CCCXLIII.—*The Interaction of Ammonium Sulphite with Certain Polybromoparaffins.*

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THE interaction of alkaline sulphites and polybromoparaffins has been studied with the object of obtaining aliphatic polysulphonic acids. The most easily obtainable bromoparaffins appeared to be αβγδ-tetrabromo-βγ-dimethylbutane and βγ-dibromobutane, and these were therefore chosen for this work. For the preparation of the former compound, pinacol, obtained from acetone (" Organic Syntheses," vol. V, p. 87), was first converted into βγ-dimethylbutadiene by distillation with a small quantity of hydrogen bromide (Kyriakides, *J. Amer. Chem. Soc.*, 1914, **36**, 987). The tetrabromide could not be obtained from this hydrocarbon in good yield by bromination in light petroleum or in carbon disulphide (compare Kondakow, *J. pr. Chem.*, 1900, **62**, 171; Courtot, *Bull. Soc. chim.*, 1906, **35**, 975), but addition proceeded smoothly in glacial acetic acid, apparently only one of the two theoretically possible, optically inactive isomerides being produced in any appreciable quantity. βγ-Dibromobutane was readily obtained by passing *n*-butyl alcohol vapour over a phosphoric acid catalyst at 400—500° and absorbing the product in bromine (King, J., 1919, **115**, 1408).

The sodium salts of the sulphonic acids prepared from these bromides were so exceedingly soluble in water that they could not be isolated from the reaction product of aqueous sodium sulphite and the halogen compound. The bromides were therefore boiled with aqueous ammonium sulphite and all inorganic salts were then completely removed from the solution by successive treatment with baryta and silver oxide; in this way the salts of the sulphonic acids were easily isolated.

Under these conditions αβγδ-tetrabromo-βγ-dimethylbutane yielded, not the corresponding tetrasulphonic acid, but a βγ-dimethylbutylenedisulphonic acid, $HO_3S{\cdot}CH_2{\cdot}CMe(SO_3H){\cdot}CMe{:}CH_2$ or

$$HO_3S{\cdot}CH_2{\cdot}CMe{:}CMe{\cdot}CH_2{\cdot}SO_3H;$$

βγ-dibromobutane, which is presumably a mixture of *meso*- and *dl*-forms, gave a mixture of two isomeric β-hydroxybutane-γ-sulphonic acids, one of which was obtained in an optically active form. Thus, although ethylene dibromide and αβγ-tribromopropane react normally with alkali sulphites, yielding ethane-αβ-disulphonic acid (Autenrieth and Rudolph, *Ber.*, 1901, **34**, 3473; Kohler, *Amer. Chem. J.*, 1897, **19**, 732) and propane-αβγ-trisulphonic acid (Schäuffelen, *Annalen*, 1868, **148**, 117; Schober, *Amer. Chem. J.*, 1904, **32**, 166) respectively, analogous compounds cannot be prepared in this way from bromobutanes.

EXPERIMENTAL.

αβγδ-Tetrabromo-βγ-dimethylbutane.—Bromine (13 c.c.; 2 mols.) in acetic acid (30 c.c.) was slowly added to βγ-dimethylbutadiene (10 g.) in acetic acid (20 c.c.). The colour of the bromine was discharged instantly at first, more slowly during the later stages, and a little hydrogen bromide was evolved. Very little heat was developed and towards the end of the addition the tetrabromide started to separate from the solution. After standing for about an hour, the product was removed by filtration, and washed first with a little acetic acid and finally with ether (yield, 28 g.). The bromide crystallised from benzene in colourless prisms, m. p. 138° (Found: C, 17·8; H, 2·5. Calc. for $C_6H_{10}Br_4$: C, 17·9; H, 2·5%). With a view to the isolation of the theoretically possible isomeric tetrabromide, the acetic acid mother-liquors were poured into water and the precipitated oil, after drying, was distilled in a vacuum: no fraction of constant boiling point could be isolated, with the exception of further quantities of the tetrabromide already described.

βγ-Dimethylbutylenedisulphonic Acid.—αβγδ-Tetrabromo-βγ-dimethylbutane (20 g.) was suspended in ammonium sulphite (50 g.) dissolved in water, and the mixture boiled under reflux during 16 hours, with the addition of small amounts of ammonium carbonate when sulphur dioxide appeared at the end of the condenser. The bromide had then almost completely dissolved and after filtration (from unchanged bromide, 2 g.), barium hydroxide (150 g.) was added and the ammonia expelled by boiling. The excess of baryta having been removed with carbon dioxide, freshly precipitated silver oxide (from 35 g. of silver nitrate) was added and the mixture well shaken. The precipitated silver bromide was filtered off, excess of barium removed as before, and the filtrate evaporated to dryness. The *barium* salt (12·5 g.; 70% of the theoretical yield) which remained proved to be that of βγ-dimethylbutylenedisulphonic acid. In further preparations the yield was increased to over 80%. The salt is extremely soluble in water and crystallised from aqueous alcohol in minute needles (Found: C, 18·15; H, 3·0; H_2O, 4·6; Ba, 34·8, 34·6. $C_6H_{10}O_6S_2Ba,H_2O$ requires C, 18·1; H, 3·0; H_2O, 4·5; Ba, 34·6%. Found in salt dried in a vacuum at 120°: Ba, 36·2. $C_6H_{10}O_6S_2Ba$ requires Ba, 36·2%). By addition of excess of bromine water to a solution of the salt and determination of the excess of bromine by titration it was found that one molecule of bromine was absorbed by 399 g. of the salt. One ethylenic linkage in the molecule requires 397·4 g. The free acid from this salt could not be obtained crystalline. The *ammonium* salt crystallised from water in glistening plates (Found: C, 26·05; H, 6·5; N, 10·05. $C_6H_{18}O_6N_2S_2$ requires C, 25·9; H, 6·5; N, 10·05%). The *sodium* salt crystallised from water, in which it is very soluble, in minute needles (Found: Na, 15·7. $C_6H_{10}O_6S_2Na_2$ requires Na, 15·9%). The *pyridine* salt crystallised from acetone–alcohol in colourless needles, m. p. 215—216° (Found: C, 48·5; H, 5·5; equiv., 201. $C_6H_{12}O_6S_2,2C_5H_5N$ requires C, 47·8; H, 5·5%; equiv., 201).

The *acid chloride* was prepared by treatment of the sodium salt (15 g.) with phosphorus pentachloride (40 g.). Reaction occurred at once with evolution of heat and the mixture became liquid. The phosphorus oxychloride was removed by distillation, and the oil which separated when the residue was poured on ice was extracted with chloroform. The dried chloroform solution on evaporation deposited colourless needles, m. p. 125—126° (Found: C, 25·2; H, 3·55; Cl, 25·3; S, 23·3. $C_6H_{10}O_4Cl_2S_2$ requires C, 25·6; H, 3·6; Cl, 25·3; S, 22·8%).

The Interaction of αβ-Dibromobutane and Aqueous Ammonium Sulphite.—The dibromide was boiled with excess of ammonium sulphite and after complete solution had occurred (22 hours) the barium salts of the sulphonic acids formed were isolated as previously described. The free acid from the barium salts was obtained as a syrup and was therefore dissolved in alcohol and neutralised with brucine. The product crystallised readily and after exhaustive fractionation from 90% alcohol two pure salts were isolated. *Fraction* A crystallised in minute colourless prisms, m. p. 270° (decomp.). It was slightly soluble in alcohol, but readily soluble in water, and proved to be the *brucine* salt of one of the possible β-hydroxybutane-γ-sulphonic acids, $CH_3\cdot CH(SO_3H)\cdot CH(OH)\cdot CH_3$ (Found: C, 59·1; H, 6·75; S, 6·1. $C_4H_{10}O_4S,C_{23}H_{26}O_4N_2$ requires C, 59·1; H, 6·6; S, 5·85%). $[\alpha]^{20°}_{5461}$ − 23·9° ($c = 0·58$)*.

This brucine salt was converted into the *barium* salt by treatment with baryta, extraction of brucine with chloroform, and precipitation of the excess of baryta with carbon dioxide. By evaporation of the filtrate the barium salt was obtained as a colourless powder very readily soluble in water (Found: H, 3·9; Ba, 30·6. $C_8H_{18}O_8S_2Ba$ requires H, 4·05; Ba, 30·9%). $[\alpha]^{20°}_{5461}$ − 5·4° ($c = 3·15$). The ammonium salt could not be obtained crystalline, but the l-*menthylamine* salt crystallised from acetone in masses of fine silky needles, m. p. 196° (Found: S, 10·45. $C_4H_{10}O_4S,C_{10}H_{21}N$ requires S, 10·35%).

Fraction B crystallised from aqueous alcohol in small needles,

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* All rotations were taken in aqueous solution.

m. p. 180—185°. It is readily soluble in hot alcohol and is apparently the salt of an acid isomeric with A (Found: C, 59·0; H, 6·7%). $[\alpha]_{5461}^{20^\circ}$ − 29·6° ($c = 0·57$). The barium salt of this acid was optically inactive.

Other fractions isolated from the original mixture could not be obtained homogeneous and further investigation was abandoned.

Summary.

Attempts to prepare paraffin polysulphonic acids from αβγδ-tetrabromo-βγ-dimethylbutane and βγ-dibromobutane by interaction with aqueous ammonium sulphite have resulted in failure: in the former case a βγ-dimethylbutylenedisulphonic acid was produced and in the latter salts of isomeric β-hydroxybutane-γ-sulphonic acids were isolated.

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