188. *Bromopiperitone.*

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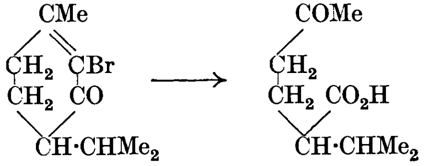
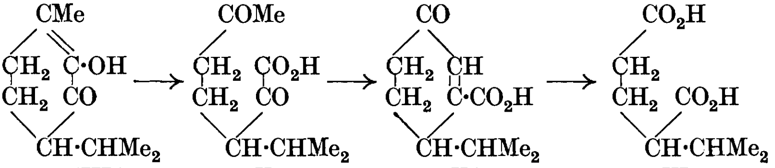
It was shown by Wallach and Hallstein (*Annalen*, 1918, **414**, 287) that when the liquid dibromide, prepared by the bromination of piperitone in acetic acid solution, was shaken with dilute potassium hydroxide solution, a crystalline monobromide, $C_{10}H_{15}OBr$, m. p. 42—43°, was formed. This bromide behaved in a somewhat remarkable manner on oxidation with potassium permanganate in alkaline solution, since it gave a keto-acid, $C_{10}H_{14}O_3$, m. p. 105—106°. Wallach and Hallstein left undetermined the constitutions of both the bromide and the keto-acid, although they suggested that the former was probably 2-bromo-Δ^1-*p*-menthen-3-one (I). We have now found this to be correct, since on oxidation with potassium permanganate in acetone solution γ-acetyl-α-*iso*propylbutyric acid (II) is obtained in excellent yield.

(I.)



(II.)

The keto acid, $C_{10}H_{14}O_3$, is undoubtedly identical with the acid having this composition which was obtained by Semmler and McKenzie (*Ber.*, 1906, **39**, 1158; compare Cusmano, *Gazzetta*, 1923, **53**, i, 158) by the oxidation of diosphenol (III) and to which they assigned the structure (V), the primary product (IV) of the oxidation undergoing cyclisation with loss of water.



(III.) (IV.) (V.) (VI.)

The identity of the acid was proved by the preparation of the oxime, which melted, as stated by Semmler and McKenzie, at 182°, whilst direct proof of its constitution was furnished by its oxidation to α-*iso*propylglutaric acid (VI).

These results are adequately explained if it is assumed that whereas in acetone solution the oxidation of the bromide proceeds normally, in alkaline solution diosphenol is first formed and then undergoes degradation in the manner observed by Semmler and McKenzie. The tendency for dibromopiperitone to pass into the monobromide and into diosphenol accounts probably for the poor yield of thymol which was obtained when it was treated with bases (Read, Watters, Robertson, and Hughesdon, J., 1929, 2071).

EXPERIMENTAL.

Bromopiperitone, m. p. 43°, was prepared as described by Wallach and Hallstein (*loc. cit.*) (Found : Br, 35·2. Calc. : Br, 34·6%). In order to obtain a good yield of the bromo-ketone it is essential that the piperitone used in its preparation should be optically inactive.

Oxidation of Bromopiperitone with Potassium Permanganate.—(1) *In acetone.* To a well-cooled solution of the bromo-ketone (11 g.) in acetone (310 c.c.), potassium permanganate (17·7 g.) was gradually added. The manganese dioxide sludge was washed with acetone to remove unchanged bromo-ketone and extracted with hot water. The aqueous alkaline extract was concentrated in a current of carbon dioxide, acidified, and extracted with ether. The oil (5·6 g.) remaining after the removal of the solvent was dissolved in methyl alcohol and mixed with semicarbazide acetate. The semicarbazone (7 g.) obtained, after crystallisation from methyl alcohol, had m. p. 156° both alone and after admixture with γ-acetyl-α-*iso*propylbutyric acid semicarbazone (Found : C, 52·3; H, 8·2. Calc. : C, 52·4; H, 8·3%). On hydrolysis with dilute sulphuric acid the semicarbazone gave γ-acetyl-α-*iso*propylbutyric acid, m. p. 42° (alone and after admixture with an authentic specimen).

(2) *In alkaline solution.* Bromopiperitone (10 g.) was oxidised

in sodium carbonate solution with potassium permanganate under the conditions used by Wallach and Hallstein (*loc. cit.*). 6-*iso*Propyl-Δ^1-*cyclo*hexen-3-one-1-carboxylic acid, obtained in excellent yield, had m. p. 104—105° after crystallisation from hot water (Found : C, 66·2; H, 7·9. Calc. : C, 65·9; H, 7·7%). The oxime, after recrystallisation from methyl alcohol, decomposed at 182—183° (Found : C, 61·2; H, 7·5. Calc. : C, 60·9; H, 7·6%). We were unable to confirm the higher m. p. 190°, recorded by Cusmano (*loc. cit.*). The semicarbazone decomposed, as stated by Wallach and Hallstein, at 225° (Found : C, 54·8; H, 7·0. Calc. : C, 55·2; H, 7·2%). The keto-acid is not attacked by sodium hypobromite solution and on oxidation with dilute nitric acid undergoes complete degradation to oxalic acid. When, however, it was oxidised with potassium permanganate in alkaline solution at 0°, α-*iso*propylglutaric acid, m. p. 95°, was obtained, identified by comparison with a specimen prepared from *dl*-piperitone.

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