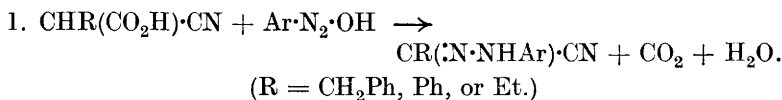


CCXIII.—*Condensation of Aryldiazonium Salts and of Alkyl Nitrites with certain Derivatives of Cyanoacetic Acid.*

By THOMAS KENNEDY WALKER.

IN extension of the investigation dealing with the action of aryl-diazonium salts on monoalkylmalonic acids (J., 1923, **123**, 2775) a study has been made of the action of these salts on monoalkylcyanoacetic acids, and of the behaviour of nitrous acid and alkyl nitrites towards the latter acids and their esters.

When solutions of aryl-diazonium salts were allowed to react with alkylcyanoacetic acids, carbon dioxide was liberated and hydrazones (type I) were produced :



On the other hand, nitrous acid and alkyl nitrites were without action on monoalkylcyanoacetic acids, whilst the esters of these acids also resisted attack to a large extent and only under one set of conditions could be made to yield oximino-derivatives, CR(:N·OH)·CN (type II). The reason for this lack of activity is not evident, for it has long been known that nitrous acid condenses with the monoalkylated malonic acids and their esters.

Based on the results obtained now and previously (*loc. cit.*), the following generalisation may be advanced: An aryldiazonium salt condenses with a compound of the type CHRXY, where X = CO₂H, CO₂R', COR', CN, and Y = CO₂H, CO₂R' (R and R' being alkyl groups); whilst an alkyl nitrite condenses with such a compound in all cases except those in which, at the same time, X = CN and Y = CO₂H.

It was deemed of interest to investigate the action of nitrosobenzene on methine compounds of the same type (CHRXY) in view of the well-known tendency of the nitroso-group to react with substances containing positively polarised hydrogen. In no case, however, could interaction be brought about, although, for the most part, condensation readily occurred with the corresponding methylene derivatives (CH₂XY).*

EXPERIMENTAL.

The difficulties experienced by Cassirer (*Ber.*, 1892, **25**, 3028) and Hessler (*Amer. Chem. J.*, 1899, **22**, 169) in monobenzylating cyanoacetic ester can be largely overcome by the use of an excess of the ester (3 mols. to 1 of benzyl chloride and 1 of sodium ethoxide). The yield is 60 per cent. of the theoretical, the production of the dibenzyl compound being negligible, and the excess of ethyl cyanoacetate can be recovered by distillation. The benzyl-ester can be converted into the benzyl-acid by shaking for 10 minutes with the necessary quantity of 20 per cent. sodium hydroxide and neutralising with cold concentrated hydrochloric acid.

Phenylpyruvonitrilephenylhydrazone (This substance and the other phenylhydrazones described below belong to type I).—A diazotised solution of aniline (3.1 gms.) in hydrochloric acid (10 c.c.) was treated with sufficient sodium acetate to remove the free mineral

* Thus, ethyl malonate and nitrosobenzene yielded *ethyl phenylimino-malonate*, colourless needles, m. p. 113.5° (Found: C = 62.9; H = 6.1; N = 5.7. C₁₃H₁₅O₄N requires C = 62.6; H = 6.0; N = 5.6 per cent.)

acid, and with an ice-cold solution, also containing sodium acetate, of benzylcyanoacetic acid (5.8 gms.) in 30 c.c. of water, carbon dioxide being evolved. The yellow syrup obtained solidified after remaining for 24 hours at 0° , and crystallised from warm alcohol in minute, buff plates, and from acetone in compact, star-like aggregates, m. p. 157° . Yield almost quantitative (Found: C = 76.3; H = 5.7; N = 18.1. $C_{15}H_{13}N_3$ requires C = 76.6; H = 5.5; N = 17.9 per cent.). Boiling 15 per cent. alcoholic potash converted it, with evolution of ammonia, into phenylpyruvic acid phenylhydrazone, m. p. 161° .

Phenylpyruvonitrile-p-tolylhydrazone.—A solution of benzylcyanoacetic acid (3.5 gms.) in an ice-cold mixture of 20 c.c. of water and 10 c.c. of alcohol was poured into a concentrated aqueous solution of *p*-toluenediazonium sulphate (1 mol.) and maintained at 0° ; finally a slight excess of sodium acetate was added. The product collected after 3 hours crystallised from boiling alcohol in slender, pale yellow prisms, m. p. 113° (decomp.) (yield 25 per cent.) or from acetone or light petroleum (Found: C = 76.8; H = 6.3; N = 17.0. $C_{16}H_{15}N_3$ requires C = 77.1; H = 6.0; N = 16.9 per cent.).

Phenylpyruvonitrile-p-nitrophenylhydrazone, obtained in small yield when a solution of diazotised *p*-nitroaniline was mixed with an aqueous solution of the sodium salt of benzylcyanoacetic acid, crystallised from chloroform in deep yellow, microscopic prisms, m. p. 167 – 168° , with frothing (Found: N = 20.2. $C_{15}H_{12}O_2N_4$ requires N = 20.0 per cent.).

Methylpyruvonitrile-p-tolylhydrazone, prepared in the same way as the corresponding derivative of phenylpyruvonitrile, melts at 143 – 144° (compare Favrel, *Compt. rend.*, 1901, **132**, 983).

Methylpyruvonitrile-p-chlorophenylhydrazone was prepared in almost quantitative yield by the same general method. It was found advantageous to carry out the diazotisation of the *p*-chloroaniline and the subsequent condensation in presence of glacial acetic acid. The substance is very sparingly soluble in the usual organic solvents. After successive crystallisations from hot glacial acetic acid and boiling benzene, it formed minute, crimson leaflets, m. p. 172° (Found: N = 20.4. $C_{10}H_{10}N_3Cl$ requires N = 20.29 per cent.).

Phenylglyoxylonitrilephenylhydrazone.—A solution of the sodium salt of ethyl phenylcyanoacetate in a small volume of ice-water was treated with a concentrated aqueous solution of crystalline benzenediazonium sulphate (1 mol.), followed by potassium carbonate (1 mol.). Recrystallised from hot glacial acetic acid and from hot acetone, the product formed sulphur-yellow needles, m. p. 152° (compare Sachs and Bry, *Ber.*, 1901, **34**, 118).

Phenylpyruvonnitrile Oxime (Type II).—Solutions of ethyl benzylcyanoacetate (4 gms.) and amyl nitrite (2.35 gms.) in 60 c.c. of dry ether and of potassium ethoxide (1 mol.) in absolute ether (Hantzsch and Lehmann, *Ber.*, 1901, **34**, 2512) were mixed at 0° and kept cold. After 48 hours, the crystalline product was washed with dry ether, when it became almost colourless; it was extremely hygroscopic, changing in the air to a dark, sticky mass. On cautious acidification, the free oxime separated as a red oil, which could not be induced to crystallise and was unstable. The *silver* salt was obtained from the potassium salt as a white, amorphous powder which slowly darkened in daylight (Found: Ag = 40.7. $C_9H_7ON_2Ag$ requires Ag = 40.42 per cent.). The constitution of the oxime was proved by the facts that on boiling with hydrochloric acid and subsequent basification it gave hydroxylamine, whilst on heating with an excess of 15 per cent. alcoholic potash for 4 hours, followed by acidification, it yielded α -oximino- β -phenylpropionic acid, m. p. 159–160°.

Methylpyruvonnitrile oxime (type II), a red oil, was obtained in the form of its potassium salt by the interaction of ethyl ethylcyanoacetate and amyl nitrite or ethyl nitrite as in the previous preparation. The salts with sodium and potassium are extremely hygroscopic, the *silver* salt is a yellowish-white powder which darkens in daylight (Found: Ag = 52.4. $C_4H_5ON_2Ag$ requires Ag = 52.65 per cent.). Attempts to prepare derivatives of this oxime resulted only in its decomposition.

Phenylglyoxylonitrile oxime (type II) was prepared in small quantity from ethyl phenylcyanoacetate by the new method, which in this case was modified in that a larger proportion of absolute alcohol was used to keep in solution ethyl phenylsodiocyanoacetate. This oxime separated from hot water in plates, m. p. 129° (compare A. Meyer, *Ber.*, 1898, **21**, 1314; Sachs, *ibid.*, 1900, **33**, 963).

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THE UNIVERSITY, MANCHESTER.

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