CLIV.—*Some Experiments with* 1 : 8-*Naphthalyl Chloride.*

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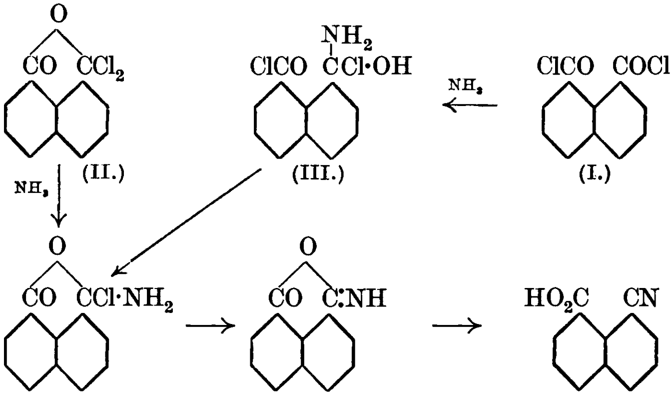
It is known that the dichlorides of several dicarboxylic acids (*e.g.*, *o*-phthalic acid) can exist in two tautomeric forms and it was therefore decided to examine 1 : 8-naphthalyl chloride (Mason, J., 1924,

125, 2116) in order to determine whether an analogous type of tautomerism could occur in this case; the examination, however, has failed to reveal the existence of more than one form, both distillation under 0·2 mm. pressure and treatment with aluminium chloride leaving the chloride unchanged.

Catalytic reduction of the chloride by Rosenmund's method (*Ber.*, 1921, **54**, 432) under conditions which gave an excellent yield of benzaldehyde from benzoyl chloride gave a complex mixture from which only naphthalic anhydride could be isolated.

The interactions of naphthalyl chloride and of phthalyl chloride with ammonia follow similar courses, but the production of 1-cyano-8-naphthoic acid can be explained equally well by either of the possible formulæ for naphthalyl chloride (I) or (II) *via* the intermediate compounds (III), (IV), and (V) (compare Staudinger, *Ber.*, 1911, **44**, 1643). It is noteworthy, however, that ammonia reacts very slowly with the chloride in benzene solution.



The action of aniline and of dimethylaniline on naphthalyl chloride followed normal lines, yielding, respectively, 1 : 8-naphthaldianilide and 1 : 8-naphthalbisdimethylanilide.

The evidence obtained therefore leaves the question of the constitution of 1 : 8-naphthalyl chloride still unsettled.

EXPERIMENTAL.

1 : 8-Naphthalyl chloride was prepared after the method of Mason (*loc. cit.*). It is advantageous to use glacial phosphoric acid as grease for the ground joint in the bromine flask in order to prevent seizing. In addition to the properties already described, naphthalyl chloride is very soluble in benzene, hot or cold. Attempts to distil it under moderately reduced pressure lead to complete decomposition

as mentioned by Mason, some carbonyl chloride being produced. The substance, however, distils unchanged at 195—200°/about 0·2 mm. when the operation is rapidly carried out on small quantities (about 10 g.).

Attempted Conversion into the Tautomeric Form.—When the acid chloride is heated for several hours with its own weight of powdered aluminium chloride in a sealed tube, no appreciable change occurs at about 86°, and complete decomposition takes place at about 115°. Since the substance can even be distilled without the other tautomeric form being produced, it is evident that the acid chloride has no great tendency to exhibit tautomerism.

1-*Cyano*-8-*naphthoic Acid.*—A solution of naphthalyl chloride (10 g.) in benzene (150 c.c.) is filtered from a trace of anhydride, and a stream of dry ammonia passed into it for 2 hours with shaking and occasional heating. Reaction readily occurs and a copious grey precipitate is formed. The benzene filtrate smells strongly of ammonia, but evolves a large quantity of hydrogen chloride after 12 hours. This phenomenon is also observed when the ammonia has been passed for a much longer period, and seems to indicate that the acid chloride is not very reactive towards dry ammonia. Concentrated aqueous ammonia and a benzene solution of the acid chloride rapidly interact, but the product is naphthalic anhydride. The above-mentioned grey precipitate is collected and shaken with hot aqueous sodium carbonate, the filtered red solution is quickly cooled and acidified with acetic acid, and the naphthalic acid produced is collected; the filtrate is then strongly acidified with hydrochloric acid, whereupon about 3 g. of the crude *cyanonaphthoic acid* separate. It crystallises from benzene–light petroleum, or from nitrobenzene, in clusters of colourless needles. It is sparingly soluble in water, moderately easily soluble in most of the usual organic solvents, and melts indefinitely with decomposition at 210—250°; the product contains naphthalimide, m. p. 300° (Found : equiv., 196·8; N, 7·1. $C_{12}H_7O_2N$ requires equiv., 197; N, 7·1%).

Cyanonaphthoic acid is very reactive. It dissolves in cold concentrated sulphuric acid with a purple fluorescence, and is gradually converted into naphthalic anhydride (m. p. 274°; mixed m. p. 274°). It dissolves readily in cold dilute sodium hydroxide solution and in warm ammonia and sodium carbonate solutions, from which it is only partly precipitated by excess of acetic acid, but completely by mineral acid. The solution in any of the alkaline reagents mentioned, when boiled for some time, deposits a large amount of crystalline matter in the heat, and the cyanonaphthoic acid is rapidly destroyed. Probably salts of naphthalic acid and of the acid amide of naphthalic acid are produced. Attempts to methylate the cyanonaphthoic acid with silver oxide and methyl iodide gave methyl naphthalate, m. p. 102° (mixed m. p. 102°).

1 : 8-*Naphthaldianilide*.—A dilute benzene solution of naphthalyl chloride is mixed with excess of aniline in benzene and the solid which slowly settles is collected after 24 hours. This is well washed with benzene and repeatedly with boiling water, and the dried substance is crystallised from nitrobenzene, from which it separates in minute, colourless needles melting with decomposition at 250—282° according to the rate of heating (Found : N, 7·9. $C_{24}H_{18}O_2N_2$ requires N, 7·65%). The substance is only sparingly soluble in low-boiling organic solvents.

1 : 8-*Naphthalbisdimethylanilide* is formed similarly, but in this case a large quantity of naphthalic anhydride is formed, which is removed by repeated extraction with boiling potassium hydroxide solution. 1 : 8-*Naphthalbisdimethylanilide* separates from nitrobenzene in minute prisms, melting sharply at 245—246° without decomposition (Found : N, 7·4. $C_{26}H_{22}O_2N_2$ requires N, 7·2%).

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