CXXXVI.—*The Oxidation of Nitrophenylcyanoacetates. Part II.*

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THE oxidation of certain nitrophenylcyanoacetates by chromic anhydride, hydrogen peroxide, and nitric acid has been studied, and the results indicate that the nature of the product depends upon the nitrophenylcyanoacetate rather than upon the agent employed. For example, of the three types of product obtained, *viz.* (*a*) ketonic ester, (*b*) substituted succinic ester, and (*c*) malonamate, ethyl 2 : 4-dinitrophenylcyanoacetate is oxidised to the type (*a*) by chromic anhydride, hydrogen peroxide, or nitric acid; ethyl *p*-nitrophenylcyanoacetate is oxidised to the type (*b*) by chromic anhydride, hydrogen peroxide, or 20% nitric acid; ethyl 2 : 4-dinitrophenylchlorocyanoacetate is converted into the type (*c*) by chromic anhydride or sulphuric acid, nitric acid and hydrogen peroxide having no action under the conditions employed; and ethyl 2 : 4 : 6-trinitrophenylchlorocyanoacetate does not react in any of these ways.

In Part I (J., 1927, 46) the oxidation by chromic anhydride was supposed to proceed through an intermediate hydroxy-ester, $R\cdot C(OH)(CN)\cdot CO_2Et$, but only in the case of a brominated 2 : 4-dinitrophenylcyanoacetate was a compound having the required composition isolated; its formation was regarded as evidence that the bromine atom was in the benzene ring and a hydroxyl group in the side chain. The similar behaviour of the corresponding chloro-compound (*loc. cit.*, p. 50) on oxidation seemed to confirm this view, but the unexpected removal of the halogen by alkali has now indicated that correct formulæ had not been assigned to the two compounds.

When the chlorination product of ethyl 2 : 4-dinitrophenylsodiocyanoacetate reacts in alcoholic solution with the silver derivative of ethyl 2 : 4-dinitrophenylcyanoacetate, some silver chloride is produced together with *ethyl* αβ-*bis*-2 : 4-*dinitrophenyl*-αβ-*dicyanosuccinate*; the yield of the latter, however, never exceeds 50%. This apparent proof of the position of the halogen atom in the chlorination product was therefore rendered indecisive by the

$$\begin{array}{ccc} C_6H_3(NO_2)_2\cdot CAg(CN)\cdot CO_2Et & & C_6H_3(NO_2)_2\cdot C(CN)\cdot CO_2Et \\ + & \longrightarrow & | \\ C_6H_3(NO_2)_2\cdot CCl(CN)\cdot CO_2Et & & C_6H_3(NO_2)_2\cdot C(CN)\cdot CO_2Et \end{array}$$

discovery that the same bisdinitrophenyldicyanosuccinate is formed, together with metallic silver, when the silver derivative of ethyl 2 : 4-

dinitrophenylcyanoacetate is boiled alone in alcohol (a synthesis believed to be without precedent; compare, however, Kharasch, *J. Amer. Chem. Soc.*, 1921, **43**, 2239). An attempt to synthesise the same succinate by the action of metallic silver upon the chlorination product alone was unsuccessful.

The position of the halogen atom in the side-chain of the product of the chlorination or bromination of ethyl 2 : 4-dinitrophenylsodiocyanoacetate was definitely established by the preparation of ethyl 2 : 4-dinitrobenzoylformate phenylhydrazone (identical with an authentic specimen; *loc. cit.*, p. 49) from both products.

The alleged hydroxy-esters obtained by the action of chromic anhydride on ethyl 2 : 4-dinitrophenylchlorocyanoacetate and ethyl 2 : 4-dinitrophenylbromocyanoacetate in acetic acid are actually ethyl dinitrophenylhalogenomalonamates, for they are also formed by means of sulphuric acid without the use of chromic anhydride, and yield 2 : 4-dinitrophenylhalogenoacetamides on elimination of the carbethoxy-group.

The compounds previously described (*loc. cit.*, pp. 49, 50) as ethyl 2 : 4-dinitrobromophenylcyanoacetate and ethyl 2 : 4-dinitrochlorophenylcyanoacetate are ethyl 2 : 4-dinitrophenylbromocyanoacetate and ethyl 2 : 4-dinitrophenylchlorocyanoacetate, respectively.

EXPERIMENTAL.

Ethyl 2 : 4-Dinitrophenylchloromalonamate, $C_6H_3(NO_2)_2{\cdot}CCl(CO{\cdot}NH_2){\cdot}CO_2Et$.—(*a*) A mixture of chromic anhydride (0·6 g.) and ethyl 2 : 4-dinitrophenylchlorocyanoacetate (2·5 g.) in 15 c.c. of glacial acetic acid was boiled for $\frac{3}{4}$ hour, some of the solvent was then distilled off, and the residue was poured into water. The product crystallised from alcohol in rhombic plates, m. p. 121°, which gave a purple coloration with alcoholic potash (Found : Cl, 10·9. $C_{11}H_{10}O_7N_3Cl$ requires Cl, 10·7%).

(*b*) A solution of 0·5 g. of ethyl 2 : 4-dinitrophenylchlorocyanoacetate in 2·5 c.c. of concentrated sulphuric acid was kept at 80° for $\frac{1}{2}$ hour and then poured into water. After crystallising from alcohol, the product, alone or when mixed with that described in (*a*), melted at 121°.

2 : 4-*Dinitrophenylchloroacetamide*, $C_6H_3(NO_2)_2{\cdot}CHCl{\cdot}CO{\cdot}NH_2$.—A solution of 1 g. of ethyl 2 : 4-dinitrophenylchlorocyanoacetate in 5 c.c. of concentrated sulphuric acid was heated at 120—130° for $\frac{1}{2}$ hour and then poured into 45 c.c. of water. A brown gum separated, from which crystals were obtained at 0°. These were boiled with charcoal in alcohol and recrystallised, giving white needles, m. p. 134°; on treatment with alcoholic sodium hydroxide, a red-

dish-purple colour developed (Found : Cl, 13·4 ; N, 16·3. $C_8H_6O_5N_3Cl$ requires Cl, 13·6 ; N, 16·2%).

Ethyl 2 : 4-*Dinitrophenylbromomalonamate*, $C_6H_3(NO_2)_2{\cdot}CBr(CO{\cdot}NH_2){\cdot}CO_2Et$. —This compound was previously prepared by method (*a*) and erroneously described as ethyl 2 : 4-dinitrobromophenylhydroxycyanoacetate (*loc. cit.*, p. 50). It has now been obtained by method (*b*). The two specimens melted separately or together at 157°.

2 : 4-*Dinitrophenylbromoacetamide* was prepared in an exactly similar manner to the chloroacetamide. It melted at 160°, and gave a deep reddish-purple coloration with alcoholic sodium hydroxide (Found : N, 14·1. $C_8H_6O_5N_3Br$ requires N, 13·8%).

Ethyl αβ-*Bis*-2 : 4-*dinitrophenyl*-αβ-*dicyanosuccinate*.—(*a*) 2·5 G. of the silver derivative of ethyl 2 : 4-dinitrophenylcyanoacetate (*loc. cit.*, p. 48) were boiled with 0·8 g. of iodine in alcohol for ¼ hour, silver iodide being formed. The hot filtered solution deposited a solid, which, after being treated with warm ether, crystallised from glacial acetic acid in colourless, hexagonal plates. The substance was not attacked by concentrated nitric acid and gave a red coloration on treatment with alcoholic sodium hydroxide (Found : C, 47·2 ; H, 3·2 ; N, 14·9. $C_{22}H_{16}O_{12}N_6$ requires C, 47·5 ; H, 2·9 ; N, 15·1%).

(*b*) 2·2 G. of the preceding silver derivative were boiled with an equivalent quantity of ethyl 2 : 4-dinitrophenylchlorocyanoacetate in 20 c.c. of alcohol for 4 hours. The product was isolated from the hot filtered solution as in method (*a*).

(*c*) 1 G. of the silver derivative of ethyl 2 : 4-dinitrophenylcyanoacetate was boiled for 2—3 hours with 10 c.c. of alcohol; metallic silver was then deposited upon the walls of the flask. The ester separated from the hot, filtered solution on cooling, and was purified as before.

The three specimens, alone or mixed, melted at 156°.

Preparation of Ethyl 2 : 4-*Dinitrophenylbenzoylformate Phenylhydrazone from Ethyl* 2 : 4-*Dinitrophenylchlorocyanoacetate and from Ethyl* 2 : 4-*Dinitrophenylbromocyanoacetate*.—Either compound in ethereal solution was slowly added, with thorough mixing, to an excess of ½*N*-sodium hydroxide, and the whole was warmed to 40—50°. The resulting solution was acidified with sulphuric acid and shaken with ether. From the extract, dried over sodium sulphate, an oil was obtained which, upon being boiled in glacial acetic acid with an excess of chromic anhydride for ½ hour and poured into water, yielded a viscous material. This was warmed in dilute acetic acid solution with a few drops of phenylhydrazine for ¼ hour; the phenylhydrazone that separated crystallised from glacial acetic acid in golden-yellow needles which melted, alone or mixed with an authentic specimen (J., 1927, 49), at 170°.

Ethyl 2 : 4 : 6-*trinitrophenylchlorocyanoacetate* was prepared by treating ethyl 2 : 4 : 6-trinitrophenylcyanoacetate in the theoretical quantity of sodium hydroxide solution with chlorine until the red colour was destroyed. The *ester* separated on warming and shaking, and was obtained in rhombic plates, m. p. 118°, by crystallisation from alcohol (Found : Cl, 9·9. $C_{11}H_7O_8N_4Cl$ requires Cl, 9·9%).

Oxidation with Nitric Acid or Hydrogen Peroxide.—(i) A solution of ethyl *p*-nitrophenylcyanoacetate (2 g.) in glacial acetic acid (10 c.c.) was heated with 2 c.c. of hydrogen peroxide on a water-bath for 20 minutes. On cooling, ethyl αβ-di-*p*-nitrophenyl-αβ-dicyanosuccinate separated; after several crystallisations from glacial acetic acid, it melted, alone or mixed with an authentic specimen (J., 1927, 49), at 209°.

Oxidation with concentrated nitric acid produced *p*-nitrobenzoic acid, but by means of 20% nitric acid at 100° ethyl αβ-di-*p*-nitrophenyl-αβ-dicyanosuccinate was obtained.

(ii) Ethyl 2 : 4-dinitrophenylcyanoacetate (3 g.) was heated with 15 c.c. of concentrated nitric acid on a water-bath for 5—10 minutes until dissolved. Water was added to the mixture, and ethyl 2 : 4-dinitrobenzoylformate then separated as a yellow oil, which solidified after cooling in ice for some time. After crystallising from glacial acetic acid and from alcohol, it melted at 89°, alone or mixed with an authentic specimen (J., 1927, 49).

0·5 G. of the ester, dissolved in a little glacial acetic acid, was heated on a water-bath with an excess of hydrogen peroxide for ¼ hour. On cooling, and dilution with water, ethyl 2 : 4-dinitrobenzoylformate separated; it was identified by the mixed melting-point method.

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