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Studies on *Cyclo*propanes

IV. On the Isomerization of 1,1-Dimethyl-2,3-dicyano-2-ethoxycarbonyl-3-*cyclo*propanecarboxamide

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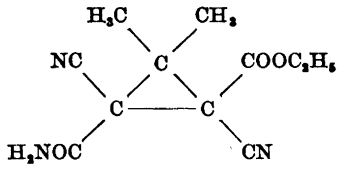
1,1-Dimethyl-2,3-dicyano-2-ethoxycarbonyl-3-*cyclo*propanecarboxamide (I) is easily rearranged to form the iminoimide II.

1,1-Dimethyl-2,3-dicyano-2-ethoxycarbonyl-3-*cyclo*propanecarboxamide (I) can be prepared from ethyl *iso*propylidenecyanoacetate and bromocyanoacetamide in alkaline solution in a way analogous to the preparations of *cyclo*propane derivatives described in Studies on *Cyclo*propanes 1—3 [1-3].

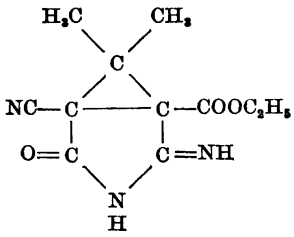
When kept in ethanol solution at room temperature for 1—2 days, the neutral I rearranges to form an amphoteric isomer, which is very weak both as an acid and as a base but can be sharply titrated in anhydrous medium with strong bases or acids. The rearrangement is strongly catalysed by bases, retarded by acids. The properties of the isomer are in accordance with the structure II. The structure III is excluded, a qualitative test on end unsaturation being distinctly negative. Thus the isomerization of I is not related to the rearrangements of the *cyclo*propanes described earlier [1,3].

The IR spectra of I and II both have an absorption band within the range characteristic of *cyclo*propane rings [4,5], I at 1 025 cm^{-1} and II at 1 005 cm^{-1}. As is to be expected the IR curve of I (in potassium bromide) shows two NH_2 stretching bands (3 150 cm^{-1} and 3 310 cm^{-1}), the spectrum of II (in potassium bromide) only one NH stretching band (3 330 cm^{-1}).

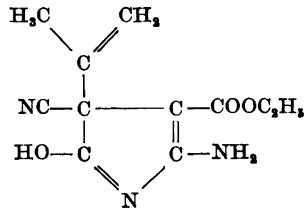
The structure II may seem strange, but ring closure with formation of iminoimides has been described earlier by, *e. g.*, Thorpe and collaborators [6-9]. Furthermore, 3,5-bridged diketopiperidines, which possess structures related to II, are stable and easily prepared as shown by Guareshi and Grande [10], Ghiglieno [11], and Wideqvist [12].



I



II



(III)

EXPERIMENTAL

Preparation of I. Sodium hydroxide (21.6 ml of 2.34 N solution) was added dropwise with stirring to a solution of ethyl *iso*propylidenecyanoacetate (7.7 g) and bromocyanoacetamide (8.2 g) in ethanol (45 ml). The precipitate formed was filtered after 5 h, washed with 50 % ethanol and air-dried. Yield of colourless product containing <50 % of I: 2.7 g. For removal of II the crude product was mixed with 5 ml of ethanol, the suspension was poured into 50 ml of 5 N hydrochloric acid, and the mixture was stirred for some minutes, filtered and washed with water and a small amount of cold ethanol. M. p. 168° (decomp.). (Found: C 56.1; H 5.6; N 17.9; O 20.3. Calc. for $C_{11}H_{13}N_3O_3$: C 56.2; H 5.6; N 17.9; O 20.4.)

The isomerization caused by bases of the neutral I to form II is so rapid that the product can be titrated as an acid in dimethylformamide solution using sodium methoxide in benzene-methanol solution as the titrant and azoviolet as the indicator. Acids retard the isomerization. Hence the compound I is stable in glacial acetic acid-chlorobenzene solution and does not consume any perchloric acid on titration using methyl violet as indicator.

Rearrangement of I to form II 1) in ethanol solution 2) in ethanol solution catalysed by alkali. 1) When a saturated ethanol solution of I was left at room temperature for a few days, colourless crystals of an isomeric, amphoteric product separated (II). In a more dilute solution the isomerization, which is almost quantitative, could be observed by UV measurements, log ε at 245 mμ increasing from 1.95 (measured in 0.05 N hydrochloric acid ethanol) to 4.06 (for a solution of recrystallized II log ε at 245 mμ was found to be 4.07). Addition of one drop of 2.5 N sodium hydroxide solution to this dilute solution of I made the isomerization complete in a few seconds. Boiling of an ethanol solution of I for ten minutes also effected isomerization. M. p. 190° (decomp.). (Found: C 56.2; H 5.8; N 17.8; O 20.4; equiv. wt on titration with perchloric acid in glacial acetic acid (solvent: chlorobenzene; indicator: methyl violet) 237; equiv. wt on titration with sodium methoxide in benzene-methanol solution (solvent: dimethylformamide; indicator: azoviolet) 236. Calc. for $C_{11}H_{13}N_3O_3$: C 56.2; H 5.6; N 17.9; O 20.4; equiv. wt 235.) II is soluble in dilute hydrochloric acid. A test on end unsaturation according to Bricker and Roberts [13] was negative.

2) A 0.83 N sodium ethoxide solution (5.38 ml) was added with stirring to the crude product from the preparation of I (1.05 g). When all crystals had dissolved (about 4 min), the solution was poured into 25 ml of 0.076 N hydrochloric acid. The colourless precipi-

tate formed was filtered and washed with water. Yield: 0.80 g. M. p. 190° (decomp.). (Found: C 56.2; H 5.6; N 17.8; O 20.5. Calc. for $C_{11}H_{13}N_3O_3$: C 56.2; H 5.6; N 17.9; O 20.4.) UV and IR curves of this product were identical with the curves of the product obtained in the preceding isomerizations.

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