

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.

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

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The plant growth hormone α -naphthaleneacetic acid is ordinarily prepared by way of α -chloromethylnaphthalene and α -naphthaleneacetoneitrile.¹ Other procedures, in our hands at least, were less satisfactory.^{2,3} The direct condensation of naphthalene with chloroacetic acid⁴ has been reported to yield naphthaleneacetic acid, and we have investigated this reaction in detail. After preliminary experiments gave poor and non-reproducible 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.

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

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Decomposition of the Isomeric Valeric Acids in the Ozonizer Discharge

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In the alpha particle bombardment of a series of straight chain aliphatic acids,² it has been observed³ 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 reported⁴ earlier for cathode ray bombardment of aliphatic hydrocarbons show a similar group to product relationship for hydrogen and methane. If the H₂/CH₄ yield ratios for the series of hydrocarbons studied are plotted *versus* the C–H/C–CH₃ bond ratios, a straight line relation-

(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) Criebl, *Chem. Ber.*, **80**, 410 (1947); *cf. C. A.*, **43**, 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).

(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).

ship is obtained. Data for the branched chain isomers, however, indicate that the relative yields of hydrogen and methane are not proportional to the fractional concentration of C-H and C-CH₃ bonds in the bombarded molecule. This selective decomposition of organic compounds by ionizing radiation has been recently discussed⁵ in terms of competing free radical and rearrangement processes.

To obtain information on the effect of isomerism on the radiation chemistry of organic acids, we have studied the decomposition of several series of isomeric acids in the ozonizer discharge which has been shown⁶ to produce chemical change by processes similar to those obtained with high-energy radiation. A previous paper⁷ reported the decomposition of the toluic acids. The present paper reports a similar study of the valeric acid isomers. Gaseous decomposition products obtained from the valeric acids in the liquid state at 0° are shown in Table I. By comparing the CH₄/H₂ yield ratios for the four isomeric acids, it is seen that the relative yield of methane to hydrogen is not proportional to the C-CH₃/C-H bond ratio in the bombarded molecule. In fact, the methane to hydrogen yield ratio for trimethylacetic acid is actually smaller than the corresponding values observed with the other three compounds. The yield of methane relative to carbon dioxide plus carbon dioxide plus carbon monoxide also shows a minimum value with the tertiary acid. Increasing substitution on the alpha carbon atom results in a decrease in the probability of methane formation with a corresponding increase in the relative yield of higher hydrocarbons. A quantitative analysis of the higher hydrocarbon fraction was not undertaken; qualitative fractionation, however, indicated the presence of ethane and hydrocarbons with higher boiling points. A more detailed discussion of these reactions will be presented in a later paper.

TABLE I

GASEOUS PRODUCTS FROM THE VALERIC ACIDS IN THE OZONIZER DISCHARGE (VOLUME %)

	<i>n</i> -Valeric		Isovaleric		Methyl-ethyl-acetic		Tri-methyl-acetic	
H ₂ O	11.5	11.3	10.7	11.2	9.3	8.3	14.5	14.8
CO ₂	10.0	10.0	10.7	9.8	10.2	10.7	18.3	19.3
CO	16.6	15.3	22.0	22.4	26.8	25.5	22.6	22.6
H ₂	54.3	54.6	40.7	40.6	38.0	40.1	17.7	17.1
CH ₄	8.8	9.0	8.2	8.4	8.3	7.8	1.8	0.5
Other ^a hydrocarbons	0.2	0.2	7.3	7.0	6.8	7.0	26.3	25.0

^a Condensable in liquid air after removing water and carbon dioxide.

Experimental

Isovaleric acid (b. p. 176–176.5°) and methylethylacetic acid (b. p. 173–174°), obtained from Eastman Kodak

(5) M. Burton, *J. Phys. Chem.*, **51**, 786 (1947).

(6) G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, Inc., New York, N. Y., 1939.

(7) C. N. Stover and W. M. Garrison, *This Journal*, **72**, 2793 (1950).

Co., were used without further purification. *n*-Valeric acid (b. p. 186.2°) was prepared by hydrolysis of *n*-valeronitrile and purified by fractional distillation. Trimethylacetic acid (b. p. 173–174°) was prepared by the method of Puntambeker and Zoellner.⁸

The all-glass discharge chamber,⁹ the temperature of which was controlled by an ice-water-bath, was connected through stopcocks to a manifold, to a product gas storage bulb, and to a Toepler pump which was used to transfer the decomposition products to a gas microanalyzer.¹⁰ The entire system could be evacuated to 10⁻⁵ mm. by a mercury diffusion pump attached to the manifold through a liquid-air trap. The transformer and experimental procedure were identical with those previously described.³

(8) "Organic Syntheses," 2nd ed., Vol. I, John Wiley and Sons, Inc., New York, 1944, p. 524.

(9) E. Warburg, *Z. tech. Physik*, **4**, 450 (1923).

(10) C. N. Stover, W. S. Partridge and W. M. Garrison, *Anal. Chem.*, **21**, 1013 (1949).

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Polymorphism of 17-Ethinylestradiol

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17-Ethinylestradiol has been described with a melting point of 146°.¹ A second polymorphic form, m. p. 183° cor., has been encountered and conditions have been found which effect the interconversion of the two forms.

Samples of pharmaceutical grade ethinylestradiol which melted in the normal manner at 146° were sometimes observed to be slightly cloudy in appearance. Sustained heating at 150 to 160° caused these samples to resolidify completely to acicular crystals. This crystalline form underwent no physical change on cooling. The melting point of this form was about 183°, at which temperature it melted completely to a clear liquid, which did not crystallize on cooling but formed a glassy mass. However, it could be made to crystallize as either the 146 or the 183° melting form by seeding with the desired form. Seeding with a mixture of both forms, even at a temperature below 140°, produced only the higher melting form.

A methanol solution prepared from the high-melting form gave the low-melting form upon concentration and cooling. The mother liquor was diluted with ether and upon standing for several days gave crystals of the high-melting form.

A sample of the 183° melting form gave the following analysis: Calcd. for C₂₀H₂₄O₂: C, 81.04; H, 8.16. Found: C, 80.80; H, 8.30. Infrared absorption spectra were determined on samples of both forms, both in chloroform solution and in mineral oil suspension.² The chloroform solutions gave identical absorption curves between 2 and 12 microns. Curves from the mineral oil

(1) Inhoffen, Logemann, Hohlweg and Serini, *Ber.*, **71**, 1024 (1938).

(2) The author is indebted to W. B. Tarpley, Research Laboratories of this company, for the absorption spectra.