The spectra of II and III in cyclohexane suggest that the monomethylated substance possesses the benzenoid structure III rather than the hemiquinone structure III′. The similarity of all of the spectra in aqueous acid solution would indicate the rupture of the lactone ring in such media. In alkaline solution where phenolate and carboxylate ions are the absorbing chromophores the data suggest that I and II exist as *p*-phenolate–carboxylate ions and III as an *o*-phenolate–carboxylate ion. The slight difference between cyclohexane and aqueous acid solutions of IV can be attributed to solvent–solute hydrogen bonding in the latter medium.

Experimental

Preparation of I, II, III and IV.—The compounds 2,4-dihydroxyphenylglyoxylic acid (I) and 2,4-dihydroxy-6-methylphenylglyoxylic acid lactone (II) were prepared by the procedures of Hunsberger, *et al.*,[1] and melted at 167–168° and 216–217°, respectively. The latter substance was methylated in the following manner.

A mixture of 1.0 g. of II and 5 ml. of methanol was prepared and 5 g. of dimethyl sulfate and a solution of 30% potassium hydroxide in water added intermittently in small portions, keeping the mixture near the neutral point. When the addition was complete (the mixture was slightly basic), water was added and the white needles that separated were recrystallized from ethanol and water to give 0.23 g. of the methyl ester of IV, m. p. 73–74°, which upon saponification gave 0.19 g. of IV, m. p. 139–141°,[1] (colorless needles from ethanol and water).

The filtrates from the crystallization of the ester were acidified and the yellow needles that separated were collected and recrystallized from ethanol and water to give 0.18 g. of III (yellow needles) m. p. 169–171°, m. m. p. with the monomethylated lactone prepared by Hunsberger,[1] 168–170°.

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Di-*n*-propylnitramide and its Isomer

BY W. R. KINGDON AND GEORGE F WRIGHT

Considerable confusion exists with respect to the compounds known as isonitramines. This is owing, firstly, to the fact that the addition products of nitric oxide with active methylenic compounds have been called isonitramine salts[1] although they are generally considered to be the salts of nitrosohydroxylamines.[2]

Secondly, such an error in nomenclature is not unexpected in view of the fact that the isonitramine structure, II, is not known with certainty but only as isomeric with the unequivocal secondary nitramide structure I, together with which it is formed when a primary nitramide salt is treated with an alkyl iodide (M is silver or potassium).

Thirdly, the confusion will not be diminished by the recent revision in nomenclature whereby I, formerly known as di-*n*-propylnitramine, is now to be classified for index purposes as di-*n*-propylnitramide. Henceforth in the present paper the older terminology will be used, since comparison must be made with the isonitramines, for which there seems at this writing to be no justification for change in nomenclature.

When both I and II are formed in the alkylation reaction, the isonitramine may be recognized by its lower boiling point and its lesser stability toward acid and alkali. Sometimes both isomers are not produced. This was the case when Thomas[3] treated silver *n*-propylnitramine with *n*-propyl iodide. He designated his single product as di-*n*-propylnitramine (b. p. 76–79° at 10 mm.). His formulation was supported by the observation[4] that the compound was stable toward hot dilute aqueous potassium hydroxide.

Secondary nitramines with saturated alkyl groups can now be prepared by direct nitration of the secondary amine.[5] When di-*n*-propylamine was nitrated in this manner the authentic di-*n*-propylnitramine was found to boil higher (103–104° at 10 mm.) than the compound reported by Thomas. Unlike Thomas' compound it melted sharply at 1.0–1.6° when it was separated entirely from di-*n*-propylacetamide and di-*n*-propylnitrosamine which were also produced by the nitration procedure.

For purposes of comparison Thomas' procedure was repeated to yield mainly the compound he reported, although a small amount (3% of theoretical) of the product of direct nitration was evidently obtained as well. This higher boiling fraction, unlike Thomas' compound, froze at a temperature below 0° and gave a positive Franchimont test for the nitramino linkage.[6] No isonitramine gives this test.

When the two compounds were heated with 5% aqueous potassium hydroxide neither decomposed appreciably, but Thomas' compound decomposed strongly with gas evolution when it was added to 70% sulfuric acid at 25°, while the product of direct nitration was quite stable toward this medium. We believe this acid test to be a better criterion for differentiation of nitramine and isonitramine than the alkali test. On this basis Thomas' compound must be the isonitramine.

Experimental[7]

n-Propyldichloramine was prepared in 71% yield (n^{24}D 1.4525, 98% electropositive chlorine) by passage of chlorine over eight hours into a solution of 33 g. (0.56 mole) of *n*-propylamine and 126 g. (1.5 moles) of sodium bicarbonate in 1 liter of water at 5–10°. The oil which settled out was washed successively with 5% aqueous sulfuric acid, 50% aqueous sulfuric acid and four times with water.

n-Propylnitramine was prepared by simultaneous and equivalent addition of 51 g. (0.4 mole) of undistilled propyldichloramine and 76 g. (1.2 moles) of 99.3% nitric acid into 204 g. (2 moles) of stirred acetic anhydride at 7–32° over fifty minutes. The addition of acid was maintained 5% ahead of the dichloramine addition. After one hour of subsequent stirring the whole was poured into a

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[1] W. Traube, *Ber.*, **27**, 1504 (1894).

[2] G. W. MacDonald and O. Masson, *J. Chem. Soc.*, **65**, 944 (1894).

[3] J. C. A. S. Thomas, *Rec. trav. chim.*, **9**, 69 (1890).

[4] H. van Erp, *Rec. trav. chim.*, **14**, 1 (1895).

[5] W. J. Chute, *et al.*, *Can. J. Research*, **26B**, 114 (1948).

[6] A. P. N. Franchimont, *Rec. trav. chim.*, **16**, 226 (1897).

[7] All melting points are corrected against known standards.

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.

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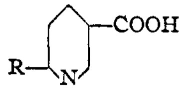
6-Iodonicotinic Acid

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).

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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).