## Ethyl 3-Amino-3-cyano-2-methylacrylate, a Product from the Reaction of Ethyl 2-Bromopropionate with Sodium Cyanide

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Ethyl 2-bromopropionate reacts with sodium cyanide to give ethyl 2-cyanopropionate (30%), a mixture of diastereoisomers of diethyl 2-cyano-2,3-dimethylsuccinate (10%), and ethyl 3-amino-3-cyano-2-methylacrylate (10%) (1).

THE reaction of sodium cyanide with ethyl 2-bromopropionate gives ethyl 2-cyanopropionate  $(30-50\%)^{1-3}$  together with a crystalline solid, m.p.  $115^{\circ}.^3$  From the molecular formula,  $C_7H_{10}N_2O_2$ , Zelinsky and Bytschichin<sup>4</sup> deduced that the compound had arisen by addition of hydrogen cyanide to the ethyl 2-cyanopropionate. The undefined nature of this compound encouraged us to examine it.

We found the major products of this reaction to be ethyl 2-cyanopropionate (30%), a mixture of the diastereoisomers of diethyl 2-cyano-2,3-dimethylsuccinate (10%), and a crystalline solid (10%), m.p. 115—117°. The <sup>1</sup>H n.m.r. spectrum of the crystalline solid in deuteriochloroform showed resonances at  $\tau$  8·7 (3H, t, J 7 Hz), 8·0 (3H, s), 5·75 (2H, q, J 7 Hz), and 4·5—3·5br (2H, exchangeable H). The i.r. spectrum in bromoform showed absorption at 3490, 3340 (NH<sub>2</sub>), 2240 (CN), 1680 (C=O), 1615 (C=C), and 1546 cm.<sup>-1</sup> and the u.v. spectrum in ethanol had  $\lambda_{max}$ . 305 nm. ( $\varepsilon$  11,640). These data are accommodated by ethyl 3-amino-3-cyano-2-methylacrylate (1). The mass spectrum showed a



molecular-ion peak  $(m/e \ 154)$  and a peak at  $m/e \ 108$  corresponding to the loss of ethanol. Such an elimination implies a cyclic transition state and suggests that, at least in the mass spectrometer, the amino and ester groups are *cis* as shown. This would be analogous with the case of 3-aminocrotonic esters which exist in the *cis*-form only.<sup>5</sup>

The acrylic ester (1) presumably arises from addition of cyanide ion to the nitrile group of ethyl 2-cyanopro-

<sup>1</sup> Y. Kakimoto and M. D. Armstrong, J. Biol. Chem., 1961, 236, 3283.

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N. Zelinsky, Ber., 1888, 21, 3168. pionate followed by protonation and tautomerisation. This is the first report of such a nucleophilic reaction.

## EXPERIMENTAL

I.r. spectra were recorded on a Unicam SP 100 spectrometer, <sup>1</sup>H n.m.r. spectra on a Varian A60A spectrometer with tetramethylsilane as an internal standard, u.v. spectra on a Perkin-Elmer 137 U.V. spectrometer, and the mass spectrum on an AEI MS9 spectrometer.

Reaction of Ethyl 2-Bromopropionate with Sodium Cyanide. –Sodium cyanide (112 g.), ethyl 2-bromopropionate (360 g.), and ethanol (1250 ml.) were heated under reflux for 24 hr.; the mixture was cooled and filtered. The filter cake was washed with ethanol (200 ml.) and the combined filtrate and washings were evaporated to dryness. The residue was extracted with ether  $(2 \times 1 \text{ l.})$  and the extracts were washed with brine (2  $\times$  200 ml.), dried, and evaporated to give a dark brown oil (210 g.). Distillation gave the following fractions. (a) Ethyl 2-cyanopropionate (76 g.), b.p. 86–90°/15 mm.,  $n_{\rm D}^{21}$  1·4120 (lit.,  $n_{\rm D}^{25}$  1·4110). (b) Ethyl 3-amino-3-cyano-2-methylacrylate (25 g.), b.p. 120-125°/15 mm., m.p. 115--117° [from chloroform-light petroleum (b.p. 60-80°)] (lit.,<sup>3</sup> 115°) (Found: C, 54.75; H, 6.65; N, 18.0; O, 21.0.  $C_7H_{10}N_2O_2$  requires C, 54.55; H, 6.65; N, 18.15; O, 20.75%). (c) Diethyl 2-cyano-2,3-dimethylsuccinate mixed diastereoisomers (30 g.), b.p. 150-155°/15 mm. (lit., 6 162-163°/20 mm.),  $n_{\rm p}^{21}$  1.4390 (lit.,<sup>6</sup> n<sub>D</sub> 1.4368).

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<sup>4</sup> N. Zelinsky and A. Bytschichin, Zhur. russk. fiz.-khim. Obshchei, 1889, **21**, 157.

 <sup>5</sup> A. Gómez Sánchez, M. Tena Aldave, and U. Scheidegger, J. Chem. Soc. (C), 1968, 2570.
<sup>6</sup> W. A. Bone and C. H. G. Sprankling, J. Chem. Soc. 1899.

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