The dodecyl, benzyl and cyclohexyl derivatives thus obtained were purified by crystallization from water. The details of the preparation and properties of the products are given in Table I. The yields reported are quite low but since they represent the result of a first synthesis on a small amount of material, considerable improvement would be expected by further refinement of reaction conditions and method of isolation of the product. In this connection it is interesting to note that the correlation of % yield with reaction time and temperature indicate that considerable increase in yield should be possible in most cases by increasing both the temperature and time of reaction.

DEPARTMENT OF CHEMISTRY
CLARK UNIVERSITY
WORCESTER, MASS.
RECEIVED MARCH 3, 1950

Preparation of α-Naphthaleneacetic Acid by the Condensation of Naphthalene with Chloroacetic Acid

BY YOSHIRO OGATA AND JIRO ISHIGURO

The plant growth hormone α-naphthaleneacetic acid is ordinarily prepared by way of α-chloromethylnaphthalene and α-naphthaleneacetonitrile.[1] Other procedures, in our hands at least, were less satisfactory.[2,3] The direct condensation of naphthalene with chloroacetic acid[4] has been reported to yield naphthaleneacetic acid, and we have investigated this reaction in detail. After preliminary experiments gave poor and nonreproducible yields, we studied the effect of many metals, metallic oxides and metal halides on this condensation and discovered that a small quantity of ferric salt was an excellent catalyst. It is probable that the small amount of iron (0.05–0.0008%) in coal tar naphthalene serves to promote the condensation in the examples previously described.[4] Metallic bromides also promote the condensation, possibly by converting chloroacetic acid into bromoacetic acid, which condenses more easily,[5] by way of hydrobromic acid.

Experimental

Materials.—Naphthalene purified by distillation, m. p. 80–80.5°, was used. Its iron content was determined by refluxing it with 2 *N* hydrochloric acid for one hour, oxidizing ferrous to ferric iron in the filtrate by means of chlorine and completing the determination colorimetrically with ammonium thiocyanate. The chloroacetic acid used melted at 61–63°. The bromoacetic acid, prepared by the bromination of acetic acid, had a boiling point of 112–117° (35 mm.).

Procedure.—Naphthalene (57.6 g.) (0.0010% iron), 14.1 g. of chloroacetic acid, 87.6 mg. of ferric oxide, and 420 mg. of potassium bromide were placed in a long-necked round-bottom flask fitted with a rubber stopper carrying a thermometer and an air-cooled tube about 1 m. long, and the mixture was boiled gently on a sand-bath for twenty hours. The best yield was obtained when the heating was controlled according to a temperature–time curve in which the temperature of reactants attained 200° after ten hours and 218° after twenty hours. After the reaction, the greater part of the unreacted naphthalene (43 g.) was recovered by distillation.[6] The residue was extracted with hot sodium hydroxide solution, cooled and filtered. Acidification of the filtrate with hydrochloric acid yielded a brownish precipitate, 19.4 g. (70%), m. p. 108–113°. Crystallization from the 250-fold amount of boiling water with the addition of small amounts of concentrated hydrochloric acid gave 9.5 g. (34% based on chloroacetic acid, 45% on naphthalene reacted), m. p. 124–126°. The melting point could be raised to 132° by repeated crystallization and showed no depression when mixed with α-naphthaleneacetic acid prepared by the chloromethylation procedure. In the absence of ferric oxide and potassium bromide no naphthaleneacetic acid was produced. With potassium bromide alone 4% and with ferric oxide alone 5% was produced. The conditions described above are optimum with regard to temperature, time, increased amounts of potassium bromide and increased ratio of chloroacetic acid to naphthalene. Bromoacetic acid condensation is more rapid, but the high cost and skin irritant properties of this substance render it less suitable than chloroacetic acid. The promoting action of several other metallic halides (*e. g.*, sodium chloride, potassium chloride, potassium iodide, hydrated aluminum chloride, hydrated aluminum bromide, hydrated ferric bromide and mercuric bromide), when mixed with ferric oxide, was also observed, but these were less effective than potassium bromide.

Acknowledgments.—The authors wish to thank the Japanese Ministry of Education, Osaka Gas Co., Professors R. Oda, S. Takei, Mr. Y. Ishikawa, and Mr. A. Fukui, without whose aid this work would not have been possible.

---

(1) *E. g.*, Cambron, *Can. J. Research*, **17B**, 10 (1939); *cf. C. A.*, **33**, 5387 (1939); Grummitt and Buck, "Organic Syntheses," Vol. XXIV, 1944, p. 30, and the literatures cited here.

(2) Griehl, *Chem. Ber.*, **80**, 410 (1947); *cf. C. A.*, **42**, 7749 (1948).

(3) Witman, U. S. Patent 2,290,401; *cf. C. A.*, **37**, 388 (1943).

(4) Wolfram, Schöring, Hausdörfer and I. G. Farbenind. A.-G., German Patent 562,391, Feb. 2, 1929; *cf. Frdl.*, **19**, 779 (1934).

(5) Demole, *Ber.*, **9**, 561 (1876).

(6) The chloroacetic acid reacted almost completely, and could not be recovered.

DEPT. OF INDUSTRIAL CHEMISTRY
KYOTO UNIVERSITY
KYOTO, JAPAN
RECEIVED NOVEMBER 30, 1949

Decomposition of the Isomeric Valeric Acids in the Ozonizer Discharge

BY WILLIAM S. PARTRIDGE[1] AND WARREN M. GARRISON

In the alpha particle bombardment of a series of straight chain aliphatic acids,[2] it has been observed[3] that the abundance of hydrogen relative to carbon dioxide plus carbon monoxide in the product gas is proportional to the ratio of C–H to C–COOH bonds in the bombarded molecule. Data reported[4] earlier for cathode ray bombardment of aliphatic hydrocarbons show a similar group to product relationship for hydrogen and methane. If the H_2/CH_4 yield ratios for the series of hydrocarbons studied are plotted *versus* the C–H/C–CH_3 bond ratios, a straight line relation-

---

(1) Department of Chemistry, University of Utah.

(2) C. W. Sheppard and V. L. Burton, THIS JOURNAL, **68**, 1636 (1946).

(3) R. E. Honig, *Science*, **104**, 27 (1946).

(4) C. S. Schoepfle and C. H. Fellows, *J. Ind. Eng. Chem.*, **23**, 1396 (1931).