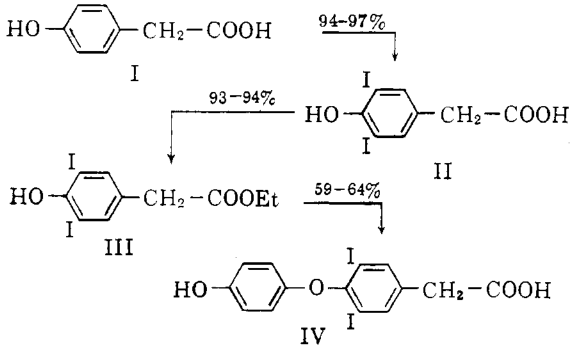
acetic acid (requiring six steps),[2] or 3-iodo-4-hydroxy-5-nitrobenzaldehyde (requiring eight steps).[3]

By means of a modified phenylation method using diaryliodonium salts,[4] we have recently prepared this compound from 4-hydroxyphenylacetic acid in three steps providing an over-all yield of 51–58%:



Experimental

4-Hydroxy-3,5-diiodophenylacetic Acid (II).—Within 1 hr., 21 ml. of 2 *N* iodine solution was added to a mixture of 15.2 g. (0.1 mole) of 4-hydroxyphenylacetic acid and 170 ml. of aqueous solution of ethylamine (15% w./v.) at 20°; after stirring for 30 min., ice was added to the solution which was then acidified with concentrated hydrochloric acid to pH 1–2 (addition of a little sodium bisulfite at pH 5–6). Cold filtration gave 38–39.2 g. (94–97% yield) of 4-hydroxy-3,5-diiodophenylacetic acid (II), m.p. 218°.

Ethyl 4-Hydroxy-3,5-diiodophenylacetate (III).—A mixture of 40.4 g. (0.1 mole) of II, 2 g. of *p*-toluenesulfonic acid, and 200 ml. of absolute ethanol was heated for 15 hr. The solution was poured onto ice and the ethyl 4-hydroxy-3,5-diiodophenylacetate (III) was filtered; yield 40.2–40.5 g. (93–94%); m.p. 121°.

Anal. Calcd. for $C_{10}H_{10}I_2O_3$: I, 58.75. Found: I, 58.8.

3,5-Diiodothyroacetic Acid (IV).—A mixture of 43.2 g. (0.1 mole) of III, 87 g. (0.2 mole) of dianisyliodonium bromide, 14 ml. of triethylamine, 15 g. of copper powder, and 90 ml. of absolute methanol was stirred at room temperature for 24 hr. After filtration of the copper, the solution was concentrated under reduced pressure; the residue was taken up by 50 ml. of benzene and washed successively with 1 *N* hydrochloric acid, water, 1 *N* sodium hydroxide, water, and 5% aqueous acetic acid; the dried, clarified benzene solution was evaporated under reduced pressure.

The residue was triturated with 150 ml. of petroleum ether (b.p. 40–60°), filtered, and heated for 3 hr. in a mixture of 160 ml. of acetic acid and 160 ml. of hydriodic acid (d = 1.7). The solution was cooled and poured into 1 l. of ice water to which a little sodium bisulfite had been added. Filtration gave 36–37.6 g. (yield 73–76%) of crude 3,5-diiodothyroacetic acid (IV), m.p. 214°. Recrystallization of IV in 53 ml. of acetic acid with 18 ml. of water and drying at 100°, under reduced pressure, gave 29.2–31.7 g. (yield 59–64%) of pure IV, m.p. 216–218°.

Anal. Calcd. for $C_{14}H_{10}I_2O_4$: I, 51.16. Found: I, 51.0. Electrophoretic control: Whatman 3 MM, 500 volts, ethanolic solution pH 12. 5 hr.: 12.0–13.3 cm. from the cathode (ultraviolet 2543 Å.).

Dianisyliodonium Bromide.—A 12.8-g. sample (0.06 mole) of potassium iodate was introduced into 50 ml. of concentrated sulfuric acid (exothermic reaction). A 5.1-g. sample (0.02 mole) of iodine was added at 15–20°. After stirring for 15 hr., the iodyl sulfate[5] was filtered, washed with acetic acid until all the sulfuric acid was eliminated, and suspended in 25 ml. of acetic acid. A mixture of 33 g. (0.6 mole) of anisol and 20 ml. of acetic anhydride was added within 1 hr. at 15–20°. Stirring was maintained for 24 hr. at room temperature and the mixture was poured onto ice. After removal of the oil by decantation, the aqueous solution was clarified with Norit, and 20 g. of potassium bromide was added to the solution. After cooling, the dianisyliodonium bromide was filtered and washed successively with water, acetone, and ether; yield 16.8–19.3 g. (40–46%); m.p. 240°.

---

[2] J. H. Wilkinson, *Biochem. J.*, **63**, 61 (1956).

[3] (a) W. Siedel and N. Nahm, *Med. u. Chem. Abhandl. med.-chem. Forschungsstätten I.G. Farbwerke Hoechst A.G.* **VI**, 249 (1958). (b) Farbwerke Hoechst, Ger. Patent 1,067,826 (1955). (c) Farbwerke Hoechst, French Patent 1,227,221 (1958).

[4] (a) F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Am. Chem. Soc.*, **75**, 2708 (1953). (b) G. Hillmann, *Zr. Naturforsch.*, **11B**, 419 (1956). (c) G. Hillmann, French Patent 1,229,626 (1956). (d) R. Michel, R. Truchot, H. Tron-Loisel, and B. Poillot, *Compt. rend.*, **250**, 2632 (1960). (e) A. Dibbo, L. Stephenson, T. Walker, and W. K. Warburton, *J. Chem. Soc.*, 2645 (1961).

[5] Warning: Do not allow contact with ether.

A New Preparation of 8-Nitro-2-naphthylamine

D. C. Morrison and Herbert P. C. Lee

Hyman Laboratories, Inc., Berkeley, California

Received March 21, 1962

The technique of preparing nitronaphthylamines by nitration of aminonaphthalenesulfonic acids, followed by desulfonation, has been used by several investigators. Nietzki and Zubelen[1] and also Bucherer and Uhlmann[2] nitrated acetylnaphthionic acid and subsequently hydrolyzed and desulfonated the product to 5-nitro-1-naphthylamine.

Ward and Pearson[3] nitrated acetylnaphthionic acid in the presence of boron trifluoride and obtained a 2-nitro derivative which was hydrolyzed and desulfonated to 2 - nitro - 1 - naphthylamine. Friedlander and Kielbasinski[4] have nitrated 1-aminonaphthalene-2-sulfonic acid but did not attempt to desulfonate the product.

In this work, the authors have nitrated Tobias acid (2-aminonaphthalene-1-sulfonic acid) at low temperatures in sulfuric acid medium and obtained a mixture of mononitro derivatives. This product was shown to consist of approximately 80–85% of the 8-nitro and 15–20% of the 5-nitro Tobias acids. It could be desulfonated to a mixture of the corresponding nitro-β-naphthylamines. 8-Nitro-2-naphthylamine can be conveniently prepared in

---

[1] R. Nietzki and J. Zubelen, *Ber.*, **22**, 451 (1889).

[2] H. Th. Bucherer and A. Uhlmann, *J. prakt. Chem.*, (II) **80**, 201 (1909).

[3] E. R. Ward and B. D. Pearson, *J. Chem. Soc.*, 3378 (1959).

[4] P. Friedlander and Kielbasinski, *Ber.*, **29**, 1978, 1982 (1896).

this manner, as after one recrystallization, the 5-isomer is essentially eliminated. The formation of as much as 85% of the 8-nitro compound compares favorably with the 50% yield of 8-nitro derivative obtained on nitration of β-naphthylphthalimide.[5,6] The removal of the phthalimide group is so difficult that the method was abandoned by Ward and Wells[6] as a preparative process for 5- or 8-nitro-2-naphthylamines. On the other hand, the nitro Tobias acids can be desulfonated easily to form these nitroamines. The production of the 8-nitro-2-naphthylamine in this way avoids the use of the carcinogenic β-naphthylamine by substitution of the presumably innocuous Tobias acid. It also provides a starting material for an alternative route to 1,7-dinitronaphthalene and to the 1,7-diamine.

The preponderance of 8-nitration may be ascribed to the peri influence of the 1-sulfonic group as naphthalene-1-sulfonic acid has long been known to nitrate in the 8 (peri) position, this being the first step in the commercial process for 8-aminonaphthalene-1-sulfonic acid (peri acid).

Prior acetylation of the amine group in Tobias acid did not change greatly the isomer distribution in the product, and no 6-nitration was observed as is the case with 2-acetylaminonaphthalene.[6,7]

The mixture of nitro Tobias acids could not be separated because of close similarity in properties. It was therefore analyzed directly.

Dinitration of Tobias acid was not successful and no identifiable product was isolated on attempted nitration of 2-aminonaphthalene-1,5-disulfonic acid (sulfonated Tobias acid).

Experimental

Nitration at 0° or above resulted in desulfonation and formation of brown amorphous material. Temperature control was therefore important and a Dry Ice-alcohol bath was used.

Nitro Tobias Acids.—Concentrated sulfuric acid (96%, 120 ml.) was cooled to −5 to −10° and treated slowly with 11.15 g. (0.05 mole) of Tobias acid with stirring. Most was soluble and the liquid was cooled further to −15° and addition of dry powdered potassium nitrate was started. A 6-g. sample (0.059 mole) of this was added in 20 min. while keeping the temperature between −10 and −16°. The brown solution was stirred 40 min. in this temperature range and then poured onto 0.5 kg. of ice. The precipitated product was filtered off and washed, and then extracted with cold dilute sodium carbonate solution. The filtered extracts were cooled to 5° and acidified with hydrochloric acid. After 3 hr. on ice, the tan crystalline powder was filtered off, washed with ice water, and dried. Two runs gave yields of 12.65 g. (94.4%) and 12.85 g. (95.9%). This product did not change on boiling its solution in sodium carbonate, but decomposed partly on storage for several months at room temperature. It was vacuum dried for analysis.

Anal. Calcd. for $C_{10}H_8SO_5$: S, 11.94. Found, S, 11.96.

Desulfonation of Nitro Tobias Acids.—A mixture of 5 g. (18.65 mmoles) of the nitrated Tobias acid and 70 ml. of 45% sulfuric acid was refluxed 40 min. It was diluted while hot to 1 l. and made alkaline with sodium hydroxide solution. The suspension was cooled to 10° for 1.5 hr., and the precipitated material filtered, washed with water, and dried; yield, 3.10 g. or 88%. The yield is poorer with nitro Tobias acid which has been stored for some time. When recrystallized once from aqueous methanol, almost all of the 5-isomer was eliminated. The 8-nitro-2-naphthylamine thus obtained, was recrystallized from aqueous methanol and from benzene-hexane, and had m.p. 104–105.5°. An intimate mixture with material obtained by the procedure of Saunders and Hamilton[7] had m.p. 104–106°. Hodgson and Ratcliffe[8] give 104.5–105°. The infrared spectrum was identical with that of authentic material.[7]

---

[5] H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 1844 (1936).

[6] E. R. Ward and P. R. Wells, *ibid.*, 4859 (1961).

[7] C. R. Saunders and C. S. Hamilton, *J. Am. Chem. Soc.*, **54**, 636 (1932).

[8] H. H. Hodgson and J. Ratcliffe, *J. Chem. Soc.*, 1040 (1949).

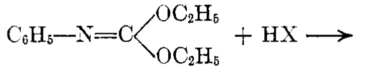
A New Type of Ring-Opening Polymerization

TERUAKI MUKAIYAMA, TAMOTSU FUJISAWA,
HIROYUKI NOHIRA, AND TERUO HYUGAJI

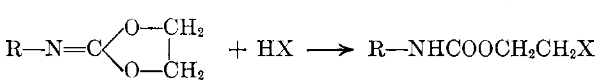
Laboratory of Organic Chemistry,
Tokyo Institute of Technology,
Meguro-Ku, Tokyo, Japan

Received March 23, 1962

The reactions of diethyl N-phenyliminocarbonate and cyclic iminocarbonates with acids, such as hydrogen chloride, carboxylic acids, and phosphoric acid, have recently been reported to afford ethyl *N*-phenylcarbamate and the corresponding esters, and compounds containing urethane and ester linkages, respectively, as shown in the following equations.[1]



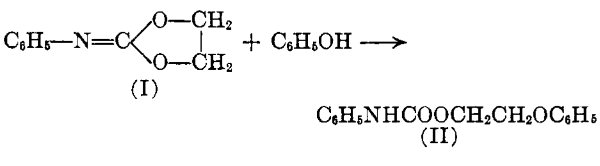
$$C_6H_5{-}N{=}C(OC_2H_5)_2 + HX \longrightarrow C_6H_5NHCOOC_2H_5 + C_2H_5X$$



$$R{-}N{=}C\langle O{-}CH_2{-}CH_2{-}O\rangle + HX \longrightarrow R{-}NHCOOCH_2CH_2X$$

Furthermore, it was found that cyclic iminocarbonates, such as ethylene N-phenyliminocarbonate and N,N'-*p*-phenylene bis(ethyleneiminocarbonate), react with phenols which are weaker acids than the acids mentioned above.

When ethylene N-phenyliminocarbonate (I) was refluxed with *p*-nitrophenol or phenol in dry benzene, β-*p*-nitrophenoxyethyl or β-phenoxyethyl N-phenylcarbamate was obtained in 53% and 55% yields, respectively.



$$\underset{(I)}{C_6H_5{-}N{=}C\langle O{-}CH_2{-}CH_2{-}O\rangle} + C_6H_5OH \longrightarrow \underset{(II)}{C_6H_5NHCOOCH_2CH_2OC_6H_5}$$

---

[1] T. Mukaiyama, T. Fujisawa, and T. Hyugaji, *Bull. Chem. Soc. Japan*, **35**, 687 (1962).