VII.—*The Oxidation of Nitrophenylcyanoacetates.*

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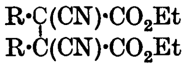
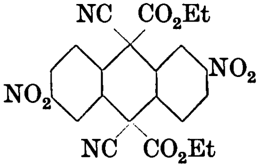
DURING an investigation on possible methods of synthesising substituted anthracenes (J., 1921, **119**, 1573; 1923, **123**, 1137), certain nitrophenylcyanoacetates were prepared and their hydrolytic and oxidation products examined. Ethyl sodiocyanoacetate was condensed with picryl chloride, 2 : 4-dinitrochlorobenzene and *p*-nitrochlorobenzene, producing ethyl 2 : 4 : 6-trinitrophenylcyanoacetate, ethyl 2 : 4-dinitrophenylcyanoacetate and ethyl *p*-nitrophenylcyanoacetate, respectively.

On oxidation, these nitrophenyl derivatives of ethyl cyanoacetate should produce first the hydroxy-esters, $R\cdot C(OH)(CN)\cdot CO_2Et$ (Meyer, *Ber.*, 1878, **11**, 1283; 1879, **12**, 2238), which would then be capable (i) of losing hydrogen cyanide and becoming ketonic esters, $R\cdot CO\cdot CO_2Et$, (ii) of reacting with unoxidised material to yield substituted succinic esters (I), or (iii) of condensing to form substituted anthracenes (II) of a particularly interesting type (compare Barnett, " Anthracene and Anthraquinone," pp. 50, 69).

(I.)



$$\begin{array}{l} R\cdot C(CN)\cdot CO_2Et \\ R\cdot C(CN)\cdot CO_2Et \end{array}$$



(II.)

Of these possibilities, (i) and (ii) have been realised. Under identical conditions, ethyl *p*-nitrophenylcyanoacetate was oxidised by chromic anhydride to the substituted succinic ester (I; $R = C_6H_4\cdot NO_2$), which was independently synthesised and its constitution verified; ethyl 2 : 4-dinitrophenylcyanoacetate gave the ketonic ester, $C_6H_3(NO_2)_2\cdot CO\cdot CO_2Et$; and ethyl 2 : 4-dinitrobromophenylcyanoacetate yielded the intermediate hydroxy-ester, $C_6H_2Br(NO_2)_2\cdot C(CN)(OH)\cdot CO_2Et$.

These nitrophenylcyanoacetates are all colourless or slightly yellow in the solid state and in dry organic solvents, but some of them develop intense colour in the presence of water and all do so when treated with alkalis.

EXPERIMENTAL.

Ethyl 2 : 4-*Dinitrophenylcyanoacetate*, $C_6H_3(NO_2)_2\cdot CH(CN)\cdot CO_2Et$.—To a solution of 2·3 g. of sodium in 40 c.c. of alcohol, 11·3 g. of ethyl cyanoacetate were added, followed by a solution of 10 g. of 2 : 4-dinitrochlorobenzene in 30 c.c. of alcohol. After the resulting red mixture had been refluxed on a water-bath for 4—5 hours, the alcohol was removed, 600 c.c. of water added, and the whole acidified with dilute nitric acid. The brown oil that separated was isolated by means of ether and, after solidifying, crystallised several times from alcohol-ligroin. The *ester* was thus obtained in colourless, crystalline needles, m. p. 66° (yield, 90%) (Found: C, 47·1; H, 3·6; N, 15·1. $C_{11}H_9O_6N_3$ requires C, 47·3; H, 3·2; N, 15·1%).

Its structure was proved by hydrolysis with concentrated hydrochloric acid; the 2 : 4-dinitrophenylacetic acid obtained melted at 179° (decomp.), alone or mixed with an authentic specimen (Radziszewski, *Ber.*, 1869, **2**, 210).

The ester gave a red solution in wet alcohol and a purple solution in concentrated sulphuric acid. Its *sodium* derivative was precipitated as a red explosive powder when the ester was treated with the theoretical weight of sodium dissolved in alcohol, and ether added (Found: Na, 7·3. $C_{11}H_8O_6N_3Na$ requires Na, 7·6%). The sodium could not be replaced directly by a radical, but was replaced by silver and then by the ethyl group.

Ethyl 2 : 4-*Dinitrophenylethylcyanoacetate*.—From the preceding sodium derivative and silver nitrate in aqueous solution, the corresponding *silver* derivative was obtained as a red powder. This was dried, and treated with an excess of ethyl iodide; after some time, ether was added and the solution was filtered and evaporated. The residual red oil, which solidified, crystallised from alcohol in colourless plates, m. p. 98° (Found: C, 50·6; H, 4·7. $C_{13}H_{13}O_6N_3$ requires C, 50·8; H, 4·2%).

2 : 4-*Dinitrophenylacetonitrile* was obtained when ethyl 2 : 4-dinitrophenylcyanoacetate was boiled with dilute hydrochloric acid during 2—3 hours. It was isolated as an oil by means of ether and crystallised from carbon tetrachloride in yellow needles, m. p. 89° (Found: C, 46·1; H, 2·6; N, 20·2. $C_8H_5O_4N_3$ requires C, 46·4; H, 2·4; N, 20·3%). Its solution in hot water was colourless but became green on the addition of alkali.

Ethyl p-*nitrophenylcyanoacetate* was prepared in the same way as the dinitro-compound, a solution of 8 g. of *p*-nitrochlorobenzene in 20 c.c. of alcohol being used and what was unchanged being filtered off before the addition of nitric acid. The product, a brown oil which could not be solidified, was converted into its *sodium* derivative in the way described above (Found: Na, 9·0. $C_{11}H_9O_4N_2Na$ requires Na, 9·0%).

The crude ester was hydrolysed with dilute and with concentrated hydrochloric acid, which produced, respectively, *p*-nitrophenylacetonitrile, m. p. 114° (compare Radziszewski, *Ber.*, 1870, **3**, 198), and *p*-nitrophenylacetic acid, m. p. 152° (Radziszewski, *Ber.*, 1869, **2**, 209). The latter was further identified by a mixed melting-point determination with an authentic specimen.

Ethyl 2 : 4 : 6-*trinitrophenylcyanoacetate* also was prepared by the same method, a solution of 12·4 g. of picryl chloride in 60 c.c. of alcohol being used. The colourless product (8·7 g.) crystallised from alcohol-ligroin in faintly pink needles, m. p. 95°, which formed red and purple solutions in water and concentrated sulphuric acid, respectively (Found: C, 40·9; H, 3·2; N, 17·5. $C_{11}H_8O_8N_4$ requires C, 40·7; H, 2·5; N, 17·3%).

Ethyl αβ-*Di*-p-*nitrophenyl*-αβ-*dicyanosuccinate* (I; R = $C_6H_4{\cdot}NO_2$).—Ethyl *p*-nitrophenylcyanoacetate (1·5 g.) or its sodium derivative was refluxed with a solution of 2·5 g. of chromic anhydride in 20 c.c. of glacial acetic acid for ¾ hour. The white solid obtained by pouring the product into cold water crystallised from glacial acetic acid in colourless needles, m. p. 209° (Found: C, 57·2; H, 3·5; N, 12·1; *M*, cryoscopic in benzene, 451. $C_{22}H_{18}O_8N_4$ requires C, 56·7; H, 3·9; N, 12·1; *M*, 466), which gave a series of colour changes when warmed with alcoholic potash.

The ester was unattacked by hot concentrated hydrochloric or nitric acid, and was easily precipitated from the latter in a very pure state. Its structure was proved as follows: 4·5 g. of the silver derivative of ethyl *p*-nitrophenylcyanoacetate, prepared from the sodium derivative by the action of silver nitrate, were heated under reflux for ½ hour with a solution of 1·7 g. of iodine in ether. The silver iodide produced and the ether were removed and the residue, after being washed with alcohol to remove the excess of iodine, was crystallised twice from alcohol and once from glacial acetic acid; the needles thus obtained melted at 209°, alone or mixed with the specimen described above.

Ethyl 2 : 4-*dinitrobenzoylformate*, $C_6H_3(NO_2)_2{\cdot}CO{\cdot}CO_2Et$, was obtained by boiling a solution of 1·5 g. of ethyl 2 : 4-dinitrophenylcyanoacetate and 2·3 g. of chromic anhydride in glacial acetic acid for 1 hour. The colourless solid obtained by pouring the product into water was crystallised from alcohol; m. p. 89° (Found: C, 44·7; H, 3·35; N, 10·85; *M*, cryoscopic in benzene, 245. $C_{10}H_8O_7N_2$ requires C, 44·8; H, 3·0; N, 10·45%; *M*, 268). The *phenylhydrazone* separated from the mixture when 1 g. of the ester was heated on a water-bath for ¼ hour together with 10 drops of phenylhydrazine dissolved in dilute acetic acid; it crystallised from alcohol in golden needles, m. p. 170° (Found: N, 15·1. $C_{16}H_{14}O_6N_4$ requires N, 15·6%). A small amount of red substance, obtained on diluting the filtrate, melted, after recrystallisation from alcohol, at 139°. By fusing it with the product of m. p. 170° it was converted into the latter, indicating that it was probably another form of the phenylhydrazone.

Ethyl 2 : 4-*dinitrobromophenylcyanoacetate* was prepared by boiling the sodium derivative of ethyl 2 : 4-dinitrophenylcyanoacetate with excess of bromine dissolved in moist ether. It crystallised from alcohol in needles, m. p. 98° (Found: C, 36·9; H, 2·7; N, 12·3; Br, 21·9. $C_{11}H_8O_6N_3Br$ requires C, 36·9; H, 2·2; N, 11·7; Br, 22·3%). This compound was originally prepared by accident in an attempt to oxidise ethyl 2 : 4-dinitrophenylcyanoacetate by bromine instead of by chromic anhydride. That the bromine atom is in the ring was established by the preparation of the following oxidation product.

Ethyl 2 : 4-*dinitrobromophenylhydroxycyanoacetate*,

$$C_6H_2Br(NO_2)_2{\cdot}C(OH)(CN){\cdot}CO_2Et,$$

was produced when ethyl 2 : 4-dinitrobromophenylcyanoacetate was treated with chromic anhydride under the conditions described for the previous oxidations. It crystallised from alcohol in colourless needles, m. p. 157° (Found : C, 35·3; H, 2·9; N, 12·6; Br, 21·4. $C_{11}H_8O_7N_3Br$ requires C, 35·3; H, 2·1; N, 11·2; Br, 21·4%).

Ethyl 2 : 4-*dinitrochlorophenylcyanoacetate* was prepared by passing chlorine into an aqueous solution of the sodium derivative of ethyl 2 : 4-dinitrophenylcyanoacetate until the red colour had been destroyed. It crystallised from alcohol in needles, m. p. 101° (Found : Cl, 11·3. $C_{11}H_8O_6N_3Cl$ requires Cl, 11·3%). The structure of this compound would appear to be sufficiently established by analogy with the corresponding bromo-derivative mentioned above. Its action with chromic anhydride is under investigation.

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