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 non-protonic 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).

ascribed the racemization to this reversible equilibrium. Heald and Williams[4] showed that hydrogen chloride adds to styrene in carbon tetrachloride containing stannic chloride at a rate ($k = 128 \times 10^{-4}$ mol.l.$^{-1}$ min.$^{-1}$) which is comparable with the rate at which the chloride racemizes in the same medium ($k = 108 \times 10^{-4}$ mol.l.$^{-1}$ min.$^{-1}$). Others[7] have claimed that the rate of addition of hydrogen chloride to styrene is too small.

To evaluate the importance of styrene in the racemization process, we have examined the exchange of α-phenyl-β,β,β-trideuteroethyl chloride, $C_6H_5CHClCD_3$ (I), with phenol. If the equilibrium with styrene were important, then I should experience a rapid decrease in deuterium content when subjected to racemizing conditions, for the exchange between deuterium chloride and phenol is known[8] to be rapid and extensive. I was allowed to go through one racemization half-life[9,3] in a phenol-benzene solution. The results (Table I) show that under the conditions of these experiments, styrene is not involved in the racemization.

TABLE I

DEUTERIUM EXCHANGE OF $C_6H_5CHClCD_3$ (1.75 MOLAR) AND PHENOL (2.16 MOLAR) IN BENZENE, 50°, 34 MINUTES

Species	Volume-%	
	Before	After
$C_6H_5CHClCD_3$	90.7 ± 0.5	90.5 ± 0.7
$C_6H_5CHClCHD_2$	9.0 ± 0.5	8.8 ± 0.7
$C_6H_5CHClCH_2D$	0.3 ± 0.1	0.7 ± 0.1
Total % of terminal hydrogens as deuterium	96.8	96.6

EXPERIMENTAL

Materials. α-Phenyl-β,β,β-trideuteroethyl chloride (I) was prepared by acetylation of benzene with trideuteroacetyl chloride, reduction of the ketone with lithium aluminum hydride, and conversion of the carbinol to the chloride with thionyl chloride, all by procedures described in the literature for the non-deuterated compounds. The deuterium content and distribution was determined mass spectrometrically[10] and is shown in column 2, Table I.

The exchange experiment. A mixture of 5 ml. of 4.32 *M* phenol in benzene and 5 ml. of 3.5 *M* I in benzene, in a glass-stoppered test tube, was kept at 50° ± 0.5° for 34 minutes. The solution then was diluted with 25 ml. of benzene and extracted immediately with 25 ml. of 5 *N* sodium hydroxide, then twice with 25-ml. portions of 3 *N* sodium hydroxide, five times with 10-ml. portions of ice-water, and dried over sodium sulfate. After removal of the benzene, 1.3 g. (60%) of the chloride was recovered, b.p. 76° at 12 mm. The mass spectrometric analysis is shown in column 3, Table I.

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(7) Böhme and Siering, *Ber.*, 71, 2372 (1938).

(8) Hart, *J. Am. Chem. Soc.*, 72, 2900 (1950).

(9) Actually, the time during which the chloride was in the phenol-benzene solution was equivalent to one half-life for the *non*-deuterated chloride.[3] Lewis and Coppinger, *J. Am. Chem. Soc.*, 76, 4495 (1954), have shown that the k_H/k_D ratio for the acetolysis at 50° of α-*p*-tolyl-β,β,β-trideuteroethyl chloride is only 1.28; this implies that the time allowed was sufficient to racemize about 40% of the trideuterated chloride, had it been optically active.

(10) Meyerson, *Appl. Spectroscopy*, 9, 120 (1955).