CVIII.—*A Contribution to the Stereochemistry of Sulphur: an Optically Active Sulphine Base.*

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FOR many years carbon was the only element known to give rise to optical activity in its compounds until Le Bel (*Compt. rend.*, 1891, 112, 724) obtained an optically active ammonium base by the fermentation of methylethylpropylisobutylammonium chloride, and later Pope and Peachey (*Trans.*, 1899, 75, 1127) obtained optically active methylallylphenylbenzylammonium iodide. In October, 1898, I commenced an investigation of the stereochemistry of sulphur, and some of the results were laid before the Society in December of the following year (*Proc.*, 1899, 15, 240; this vol., 160). The preparation of crystalline salts of methylethylthetine with certain optically active acids and bases was attempted, but without success. Profiting by the experience of Le Bel and Wedekind (*Zur Stereochemie des Stickstoffes*, Leipzig, 1899), attempts were also made to obtain sulphines containing more complex radicles, and it has been found that ω -bromacetophenone and bromodeoxybenzoin react with the sulphides of the fatty series, forming sulphine bromides containing a phenacyl and a desyl group

respectively : $\text{R} \begin{array}{c} \diagup \\ \text{S} \\ \diagdown \end{array} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \\ \text{Br} \end{array}$ and $\text{R} \begin{array}{c} \diagup \\ \text{S} \\ \diagdown \end{array} \begin{array}{c} \text{CH}(\text{C}_6\text{H}_5) \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \\ \text{Br} \end{array}$

The investigation of these substances has been completed, and a paper describing the results obtained will shortly be laid before the Society. The sulphine bromide prepared from methyl ethyl sulphide and ω -bromacetophenone, $\text{C}_2\text{H}_5 \begin{array}{c} \diagup \\ \text{S} \\ \diagdown \end{array} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \\ \text{Br} \end{array}$, contains an asymmetric sulphur atom, and on account of its high molecular weight and comparative stability seemed more suitable for resolution into active components than any other sulphine base hitherto obtained. The salts of this sulphine, with the following acids, were therefore prepared, tartaric, malic, antimonyltartaric, camphoric, and orthomethyl camphoric ester, but were not obtained in the crystalline state. The great efficacy of the camphorsulphonic acids in resolving inactive bases into their optically active components had been pointed out by Pope, who applied them with brilliant success to asymmetric nitrogen (*loc. cit.*) and tin (Proc., 1900, 16, 42) compounds. He also prepared (Proc., 1900, 16, 12, 43) the *d*-camphorsulphonate and *d*- α -bromocamphorsulphonate of methylethylthetine, and found these salts to be crystalline, but was not successful in effecting a resolution of the base with their aid. Having exhausted all other easily obtainable active acids, I finally applied α -bromocamphorsulphonic acid to the resolution of methylethylphenacylsulphine bromide and was successful, but, not wishing to interfere with Mr. Pope's work on this subject, I have refrained from publishing the results until he should have arrived at some definite conclusion in the matter. This has been attained (Pope and Peachey, this vol., 1072), and the following results are therefore laid before the Society, with Mr. Pope's acquiescence.

When methylethylphenacylsulphine bromide is treated in absolute alcoholic solution with the requisite amount of silver *d*-bromocamphorsulphonate, two salts are obtained, the less soluble having a molecular rotation of $+250^\circ$ and the more soluble a rotation of $+289^\circ$. Since the molecular rotation of *d*-bromocamphorsulphonic acid in dilute aqueous solution is about $+270^\circ$ (Walden, *Zeit. physikal. Chem.*, 1894, 15, 196), it is to be expected that the two salts should contain lævo- and dextro-base respectively. This was found to be the case, *l*- and *d*-picrates being obtained from the two bromocamphorsulphonates. The sulphine bromide produced by the interaction of methyl ethyl sulphide and bromodeoxybenzoin, namely,

contains both an asymmetric sulphur and carbon atom. It is therefore possible that the product should consist of two inactive stereo-

isomeric bromides, each of which should be separable into active components. However, when the above sulphine was examined by means of its picrate, it appeared to be homogeneous. It may be concluded that, in salts of sulphine bases, the four radicles which are directly united to the sulphur atom do not lie in the same plane with it, but are probably present in some tetrahedral arrangement.

i-Methylethylphenacylsulphine Bromide,
 $S(CH_3)(C_2H_5)(CH_2 \cdot CO \cdot C_6H_5)Br.$

Nineteen grams of bromacetophenone were added to 9 grams of methyl ethyl sulphide contained in a flask provided with a reflux condenser. Solution took place with absorption of heat, but in a short time the mixture became warm, and was cooled to prevent loss of sulphide. After standing overnight, the whole had solidified to a hard, colourless glass, which consisted of the almost pure sulphine bromide in nearly theoretical quantity, namely, 23 grams. The bromide is very soluble in alcohol, but only sparingly so in water, and is insoluble in ether. Many unsuccessful attempts were made to obtain it in the crystalline state.

The *platinichloride* was precipitated as a light, buff-coloured powder on the addition of platinic chloride to the aqueous solution of the sulphine chloride; when purified, it melted at 173—174°. On analysis :

0.1848 gave 0.0448 Pt. Pt = 24.24.

0.2226 „ 0.0538 Pt. Pt = 24.17.

$(C_{11}H_{15}OSCl)_2PtCl_4$ requires Pt = 24.42 per cent.

i-Methylethylphenacylsulphine Picrate,

—The alcoholic solution of the bromide was treated with the requisite amount of picric acid dissolved in alcohol. After standing for a short time, the picrate was precipitated as a yellow, crystalline powder, very soluble in acetone, but insoluble in water. It is deposited from a mixture of acetone and alcohol as shining, yellow needles melting at 118—119°. On analysis :

0.2037 gave 19.05 c.c. of moist nitrogen at 26° and 764 mm. N = 10.4.

$C_{17}H_{17}O_8N_3S$ requires N = 9.93 per cent.

d- and l-Methylethylphenacylsulphine d-Bromocamphorsulphonate.

An alcoholic solution of methylethylphenacylsulphine bromide was boiled for a quarter of an hour with the calculated quantity of silver *d*-bromocamphorsulphonate in a flask provided with a reflux condenser. After rapidly removing the silver bromide by filtration, the

greater part of the alcohol was distilled off. The residue, on cooling, yielded an abundant crop of crystals.

By fractionally crystallising this from alcohol, a sparingly soluble salt, *l*-methylethylphenacylsulphine *d*-bromocamphorsulphonate, was easily obtained. It consisted of colourless needles very sparingly soluble in cold acetone and melting at 194–195°.

0.3695 gram dissolved in 25 c.c. of water gave $\alpha + 1.47^\circ$ in a 2-decimetre tube at 19°, whence $[\alpha]_D + 49.7^\circ$ and $[M]_D + 251.0^\circ$.

After further crystallisation, a specimen was obtained showing the following optical behaviour :

0.3186 gram dissolved in 25 c.c. of water gave $\alpha + 1.26^\circ$ in a 2-decimetre tube at 20°, whence $[\alpha]_D + 49.5^\circ$ and $[M]_D + 250^\circ$.

d-Methylethylphenacylsulphine *d*-bromocamphorsulphonate was contained in the alcoholic mother liquors, and was obtained therefrom as a white, crystalline precipitate, soluble in water and alcohol, but only sparingly so in cold acetone. It was deposited from acetone in fine silky needles melting at 183–184°. The purest specimen which could be obtained was examined in the polariscope with the following result :

0.4394 gram dissolved in 25 c.c. of water gave $\alpha + 2.01^\circ$ in a 2-decimetre tube at 18°, whence $[\alpha]_D + 57.2^\circ$ and $[M]_D + 288.8^\circ$.

These results point to the fact that the molecular rotation of the basic sulphine radicle in aqueous solution is approximately 20°.

l-Methylethylphenacylsulphine picrate,

—On adding the requisite amount of picric acid contained in saturated alcoholic solution to *l*-methylethylphenacylsulphine *d*-bromocamphorsulphonate, a yellow, crystalline precipitate was slowly formed. After allowing to stand for 2–3 hours, this was collected and recrystallised from acetone, being deposited in golden-yellow needles melting at 125°. When examined in the polariscope, it showed the following behaviour :

0.5168 gram dissolved in 25 c.c. of acetone gave $\alpha - 0.38^\circ$ in a 2-decimetre tube, whence $[\alpha]_D - 9.2^\circ$ and $[M]_D - 38.9^\circ$.

Another specimen showed the following rotation :

0.2988 gram dissolved in 10 c.c. of acetone gave $\alpha - 0.28^\circ$ in a 1-decimetre tube, whence $[\alpha]_D - 9.3^\circ$ and $[M]_D - 39.3^\circ$.

The following analytical results were obtained :

0.1590 gave 14.7 c.c. of moist nitrogen at 25° and 760 mm. $N = 10.3$.

$C_{17}H_{17}O_8N_3S$ requires $N = 9.93$ per cent.

d-Methylethylphenacysulphine picrate,

was prepared by precipitating the alcoholic solution of *d*-methylethylphenacysulphine *d*-bromocamphorsulphonate with picric acid; it crystallised in bright yellow needles melting at 123–124°.

0.5411 gram dissolved in 25 c.c. of acetone gave $\alpha + 0.31^\circ$ in a 2-decimetre tube, whence $[\alpha]_D + 7.2^\circ$.

A purer specimen showed the following behaviour:

0.1963 gram dissolved in 10 c.c. of acetone gave $\alpha + 0.16^\circ$ in a 1-decimetre tube, whence $[\alpha]_D + 8.1^\circ$ and $[M]_D + 34.2^\circ$.

On analysis the following numbers were obtained:

0.1872 gave 17.2 c.c. moist nitrogen at 23° and 760 mm. $N = 10.3$.

$\text{C}_{17}\text{H}_{17}\text{O}_8\text{N}_3\text{S}$ requires $N = 9.93$ per cent.

Methylethyldeysulphine Bromide, $\text{S}(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{C}_{14}\text{H}_{11}\text{O})\text{Br}$.

Bromodeoxybenzoin was dissolved in rather more than the theoretical amount of methyl ethyl sulphide. After standing for 24 hours, the mass had solidified, but it was found to be exceedingly difficult to obtain the sulphine bromide in a pure state from the product.

The *platinichloride* was prepared and, after purification, melted at 177° with decomposition. The following analytical results were obtained:

0.1257 gave 0.0258 Pt. $\text{Pt} = 20.52$.

0.1325 „ 0.0273 Pt. $\text{Pt} = 20.60$.

$(\text{C}_{17}\text{H}_{19}\text{SCl})_2\text{PtCl}_4$ requires $\text{Pt} = 20.52$ per cent.

Methylethyldeysulphine picrate,

—The somewhat impure bromide, prepared as just described, was completely converted into the picrate by means of a saturated alcoholic picric acid solution. A bright yellow, heavy, crystalline precipitate separated, which, on fractional recrystallisation from alcohol, appeared to be homogeneous. The pure picrate was deposited from alcohol as yellow leaflets melting at 162°.

The following analytical results were obtained:

0.1950 gave 15.1 c.c. of moist nitrogen at 25.5° and 763 mm. $N = 8.6$.

$\text{C}_{23}\text{H}_{21}\text{O}_8\text{N}_3\text{S}$ requires $N = 8.4$ per cent.

In conclusion, I wish to express my indebtedness to R. Moritz,

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