A Simplified Synthesis of α-Phenylcinnamic Acid and α-Phenyl-*p*-nitrocinnamic Acid[1]

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Benzaldehyde or *p*-nitrobenzaldehyde can be condensed with phenylacetic acid in the presence of tertiary amines with about the same yields as the Perkin reaction.[2] The advantage of this synthesis is that it does not require the anhydrous sodium salt, nor is it carried out at the high temperature of the Perkin reaction. The method is an application of one used by Bakunin and Peccerillo[3] for the synthesis of α-phenyl-*o*-nitrocinnamic acid.

A comparison of triethylamine, tri-*n*-propylamine and tri-*n*-butylamine as catalysts in the preparation of α-phenyl-*p*-nitrocinnamic acid was made. The yields in three identical experiments except for catalyst were: triethylamine, 52%; tripropylamine, 56%; tributylamine, 33%.

When the reactions were carried out with *p*-nitrophenylacetic acid in place of phenylacetic acid a successful condensation was obtained only with benzaldehyde.

Experimental

α-Phenylcinnamic Acid.[1]—Twelve cc. of benzaldehyde, 11 g. of phenylacetic acid, 23 cc. of acetic anhydride and 8 cc. of tripropylamine[4] were heated together on a steam-bath for ten hours. The reaction mixture was then poured into a dilute (10%) hydrochloric acid solution. The solid which precipitated was dissolved in benzene (125 cc.). This solution was extracted three times with 100-cc. portions of 5% sodium hydroxide. The aqueous solution was acidified with hydrochloric acid to precipitate the crude product. Two recrystallizations from a mixture of equal volumes of benzene and ligroin yielded 9.0 g. (50%) of phenylcinnamic acid, m. p. 172°.

α-Phenyl-*p*-nitrocinnamic Acid.[5]—A mixture of 3.0 g. of *p*-nitrobenzaldehyde,[6] 2.7 g. of phenylacetic acid, 5.7 cc. of acetic anhydride and 2.8 cc. of triethylamine was heated on a steam-bath for four hours. The resulting solution was made basic with sodium carbonate solution and then filtered while warm. The filtrate was acidified with hydrochloric acid. The precipitate was removed by filtration and recrystallized from ethyl alcohol. A yield of 3.6 g. (66%) of product, m. p. 208°, was obtained. A second recrystallization gave a 3.3 g. (61%) of α-phenyl-*p*-nitrocinnamic acid of m. p. 213°.

Smaller amounts were used in similar experiments to determine the relative merits of triethylamine, tripropylamine[4] and tributylamine[4] as catalysts.

When 3.6 g. of *p*-nitrophenylacetic acid (Eastman Kodak Co.) was used instead of phenylacetic acid in the above procedure, a negligible precipitate was obtained on acidification.

α-*p*-Nitrophenylcinnamic Acid.[7]—A mixture of 3.0 cc. of benzaldehyde, 3.6 g. of *p*-nitrophenylacetic acid, 5.7 cc. of acetic anhydride and 2.8 cc. of triethylamine was heated for ten hours. The red solution was poured into a 10% hydrochloric acid solution. The resinous mass obtained in this manner was extracted with ether. The yellow crystals not soluble in ether were recrystallized from ethyl alcohol. A yield of 0.7 g. (13%) of α-*p*-nitrophenylcinnamic acid, m. p. 224° was obtained.

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[1] Part of the M.S. thesis of Eugene A. Hausman, August, 1947.

[2] Johnson, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 252.

[3] Bakunin and Peccerillo, *Gazz. chim. ital.*, **65**, 1145 (1935).

[4] Supplied through the courtesy of Sharples Chemicals, Inc.

[5] Bakunin, *Gazz. chim. ital.*, **25**, I, 146 (1895).

[6] Liebermann and Connor, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 441.

[7] Borsche, *Ber.*, **42**, 3597 (1909).

Chlorination of Thiophenes with Sulfuryl Chloride

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In an attempted preparation of 3-thenyl chloride from 3-methylthiophene it was found that sulfuryl chloride did not react with alkyl thiophenes as it does with alkyl benzenes. Kharasch and Brown[1] reported a high yield of benzyl or benzal chloride, depending on the mole ratio of reactants, on treatment of toluene with sulfuryl chloride in the presence of small amounts of benzoyl peroxide. No nuclear substitution occurred. The reactive thiophene nucleus yielded only nuclear substitution products in high yield on chlorination of 2- and 3-methylthiophene by this procedure. Thiophene was also readily chlorinated by this method. The chlorinations were effected in similarly high yields in the absence of the peroxide catalyst. The chlorination of thiophene has been reported previously using sulfuryl chloride in the presence of aluminum chloride.[2]

Experimental

Chlorination of 3-Methylthiophene.—To a solution of 98 g. (1.0 mole) of 3-methylthiophene was added 140 g. (1.03 mole) of sulfuryl chloride. Spontaneous refluxing commenced during the addition and continued throughout the addition, about one-half hour being required. The solution was then heated to reflux for one additional hour. Fractionation of the product yielded 104 g. (79%) of 2-chloro-3-methylthiophene, b. p. 153–155° (754 mm.). Vacuum distillation yielded a product with an odor of chlorotoluene, b. p. 154–155° (742 mm.), 54° (19 mm.); $n^{20}\mathrm{D}$ 1.5408, d^{25}_{4} 1.2281. The physical constants are in accordance with those previously reported.[3]

Chlorination of Thiophene and 2-Methylthiophene.—These compounds were chlorinated by the same procedure as described above. The yield of 2-methyl-5(?)-chlorothiophene from 2-methylthiophene was 77% theory, b p. 154–155° (742 mm.), 55° (19 mm.); $n^{20}\mathrm{D}$ 1.5372, d^{25}_{4} 1.2147. This is the same compound obtained by Opolski[4] on direct chlorination of 2-methylthiophene.

Three moles of thiophene on treatment with three moles of sulfuryl chloride yielded on distillation 0.8 mole of unchanged thiophene, 1.3 moles of 2-chlorothiophene (43%), and 0.3 mole of 2,5-dichlorothiophene (10%). Higher chlorination products were not identified.

2-Chlorothiophene.—B. p. 127–129° (742 mm.), 56° (56 mm.); $n^{20}\mathrm{D}$ 1.5490, d^{26}_{4} 1.2923.

2,5-Dichlorothiophene.—B. p. 160–162° (742 mm.), 64.5° (25 mm.); $n^{20}\mathrm{D}$ 1.5627, d^{27}_{4} 1.4486.

The physical constants for the mono- and dichlorothiophenes are in agreement with those previously reported.[5]

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[1] Kharasch and Brown, THIS JOURNAL, **61**, 2142 (1939).

[2] Tohl and Eberhard, *Ber.*, **26**, 2947 (1893).

[3] Opolski, *Ans. Akad. Wiss. Krakau*, 548 (1905); *Chem. Zentr.*, **76**, II, 1796 (1905).

[4] Opolski, *Ans. Akad. Wiss. Krakau*, 730 (1904); *Chem. Zentr.*, **76**, I, 1255 (1905).

[5] "Thiophene Chemicals," Socony-Vacuum Oil Co., Inc., New York, N. Y., 1946.