433. *Alicyclic Glycols. Part IV. Toluene-*p*-sulphonyl and Methanesulphonyl Derivatives of* cyclo*Hexane-*1 : 3*-diol.*

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Mono- and di-toluene-*p*-sulphonyl and -methanesulphonyl derivatives of the *cis*- and the *trans*-form of *cyclo*hexane-1 : 3-diol have been prepared. In reactions with alkali, potassium acetate, sodium benzoate, and lithium chloride, elimination occurs, in some cases exclusively, and unsaturated products are formed. With sodium iodide, replacement more readily takes place, leading to the formation of 1 : 3-di-iodo*cyclo*hexane from the disulphonates.

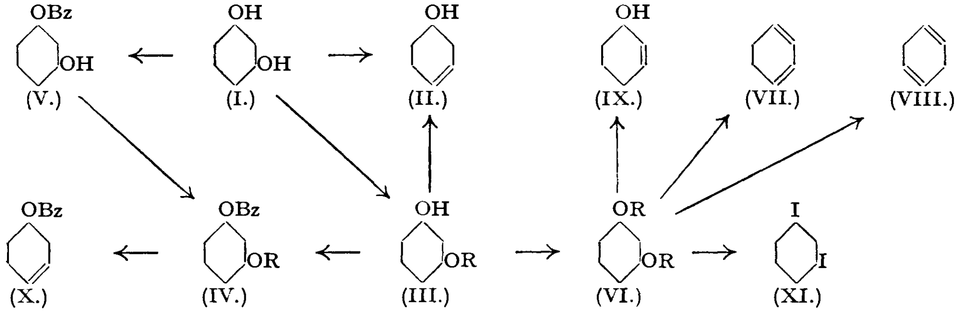
In Parts I and II (Clarke and Owen, *J.*, 1949, 315; Owen and Robins, *ibid.*, p. 320) the properties of some derivatives, in particular the sulphonate esters, of *cyclo*hexane-1 : 2- and -1 : 4-diol were considered. This investigation has now been extended to *cyclo*hexane-1 : 3-diol, the chemistry of which has been sporadically studied by earlier workers. Most of these obtained the diol by hydrogenation of resorcinol, generally in poor yield owing to the simultaneous occurrence of hydrogenolysis, which appears to take place particularly readily with 1 : 3-glycols (cf. Connor and Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 4678). The most extensive investigations were made by Palfray and Sabetay (*Bull. Soc. chim.*, 1928, [iv], **43**, 895), Rothstein, Palfray, and Sontag (*ibid.*, 1929, [iv], **45**, 683; *Compt. rend.*, 1929, **189**, 188), and Rothstein (*Ann. Chim.*, 1930, [x], **14**, 461). Many esters and ethers were prepared; most of these were liquids, but a solid dibenzoate was described, the *cis*- and the *trans*-form of which were separated by fractional crystallisation; these benzoates were very resistant to hydrolysis, but eventually, with some difficulty, the *cis*- and the *trans*-diol were obtained. Lindemann and Baumann (*Annalen*, 1929, **477**, 78) also succeeded in separating the dibenzoates, but failed to effect their hydrolysis; they obtained the *cis*- and the *trans*-diol from the bisphenylurethanes and bistriphenylmethyl ethers. The latter derivatives were also used for this purpose by Coops, Dienske, and Aten (*Rec. Trav. chim.*, 1938, **57**, 303). The most recent work is that of Rigby (*J.*, 1949, 1586, 1588) who separated the stereoisomers by fractional crystallisation from acetone; he also resolved the *trans*-diol, thus providing the first conclusive proof of the stereochemical structures (the failure of Lindemann and Baumann to resolve the *cis*-diol cannot be regarded as satisfactory evidence). It is interesting that these were originally allocated on the basis of the relative melting points of derivatives, on the assumption that *cis*- had melting points lower than *trans*-forms; by chance, this happened to be so for all derivatives described at the time, but, as will be evident in the sequel, this supposition is not always correct.

Resorcinol was hydrogenated in methanol over Raney nickel. Hydrogenolysis always occurred, a considerable amount of *cyclo*hexanol being formed, but the *cyclo*hexane-1 : 3-diol (yield, 45%) was readily purified by fractional distillation. Apart from the rather tedious nature of the process, little difficulty was found in the preparation and separation of the *cis*- and the *trans*-dibenzoate. The only previously successful hydrolysis of these esters had been carried out by Rothstein (*loc. cit.*), and we have confirmed his observation that with boiling alcoholic potassium hydroxide a long period of heating is necessary. In the case of *cyclo*hexane-1 : 4-diol, however, it had been found (Owen and Robins, *loc. cit.*) that a particularly satisfactory method for the preparation of the diols from the *cis*- and the *trans*-diacetate was catalytic alcoholysis by a trace of sodium methoxide in cold methanol. This procedure failed completely with the 1 : 3-dibenzoates, thus providing a further illustration of their greater stability, but at 50° alcoholysis proceeded smoothly, and in excellent yields; the ease of isolation by this method is in marked contrast to the drastic and much less efficient hydrolytic process.

Rothstein (*loc. cit.*) made the rather remarkable claim that benzoylation of the pure *cis*-diol is accompanied by partial inversion and gives some *trans*-dibenzoate. No experimental details were given, nor was there any indication of the method of benzoylation which brought about this change, and it is more probable that his *cis*-diol was impure and contained some of the *trans*-isomer. Lindemann and Baumann (*loc. cit.*), and Rigby (*loc. cit.*), obtained only the *cis*-dibenzoate from the *cis*-diol, and we have confirmed their results.

By dehydration of *cyclo*hexane-1 : 4-diol over alumina, Olberg, Pines, and Ipatieff (*J. Amer. Chem. Soc.*, 1944, **66**, 1096) obtained 1 : 4-epoxy*cyclo*hexane. However, with the 1 : 3-diol (I) no oxide could be detected, the main product being *cyclo*hexen-4-ol (II).

From the appropriate form of the diol, the following new solid derivatives were prepared by standard methods : *cis*-bisphenylurethane, *cis*- and *trans*-dimethanesulphonates, *cis*- and *trans*-ditoluene-*p*-sulphonates. The formation of monoesters took place less readily than in the 1 : 4-series (cf. Owen and Robins, *loc. cit.*). Thus, the 1 : 3-diol reacted only very slowly with 1 mole of toluene-*p*-sulphonyl chloride in pyridine at 0°, and it was necessary to allow the reaction to proceed at room temperature for 3 days in order to obtain the monotoluene-*p*-sulphonate (III). The products from the *cis*- and the *trans*-diol were oils, but on benzoylation gave the crystalline benzoate toluene-*p*-sulphonates (IV). Methanesulphonyl chloride is considerably more reactive than toluene-*p*-sulphonyl chloride, and to avoid excessive formation of the dimethanesulphonates much milder conditions were necessary; these monoesters also were liquids, but on benzoylation gave crystalline benzoate methanesulphonates.



(R = Me·SO$_2$ or *p*-Me·C$_6$H$_4$·SO$_2$)

A mixture of the stereoisomeric monobenzoates was prepared by Rothstein (*loc. cit.*), apparently in poor yield, by treatment of the mixed 1 : 3-diol with 1 mole of benzoyl chloride in the absence of any base. Dimroth and Resin (*Ber.*, 1942, **75**, 322) also prepared some monoesters of the 1 : 3-diol in their search for a route to 3-hydroxy*cyclo*hexanone, but the individual *cis*- and *trans*-monobenzoates were first prepared by Rigby (*loc. cit.*), by partial hydrolysis of the respective dibenzoates. By applying the method used successfully in the 1 : 4-series (Owen and Robins, *loc. cit.*) we have independently obtained the pure *cis*- (yield, 60%) and *trans*-monobenzoates (yield, 42%) (V) ; both were oils, but were characterised by methanesulphonation and toluene-*p*-sulphonation to give the crystalline derivatives (IV) identical with those obtained by benzoylation of the monomethanesulphonates and monotoluene-*p*-sulphonates. The monobenzoates also gave the crystalline phenylurethanes subsequently described by Rigby, one of which, m. p. 167°, derived from the *cis*-compound, is probably identical with the substance m. p. 168—169°, of hitherto unknown configuration, obtained by Rothstein from his mixed monobenzoate.

The melting points of the new derivatives are recorded in the Table, and it is of interest that in every case where both forms are solid the *cis*-form has the higher value.

Derivatives of cyclo*hexane*-1 : 3-*diol.*

	M. p.			M. p.	
	cis-.	*trans*-.		*cis*-.	*trans*-.
Ditoluene-*p*-sulphonate	108°	92°	Benzoate methanesulphonate ...	104°	65°
Dimethanesulphonate	125	97·5	Benzoate toluene-*p*-sulphonate	97	89
Toluene-*p*-sulphonate methanesulphonate	—	85	Benzoate phenylurethane	167	112
			Bisphenylurethane	—	72—73

In previous papers in this series, attention was drawn to the possibility of the formation of epoxy*cyclo*hexanes by intramolecular loss of a sulphonic acid from a monosulphonyl ester of a diol, and such a reaction was shown to occur with the 1 : 2-, but not with the 1 : 4-diol; the behaviour of the 1 : 3-derivatives was therefore of particular interest. Since the elimination of a sulphonyloxy-group in oxide formation is accompanied by inversion on the carbon atom carrying that group, the compound most likely to yield the 1 : 3-epoxide on treatment with alkali is the *trans*-monotoluene-*p*-sulphonate (or monomethanesulphonate) (III). This compound, in cold methanol, reacted with 1 mole of sodium methoxide, and sodium toluene-*p*-sulphonate was rapidly formed, but the main product was *cyclo*hexen-4-ol (II); the reaction therefore takes the same course as with the 1 : 4-compound.

The *cis*- and the *trans*-dimethanesulphonate (VI), with hot aqueous alkali, gave a mixture of *cyclo*hexa-1 : 3- (VII) and -1 : 4-diene (VIII) and *cyclo*hexen-3-ol (IX), elimination and replacement reactions having taken place. When the dimethanesulphonates were treated with potassium acetate in boiling ethanol, free acid was liberated, indicating the occurrence of elimination or alcoholysis, and the only recognisable products were *cyclo*hexadienes, there being no evidence for the formation of any diacetate, as had been observed in the 1 : 4-series. Furthermore, the *cis*- and the *trans*-ditoluene-*p*-sulphonate, and the *cis*-dimethanesulphonate, with sodium benzoate in methanol gave only *cyclo*hexadienes and the theoretical amount of benzoic acid.

Several derivatives were treated with lithium chloride in boiling ethanol: in no case was substitution observed, the elimination reaction being dominant. The *trans*-monotoluene-*p*-sulphonate (III) gave *cyclo*hexen-4-ol (II); the *cis*- and the *trans*-benzoate toluene-*p*-sulphonate (IV) gave *cyclo*hexen-4-yl benzoate (X); the *cis*- and the *trans*-ditoluene-*p*-sulphonate and the *trans*-dimethanesulphonate (VI) gave *cyclo*hexadienes. Some substitution, however, occurred with sodium iodide in acetone, and 1 : 3-di-iodo*cyclo*hexane (XI) was obtained from the *trans*-ditoluene-*p*-sulphonate and from the *cis*- and the *trans*-dimethanesulphonate; the product in each case was a liquid, so that no conclusion could be drawn about its stereochemical homogeneity. Substitution also occurred when the *cis*- and the *trans*-benzoate toluene-*p*-sulphonate (IV) reacted with sodium iodide, but the resulting benzoate iodide could not be separated from accompanying unsaturated material. The di-iodide (XI) is possibly the first 1 : 3-dihalogeno-*cyclo*hexane to be described, since, according to Rothstein (*loc. cit.*), attempts to prepare 1 : 3-dichloro- and 1 : 3-dibromo-*cyclo*hexane by reaction of the 1 : 3-diol with the appropriate hydrogen halide have always given 1 : 4-dihalogeno*cyclo*hexanes. It is unlikely that any such rearrangement would occur under the present conditions; furthermore, both stereoisomeric forms of 1 : 4-di-iodo*cyclo*hexane are crystalline solids, whereas the di-iodide now obtained is a liquid.

Considering the results as a whole, it is clear that in the reactions of the sulphonyl esters of *cyclo*hexane-1 : 3-diol elimination takes place even more readily than with derivatives of the 1 : 2- and 1 : 4-diols. This is particularly evident in the reactions with lithium chloride, in which replacement of a sulphonyloxy-group by chlorine occurs readily in the 1 : 2- and the 1 : 4-, but not in the 1 : 3-, series.

The formation of *cyclo*hexen-3-ol (IX) from the dimethanesulphonates (VI) is of interest, since in the other instances when a *cyclo*hexenol was formed it was the isomer (II). At first sight it may appear that (IX) could be formed *via* (II) by isomerisation under the alkaline conditions of the reaction, since it is known that βγ-unsaturated alcohols undergo such changes in the presence of alkali (cf. Hargreaves and Owen, *J.*, 1947, 753, 756). The present conditions, however, are much milder than are usually necessary to bring about the isomerisation, and (II) was in fact unchanged by being heated at 100° with 10% aqueous alkali. The elimination to give (IX) rather than (II) must therefore be a consequence of the presence of the two sulphonyloxy-groups in the molecule.

EXPERIMENTAL.

cis- *and* trans-cyclo*Hexane*-1 : 3-*diol*.—Resorcinol (200 g.) in methanol (200 c.c.) was hydrogenated at 130°/120 atm. over Raney nickel (*ca.* 20 g.), prepared by the method of Pavlic and Adkins (*J. Amer. Chem. Soc.*, 1946, **68**, 1471). The rate of absorption depended on the freshness of the catalyst, but was usually substantially complete after *ca.* 24 hours; with one particularly active batch, most of the absorption had occurred within 10 hours, and prolongation of the reaction then led to almost complete hydrogenolysis. The solution was diluted with more methanol, filtered, and concentrated; fractional distillation then gave a considerable amount of *cyclo*hexanol, b. p. 88°/25 mm. (phenylurethane, m. p. 82°), followed by *cyclo*hexane-1 : 3-diol, b. p. 130—140°/6 mm., n_D^{19} 1·5015, as a viscous oil. There was a small residue (*ca.* 10 g.) of resorcinol. The average yield of diol was 100 g.

The oil (97·5 g.) was dissolved in pyridine (350 g.), and benzoyl chloride (285 g.) was slowly added, with stirring, at 0°. The mixture was left overnight at room temperature, then heated on the steam-bath for an hour, cooled, and diluted with 4N-sulphuric acid (2 l.). The precipitated oil was taken up in chloroform, and the extract was washed with dilute sulphuric acid, aqueous potassium carbonate, and finally with water, dried (Na_2SO_4), and evaporated to an oil, which on treatment with ethanol (40 c.c.) partly crystallised. The solid (100 g.) was collected, and on recrystallisation from methanol gave the *trans*-dibenzoate as plates, m. p. 124°. The ethanolic solution was concentrated, treated with a little light petroleum (b. p. 40—60°), and set aside in the refrigerator; it slowly crystallised, and after trituration with cold methanol the solid was recrystallised from the minimum amount of boiling methanol to give short thick needles of the *cis*-dibenzoate, m. p. 67·5°, depressed to 58° on admixture with the *trans*-isomer.

The *trans*-dibenzoate (50 g.) was dissolved in dry methanol (150 c.c.), and a 5% solution of sodium in dry methanol (0·5 c.c.) was added. The mixture, protected from moisture, was warmed at *ca.* 50° for 24 hours. Water (0·5 c.c.) was then added, and the alkali was neutralised with carbon dioxide. Filtration, and removal of methanol by distillation, gave a liquid which on fractionation gave methyl benzoate, b. p. 91°/15 mm., and the *trans*-diol (14 g., 79%), b. p. 140—142°/15 mm.; the latter solidified, and on recrystallisation from ethyl acetate formed plates, m. p. 115·5°. The *bisphenylurethane* of *trans-cyclo*hexane-1 : 3-diol crystallised from light petroleum (b. p. 80—100°) in fine needles, m. p. 72—73° (Found: C, 68·0; H, 6·0. $C_{20}H_{22}O_4N_2$ requires C, 67·8; H, 6·3%).

The *cis*-dibenzoate (29 g.) was treated in a similar way. On removal of the methanol, however, the *cis*-diol crystallised from the methyl benzoate solution. Light petroleum (b. p. 40—60°) (150 c.c.) was therefore added, and the diol was filtered off and washed with light petroleum (yield, 9·2 g.). Recrystallisation from acetone gave 8·7 g. (84%), m. p. 85·5°. A portion (1·0 g.) was benzoylated under the conditions used for the mixed diol; recrystallisation of the product from methanol gave 2·5 g. (90%) of *cis*-dibenzoate, m. p. and mixed m. p. 67°, with no indication of any *trans*-isomer.

Dehydration of cyclo*Hexane*-1 : 3-*diol*.—The mixed diol (21 g.) and activated alumina (15 g.) were heated, in an oil-bath at *ca.* 240°, in a flask fitted with a short fractionating column, the distillate being collected during 20 hours. Water (1·8 g.) was separated from the organic layer, and the latter was dried (Na_2SO_4) and distilled to give *cyclo*hexen-4-ol (8·0 g.), b. p. 160—163°, n_D^{22} 1·4810, characterised as the α-naphthylurethane, m. p. 128·5°.

Ditoluene-p-*sulphonates*.—(*a*) The *trans*-diol (6·0 g.), toluene-*p*-sulphonyl chloride (19·6 g.), and pyridine (100 c.c.) were set aside overnight and the solution, containing much pyridine hydrochloride, was then diluted with chloroform (150 c.c.) and washed with 4N-sulphuric acid (2 × 200 c.c.), followed by water. The chloroform solution was dried (Na_2SO_4) and evaporated to an oil, which solidified. The trans-*ditoluene*-p-*sulphonate* crystallised from methanol in rectangular plates (18·9 g., 86%), m. p. 90°, raised on further crystallisation to 92° (Found: C, 56·8; H, 5·6. $C_{20}H_{24}O_6S_2$ requires C, 56·6; H, 5·7%).

(*b*) The *cis*-diol (2·0 g.), similarly treated, gave the cis-*ditoluene*-p-*sulphonate* (6·55 g., 88·5%), which crystallised from chloroform–light petroleum (b. p. 80—100°) in plates, m. p. 108°, depressed to 84—85° on admixture with the *trans*-derivative (Found: C, 56·9; H, 6·1%).

Dimethanesulphonates.—(*a*) Methanesulphonyl chloride (9·9 g.) was slowly added to a stirred solution of the *trans*-diol (5·0 g.) in pyridine (50 c.c.) at 0°; the solution was then set aside overnight and worked up as for the ditoluene-*p*-sulphonyl derivative. The trans-*dimethanesulphonate* (11·4 g., 97%) solidified on removal of the chloroform and crystallised from methanol in rosettes of needles, m. p. 97·5° (Found: C, 35·6; H, 5·8. $C_8H_{16}O_6S_2$ requires C, 35·3; H, 5·9%).

(*b*) The *cis*-diol (1·25 g.) similarly gave the cis-*dimethanesulphonate* (2·5 g., 85%), which crystallised from methanol in needles, m. p. 125° (Found: C, 35·3; H, 6·1%). A mixed m. p. with the *trans*-derivative was 86—87°.

It was possible to separate the *cis*- and the *trans*-dimethanesulphonate, prepared from the mixed diol in a similar way, by fractional crystallisation from methanol, the *cis*-compound being the less soluble. Both were soluble in hot water, but only the *trans*-derivative readily crystallised on cooling.

Monobenzoates.—(*a*) Benzoyl chloride (5·8 g.) in pure chloroform (150 c.c.) was added during 4 hours to a stirred solution of the *trans*-diol (4·8 g.) in pyridine (50 c.c.) at −10°. The solution was set aside at room temperature overnight and then washed successively with dilute sulphuric acid and aqueous sodium carbonate, dried (Na_2SO_4), and evaporated to an oil, which deposited some crystalline material. The whole product was dissolved in the minimum amount of boiling methanol; when cooled, the *trans*-dibenzoate (2·2 g.), m. p. 122°, separated and was removed. The methanol solution was then evaporated to an oil, which on distillation gave the *trans*-monobenzoate (3·8 g., 42%), b. p. 120—130° (bath)/0·005 mm., as a viscous oil. A small portion, treated with phenyl *iso*cyanate in the usual way, gave the *trans*-benzoate phenylurethane, which crystallised from benzene–light petroleum (b. p. 60—80°) in rosettes of needles, m. p. 112° (Found: C, 70·9; H, 6·1. Calc. for $C_{20}H_{21}O_4N$: C, 70·8; H, 6·25%). Treatment of another portion with acetyl chloride in pyridine gave the trans-*acetate benzoate* as an oil, b. p. 85—90°/0·0004 mm. (Found: C, 68·9; H, 7·2. $C_{15}H_{18}O_4$ requires C, 68·7; H, 6·9%).

(*b*) The *cis*-diol, on benzoylation under similar conditions, gave the *cis*-monobenzoate (60%), b. p. 130—135° (bath)/0·003 mm. It gave a phenylurethane, m. p. 167°.

Benzoate Toluene-p-*sulphonates*.—The *trans*-monobenzoate (3·8 g.) was treated overnight with toluene-*p*-sulphonyl chloride (3·3 g.) in pyridine (30 c.c.) and worked up in chloroform (60 c.c.) as previously described. The trans-*benzoate toluene*-p-*sulphonate* (4·65 g., 72%) crystallised from light petroleum (b. p. 80—100°) in plates, m. p. 89° (Found: C, 64·4; H, 6·1. $C_{20}H_{22}O_5S$ requires C, 64·2; H. 5·9%). Similar treatment of the *cis*-monobenzoate (2·0 g.) gave the cis-*benzoate toluene*-p-*sulphonate* (2·8 g., 82·5%), which crystallised from methanol in fine needles, m. p. 97° (Found: C, 63·7; H, 5·7%). On admixture of this with the *trans*-compound the m. p. was depressed to 78—80°.

Benzoate Methanesulphonates.—These were prepared in a similar way to the preceding compounds. The trans-*benzoate methanesulphonate* (83%) formed needles, m. p. 65°, from light petroleum (b. p. 80—100°) (Found: C, 56·4; H, 6·0. $C_{14}H_{18}O_5S$ requires C, 56·4; H, 6·1%). The cis-*benzoate methanesulphonate* (92%) crystallised from light petroleum (b. p. 80—100°) in needles, m. p. 104° (Found: C, 56·7; H, 6·6%).

*Monotoluene-*p*-sulphonates.*—A solution of toluene-*p*-sulphonyl chloride (28·6 g.) in pyridine (60 c.c.) was added during 5 hours to a stirred solution of the *trans*-diol (17·4 g.); the mixture was then set aside for 3 days. Chloroform (250 c.c.) was then added, and after the pyridine had been washed out as previously described the dried solution was evaporated to an oil. This was dissolved in light petroleum (b. p. 60—80°) containing a few drops of chloroform, and seeded with the *trans*-ditoluene-*p*-sulphonate, whereupon a small amount of this substance crystallised and was removed. Evaporation then gave the trans-*monotoluene-*p*-sulphonate* as an oil (25 g.) which was clarified by dissolution in chloroform, shaking with charcoal, filtration, and evaporation to an almost colourless viscous liquid (Found: S, 10·5. $C_{13}H_{18}O_4S$ requires S, 11·85%). The *cis*-monotoluene-*p*-sulphonate, similarly prepared, was also an oil.

Treatment of these derivatives with benzoyl chloride in pyridine gave the corresponding benzoate toluene-*p*-sulphonate, *cis*-, m. p. 97°, and *trans*-, m. p. 89°, identical with those described above.

Monomethanesulphonates.—A solution of methanesulphonyl chloride (1 g.) in pure chloroform (80 c.c.) was added during 3 hours to a stirred solution of the *trans*-diol (1·0 g.) in pyridine (20 c.c.) at −20°. The solution was set aside at room temperature overnight and then stirred with sodium hydrogen carbonate (1 g.) and a few drops of water until neutral. The solution was then shaken with anhydrous sodium sulphate, filtered, and evaporated to an oil, which was dissolved in the minimum amount of boiling methanol. On cooling, some *trans*-dimethanesulphonate (0·37 g., m. p. 97°) crystallised and was removed. Evaporation of the solution then gave the crude *trans*-monomethanesulphonate as a viscous water-soluble oil, which could not be distilled without decomposition. The *cis*-monomethanesulphonate had similar properties.

Treatment of these derivatives with benzoyl chloride in pyridine gave the *trans*-, m. p. 64°, and the *cis*-form, m. p. 103°, respectively of the benzoate methanesulphonate, identical with those previously described.

The *trans*-monomethanesulphonate (0·4 g.) with toluene-*p*-sulphonyl chloride (0·4 g.) in pyridine gave the trans-*methanesulphonate toluene-*p*-sulphonate*, which crystallised from ethanol in laths, m. p. 85° (Found: C, 48·1; H, 6·0. $C_{14}H_{20}O_6S_2$ requires C, 48·3; H, 5·8%). The *cis*-monomethanesulphonate on similar treatment gave an oil.

Reaction of the trans-*Monotoluene-*p*-sulphonate with Sodium Methoxide.*—A 5% solution of sodium in methanol (25 c.c.) was added to the derivative (14·8 g.) in methanol (50 c.c.). Sodium toluene-*p*-sulphonate began to separate after a few minutes. After the mixture had been left for 2 days at room temperature, a few drops of water were added and the residual alkali was neutralised with carbon dioxide. The solution was filtered, and the methanol was removed by distillation through a short fractionating column; the distillate was unsaturated. Distillation of the residue gave a main fraction (4·1 g.), b. p. 94—115°/70 mm., which on redistillation gave *cyclo*hexen-4-ol, b. p. 160—165°, n_D^{25} 1·4806, characterised as the α-naphthylurethane, m. p. 128°.

Reaction of the Dimethanesulphonates with Alkali.—The *cis*-derivative (10 g.) was stirred for 2½ hours at 90° with 5% aqueous sodium hydroxide (120 c.c.), in which it was appreciably soluble. A slow stream of nitrogen was passed through the flask and reflux condenser, and thence, through a calcium chloride tube, to a solution of bromine in carbon tetrachloride. From the latter solution there was obtained the tetrabromide of *cyclo*hexa-1 : 4-diene, m. p. 188°. The alkaline solution was extracted with ether (4 × 50 c.c.), the extracts were dried (Na_2SO_4) and evaporated, and the residual unsaturated oil (3 g.) was distilled to give *cyclo*hexen-3-ol (75%), b. p. 160—165°, n_D^{30} 1·4777, characterised as the phenylurethane, m. p. 107°, and the α-naphthylurethane, m. p. 155° (Willstätter and Sonnenfeld, *Ber.*, 1913, **46**, 2952, give 107° and 156°).

The *trans*-dimethanesulphonate (10 g.) on similar treatment gave 1·0 g. (28%) of *cyclo*hexen-3-ol. For half of the reaction period the stream of nitrogen was passed through pure ethanol, spectroscopic examination of which then showed the presence of *cyclo*hexa-1 : 3-diene (light absorption max., 2580 A.); in addition, the tetrabromide, m. p. 188°, of *cyclo*hexa-1 : 4-diene was obtained as before. In view of the much smaller yield of *cyclo*hexen-3-ol, the aqueous residues were examined for *cyclo*hexane-1 : 3-diol, but none was detected.

After a similar experiment, the *trans*-ditoluene-*p*-sulphonate was recovered quantitatively. The non-reactivity is probably due to its insolubility in aqueous alkali.

Reaction of the Dimethanesulphonates with Potassium Acetate.—A solution of the *trans*-derivative (2·2 g.) and anhydrous potassium acetate (3·9 g.) in ethanol (60 c.c.) was heated under reflux for 24 hours. A bromine absorption train was used, as previously described, and from it the tetrabromide, m. p. 188°, was recovered. The alcoholic solution (which now contained free acetic acid) was diluted with water and neutralised by titration with 0·216N-sodium hydroxide (42·6 c.c., corresponding to the formation of 1·2 moles of acid). Most of the alcohol was then distilled off, and the residual aqueous solution was extracted with chloroform; only unchanged *trans*-dimethanesulphonate (0·7 g.), m. p. 95°, was obtained.

Similar results were obtained with the *cis*-dimethanesulphonate, which was heated for 40 hours; 1·5 moles of acetic acid were liberated, and the tetrabromide, m. p. 188°, was isolated as before.

Reaction of the Disulphonates with Sodium Benzoate.—The *cis*-dimethanesulphonate (1·0 g.) and sodium benzoate (2·7 g.) were heated under reflux in methanol (60 c.c.) for 50 hours. Tetrabromo*cyclo*hexane, m. p. 187°, was obtained, as previously described, from a bromine absorption train. The solution was diluted with water, concentrated to remove methanol, and extracted with ether to yield benzoic acid (0·9 g., 2 moles), m. p. 120°.

Essentially the same results were obtained with the *cis*- and the *trans*-ditoluene-*p*-sulphonate.

Reactions with Lithium Chloride.—(*a*) The *trans*-monotoluene-*p*-sulphonate (4·0 g.) and lithium chloride (2·0 g.) were heated under reflux in ethanol (65 c.c.) for 40 hours. The solvent was then distilled off through a fractionating column (the distillate was unsaturated), and the semi-solid residue was diluted with water (20 c.c.) and extracted with ether (3 × 40 c.c.). The dried (Na_2SO_4) extracts were evaporated to an oil (1·7 g.), which contained combined sulphur but no halogen; on distillation, some *cyclo*hexen-4-ol (0·71 g., 49%), b. p. 95—102°/60 mm., was obtained before the residue, which probably contained some unchanged toluene-*p*-sulphonate, decomposed. The *cyclo*hexenol was identified by formation of the α-naphthylurethane, m. p. 128°.

(*b*) A solution of the *trans*-benzoate toluene-*p*-sulphonate (1·0 g.) and lithium chloride (0·35 g.) in ethanol (25 c.c.) was heated under reflux for 40 hours and then concentrated to small bulk. The residue was diluted with water and extracted with chloroform, to give an unsaturated oil (0·53 g.), b. p. 80° (bath)/0·001 mm., n_D^{23} 1·5218, which contained no halogen. It was hydrolysed by being heated with 10% aqueous potassium hydroxide for 4 hours on the steam-bath, and gave *cyclo*hexen-4-ol, characterised as the 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 100—101°.

Similar results were obtained with the *cis*-benzoate toluene-*p*-sulphonate.

(*c*) The *trans*-ditoluene-*p*-sulphonate (1·0 g.) and lithium chloride (0·5 g.) were heated under reflux in ethanol (35 c.c.) for 24 hours, a stream of nitrogen being passed through the apparatus and into a solution of bromine in carbon tetrachloride. From the latter, there were obtained needles of tetrabromo*cyclo*hexane (0·25 g., corresponding to a 30% yield of *cyclo*hexa-1 : 4-diene), m. p. 180°, raised on recrystallisation from acetone to m. p. 188°. The alcohol was distilled off, and the residue was dissolved in water (40 c.c.); extraction with ether (3 × 70 c.c.) gave no product.

No chlorine-containing product was obtained on repetition of the experiment (i) with a period of heating of only 3 hours, when 65% of the ditoluene-*p*-sulphonate was recovered unchanged; (ii) when the reaction was carried out in a sealed tube at 150° for 2 hours, or (iii) under the original conditions, with either the *cis*-ditoluene-*p*-sulphonate or the *trans*-dimethanesulphonate.

Reactions with Sodium Iodide.—(*a*) The *cis*-ditoluene-*p*-sulphonate (1·0 g.), sodium iodide (1·8 g.), and pure acetone (25 c.c.) were heated in a sealed tube for 1 hour at 100°. The dark brown solution was filtered from sodium toluene-*p*-sulphonate (0·73 g., 80%) and was concentrated to a semi-solid residue; this was diluted with water (25 c.c.) and extracted with ether (3 × 35 c.c.). The extracts were washed with aqueous sodium thiosulphate to remove free iodine, dried (Na_2SO_4), and evaporated below 40° under reduced pressure to give a colourless oil. Distillation at 65° (bath)/0·0001 mm., gave 1 : 3-*di-iodo*cyclo*hexane* (0·37 g., 47%), n_D^{23} 1·6225 (Found: I, 76·5. $C_6H_{10}I_2$ requires I, 75·6%).

A compound with similar properties was obtained (i) from the *cis*-dimethanesulphonate by heating it with sodium iodide in acetone under reflux for 100 hours, and (ii) from the *trans*-ditoluene-*p*-sulphonate by heating under reflux for 20 hours or at 100° for 2 hours.

(*b*) The *trans*-benzoate toluene-*p*-sulphonate (1·5 g.), sodium iodide (1·5 g.) and acetone (40 c.c.) were heated in a sealed tube for 3 hours at 100°. Sodium toluene-*p*-sulphonate (0·66 g., 84%) was removed, and the acetone solution was worked up as before to give an almost colourless oil (1·2 g.). Unchanged starting material (0·15 g.) was separated from this by crystallisation from aqueous methanol, and the recovered oil was distilled at 80° (bath)/0·0004 mm. to give a colourless liquid (1·0 g.), n_D^{22} 1·5514, which contained iodine (Found: I, 16·9%) but no sulphur. It was, however, unsaturated and could not be further purified. Similar results were obtained with the *cis*-derivative.

Stability of cyclo*Hexen-4-ol.*—Prepared by dehydration of *cyclo*hexane-1 : 4-diol with sulphuric acid (cf. Senderens, *Compt. rend.*, 1925, **180**, 191), *cyclo*hexen-4-ol had b. p. 162—163°, n_D^{21} 1·4860, and gave the phenylurethane, m. p. 81°. A portion of the alcohol (1·3 g.) was stirred under reflux with 10% aqueous sodium hydroxide (20 c.c.) at 100° for 5 hours. Light petroleum (b. p. 40—60°) was then added, and the organic layer was removed, dried ($CaCl_2$), and evaporated to an oil, which on distillation gave only *cyclo*hexen-4-ol (0·85 g.), b. p. 162—164°, n_D^{22} 1·4852, characterised as the phenylurethane, m. p. and mixed m. p. 81°. (The phenylurethane of *cyclo*hexen-3-ol has m. p. 107°.)

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