well-stirred slurry of 150 g. of sodium sulfite in ice and water. The *p*H was adjusted to 10; an ether extract of this solution was discarded. The cold aqueous phase was then acidified with acetic acid and extracted with ether. This extract (dried with calcium chloride) was distilled, finally at 90–111° under 13 mm. The 19.8 g. (47% yield) of distillate melted at −29 to −21° and gave a positive Franchimont test.

This nitramine was best preserved by conversion to the potassium salt in 71% yield. This salt precipitated as platelets when an absolute ethanol solution was treated with an equivalent of absolute ethanolic potassium hydroxide and then with an equal volume of dry ether. By treatment of this salt in aqueous solution the silver salt could be precipitated just prior to use after it was washed with ethanol and ether.

Di-*n*-propylnitramine. A. From Silver *n*-Propylnitramine.—A suspension of 13.6 g. (0.06 mole) of silver salt in 9.4 g. (0.06 mole) of *n*-propyl iodide and 70 cc. of U. S. P. ether was stirred for two days at room temperature. After filtration the solution was distilled, finally at 7–8 mm. to yield 4.8 g. of di-*n*-propylisonitramine (Thomas' compound), b. p. 63–67°, $n^{22}\mathrm{D}$ 1.4370. This compound (53% yield) gave a negative Franchimont test and would not freeze at Dry Ice temperature. A distillation fraction of 0.3 g., b. p. 89–100°, $n^{22}\mathrm{D}$ 1.4542, was then obtained. This product was evidently di-*n*-propylnitramine, since it gave a positive Franchimont test. It froze easily above Dry Ice temperature and a rough mixed melting point with authentic di-*n*-propylnitramine was not lowered.

B. From Di-*n*-propylamine.—Proportionate addition of 17.4 g. (0.27 mole) of 99% nitric acid and 25.3 g. (0.25 mole) of di-*n*-propylamine to a stirred solution of 150 g. (2.5 moles) acetic acid, 30.6 g. (0.3 mole) of acetic anhydride and 2.75 g. (0.035 mole) of acetyl chloride at 20° over one hour. After fifteen hours of subsequent stirring the excess anhydride was hydrolyzed with a little water and the acetic acid distilled off under 16 mm. The residue was suspended in 200 cc. of water, acidified to *p*H 2–3 and extracted with ether. This ether solution was extracted 5 times with a total of 125 cc. of 12% hydrochloric acid. When this aqueous extract was made basic to *p*H 10 and extracted with ether, subsequent distillation finally at 20 mm. yielded 1.7 g. (5% yield) of di-*n*-propylacetamide, b. p. 105–108°.

The acid extracted ether solution was evaporated to leave an oil which was extracted 4 times with 3-cc. portions of concd. hydrochloric acid. Dilution and neutralization of these acid extracts yielded the ether-soluble di-*n*-propylnitrosamine which boiled at 84–88° (10 mm.) after drying with Drierite and evaporation of the ether. The refractive index of this 2.8-g. yield (9%) was $n^{20}\mathrm{D}$ 1.4468.

The oil remaining after extraction with concd. hydrochloric acid was neutralized and dried in ether solution with Drierite. Evaporation of the ether left 20.2 g., $n^{20}\mathrm{D}$ 1.4540, of crude nitramine, m. p. −11°. This 56% crude yield was badly contaminated with organic chlorides. It was boiled with 5 times its volume of 70% nitric acid for fifty minutes, then separated (46% yield), neutralized, dried and distilled at 103–104° (10 mm.) to give a halogen-free product, $n^{20}\mathrm{D}$ 1.4559, m. p. 1.0–1.6° in 35% yield. The Franchimont test was positive.

Anal. Calcd. for $C_6H_{14}N_2O_2$: C, 49.3; H, 9.59; N, 19.2. Found: C, 49.9; H, 10.0; N, 19.4.

CHEMICAL LABORATORY
UNIVERSITY OF TORONTO
TORONTO, CANADA
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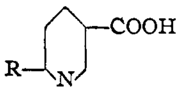
6-Iodonicotinic Acid

BY ERWIN KLINGSBERG[1]

It seemed that the well-known activity of α- and γ-pyridyl halides would make possible the conversion of 6-chloronicotinic acid (I) into 6-iodonicotinic acid (II) under the conditions of the Finkelstein reaction.[2]


(I) R = Cl
(II) R = I

In an experiment with sodium iodide and acetone, it was found that replacement was inconveniently slow. When ethyl methyl ketone was used as the solvent, the reaction proceeded smoothly to give a quantitative yield of the hitherto unreported acid (II).

Acetonylacetone shows solvent properties for sodium iodide, and preliminary experiments performed here indicate that it may be used conveniently for similar iodine exchange reactions at still higher temperatures.

Experimental

6-Iodonicotinic Acid (II).—Twenty-one grams (0.13 mole) of 6-chloronicotinic acid (I) and 40 g. (0.27 mole) of sodium iodide are refluxed for forty-eight hours in 350 ml. of ethyl methyl ketone. The solvent is evaporated and the salts removed from the residue by leaching with water containing a little bisulfite. There is obtained a quantitative yield of 6-iodonicotinic acid (II), m. p. 189–190°, which may be recrystallized from water or dilute ethanol without significant change in m. p.

Anal. Calcd. for $C_6H_4O_2NI$: C, 28.94; H, 1.62; neut. equiv., 249. Found: C, 29.39; H, 1.99; neut. equiv., 253.

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[1] Present address: Calco Chemical Division, American Cyanamid Co., Bound Brook, N. J.

(2) Finkelstein, *Ber.*, **43**, 1528 (1910).

CHEMICAL RESEARCH DIVISION
SCHERING CORPORATION
BLOOMFIELD, NEW JERSEY
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Alcoholysis of Penta- and Hexachloroacetone

BY MARSHALL KULKA

The reduction of chloral[1] and 1,1,1-trichloroacetone[2] to trichloroethanol and 1,1,1-trichloropropan-2-ol, respectively, can be achieved in high yield by means of aluminum ethylate in absolute ethanol. An attempt to reduce pentachloroacetone or hexachloroacetone in a similar manner failed. Heating pentachloroacetone with a small amount of aluminum ethylate in ethanol resulted in alcoholysis with the formation of chloroform and ethyl dichloroacetate. Hexachloroacetone cleaved similarly to chloroform and ethyl trichloroacetate. This behavior is analogous to the well known cleavage of trihalomethyl ketones by aqueous alkali.

Experimental

A solution of pentachloroacetone (50 g.), aluminum ethylate (2 g.) and absolute ethanol (50 cc.) was heated under reflux for five hours. Then it was distilled and the fraction boiling at 60–78° was washed with water, dried over calcium chloride and distilled. The colorless distillate (18 g.) had the odor, the boiling point and the refrac-

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(1) Chalmers, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 598.

(2) Meerwein, Hinz, Majert and Sönke, *J. prakt. Chem.*, **147**, 226 (1936).