

THE FORMATION OF DERIVATIVES OF
CYCLOPROPANE-1,2-DICARBOXYLIC ACID FROM ACRYLONITRILE
AND METHYL CHLOROACETATE UNDER THE EFFECT
OF SODIUM AMALGAM

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The reaction of methyl chloroacetate and acrylonitrile with sodium amalgam in the presence of one equivalent of water gives rise to a mixture of methoxypropionitrile and a mixture of methyl esters of *cis*- and *trans*-2-cyanocyclopropanecarboxylic acids.

For a direct preparation of the esters of 4-cyano-3-butenic acid a radical reaction is described in the literature¹ between methyl chloroacetate, acrylonitrile and sodium amalgam in the presence of water. After having carried out this reaction we determined by gas chromatography that the product contained four substances. In addition to methyl chloroacetate and 3-methoxypropionitrile a substance was also present the elemental analysis of which corresponded to that of methyl 4-cyano-3-butenate. However, our substance lacks an absorption maximum in the UV region up to 210 nm. According to IR spectra it does not contain a double bond, and the absorption bands indicate the presence of a saturated nitrile and a COOR group and a cyclopropane ring². According to NMR spectrum of the substance it does not contain vinylic protons, but the spectrum cannot be assigned unequivocally to the supposed structure of 2-cyanocyclopropanecarboxylic acid ester. Therefore, the substance was hydrolysed affording *trans*-1,2-cyclopropanedicarboxylic acid. The content of the fourth substance present in the above mixture was low; elemental analysis again corresponded to methyl 2-cyanocyclopropanecarboxylate, the IR and NMR spectra again excluded the presence of a double bond, and thus it may be assumed that it is the *cis*-isomer of the above mentioned compound.

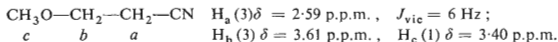
In view of the presence of 3-methoxypropionitrile the molar amount of which (in g-mol) was equal to that of the water present at the beginning of the reaction it is evident that the reaction does not take place by a radical mechanism, but by an ionic one. 3-Methoxypropionitrile is formed by addition of the methoxide ion to acrylonitrile³; the methoxide ion is formed on hydrolysis of the ester group with the hydroxyl ion formed from water and sodium amalgam. The formation of cyclo-

propane derivative probably takes place by Michael addition of the $(\text{Cl}-\text{CH}-\text{COCH}_3)^{-}$ anion (formed from methyl chloroacetate and hydroxide or methoxide ion) to acrylonitrile and subsequent elimination of the chlorine anion, under simultaneous cyclisation. Similar reactions leading to cyclopropane derivatives are described in literature^{4,5}.

EXPERIMENTAL

Reactions and Isolations of Products

Following the literature data¹ 414 ml (333 g; 6.3 mol) of acrylonitrile were mixed with 484 ml (520 g; 5.5 mol) of methyl chloroacetate and 5 ml (0.278 mol) water. Sodium amalgam (from 111.5 g, *i.e.* 4.85 mol, of sodium and 3.700 g of mercury) was then added in portions keeping the temperature below 50°C. After the addition the mixture was stirred for one hour and allowed to stand overnight. Mercury was then separated and the solid residue washed with seven 100 ml portions of ether. The solid residue was then mixed with ether and water was added to bring sodium chloride into solution. The ethereal layer was separated and combined with the previous extracts. After drying over magnesium sulfate and distillation a fraction of b.p. 37–70°C/18 Torr was obtained (a mixture of four substances according to gas chromatography) which was submitted to rectification of a 1 m long column of 18 mm diameter, filled with stainless-steel helices. The following pure fractions were obtained: 1. A compound of b.p. 38°C/21 Torr, yield 46 g, the spectrum identical with that of methyl chloroacetate. 2. A compound of b.p. 62°C/17 Torr, yield 19.4 g. For $\text{C}_4\text{H}_7\text{NO}$ (85:1) calculated: 56.45% C, 8.29% H; found: 56.50% C, 8.46% H. Mass spectrum: molecular peak m/e 85, further a peak of m/e 84 the intensity of which was 70% of the base peak, characteristic of nitriles. Further peaks were at m/e 26 (CN), a small peak at m/e 31 indicating the presence of the OCH_3 group, at m/e 45 ($-\text{CH}_2\text{OCH}_3$), and 40 ($-\text{CH}_2\text{CN}$). These data indicate the structure $\text{CH}_3\text{O}-\text{CH}_2-\text{CH}_2-\text{CN}$ which was confirmed by the NMR spectrum (Varian 100 Mc). Deuteriochloroform was used as solvent, tetramethylsilane as internal reference.



The IR spectrum of the substance was identical with that of 3-methoxypropionitrile, described in literature^{6,7}. 3. Compound of b.p. 101°C/20 Torr, yield 10 g. For $\text{C}_6\text{H}_7\text{NO}_2$ (125:1) calculated: 57.59% C, 5.64% H, 11.29% N; found: 57.55% C, 5.88% H, 11.38% N. IR spectrum: 2250 cm^{-1} (CN), 1745 cm^{-1} (C=O), 655, 1020, 3020 and 3109 cm^{-1} (bands characteristic of cyclopropane ring²). The NMR spectrum is complex and not of the first order; it is very close to the NMR spectrum of the analogous ethyl ester⁸: multiplet $\delta = 1.36-1.67$ p.p.m. (2 H, CH_2 in cyclopropane); multiplet $\delta = 1.80-2.0$ p.p.m. (1 H, CH in cyclopropane), multiplet $\delta = 2.12-2.31$ p.p.m. (1 H, CH in cyclopropane), singlet $\delta = 3.69$ p.p.m. (3 H, COOCH_3). The substance does not absorb in the UV region above 210 nm. 4. A compound present only in small amount. It was obtained by preparative gas chromatography (polyethyleneglycol sebacate on celite, temperature 180–190°C) from the distillation residue of another experiment. For $\text{C}_6\text{H}_7\text{NO}_2$ (125:1) calculated: 57.59% C, 5.64% H, 11.29% N; found: 57.64% C, 5.95% H, 11.67% N. NMR spectrum: multiplet $\delta = 1.27-2.16$ p.p.m. (4 H, cyclopropane); singlet $\delta = 3.72$ p.p.m. (3 H, COOCH_3). IR spectrum: 2275 cm^{-1} (CN), 1746 cm^{-1} (C=O), 868 and 1010 cm^{-1} (cyclopropane ring absorption²).

Hydrolysis of the Methyl Ester of *trans*-2-Cyanocyclopropanecarboxylic Acid

Compound 3 (1 g) was refluxed with 50 ml of 4M-NaOH. The obtained solution was filtered, acidified with hydrochloric acid and evaporated. The residue, m.p. 165–175°C, was dissolved in a small amount of water and the solution was extracted with 10 ml of ether. After drying over magnesium sulfate the extract was concentrated to give 0.9 g of substance melting at 169–176°C (sublimates from 120°C, distills at 165°C). After crystallisation from 22 ml of ether (charcoal) and 10 ml hexane the yield was 0.4 g, m.p. 172–175°C (from 120°C distillation of the liquid and sublimation). After resublimation in a vacuum (water pump), m.p. 171.5–174°C (from 100°C the liquid distills, later sublimation). Literature⁸ gives m.p. 172–174°C. For C₅H₆O₄ (130.1) calculated: 46.16% C, 4.65% H; found: 46.38% C, 4.65% H. IR spectrum in the 800 to 1100 cm⁻¹ region is in good agreement with that from the literature².

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