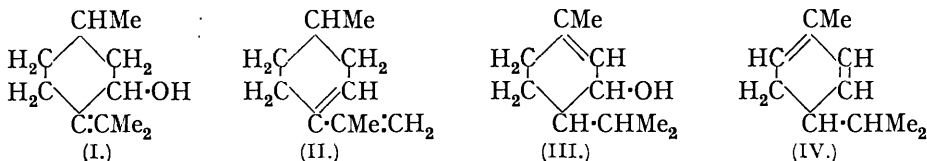


63. *d*- $\Delta^{3,8(9)}$ -*p*-Menthadiene from *d*-Pulegone.

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CURRENT investigations in the carvone and menthone series have shown that  $\alpha\beta$ -unsaturated alicyclic ketones are often reduced only with difficulty by the method of Ponndorf (*Z. angew. Chem.*, 1926, **39**, 138), and, further, that the resulting  $\alpha\beta$ -unsaturated alcohols sometimes undergo ready dehydration, yielding terpenes. The work now described shows that both of these conditions hold for pulegone. No pulegol was found, the sole product of the reaction being a terpene: this yielded  $\beta$ -methyladipic acid upon oxidation, and in its physical and chemical properties resembled closely *d*- $\Delta^{3,8(9)}$ -*p*-menthadiene (II) described by Perkin and his collaborators (J., 1906, **89**, 848; 1911, **99**, 537). The high rotatory power,  $[\alpha]_D^{14.2} + 140.6^\circ$ , of the terpene from *d*-pulegone confirms Perkin's supposition (*loc. cit.*, p. 538) that the specimens prepared from ethyl *d*- $\Delta^1$ -tetrahydro-*p*-toluate had racemised to some extent.

The mode of dehydration of the intervening pulegol (I) is of particular interest, since it is a  $\gamma$ -elimination analogous to the arresting dehydration of piperitol (III) to  $\alpha$ -phellandrene (IV) (J., 1930, 2773; and later unpublished observations):



It seemed possible that the above terpene might be identical with the supposedly new terpene obtained by the action of 50% sulphuric acid on citronellal (Horiuchi, *Mem. Coll. Sci. Kyoto*, 1928, **11**, No. 3, 176), but this idea derived no support from a comparison of the observed physical constants.

*d*-Pulegone (80 g.;  $[\alpha]_D^{15} + 23.60^\circ$ ) reacted only slowly with aluminium isopropoxide in dry isopropyl alcohol (cf. Ponndorf, *loc. cit.*). The product, apart from unchanged ketone, distilled at  $79\text{--}93^\circ/13$  mm. (24.1 g.); this fraction yielded no ester when treated with benzoyl chloride in dry pyridine. After extraction with hot aqueous sodium bisulphite solution in presence of alcohol, the residual terpene (10.2 g.) had b. p.  $70\text{--}72^\circ/13$  mm.,  $n_D^{17} 1.4961$ ,  $\alpha_D^{15} (1\text{-dcm. tube}) + 118.3^\circ$ ,  $d_4^{17} 0.8615$ ; when further purified by repeated distillation from metallic sodium, it had b. p.  $69^\circ/14$  mm.,  $n_D^{14.2} 1.4966$ ,  $d_4^{14.2} 0.8585$ ,  $[R_L]_D 46.37$  (calc., 45.24; exaltation, 1.13),  $\alpha_D^{14.2} + 120.7^\circ$ ,  $[\alpha]_D^{14.2} + 140.6^\circ$ . No solid derivatives were obtained with bromine or hydrogen chloride; the nitrosochloride and nitrosite were oils; titration with bromine in dry carbon tetrachloride showed addition of 1 mol., followed by substitution (Perkin, *loc. cit.*).

Since oxidation with 1% ice-cold potassium permanganate in aqueous solution was inconclusive, an ice-cooled solution of the terpene (11.6 g.) in acetone (120 c.c.) was treated gradually (5 hours) with powdered potassium permanganate (27.8 g.). The collected precipitate

was freed from terpene and acetone by steam distillation, and extracted repeatedly with boiling water. The aqueous solution was concentrated, with passage of carbon dioxide; its ethereal extract then gave a brown oil smelling of acetic acid, and this crystallised partly when kept in a vacuum desiccator over potassium hydroxide. The solid (1.3 g.) was separated on porous plate and boiled with pure aniline (2 c.c.); the crystalline product upon recrystallisation from warm alcohol yielded a microcrystalline powder, m. p. 196° (Found: C, 73.1; H, 7.1. Calc. for  $C_{19}H_{22}O_2N_2$ : C, 73.5; H, 7.2%). According to Markownikow (*Annalen*, 1904, 336, 301), the dianilide of optically active  $\beta$ -methyladipic acid melts at 198—200°.

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