nol were mixed, warmed to 50° for 10 min., allowed to stand 1 hr. at room temperature, and then reheated to 60°, and concentrated hydrochloric acid was added with stirring until the *p*H dropped to 1. The mixture was stirred and heated at 60° for 2 hr. longer and then cooled in an ice bath. The precipitated phthalhydrazide was filtered off and the filtrate was adjusted to pH 10 with saturated aqueous sodium hydroxide solution. The basic solution was mixed with 2 g. of sodium chloride and extracted with ether for 5 hr. in a continuous extractor, and the extract was dried over anhydrous potassium carbonate. Concentration of the extract to a small volume and addition of 5% ethanolic hydrochloric acid caused the precipitation of 2.54 g. (41%) of BAPN hydrochloride, m.p. 165–166°. The m.p. of this salt has been reported to be 164°.[9] Analysis with the mass spectrometer showed 15.4 atom per cent N^{15} excess in this product.[10]

β-Aminopropionitrile-1-C.[14] C^{14} Barium carbonate was converted to C^{14} potassium cyanide by the method of McCarter.[11] Yields varied from 82 to 84%.

A mixture of the radioactive potassium cyanide from 100 mg. of barium carbonate (specific activity 1 mc. per millimole), 14.8 g. of nonradioactive potassium cyanide, and 19.5 g. of ethylene chlorohydrin was stirred continuously at 55° and 6.5 ml. of water was added dropwise during a period of 1.75 hours.[12] Stirring was continued while the mixture was maintained at 55° for 45 min. after addition of the water was complete and then at 60° for 3 hr. longer. The reaction mixture was then extracted five times with 15-ml. portions of acetone, and the extract was fractionally distilled. Ethylene cyanohydrin distilled as a colorless liquid, 7.48 g. (44%), b.p. 223–224°.

The above product and 0.75 g. of aluminum dust were placed in a 50-ml. conical flask fitted with a reflux condenser and with a second condenser arranged for downward distillation.[12] Steam was passed through the reflux condenser and the flask was heated in an oil bath at 180° until distillation ceased (*ca.* 3 hr.). The distillate was collected in a centrifuge tube chilled in dry ice. The oil bath temperature was then raised to 280° and held there until dehydration was complete (total heating time 8 hr.). Decantation of the upper oily layer in the receiver from the lower frozen water layer gave 4.4 g. (79%) of radioactive acrylonitrile.

This material without further purification was placed in a sealed tube with 16 ml. of concentrated ammonium hydroxide and shaken for a few minutes until a homogeneous solution was formed. After 20 hr. at room temperature the contents of the tube were distilled to yield 1.40 g. (24%) of V, b.p. 69–70° (8 mm.), plus 2.28 g. (45%) of the bis compound, VI, b.p. 180–192° (8–10 mm.).[13] Each was converted to the hydrochloride with ethanolic hydrogen chloride in quantitative yield. The salt of V consisted of glistening white platelets, m.p. 165–166°, while that from VI appeared as fine white needles, m.p. 149–150°. These m.p. values have been reported as 164° and 148°, respectively.[9] The specific activity of the hydrochloride of V was 0.46 μc. per mg., and of that from VI was 0.48 μc. per mg.

Reaction of N-(β-haloethyl)phthalimides with sodium or potassium cyanide. In a typical experiment 8 g. of N-(β-bromoethyl)-phthalimide, (III),[14] 2.6 g. of potassium cyanide, and 140 ml. of 80% ethanol were continuously stirred and refluxed for 24 hr. The clear red-brown solution was concentrated to dryness at reduced pressure and the residue was extracted with boiling dioxane. The residue from evaporation of the dioxane extract was crystallized from water to give 2.6 g. of large plates, m.p. 125–126°. A recrystallized sample, m.p. 127–129°, proved to be identical with N-(β-hydroxyethyl)phthalimide, (II).[14] No other definite product could be isolated.

A repetition of this experiment using N,N-dimethylformamide as the solvent in place of 80% ethanol gave an 11% yield of impure N-(β-cyanoethyl)phthalimide, (IV), m.p. 139–144°, (pure IV melts at 151–152°). Extending the reaction time to 70 hr. at 120–130° gave no better results. When the procedure of Sakami *et al*[15] involving the use of acetone-free methanol as solvent was tried, unchanged III was recovered. When N-(β-chloroethyl)phthalimide[16] was refluxed with sodium cyanide in 50% ethanol, the mixture darkened rapidly and no definite product could be isolated. Reaction of N-(β-iodoethyl)phthalimide[17] with potassium cyanide in 95% ethanol gave II as the only product.

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[9] A. P. Terent'ev, K. I. Chursina, and A. N. Kost, *J. Gen. Chem.*, (*USSR*) **20,** 1073 (1950).

[10] The authors wish to thank Mr. Michael Bach for making this measurement.

[11] J. A. McCarter, *J. Am. Chem. Soc.*, **73,** 483 (1951).

[12] C. H. G. Hands and B. Y. Walker, *J. Soc. Chem. Ind.*, **67,** 458 (1948).

[13] S. R. Buc, *Org. Syntheses*, **27,** 3 (1947).

[14] T. O. Soine, *J. Am. Pharm. Assoc.*, **33,** 141 (1944).

[15] W. Sakami, W. E. Evans, and S. Gurin, *J. Am. Chem. Soc.*, **69,** 1110 (1947).

[16] H. Wenker, *J. Am. Chem. Soc.*, **59,** 422 (1937).

[17] E. E. Blaise, and A. Cornillot, *Compt. rend.*, **178,** 1186 (1924).

Anomalous Hofmann Elimination Reactions

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Weinstock[1] questions the conclusion of Ingold and Rogers[2] and in particular suggests that the alleged new *cis-trans* isomer, m.p. 107–8°, of the previously described α-benzylcrotonic acid (m.p. 99°) which these authors describe, is, in fact, 1-benzylcyclopropanecarboxylic acid. Such a possibility was considered by Rogers[3] and rejected for two reasons: the absorption of more hydrogen (3.25 atoms) on catalytic reduction in aqueous solution over Adam's platinum oxide catalyst than was required for full hydrogenation of the benzene ring system; and the isolation,[2] following ozonolysis in chloroform at 0° for 2 hr., of acetaldehyde as its 2,4-dinitrophenylhydrazone, m.p. 154°, raised on admixture with authentic material of m.p. 163°, and depressed by mixture with the dinitrophenylhydrazone of formaldehyde.

Small samples of both isomers being available, it has been possible to decide the point in the light of modern spectroscopic knowledge. The infrared absorption of the alleged isomer m.p. 107° not only differs greatly from that of the isomer m.p. 99°, but shows the peak at 9.70 μ, already recorded for 1-benzylcyclopropanecarboxylic acid by Piehl and Brown,[4] which Slabey[5] has shown to be charac-

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[1] Weinstock, *J. Org. Chem.*, **21,** 540 (1956).

[2] Ingold and Rogers, *J. Chem. Soc.*, 722 (1935).

[3] Rogers, Thesis "The mechanism of the reduction of unsaturated organic compounds," London, 1934, pp. 40 & 79.

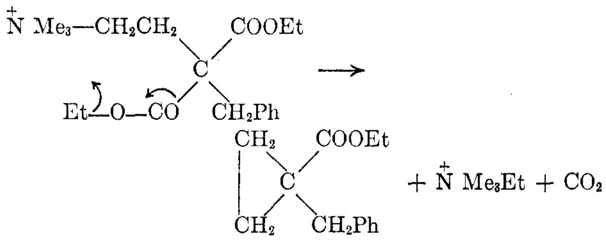
[4] Piehl and Brown, *J. Am. Chem. Soc.*, **75,** 5026 (1953).

[5] Slabey, *J. Am. Chem. Soc.*, **76,** 3605 (1954).

teristic of 1,1-disubstituted cyclopropanes; all six peaks recorded by the former authors are present, with maximum deviation of ±0.1 μ.

Ultraviolet absorption also confirms the supposition of Weinstock. Both compounds show a weak maximum at 260 mμ, but in the case of α-benzylcrotonic acid (m.p. 99°) only there is very considerable overlapping end absorption due to the conjugated carboxylic acid system.

Despite the unexplained results of the ozonolysis experiment, these observations confirm Weinstock's assertion that there is no evidence that the thermal degradation of 3,3-dicarboethoxy-4-phenylbutyltrimethylammonium iodide or ethoxide proceeds by a Wagner-Meerwein rearrangement. But rather than formulate the mechanism as Weinstock has done, it is preferred to represent it as an intramolecular 1,3 elimination process:



According to this one would not expect a 4,4-dicarboethoxybutyl quaternary ammonium salt to give cyclobutane derivatives on thermal decomposition under non-hydrolytic conditions, whereas in Weinstock's formulation it would be just as probable as in the case of the lower homolog. Furthermore the special function of the carboethoxy group explains why in this example and the closely related one[6] which Weinstock quotes, cyclopropane derivatives are formed so readily while 3-phenylpropyltrimethylammonium hydroxide reacts normally.

These results do not substantially weaken the argument of Ingold and Rogers[7] in support of the views of Burton and Ingold on the mechanism of reduction by sodium amalgam.

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[6] Rinderknecht and Niemann, *J. Am. Chem. Soc.*, **73**, 4259 (1951).

[7] Ingold and Rogers, *J. Chem. Soc.*, 717 (1935).