# CXCVI.—*The Action of Bromine Water on Certain Olefinic Hydrocarbons and Ethers.*

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From the series of researches indicated in a recent communication (this vol., p. 745), it has become evident that wide use may be made of chlorine water and bromine water as reagents for the addition of hypochlorous and hypobromous acids to olefinic substances. The present paper describes the application of bromine water in this way to styrene and a number of related aromatic ethers, and also to amylene and *dl*-$\Delta^3$-menthene. Since the first-named group yields bromohydrins which are not readily affected by hot water, it has been possible to adduce four further examples in which the yield of bromohydrin is increased by raising the temperature during the reaction with bromine water. Under the conditions adopted, the percentage yields of bromohydrin obtained at the ordinary temperature and at about 90°, respectively, were as follows: styrene, 77·9, 96·7; anethole, 47·9, 76·1; safrole, 65·2, 69·2; *iso*safrole, 67·0, 72·8. Taking into account the behaviour of oleic acid and indene (*loc. cit.*), it thus appears to be a general rule that when the halogenohydrin is stable towards hot water the ratio halogenohydrin/dihalogenide increases with rise of temperature. The yield of halogenohydrin is increased also by dilution. At concentrations from about 0·1 to 0·2 gram-molecule per litre, yields of more than 90% of the amounts of bromohydrin theoretically possible have now been obtained by the action of bromine water on the following substances: ethylene, sodium maleate, sodium fumarate, itaconic acid, indene, styrene, cinnamic acid, methylcoumaric acid, and methylcoumarinic acid. Of the other substances investigated, maleic acid and allyl alcohol gave yields of more than 85%; and amylene, anethole, safrole and *iso*safrole gave from about 70% to 80%, *dl*-$\Delta^3$-menthene 62·9%, and oleic acid 51·5%.

It has already been pointed out that the reactions in question may be used, *inter alia*, for the rapid and convenient preparation of aldehydes and ketones from olefinic substances, *e.g.*, of phenylacetaldehyde from cinnamic acid, and of β-hydrindone from indene (J., 1921, **119**, 1775; 1922, **121**, 2551); we describe below a similar conversion of amylene (trimethylethylene) into trimethylethylene oxide and methyl *iso*propyl ketone. We have also taken occasion to prepare certain αβ-amino-alcohols by the action of cold concentrated ammonia on the corresponding bromohydrins. Thus, styrene yields β-hydroxy-β-phenylethylamine; since the same base has been obtained by reducing *iso*nitrosoacetophenone (Kolshorn, *Ber.*, 1904, **37**, 2483), the position of the amino-group and the mode of addition of the hypobromous acid are thereby established. In a similar way, we have prepared β-hydroxy-β-*p*-methoxyphenyl-*iso*propylamine (m. p. 84°) from anethole, and have moreover resolved it into optically active components (m. p. 80—81°). β-Hydroxy-α-*p*-methoxyphenylpropylamine has been described by Takeda and Kuroda (*J. Pharm. Japan*, 1919, 561); our substance appears to be identical with an isomeric alkamine (m. p. 80°), of undetermined constitution, prepared by these authors. By applying the same method to amylene we have been able to prepare γ-amino-β-hydroxy-β-methylbutane, an asymmetrically constituted base which we have as yet been unable to submit to optical resolution.

## EXPERIMENTAL.

*The Action of Bromine Water on Styrene.*—(1) To 500 c.c. of water, maintained at about 90°, were added four successive portions of 5 g. of styrene. To the mixture, thoroughly emulsified in each instance by vigorous shaking, a 7% solution of bromine in aqueous potassium bromide (10%) was added with moderate rapidity until the attainment, after continued shaking, of a permanent yellow tint. The amount of bromine added at each stage was noted, and its distribution was determined by titrating the resulting hydrobromic acid in a small measured volume of the aqueous solution with standard sodium bicarbonate.

The proportion of bromine converted into bromohydrin and hydrobromic acid declined in the successive stages from 97·6% to 94·9%, and of the total amount of bromine added (25·85 g.), 96·7% reacted in this way, leaving only 3·3% to function in the formation of dibromide. From these results it is also apparent that of the 20 g. of styrene used, only 16·8 g. reacted, owing possibly to the presence of polymerisation products.* Extraction with ether yielded a limpid, amber-coloured liquid (35 g.), having $n_D^{17^\circ}$ 1·5780. The bulk of the product (21 g.), distilling at 109—110°/2 mm., and having $n_D^{17^\circ}$ 1·5800, $d_{4^\circ}^{20^\circ}$ 1·4994, consisted of styrene bromohydrin, or β-*hydroxy*-β-*phenylethyl bromide*, $OH{\cdot}CHPh{\cdot}CH_2Br$. This substance is a heavy, colourless liquid, with an irritating odour; it is almost insoluble in water (Found: Br, 40·0. $C_8H_9OBr$ requires Br, 39·8%). It was impracticable to distil the product of the reaction at 10 mm., owing to decomposition.

(2) Upon conducting the operation at the ordinary temperature, the yield of bromohydrin fell to 77·9%, and the extracted oily product deposited crystals of styrene dibromide (αβ-dibromo-α-phenyl-

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* The original styrene distilled completely between 78° and 85°, and 80% passed over between 80° and 83°.

ethane) when kept (m. p. 74—75°) (Found: Br, 60·1. Calc. for $C_8H_8Br_2$: Br, 60·4%). Attempts to prepare the bromohydrin from the dibromide by digestion with aqueous alcohol or acetone in presence of calcium carbonate were unsuccessful, the dibromide remaining practically unaltered after 10 hours. It is thus improbable that the enhanced yield of bromohydrin at the higher temperature is due to partial hydrolysis of the dibromide.

β-*Hydroxy*-β-*phenylethylamine*, $OH{\cdot}CHPh{\cdot}CH_2{\cdot}NH_2$.—Styrene bromohydrin (10 g.) was shaken mechanically with concentrated aqueous ammonia (50 g.) for 10 hours. The excess of ammonia was then removed by spontaneous evaporation in an open dish, and the oily by-products (including bromostyrene) by subsequent extraction with ether. The concentrated aqueous residue yielded a brownish-yellow syrup (1·7 g.) when basified with potassium hydroxide and extracted with ether. This product consisted of the free hydroxy-amine, and when submitted to the Schotten-Baumann reaction with benzoyl chloride it readily gave the corresponding benzoyl derivative, m. p. 143° (*Ber.*, 1904, **37**, 2483) (Found: C, 74·2; H, 6·5. Calc. for $C_{15}H_{15}O_2N$: C, 74·7; H, 6·2%).

*The Action of Bromine Water on Anethole.*—(1) To 10 g. of anethole emulsified in 250 c.c. of water at about 90° was gradually added bromine (10·85 g.; 1 mol.) dissolved in aqueous potassium bromide (10 g. in 150 c.c.), the mixture being shaken vigorously throughout the process. A determination of the resulting hydrobromic acid showed that 76·1% of the bromine had reacted to form this substance and the bromohydrin. The pasty product, when extracted with ether and dried (17 g.), deposited crystals of anethole dibromide (m. p. 67°). The residual viscid syrup, which had a very irritating odour, decomposed when heated in a vacuum apparatus.

(2) When the operation was repeated at the ordinary temperature, a suspension of finely powdered anethole in water being used, only 47·9% of the bromine reacted to form bromohydrin and hydrobromic acid, and a larger proportion of crystalline anethole dibromide was isolated from the product. In both instances the calculated quantity of bromine reacted with the anethole.

β-*Hydroxy*-β-p-*methoxyphenyl*iso*propylamine*,

$$MeO{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CHMe{\cdot}NH_2.$$

—Anethole bromohydrin (50 g.), prepared from anethole dibromide (*Ber.*, 1905, **38**, 3470), was shaken for 3 days with concentrated ammonia (250 g.). After the product had been exposed over-night in an open dish, the residual oil was extracted with ether; the aqueous washings of the ethereal extract were added to the original aqueous liquor, and most of the water was removed by evaporation on the water-bath. The free base, isolated in the usual way, formed a viscid syrup (7 g.), which gradually crystallised; the colourless product obtained by washing with ether melted at 84°. The base is insoluble in light petroleum, moderately easily soluble in ether, and readily soluble in water. The *hydrochloride*, after recrystallisation from acetone, melted at 182°; it is very soluble in alcohol or water (Found: Cl, 16·3. $C_{10}H_{15}O_2N,HCl$ requires Cl, 16·3%). The *benzoyl* derivative crystallised from alcohol in fine needles, m. p. 159°; the *benzylidene* derivative is a viscid syrup.

The crude *d*-camphorsulphonate had $[\alpha]_D$ +15·0°, $[M]_D$ +62°, in 1% aqueous solution. After two fractional recrystallisations from hot absolute alcohol, this salt yielded large colourless prisms of d-β-*hydroxy*-β-p-*methoxyphenyl*iso*propylamine* d-*camphorsulphonate*, m. p. 194—195°, $[\alpha]_D$ +20·5°, $[M]_D$ +85°; the rotatory power was unaltered by further recrystallisation. d-β-*Hydroxy*-β-p-*methoxyphenyl*iso*propylamine* separates from ether in needles, m. p. 80—81°. The following determinations of optical rotatory power were made at 15°: $[\alpha]_D$ +4·6°, $[M]_D$ +8° (water, *c* 1·0); $[\alpha]_D$ +13·9°, $[M]_D$ +25° (methyl alcohol, *c* 1·0); $[\alpha]_D$ +18·4°, $[M]_D$ +33° (ethyl alcohol, *c* 0·6); $[\alpha]_D$ +22·9°, $[M]_D$ +41·5° (benzene, *c* 1·2); $[\alpha]_D$ +21·7°, $[M]_D$ +39° (acetone, *c* 0·6). The *hydrochloride*, m.p. 171—172°, had $[\alpha]_D$ +14·7°, $[M]_D$ +32°, in water (*c* 0·9) (Found: Cl, 16·3%). The *benzoyl* derivative crystallised from alcohol in fine needles, m. p. 153—154°; a 0·5% alcoholic solution showed no measurable optical activity when examined in a 2-dcm. tube in sodium light.

The crude d-α-*bromocamphorsulphonate* of the inactive base formed large prisms, m. p. 103°.

*The Action of Bromine Water on Safrole.*—A procedure was adopted exactly similar to that described for anethole. At about 90°, 69·2% of the added bromine was used in the formation of bromohydrin and hydrobromic acid, and at the ordinary temperature the proportion fell to 65·2%. In both instances the calculated amount of bromine was absorbed, and 10 g. of safrole yielded 17 g. of a dark brown, viscid syrup with an irritating odour; when kept for a while, this deposited colourless needles of *safrole dibromide*, which melted at 87° after being collected and washed with ether (Found: Br, 49·1. $C_{10}H_{10}O_2Br_2$ requires Br, 49·7%). The dibromide obtained by brominating safrole in chloroform and other organic solvents was a liquid which could not be induced to crystallise.

*The Action of Bromine Water on* iso*Safrole, Eugenol, and* iso*Eugenol.*—*iso*Safrole behaved very similarly to safrole, the proportions of bromine functioning in the formation of bromohydrin and hydrobromic acid being 72·8% at 90° and 67·0% at the ordinary temperature.

Upon treating *iso*safrole bromohydrin (50 g.; compare *Ber.*, 1905, **38**, 3469) with concentrated ammonia, in the way described for styrene bromohydrin, it yielded a viscid oil (6 g.), which appeared to consist of β-*amino-α-hydroxydihydro*iso*safrole*,

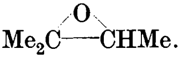
$$CH_2O_2{:}C_6H_3{\cdot}CH(OH){\cdot}CHMe{\cdot}NH_2.$$

The *hydrochloride* separated from acetone in colourless needles, m. p. 154° (Found : Cl, 15·2. $C_{10}H_{13}O_3N,HCl$ requires Cl, 15·3%).

Eugenol and *iso*eugenol yielded indefinite tarry products when treated with bromine water, even when the mixtures were cooled in ice-water; this result is probably to be associated with the phenolic character of these ethers.

*The Action of Bromine Water on Amylene.*—The commercial amylene used in this work consisted mainly of trimethylethylene (b. p. 37°); 10% distilled below 34°, 77% between 34° and 40°, and 8% between 40° and 50°. The crude amylene (10 g.) was emulsified with water (200 c.c.) at the ordinary temperature and treated gradually, in the usual way, with a solution of bromine (22·9 g.; 1 mol.) in water (300 c.c.) containing dissolved potassium bromide (20 g.). A permanent yellow tinge was produced after the addition of 73·3% (220 c.c.) of this solution; so that 26·7% of the hydrocarbon mixture appeared to be unaffected by bromine water. Titration disclosed that 78·9% of the added bromine had reacted to form bromohydrin and hydrobromic acid. The product was isolated, by extraction with ether, as a limpid, pale yellow liquid (18 g.) with an irritating odour. After three successive fractional distillations under diminished pressure, this material gave a 50% yield of a colourless liquid which distilled completely at 45—46°/12 mm. and appeared to be identical with the amylene bromohydrin (γ-bromo-β-hydroxy-β-methylbutane) prepared by Mokiewsky (*J. Russ. Phys. Chem. Soc.*, 1898, **30**, 900) (Found: Br, 48·1. Calc. for $C_5H_{11}OBr$ : Br, 47·9%).

*γ-Amino-β-hydroxy-β-methylbutane*, $OH{\cdot}CMe_2{\cdot}CHMe{\cdot}NH_2$.—Upon shaking amylene bromohydrin (40 g.), prepared as above, for 24 hours in a stoppered bottle with concentrated ammonia (200 g.) the oily layer gradually diminished but did not disappear completely. Excess of ammonia was allowed to evaporate in an open dish, and the oil was extracted with ether; when recovered, it had $n_D^{18^\circ}$ 1·5043 and contained no bromohydrin or base. The aqueous layer, when evaporated to small bulk, basified, and extracted with ether, yielded a brown oil (11·5 g.) with a strong basic odour; the bulk of this product distilled at 60—62°/16 mm. as a pale yellow oil. The *chloroplatinate* separated from a strong aqueous solution in orange prisms, m. p. 186° (decomp.) [Found: Pt, 31·8. $(C_5H_{13}ON)_2,H_2PtCl_6$ requires Pt, 31·7%]. The *benzoyl* derivative was obtained as an oil, and the p-*nitrobenzoyl* derivative melted indefinitely at about 65°. The d-α-*bromocamphorsulphonate* crystallised from acetone in felted masses of colourless needles, m. p. 170°; systematic fractional crystallisation from this solvent yielded fractions with values of $[\alpha]_D$ ranging from +61° to +66° in dilute aqueous solution, but no appreciable optical rotation was discernible in dilute alcoholic solutions of specimens of the free base regenerated from such fractions. The d-*camphorsulphonate* separated from ethyl acetate in glistening plates, m. p. 144°; fractional crystallisation of this salt also failed to yield an indication of the optical resolution of the base.

*Trimethylethylene Oxide* (βγ-oxy-β-methylbutane),  $Me_2C\overset{O}{\text{——}}CHMe$. —Upon heating amylene bromohydrin with potassium hydroxide dissolved in methyl or ethyl alcohol, it proved impracticable to separate the resulting trimethylethylene oxide from the solvent. Accordingly, the bromohydrin (200 g.) was added to potassium hydroxide (70 g.) dissolved in water (500 c.c.), the mixture being heated for ½ hour on the water-bath under reflux, with frequent shaking. After the upper oily layer had been separated, the aqueous liquid was distilled until no more oil passed over; upon adding the distillate to the oily layer, drying the mixture with sodium sulphate, and distilling it, the whole (53 g.) passed over at 74—78°. From this result, taken in conjunction with the observed values $d_{4^\circ}^{20^\circ}$ 0·8277, $d_{4^\circ}^{0^\circ}$ 0·8288, and $n_D^{18^\circ}$ 1·3896, the product appeared to be identical with trimethylethylene oxide described by Eltekow (*J. Russ. Phys. Chem. Soc.*, 1882, **14**, 361).

*Methyl* iso*Propyl Ketone*, $CHMe_2{\cdot}COMe$.—Heat was evolved upon adding trimethylethylene oxide to dilute sulphuric acid, and the product which was isolated after the mixture had been boiled for 2 hours under reflux consisted of a mixture of methyl *iso*propyl ketone and the corresponding glycol. The ketone was prepared in better yield (10 g.) by heating amylene bromohydrin (25 g.) with litharge (50 g.) and lead chloride (10 g.) at 200° for 7 hours in a sealed tube; it was also formed by heating the bromohydrin with water at 100° (compare *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 287).

*The Action of Bromine Water on* dl-$\Delta^3$-*Menthene.*—We are indebted to Dr. G. J. Robertson, of this College, for the particulars of a method devised by him for preparing *dl*-$\Delta^3$-menthene (compare Milobedzki and Kolitowska, *Roczniki Chem.*, 1926, **6**, 67):

*dl*-Menthol (31·2 g.) was added gradually to phosphorus trichloride (27·5 g.; 1 mol.), the container being cooled in water. The clear liquid was then heated slowly to 80° and kept at that temperature for about an hour, until the evolution of hydrogen chloride had practically ceased. The product was poured into ice-water, and the oil was extracted with ether, washed with water, and dried over sodium sulphate. After two fractional distillations under diminished pressure, *dl*-$\Delta^3$-menthene,* b. p. 60—62°/15 mm., was obtained in good yield (23 g.).

*dl*-$\Delta^3$-Menthene (10 g.), emulsified with ice-water (250 g.) by vigorous shaking in a stout glass bottle, was treated gradually in the usual way with bromine (11·6 g.; 1 mol.) dissolved in an aqueous solution (150 c.c.) of potassium bromide (10 g.). The bromine was decolorised at once, and the calculated amount was readily absorbed; 62·9% was found by titration to have reacted in the formation of hydrobromic acid and bromohydrin. The product was isolated by extraction with ether as an amber-coloured oil (16 g.), having $n_D^{13°}$ 1·5111; it decomposed when submitted to vacuum distillation (Found: Br, 42·6. A mixture of 62·9% $C_{10}H_{19}OBr$ and 37·1% $C_{10}H_{18}Br_2$ requires Br, 42·5%). The utilisation of this product as a source of substances of interest in the chemistry of terpenes is under investigation.

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