CXLIV.—*Studies of the Terpenes and Allied Compounds.*
The Sulphonation of Camphor. III. The Optical
Inversion of Camphor and the Mechanism of
Hetero- and Meso- sulphonation, of Homo- and
Hetero-bromination, and of Dehydration.

By HENRY E. ARMSTRONG and MARTIN T. LOWRY.

THE formation of *isocamphoronic acid*, $\text{CH}_2\text{X}\cdot\text{CH}(\text{CMe}_2\text{X})\cdot\text{CH}_2\text{X}$ ($\text{X}=\text{CO}_2\text{H}$), on oxidising β -bromocamphor, would appear to be almost conclusive proof that the bromine atom is not present in a methyl group; consequently, of the two formulæ which, as Forster has pointed out (this vol., 267), account for the conversion of β -bromocamphor into campholenic acid by the action of alcoholic potash, that which he preferred is to be regarded as highly probable, namely:

It is improbable that both of the "pentaphane" rings (Armstrong, Proc., 1890, 6, 227) in β -bromocamphor would be broken if the bromine were present in a methyl group—especially in view of the results obtained by Kipping on oxidising the π -derivative.

Until proof to the contrary be given, it may therefore be assumed that, of the three series of derivatives of camphor now known:

- the α - or *homo-ketonic* series is that in which hydrogen is displaced in the methylene group next the CO group;
- the β - or *hetero-ketonic* series, that in which hydrogen is displaced in the methylene group next the "mono-methylated" carbon atom;
- and the π - or *meso*-series, that in which hydrogen is displaced in one of the median methyl groups.

There can be little doubt that the Reychler sulphonic acid belongs to the β - or hetero-ketonic series; were it an α -compound, it can scarcely be doubted that it would yield some camphoric acid on oxidation.

The manner in which the β - and π -derivatives are formed merits special consideration.

As we have previously remarked, the ketonic group is probably in all cases the "centre of attraction," the point of departure of all changes. The formation of the homo-ketonic α -derivatives—alpha-

bromination, for example—may be pictured as taking place in the following manner :

In discussing the conversion of $\alpha\alpha'$ -dibromocamphor into $\alpha\beta$ -dibromocamphor, and similar changes, under the influence of hydrogen bromide (Swarts), it is important to take into account the evidence recently brought forward by Forster favouring the conclusion that the carbon atoms in camphor are so situated that a trimethylene ring or triphane is easily formed by the union of the two carbon atoms on either side of the monomethylated carbon atom in camphor.

The introduction of the bromine into the β -position, in fact, may be pictured as involving the following changes in the $\text{CH} \cdot \text{CHMe} \cdot \text{CO}$ group:

A similar explanation may be given of the formation of the β -sulphonic acid. The sulphonating agent is apparently an acetyl-sulphuric acid which on combining with the ketonic group would give rise to a compound containing the group

convertible by loss of sulphuric acid into the triphane derivative:

By a reversible process, the latter might pass over into the β -acid, becoming first $\text{CH}(\text{SO}_3\text{H}) \cdot \text{CMe} \cdot \text{C}(\text{OAc})_2$ and then $\text{CH}(\text{SO}_3\text{H}) \cdot \text{CMe} \cdot \text{CO}$.

In undergoing conversion into $\alpha\beta$ -dibromocamphor, $\alpha\alpha'$ -dibromocamphor must obviously be reduced by the hydrogen bromide at some stage in the process and the CBr_2 group converted into the CHBr group of α -bromocamphor; the change may be pictured as taking place in the following manner :

Whether this change occurs initially or whether—and to what extent—tribromination precedes reduction is open to question, but the latter is perhaps the more probable, inasmuch as camphor cannot be directly tribrominated in any complete manner although tribromocamphor is readily formed as a by-product on oxidising $\alpha\beta$ -dibromo-

But an acid thus produced would be optically active like camphor. To account for the racemisation, it is necessary to postulate the occurrence of changes affecting both the asymmetric carbon atoms in camphor.

The asymmetry of the carbon atom next the ketonic group might readily be reversed in sign by "enolisation," owing to the presence of the hydrogen introduced in breaking the ring; but the "reversed" compound could not take part in the re-formation of camphorsulphonic acid. On this account, and because the product of sulphonation is mainly racemic, it is necessary to suppose that a further change takes place involving the reversal of the asymmetry of the second carbon atom. This may be accounted for by supposing that, under the influence of the acid, dihydroeucarvene—or, more probably, the isodynamic dihydroeucarvenol—is produced, and that equilibrium is established, not only between this compound and dihydrocarvene, but also with camphor, as shown in the following scheme:

Both the forms of dihydrocarvene required to give the two forms of camphor would then be present.

In justification of this argument, Butlerow's experiments (*Annalen*, 1877, 189, 44) on the oxidation of *isodibutylene* may be quoted, in which it was shown that under the influence of sulphuric acid *isodibutylene* is converted into an isomeride, an equilibrium being established between the two compounds, so that products of oxidation are obtained which are derived, not merely from the hydrocarbon taken, but also from an isomeride. And not only was this the case, but evidence was also obtained of the presence of two alcohols in equilibrium with the hydrocarbons:

Leading, as it does, to a highly racemised product, the sulphonation of camphor must therefore be regarded as a process involving a complex series of changes in which equilibrium is established between no less than three isomeric ketones, and the proportion of dihydroeucarvone present must be the determining factor in regulating the extent to which racemisation takes place. It is of interest to note to how great an extent the presence of bromine in the α -position determines the equilibrium in one direction, so that scarcely any racemisation is effected when bromocamphor is sulphonated.

The formation of acetyl-*o*-xylene (together with carvenone) by the action of sulphuric acid on camphor (Armstrong and Kipping) may almost be regarded as proof that the rupture of the median ring is accomplished through the intervention of the ketonic group. Whilst we did not think it necessary to postulate the formation of a direct linkage between the ketonic carbon and a median methyl, such a linkage must evidently arise if the transference of a methyl group from the one position to the other is to be explained. The following scheme may serve in a measure to indicate the course of change :

It is well known that by the action of "dehydrating" agents on camphor, a variety of benzenes are formed (compare Armstrong and Miller, *Ber.*, 1883, 16, 2255), and that when care is taken to carry out the decomposition at as low a temperature as possible, the products appear to be practically all C_{10} derivatives—of which four are formed: cymene, metacymene, 1:2:4-dimethylethylbenzene, and 1:2:3:5-tetramethylbenzene; higher and lower benzenes are only formed when the conditions are such as to favour the occurrence of secondary changes. It is therefore probable that the transference of methyl groups involved in the production of several of the hydrocarbons may be conditioned by reversible *intramolecular* changes such as are contemplated above, rather than by a succession of analytic and synthetic operations of the type determined by aluminium chloride, for example,

The production of metacymene by means of phosphorus pentasulphide and of zinc chloride may be accounted for if it be supposed that a triphane ring is first formed by the interaction of the ketonic group and the (ortho) methyl group attached to the contiguous carbon atom; and that this ring is subsequently broken in such a manner that methyl becomes attached to the carbon atom of the ketonic group, meta to the propyl group formed by scission of the linkage across the hexaphane system. This argument is equally applicable in explanation of the oxidation of the ortho-methyl group which is involved in the formation of ketopinic acid from chlorocamphane (turpentine hydrochloride), and of camphoic acid from camphene.

To explain the formation of tetramethylbenzene, one of the chief products of the action of iodine, and which is also formed by the action of zinc chloride and of phosphorus pentasulphide on camphor, it is necessary to suppose that both the meso-methyls may be brought into connection with the hexaphane system. Assuming that one of the methyls were transferred to the "ketoposition" in the manner shown above, in discussing the formation of acetyl-o-xylene, a compound would be formed from which the elements of a molecule of water might be withdrawn in two ways: either in such a way as to give rise to the formation of the group $\text{CH}_2:\dot{\text{C}}$ from the median $\cdot\dot{\text{C}}\text{-OH}$ group, or in such a way as to involve the coupling of the ketonic group with the β -carbon atom. If, in either case, the change were to be reversed, hydroxy-compounds would be formed (either π' or β), which would give rise, if deprived of the elements of water, to a $(\pi'\beta)$ -tetraphane derivative, corresponding to the $\pi\beta$ -compound formulated on page 1473. If the tetraphane ring thus formed were subsequently broken, so as to sever the connection between the median carbon atom of camphor and that which had previously been associated with it in the form of methyl, the methyl group would be transferred to the β -position; three methyl groups would then be contiguous.

The production of benzenes from camphor in the manner contemplated involves the withdrawal of hydrogen at some stage in the process; it is unnecessary to discuss the manner in which this may take place, but it may be pointed out that, however carefully the operation be conducted, a large proportion of resinous matter is always formed, and it may be that the withdrawal of hydrogen is in some way connected with the formation of this; it is noteworthy that even zinc chloride gives rise to the production of a not inconsiderable amount of the saturated hydrocarbon, $\text{C}_{10}\text{H}_{20}$.

Lastly, it is of interest to note, as a further illustration of the influence of bromine as a depressant of activity, that bromocamphor does

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not give rise to hydrocarbons under the influence of dehydrating agents.

We are inclined to think that the views advanced in this communication may be of some value in arriving at the synthesis of camphor and that the recognition of reversible changes as playing a part in the formation of camphor and terpene derivatives generally may be of importance.

CHEMICAL DEPARTMENT,
CITY AND GUILDS OF LONDON INSTITUTE,
CENTRAL TECHNICAL COLLEGE.