Chemistry. — *"Optical resolution of chlorobromoacetic acid."* By H. J. BACKER and H. W. MOOK. (Communicated by Prof. F. M. JAEGER.)

Chlorobromo- and chloroiodomethanesulphonic acids show a remarkable difference.

POPE and READ [1]) resolved the latter acid into its enantiomorphic components, which were completely stable. They did not, however, succeed in resolving the chlorobromo-compound.

After it had been shown, that in the analogous case of chlorosulphoacetic acid the failure was not due to partial racemy of the alkaloidal salts as had been supposed before [2]), but that it was caused by a strong tendency to racemisation [3]), this same cause was accepted by READ and McMATH [4]) for the chlorobromomethanesulphonic acid. They stated, that under special conditions salts of different rotation were formed, but that in aqueous solutions only inactive mixtures could be obtained.

This striking difference between the chlorobromo- and chloroiodo-compounds raises the question, whether perhaps the close chemical analogy of chlorine and bromine might prevent resolution or promote racemisation.

In the literature we only found two examples of resolvable chlorobromo-carboxylic acids, the asymmetry of which is due to the carbon atom bearing chlorine and bromine, namely fluorochlorobromoacetic acid $CFClBr.CO_2H$ [5]) and methylchlorocyclohexyl-chlorobromoacetic acid $C_7H_{12}Cl.CClBr.CO_2H$ [6]).

In both acids the asymmetric carbon atom has no hydrogen atom and yet in the first case the tendency to racemisation is so strong, that the active acids could not be separated from the alkaloid salts of different rotation.

To test the influence of chlorine and bromine attached to an asymmetric carbon atom, we have now examined one of the simplest examples namely chlorobromoacetic acid, $ClBrCH.CO_2H$.

This compound, which is closely analogous in structure with chlorobro-

[1]) Journ. chem. Soc. **105,** 811 (1914).

[2]) POPE and READ, Journ. chem. Soc. **93,** 796 (1908).

[3]) BACKER and BURGERS, These Proc. **28,** 64 (1925).

[4]) Journ. chem. Soc. **127,** 1572 (1925).

[5]) SWARTS, Bull. Ac. r. Belg. [3], **31,** 28 (1896); Mém. cour. Ac. Belg. **54** (1896).

[6]) PERKIN and POPE, Journ. chem. Soc. **99,** 1527 (1911).

momethanesulphonic acid ClBrCH.SO$_3$H, may be prepared from commercial trichloroethylene [1]).

To effect its resolution the method of „cold crystallisation" [2]) was applied to various alkaloidal salts.

With brucine a laevorotatory acid was obtained, whilst quinine gave a dextrorotatory compound.

The latter alkaloid gave the best results.

Since neutralisation of the carboxyl group in the sulphocarboxylic acids causes a considerable change in molecular rotation, it was important to determine the influence of neutralisation in this case.

It was found, that the salts show a rotation of about the same value as that of the acid, but in the opposite direction.

The highest molecular rotation for the D-line, so far observed, is $+8°$ for the free acid and $—8°$ for the ammonium salt.

Further experiments on the dispersion are in progress, which may perhaps give a greater rotation.

In the first place we were interested in the tendency to racemisation; it proved to be not so great as might have been expected.

A solution of the ammonium salt did not racemise in 24 hours, even in the presence of a molecule of sodium hydroxide.

After heating for half an hour on a water bath the alkaline solution was half racemised.

For a solution of the ammonium salt, containing 0.089 G.mol. per litre, kept at ordinary temperature from October 1925 until June 1926, the rotation had diminished to half the original value.

Thus a compound with chlorine and bromine, attached to an asymmetric carbon atom, has now been resolved into its enantiomorphs; further in the case examined racemisation of the active components was slow.

Org. Chem. Laboratory of the State University.

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[1]) Method of CROMPTON, Compare W. H. VAN MELS, Dissertation Groningen, 26 June 1926, p. 48.
[2]) These Proc. **28,** 64 (1925).