moderate warming in the presence of a carbon dioxide atmosphere. The reaction was allowed to proceed at the boiling point of ether (due to the heat of reaction) and from a 0.2-mole run there was obtained 6.5 g., or a 20% yield of methyl atropic acid. There is then a restricted optimal temperature range, below which the reaction is virtually stopped, and above which the yield of acid drops.

Summary

Methyl atropic acid is obtained when cinnamyl chloride and carbon dioxide are added to magnesium in ether. The formation of this acid probably is due to the rearrangement of cinnamylmagnesium chloride.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SOME BROMINE DERIVATIVES OF PENTANOIC AND HEXANOIC ACIDS

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RECEIVED APRIL 16, 1927 PUBLISHED JULY 5, 1927

The ω-halogen derivatives of pentanoic and hexanoic acids are of some interest in connection with the preparation of compounds related to ornithine and lysine. Several methods of synthesis are already available but they are not entirely satisfactory in all details.

5-Bromopentanoic acid has been prepared by Cloves[1] by heating 5-phenoxypentanoic acid with concd. hydrobromic acid in a sealed tube at 145°. The 5-phenoxypentanoic acid is best prepared by Gabriel's method[2] from diethyl phenoxypropylmalonate. This ester has been described in several papers[2,3] and the yields are said to be about 55% when γ-chloropropylphenyl ether is condensed with the sodium derivative of malonic ester.

All of these reactions have been reinvestigated and the methods and yields have been improved. Thus, in the preparation of diethyl phenoxypropylmalonate, the use of γ-bromopropylphenyl ether in place of the chloro compound has increased the yield of the ester to about 70–80%. The 5-phenoxypentanoic acid has been reacted with 48% hydrobromic acid without the use of sealed tubes to give better than 60% of the calculated amount of 5-bromopentanoic acid. A more direct preparation of this bromo acid was developed, in which the diethyl phenoxypropylmalonate was treated directly with 48% hydrobromic acid. The yield based on the ester is 65–69%.

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[1] Cloves, *Ann.*, **319**, 367 (1901).

[2] Gabriel, *Ber.*, **25**, 418 (1892).

[3] (a) Funk, *Ber.*, **26**, 2569 (1893). (b) Granger, *Ber.*, **28**, 1199 (1895). (c) Günther, *Ber.*, **31**, 2136 (1898).

2,5-Dibromopentanoic acid has been prepared previously from diethyl α,δ-dibromopropylmalonate by hydrolysis with concd. hydrobromic acid.[4] It has been found that the bromination of 5-bromopentanoic acid in the presence of a small amount of phosphorus tribromide[5] proceeds smoothly to give the 2,5-dibromo acid. An attempt was made to obtain this acid by first brominating phenoxypropylmalonic acid and then removing carbon dioxide and splitting the ether acid with hydrobromic acid. This method was not at all satisfactory. Apparently, bromine enters the benzene ring and the resulting mixture of products is very hard to purify. Practically no pure 2,5-dibromopentanoic acid could be isolated from this reaction.

In a previous paper[6] from this Laboratory a solid compound thought to be 2,6-dibromohexanoic acid was described. It was prepared by the bromination of phenoxybutylmalonic acid, followed by the elimination of carbon dioxide and the splitting of the ether with hydrobromic acid. The compound was so different in its physical properties from those of the 2,5-dibromopentanoic acid prepared in this work that it was thought advisable to prepare a sample of 2,6-dibromohexanoic acid by the bromination of 6-bromohexanoic acid. This was done and the pure 2,6-dibromo acid was obtained as a heavy liquid. The compound previously described is undoubtedly not a simple hexanoic acid derivative.

The acid chlorides and ethyl esters of 5-bromopentanoic acid and of 2,5-dibromopentanoic acid have been prepared and are described in the Experimental Part.

Experimental Part

Diethyl Phenoxypropylmalonate.—The usual procedure for the alkylation of malonic ester was followed.[7] The quantities used were 2.5 liters of absolute alcohol, 69 g. of sodium, 720 g. of diethyl malonate and 645 g. of γ-bromopropylphenyl ether. The product was collected at 185–189° (4 mm.). The yield varied from 615 to 710 g., or 70–80%. The product did not solidify at ordinary temperatures. Its purity was shown by the saponification number 148.6, whereas the calculated value is 147; d_{26}^{26}, 1.0858; n_D^{21}, 1.488; M_D calcd., 77.45; found, 78.00.

5-Phenoxypentanoic Acid.—This product was prepared by Gabriel's[2] method in yields of 87–93%, based on the ester. It boiled at 175° (4 mm.) and melted at 65–66°.

5-Bromopentanoic Acid from 5-Phenoxypentanoic Acid.—A 1-liter flask was fitted

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[4] (a) Willstätter and Ettlinger, *Ann.*, **326**, 101 (1903). (b) Fischer and Suzuki, *Ber.*, **37**, 2843 (1904).

[5] Compare the method of Clarke and Taylor for α-bromocaproic acid, "Organic Syntheses," John Wiley and Sons, New York, **1925**, vol. 4, p. 9.

[6] Marvel, MacCorquodale, Kendall and Lazier, THIS JOURNAL, **46**, 2842 (1924).

[7] Ref. 5, p. 11.

by means of a ground-glass connection to a 1-meter fractionating tube leading to a condenser set for distillation. In this flask were placed 330 g. of 5-phenoxypentanoic acid and 500 cc. of 48% hydrobromic acid. The mixture was boiled over a flame at such a rate that the temperature at the head of the fractionating column was maintained at 115–120°, thus allowing water and phenol to distil out of the reaction mixture. The reaction was complete in five to eight hours, as no more phenol distilled. The reaction mixture was diluted with about 500 cc. of water and the 5-bromopentanoic acid was collected in ether. The ether extract was separated and evaporated and the residue was distilled under reduced pressure. The yield of acid boiling at 123–131°, at 6 mm., was 195–200 g., or 63–64%. On cooling, the product solidified; m. p., 38–39°.

5-Bromopentanoic Acid from Diethyl Phenoxypropylmalonate.—In the same way, 455 g. of diethyl phenoxypropylmalonate was treated with 300 cc. of 48% hydrobromic acid. The ester hydrolyzed and the ethyl alcohol was largely converted to ethyl bromide. Large quantities of carbon dioxide were evolved so that considerable foaming occurred in the early part of the reaction. When most of the ethyl bromide had distilled, another lot of 400 cc. of hydrobromic acid was added to the reaction mixture and the heating was then continued. When no more phenol distilled, the product was isolated as described before. The yield of pure acid, b. p. 142–145°, at 13 mm., was 182–193 g., or 65–69%; m. p., 38–39°.

Ethyl 5-Bromopentanoate.—Cloves[1] has esterified 5-bromopentanoic acid with ethyl alcohol, using dry hydrogen chloride as a catalyst. He collected and analyzed a fraction boiling at 120–176°, at 15 mm. No other physical properties were recorded.

A mixture of 50 g. of the bromo acid, 300 cc. of absolute alcohol and 5 g. of concd. sulfuric acid was refluxed for about two hours. The excess of alcohol was then distilled, the remaining crude ester dissolved in ether, washed with sodium carbonate solution and distilled. The yield of ester, b. p. 94–97°, at 7 mm., was 34–42 g., or 58–72%; d^{24}_{24}, 1.3191; $n^{24°}_{D}$, 1.4580; M_D, calcd., 43.85; found, 43.23.

5-Bromopentanoyl Chloride.—A mixture of 50 g. of 5-bromopentanoic acid and 90 g. of thionyl chloride was refluxed for about two hours and then distilled. The yield of pure acid chloride, b. p. 102–104°, at 15 mm., was 45 g., or 80%; d^{27}_{4}, 1.5010; n^{26}_{D}, 1.4879; M_D, calcd., 37.93; found, 38.29.

Anal. Subs., 0.1192, 0.4283: 6.80, 24.65 cc. of 0.1737 N $AgNO_3$. Calcd. equivalents of halogen: 0.001196, 0.004284. Found: 0.001180, 0.004265.

When treated with 30 g. of absolute alcohol, the above acid chloride gave 42 g. of the ethyl ester; b. p., 106–110°, at 20 mm.; yield, 89%.

2,5-Dibromopentanoic Acid.—A mixture of 53 g. of 5-bromopentanoic acid and 0.5 cc. of phosphorus tribromide was placed in a flask fitted to a reflux condenser by means of a ground-glass joint. Through the condenser, 60 g. of dry bromine was added. Some hydrogen bromide was evolved at room temperature. The flask was placed in an oil-bath at 70–80° for about 15 hours and finally heated for a few minutes at 110° to drive out most of the dissolved hydrogen bromide. The material was then transferred to a Claisen flask and distilled under reduced pressure. The yield of dibromo acid, b. p. 150–152°, at 5 mm., was 69 g., or 91%. The boiling point given in the literature[4b] is 171–174°, at 13–15 mm. The neutral equivalent for the acid prepared above was found to be 261; calcd., 260; d^{25}_{4}, 1.8629; n^{25}_{D}, 1.5347; M_D, calcd., 42.47; found, 43.42.

2,5-Dibromopentanoyl Chloride.—In a flask fitted to a reflux condenser by means of a ground-glass joint was placed 150 g. of 5-bromopentanoyl chloride. Through the condenser 160 g. of dry bromine was added, over a period of two hours. The mixture was heated overnight on a steam-bath and then distilled under reduced pressure. Some unchanged 5-bromopentanoyl chloride distilled first and then the dibromo acid chloride was collected at 138–145°, at 15 mm.; yield, 162 g., or 77%. The boiling point reported here is somewhat higher than that given by Fischer and Suzuki.[4b]

Ethyl 2,5-Dibromopentanoate.—A mixture of 430 g. of 5-bromopentanoic acid and 275 g. of thionyl chloride was allowed to react and the excess of thionyl chloride was then distilled. The residue was brominated with 420 g. of dry bromine. The crude 2,5-dibromopentanoyl chloride thus obtained was treated with 350 cc. of absolute ethyl alcohol. The ester was distilled under reduced pressure. The yield of ester, b. p. 128–135°, at 14 mm., was 400 g., or 58%. On redistillation most of the product boiled at 133–135°, at 14 mm.; d_4^{25}, 1.6289; n_D^{25}, 1.4947, M_D, calcd., 50.51. Found: 51.53.

Anal. Subs., 0.4516, 0.4182: 18.00, 16.77 cc. of 0.1737 N $AgNO_3$. Calcd. for $C_7H_{12}Br_2O_2$: Br, 55.6. Found: 55.4, 55.4.

6-Bromohexanoic Acid.—A mixture of 153 g. of diethyl phenoxybutylmalonate and 500 cc. of 48% hydrobromic acid was treated as described for the preparation of 5-bromopentanoic acid. The yield of product, b. p. 160–168°, at 18 mm., was 60 g., or 62%.

2,6-Dibromohexanoic Acid.—The general procedure used was that described for the bromination of 5-bromopentanoic acid. From 25 g. of 6-bromohexanoic acid, 24 g. of dry bromine and 3 cc. of phosphorus tribromide, there was obtained 28 g., or 80%, of 2,6-dibromohexanoic acid; b. p., 158–160°, at 4 mm.; n_D^{21}, 1.5245; d_4^{21}, 1.7897; M_D, calcd., 47.09; found, 46.88.

Anal. Subs., 0.1954, 0.2492: 8.23, 10.49 cc. of 0.1737 N $AgNO_3$. Calcd. for $C_6H_{10}O_2Br_2$: Br, 58.39. Found: 58.53, 58.50.

Summary

1. Improved methods for the preparation of 5-bromopentanoic acid and 2,5-dibromopentanoic acid and their esters and acid chlorides have been described.
2. It has been shown that the earlier description of 2,6-dibromohexanoic acid is in error and the correct description of this compound has been given.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WEST VIRGINIA UNIVERSITY]

THE ALKALINE OXIDATION OF ALPHA-NITRONAPHTHALENE

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RECEIVED MAY 11, 1927 PUBLISHED JULY 5, 1927

Since it has been known for a long time that in the oxidation of α-nitronaphthalene in an acid medium, 3-nitrophthalic acid is the principal product,[2] it seemed logical to expect that the oxidation with alkaline permanganate should yield a nitrophthalonic acid, which could be converted into 3- or 6-nitrophthalaldehyde acid by procedure analogous to that used by Fuson[3] for the preparation of phthalaldehyde acid from phthalonic acid. On carrying out the oxidation, however, it was found that the nitrated ring was attacked.

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[1] National Research Fellow in Chemistry.

[2] Beilstein and Kurbatow, *Ann.*, **202,** 217 (1880).

[3] Fuson, THIS JOURNAL, **48,** 1093 (1926).