# *Some Reactions of Ethyl Cyanoacetate.*

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The action of *N*-bromosuccinimide on ethyl cyanoacetate yields ethyl dibromocyanoacetate, which is also obtained together with dibromoacetonitrile by the action of bromine in the presence of magnesium oxide, the proportions of the products being dependent upon the amount of magnesium oxide used. Oxidation of ethyl cyanoacetate by selenium dioxide gives diethyl *trans*(?)-1 : 2-dicyanoethylene-1 : 2-dicarboxylate.

In unsuccessful attempts to prepare ethoxalyl cyanide, $EtO_2C{\cdot}CO{\cdot}CN$, or a derivative of this (see also Diels, Gärtner, and Kaack, *Ber.*, 1922, **55**, 3439), a number of reactions of ethyl cyanoacetate has been studied.

Ethyl dibromocyanoacetate has been prepared for the first time and is best obtained by the reaction of *N*-bromosuccinimide (2 mols.) with ethyl cyanoacetate (1 mol.) in carbon tetrachloride solution. Photocatalysed bromination of ethyl cyanoacetate in organic solvents by bromine (2 mols.) was incomplete and the product decomposed during washing to remove unchanged bromine. Bromination by bromine (2 mols.) in aqueous solution in the presence of magnesium oxide (1 mol., as acid absorbent) led to the reaction of the magnesium oxide completely after the addition of only one mol. of bromine, and carbon dioxide was evolved during the subsequent addition of the second mol. The product on fractionation gave ethyl dibromocyanoacetate and dibromoacetonitrile in approximately equimolecular amounts. When magnesium oxide (2 mols.) was used, and the reaction was completed by acidification after the addition of the bromine, the product was predominantly dibromoacetonitrile and this offers an easy route to the latter compound, previously obtained by dehydration of dibromoacetamide by phosphoric oxide (Steinkopf, *Ber.*, 1905, **38**, 2695; Ghigi, *Gazzetta*, 1941, **71**, 641).

Several attempts were made to replace the bromine atoms in ethyl dibromocyanoacetate, but treatment with alkaline reagents, *e.g.*, sodium ethoxide in ethanol, or ethanolic potassium acetate, led to rapid darkening of the mixture, and only small amounts of unidentified volatile liquid products could be separated from the large amounts of tar formed. This behaviour in the presence of alkaline reagents accounts for the decomposition during the washing to remove bromine left after the photobromination experiments.

In view of recent observations by Mel'nikov and Baskakov (*Doklady Akad. Nauk S.S.S.R.*, 1952, **85**, 337; *Chem. Abs.*, 1953, **47**, 7461) on the oxidation of nitriles by selenium dioxide, it is unlikely that ethoxalyl cyanide, if formed by the action of selenium dioxide on ethyl cyanoacetate, would survive in the reaction mixture. Selenium dioxide reacted with ethyl cyanoacetate in ethanol at 100°, but the product was a seleniferous material, largely undistillable. When selenium dioxide was heated with ethyl cyanoacetate alone at 120—125° [the conditions used by Astin, Newman, and Riley (*J.*, 1933, 391) for the comparable oxidation of ethyl malonate to ethyl mesoxalate] and the product was distilled, two fractions were obtained, the larger of which was unchanged ethyl cyanoacetate, contaminated with selenium compounds. The second fraction was a solid, $(C_5H_5O_2N)_x$, m. p. 117—117·5°, which corresponds closely with the m. p. recorded for triethyl 1 : 2 : 3-tricyano*cyclo*propane-1 : 2 : 3-tricarboxylate. The latter had been prepared by, *inter al.*, Errera and Perciabosco (*Ber.*, 1901, **34**, 3708) in variable yield by the reaction of bromine, iodine, or ethyl monobromocyanoacetate upon ethyl sodiocyanoacetate in ether. In the present study, when all the sodium was made to react with ethyl cyanoacetate before the addition of the bromo-ester, none of the *cyclo*propane ester was formed but, when free sodium was present, this ester was obtained and this result, taken together with the difficulty found in causing complete reaction of the metal with the ester, probably explains the variable yields reported by the earlier workers; the *cyclo*propane ester melted at 123·5—124°, but its mixed m. p. with the product, $(C_5H_5O_2N)_x$, was 99—99·5°. Prolonged hydrolysis of the compound with 6N-potassium hydroxide solution gave ammonia, but no product could be isolated. The compound was recovered unchanged when treated with ethanolic hydrogen chloride, either in the cold or under reflux, and with ethanolic sulphuric acid (approx. 5N) at 210°. A small amount was also recovered from an attempted reaction between it and ethanolic sulphuric acid (5N) at 170° but the main product was an oil, probably a mixture of two or more compounds.

With ethanolic hydrazine hydrate, the compound of m. p. 117—117·5° readily formed a dihydrazide. A molecular-weight determination on the original compound showed $x = 2$; therefore the action of selenium dioxide on ethyl cyanoacetate yields diethyl 1 : 2-dicyanoethylene-1 : 2-dicarboxylate. Treatment of the compound with magnesium *n*-propoxide in *n*-propanol (Linstead and Whalley, *J.*, 1952, 4839) did not yield any tetra-azaporphin-like pigment and on this account the geometric configuration is thought, provisionally, to be *trans*.

## EXPERIMENTAL

*Ethyl Dibromocyanoacetate.*—(*a*) Ethyl cyanoacetate (33·9 g.) in carbon tetrachloride (300 ml.) was heated under reflux with *N*-bromosuccinimide (106·8 g.) and benzoyl peroxide (0·5 g.) for 16 hr. Succinimide was removed by filtration, the solvent evaporated, and the residue distilled, yielding *ethyl dibromocyanoacetate* as a colourless liquid (73 g.), b. p. 70—72°/1·3 mm., $n^{18}$ 1·4957 (Found : C, 22·1; H, 2·1; N, 5·2; Br, 59·1. $C_5H_5O_2NBr_2$ requires C, 22·1; H, 1·85; N, 5·2; Br, 59·0%).

(*b*) Ethyl cyanoacetate (56·6 g.) was stirred with water (350 ml.), in which was suspended magnesium oxide (21 g.), while bromine (160 g., 2 mols.) was added dropwise. After addition of half the volume of bromine, all the magnesium oxide had dissolved and effervescence ($CO_2$) became pronounced. The mixture was kept overnight, the oil separated, and the aqueous residue extracted with carbon tetrachloride. The combined oil and carbon tetrachloride solution were washed with sodium carbonate and sodium thiosulphate solutions successively and dried ($MgSO_4$). The solvent was evaporated, and the residue fractionally distilled through a Vigreux column (10 cm.), to yield dibromoacetonitrile (35·1 g.), b. p. 30°/1·6 mm., $n^{18}$ 1·5429 (Ghigi, *loc. cit.*, gives b. p. 67—69°/20 mm.) (Found : C, 12·1; H, 0·55; N, 6·9; Br, 80·5. Calc. for $C_2HNBr_2$ : C, 12·1; H, 0·5; N, 7·0; Br, 80·4%), and ethyl dibromocyanoacetate (44·8 g.), b. p. 76—77°/2 mm., $n^{18}$ 1·4960.

*Dibromoacetonitrile.*—Ethyl cyanoacetate (56·6 g.), magnesium oxide (42 g.), and water (350 ml.) were stirred together at room temperature, while bromine (160 g.) was added dropwise. At the end of the addition the mixture was acidified with concentrated hydrochloric acid (Congo-red), carbon dioxide being evolved. The solution was extracted with carbon tetrachloride, and the extract washed successively with sodium carbonate and sodium thiosulphate solutions and dried ($MgSO_4$). The solvent was evaporated and the residue was fractionally distilled, yielding dibromoacetonitrile (58·2 g.), b. p. 68—70°/20 mm., and ethyl dibromocyanoacetate (8·4 g.), b. p. 120—123°/20 mm.

*Diethyl* trans(?)-1 : 2-*Dicyanoethylene*-1 : 2-*dicarboxylate.*—A mixture of ethyl cyanoacetate (50 g.) and selenium dioxide (25 g.) was heated under reflux at 120—125° in an oil-bath for 2 hr., during which the mixture effervesced and selenium separated. When cool, the liquid was decanted from the selenium residues and fractionally distilled. The major fraction (31·1 g.), b. p. 86—94°/12 mm., smelled strongly of selenium compounds and was identified as impure ethyl cyanoacetate by conversion into cyanoacetamide, m. p. and mixed m. p. 119—120°. The fraction (6·8 g.), b. p. 120—200°/12 mm., solidified when cool and crystallised from ethanol, to yield *diethyl* 1 : 2-*dicyanoethylene*-1 : 2-*dicarboxylate* as colourless needles, m. p. 117—117·5° (corr.) [Found : C, 54·4; H, 4·6; N, 12·7%; *M* (Rast), 226. $C_{10}H_{10}O_4N_2$ requires C, 54·05; H, 4·5; N, 12·6%; *M*, 222]. The compound decolorised bromine water on being heated, and slowly liberated ammonia in boiling 6N-potassium hydroxide. The *dihydrazide*, prepared by using hydrazine hydrate (100%) in ethanol, crystallised from 95% ethanol as flat needles, m. p. 211·5° (decomp.) (Found : C, 40·0, 39·9; H, 5·0, 5·1; N, 34·6. $C_6H_6O_2N_6,C_2H_5{\cdot}OH$ requires C, 40·0; H, 5·0; N, 35·0%). When heated in a vacuum in an attempt to remove solvent, the compound sublimed.

*Triethyl* 1 : 2 : 3-*Tricyano*cyclo*propane*-1 : 2 : 3-*tricarboxylate*.—Sodium wire (6 g.) in dry ether (100 ml.) was treated with ethyl cyanoacetate (29 g.). Next day, when only some of the sodium had reacted, ethyl monobromocyanoacetate (50·8 g.) was added, and the mixture kept with intermittent shaking for 2 days. The product, isolated as described by Errera and Perciabosco (*loc. cit.*), crystallised from ethanol to yield colourless needles (7·5 g.), m. p. 123·5—124° (corr.) (Errera and Perciabosco, *loc. cit.*, give m. p. 119·5; Goldthwaite, *Amer. Chem. J.*, 1903, **30**, 465, gives 122°); mixed m. p. with the ethylene (above), 99—99·5° [Found : C, 54·4; H, 4·5; N, 12·8%; *M* (Rast), 340. Calc. for $C_{15}H_{15}O_6N_3$ : C, 54·05; H, 4·5; N, 12·6%; *M*, 333]. The compound did not decolorise bromine water even when heated.

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