ON THE ACTION OF NITROUS ANHYDRIDE UPON ORGANIC COMPOUNDS.

By L. H. Friedburg and John A. Mandel.

(*Second Paper.*)

Before taking up the study of the reaction of nitrous anhydride upon benzaldehyde, we submitted diphenyl and benzonitrile to the same reaction under the conditions already given.

Diphenyl and Nitrous Anhydride.—Diphenyl was prepared by the method of Berthelot,[2] as modified by G. Schultz[3] and by H. Hübner.[4] A piece of ¾-inch gas pipe about two feet long was filled with pieces of pumice of about half the size of a pea and heated in an ordinary combustion furnace so that a length of four decimetres in the middle of the pipe were kept at a bright red heat. One of its ends was tightly connected with a flask in which benzol was kept gently boiling on a water bath. A current of carbon dioxide was allowed to pass through the benzol and with the vapor through the heated pipe. The other end of the pipe was connected with two well cooled flasks. In these the gases were condensed. The second flask carried in addition a piece of glass tube to lead away uncondensed gases into the chimney. After all of the benzol had passed through the hot iron tube, the liquid from the flasks was returned to the flask from which the benzol had been distilled and two-thirds of it were again vaporized

[1] J. Am. Chem. Soc., **12**, 1.
[2] Comptes rendus, **63**, *788, et seq.*
[3] Ann. Chem. (Liebig), **174**, *201*, and Ber. chem. Ges., **7**, *52*.
[4] Ann. Chem. (Liebig), **209**, *333*.

through the hot pipe. This last distillation was repeated once more. The liquids collected, containing diphenyl and unchanged benzol were united and the benzol driven off on a water bath. The residue was put into a flask with hot water, boiled, and the diphenyl distilled with steam. A good Liebig's condenser served for condensing the compound which was collected on a filter, pressed, dried and crystallized once from alcohol. Thus diphenyl was easily and abundantly obtained chemically pure and in flat, shining crystals of a snowy white.

Diphenyl, dissolved in carbon disulphide, was then treated (in the manner described in our first paper) with nitrous anhydride. The brown vapors having totally disappeared, the carbon disulphide was driven off on a water bath and the residue distilled in a current of steam, to separate the products formed from unattacked diphenyl which was condensed and regained in the cooler. The residue in the distilling flask contained an oily substance, heavier than water and but slightly soluble in it. The faintly yellow colored, watery solution was poured off and the oily mass solidified slowly. It was dissolved in alcohol.

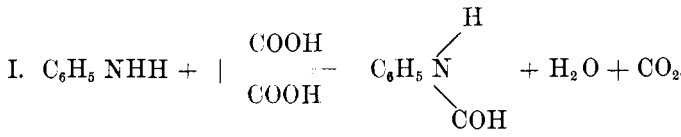
A crop of brown crystals was obtained the following day. These were redissolved in alcohol and soon deposited in long, colorless, brilliant needles which proved to be paramononitrodiphenyl of the exact melting point 113° C. The mother liquor was allowed to crystallize and deposited warty crystals, almost brick red, which as yet were not pure enough to identify. As far as our observations go, they do *not* seem to be the isomononitrodiphenyl of melting point 37° C.

Benzonitrile and Nitrous Anhydride.—The preparation of benzonitrile was made a special study. The methods which lead to it, are of but little practical value, except that of Krüss.[5] Our original intention was to follow the prescription of A. W. Hofmann,[6] to treat aniline with perfectly anhydrous oxalic acid. Previous experience had given us some benzonitrile in this manner, but we were astonished in this case (although working most carefully and using varied proportions) to obtain no benzonitrile *at all*, but an

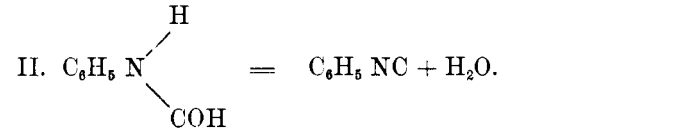
[5] Ber. chem. Ges. **17**, *1767*.

[6] Comptes rendus, **64**, *387*; Ann. Chem. (Liebig) **142**, *125*.

abundance of phenylcarbylamine (isobenzonitrile) of offensive odor. The chemical equations for this reaction speak more simply for the result.



$$\text{I. } C_6H_5NHH + \left|\begin{matrix}COOH\\COOH\end{matrix}\right. = C_6H_5\overset{H}{\underset{COH}{N}} + H_2O + CO_2.$$



$$\text{II. } C_6H_5\overset{H}{\underset{COH}{N}} = C_6H_5NC + H_2O.$$

We, therefore, resorted to Krüss' method (*loc. cit.*), which consists in heating to 190° C. two mols. of benzoïc acid with one mol. of lead sulphocyanide, well mixed in a large retort, to which a Liebig condenser is attached. Amongst other products, formed simultaneously, benzonitrile distills over, rather impure from presence of sulphur compounds. It is quite difficult to remove these latter by fractional distillation alone, but we easily obtained a product entirely free from sulphur, and boiling constantly at + 190° C., by shaking the impure oil vigorously for some time with pure metallic mercury. Benzonitrile thus prepared was used by us, and, as we shall have to repeat the reaction, will be used in future, so that the above description of its preparation will serve as a reference. The experiment did not lead to any notable reaction and we intend to repeat it, but with the difference of working in pressure tubes at high temperatures. The same will be done with diphenyl and nitrous anhydride.

Benzaldehyde and Nitrous Anhydride.—The product of reaction was *not* a substitution product, but the aldehyde was simply oxidized to benzoïc acid. We shall consequently repeat this experiment also in sealed tubes at higher temperatures.

Aromatic Acids and Nitrous Anhydride.—Benzoïc and phthalic acids were used. Neither of these are soluble enough in carbon disulphide to permit of an adequate reaction. A mere trifle was acted upon in both cases. The experiment was repeated, using alcohol as a solvent for the acids. The reaction was better, but

too much nitrous ether was formed and, in the case of benzoïc acid, benzoïc ether in addition. Substitution products formed in these reactions.

The benzoïc acid, treated with carbon disulphide and nitrous anhydride, *without* using alcohol as a solvent, furnished a *nitroso* compound, the barium salt of which was prepared after we had carefully driven off the unattacked benzoïc acid by persistent boiling, continued for nearly a week, replacing the water at intervals. The acid, separated from its barium salt by means of sulphuric acid, melted at 114° C. The barium salt is very sparingly soluble in alcohol, but easily in water, yielding an amber-yellow solution from which the salt crystallized in a few days. A barium determination, using 0.1949 grm. of the crystals, was made, and 0.0953 grm. barium sulphate were obtained. Theory demands 28.98 per cent. Ba for barium *nitroso*benzoate of the formula

$$(C_6H_4.NO.COO)_2.Ba + 2H_2O.$$

We found, according to the figures given: 28.73 per cent.

We have thus found a direct way of preparing nitroso acids, at least nitrosobenzoïc acid, which we shall now try to obtain in larger quantities, using sealed tubes, if possible, for the reaction.

The alcoholic solution of phthalic acid, when acted upon by nitrous anhydride, furnished a yellow oil which solidified after several weeks. It could not yet be used for any determination.

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DETERMINATIONS OF THE FIRING POINTS OF VARIOUS EXPLOSIVES.

BY CHARLES E. MUNROE.

For this purpose an apparatus devised by Mr. Horsley,* was used which consisted of an iron stand with a ring support holding a hemispherical iron vessel in which paraffine or tin was put.

**Trans. Soc. Eng. (Eng.) 1872, page 15.*