(1.2 g.) was dissolved in 60 ml. of dry ethyl chloride and treated at −60° for two hours with a stream of oxygen containing about 3% of ozone. The ethyl chloride was evaporated over water at room temperature. The ozonide was decomposed in boiling water and the escaping gasses were passed into an aqueous alcohol solution of "dimedon" (5,5-dimethyl-1,3-cyclohexanedione). After standing, needles of the dimedon derivatives of formaldehyde precipitated, m.p. 190.5–191.50°. A mixture melting point showed no depression.

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The Halodecarboxylation of Cyanoacetic Acid

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The current interest in halodecarboxylation[1] reactions is reflected in the number of relevant papers in recent journals.[2] A novel example of this type reaction occurs when cyanoacetic acid (or its potassium salt) is treated with an N-halosuccinimide in water. Dihaloacetonitriles are formed in good yield in an extremely facile manner. This is believed to be the simplest route to these halonitriles.[3,4a,b,c]

Cyanoacetic acid and the N-halosuccinimide are mixed in a molar ratio of 1:2[5] in water (about 100 ml. per 0.1 mole of reactants). Upon stirring for a short time at room temperature, a mildly exothermic reaction ensues with evolution of carbon dioxide. In 10–15 minutes, the clear solution is completely free of solid and has a bottom phase of the dihaloacetonitrile, which may be either separated or extracted from the aqueous phase, dried, and distilled.

In this manner, dibromoacetonitrile and dichloroacetonitrile were obtained from the corresponding N-halosuccinimide in 75% and 60% yields, respectively.

The discussion of mechanism for this transformation is at present somewhat speculative, but some relevant facts are known: the reaction also proceeds essentially as described with potassium cyanoacetate,[6] but fails to occur under these conditions with chloroacetonitrile, and α-cyanopropionic acid or its anion. Such results indicate: (1) that the reaction may proceed *via* the acid anion, the route generally believed taken in similar decarboxylations;[7] (2) that the presumed first intermediate, monohalocyanoacetic acid, does not decarboxylate to a monohaloacetonitrile *prior* to further halogenation;[8] and (3) that α-hydrogen atoms reduced in lability are unreactive in such halodecarboxylations.[9]

The following mechanism is in accordance with such facts.

$$\mathrm{NCCH_2CO_2H} \rightleftharpoons \mathrm{NCCH_2CO_2^{\ominus}} + \mathrm{H^{\oplus}}$$

$$\mathrm{NCCH_2CO_2^{\ominus}} + 2\ \mathrm{X{-}N}\langle\ \longrightarrow\ [\mathrm{NCCX_2CO_2^{\ominus}}] + 2\ \mathrm{H{-}N}\langle$$

$$[\mathrm{NCCX_2CO_2^{\ominus}}] \longrightarrow [\mathrm{NCCX_2}]^{\ominus} + \mathrm{CO_2}$$

$$[\mathrm{NCCX_2}]^{\ominus} + \mathrm{H_2O} \longrightarrow \mathrm{NCCHX_2} + \mathrm{OH^{\ominus}}$$

$$\mathrm{H^{\oplus}} + \mathrm{OH^{\ominus}} \longrightarrow \mathrm{H_2O}$$

In an alkaline medium, the carbon dioxide is retained as bicarbonate ion.

EXPERIMENTAL[10]

Materials. The *cyanoacetic acid* and *N-halosuccinimides* were commercial products used as received. *Chloroaceto-*

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[1] This name for the reaction also known as "halogenative decarboxylation" is in accordance with suggestions for nomenclature reported by Patterson, *Chem. Eng. News*, **32**, 4019 (1954).

[2] *Inter alia*, see Grovenstein, Jr., and Lee, *J. Am. Chem. Soc.*, **75**, 2639 (1953); Grovenstein, Jr., and Theophilou, *J. Am. Chem. Soc.*, **77**, 3795 (1955); Grovenstein, Jr., and Henderson, Jr., *J. Am. Chem. Soc.*, **78**, 569 (1956); Price and Berman, *Am. Chem. Soc. Abst.*, Cincinnati Meeting, March, 1955, p. 12N; Wilt, *J. Am. Chem. Soc.*, **77**, 6397 (1955).

[3] van't Hoff, *Ber.*, **7**, 1382, 1571 (1874), reported the production of dibromoacetonitrile by the action of bromine on cyanoacetic acid. He listed the nitrile as a solid, m.p. 142°. Steinkopf (*loc. cit.*) repeated the work and showed van't Hoff's nitrile to be impure dibromoacetamide, m.p. 153°.

[4] The dihalonitriles have customarily been prepared by a dehydration of the corresponding amide, essentially as described by (a) Bisschopinck, *Ber.*, **6**, 731 (1873); (b) Steinkopf, *Ber.*, **38**, 2695 (1905); **41**, 2541 (1908); and (c) Steinkopf and Bohrmann, *Ber.*, **40**, 1638 (1907). This reaction is troublesome and the yield of pure material in these cases is generally only 25–40%.

[5] The *same* reaction occurs (though in lower yield) when a molar ratio of 1:1 is used. This fact has mechanistic importance (*cf.* footnote 8).

[6] Potassium bicarbonate, rather than carbon dioxide, is produced in this case and the reaction mixture colors considerably.

[7] *Cf.* Hine, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 283–284 and the references cited therein. A *general mechanism* involving cyanoacetate ion is therefore favored by precedent over *separate mechanisms* for the acid and anion, although presumably both undissociated acid and acid anion are present in the systems used here. Separate mechanisms for each case are therefore not precluded.

[8] The production of *dihalo-* and not *trihalo-* acetonitriles when a 1:1 molar ratio of acid and N-haloimide is used also indicates that monohaloacetonitriles are not intermediates. For the existence of such a reaction path would imply that monohaloacetonitriles are halogenated faster than dihaloacetonitriles. Such a rate order is the reverse of that observed in similar reactions such as the haloform reaction or the halogenation of ketones. *Cf.* Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 240–241.

[9] Correspondingly, when activation is present, the reaction is facilitated. Thus malonic acid has recently been converted in 78% yield to dichloroacetic acid *via* the reaction described here (work performed by Mr. A. Danielzadeh and the author).

[10] All melting points and boiling points are uncorrected. Analyses were performed by the Galbraith Laboratories, Knoxville, Tennessee.

nitrile was prepared by dehydration of commercial chloroacetamide with phosphorus pentoxide (51% yield, b.p. 124–125°, n_D^{25} 1.4195, d_4^{20} 1.192). *α-Cyanopropionic acid* was synthesized from commercial α-bromopropionic acid as described by Hoffmann and Barbier.[11] A 45% yield of pure material was obtained, b.p. 112–113° at 1 mm., n_D^{23} 1.432, d_4^{20} 1.146, MR_D. Calc'd: 22.0. Found: 22.4.

Anal. Calc'd for $C_4H_5NO_2$: C, 48.48; H, 5.09; N, 14.14. Found: C, 48.65; H, 5.17; N, 14.21.

Bromodecarboxylation of cyanoacetic acid. Cyanoacetic acid (8.5 g., 0.1 mole) and N-bromosuccinimide (35.6 g., 0.2 mole) were mixed in cold water (100 ml.) and stirred by means of a magnetized stirring bar. Within 5–10 minutes, the solution clouded and a slightly exothermic reaction commenced with evolution of carbon dioxide. The sustaining reaction was complete after another 5–10 minutes, after which time the mixture was allowed to settle into two liquid phases. The bottom dibromoacetonitrile phase was separated directly and the top aqueous phase was extracted twice with small portions of ether. After having been dried over sodium sulfate, the combined oil and ethereal extracts were freed of ether by distillation from a water-bath and the residual dibromoacetonitrile was purified by distillation under reduced pressure. The nitrile distilled as a colorless oil (colors on standing), b.p. 68–69° at 24 mm., n_D^{25} 1.5423, d_4^{20} 2.369, MR_D. Calc'd: 26.7. Found: 26.4, Wt. 14.9 g. (75% yield). Literature[4b] b.p. 67–69° at 24 mm.

Anal. Calc'd for C_2HBr_2N: Br, 80.37. Found: Br, 80.59.

Chlorodecarboxylation of cyanoacetic acid. In a similar fashion, cyanoacetic acid (8.5 g., 0.1 mole) was treated in water with N-chlorosuccinimide (26.7 g., 0.2 mole). The reaction was complete in 10–15 minutes. Isolation of the nitrile was accomplished as in the preceding experiment and yielded colorless dichloroacetonitrile, b.p. 112–113° at atmospheric pressure, n_D^{25} 1.4391, d_4^{20} 1.369, MR_D. Calc'd: 20.9; Found: 21.2, Wt. 6.0 g. (60% yield). Literature[3a] b.p. 112–113° at atmospheric pressure.

Anal. Calc'd for C_2HCl_2N: Cl, 64.49. Found: Cl, 64.35.

Similar results were also obtained when the molar equivalent of potassium cyanoacetate was substituted for cyanoacetic acid in the above experiments. In these cases, however, no carbon dioxide evolution was noted and the aqueous phase reddened. The work-up as described yielded the dihaloacetonitriles with no significant differences in yields. The aqueous phases from these reactions liberated carbon dioxide on acidification, indicating the presence of bicarbonate (or less probably, carbonate) ion.

Characterization of the dihaloacetonitriles. Dichloroacetonitrile. The nitrile (5.5 g., 0.05 mole) was refluxed for four hours in methanol (8 ml.) containing water (2 ml.) and concentrated sulfuric acid (3 ml.). Methanol (6 ml.) was recovered by distillation. The residual material was treated with water (30 ml.), separated, and the lower ester layer was washed with dilute bicarbonate solution. Distillation of the dried material gave unreacted nitrile, b.p. 90–115°, 10% recovery, and methyl dichloroacetate, b.p. 137–140°, n_D^{25} 1.4400, d_4^{20} 1.361, 75% yield. The ester, when shaken with cold concentrated ammonia, yielded crystalline dichloroacetamide quickly in essentially quantitative yield. The amide sublimed (1 mm., 120° bath) as thick rods, m.p. 97–98°, undepressed when admixed with authentic material. Literature[12] m.p. 98°.

Dibromoacetonitrile. The nitrile (9.95 g., 0.05 mole) gave colorless methyl dibromoacetate (b.p. 60° at 9 mm., n_D^{25} 1.5234, d_4^{20} 2.221, 80% yield) when methanolyzed as described above. Dibromoacetamide (m.p. and mixture m.p. 153–154°, literature[4b] m.p. 153°) resulted in a near quantitative yield upon ammonolysis of the ester.

Attempted chlorination of chloroacetonitrile. Chloroacetonitrile (3.78 g., 0.05 mole), water (50 ml.), and N-chlorosuccinimide (6.68 g., 0.05 mole) were magnetically stirred at room temperature. No reaction occurred after 1½ hours. The N-chlorosuccinimide was recovered by filtration (Wt. 5.4 g., 81% recovery). The aqueous solution had the odor of hypochlorous acid from the slow hydrolysis of the chloroimide.

Attempted halodecarboxylation of α-cyanopropionic acid. α-Cyanopropionic acid (1 g., 0.01 mole) and N-bromosuccinimide (1.8 g., 0.01 mole) were stirred in water as described. After 30 minutes, the N-bromoimide was hydrolyzed to yellow hypobromous acid with no other observable reaction. Extraction with ether yielded as the only isolable material only unreacted cyanoacid (essentially quantitative recovery), identified by hydrolysis with concentrated hydrochloric acid at room temperature for four days to isosuccinic acid, m.p. 128–129.5° (dec.). Literature[13] m.p. 120–135° (dec.).

The reaction of α-cyanopropionic acid with N-chlorosuccinimide gave results comparable to those just noted. Attempts to obtain the reaction by using potassium α-cyanopropionate with either N-bromo- or N-chloro-succinimide were not successful. Hydrolysis of both the haloimides and the cyanoacid occurred and no evidence of nitrile formation was observed.

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[11] Hoffmann and Barbier, *Bull. soc. chim. Belg.*, **45**, 565 (1936); cf. C. A., **31**, 9192 (1937). The abstract gives the boiling point of α-cyanopropionic acid as 93.4° at 10.5 mm. The present author considers this in error.

[12] Shriner and Fuson, *The Identification of Organic Compounds*, Third Edition, John Wiley and Sons, New York, N. Y. (1948), p. 231.

[13] Meyer and Bock, *Ann.*, **347**, 100 (1906).

The Role of Styrene in the Racemization of α-Phenethyl Chloride

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Optically active α-phenethyl chloride is known to racemize in polar solvents such as liquid sulfur dioxide,[1] formic acid,[2] and phenol[3] and in non-polar solvents such as carbon tetrachloride, provided Lewis acids are present.[4] α-Mesitylethyl chloride racemizes unimolecularly even in the non-polar nonprotonic solvent acetone.[5] Although it is generally presumed that the racemization proceeds by a rate-determining ionization of the carbon-chlorine bond, the importance of the possible equilibrium of the carbonium ion thus formed with styrene and a proton has not been evaluated, and earlier workers[6]

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[1] Bergmann and Polanyi, *Naturwissenschaften*, 21, 378 (1933).

[2] Bodendorf and Böhme, *Ann.*, **516**, 1 (1935).

[3] Hart and Spliethoff, *J. Am. Chem. Soc.*, **77**, 833 (1955).

[4] Heald and Williams, *J. Chem. Soc.*, 362 (1954) and earlier references cited there.

[5] Charlton and Hughes, *J. Chem. Soc.*, 2939 (1954).

[6] Hughes, Ingold, and Scott, *J. Chem. Soc.*, 1271 (1937).