IV.—*Studies of the Terpenes and Allied Compounds.* *New Derivatives from α -Dibromocamphor.*

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Introductory.

THE behaviour of α -dibromocamphor towards nitric acid was studied more than 10 years ago by Kachler and Spitzer, who allowed a mixture of equal parts of concentrated and fuming acid to act on dibromocamphor during a protracted period (*Monatsh.*, 1883, **4**, 554); they recorded the formation of dinitrobromomethane, camphoronic acid, $C_9H_{12}O_6$, hydroxycamphoronic acid, $C_9H_{12}O_6$, and a small quantity of a crystalline substance melting at $87-88^\circ$, which may have the composition $C_{24}H_{33}BrN_4O_{12}$. From β -dibromocamphor and fuming nitric acid the same investigators obtained a nitro- β -dibromocamphor melting at 130° (*Monatsh.*, 1882, **3**, 218; **4**, 566).

In the hope that light would be thrown on the structural relationship existing between α -dibromocamphor and the β -modification, Dr. Armstrong suggested that an attempt should be made to obtain a nitro-derivative from the former, isomeric with nitro- β -dibromocamphor. On subjecting α -dibromocamphor to the action of fuming nitric acid (density 1.52), it was soon observed that a somewhat remarkable change takes place; the substance is rapidly dissolved by the acid, and at first the temperature falls, but then gradually rises spontaneously to about 70° , when dense, ruddy fumes are liberated in large volume. From the oily product, a crystalline substance is isolated without difficulty, in quantity amounting to about 10 per cent. of the material used; it is free from nitrogen, and has the composition $C_{10}H_{14}Br_2O_2$.*

The conditions which affect the production of this substance afford no clue to its chemical nature. A careful study of the derivatives to which it gives rise, however, reveals its lactonic character, the single oxygen atom by which its empirical formula differs from that of dibromocamphor appearing to enter the ring between the carbonyl group and one of the neighbouring carbon atoms. There is every

* In a preliminary notice of the investigation (*Proc.*, 1895, **4**), this substance was described as having the composition $C_{10}H_{12}Br_2O_2$. Study of its derivatives having shown that it must be represented by the formula $C_{10}H_{14}Br_2O_2$, the numbers required by this expression were calculated, and were found to agree more closely with the analytical results already announced (*loc. cit.*) than does the percentage composition of a substance having the formula $C_{10}H_{12}Br_2O_2$.

reason to suppose that the bromine atoms occupy relatively the same position as in α -dibromocamphor, it being unlikely that the formation of the new compound affords an instance of rebromination, as, although bromine is liberated in the course of the action, the presence of silver nitrate does not interfere with the production of the substance; moreover, addition of bromine to the nitric acid used, does not augment the yield. A noteworthy fact in connection with this change is the importance of using the strongest nitric acid procurable; in carrying out the investigation it has been customary to distil 500 c.c. of commercial fuming nitric acid (density 1.52) from 200 c.c. of concentrated sulphuric acid, the operation being interrupted when 400 c.c. has passed over.

The dibromolactone obtained in the manner indicated gives rise to an interesting series of compounds, and before passing on to the experimental matter with which the present communication deals, it appears desirable to give a brief sketch of these substances, and the manner in which they are related to one another.

The properties of the initial compound are most characteristic. It crystallises very readily from organic solvents, forming long, prismatic needles melting at 152° ; cold, concentrated sulphuric acid has no action on it, and it may be crystallised from hot, fuming nitric acid. The substance is indifferent towards phenylhydrazine, aniline, benzoic chloride, acetic anhydride, and hydroxylamine, but is attacked by alkalis with great readiness. Thus alcoholic potash eliminates bromine, giving rise to a lactone of the formula $C_{10}H_{14}O_3$, which, under the influence of a boiling solution of barium hydroxide, yields the acid $C_{10}H_{16}O_4$, melting at 203° . As will be seen from its empirical formula, the lactone $C_{10}H_{14}O_3$ cannot be regarded as the substance of which the dibromolactone is a haloid derivative, and this is also shown by the fact that, on brominating the lactone, only one atom of the halogen enters the molecule, a derivative of the composition $C_{10}H_{13}BrO_3$ being formed. It seems probable that the production of the lactone involves the displacement of bromine by hydroxyl groups, and the subsequent elimination of the elements of water.

Whilst alkalis eliminate both bromine atoms from the dibromolactone, only one is removed by reducing agents. Simultaneously, however, the lactone ring is split, and an unsaturated monobromocarboxylic acid is produced. This substance, which has the formula $C_{10}H_{15}BrO_2$, melts at 159° ; it forms well-defined salts, and has marked acidic characteristics, dissolving in a cold, aqueous solution of sodium carbonate, liberating carbon dioxide, and although but sparingly soluble in boiling water, the solution is distinctly acid towards litmus. Its unsaturated character is revealed by the behaviour of a solution containing sodium carbonate towards potassium

permanganate, which it immediately decolorises, and also by the readiness with which bromine dissolved in chloroform is decolorised when mixed with a solution of the acid in the same medium. The product of the latter change consists entirely of a dibromolactone, which it is to be supposed is formed by the elimination of hydrogen bromide from a tribromocarboxylic acid, incapable of existing in the free state. Fittig has shown that a similar behaviour towards bromine is characteristic of $\beta\gamma$ -unsaturated acids, which take up two atoms of the halogen, and at once part with hydrogen bromide, yielding a β -bromo- γ -lactone.

The behaviour of the monobromocarboxylic acid towards sulphuric acid affords further evidence in favour of the view that it is a $\beta\gamma$ -unsaturated acid. It is characteristic of these substances that, when subjected to the influence of sulphuric acid, they are converted into the isomeric lactones, the investigations of Fittig and his pupils having shown that this behaviour is generally manifest in the aliphatic series, but is not met with among aromatic compounds (*Ber.*, 1894, 27, 2668). When this test is applied to the acid from camphor, it is found to be converted by sulphuric acid into an isomeride which crystallises in magnificent, lustrous plates, melting at 93—94°. It has the properties of a lactone, and, on hydrolysis, yields an acid free from bromine. The bromolactone is a saturated compound, being indifferent towards bromine, and fuming nitric acid has no action on it, whereas the isomeric bromocarboxylic acid readily yields a nitro-compound.

Although the halogen in the bromocarboxylic acid resists the action of such reducing agents as zinc and acetic acid, sodium and alcohol, or tin and hydrochloric acid, the bromine is completely eliminated when a solution of the sodium salt is submitted to prolonged treatment with sodium amalgam at the temperature of boiling water. The product, which has the formula $C_{10}H_{16}O_2$, melts at 161°, and exhibits the character of a $\beta\gamma$ -unsaturated acid. It dissolves in a cold aqueous solution of sodium carbonate, liberating carbon dioxide, and the solution in hot water is acid towards litmus; potassium permanganate is immediately decolorised when added to a cold, alkaline solution of the acid. The solution in chloroform at once decolorises bromine dissolved in the same medium, and hydrogen bromide is liberated, a monobromolactone of the composition $C_{10}H_{15}BrO_2$ being formed, which melts at 62°, and is isomeric with the bromolactone obtained directly from the bromocarboxylic acid.

When the carboxylic acid, $C_{10}H_{16}O_2$, is dissolved in concentrated sulphuric acid, it is transformed into an isomeric lactone which melts at 176—177°; it resembles camphor in appearance, has the odour of that substance, and sublimes slowly at 100°. Its properties are lac-

tonic, and it gives rise to an acid, $C_{10}H_{18}O_3$, which crystallises in lustrous needles, and melts at 179° .

Nomenclature.—The desirability of being in a position to refer without confusion to these substances has rendered necessary the adoption of some convenient system of nomenclature. On consideration of their empirical formulæ, it will be seen that the compounds in question arrange themselves into two classes, typified on the one hand by the carboxylic acid, $C_{10}H_{16}O_2$, formed from the bromocarboxylic acid obtained from the original dibromolactone by means of alcoholic ammonia and zinc dust, and on the other from the isomeric lactone to which the acid gives rise under the influence of concentrated sulphuric acid. It is proposed that reference be made to the new acid as *camphorenic acid*, a name which indicates, by the syllable *en*, the unsaturated nature of the substance. The isomeric lactone will be called *campholid*, the termination *olid* indicating, according to systematic nomenclature, a compound of lactonic character. The product of the action of fuming nitric acid on α -dibromo-camphor is, therefore, *dibromocampholid*, and the acid obtained on reducing this substance will be called *bromocamphorenic acid*. It is proposed to indicate the isomerism exhibited by the product of the action of sulphuric acid on bromocamphorenic acid, and the compound obtained from camphorenic acid and bromine, by referring to these substances as α -monobromocampholid and β -monobromocampholid respectively.

The generic relationship which runs through the new group of compounds will be, perhaps, more clearly illustrated by the following scheme, intended to represent the steps by which it is possible to pass from one compound to another.

In view of the relation between dibromocampholid and campholid

itself, it was to be expected that, when brominated, the latter would either give rise to the former, or become converted into one of the isomeric monobromo-derivatives. Campholid, however, is not attacked by bromine at 100° , and the two monobromo-derivatives are also indifferent towards the halogen; moreover, camphorenic acid and the sodium salt are converted by bromine into β -monobromocampholid, no trace of dibromocampholid being formed. When, however, the methylic salt of camphorenic acid is brominated, a mixture of mono- and dibromocampholid is formed. This is most likely owing to the effect produced on the neighbouring methenyl group by neutralising the carboxyl radicle. While this is free, bromination does not take place, and the halogen merely saturates the ethylenic linking, whereupon hydrogen bromide is eliminated, and this change leads to the formation of a monobromolactone; when, however, the carboxyl radicle is rendered inactive by the introduction of the methyl group, substitution occurs in the neighbouring methenylic residue at the same time, and the usual addition of bromine also takes place, the ethylenic linking becoming saturated, and this being followed by elimination of methylic bromide, the closing of the ring is effected, and a dibromolactone is formed.

Specific Rotatory Power.—The lactones and unsaturated acids with which the present communication deals, are all optically active, and their examination has afforded striking evidence of the alteration in rotatory power attending ring formation. It has been already observed in the case of several acids belonging to the sugar group that the formation of the lactone ring involves a very marked alteration in the behaviour towards polarised light; for instance, whilst gluconic acid has the specific rotatory power $[\alpha]_D = -1.74^{\circ}$ (*Annalen*, 1892, **271**, 78), the lactone has $[\alpha]_D = +68.2^{\circ}$ (*Ber.*, 1890, **23**, 2626), and mannosaccharic acid, which is very feebly active, forms a double lactone which has $[\alpha]_D = +201.8^{\circ}$ (*Ber.*, 1891, **24**, 541). It is, therefore, interesting to observe that the changes involved in the production of such lactones as campholid and its bromo-derivatives are also attended with radical alterations in specific rotatory power. With regard to campholid, whilst camphorenic acid has $[\alpha]_D = +179.4^{\circ}$ in chloroform, the isomeric lactone has $[\alpha]_D = +27.4^{\circ}$ in the same medium. Bromocamphorenic acid has, in chloroform, the specific rotatory power $[\alpha]_D = +144.1^{\circ}$, whilst the isomeric α -bromocampholid has $[\alpha]_D = +10.9^{\circ}$; β -bromocampholid, the formation of which involves elimination of hydrogen bromide from brominated camphorenic acid, has the specific rotatory power $[\alpha]_D = +3.5^{\circ}$ when dissolved in a certain proportion of chloroform, becoming inactive when the solution is more concentrated.

Although systematic investigation of the influence exerted by the

solvent on the specific rotatory power of these substances must be postponed for the present, experiment has shown that in the case of bromocamphorenic acid and β -bromocampholid, the use of benzene instead of chloroform is attended with a marked change in the rotation, and to a smaller extent dibromocampholid is affected in the same way. Thus the latter substance has $[\alpha]_D = +64.5^\circ$ in chloroform, a solution of identical concentration in benzene giving $[\alpha]_D = +69.8$. Bromocamphorenic acid has $[\alpha]_D = +144.1^\circ$ in chloroform, and $+161.3^\circ$ in benzene, whilst β -bromocampholid has $[\alpha]_D = +3.5^\circ$ in chloroform, and -21.2° in benzene. It would be possible to quote many instances of the influence on rotatory power which the nature of the medium exerts, for example, the recent observation of Herzfeld (*Ber.*, 1895, **28**, 440), regarding the specific rotatory power of octacetylmaltose, which has been determined in chloroform and benzene, and is found to be $[\alpha]_D = +61.0$ and $[\alpha]_D = +76.5^\circ$ in the respective media. Whilst in this instance it is merely degree of rotation which is affected, rare observations of alteration in sign have been recorded; thus Freundler (*Compt. rend.*, 1890, **117**, 556), determining the specific rotatory power of propylic diacetyltartrate, found $[\alpha]_D = +36.7^\circ$ in carbon bisulphide, and -2.6° in bromoform. The camphor series, moreover, affords a still more striking instance of this phenomenon. α -Nitrocamphor has the specific rotatory power $[\alpha]_j = -7.5^\circ$ in alcohol, and $[\alpha]_j = -140^\circ$ in chloroform, whilst in the case of the β -modification, the value of $[\alpha]_j$ is $+7.5^\circ$ in alcohol, and -7.5° in benzene.

EXPERIMENTAL.

Dibromocampholid, $C_{10}H_{14}Br_2O_2$.

One hundred grams of recrystallised α -dibromocamphor are placed in a capacious flask (80 oz.), and covered with 200 c.c. of the strongest fuming nitric acid. The temperature of the liquid is at first sensibly reduced, and gradually rises spontaneously to about 70° , at which point a violent action takes place, rendered evident by vigorous evolution of ruddy fumes, and the generation of much heat. When all action ceases, the liquid is allowed to cool; on pouring it into a large volume of cold water, a heavy, brown oil separates, which is washed two or three times with cold water, and subsequently agitated for about 10 minutes with boiling water. As a consequence of this treatment it becomes very viscous, and acquires a pale yellow colour; when freed from water it readily dissolves in twice its bulk of boiling spirit, and the liquid solidifies to a crystalline magma on cooling. After expressing the oily mother liquor, the residue is washed two or three times with cold alcohol, and then recrystallised

from the minimum quantity of boiling spirit. Dibromocampholid is thus obtained in magnificent, lustrous needles, which frequently attain to more than an inch in length; it melts at 152° .

The following results were obtained on analysis.

0.1419 gave 0.1918 CO_2 and 0.0560 H_2O . $\text{C} = 36.86$; $\text{H} = 4.38$.

0.2071 „ 0.2806 CO_2 and 0.0814 H_2O . $\text{C} = 36.95$; $\text{H} = 4.36$.

0.1044 „ 0.1203 AgBr. $\text{Br} = 48.84$.

0.1076 „ 0.1244 AgBr. $\text{Br} = 49.13$.

0.1854 „ 0.2133 AgBr. $\text{Br} = 49.20$.

$\text{C}_{10}\text{H}_{14}\text{Br}_2\text{O}_2$ requires $\text{C} = 36.81$; $\text{H} = 4.29$; $\text{Br} = 49.08$ per cent.

Although many attempts have been made to increase the yield of this substance by varying the conditions attending its formation, it has never been obtained in quantities exceeding in weight 11 per cent. of the material used. Thus it is found that the use of smaller quantities of dibromocamphor (5, 10 or 20 grams), or of a greater proportion of nitric acid, has no influence on the relative amount of the product, nor is the yield augmented on checking the vigour of the action by immersing the flask in cold water. If nitric acid, having a lower density than 1.52 be taken, no spontaneous rise of temperature is observed, and almost the whole of the dibromocamphor can be easily recovered from the oil obtained on pouring the solution into cold water.

As it appeared not unlikely that the formation of the compound involved a liberation of bromine and the consequent bromination of an intermediate product, finely powdered silver nitrate was dissolved in the strongest fuming nitric acid, which was then allowed to act on α -dibromocamphor. Silver bromide was obtained in quantity representing 30 per cent. of the halogen available, but the yield of dibromocampholid was unaltered; when, moreover, 20 c.c. of bromine was added to the quantity of nitric acid usually taken, action proceeded in the ordinary manner, but no increase in yield was observed.

Dibromocampholid is insoluble in water, and scarcely soluble in cold alcohol, but dissolves in the boiling solvent, and also in ether, chloroform, petroleum, acetone, and glacial acetic acid; it crystallises from ethylic acetate in magnificent, long, transparent prisms, belonging to the orthorhombic system. It sublimes at a high temperature, and is somewhat volatile in an atmosphere of steam. The compound is indifferent towards bromine, and dissolves in concentrated sulphuric and fuming nitric acids without undergoing change, crystallising from the latter in long, transparent needles. It is in many respects a remarkably inert substance, and crystallises unaltered from boiling aniline, phenylhydrazine, acetic anhydride, or benzoic chloride; when it is heated, however, with an aqueous solu-

tion of sodium carbonate and alcohol, bromine is removed; and the halogen is also eliminated when the substance is heated for some time with a mixture of equal parts of nitric acid (density 1.42) and water. Dibromocampholid undergoes no change when the solution in glacial acetic acid is boiled for several hours with hydroxylamine hydrochloride.

The specific rotatory power of a solution containing 1.0269 grams in 25 c.c. of chloroform was determined in a 2-decimetre tube at 11° ; the mean of six concordant readings gave $\alpha_D = +5^{\circ} 18'$, whence $[\alpha]_D = +64.5^{\circ}$. It has been already stated that the influence which the nature of the solvent exerts on the rotatory power of dibromocampholid is more feeble than in the case of β -bromocampholid and bromocamphorenic acid; a solution in benzene of the above concentration gave $\alpha_D = +5^{\circ} 40'$ at 15° , whence $[\alpha]_D = +69.8^{\circ}$.

Hydrolysis of Dibromocampholid.

It has been already mentioned that elimination of halogen from dibromocampholid is readily effected by alkalis. The result of treatment with alkaline hydrolytic agents is the production of an acid having the formula $C_{10}H_{16}O_4$, the lactone $C_{10}H_{14}O_3$ being obtained as an intermediate product, in quantity varying according to the experimental conditions. Alcoholic potash is the agent most favourable to the formation of the lactone, whilst aqueous solutions of barium and sodium hydroxide give rise almost exclusively to the acid; the action of these alkalis on dibromocampholid will be therefore described in the order named.

Action of Alcoholic Potash on Dibromocampholid.—Twenty grams of the finely powdered substance are covered with about 50 c.c. of boiling alcohol, and heated for three hours in a reflux apparatus with 23 c.c. of an aqueous, 50 per cent. solution of caustic potash, which is added to the alcoholic liquid in small quantities at a time. The substance gradually dissolves, and the alkalinity produced by each fresh addition of potash is allowed to disappear before any more is added. The clear, red liquid, which is faintly alkaline, is allowed to cool, filtered from the potassium bromide which crystallises out along with unaltered substance (about 0.5 gram), reduced to small bulk by evaporation, and set aside for 48 hours. The crystalline substance which separates during this time is freed from oil, washed two or three times with cold petroleum, and recrystallised from hot alcohol; it is thus obtained in lustrous plates, and melts at 174° . From the analytical results, it will be seen that the compound has the formula $C_{10}H_{14}O_3$.

0.1703 gave 0.4097 CO₂ and 0.1183 H₂O. C = 65.60; H = 7.71.

0.1227 „ 0.2946 CO₂ and 0.0839 H₂O. C = 65.48; H = 7.60.

C₁₀H₁₄O₃ requires C = 65.93; H = 7.68 per cent.

A solution of 1.1826 grams in 25 c.c. of chloroform was examined at 15° in a 2-decimetre tube; the rotation $\alpha_D = -11^\circ 6'$, whence $[\alpha]_D = -117.3^\circ$.

The lactone is somewhat soluble in cold water, from which it crystallises in thick, transparent prisms; it fuses to an oil in boiling water, which dissolves it readily, forming a neutral solution. Although insoluble in cold alkalis, it dissolves readily when the solution is boiled, and no precipitate is formed on acidifying the cold liquid; it crystallises unchanged from boiling, aqueous ammonia. Phenylhydrazine has no action on it, and it is indifferent towards boiling acetic anhydride.

The bromo-derivative, C₁₀H₁₃BrO₃, is obtained by the action of bromine on the lactone. When the dry substance is covered with the halogen, no change takes place at first, but after remaining in contact for about a minute, action occurs quite suddenly, hydrogen bromide being liberated. The solid product is treated with sulphurous acid, washed several times with cold water, and finally crystallised from a considerable quantity of boiling alcohol, which deposits it, on cooling, in slender, lustrous needles melting at 196—197°. The following results were obtained on analysis.

0.1406 gave 0.2375 CO₂ and 0.0657 H₂O. C = 46.06; H = 5.18.

0.1460 „ 0.1062 AgBr. Br = 30.91.

C₁₀H₁₃BrO₃ requires C = 45.98; H = 4.98; Br = 30.65 per cent.

The bromolactone does not dissolve in water; it is insoluble in cold alkalis, but dissolves when the solution is boiled, and no precipitate is formed on acidifying the cold liquid. The halogen is eliminated on treatment with hot, alcoholic ammonia and zinc dust.

Hydrolysis of the Lactone.—2.5 grams of the lactone were heated in a reflux apparatus for an hour with 40 c.c. of aqueous barium hydroxide containing 3 grams of the crystallised hydrate. A current of carbonic anhydride was passed through the filtered liquid, and, after being boiled for a few minutes, the solution was freed from barium carbonate by filtration, and evaporated on the water bath until crystals began to separate; the substance thus obtained is the barium salt of the acid C₁₀H₁₆O₄, which is more conveniently obtained in the manner about to be described.

Action of Barium Hydroxide on Dibromocampholid.—The finely powdered substance is treated with successive quantities of a boiling, concentrated solution of barium hydroxide, in a flask provided with a reflux condenser; as long as any of the substance remains

undissolved, the alkalinity produced by a fresh portion of the hydrate is destroyed on boiling the liquid for a few minutes. When a clear solution is obtained, it is allowed to cool, filtered from a small quantity of unaltered dibromocampholid, reduced to a small bulk by evaporation in an open basin, cooled, and, after acidification with concentrated hydrochloric acid, repeatedly extracted with ether. On evaporating the ether, after agitating the solution with fused calcium chloride, a pale yellow substance is obtained, which crystallises from a mixture of ether and petroleum in minute, transparent rhombohedra, and melts, evolving gas, at 203° . The following results were obtained on analysis.

0.1716 gave 0.3742 CO_2 , and 0.1312 H_2O . $\text{C} = 59.47$; $\text{H} = 8.49$.

$\text{C}_{10}\text{H}_{16}\text{O}_4$ requires $\text{C} = 60.00$; $\text{H} = 8.00$ per cent.

The acid is very readily soluble in cold water, forming a strongly acid solution, which dissolves potassium carbonate with evolution of carbon dioxide; the alkaline liquid immediately decolorises a cold solution of potassium permanganate. It is extremely soluble in alcohol, chloroform, ethylic acetate, and organic solvents generally, excepting petroleum, in which it is insoluble. A solution in chloroform does not decolorise bromine, but on boiling the liquid a violent disengagement of hydrogen bromide occurs, and a colourless *dibromoderivative* is formed, which crystallises from alcohol in feathery aggregates, and melts at 159 – 160° ; this substance is insoluble in cold alkalis.

The *barium* salt is obtained by dissolving barium carbonate in a hot, aqueous solution of the acid; it is also formed on hydrolysing the lactone, $\text{C}_{10}\text{H}_{14}\text{O}_3$, with aqueous barium hydroxide. The solution is evaporated until the salt separates in white needles; the crystals are collected, washed with alcohol, and dried at 100° .

0.1501 gave 0.0641 BaSO_4 . $\text{Ba} = 25.11$.

0.1512 „ 0.0642 BaSO_4 . $\text{Ba} = 24.97$.

$(\text{C}_{10}\text{H}_{15}\text{O}_4)_2\text{Ba}$ requires $\text{Ba} = 25.60$ per cent.

The barium salt is very soluble in cold water, but is insoluble in alcohol, acetone, and ethylic acetate; the aqueous solution has an intensely bitter taste.

Action of Sodium Hydroxide on Dibromocampholid.—The substance dissolves slowly in a boiling aqueous solution of sodium hydroxide, and, on evaporating the filtered liquid, rendering acid with concentrated hydrochloric acid, and extracting several times with ether, the foregoing acid, $\text{C}_{10}\text{H}_{16}\text{O}_4$, is obtained on evaporating the solvent. If, however, the action of sodium hydroxide be allowed to proceed for a few minutes only, and the filtered liquid be extracted with ether

previous to acidification, the lactone, $C_{10}H_{14}O_3$ (m. p. 174°), is obtained.

An attempt was made to hydrolyse dibromocampholid by means of dilute sulphuric acid. The powdered substance was treated with boiling sulphuric acid (2 parts of concentrated acid in 10 parts of water) for six hours in a flask provided with a reflux condenser, but the greater part of the substance remained undissolved, and when recrystallised from alcohol melted at 152° .

Bromocamphorenic acid, $C_{10}H_{15}BrO_2$.

Fifty grams of dibromocampholid are covered with about 100 c.c. of boiling alcohol in a capacious flask, and to the liquid are added successively small quantities of zinc dust, and strong, aqueous ammonia, the temperature being maintained meanwhile on the water bath, until a portion of the clear, ammoniacal solution no longer becomes turbid when diluted with water. The liquid is then decanted from undissolved zinc, largely diluted with water, and finally acidified with dilute sulphuric acid, when a white, flocculent precipitate immediately separates; this is collected, washed several times with cold water, and dissolved in a small quantity of hot spirit, from which it crystallises in thin, lustrous plates. It frequently happens that on diluting the ammoniacal liquid, a yellowish-white, granular precipitate is thrown down; this consists of the zinc salt, which is invariably produced when the solution remains in contact with hot ammonia and zinc dust for a period longer than that necessary for reduction. In this case, the product is washed with cold water, and dissolved in dilute caustic soda, the solution being then precipitated with sulphuric acid.

The bromocarboxylic acid is readily soluble in cold alcohol, from which it crystallises in transparent, six-sided plates, melting at 159° ; it dissolves readily in organic solvents, separating in well-formed crystals from glacial acetic acid and petroleum. It is insoluble in cold water, but dissolves sparingly on boiling, forming an acid solution; it is volatile in an atmosphere of steam, and sublimes at a high temperature. Analysis gave the following results.

0.1685 gave 0.3016 CO_2 , and 0.0922 H_2O . C = 48.81; H = 6.08.

0.1152 „ 0.0877 AgBr. Br = 32.35.

0.1175 „ 0.0897 AgBr. Br = 32.44.

$C_{10}H_{15}BrO_2$ requires C = 48.58; H = 6.07; Br = 32.38 per cent.

A solution of 1.0060 gram in 25 c.c. of chloroform at 11° gave a rotation $\alpha_D = +11^\circ 36'$, this being the average of seven concordant readings; the specific rotatory power is, therefore, $[\alpha]_D = +144.1^\circ$. Dilution of the liquid appears to be without influence on the specific

rotatory power, as a solution containing 0.7247 gram in 25 c.c. of chloroform at 14° gave a rotation $\alpha_D = +8^{\circ} 22'$; this corresponds with a specific rotatory power $[\alpha]_D = +144.3^{\circ}$, a result sufficiently close to the one already given to show the constancy of this property between the limits indicated. The influence exerted by the nature of the medium is revealed when benzene is used as a solvent; a solution containing 0.7850 gram of bromocamphorenic acid in 25 c.c. of benzene at 15° gave a rotation $\alpha_D = +10^{\circ} 8'$, whence $[\alpha]_D = +161.3^{\circ}$.

The acid dissolves readily in cold alkalis, and it is also soluble in a cold, aqueous solution of sodium carbonate, carbon dioxide being liberated. No coloration is developed when ferric chloride is added to the dilute alcoholic solution, and it is indifferent towards Fehling's solution; the alkaline solution immediately decolorises potassium permanganate. The substance may be heated for an hour with boiling aniline without undergoing change, and a boiling alcoholic solution of sodium ethoxide has no action on it; when boiled during three hours with an aqueous solution of caustic soda, it is precipitated unchanged on adding acid, and silver nitrate produces no turbidity in the filtrate. A solution in chloroform immediately decolorises bromine in the same medium, and on evaporating the solvent dibromocampholid is obtained; the latter is also formed when bromine is added to the dry solid, much heat being generated, and hydrogen bromide evolved. Bromocamphorenic acid undergoes no change when allowed to remain for many days in contact with glacial acetic acid saturated with hydrogen bromide. The acid is indifferent towards hydroxylamine, benzoic chloride, and acetic anhydride, and undergoes no change when heated in a sealed tube with ammonia (sp. gr. 0.880) for five hours at 170° .

Monobromocamphorenic acid may be also prepared by reducing dibromocampholid with zinc dust and glacial acetic acid. The following salts have been obtained.

The *barium* salt is prepared by dissolving the acid in the minimum quantity of an aqueous solution of barium hydroxide, and evaporating the liquid till crystals form. It separates from the concentrated solution in lustrous plates, and in nodular aggregates when slowly deposited. From a specimen dried at 100° , the following analytical results were obtained.

0.2535 gave 0.0890 BaSO_4 . Ba = 20.64.

0.1963 „ 0.0706 BaSO_4 . Ba = 20.64.

$(\text{C}_{10}\text{H}_{14}\text{BrO}_2)_2\text{Ba} + 2\text{H}_2\text{O}$ requires Ba = 20.60 per cent.

On analysing the same preparation dried at 130° ,

0.2003 gave 0.0733 BaSO_4 . Ba = 21.52.

0.2148 „ 0.0796 BaSO_4 . Ba = 21.79.

$(\text{C}_{10}\text{H}_{14}\text{BrO}_2)_2\text{Ba}$ requires Ba = 21.78 per cent.

The *silver* salt is obtained by adding a slight excess of silver nitrate to an aqueous solution of the crystallised barium salt. The colourless precipitate is washed successively with water, alcohol, and ether, and dried at 50° . It is sparingly soluble in water, and dissolves with difficulty in boiling alcohol, from which it crystallises in lustrous needles. The dry salt darkens very slowly on exposure to light, but quickly blackens when treated with boiling water; it does not explode when heated suddenly. Analysis gave the following results.

0.2294 (precipitated) gave 0.1211 AgBr. Ag = 30.30.

0.0652 (crystallised) „ 0.0346 AgBr. Ag = 30.46.

$C_{10}H_{14}BrO_2Ag$ requires Ag = 30.50 per cent.

The *zinc* salt is obtained as a yellowish, granular precipitate when an alcoholic solution of the acid is boiled for some time with ammonia and zinc dust; it is also produced on adding an aqueous solution of zinc chloride to a neutral solution of the ammonium salt. The zinc salt is scarcely soluble in water, and but sparingly soluble in cold alcohol; it is more readily soluble in hot alcohol, and crystallises from acetone in tufts of minute, transparent needles. On adding water to the hot, alcoholic solution, and allowing the liquid to cool, the salt is obtained in stumpy prisms. It dissolves in alkalis, the solutions yielding the acid when acidified. When heated at $130-140^{\circ}$, the salt yields a colourless, crystalline sublimate of the acid. This behaviour is explained by its composition, which analysis shows to be represented by the formula $(C_{10}H_{14}BrO_2)_2Zn + C_{10}H_{15}BrO_2$.

0.2626 gave 0.0274 ZnO. Zn = 8.35.

$(C_{10}H_{14}BrO_2)_2Zn + C_{10}H_{15}BrO_2$ requires Zn = 8.08 per cent.

$(C_{10}H_{14}BrO_2)_2Zn$ requires Zn = 11.67 per cent.

The *ammonium* salt exists only in dilute, aqueous solution; if this is evaporated, or saturated with carbon dioxide, the salt is decomposed, and the acid separates.

The *copper* salt is obtained by adding copper sulphate dissolved in water to the neutral, aqueous solution of the ammonium salt, a bluish-green, flocculent precipitate being formed; when this is boiled with alcohol, a green solution is produced, and on adding a small quantity of water to the hot liquid and allowing it to cool, minute green needles are deposited.

The *methylic* salt is not formed when a solution of the acid in methylic alcohol is saturated at common temperatures with hydrogen chloride. It is prepared by dissolving 3 grams of the acid in a boiling solution of sodium methoxide in methylic alcohol containing 0.3 gram of sodium, and adding small quantities of methylic iodide until a few drops of the liquid, when diluted with water, no longer yield a

solid precipitate on acidification. The excess of methylic iodide having been removed, the liquid is diluted with water, and the colourless oil which is thrown down is washed two or three times with cold water, and extracted with ether; after being dried with calcium chloride, the solvent is evaporated, and the residual oil distilled. It boils at 255° under a pressure of 767.5 mm. The salt was analysed with the following result.

0.1792 gave 0.3379 CO_2 and 0.1078 H_2O . C = 51.4; H = 6.7.

$\text{C}_{10}\text{H}_{14}\text{BrO}_2\cdot\text{CH}_3$ requires C = 50.5; H = 6.5 per cent.

The methylic salt is a colourless, somewhat viscous oil, heavier than water, having a fragrant odour suggestive of camphor; it is volatile in an atmosphere of steam, the vapour being pungent and exhilarating. The salt is hydrolysed when heated with boiling alcoholic potash for six hours; it burns on platinum foil with a luminous, smoky flame, leaving no residue. The solution in chloroform immediately decolorises bromine, and, on evaporating the liquid, dibromocampholid is left.

Oxidation of Bromocamphorenic acid.

It has been already stated that the acid dissolved in an aqueous solution of sodium carbonate immediately decolorises potassium permanganate; an attempt was therefore made to obtain an oxidation product by means of this agent.

Twenty grams of finely powdered bromocamphorenic acid was suspended in 200 c.c. of boiling water, sodium carbonate being added until a clear solution was obtained; the liquid was then cooled to about 0° and mixed with an ice-cold, 2 per cent. solution of potassium permanganate, which was added in portions of 100 c.c. Crushed ice was also added to the liquid in order to maintain the temperature at 0° , and when 1,500 c.c. of the permanganate solution (corresponding to more than twice the molecular proportion) had been added, the liquid was allowed to remain for an hour surrounded with melting ice. After the removal of manganese dioxide, the clear liquid was concentrated to 200 c.c., acidified with concentrated hydrochloric acid, and the yellow solution extracted several times with ether. The pink syrup left on evaporating the united extracts rapidly solidified on being rubbed with a glass rod; the product was washed with hot ethylic acetate, and the colourless, insoluble portion dissolved in ether, which, when mixed with the same bulk of ethylic acetate, deposited the substance in groups of brilliant transparent prisms. The compound melts and evolves gas at 184° , and, after having been allowed to cool, melts at $84\text{--}85^{\circ}$; a specimen of the fused substance, however, after recrystallisation from dilute alcohol, melted at 184° .

0.1594 gave 0.3018 CO₂ and 0.0988 H₂O. C = 51.63; H = 6.85.

0.1559 „ 0.2967 CO₂ and 0.0944 H₂O. C = 51.91; H = 6.73.

C₁₀H₁₆O₆ requires C = 51.72; H = 6.90 per cent.

The oxidation product has the properties of a dibasic acid; it is strongly acid towards litmus, dissolves readily in alkalis, and with effervescence in alkali carbonates, and the aqueous solution. It dissolves readily in cold alcohol and ether, being but sparingly soluble in cold ethylic acetate; the solution in boiling water deposits rosettes of minute, transparent prisms as the liquid cools.

The *silver* salt was obtained as a pale yellow precipitate on adding silver nitrate in slight excess to a neutral solution of the ammonium salt; after being collected and washed successively with water, alcohol, and ether, the salt was dried in the desiccator. It darkens when exposed to light, or when heated for a few minutes in the water oven; there is no explosion when the salt is suddenly heated. Probably owing to the unstable character of the salt, which gradually darkens even in a desiccator protected from light, analysis of the substance gave somewhat unsatisfactory results, which seem to indicate, however, that the acid contains two carboxylic groups.

0.1402 gave 0.0726 Ag. Ag = 51.78.

0.1926 „ 0.0998 Ag. Ag = 51.87.

C₁₀H₁₄O₆Ag₂ requires Ag = 48.65 per cent.

C₁₀H₁₃O₆Ag₃ „ Ag = 58.58 „

α-Monobromocampholid, C₁₀H₁₅BrO₂.

In the introduction, it was mentioned that bromocamphorenic acid shows the behaviour which aliphatic $\beta\gamma$ -unsaturated acids exhibit, when brought in contact with sulphuric acid, undergoing molecular rearrangement, and being converted into the isomeric lactone.

Finely divided bromocamphorenic acid is added in small quantities at a time to five times its weight of concentrated sulphuric acid, which is continuously stirred during the operation. Heat is developed, the substance gradually becoming dissolved, and when a clear solution is obtained, the pale brown liquid is poured into a large volume of cold water; a white, crystalline precipitate at once separates, and this is collected, and washed several times with cold water. If the substance is added too quickly to the acid, liberation of a small quantity of hydrogen bromide is observed, but this may be avoided by preventing a sudden rise in the temperature of the liquid. The lactone crystallises from hot alcohol in magnificent, lustrous plates, separating from concentrated solutions in long, slender needles; it melts at 93—94°.

0.1575 gave 0.2805 CO_2 and 0.0878 H_2O . $\text{C} = 48.57$; $\text{H} = 6.19$.

0.1537 „ 0.1183 AgBr . $\text{Br} = 32.71$.

$\text{C}_{10}\text{H}_{15}\text{BrO}_2$ requires $\text{C} = 48.58$; $\text{H} = 6.07$; $\text{Br} = 32.38$ per cent.

The compound dissolves readily in organic solvents, and is soluble in boiling water, from which it separates as the liquid cools; it may be conveniently crystallised from a mixture of petroleum and alcohol, being obtained from this medium in thin, lustrous plates. It is volatile in an atmosphere of steam.

Apart from its neutral character, the properties of α -monobromocampholid differ very widely from those of bromocamphorenic acid. The lactone is insoluble in cold alkalis, and dissolves in bromine without undergoing change; it is indifferent towards a boiling mixture of glacial acetic and fuming nitric acids, whilst this treatment converts bromocamphorenic acid into a nitro-compound. Potassium bromide separates immediately when a concentrated, aqueous solution of caustic potash is added to the boiling solution in alcohol, the original acid, in boiling alcoholic solution, being indifferent towards metallic sodium. So easily is bromine eliminated from the lactone that, on digesting it for a considerable period with boiling water, and filtering the cold liquid, a precipitate is at once formed on adding silver nitrate to the acidified solution.

The conversion of bromocamphorenic acid into the isomeric lactone is attended with a remarkable alteration in the specific rotatory power. A solution of 0.9549 gram of α -bromocampholid in 25 c.c. of chloroform was examined in a 2-decimetre tube at 21° ; a rotation $\alpha_D = +0^\circ 50'$ was observed as the mean of seven concordant readings, whence $[\alpha]_D = +10.9^\circ$.

Hydrolysis of α -Monobromocampholid.—The lactonic character of the substance is revealed on treatment with an aqueous solution of barium hydroxide. After remaining in contact with the boiling agent in a reflux apparatus for three hours, the lactone becomes dissolved, and the alkalinity of the liquid is gradually destroyed; on evaporating the solution which has been cooled and filtered, a barium salt crystallises in prismatic needles. It was dried at 130° for half an hour, and analysed with the following result.

0.1320 gave 0.0611 BaSO_4 . $\text{Ba} = 27.21$.

$(\text{C}_{10}\text{H}_{15}\text{O}_3)_2\text{Ba}$ requires $\text{Ba} = 27.23$ per cent.

On acidifying a solution of the barium salt, the acid is obtained as a colourless, viscous oil, which rapidly becomes hard and crystalline. It separates from a mixture of petroleum and ethylic acetate in transparent prisms, and melts at 195° ; it is very readily soluble in water, alcohol, ether, and acetic acid, but is insoluble in petroleum. The aqueous solution dissolves sodium carbonate with effervescence

the liquid having no reducing action on ice-cold potassium permanganate.

Camphorenic acid, $C_{10}H_{16}O_2$.

Bromocamphorenic acid is readily attacked by sodium amalgam, especially at slightly elevated temperatures.

Fifty grams are suspended in 200 c.c. of boiling water and vigorously agitated during the addition of 4 per cent. sodium amalgam in small quantities. It is necessary that the liquid should remain at the temperature of boiling water, otherwise the reduction is incomplete, and a mixture of the new compound with unaltered substance is obtained; as the separation of the latter is extremely tedious, the observance of this precaution is of some importance. For the quantity mentioned, about 500 grams of amalgam will be found sufficient, and when this amount has been added, if a drop of the liquid becomes solid when placed on a watch glass, it is decanted from the mercury and allowed to cool. The paste of fibrous needles thus obtained, consisting of the sodium salt of the reduction product, is collected, the alkaline liquid being removed by filtering through asbestos. On dissolving the salt in water, and adding dilute sulphuric acid, a white, flocculent precipitate is formed, which is collected and washed thoroughly with cold water. In order to completely remove the last traces of the original substance, the precipitated carboxylic acid is again agitated with 50 grams of sodium amalgam, the separation and decomposition of the sodium salt being repeated; as the latter only crystallises from strongly alkaline solutions, it is generally found necessary after this supplementary treatment with the amalgam to add sodium carbonate to the hot liquid until the sodium salt begins to separate. The acid, on being crystallised from hot alcohol, separates in long, slender needles; it melts at 161° .

0.1500 gave 0.3925 CO_2 and 0.1314 H_2O . $C = 71.36$; $H = 9.73$.

$C_{10}H_{16}O_2$ requires $C = 71.43$; $H = 9.52$.

The substance is very soluble in organic solvents, and dissolves to some extent in boiling water, being insoluble in the cold; it crystallises from ether in transparent prisms which become opaque in the water oven. It is volatile in an atmosphere of steam, and sublimes when heated, the vapour having a faint, camphor-like odour.

A solution of 1.1840 gram in 25 c.c. of chloroform was examined in a 2-decimeter tube at 18° ; it exhibited a rotation of $\alpha_D = +17^\circ$, and the specific rotatory power is, therefore $[\alpha]_D = +179.4^\circ$. The substance dissolves readily in cold, aqueous alkalis, and in a cold solution of sodium carbonate, carbon dioxide being evolved; the solution in hot water is acid, and potassium permanganate is immedi-

ately decolorised when added to the cold solution containing sodium carbonate. Boiling acetic anhydride has no action on the acid, which is also indifferent towards benzoic chloride.

The *sodium* salt, which separates from a strongly alkaline solution in tough, fibrous masses, is extremely soluble in water, and may be recrystallised from ethylic acetate, separating from this solvent in lustrous, silky needles; a specimen obtained in this way was analysed with the following result.

0.2395 gave 0.0948 Na_2SO_4 . $\text{Na} = 12.82$.

0.2940 „ 0.1161 Na_2SO_4 . $\text{Na} = 12.79$.

$\text{C}_{10}\text{H}_{15}\text{O}_2\text{Na}$ requires $\text{Na} = 12.10$ per cent.

The somewhat unsatisfactory character of these numbers is most probably due to slight decomposition taking place at the temperature of boiling ethylic acetate, as the crystallised salt does not redissolve completely in that solvent, and the solution in cold water is strongly alkaline.

The *zinc* salt resembles that of bromocamphorenic acid; it is obtained on adding zinc chloride dissolved in water to a neutral solution of the ammonium salt.

The *methylic* salt is not formed when a solution of the acid in methylic alcohol is saturated at common temperatures with hydrogen chloride, but it can be prepared by dissolving the sodium salt in methylic alcohol and heating the solution with methylic iodide for several hours in a reflux apparatus; on diluting the liquid with water, and extracting with ether, a colourless oil is obtained which boils at 215° under a pressure of 767.5 mm. It is viscous, and heavier than water, and burns on platinum foil with a luminous, smoky flame, leaving no residue; it dissolves readily in alcohol, but is insoluble in water. The salt is volatile in an atmosphere of steam, and the vapour has a very sweet, camphor-like odour; it is hydrolysed when heated with alcoholic potash for several hours in a reflux apparatus.

Its behaviour towards bromine is somewhat remarkable. Whilst by direct bromination of the original acid only one atom of bromine is introduced into the molecule, the methylic salt is violently acted on by the halogen, and is at once converted into dibromocampholid, a certain quantity of β -monobromocampholid (see below) being produced at the same time.

Anhydride of Camphorenic Acid, $\text{C}_{20}\text{H}_{30}\text{O}_3$.

Phosphorus pentachloride acts readily on camphorenic acid, but on pouring the liquid into cold water, or cold aqueous ammonia, and acidifying the solution, the unaltered substance is precipitated; if,

however, dry ammonium carbonate be substituted for the free alkali, only a portion of the camphorenic acid is recovered unchanged, the remainder being converted into a non-nitrogenous compound having the formula of camphorenic anhydride.

Five grams of the acid was intimately mixed with 7.5 grams of phosphorus pentachloride, this quantity being in slight excess of the amount calculated for one molecular proportion. A violent action took place, and the mixture became liquid; in this condition it was poured on to finely powdered ammonium carbonate, and when the pasty mass at first obtained had become solid, the product was thrown into cold water, in which the greater part dissolved. The insoluble portion was then removed, washed several times with cold water, and recrystallised from alcohol; it separates from concentrated solutions in snow-white plates, and melts at 84—85°.

0.1334 gave 0.3692 CO₂ and 0.1148 H₂O. C = 75.42; H = 9.55.
C₂₀H₃₀O₃ requires C = 75.47; H = 9.43 per cent.

From the above quantity of camphorenic acid, two grams of the anhydride was obtained, rather more than this amount of the unaltered acid being recovered from the alkaline filtrate on acidification.

The anhydride is indifferent towards boiling water, and may be mixed with alcoholic potash without undergoing hydrolysis. It is very readily soluble in organic solvents, and is volatile in an atmosphere of steam.

β-Monobromocampholid, C₁₀H₁₅BrO₂.

Whilst bromination of bromocamphorenic acid gives rise to dibromocampholid, camphorenic acid is converted into a bromolactone isomer with the monobromocampholid already described as arising from the action of concentrated sulphuric acid on bromocamphorenic acid.

Camphorenic acid is dissolved in cold chloroform, and bromine is added from a burette until the colour of the halogen is no longer destroyed. Before this stage is reached, heat is developed and hydrogen bromide evolved, and, on evaporating the solvent, a pale yellow oil is obtained, which rapidly solidifies to a crystalline cake; this is drained on porous earthenware, crystallised from chloroform, and finally from ether. The substance melts at 62°.

The following results were obtained on analysis.

0.1453 gave 0.2591 CO₂ and 0.0800 H₂O. C = 48.63; H = 6.11.

0.1620 „ 0.1241 AgBr. Br = 32.55.

C₁₀H₁₅BrO₂ requires C = 48.58; H = 6.07; Br = 32.38 per cent.

β-Monobromocampholid is also formed when bromine is added to the dry sodium salt of camphorenic acid. The action is violent,

being accompanied by a hissing noise, and the development of much heat; liberation of hydrogen bromide is, however, not observed. The new isomeride is extremely soluble in organic solvents, and crystallises from ether in hard, transparent prisms; it separates from dilute acetic acid in thin, lustrous plates, and the concentrated solution in alcohol deposits long, striated prisms. The substance is somewhat volatile at 100° , the vapour having a pleasant odour resembling that of α -dibromocamphor; it is volatile in an atmosphere of steam.

Attention has been already drawn to the fact that dibromocampholid is converted into bromocamphorenic acid under the influence of alcoholic ammonia and zinc dust. An analogous change takes place when β -bromocampholid is reduced in this manner, camphorenic acid being formed. The lactone is indifferent towards bromine, and is attacked very slowly by hydrolytic agents.

The specific rotatory power of β -bromocampholid has been the subject of comment in the introductory portion of this paper, it having been observed that the concentration of the solution and the nature of the solvent exert a marked influence on this property. 1.0179 gram dissolved in 25 c.c. of chloroform, at 15° , was found to be inactive, whilst a solution containing 0.7006 gram, in 25 c.c. at the same temperature, gave $\alpha_D = +0^{\circ} 12'$ as the mean of seven concordant readings, whence $[\alpha]_D = +3.5^{\circ}$. A very different result, however, was obtained on using benzene as a solvent, although in the case of this medium concentration has but slight influence on the rotatory power. Thus, a solution containing 0.8810 gram, in 25 c.c. of benzene at 16° , gave $\alpha_D = -1^{\circ} 30'$ as the mean of six concordant readings, corresponding to a specific rotatory power $[\alpha]_D = -21.2^{\circ}$, whilst 1.3711 gram, dissolved in 25 c.c. at the same temperature, gave $\alpha_D = -2^{\circ} 18'$, whence $[\alpha]_D = -21.0^{\circ}$.

Campholid, $C_{10}H_{16}O_2$.

The transformation of bromocamphorenic acid into the isomeric α -bromocampholid finds a parallel in the conversion of camphorenic acid into campholid under the influence of concentrated sulphuric acid. In describing the preparation of camphorenic acid, attention was drawn to the importance of effecting complete reduction of the bromocamphorenic acid, and as an instance of the tenacity with which bromine remains in the product, it may be mentioned that a specimen of campholid, obtained from camphorenic acid containing a small quantity of the halogen, was found to retain an appreciable amount of the impurity after passing successively through the operations entailed in its preparation for analysis, namely, dissolution in sulphuric acid, crystallisation, and sublimation. It is possible, how-

ever, to obtain a pure specimen of campholid by boiling the crude product during several minutes with alcoholic potash, and precipitating the lactone by water.

Camphorenic acid, which has been reduced to powder, is added in small quantities to about five times its bulk of concentrated sulphuric acid; as the substance dissolves, the temperature rises slightly. When clear, the pale yellow solution is poured into a large volume of cold water, and the white, flocculent precipitate is collected, washed several times with cold water, and boiled during a few minutes with alcoholic potash, to which a considerable quantity of cold water is then added. After being washed carefully with cold water, the product is dried on porous earthenware, and crystallised from hot petroleum, separating as the solvent cools in minute, colourless crystals; it melts at 176—177°. The following results were obtained on analysis.

0.1020 gave 0.2660 CO₂ and 0.0907 H₂O. C = 71.12; H = 9.88.

C₁₀H₁₆O₂ requires C = 71.43; H = 9.52 per cent.

Campholid has the odour of camphor, and closely resembles that substance in appearance, moderate pressure converting it into a translucent mass, which, however, does not exhibit on the surface of water, the gyratory motion peculiar to camphor. It is an extremely volatile substance, and sublimes slowly below 100°; when heated at the melting point, however, sublimation is extremely rapid, and if the vapour is allowed to cool very slowly, campholid is deposited in beautiful, fern-like aggregates, composed of elongated octohedra. The substance is very volatile in an atmosphere of steam, and the camphor-like odour of the hot vapour is extremely powerful.

Campholid dissolves in most organic solvents with great readiness, and has not as yet been obtained in crystals having well defined geometrical structure; it is less readily soluble in cold petroleum, from which it separates in feathery aggregates when evaporation of the solvent is slow. The lactone is indifferent towards bromine, and is very slowly attacked by hydrolytic agents.

A solution containing 1.0011 gram of campholid in 25 c.c. of chloroform was examined in a 2-decimeter tube at 17°; the mean of seven concordant observations gave $\alpha_D = +2^\circ 12'$, which corresponds to the specific rotatory power $[\alpha]_D = +27.4^\circ$.

Hydrolysis of Campholid.

At one stage of the investigation, before the lactonic character of campholid was recognised, it was anticipated that the carbonyl group would possess ketonic properties, and an attempt was accordingly made to prepare an oxime; the product, however, consisted of a non-

nitrogenous substance, which evidently arises from addition of the elements of water to the campholid molecule, the action being most likely due to the influence of alcoholic potash.

1.7 gram of the lactone was dissolved in alcohol containing 2 grams of potassium hydroxide; 1 gram of hydroxylamine hydrochloride was then added, and the liquid heated for $1\frac{1}{2}$ hour on the water bath, alcohol being added from time to time. It was then evaporated, the residue being treated with water in order to separate the product from insoluble matter consisting of the unaltered lactone. On reducing the filtered liquid to small bulk, and rendering it acid with concentrated hydrochloric acid, a pale, yellow oil separated, which rapidly became crystalline and hard when rubbed with a glass rod; after being washed and dried, the product was crystallised from hot ethylic acetate, which dissolves it readily, allowing it to separate in magnificent, lustrous needles as the liquid cools. The substance melts to a clear liquid at 179° , and evolves gas at this temperature.

0.1612 gave 0.3798 CO_2 and 0.1376 H_2O . $\text{C} = 64.25$; $\text{H} = 9.48$.

0.1743 „ 0.4090 „ „ 0.1577 „ $\text{C} = 64.00$; $\text{H} = 10.05$.

$\text{C}_{10}\text{H}_{18}\text{O}_3$ requires $\text{C} = 64.51$; $\text{H} = 9.67$ per cent.

The acid dissolves readily in organic solvents, but is only sparingly soluble in water; it dissolves in an aqueous solution of sodium carbonate, and the liquid thus obtained does not decolorise potassium permanganate immediately in the cold.

The *barium* salt was prepared by the protracted action of a hot aqueous solution of barium hydroxide on campholid; it separated in white scales on evaporating the solution, and was found on analysis to contain 26.47 per cent. of barium, the percentage required by the formula $(\text{C}_{10}\text{H}_{17}\text{O}_3)_2\text{Ba}$ being 26.00.

Theoretical.

Although our knowledge of the structure of camphor is not sufficiently accurate to render the constitutional expression of the new derivatives a simple exercise, it may not be altogether unprofitable to discuss the relationship which they exhibit among themselves.

It may be safely assumed that the complex $\cdot\text{CHBr}\cdot\text{CO}\cdot$ occurs in bromocamphor, and there appears to be no evidence opposed to the view that the group $\cdot\text{CBr}\cdot\text{CHBr}\cdot\text{CO}\cdot$ is present in α -dibromocamphor; with this provision, the development of a scheme illustrating the mutual connection between these new compounds would present no great difficulty, were it not for the fact that the tendency of recent investigation is to show that the carbonyl group occurs in camphor as the member of a ring containing five carbon atoms. Thus

F. Tiemann (*Ber.*, 1895, **28**, 2182) has advanced the conclusion that camphor must be represented constitutionally by the formula

Assuming that α -dibromocamphor contains the group already indicated, this conception demands the representation of dibromocampholid by one of the formulæ

Neither of these expressions, however, is in accordance with the properties of the substance. The bromocarboxylic acids derived from them would be $\gamma\delta$ -acids, having the constitution expressed by the formulæ

respectively. A systematic study of the properties of $\gamma\delta$ -unsaturated acids as a class has been hitherto impossible, owing to the lack of general methods of preparation. In the aliphatic series, however, allylacetic acid has been obtained, and is found to yield $\gamma\delta$ -dibromovaleric acid on bromination (*Annalen*, 1881, **208**, 100), and γ -bromovaleric acid when combined with hydrogen bromide. The former substance has no tendency to pass spontaneously into a δ -lactone, whilst boiling water converts γ -bromovaleric acid into the lactone of γ -hydroxyvaleric acid. The slight evidence available, therefore, seems opposed to the view that $\gamma\delta$ -unsaturated acids behave in the same way as those containing the ethylenic linking in the $\beta\gamma$ -position, and it is probable that if elimination of hydrogen bromide did follow immediately on the addition of bromine, as is the case with the latter class, the result would be the same as among these acids, so far as the structure of the lactone-ring is concerned, that is to say, γ -lactones would be formed. Assuming this to be the case, bromocamphorenic acid should yield a dibromolactone, having the constitution expressed by one of the following formulæ.

But it has been already stated that dibromocampholid is the product of this change, and if the constitution of that substance is to be represented by the latter scheme, the former being obviously inappropriate, it must be assumed that under the influence of nitric acid, the

ring $\begin{array}{c} \cdot\text{CH}\cdot\text{CHBr}\cdot\text{CO} \\ | \quad \quad | \\ \text{CH}_2 \text{---} \text{CBr}\cdot \end{array}$ opens, and then re-closes, forming the complex $\begin{array}{c} \text{CH}\cdot\text{CHBr}\cdot\text{CO} \\ | \quad \quad | \\ \cdot\text{CHBr}\cdot\text{CH}\text{---}\text{O} \end{array}$, an assumption which seems scarcely tenable.

There is, moreover, another obstacle regarding the constitution of dibromocampholid as represented by the second of the above expressions. Camphorenic acid would have the constitution

whilst the formula

would represent the structure of campholid, and it will be at once noticed that these expressions have been already adopted by Tiemann (*loc. cit.*) in explaining the behaviour of β -campholenic acid and dihydrocampholenolactone, to which camphorenic acid and campholid bear no resemblance, although they are respectively isomeric with these substances.

Whatever conclusion is arrived at regarding the constitution of camphor itself, the relationship between the new derivatives will meet with explanation if the view be taken that dibromocampholid contains

the group $\begin{array}{c} \cdot\text{CBr}\cdot\text{CHBr}\cdot\text{CO} \\ | \quad \quad | \\ \text{C} \text{---} \text{O} \end{array}$. The changes which result in the produc-

tion of bromocamphorenic acid from dibromocampholid most probably involve hydrolysis of the lactone ring, substitution of hydrogen for bromine, and elimination of the elements of water, as indicated in the following manner.

The last of these expressions represents the complex occurring in bromocamphorenic acid, and assuming that an acid of this nature would exhibit the behaviour of aliphatic $\beta\gamma$ -unsaturated acids, the action of bromine and sulphuric acid would give rise to compounds containing the groups

peculiar to dibromocampholid and α -monobromocampholid respectively. Under the influence of the same agents, camphorenic acid would yield compounds in which occur the groups

which are most likely present in β -bromocampholid and campholid respectively. The steps by which reduction of the former gives rise to camphorenic acid, would then be parallel with those changes which result in the production of bromocamphorenic acid from dibromocampholid.

It is anticipated that oxidation of the new derivatives will throw light on their constitution, and experiments are being now carried on in this direction.

I cannot conclude this paper without expressing my indebtedness to Professor Armstrong and Dr. Kipping, not only for the interest they have exhibited in the progress of the work, but also for the valuable advice of which I have frequently had the benefit.

Note by Dr. Armstrong.—I desire to take this opportunity of pointing out that the investigation of the derivatives of camphor containing halogens, is at present being pursued in a variety of directions in my laboratory. Although, as Dr. Forster says, there is no evidence opposed to the view that the bromine atoms in α -dibromocamphor are attached to different carbon atoms, and the peculiar readiness with which one is eliminated, lends much support to this view, there are not a few facts which are difficult to reconcile with such a conclusion. Dr. Forster's work—interesting as are the results—has not thrown the light on this question I had anticipated. It is to be expected that the investigation of the nitrocamphor derivatives, and of the derivatives containing two different halogens, as well as the comparison of α - with β -dibromocamphor, will afford evidence of the desired character. The important discovery of a *cis*- and *trans*-nitrobromocamphor made by Drs. Kipping and Lapworth (Proc., No. 157, 209), is of special interest in this connection. I may mention that Dr. Lapworth has proved that when α -dibromocamphor and bromochlorocamphor are sulphonated, the halogen is partially displaced, products different from those investigated by Kipping and Pope being formed. β -Dibromocamphor has also given interesting results.

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