# 74. *Alicyclic Glycols. Part I. Toluene*-p-*sulphonyl and Methanesulphonyl Derivatives of* cyclo*Hexane*-1 : 2-*diol.*

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The *monotoluene*-p-*sulphonates* and *monomethanesulphonates* of *cis*- and *trans-cyclo*hexane-1 : 2-diol have been prepared. The *trans*-compounds are very much more reactive than the *cis*-, and with alkali, sodium iodide, or lithium chloride, give *cyclo*hexene oxide, *trans*-2-iodo*cyclo*hexanol, or *trans*-2-chloro*cyclo*hexanol, respectively. The *cis*-compounds, with alkali, give *cyclo*hexanone, and, with the aqueous reagent, *cis-cyclo*hexane-1 : 2-diol, and react only slowly with sodium iodide or lithium chloride. Replacement of the sulphonyloxy-group in the *trans*-series results in overall retention of configuration, probably as a result of two successive inversions, whilst in the *cis*-series, where formation of an intermediate cyclic compound is less likely, a single inversion of configuration occurs. The reactions are compared with those involving replacement of toluene-*p*-sulphonyl groups in the carbohydrate field.

SIMPLE esters of sulphonic acids, such as the alkyl toluene-*p*-sulphonates, on treatment with alcoholic alkali or alkoxide, usually give ethers :

$$\mathrm{R{\cdot}O{\cdot}Ts + R'{\cdot}ONa \longrightarrow R{\cdot}O{\cdot}R' + Ts{\cdot}ONa\ (Ts = \textit{p}\text{-}CH_3{\cdot}C_6H_4{\cdot}SO_2)}$$

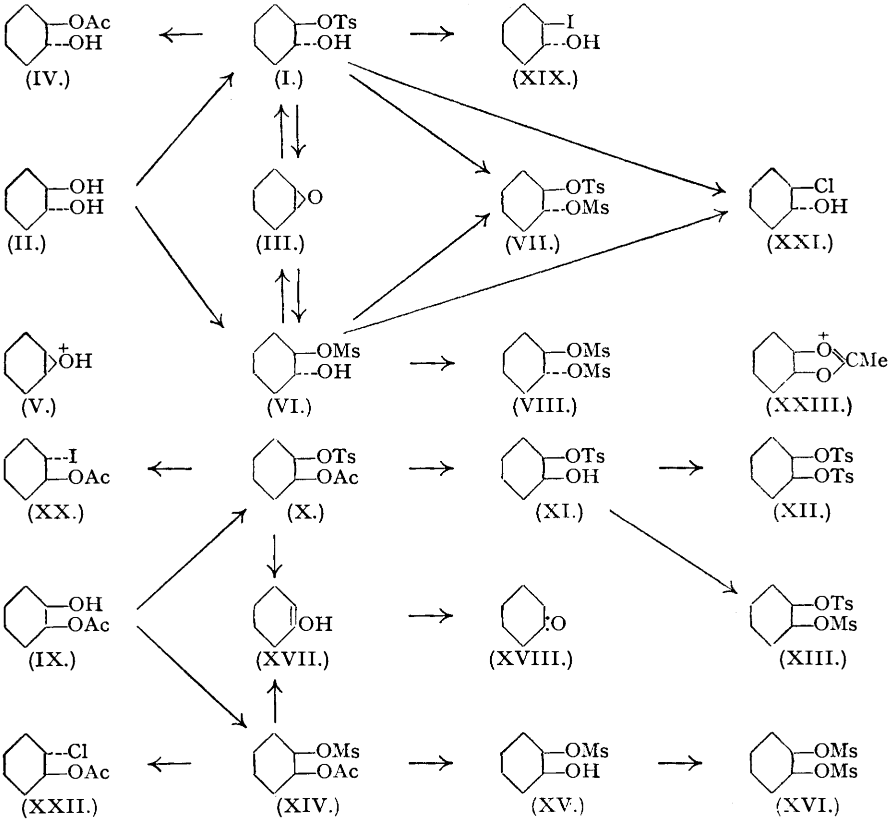
although olefins also are sometimes formed, by intramolecular loss of toluene-*p*-sulphonic acid, particularly when the derivative is of a secondary alcohol (Ferns and Lapworth, *J.*, 1912, **101**, 273; Phillips, *J.*, 1923, **123**, 44). In the alicyclic series, Hückel and his co-workers (*Annalen*, 1930, **477**, 143; 1937, **533**, 1) have studied the behaviour of a few simple monotoluene-*p*-sulphonates. *cyclo*Hexyl toluene-*p*-sulphonate, for example, gave only *cyclo*hexene when treated with dilute acids or alkalis, or with sodium acetate, the tendency towards olefin-formation entirely preventing substitution. The toluene-*p*-sulphonates of menthol and β-decalol also gave considerable amounts of the corresponding olefins, menth-3-ene and octalin respectively, when boiled with alcoholic potassium acetate, though small amounts of the ethyl ethers and acetates were also produced.

With monotoluene-*p*-sulphonates of polyhydroxy-compounds it is clear that the formation of ethers can also occur by intramolecular reaction, to yield anhydro-derivatives containing oxide rings; the α-toluene-*p*-sulphonate of glycerol, for example, on treatment with sodium methoxide gives 2 : 3-epoxypropanol (Fischer and Sowden, *J. Amer. Chem. Soc.*, 1942, **64**, 1291). if, however, the polyhydroxy-compound is cyclic, the stereochemical disposition of the toluene-*p*-sulphonyl group with reference to the hydroxyl group will evidently influence the tendency for such oxide-formation to occur. In the carbohydrate field, in which very extensive investigations of this nature have been carried out (cf. Peat, " Advances in Carbohydrate Chemistry ", Vol. II, p. 38) it has been firmly established that the formation of a 1 : 2-anhydro-ring is accompanied by inversion of configuration at the carbon atom originally carrying the toluene-*p*-sulphonyl group ; consequently, for anhydro-ring formation of this type to occur it is necessary that there should be a *trans*-disposition between the toluene-*p*-sulphonyl and the adjacent hydroxyl (or potential hydroxyl) group. If this condition is not satisfied, then (unless some other type of oxide-ring formation is possible) the toluene-*p*-sulphonyl group is usually very resistant towards alkaline reagents, though under vigorous conditions it may undergo hydrolysis or ammonolysis without inversion.

Comparatively little is yet known about the behaviour of esters of methanesulphonic acid under similar conditions, but from the evidence so far available it appears that the above conclusions apply also to the methanesulphonyl derivatives of carbohydrates.

There is practically no information about the behaviour of analogous toluene-*p*-sulphonyl and methanesulphonyl derivatives of polyhydroxy-alicyclic compounds. Amongst the simple alicyclic diols, only one monotoluene-*p*-sulphonate (I) has been described. This was obtained by Criegee and Stanger (*Ber.*, 1936, **69**, 2753) by partial toluene-*p*-sulphonation of *trans-cyclo*hexane-1 : 2-diol (II) and also by scission of *cyclo*hexene oxide (III) with toluene-*p*-sulphonic acid, a reaction accompanied by the expected inversion ; their attempts to prepare the *cis*-monotoluene-*p*-sulphonate from the *cis*-diol were unsuccessful. On treatment of the *trans*-monotoluene-*p*-sulphonate (I) with potassium acetate in methanol, they obtained the *trans*-monoacetate (IV), and since a direct replacement of toluene-*p*-sulphonyl by acetyl would be expected to give the *cis*-monoacetate, by a single inversion, they postulated the intermediate formation of *cyclo*hexene oxide (III), which with the liberated acetic acid was supposed to undergo the usual ring-opening to give the *trans*-monoacetate ; an appreciable amount of the oxide was in fact detected in the reaction mixture. The more recent papers by Winstein and his co-workers

(*J. Amer. Chem. Soc.*, 1942, **64**, 2780, 2787, 2791, 2792, 2796; 1943, **65**, 613, 2196) have dealt in considerable detail with the influence of a neighbouring *trans*-group on reactivity, and have provided a comprehensive explanation for the inversion or non-inversion accompanying the replacement of a group in such compounds under various conditions. The results observed by Criegee and Stanger can thus be explained by postulating the intermediate formation of (V), rather than of *cyclo*hexene oxide itself. It was nevertheless probable that the *trans*-monotoluene-*p*-sulphonate could be converted into the oxide under appropriate conditions, and, as part of a general investigation on alicyclic diols, we have prepared the *cis*- and *trans*-forms of the monotoluene-*p*-sulphonyl and of the monomethanesulphonyl derivatives of *cyclo*hexane-1 : 2-diol, and have studied their properties.



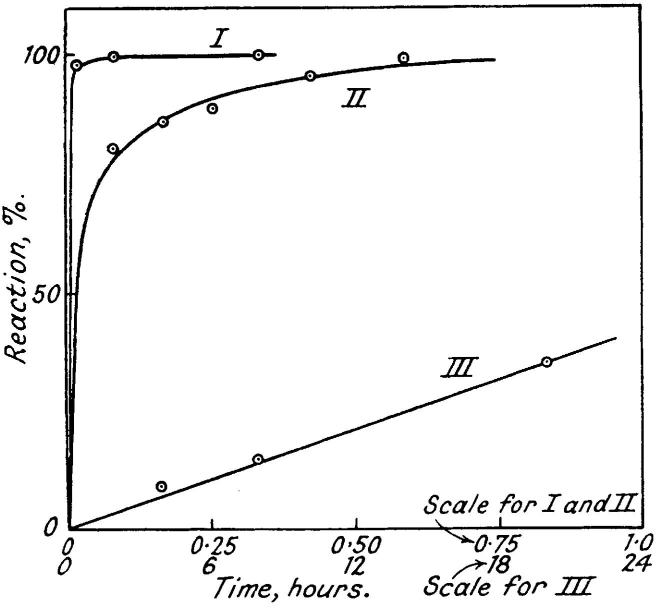
The trans-*monomethanesulphonate* (VI) was obtained in high yield by reaction of methanesulphonic acid with *cyclo*hexene oxide, the ring-opening being accompanied by the expected inversion. The product was identical with that isolated, in poor yield, by the action of 1 mol. of methanesulphonyl chloride on the *trans*-diol in pyridine solution, and with toluene-*p*-sulphonyl chloride it gave the trans-*toluene*-p-*sulphonate-methanesulphonate* (VII), also obtained by methanesulphonation of the known *trans*-monotoluene-*p*-sulphonate (I). With excess of methanesulphonyl chloride, the *trans*-diol gave the trans-*bismethanesulphonate* (VIII).

The bistoluene-*p*-sulphonate of *cis-cyclo*hexane-1 : 2-diol has already been described by Criegee and Stanger (*loc. cit.*), who reported that this diol, unlike the *trans*-isomer, could not be converted into a monotoluene-*p*-sulphonate by the use of 1 mol. of toluene-*p*-sulphonyl chloride. We have now succeeded in preparing this mono-derivative by an indirect route from the *cis*-monoacetate (IX), which on toluene-*p*-sulphonation yielded the cis-*toluene*-p-*sulphonate-acetate* (X). When this was treated with cold methanolic hydrogen chloride it was smoothly deacetylated to give the cis-*monotoluene*-p-*sulphonate* (XI) as a liquid, characterised by conversion into the *cis*-bistoluene-*p*-sulphonate (XII) and also by methanesulphonation to give the cis-*toluene*-p-*sulphonate-methanesulphonate* (XIII). Similarly, methanesulphonation of the *cis*-monoacetate

(IX) gave the cis-*methanesulphonate-acetate* (XIV), and thence, by deacetylation, the cis-*monomethanesulphonate* (XV); this was characterised by conversion into the cis-*bismethanesulphonate* (XVI), also obtained by direct methanesulphonation of the *cis*-diol.

Treatment of the *trans*-monotoluene-*p*-sulphonate (I) or the *trans*-monomethanesulphonate (VI) with cold methanolic sodium methoxide gave *cyclo*hexene oxide (III). On the other hand, similar reactions on the *cis*-toluene-*p*-sulphonate-acetate (X) and on the *cis*-methanesulphonate-acetate (XIV) gave *cyclo*hexanone (XVIII), evidently formed *via* its enol (XVII); clearly, therefore, the second general type of reaction, olefin-formation, can occur in this series when oxide-formation is not possible. There was also a very striking difference between the *cis*- and the *trans*- series in their rates of reaction with cold 0·1N-alcoholic alkali; oxide-formation from the *trans*-compounds was complete within a few minutes, whilst the production of *cyclo*hexanone from the *cis*-isomers proceeded very slowly under these conditions (see Figure). This difference in behaviour is akin to that observed by Bartlett (*J. Amer. Chem. Soc.*, 1935, **57**, 220) in the reactions of the *cis*- and *trans*-2-chloro*cyclo*hexanols with alkali. When the *trans*-monotoluene-*p*-sulphonate (I) was heated with aqueous alkali it gave *trans*-*cyclo*hexane-1 : 2-diol in 58% yield, together with some formyl*cyclo*pentane; *cyclo*hexene oxide was an evident intermediate in this reaction. The *cis*-toluene-*p*-sulphonate-acetate (X) under these conditions gave *cyclo*hexanone (64%) and the *cis*-diol (22%). The formation of *cis*-diol in the latter reaction is of interest, since it indicates that the toluene-*p*-sulphonyloxy-group can be replaced by hydroxyl *without inversion*; this has already been observed in the carbohydrate field, where, for example, 3-toluene-*p*-sulphonyl di*iso*propylidene glucose can be hydrolysed, though with considerable difficulty, into di*iso*propylidene glucose (Oldham and Robertson, *J.*, 1935, 685). In the carbohydrate examples, however, there does not appear to be any evidence of the occurrence of the elimination reaction, leading to the formation of ketones.

*Reaction of sulphonic esters of* cyclo*hexane*-1 : 2-*diol with alkali.*



I, trans-*Monomethanesulphonate*; II, trans-*monotoluene*-p-*sulphonate*; III, cis-*monotoluene*-p-*sulphonate*.

A reaction which has assumed considerable importance in carbohydrate chemistry, but which has only recently found application in other fields (see, *e.g.*, Ruzicka, Szpilfogel, and Jeger, *Helv. Chim. Acta*, 1946, **29**, 1520), is that which occurs between a primary toluene-*p*-sulphonyl group and sodium iodide, the toluene-*p*-sulphonyloxy-residue being replaced by iodine, with quantitative precipitation of sodium toluene-*p*-sulphonate. The diagnostic value of this reaction is the basis of the so-called " Oldham–Rutherford rule " (Oldham and Rutherford, *J. Amer. Chem. Soc.*, 1932, **54**, 366) since a secondary toluene-*p*-sulphonyl group was found to be unaffected by the reagent. Some exceptions to this generalisation have been reported (Bell, Friedmann, and Williamson, *J.*, 1937, 252; Tipson and Cretcher, *J. Org. Chem.*, 1943, **8**, 95; Ness, Hann, and Hudson, *J. Amer. Chem. Soc.*, 1944, **66**, 1901), and it now appears that a secondary toluene-*p*-sulphonyl group may be reactive towards sodium iodide if it is contiguous to one in a primary position; there are also a few instances (cf. Hockett *et al.*, *ibid.*, 1946, **68**, 930) of an isolated secondary toluene-*p*-sulphonyl group reacting with sodium iodide. According to Helferich and Gnüchtel (*Ber.*, 1938, **71**, 712) a secondary methanesulphonyl group is not so resistant.

Quite recently, Tipson, Clapp, and Cretcher (*J. Org. Chem.*, 1947, **12**, 133) have shown that the toluene-*p*-sulphonates of some secondary aliphatic alcohols, and of *cyclo*hexanol, borneol, and menthol, react with sodium iodide to form sodium toluene-*p*-sulphonate; evidently the secondary toluene-*p*-sulphonyl group in these compounds is considerably more reactive than a similar group in a carbohydrate molecule, although the other products of the reaction were not identified. It has now been found that the *trans*-monotoluene-*p*-sulphonate (I) reacts readily with sodium iodide in acetone solution at 85° to give, after 5 hours, a high yield of sodium toluene-*p*-sulphonate, and from the reaction products it was possible to isolate *trans*-2-iodo*cyclo*hexanol (XIX) as its 3 : 5-dinitrobenzoate m. p. 157°. Sodium methanesulphonate was also formed from the *trans*-monomethanesulphonate under similar conditions, though the yield of iodo*cyclo*hexanol was too low for characterisation; in both cases, unsaturated products, probably *cyclo*hexanone and *cyclo*hexadienes, were also produced. A much lower reactivity was observed with the *cis*-toluene-*p*-sulphonate-acetate (X), which required 15 hours at 100° to give 72% of sodium toluene-*p*-sulphonate; the resulting 2-iodo*cyclo*hexyl acetate (XX) was shown to be the *trans*-form by deacetylation to *trans*-2-iodo*cyclo*hexanol. A similarly low reactivity was also shown by the *cis*-methanesulphonate-acetate (XIV).

Experiments were also carried out on the replacement of toluene-*p*-sulphonyl and methanesulphonyl groups by chlorine, and it was found that the *trans*-monotoluene-*p*-sulphonate (I) and the *trans*-monomethanesulphonate (VI) reacted smoothly with alcoholic lithium chloride to give *trans*-2-chloro*cyclo*hexanol (XXI) in *ca.* 60% yield, the tendency for substitution, rather than elimination, being predominant, unlike the situation in the reactions with sodium iodide. The *cis*-methanesulphonate-acetate (XIV) reacted less readily to give *trans*-2-chloro*cyclo*hexyl acetate (XXII), identified by methanolysis with methanolic hydrogen chloride to *trans*-2-chloro*cyclo*hexanol.

In the *cis*-compounds, the replacement of the sulphonyloxy-group is clearly accompanied by inversion; the apparent non-occurrence of inversion in the *trans*-series is undoubtedly due to the intermediate formation, by one inversion, of a cyclic compound (V) or (XXIII) (cf. Winstein *et al.*, *loc. cit.*) followed by its scission, involving a second inversion, and consequent overall retention of configuration. Winstein and Buckles, (*J. Amer. Chem. Soc.*, 1942, **64**, 2780) have observed that *cis*-2-chloro*cyclo*hexyl acetate is unaffected by silver acetate under conditions in which the *trans*-isomer readily gives *trans*-1 : 2-diacetoxy*cyclo*hexane, and have implied that the low reactivity of the *cis*-derivative is due to its inability to form an intermediate ring-compound. This view is applicable also to our own observations on the much greater reactivity of the *trans*-methanesulphonates and *trans*-toluene-*p*-sulphonates towards alkali, sodium iodide, and lithium chloride.

## EXPERIMENTAL.

trans-cyclo*Hexane*-1 : 2-*diol*.—This was obtained by saponification of the *trans*-monoacetate, a by-product in the preparation of the monotoluene-*p*-sulphonate from *cyclo*hexene (cf. Criegee and Stanger, *loc. cit.*).

cis-cyclo*Hexane*-1 : 2-*diol*.—(i) A suspension of *cyclo*hexene (10 g.) in a solution of sodium chlorate (17 g.) in water (200 c.c.) containing osmium tetroxide (0·1 g.) was vigorously stirred for 9 hours at 50°. The cooled solution was then extracted twice with benzene to remove catalyst, and then evaporated to dryness. Extraction of the residue with boiling chloroform gave the *cis*-diol (6·5 g.), m. p. 98° after one recrystallisation from carbon tetrachloride. This method was used by Böeseken and Giffen (*Rec. Trav. chim.*, 1920, **39**, 183), but no yield was recorded.

(ii) A solution of potassium permanganate (40 g.) and magnesium sulphate (30 g., anhydrous) in water (800 c.c.) was added gradually to a vigorously stirred suspension of *cyclo*hexene (26 g.) in ethanol (600 c.c.) during 1·5 hours, the temperature being kept between −15° and −20°. After filtration, the solution was concentrated to small bulk, saturated with salt, and extracted with chloroform to yield the *cis*-diol (12 g., 33%), m. p. 98°. Markownikoff (*Annalen*, 1898, **302**, 21) obtained a yield of 18%.

*Derivatives of* trans-cyclo*Hexane*-1 : 2-*diol*.—Treatment of the diol with slight excess of methanesulphonyl chloride in pyridine solution for 12 hours at ordinary temperature gave the trans-*dimethanesulphonate*, which crystallised from methanol in needles, m. p. 135° (Found : C, 35·9; H, 6·0. $C_8H_{16}O_6S_2$ requires C, 35·3; H, 5·9%). Similar treatment of the *trans*-monotoluene-*p*-sulphonate, prepared by the method of Criegee and Stanger (*loc. cit.*), gave the trans-*toluene*-p-*sulphonate-methanesulphonate*, which crystallised from methanol in rosettes of needles, m. p. 108·5° (Found : C, 48·7; H, 6·0. $C_{14}H_{20}O_6S_2$ requires C, 48·3; H, 5·8%).

To a solution of *cyclo*hexene oxide (1·75 g.) in dry ether (25 c.c.) a solution of methanesulphonic acid

(1·75 g.) in ether (10 c.c.) was gradually added, with cooling. After an hour at 20°, removal of the solvent gave a quantitative yield of the trans-*monomethanesulphonate*, which crystallised from light petroleum (b. p. 80—100°) in fine needles, m. p. 79° (Found : C, 43·3; H, 7·4. $C_7H_{14}O_4S$ requires C, 43·3; H, 7·3%). With toluene-*p*-sulphonyl chloride in pyridine solution, this readily gave the *trans*-toluene-*p*-sulphonate-methanesulphonate, m. p. 108·5°, identical with that described above. The same monomethanesulphonate was also isolated, in 12% yield, by fractional crystallisation from carbon tetrachloride of the mixture of products obtained by treatment of the *trans*-diol in pyridine solution with one mol. of methanesulphonyl chloride.

*Derivatives of* cis-cyclo*Hexane*-1 : 2-*diol*.—With a slight excess of methanesulphonyl chloride in pyridine solution, the cis-*bismethanesulphonate* was obtained, which crystallised from methanol in rosettes of needles, m. p. 85·5° (Found : C, 35·5; H, 6·0. $C_8H_{16}O_6S_2$ requires C, 35·3; H, 5·9%).

The *trans*-toluene-*p*-sulphonate-acetate, isolated as a by-product in the preparation of the *trans*-monotoluene-*p*-sulphonate (cf. Criegee and Stanger, *loc. cit.*) was converted by treatment in alcoholic solution with calcium carbonate into the *cis*-monoacetate, according to the method of Winstein and Buckles (*loc. cit.*). The product was isolated by concentration of the filtered solution, dilution with water, and extraction with ether; it had b. p. 110—113°/11 mm., $n_D^{20^\circ}$ 1·4623. This monoacetate (11·2 g.) dissolved in pyridine (60 c.c.) was treated with toluene-*p*-sulphonyl chloride (15 g.) and left overnight. Chloroform (250 c.c.) was then added, and the solution was washed with dilute sulphuric acid and finally with water. After drying, removal of solvent gave the cis-*toluene*-p-*sulphonate-acetate*, which crystallised from methanol in prisms, m. p. 80°, depressed to *ca.* 60° on admixture with the *trans*-isomer mentioned above (Found: C, 57·6; H, 6·3. $C_{15}H_{20}O_5S$ requires C, 57·65; H, 6·5%). Similar treatment of the *cis*-monoacetate (8 g.) in pyridine (30 c.c.) with methanesulphonyl chloride (6·4 g.) gave the cis-*methanesulphonate-acetate*, which crystallised from methanol in large prisms, m. p. 64° (Found : C, 45·7; H, 6·9. $C_9H_{16}O_5S$ requires C, 45·7; H, 6·8%).

The *cis*-toluene-*p*-sulphonate-acetate (1·1 g.) was dissolved in 0·2% methanolic hydrogen chloride (20 c.c.) and left at 20° overnight. After neutralisation with sodium hydrogen carbonate and removal of solvent, the residue was taken up in chloroform, dried ($Na_2SO_4$), and then evaporated to give the cis-*monotoluene*-p-*sulphonate* as a viscous oil (yield, almost theoretical) (Found : S, 11·8. $C_{13}H_{18}O_3S$ requires S, 11·8%). A portion, with toluene-*p*-sulphonyl chloride in pyridine, furnished the *cis*-bis-toluene-*p*-sulphonate m. p. 129°, whilst with methanesulphonyl chloride in pyridine it gave the cis-*toluene*-p-*sulphonate-methanesulphonate*, prisms from aqueous ethanol, m. p. 75° (Found : C, 48·25; H, 5·9. $C_{14}H_{20}O_6S_2$ requires C, 48·3; H, 5·8%).

Deacetylation of the *cis*-methanesulphonate-acetate under similar conditions gave the cis-*monomethanesulphonate* as a water-soluble viscous oil, b. p. *ca.* 80°/0·0001 mm. (Found : S, 16·5. $C_7H_{14}O_4S$ requires S, 16·5%). A portion, treated in pyridine solution with methanesulphonyl chloride, gave the *cis*-bismethanesulphonate, m. p. and mixed m. p. 85·5°.

*Reactions of the Monotoluene*-p-*sulphonates and Monomethanesulphonates with Alkali*.—(i) The *trans*-monotoluene-*p*-sulphonate (19·7 g.) in methanol (60 c.c.) was treated with methanolic sodium methoxide (34 c.c.; 2·17 N) at room temperature overnight; sodium toluene-*p*-sulphonate had then separated from the solution, which was still alkaline to phenolphthalein. After neutralisation with carbon dioxide, and filtration, the methanol was removed by distillation through a 6-inch Vigreux column; it nevertheless had a strong odour of *cyclo*hexene oxide. The liquid residue was diluted with ether (100 c.c.), washed with water, and dried ($Na_2SO_4$). After removal of ether through the Vigreux column, the residual *cyclo*hexene oxide distilled at 130—132°, $n_D^{20^\circ}$ 1·4491 (yield 1·6 g.). It was characterised by reaction with methanesulphonic acid, under the conditions already described, to give the *trans*-monomethanesulphonate, m. p. 79°.

(ii) The *trans*-monomethanesulphonyl derivative (18 g.), on similar treatment, gave 1·5 g. of *cyclo*hexene oxide, b. p. 129—131°, $n_D^{21^\circ}$ 1·4492.

(iii) The *cis*-toluene-*p*-sulphonate-acetate (19 g.) on treatment in methanol solution with methanolic sodium methoxide (28·4 c.c., 2·17N) at room temperature overnight gave *cyclo*hexanone, 2·9 g., b. p. 155°, characterised as the semicarbazone, m. p. 165·5°, and the 2 : 4-dinitrophenylhydrazone, m. p. 161°. It is noteworthy that only one equivalent of methoxide was required; the acetyl group is removed as methyl acetate by catalytic alcoholysis.

(iv) The *cis*-methanesulphonate-acetate (7 g.) similarly yielded *cyclo*hexanone, 1·3 g., b. p. 150—160°.

(v) The *trans*-monotoluene-*p*-sulphonate (16 g.) in 0·5N-aqueous sodium hydroxide (119 c.c.) was stirred at 85—90° for 2·5 hours. A strong odour of *cyclo*hexene oxide was observed during the first ½ hour. The clear neutral solution was extracted once with chloroform (20 c.c.) to yield a trace of an oil which gave a positive Schiff test for aldehyde, and gave *formyl*cyclo*pentane* 2 : 4-*dinitrophenylhydrazone*, orange plates from methanol, m. p. 158° (Found : N, 19·9. $C_{12}H_{14}O_4N_4$ requires N, 20·1%). The aqueous solution, on evaporation to dryness and extraction of the solid residue with chloroform, gave *trans-cyclo*hexane-1 : 2-diol (3·94 g.; 58%), m. p. 100°, raised to 104° on recrystallisation.

(vi) The *cis*-toluene-*p*-sulphonate-acetate (9·0 g.) in 0·5N-sodium hydroxide (115 c.c.) was stirred at 85—90° for 7 hours. The cooled solution was then saturated with salt and extracted with ether to yield *cyclo*hexanone (1·8 g.; 63·7%), b. p. 155° (semicarbazone, m. p. 165°). Evaporation of the aqueous portion to dryness, followed by extraction with chloroform, gave *cis-cyclo*hexane-1 : 2-diol (0·75 g.; 22·4%), m. p. 92°, raised to 94° on admixture with an authentic sample of m. p. 98°. It was characterised by conversion into the *cis*-bismethanesulphonate, m. p. and mixed m. p. 85°.

(vii) Quantitative experiments on the rates of reaction with alkali of the *trans*-monomethanesulphonate, *trans*-monotoluene-*p*-sulphonate, and *cis*-monotoluene-*p*-sulphonate were carried out according to the following procedure. The compound (0·025 mol.) was dissolved in methanol (25 c.c.) and treated with methanolic potassium hydroxide (25 c.c., 0·2N; 100% excess). The solution was kept at 17°, the progress of the reaction, measured by the consumption of alkali, being followed by withdrawal of 10 c.c. portions and titration with standard acid. The results are shown in the figure.

*Reactions with Sodium Iodide*.—(i) The *trans*-monotoluene-*p*-sulphonate (5 g.) and sodium iodide (8 g.) in acetone (50 c.c.) were heated in a sealed tube at 85° for 5 hours. Sodium toluene-*p*-sulphonate

(2·9 g., 81%) was removed by filtration, and the acetone distilled off through a Vigreux column; the distillate was unsaturated towards bromine in carbon tetrachloride. The residue, which contained free iodine, was diluted with water (20 c.c.) and extracted with four 40-c.c. portions of ether. The extracts were washed with aqueous sodium thiosulphate until colourless, then dried ($Na_2SO_4$) and evaporated to an oil (1·75 g.). Distillation at 50—60° (bath temp.)/0·001 mm. gave a pale yellow oil (0·65 g.), the residue consisting of unchanged monotoluene-*p*-sulphonate. The distillate (Found : I, 30·8%) contained 2-iodo*cyclo*hexanol, which could not be isolated in the pure state, but was identified by formation of its 3 : 5-dinitrobenzoate, crystallising from ethanol in needles, m. p. 157° (Found : I, 30·2. Calc. for $C_{13}H_{13}O_6N_2I$ : I, 30·2%). Tiffeneau and Tchoubar (*Compt. rend.*, 1938, **207**, 918) give m. p. 157° for this derivative of *trans*-2-iodo*cyclo*hexanol.

(ii) Under the same conditions, the *trans*-monomethanesulphonate (5 g.) gave 2·2 g. of sodium methanesulphonate (74%), but the small amount of iodine-containing oil, which was obtained on distillation, could not be effectively separated from unchanged monomethanesulphonate.

(iii) Under the same conditions, the *cis*-toluene-*p*-sulphonate-acetate gave only 6·5% of sodium toluene-*p*-sulphonate, but when this compound (1·5 g.) was heated with sodium iodide (2·2 g.) in acetone (15 c.c.) at 100° for 15 hours, the sodium toluene-*p*-sulphonate collected from the cooled solution amounted to 0·67 g. (72%). The product was worked up to give an oil (0·5 g.) which on distillation at 80° (bath temp.)/0·0001 mm. gave a sulphur-free oil (0·17 g.) and a residue (0·3 g.) of unchanged toluene-*p*-sulphonate-acetate. The 2-iodo*cyclo*hexyl acetate (0·15 g.) was deacetylated by being kept overnight in 0·2% methanolic hydrogen chloride (1 c.c.). Removal of solvent than gave an oil (0·1 g.) which was treated with 3 : 5-dinitrobenzoyl chloride (0·12 g.) in pyridine (1 c.c.). The solid derivative contained some methyl 3 : 5-dinitrobenzoate, evidently formed from a trace of residual methanol, but by several fractional crystallisations from methanol, the less soluble material being discarded on each occasion, a small quantity of *trans*-2-iodo*cyclo*hexyl 3 : 5-dinitrobenzoate was obtained. It had m. p. 153°, and was insufficient for a further recrystallisation, but the m. p. was raised to 156° on admixture with an authentic sample of m. p. 157°. Brunel (*Ann. Chim. Phys.*, 1905, **6**, 217) described a 2-iodo*cyclo*hexyl acetate to which he allocated a *cis*-configuration, but in the light of more recent evidence this was almost certainly the *trans*-compound, and therefore identical with that obtained above.

(iv) The *cis*-methanesulphonate-acetate (1·65 g.) on being heated with sodium iodide (3·15 g.) in acetone (20 c.c.) at 100° for 16 hours gave 0·7 g. (85%) of sodium methanesulphonate. The product distilled at 80° (bath temp.)/0·0002 mm., as an oil (0·58 g.) containing iodine and sulphur, and was evidently contaminated with unchanged methanesulphonate. It was deacetylated with methanolic hydrogen chloride as above, but the presence of methanesulphonate prevented the isolation of any crystalline derivatives of the iodo-compound.

*Reactions with Lithium Chloride.*—(i) A solution of the *trans*-monotoluene-*p*-sulphonate (5 g.) and lithium chloride (2·4 g.) in ethanol (100 c.c.) was refluxed for 30 hours, and then concentrated to small volume, diluted with water (25 c.c.), and extracted thrice with 30-c.c. portions of chloroform. The extracts, after being dried ($Na_2SO_4$), were evaporated to an oil, which on distillation furnished *trans*-2-chloro*cyclo*hexanol (1·6 g.; 64%), b. p. 81—85°/14 mm., $n_D^{20°}$ 1·4850, characterised as the α-naphthylurethane, m. p. 165°. Bartlett (*loc. cit.*) recorded m. p. 165°.

(ii) Similar treatment of the *trans*-monomethanesulphonate (2 g.) gave 0·8 g. (57·5%) of *trans*-2-chloro*cyclo*hexanol (α-naphthylurethane, m. p. 165°).

(iii) The *cis*-methanesulphonate-acetate (4 g.), under the same conditions, gave only 0·6 g. (20%) of 2-chloro*cyclo*hexyl acetate, b. p. 105—110°/25 mm., which was deacetylated by treatment with 0·2% methanolic hydrogen chloride at room temperature for 15 hours. The resulting 2-chloro*cyclo*hexanol was identified as the *trans*-form by conversion into the α-naphthylurethane, m. p. and mixed m. p. 165°.

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