The Formation of o-*Xylene through* 4 : 5-*Dimethylene*cyclo*hexene.*

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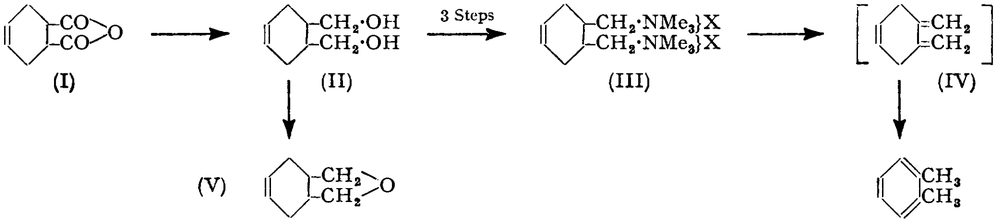
o-Xylene is obtained when 4 : 5-dimethylene*cyclo*hexene is the formal product of the Hofmann degradation of the dimethohydroxide of 4 : 5-di-(dimethylaminomethyl)*cyclo*hexene.

The aim of this investigation was to isolate 4 : 5-dimethylene*cyclo*hexene (IV) and determine the heat of its conversion into *o*-xylene. In fact, the conversion was, from the practical point of view, spontaneous.

Reduction of *cis-cyclo*hexene-4 : 5-dicarboxylic anhydride (I) or of methyl *cis-cyclo*hexene-4 : 5-dicarboxylate with lithium aluminium hydride in ethereal solution gave *cis*-4 : 5-bishydroxymethyl*cyclo*hexene (II). This, following the general procedure of Haggis and Owen (*J.*, 1953, 389), was converted by the action of toluene-*p*-sulphonyl chloride in pyridine solution into the ditoluene-*p*-sulphonate, which with sodium iodide in acetone gave the di-iodide. Combination of this compound with two mols. of trimethylamine gave the quaternary iodide (III; X = I) and, when the dihydroxide (III; X = OH) was heated, *o*-xylene was formed. For identification it was converted into 3 : 4-dimethylbenzenesulphonamide.



An attempt to obtain dimethylene*cyclo*hexene by the Tschugaeff xanthate process was abortive, probably owing to the difficulty of forming the disodium derivative of the diol. 4 : 5-Bishydroxymethyl*cyclo*hexene readily passed into the corresponding cyclic ether, *cis*-2 : 3 : 4 : 5 : 1′ : 4′-hexahydro-3 : 4-benzofuran (V), for example, on distillation, or in presence of dilute sulphuric acid. The cyclic ether was formed during the abovementioned preparation of the ditoluene-*p*-sulphonate of the diol.

Experimental

Methyl cis-cyclo*Hexene*-4 : 5-*dicarboxylate.*—A mixture of *cis-cyclo*hexene-4 : 5-dicarboxylic anhydride (48 g.), absolute methyl alcohol (500 c.c.), and concentrated sulphuric acid (20 c.c.) was boiled under reflux for 7 hr. Most of the alcohol was distilled off and the remaining liquid was poured into twice its volume of water and then neutralised with solid sodium hydrogen carbonate. The oil which separated was extracted with ether. The ethereal extracts were dried ($MgSO_4$), and the ether was distilled off. The ester (56·5 g., 90%) had b. p. 116—117°/5·5 mm., n_D^{25} 1·4726. This procedure is less complicated than that described by Cope and Herrick (*J. Amer. Chem. Soc.*, 1950, **72**, 983).

cis-4 : 5-*Bishydroxymethyl*cyclo*hexene.*—(*a*) A solution was made of lithium aluminium hydride (7·5 g., 1·2 mols.) in anhydrous ether (500 c.c.). *cis-cyclo*Hexene-4 : 5-dicarboxylic anhydride (25 g.. 1 mol.) was added by extraction from a Soxhlet thimble. The mixture was thereafter boiled for an hour. Water and 5% (v/v) sulphuric acid were added until the mixture cleared. The ethereal layer, together with three ethereal extracts of the aqueous layer, was dried (K_2CO_3) and the ether distilled off. The pale-yellow viscous residue was distilled and 10 g. of colourless viscous liquid, b. p. 169—170°/11 mm., n_D^{25} 1·5092, were obtained. A further 4 g. of product were obtained by exhaustive ether-extraction of the aqueous layer. The total yield of *diol* was 14 g. (60%) (Found : C, 67·6; H, 10·2. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%).

(*b*) Methyl *cis-cyclo*hexene-4 : 5-dicarboxylate (55 g., 1 mol.) was added dropwise to a mixture of lithium aluminium hydride (13·5 g., 1·3 mols.) in anhydrous ether (400 c.c.). Water and then dilute hydrochloric acid were added and the ethereal layer separated. The aqueous layer was extracted continuously for 24 hr. with ether. The combined ethereal extracts after being dried (K_2CO_3) were evaporated and the residue was distilled. The diol (30 g., 76%) had b. p. 168–170°/11 mm.

Ditoluene-p-*sulphonate of* cis-4 : 5-*Bishydroxymethyl*cyclo*hexene.*—An ice-cold solution of toluene-*p*-sulphonyl chloride (110 g.) in dry pyridine (350 c.c.) was added gradually to a cooled solution of bishydroxymethyl*cyclo*hexene (37·7 g.) in dry pyridine (100 c.c.). Twelve hours later the mixture was poured into an excess of dilute hydrochloric acid. An oil separated and solidified. The whole was extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution, then with water, and finally dried ($MgSO_4$). Removal of the chloroform by distillation gave an oil, which from methanol gave needles (23 g., 19%), m. p. 94·5° (Found : C, 58·7; H, 5·5; S, 14·6. $C_{22}H_{26}O_6S_2$ requires C, 58·6; H, 5·8; S, 14·2%).

cis-4 : 5-*Bisiodomethyl*cyclo*hexene.*—A mixture of the sulphonic *ester* (23 g.) and sodium iodide (33 g.) in dry acetone (360 c.c.) was boiled under reflux for 16 hr. The precipitated sodium toluene-*p*-sulphonate was filtered off (yield 97%) and the acetone was removed in a vacuum. Addition of water gave a heavy oil, which was dissolved in chloroform. The solution was washed with aqueous sodium thiosulphate and then with water. The dried ($MgSO_4$) solution was freed from chloroform and gave the di-iodo-compound (17·5 g., 95%).

cis-4 : 5-*Di*(*dimethylaminomethyl*)cyclo*hexene Dimethiodide.*—A solution in dry acetone (50 c.c.) of the above di-iodo-compound (17·5 g.) was added dropwise to a gently boiling solution of trimethylamine in acetone. The mixture was boiled under reflux for 3 hr., and the acetone was then distilled off. The residue, after treatment with dry ether, gave a solid *dimethiodide,* which after crystallisation from ethanol had m. p. 158—160° (decomp.) (0·8 g.) (Found : I, 52·6; 52·2. $C_{14}H_{30}N_2I_2$ requires I, 52·9%). Some unchanged di-iodo-compound (14 g.) was recovered. When the bisiodomethyl*cyclo*hexene (1·5 g.) was heated with trimethylamine (2 g.) in dry acetone (6 c.c.) at 100° for 2 hr. (sealed glass tube), 0·8 g. (40%) of quaternary iodide was obtained.

Formation of o-*Xylene.*—The quaternary di-iodide (21 g.) was shaken for 2 hr. with moist silver oxide prepared from silver nitrate (40 g.). The mixture was filtered and the residue well washed with water. The washings and the filtrate were combined and distilled. When about 20 c.c. of liquid remained, an oil began to distil. When no more appeared the oil was separated, dried ($MgSO_4$), and distilled from sodium. *o*-Xylene (2 g.), b. p. 143°, n_D^{25} 1·5017, was obtained.

The *o*-xylene was converted into 3 : 4-dimethylbenzenesulphonamide by the method of Huntress and Autenrieth (*J. Amer. Chem. Soc.*, 1941, **63**, 3446) and Huntress and Carten (*ibid.*, 1940, **62**, 511). The sulphonamide crystallised from ethanol in plates, m. p. and mixed m. p. 144—145°.

cis-2 : 3 : 4 : 5 : 1′ : 4′-*Hexahydro*-3 : 4-*benzofuran.*—A mixture of bishydroxymethyl*cyclo*hexene (20 g.) and naphthalene-2-sulphonic acid (3 g.) was distilled. The distillate was saturated with sodium chloride, the layers were separated, and the oil was again heated with the sulphonic acid. Fractionation of the organic material obtained gave 3·8 g. of the *benzofuran*, b. p. 178–179°, n_D^{25} 1·4888 (Found : C, 77·6; H, 9·6. $C_8H_{12}O$ requires C, 77·4; H, 9·7%).

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