting points were observed on a calibrated micro hot stage. Microanalyses were performed by Dr. S. M. Nagy and associates of the Massachusetts Institute of Technology. Infrared spectra, in potassium bromide, were recorded with Perkin-Elmer models 21 and 137. Only those maxima of significance in interpretation are mentioned. Bands not of full intensity are designated as medium (m) or weak (w). Woelm nonalkaline aluminum oxide was used for chromatographic separations. Starting phthalimides were prepared with potassium phthalimide in dimethylformamide at 25°. The following abbreviated conventions are adopted in the experimental descriptions: "at 25°" = at ordinary temperature; "concentrated" = concentrated under diminished pressure with a Rinco rotating evaporator; "dried" = dried in a vacuum desiccator; "stirred" = stirred by means of a magnetic apparatus; "petroleum ether" = petroleum ether (b.p. 30–60°).

(9) R. H. F. Manske, *Org. Syntheses*, **Coll. Vol. II**, 83 (1943).

m.p.[10] 152–155°). A benzene solution of the dried residue (600 mg.) was chromatographed over 18 g. of aluminum oxide to give the fractions: (1) benzene: 250 mg.; (2) ether: 150 mg.; (3) ether-methanol (95:5): 160 mg. Fractions 1 and 2 were combined and recrystallized from aqueous isopropyl alcohol to afford 280 mg. (25%) of tetragonal prisms of 2-benzyl-3-isopropoxy-1-isoindolinone (II), m.p. 65–66°; infrared spectrum: 3.50 (m) (isopropyl), 6.00 μ (tertiary amide), absence of hydroxyl absorption.

Anal. Calcd. for $C_{18}H_{19}NO_2$ (281.34): C, 76.84; H, 6.81; N, 4.98. Found: C, 76.72; H, 6.91; N, 5.01.

Fraction 3, from dichloromethane–petroleum ether (b.p. 30–60°), gave 145 mg. (15%) of glistening needles of 2-benzyl-3-hydroxy-1-isoindolinone (III); m.p.[5] 145–146°; infrared spectrum: 3.0 (OH), 6.0 μ (tertiary amide).

Anal. Calcd. for $C_{15}H_{13}NO_2$ (239.26): C, 75.30; H, 5.48; N, 5.85. Found: C, 75.09; H, 5.54; N, 5.95.

2-Benzyl-3-hydroxy-1-isoindolinone (III) from 2-benzyl-3-isopropoxy-1-isoindolinone (II). A solution of 281 mg. (0.001 mole) of II in 30 ml. of aqueous 1*N* hydrochloric acid was heated under reflux for 2 hr. After 40 hr. at 0°, the precipitate was collected, washed with water, and dried. Recrystallization from dichloromethane–petroleum ether gave 175 mg. (73%); m.p. 140–145°. When the neutral fraction (280 mg.) from sodium borohydride reduction of 0.002 mole of *N*-benzylphthalimide (under conditions described above) was heated with aqueous 1*N* hydrochloric acid, 200 mg. (42%) of 2-benzyl-3-hydroxy-1-isoindolinone (III) was isolated directly.

o-Hydroxymethyl-N-benzylbenzamide (IV) *from 2-benzyl-3-hydroxy-1-isoindolinone* (III). To a solution of 96 mg. (0.0004 mole) of III and 2 ml. of water in 10 ml. of isopropyl alcohol was added 62 mg. (0.0016 mole) of sodium borohydride. After the mixture had been stirred for 18 hr. at 25°, 0.5 ml. of aqueous 6*N* hydrochloric acid was added dropwise. The solution was concentrated to give a residue which was diluted with water and extracted with ether. The organic phase was washed with dilute ammonia and with water and was concentrated. Recrystallization of the dried residue from dichloromethane-petroleum ether gave 86 mg. (90%). The analytical sample, from ethyl acetate, melted at 137–139°; infrared spectrum: 3.05 (OH and NH), 6.15, 6.45 μ (secondary amide).

Anal. Calcd. for $C_{15}H_{15}NO_2$ (241.28): C, 74.66; H, 6.27; N, 5.81. Found: C, 74.76; H, 6.22; N, 5.83.

o-Hydroxymethyl-N-benzylbenzamide (IV) *from phthalide* (V). A solution of 72 mg. (0.0005 mole) of phthalide (V) and 535 mg. (0.005 mole) of benzylamine in 2 ml. of water was heated under reflux for 3 hr. After 15 hr. at 0°, the precipitate was collected, washed with water, and dried to give 20 mg. (17%)[11]; m.p. 131–133°; infrared spectrum identical with that of the product from sodium borohydride reduction of III.

N-Benzylphthalimide (I) *from o-hydroxymethyl-N-benzylbenzamide* (IV). A suspension of 200 mg. of manganese dioxide[12] in 8 ml. of chloroform containing 48 mg. (0.0002 mole) of IV was stirred for 15 hr. at 25°. The filtrate from the manganese dioxide was concentrated. The infrared spectrum of the crystalline residue was indistinguishable from that of *N*-benzylphthalimide (I): 5.70, 5.90, 13.9, 14.4 μ (phthalimide). Three recrystallizations from dichloromethane–petroleum ether left 25 mg., m.p. 100–115°. Treatment of IV with one oxidizing equivalent of chromic acid in acetic acid gave *N*-benzylphthalimide as the sole crystalline product.

2-Phenyl-3-hydroxy-1-isoindolinone from N-phenylphthalimide. A solution of 223 mg. (0.001 mole) of *N*-phenylphthalimide (commercial product) and 156 mg. (0.004 mole) of sodium borohydride in 100 ml. of isopropyl alcohol was stirred for 18 hr. at 25°. After 1 ml. of aqueous 6*N* hydrochloric acid had been added dropwise, the solution was concentrated to give a residue which was diluted with water and extracted with ether. The organic phase was washed with dilute ammonia and with water and was concentrated. (Acidification of the ammoniacal solution gave 45 mg. of *N*-phenylphthalamidic acid, m.p.[13] 155–158°.) A benzene solution of the dried product (140 mg.) was chromatographed over 4.2 g. of aluminum oxide to give the fractions: (1) benzene: 50 mg.; (2) benzene-ether (1:1): 55 mg. Fraction 2 was recrystallized from aqueous methanol to afford 45 mg. (20%); m.p.[5] 170–172°; infrared spectrum: 3.05 (OH), 6.05 μ (tertiary amide).

Anal. Calcd. for $C_{14}H_{11}NO_2$ (225.24): C, 74.65; H, 4.92; N, 6.22. Found: C, 74.65: H, 4.91; N, 6.21.

o-Hydroxymethyl-N-phenylbenzamide from N-phenylphthalimide. A solution of 669 mg. (0.003 mole) of *N*-phenylphthalimide, 468 mg. (0.012 mole) of sodium borohydride, and 15 ml. of water in 75 ml. of isopropyl alcohol was stirred for 15 hr. at 25°. After the mixture had been acidified dropwise with 3 ml. of aqueous 6*N* hydrochloric acid and had been concentrated, the residue was diluted with water and extracted with ether. The organic phase was washed with dilute ammonia and with water and was concentrated. Recrystallization of the dried residue from dichloromethane–petroleum ether gave 300 mg. (44%); m.p. 130–132°; infrared spectrum: 3.00–3.05 (OH and NH), 6.05, 6.50 μ (secondary amide).

Anal. Calcd. for $C_{14}H_{13}NO_2$ (227.25): C, 73.99; H, 5.77; N, 6.16. Found: C, 73.65; H, 5.70; N, 6.00.

2-Phenylethyl-3-isopropoxy-1-isoindolinone and 2-phenylethyl-3-hydroxy-1-isoindolinone from N-phenylethylphthalimide. A solution of 500 mg. (0.002 mole) of *N*-phenylethylphthalimide[14] and 312 mg. (0.008 mole) of sodium borohydride in 200 ml. of isopropyl alcohol was stirred for 16 hr. at 25°. After 2 ml. of aqueous 6*N* hydrochloric acid had been added dropwise, the solution was concentrated to give a residue which was diluted with water and extracted with ether. The organic phase was washed with dilute ammonia and with water and was concentrated. (Acidification of the ammoniacal extract gave 140 mg. (26%) of *N*-phenylphthalamidic acid, m.p. 150–153°.

Anal. Calcd. for $C_{16}H_{15}NO_2$ (269.29): N, 5.20. Found: N, 5.31. A benzene solution of the dried residue was chromatographed over 12 g. of aluminum oxide to give the fractions: (1) benzene: 170 mg.; (2) ether: 130 mg.; (3) ether-methanol (95:5): 40 mg. Fraction 2 gave, from aqueous isopropyl alcohol, 90 mg. (15%) of 2-phenylethyl-3-isopropoxy-1-isoindolinone. Recrystallization from aqueous methanol afforded extraordinarily long, slender needles; m.p. 55–57°; infrared spectrum: 3.45 (isopropyl), 5.90 μ (amide).

Anal. Calcd. for $C_{19}H_{21}NO_2$ (295.37): C, 77.26; H, 7.17; N, 4.74. Found: C, 77.16; H, 7.16; N, 4.89.

Fraction 3 gave, from dichloromethane–petroleum ether, 30 mg. (6%) of 2-phenylethyl-3-hydroxy-1-isoindolinone. The analytical sample, from aqueous methanol, melted at 163–166°; infrared spectrum: 3.00 (OH), 6.00 μ (tertiary amide).

Anal. Calcd. for $C_{16}H_{15}NO_2$ (253.29): C, 75.87; H, 5.97; N, 5.53. Found: C, 76.08; H, 6.04; N, 5.42.

o-Hydroxymethyl-N-isopropylbenzamide from N-isopropylphthalimide. A solution of 378 mg. (0.002 mole) of *N*-isopropylphthalimide,[15] 312 mg. (0.008 mole) of sodium boro-

(10) S. Gabriel and W. Landsberger, *Ber.*, **31**, 2740 (1898).

(11) This yield doubtless could be improved by modification of conditions; *cf.* the preparation of *o*-hydroxymethyl-*N*-methylbenzamide from phthalide and aqueous methylamine: W. Theilacker and H. Kalenda, *Ann.*, **584**, 87 (1953); **597**, 95 (1955).

(12) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, H. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc*, 1094 (1952).

(13) T. Zincke and T. Cooksey, *Ann.*, **255**, 375 (1889).

(14) H. R. Ing and R. H. F. Manske, *J. Chem. Soc.*, 2350 (1926).

(15) S. Gabriel, *Ber.*, **24**, 3106 (1891).

hydride and 10 ml. of water in 50 ml. of isopropyl alcohol was stirred for 18 hr. at 25°. After 2 ml. of aqueous 6*N* hydrochloric acid had been added dropwise, the solution was concentrated to give a residue which was diluted with water and extracted with ether. The organic phase was washed with dilute ammonia and with water and was concentrated. Recrystallization of the dried residue from dichloromethane–petroleum ether afforded 300 mg. (78%) of long needles; m.p. 111–113°; infrared spectrum: 3.00 (OH and NH), 6.10, 6.50 μ (secondary amide).

Anal. Calcd. for $C_{11}H_{15}NO_2$ (193.24): C, 68.37; H, 7.82; N, 7.25. Found: C, 68.76; H, 7.95; N, 7.15.

3-Isopropoxy-1-isoindolinone from phthalimide. To a solution of 441 mg. (0.003 mole) of phthalimide in 300 ml. of isopropyl alcohol was added 468 mg. (0.012 mole) of sodium borohydride. After the mixture had been stirred for 18 hr. at 25°, 3 ml. of aqueous 6*N* hydrochloric acid was added dropwise. The solution was kept at 25° for 24 hr. to ensure completion of isopropyl ether formation. After 10 ml. of 6*N* ammonia had been added, the solution was concentrated to give a residue which was extracted with ether. The organic phase was washed with dilute ammonia and with water and was concentrated to give a product which was dissolved in 10 ml. of isopropyl alcohol containing 1 ml. of aqueous 3*N* potassium hydroxide. After 10 min. at reflux temperature to ensure hydrolysis of traces of phthalide, the solution was concentrated to give a residue which was diluted with 5 ml. of water. After 15 hr. at 0°, the precipitate was collected, washed with water, and dried to give 200 mg. (35%); m.p. 125–128°. Recrystallization from water gave heavy prismatic needles, m.p. 133–134° (*cf.* ref. 5: 125°); infrared spectrum: 3.05 (NH), 5.90, 6.00 μ (amide).

Anal. Calcd. for $C_{11}H_{13}NO_2$ (191.22): C, 69.09; H, 6.85; N, 7.33. Found: C, 69.10; H, 6.79; H, 7.30.

Phthalide (V) *from phthalimide.* To a solution of 588 mg. (0.004 mole) of phthalimide and 20 ml. of water in 100 ml. of isopropyl alcohol was added 624 mg. (0.016 mole) of sodium borohydride. After the mixture had been stirred for 20 hr. at 25°, 5 ml. of aqueous 6*N* hydrochloric acid was added dropwise. The solution was concentrated to give a residue which was dissolved in 7 ml. of hot water. After 15 hr. at 0°, the precipitate was collected, washed with water, and dried. A benzene solution of the 1 g. of solid (which contained boric acid) was poured through a column of 30 g. of aluminum oxide. The residue from concentration of the benzene eluate was recrystallized from dichloromethane–petroleum ether to give 320 mg. (60%) of small transparent plates; m.p. 72–73°[7]; infrared spectrum: 5.70 μ (lactone).

Acknowledgment. The assistance of Grace Swanson is gratefully acknowledged. The work was supported by the National Heart Institute of the National Institutes of Health (H-2205) and by the Eugene Higgins Trust.

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Pyridine 1-Oxides. VIII. Hydrolysis of 4-Nitro-3-picoline[1]

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Received December 1, 1960

During the course of our investigations of pyridine 1-oxides, it was noticed that freshly distilled 4-nitro-3-picoline,[3] when left at room temperature for several days partially exposed to the atmosphere, slowly deposited a light yellow solid. This observation had not been made by Herz and Tsai.[3] Suction filtration of the mixture gave unchanged 4-nitro-3-picoline as the filtrate, but separation of the solid material in this manner seemed to accelerate the formation of more solid in the filtrate. The rate of solid formation was increased by the presence of water but not by bubbling oxygen through the oil. The yellow solid was insoluble in ethanol but very soluble in water; the *p*H of the solution was 3. By contrast, 4-nitro-3-picoline is very soluble in ethanol but insoluble in water.

Addition of alkali to the aqueous solution of the solid followed by extraction with benzene and then with chloroform (see Experimental) effected a separation of the yellow solid into two crystalline compounds. Both exhibited absorption bands at 1645 cm.$^{-1}$ in the infrared characteristic of the carbonyl stretching band in pyridones (1650–1630 cm.$^{-1}$ [4]) Microanalytical data then allowed the assignment of the structure 3-methyl-4-pyridone (I. R = —CH_3) to the lower melting solid (m.p. 92–94°) and the structure 1-(3′-methyl-4′-pyridyl)-3-methyl-4-pyridone (II. R = —CH_3) to the higher melting solid (m.p. 197–198°). An authentic sample of 3-methyl-4-pyridone was made for comparison by catalytic reduction of 4-hydroxy-3-picoline-1-oxide, which in turn was prepared by alkaline hydrolysis of 4-chloro-3-picoline 1-oxide.

Recrystallization of the original yellow solid from methanol yielded two different crystalline compounds, of which one was obtained pure by hand separation of the crystals. This proved to be the nitric acid salt of 3-methyl-4-pyridone (I. R = —CH_3); an authentic sample was prepared independently by treatment of 3-methyl-4-pyridone with dilute nitric acid. The origin of the nitric acid is not known with certainty, although it seems probable that it must have arisen by air oxidation of the nitrous acid formed during the hydrolysis of 4-nitro-3-picoline and of III (see below).

It has been reported by den Hertog[5] that 4-nitropyridine behaves similarly upon standing. Analogous products (I and II. R = H) were obtained and the suggestion was made that these products arose as outlined on page 3002.

It appears that the above displacement and hydrolytic reactions may be general for 4-nitropyridines, and care should be taken in storing and handling such compounds to exclude all traces of moisture.

(1) For the previous paper in this series, see E. C. Taylor and J. S. Driscoll, *J. Org. Chem.*, 25, 1716 (1960).

(2) Parke, Davis and Company Fellow in Chemistry, 1957–1958; Monsanto Chemical Company Fellow, 1958–1959.

(3) W. Herz and L. Tsai, *J. Am. Chem. Soc.*, 76, 4184 (1954).

(4) T. N. Sheinker and Y. I. Pomerantsev, *Zhur. Fiz. Khim.*, 30, 79 (1956).

(5) H. J. den Hertog, F. W. Broekman, and W. P. Combé, *Rec. trav. chim.*, 70, 105 (1951).