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LIX.—*A New Monobromocamphor.*

By J. E. MARSH.

Action of Bromine on Camphor.

THE action of bromine on camphor may be said to be a commercial process for the production, for pharmaceutical purposes, of the ordinary monobromocamphor. The yield of the bromocamphor is, in the first instance, a relatively small one. There accompanies the crystalline bromocamphor a considerable quantity of an oil which, according to Swarts, is the hydrobromide of bromocamphor,

$$6C_{10}H_{15}BrO + HBr.$$

By distilling this oil, the yield of bromocamphor is, as is known, materially increased. The existence of such a compound as that supposed by Swarts is open to serious doubt. In the first place, it is unlikely that bromocamphor should form a compound with hydrobromic acid, and still less likely that 6 mols. of the one should combine with 1 mol. of the other. I shall endeavour in this paper to show that the action of bromine on camphor is such as to give two isomeric monobromocamphors. These are in approximately equal quantity, of which one, the iso- or β-bromocamphor, is readily converted by distillation, under ordinary pressure, into the other, namely, the ordinary or α-bromocamphor; and the increased production of the α-bromocamphor by distilling the above-mentioned oil is to be explained by the conversion of the β- into the α-isomer.

Preparation of the Iso- or β-Monobromocamphor.

The new isomer is best prepared by the action of bromine on camphor in presence of alcohol, the diluent alcohol, which was also employed by Swarts, appearing to facilitate the subsequent separation of the two isomers. This separation is in any case a difficult one, and I am unable to state positively that I have obtained the new isomer absolutely free from the ordinary modification. This I judge from the slight variations which specimens of the same melting point show in respect of rotatory power, or, perhaps it would be more correct to say that a slight admixture of the ordinary isomer affects the melting point much less than the rotatory power.

The β-isomer is extremely soluble in alcohol, and is separated from the α-modification by fractional crystallisation from alcohol. It is further separated from unaltered camphor by distillation *in vacuo*,

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when it distils unaltered at about 130° under 10 mm., or 140° under 20 mm. pressure. The α-isomer distils under the same circumstances at substantially the same temperature.

When bromine acts on camphor in presence of alcohol, the substitution appears to take place at once, regularly and quietly, without the formation, and subsequent decomposition at a high temperature, of the additive compound $C_{10}H_{16}OBr_2$. Whereas, when bromine acts on camphor alone, the additive compound formed at first decomposes, as is known, on raising the temperature, with some violence and with evolution of torrents of hydrobromic acid. The new isomer is also formed by this latter method, and at the same time I have obtained a liquid of boiling point about 160° under 20 mm. pressure, apparently a single substance, which contains an amount of bromine just midway between mono- and di-bromocamphor.

Estimation of Bromine.

Found.		Calculated for	
I.	II.	$C_{10}H_{15}BrO$.	$C_{10}H_{14}Br_2O$.
42·7 p. c.	42·7 p. c.	34·6 p. c.	51·6 p. c.

I hope to return to the investigation of this substance.

Properties of β-Monobromocamphor.

The β-monobromocamphor, as obtained after distillation in vacuo, forms on solidifying an almost transparent mass, easily breaking up into a soft, granular powder, very different in appearance from the hard crystals of the ordinary modification. It melts about 61° C. I have obtained it crystallised from dilute alcohol in feathery crystals which bind together when dry, forming tough, camphor-like masses. It is very soluble in alcohol, chloroform, carbon bisulphide, petroleum spirit, and glacial acetic acid, and separates on evaporation in the crystalline form.

It is volatile in the steam from boiling water, as is also the ordinary isomer.

It rotates the plane of polarised light to the right, but to a much less extent than the α-modification. I have found in alcoholic solution, $[\alpha]_D = +34·9°$ and $+40°$, while the ordinary modification gives $[\alpha]_D = +139°$ (De Montgolfier).

Determination of Bromine.

I have made several determinations of bromine in the new substance, of which the theoretical percentage is 34·6. A specimen prepared with alcohol as a diluent, and distilled *in vacuo* and rotated

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+34·9° gave 35·3 and 35·5 per cent. of bromine. It might, during the distillation, have mechanically enclosed some hydrobromic acid. Another specimen which had been crystallised from alcohol gave 35·1 per cent. Swarts' compound of 6 mols. bromocamphor and 1 mol. of hydrobromic acid requires 38·1 per cent. of bromine.

Distillation of β-Monobromocamphor under Ordinary Pressure.

When distilled under ordinary pressure, the new isomer begins to boil at 250°, and distils fairly constant at 265°; the distillate crystallised from alcohol gives the hard crystals characteristic of the ordinary modification, and melting about 76°. During the distillation there is a slight evolution of HBr, and a small carbonaceous residue is left in the retort. The conversion of one isomer into the other by distillation is not complete, and a more detailed examination was made as to the extent of the change.

A specimen of the isomeric β-bromocamphor, which had been distilled *in vacuo* and gave a specific rotation of +34·9°, was distilled slowly under ordinary pressure; the distillate gave now a specific rotation of +96°. Subjected to a second distillation, the new distillate gave a specific rotation of +98°. The distillate was dissolved in alcohol, and gave crystals of the ordinary modification and of specific rotation +135°, while on further evaporation a residue was obtained of specific rotation +56°; this residue again distilled gave a distillate* of specific rotation +76°. The alcoholic solution, on boiling down again, gave a crystallisation closely resembling the ordinary monobromocamphor.

It is thus evident that the β- is converted into the α-modification by distilling at ordinary pressure, while no change is effected by distilling *in vacuo;* that this change in any case is not complete, but would probably become so by separating the already formed α-isomer after each distillation.

Nature of the Isomerism and of the Isomeric Change.

The relations subsisting between the two isomeric bromocamphors render it extremely probable that we have here another instance, not of structural but of geometrical isomerism. The conversion of one isomer into the other by the action of heat recalls the similar conversion in the case of lævocamphoric acid and of fumaric acid. That the bromine-atom in the ordinary bromocamphor is attached to

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* On removing this substance from the desiccator, it was accidently moistened with strong sulphuric acid. It was, however, immediately recovered, not being in contact with the acid many seconds, and suffered no apparent change.

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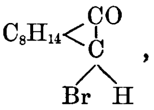
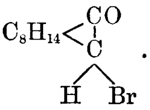
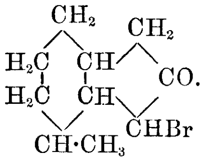
he carbon-atom, which is united to the CO-group, is rendered evident from the oxidation of this body to camphoric acid. The formula then which I have given for camphor (*Proc. Roy. Soc.*, **47**, 6) accounts perfectly for two stereographically isomeric monobromocamphors, and they may be represented by the condensed formulæ





and they will both have the same structural formula represented by



As to the particular space symbol which belongs to each isomer, we have no direct evidence; but it seems probable, from analogy, that the more stable of the two, namely, the ordinary bromocamphor, will be the one in which the bromine approaches more nearly the positive hydrocarbon groupings. The hexamethylene ring does not lie in the same plane with the pentamethylene ring, but inclined to it at an angle. The bromine-atom in the ordinary α-bromocamphor will then lie on the same side of the pentamethylene ring plane as the hexamethylene ring, while in the β-isomer the bromine-atom will be on the other side.

As to the mode in which the isomeric change is effected, Wislicenus has, in his well-known memoir, "Ueber die räumliche Anordnung, u. s. w.," attempted to explain the conversion of one stereometric isomer into the other in the case of the olefine-derivatives, by supposing the double linking to open out: then an exchange of groups occurs, the double linking is again formed, and the isomeric body obtained.

Von Baeyer has pointed out the objection to this view in the case of the hexahydroterephthalic acids, where there is no double linking. The same objection would apply to an isomeric change of this nature in the camphor series. Now these isomeric changes only occur, so far as is yet known, in cases where there is an oxygen-atom doubly linked to carbon, and situated in one of the groups which govern the isomerism. It may be, then, that this oxygen-atom, under the influence of heat or of certain reagents, passes into its unstable hydroxyl form, and, on returning to its original carbonyl state, gives not the original substance, but its isomer.

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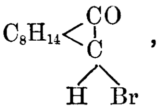
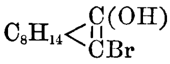
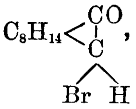
Thus we should have, in the case of the bromocamphors,



β-Bromocamphor.

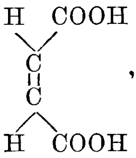


Unstable transition compound.

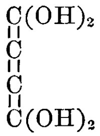


α-Bromocamphor.

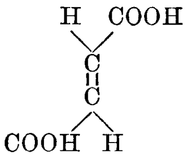
and similarly, in the case of maleic and fumaric acids,



Maleic acid.



Unstable transition compound.



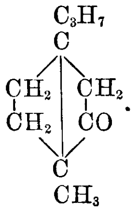
Fumaric acid.

The possibility of such isomeric change would then be confined to bodies which contain doubly-linked oxygen (or its equivalent, *e.g.*, sulphur or the imidogen radical) capable of yielding an unstable transition compound. These views, though they have been for some time in my mind, I cannot claim priority for, as E. Beckmann (*Annalen*, **250**, 365) has published a precisely similar explanation of the isomeric change in the case of the menthones. Dr. Beckmann, however, does not appear to have considered the far-reaching consequences to which his happy conception leads.

Note on the Constitution of Camphor.

Dr. Bamberger has published formulæ for camphor and camphoric acid (*Ber.*, **23**, 218), and believes that the latter is "wie es wohl meist angenommen wird"—a tetramethylene-derivative. Dr. Bamberger may possess some special information that his view has been generally accepted, but unfortunately he gives no references.

The formula which Dr. Bamberger gives for camphor is identical with that previously proposed by Wallach (*Annalen*, **230**, 269). It is a little difficult to interpret.



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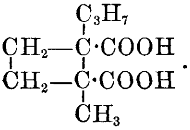
Does the formula represent simply an unsaturated derivative of hexamethylene, or does it represent two tetramethylene rings? In the latter case there is no special reason for retaining a hexagonal form, and the formula is without any analogy among synthetic compounds. That alone would not be sufficient to condemn it. The condemnation lies in the formula for camphoric acid derived from the above camphor formula. This formula represents camphoric acid as a tetramethylene derivative,



$$\begin{array}{llll} & & C_3H_7 & \\ & & | & \\ CH_2 & — & C & \cdot COOH \\ | & & | & \\ CH_2 & — & C & \cdot COOH \\ & & | & \\ & & CH_3 & \end{array}.$$

We have no evidence that camphoric acid is a tetramethylene-derivative. On the other hand, we have evidence that it is a hexamethylene-derivative, in that it yields, on hydrolysis, carbonic acid and hexahydroxylene—

$$C_{10}H_{16}O_4 = 2CO_2 + C_6H_{10}(CH_3)_2.$$

Further, if camphoric acid has the tetramethylene formula, then it is also a substituted succinic acid, and should yield a fluorescent compound with resorcin. I have not been able to obtain any such fluorescent body from camphoric acid.

A Sulphonic Acid of Monobromocamphor.

In conclusion, I may add that I have obtained a sulphonic acid by treating the ordinary bromocamphor dissolved in chloroform with chlorosulphonic acid. Neither the barium nor potassium salt appears to crystallise; the potassium salt forms on evaporation a syrupy product which, when dried at over 100°, gives a yellowish, very deliquescent powder. The bromine and sulphur in this were determined, and agree very fairly with the formula. Thus:

Per cent. sulphur found	9·51 p. c. and 9·33 p. c.
Calculated for $C_{10}H_{14}BrOSO_3K$......	9·17 „

I hope to investigate the substance further.

University Laboratory, Oxford.