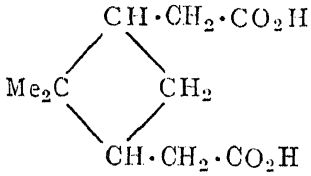
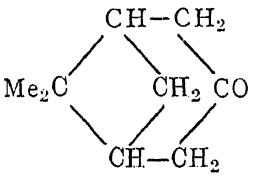
## The Synthesis of *trans sym.*-Homopinic Acid.

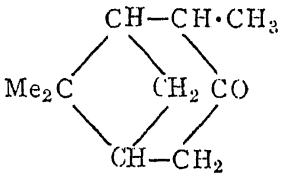
THE Synthesis of *trans sym.*-Homopinic Acid (I) has now been effected in the course of our attempts to synthesise *iso*nopinone (II) and pinocamphone (III).



(I)

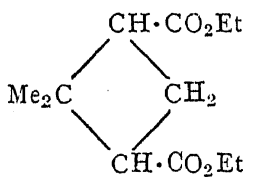


(II)

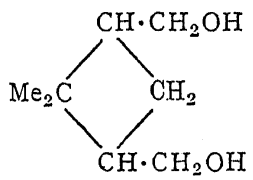


(III)

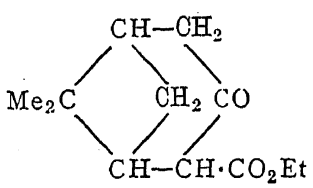
Ostling[1] reduced *cis*-diethyl norpinate (IV) by means of sodium and absolute alcohol and obtained the glycol (V), b.p. 150–52°/15 mm.; but no details of his experiments and yields are available. It has now been found that reduction with sodium and absolute alcohol at 140° (Ostling's condition) gives the glycol in about 10–20 per cent. yield together with some by-products, whereas by adding sodium all at once to the ester in absolute alcohol (moisture less than 0·01 per cent.) obtained according to the method of Manske[2] the glycol is obtained in about 75 per cent. yield with no by-products. The significant observation is made that both the *cis*- and *trans*-esters furnish the same glycol, b.p. 125–28°/4 mm. (identical with that of Ostling) which has now been proved to be of the *trans*-configuration by oxidation with permanganate to *trans*-norpinic acid. With $PBr_3$ in dry chloroform solution the glycol gives the corresponding dibromide, b.p. 100–102°/4 mm. with a very characteristic terpene like odour. This on refluxing with alcoholic sodium cyanide for 12 hours gives the corresponding dinitrile, b.p. 142–45°/6 mm., which on hydrolysis with boiling 20 per cent. potash yields *trans sym.*-homopinic acid, m.p. 120–21° (dianilide, m.p. 219–20°). This acid is remarkably stable, distilling unchanged over barium hydroxide. With acetic anhydride under the usual conditions (Blanc) it does not give a ketone but only the double anhydride[3] which with water gives the acid (I). The diethyl ester of (I), b.p. 131–32°/4 mm. gives on prolonged boiling with sodium in xylene solution traces of a product exhibiting properties of a $\beta$-ketonic ester. The cyclisation does not proceed in the desired direction to yield the ester (VI) obviously due to the acid (I) possessing the *trans*-configuration. A study of the model also shows that the formation of the bi*cyclo*-(1 : 1 : 3)-heptane ring by the locking of the *trans* valencies in 1 : 3-positions of *cyclo*butane is not possible.[4]



(IV)

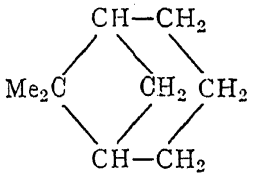


(V)

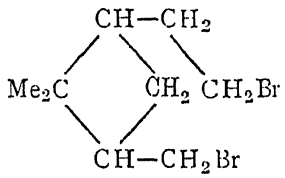


(VI)

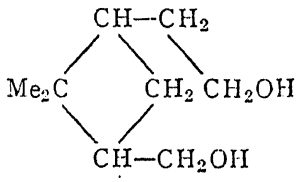
In the light of the results obtained in this investigation, Ostling's failure (*loc. cit.*) in getting nopinane (VII) from the dibromide (VIII), can reasonably be explained as due to his glycol (IX) being of the *trans* form



(VII)



(VIII)



(IX)

the change of configuration occurring during the reduction of pinic ester with sodium and alcohol. Work on the synthesis of *cis-sym.*-homopinic acid is in progress.

This work was done with experimental collaboration of Messrs. D. K. Sankaran and V. K. Subramanian.

P. C. GUHA.
K. GANAPATHI.

Department of Organic Chemistry,
Indian Institute of Science,
Bangalore,
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