CCCLII.—*The Two* o-*Cyanocinnamic Acids.*

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Although the two theoretically possible stereoisomeric forms of *o*-cyanocinnamic acid exist, only one form of *o*-carboxycinnamic acid is known, and this is obtained when either of the cyano-acids is hydrolysed (Edwards, J., 1926, 816). It gives the lactone of β-*o*-carboxyphenylhydracrylic acid on heating or on treatment with dehydrating agents, and attempts to prepare the true anhydride failed.

The *o*-cyanocinnamic acid melting at 256° can be obtained in 36% yield by heating the sodium salt of 1-nitroso-2-naphthol with a solvent of suitable boiling point, whereas with the use of sand as diluent (D.R.-P. 116,123) the yield is not more than 5% (Gabriel, *Ber.*, 1916, **49**, 1611). The *o*-cyanocinnamic acid melting at 137° has been prepared after D.R.-P. 411,955 by the action of *p*-toluenesulphonyl chloride on 1-nitroso-2-naphthol in the presence of aqueous alkali. During a large-scale preparation in which the heating during evaporation was very prolonged, an appreciable quantity of acetophenone-*o*-carboxylic acid was produced, possibly owing to the following changes in the $CH{:}CH{\cdot}CO_2H$ group of the carboxycinnamic acid formed by hydrolysis of the cyanocinnamic acid initially produced: $\cdot CH{:}CH{\cdot}CO_2H \longrightarrow \cdot C(OH){:}CH{\cdot}CO_2H \longrightarrow \cdot CO{\cdot}CH_2{\cdot}CO_2H \longrightarrow \cdot CO{\cdot}CH_3$. It is, however, not clear whether the atmosphere or part of the nitrosonaphthol is the oxidising agent, and this abnormal reaction will be further examined.

Experimental.

The Preparation of o-*Cyanocinnamic Acid* (m. p. 256°).—A series of experiments was carried out with *p*-cymene, *o*-nitrotoluene, and nitrobenzene as solvents and the following process was found satisfactory. The dry, finely powdered sodium salt of 1-nitroso-2-naphthol (20 g.) and nitrobenzene (120 c.c.) were heated at 205° for 2 hours. The dark mixture was shaken with a warm aqueous solution of sodium acetate, and the aqueous portion was boiled with animal charcoal and acidified with hydrochloric acid; the buff-coloured precipitate obtained (yield, 6½ g. or 36%) crystallised from nitrobenzene in colourless needles, m. p. 256° (decomp.).

This *o*-cyanocinnamic acid sublimes almost unchanged at 225°/1 mm. It is not attacked by cold concentrated sulphuric acid exposed to air, and no trace of an acid amide is formed on prolonged standing. Hydrolysis with concentrated aqueous alkaline solutions gives a large quantity of tar and only a small amount of *o*-carboxycinnamic acid (m. p. 184°). The identity of this carboxycinnamic acid with that from *o*-cyanocinnamic acid (m. p. 137°) was proved by the method of mixed melting points.

Preparation of o-*Cyano*allo*cinnamic Acid* (m. p. 137°) *after* D.R.-P. 411,955.—To a solution of 1-nitroso-2-naphthol (from 50 g. of β-naphthol *) in aqueous sodium hydroxide [45 g. (3¼ mols.) in 1 l.] at 75°, *p*-toluenesulphonyl chloride (65 g.) was added all at once. The temperature was then rapidly raised to 100° and maintained for 15 minutes; a vigorous reaction began at 85°. Some tar was filtered off when cold, and after acidification a large, orange-yellow precipitate settled out. When this was crystallised from hot water, 15 g. of cyanocinnamic acid (m. p. 137°) were obtained, and subsequently 6 g. of a yellow, granular material.

Acetophenone-o-*carboxylic Acid.*—In a preliminary experiment (1-nitroso-2-naphthol from 200 g. of β-naphthol; 10 l. of water; 3¼ mols. of sodium hydroxide; 320 g. of *p*-toluenesulphonyl chloride) the procedure was as described above. After the 15 minutes' heating at 100°, the mixture was rapidly cooled to 40° with ice. A large amount of a green substance like the sodium salt of nitrosonaphthol was left. The filtrate from this was evaporated to 4½ litres, and the green substance (assumed to be the sodium salt of nitrosonaphthol) then added together with the requisite amounts of sodium hydroxide and toluenesulphonyl chloride. The mixture was kept at 100° for 15 minutes, and on cooling, a green precipitate was again formed. The filtrate when acidified with hydrochloric acid gave much tar, and after the removal of this the solution was again made alkaline with sodium hydroxide solution; a dark substance slowly separated from the deep red solution. This solution was concentrated and acidified with hydrochloric acid, whereby, instead of *o*-carboxycinnamic acid, a deep red oil was produced. This was extracted with ether, the ether removed, and the pasty residue crystallised from water, 20 g. of crude crystalline acetophenone-*o*-carboxylic acid being obtained. This crystallised from benzene in colourless prisms, which melted at 114—115° and had a sweet taste (Found: equiv., 165·4; M, by Rast's method, 163, 171; H, 5·2. Calc. for $C_9H_8O_3$: equiv. and M, 164; H, 4·9%) (compare Gabriel and Michael, *Ber.*, 1877, **10**, 1554. Rule and Smith, J., 1926, 556, record m. p. 112°). The *oxime* crystallised from alcohol in colourless needles, m. p. 156—157°, and the p-*nitrophenylhydrazone* in minute, yellow, felted needles, m. p. 211°. The *phenylhydrazone*

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* β-Naphthol is nitrosated in about 85% yield after Lagodzinski and Hardine (*Ber.*, 1894, **27**, 3075), and is most conveniently used moist. The nitrosonaphthol is difficult to dry completely, and the sodium salt when dry is very sternutatory.

is too soluble in water to be a convenient derivative for identification. The acid was smoothly converted into phthalic acid by oxidation with permanganate solution.

Properties and Derivatives of o-*Cyano*allo*cinnamic Acid.*—On being heated slightly above its melting point under 1 mm. pressure, this acid distils with some decomposition. The oily distillate, which has the odour of styrene, contains the isomeric *o*-cyanocinnamic acid, m. p. 256°. The *allo*-acid is easily hydrolysed to the corresponding dicarboxylic acid (m. p. 184°).

o-*Cyano*allo*cinnamyl chloride* is best prepared by heating the corresponding acid with a slight excess of thionyl chloride for 1 hour; the excess of thionyl chloride is then removed in a vacuum. The residual acid chloride crystallises from petroleum (b. p. 120°) in colourless needles, 2 cm. long (Found: Cl, 18·4. $C_{10}H_6ONCl$ requires Cl, 18·5%). It melts at 50°, and is extremely soluble in benzene, ether, or dichloroethylene, and sparingly soluble in cold light petroleum. Ethyl and methyl alcohol convert it into the ethyl and methyl esters of the lactone of β-*o*-carboxyphenylhydracrylic acid (Roth, *Ber.*, 1914, **47**, 1598), m. p. 76° and 62°, respectively.

The authors wish to thank Mr. F. C. Woods, M.Sc., for assistance in preparing the *o*-cyanocinnamic acid of m. p. 256°.

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