771. *Alicyclic Glycols. Part VII.** cyclo*Pentane*-1 : 3-*diol. Anionotropic Rearrangement in Some Reactions of* 3 : 5-*Dibromo*cyclo*pentene.*

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A re-investigation of the methods used by earlier workers for the synthesis of *cyclo*pentane-1 : 3-diol has shown that in all cases the products contain considerable proportions of *cyclo*pentane-1 : 2-diol.

Replacement of bromine by acetoxyl in *cis*- and in *trans*-3 : 5-dibromo*cyclo*pentene (VIII) has been studied under various conditions. When potassium acetate or silver acetate in acetic acid is used, the normal product, 3 : 5-diacetoxy*cyclo*pentene, is accompanied by 3 : 4-diacetoxy*cyclo*pentene, formed by anionotropic rearrangement; the configuration of the rearranged product is *cis* if the reaction is carried out in the presence of water, but *trans* if anhydrous acetic acid is used, irrespective of the configuration of the original dibromide. This can be explained by the assumption that the anionotropic change occurs when the first bromine atom is replaced, to give *trans*-3-acetoxy-4-bromo*cyclo*pentene (X), which then forms a cyclic intermediate (XI) of the Winstein type. When the dibromide reacts with tetraethylammonium acetate in acetone, rearrangement does not occur, and deacetylation and hydrogenation of the product gives only *cyclo*pentane-1 : 3-diol; in this way the pure *cis*- and *trans*-forms have been prepared for the first time.

The ditoluene-*p*-sulphonate of *trans*-*cyclo*pentane-1 : 3-diol reacts readily with potassium acetate, potassium *p*-nitrobenzoate, or sodium iodide, to give the corresponding 1 : 3-*trans*-derivatives; although some *cyclo*pentadiene is also formed the proportion of substitution to elimination is greater than for any other alicyclic toluene-*p*-sulphonate. The dimethanesulphonate with aqueous alkali gives *cyclo*pent-2-enol. The monotoluene-*p*-sulphonate of *trans*-*cyclo*pentane-1 : 3-diol shows very low reactivity in comparison with the corresponding 1 : 2-compound.

In contrast to the *cyclo*pentane-1 : 2-diols, the two stereoisomers of which have been known and studied for many years (cf. preceding paper), comparatively little is known about the *cyclo*pentane-1 : 3-diols, and the available information is in many respects of doubtful accuracy.

Dane, Schmitt, and Rautenstrauch (*Annalen*, 1937, **532**, 29) oxidised *cyclo*pentene (I) with selenium dioxide in acetic anhydride and obtained a mixture of mono- and di-acetoxy*cyclo*pentene; deacetylation and hydrogenation of the supposed di-ester (II) gave a product (bisphenylurethane, m. p. 195°) which should evidently be a *cyclo*pentane-1 : 3-diol (III). Criegee and Beucker (*ibid.*, 1939, **541**, 218), by oxidation of *cyclo*pentadiene (IV) with phenyl iodosoacetate in acetic acid, obtained a mixture of 3 : 4- (V) and 3 : 5-diacetoxy*cyclo*pentene (II), which was hydrolysed and hydrogenated to give a mixture of almost equal parts of *cyclo*pentane-1 : 2- and -1 : 3-diol; the 1 : 2-diol (VI) was destroyed with lead tetra-acetate, and the remaining 1 : 3-diol (III) was shown to be a mixture of stereoisomers by conversion into two bisphenylurethanes, m. p.s 173° and 145° respectively. Milas and Maloney (*J. Amer. Chem. Soc.*, 1940, **62**, 1841) treated *cyclo*pentadiene with hydrogen peroxide in dry *tert.*-butyl alcohol in the presence of osmic acid, and isolated a product,

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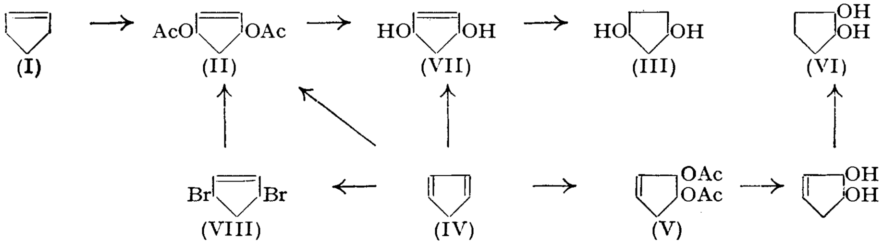
* Part VI, preceding paper.

formulated as *cis-cyclo*pent-2-ene-1 : 4-diol (VII), which on hydrogenation was said to give a *cyclo*pentane-1 : 3-diol, the bisphenylurethane of which had m. p. 168—171°.



Blomquist and Mayes (*J. Org. Chem.*, 1945, **10**, 134) treated *cis*-3 : 5-dibromo*cyclo*pentene (VIII) with potassium acetate in acetic acid and isolated an unsaturated diacetate, assumed to be *cis*-(II), which on deacetylation and hydrogenation gave a *cyclo*pentanediol (bisphenylurethane, m. p. 171°). Similar reaction of the *trans*-dibromide, but with silver acetate in acetic acid, likewise gave an unsaturated diacetate, deacetylation and hydrogenation of which gave another *cyclo*pentanediol (bisphenylurethane, m. p. 184°) in very poor yield. Both diols were assumed to be 1 : 3-compounds, and to have been formed with overall retention of configuration.

Consideration of the melting points of the bisphenylurethanes of the alleged 1 : 3-diols reported by these various investigators shows that four different values are recorded, even on the assumption that those of m. p. 168—171°, 171°, and 173° are essentially identical with one another. A complete re-investigation of the problem was therefore undertaken.

Repetition of the procedure of Dane *et al.* gave the unsaturated diacetate in improved yield. The saturated diol prepared from this material reacted to the extent of 64% with aqueous sodium metaperiodate, thus showing it to be a mixture of 1 : 2- and 1 : 3-diols, and not, as claimed, a pure 1 : 3-compound. When the method of Milas and Maloney was used, the saturated product contained 53% of 1 : 2-diol; the preparation was undertaken thrice, with the same result, and the non-reactivity towards lead tetra-acetate claimed by Milas and Maloney is inexplicable. Their reported formation of a benzylidene derivative cannot, of course, be taken as evidence that no 1 : 2-diol was present.

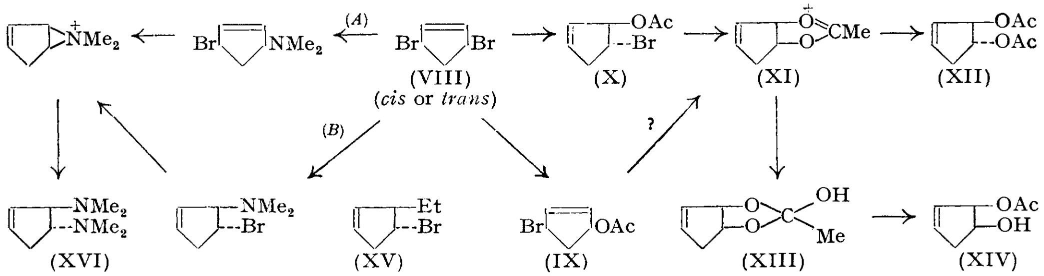
The work of Blomquist and Mayes was then repeated, *cis*-3 : 5-dibromo*cyclo*pentene being prepared from *cyclo*pentadiene in improved yield (over 80%). Reaction with potassium acetate in acetic acid gave an unsaturated diacetate which on deacetylation and hydrogenation furnished a *cyclo*pentanediol; this by periodate titration was found to contain 63% of the 1 : 2-isomer, confirmed by toluene-*p*-sulphonation, and isolation of the crystalline ditoluene-*p*-sulphonate of *trans-cyclo*pentane-1 : 2-diol (cf. Part VI, previous paper). By using the crude *cis*-dibromide in the replacement reaction the overall yield of unsaturated diacetate was raised to 63% (cf. 14% by Blomquist and Mayes on the two stages).

Reaction of the *trans*-dibromide with silver acetate in acetic acid, followed by deacetylation and hydrogenation of the product, gave a diol *which consisted almost entirely* (93%) *of* 1 : 2-*compound* and which readily gave the di-*p*-nitrobenzoate of *cis-cyclo*pentane-1 : 2-diol. Since this derivative is the most soluble of all the di-*p*-nitrobenzoates of the isomeric *cyclo*pentanediols (cf. previous paper for the 1 : 2-series; the authentic 1 : 3-compounds are described below) the diol must have been nearly pure *cis*-1 : 2-isomer.

It has thus been found that all earlier methods for the preparation of *cyclo*pentane-1 : 3-diol give mixtures, most of which are actually richer in the 1 : 2-isomer. Whilst the 1 : 2-diol formed in the hydroxylation of *cyclo*pentadiene may arise by direct 1 : 2-addition, its formation in Dane's method or from the 1 : 3-dibromides must involve rearrangement. In the investigation of Blomquist and Mayes's route, the deacetylation and hydrogenation stages were interchanged without appreciable effect on the proportions of 1 : 2- and 1 : 3-diols encountered in the final product, and there can be no doubt that the 1 : 2-compound must be formed by anionotropic rearrangement during the conversion of the dibromides into the unsaturated diacetates. Since completion of this work, the formation of 1 : 2-compounds from 3 : 5-dibromo*cyclo*pentene has been reported in its reactions with ethylmagnesium bromide (Barber and English, *J. Amer. Chem. Soc.*, 1951, **73**, 746) and with dimethylamine (Cope, Estes, Emery, and Haven, *ibid.*, p. 1199; see also Ried and Yost, *ibid.*, 1950, **72**, 1807).

The fact that the 1 : 2-diol formed in our experiments was *cis* from the *trans*-1 : 4-dibromide, and *vice versa*, showed that there was a marked stereochemical specificity in the rearrangement, which apparently resulted in overall inversion. However, in these experiments it so happened that the reaction of the *cis*-dibromide with potassium acetate in acetic acid was carried out in the presence of some acetic anhydride, *i.e.*, under anhydrous conditions, whereas interaction of the *trans*-dibromide with silver acetate was done in ordinary acetic acid without exclusion of moisture. Further experiments were therefore carried out, as follows. Treatment of the *cis*-dibromide with silver acetate in *moist* acetic acid, followed by the usual deacetylation and hydrogenation, gave a product which contained 81% of 1 : 2-diol and readily gave derivatives of *cis*-*cyclo*pentane-1 : 2-diol; *i.e.*, the configuration was the opposite of that found under the original dry conditions. Furthermore, the *trans*-dibromide, with silver acetate in *dry* acetic acid, gave a product (containing 42% of 1 : 2-diol) which by fractional crystallisation of the ditoluene-*p*-sulphonates was shown to include *trans*-1 : 2-, *cis*-1 : 3-, and *trans*-1 : 3-*cyclo*pentanediols; owing to the practical difficulties involved in the separation of these three stereoisomers, it cannot be claimed, though it is very probable, that the *cis*-1 : 2-compound was entirely absent, but there is no doubt that the 1 : 2-diol produced was mainly the *trans*-form. It is therefore established that *irrespective of the configuration of the dibromide* the *cis*-1 : 2-diol is formed when water is present, and the *trans*-1 : 2-diol under anhydrous conditions.

There are two possible ways in which the 1 : 2-product can be formed, depending upon the stage at which rearrangement occurs, and the intermediate can be either 3-acetoxy-5-bromo- (IX) or 3-acetoxy-4-bromo-*cyclo*pentene (X). The dependence of the configuration of the 1 : 2-diol on the presence or absence of water suggests the operation of a mechanism similar to that proposed by Winstein and Buckles (*ibid.*, 1942, **64**, 2780, 2787) to explain the formation of either *cis*- or *trans*-derivatives of *cyclo*hexane-1 : 2-diol, in wet or dry acetic acid respectively, from *trans*-1-acetoxy-2-bromo*cyclo*hexane and silver acetate. Evidence for the applicability of Winstein's reasoning to the *cyclo*pentane field has been presented in Part VI (preceding paper), and in the present instance a cyclic intermediate (XI) in dry acetic acid would undergo acetolysis with inversion to give the *trans*-diacetate (XII), whereas in the presence of water the formation of the orthoacetate (XIII) would lead to the *cis*-monoacetate (XIV), and, by further esterification, to the *cis*-diacetate. If (XI) is derived from (X), the latter must have the *trans*-configuration shown in order that cyclisation can be accompanied by the usual inversion on the carbon atom carrying the halogen, and it seems likely that an anionotropic rearrangement (VIII) ⟶ (X) might give a *trans*-product preferentially (from either *cis*- or *trans*-dibromide) because of steric hindrance by the remaining bromine atom, which would lead to opposite-side attack on the adjacent carbon atom. This is supported by the important observation by Barber and English (*loc. cit.*), for which they offer a similar explanation, that either *cis*- or *trans*-(VIII) with ethylmagnesium bromide gives a 4-bromo-3-ethyl*cyclo*pentene which is almost certainly the *trans*-compound (XV). The possible formation of (XI) by the other route, from (IX), is a



type of reaction for which no analogy appears to exist, but if it occurs it would probably be independent of the configuration of (IX) and hence of the original dibromide. In the absence of further evidence, however, we regard the route (VIII) $\longrightarrow$ (X) as the more probable. In this connection it may be pointed out that the formation of *trans*-3 : 4-bisdimethylamino*cyclo*pentene (XVI) from both *cis*- and *trans*-(VIII) could be explained not only by the mechanism (*A*) suggested by Cope *et al.* (*loc. cit.*), but by the alternative (*B*).

Roberts, Young, and Winstein (*ibid.*, p. 2157), in their studies on the replacement reactions of the butenyl chlorides, found that anionotropic rearrangement was inhibited in non-hydroxylic solvents (cf. Steigmann and Hammett, *ibid.*, 1937, **59**, 2536) and that with potassium acetate in acetic anhydride, or tetraethylammonium acetate in acetone, reaction occurred exclusively by the S_N2 mechanism to give the normal acetates. In our own experiments, described above, it had been observed that the proportion of 1 : 2-diol was less in those reactions when dry acetic acid had been used, and it was found that when *trans*-3 : 5-dibromo*cyclo*pentene was treated with potassium acetate in boiling acetic anhydride the product, after the usual deacetylation and hydrogenation, contained only 26% of 1 : 2-diol. Even better results were obtained with tetraethylammonium acetate in acetone; the *trans*-dibromide reacted very smoothly, the replacement of halogen, even at 0°, being complete in an hour [this illustrates the high reactivity of the dibromide compared with that of 1-methylallyl chloride towards the same reagent, for which 7 days at reflux temperature were required for complete reaction (Roberts, Young, and Winstein, *loc. cit.*)]. The resulting unsaturated diacetate was deactylated and hydrogenated, to give a pure *cyclo*pentane-1 : 3-diol, m. p. 40°, which was quite free from 1 : 2-diol. This process therefore represents the first satisfactory method for the synthesis of this elusive compound. The evidence for the allocation of the *trans*-configuration to the solid 3 : 5-dibromide by Thiele (*Annalen*, 1900, **314**, 296) appears to be sound, and on the usual assumption that bimolecular replacement of each halogen atom occurs with inversion the resulting 1 : 3-diol can be assigned the *trans*-structure. It gave a bisphenylurethane the m. p. (162—163°) of which was different from all the alleged 1 : 3-derivatives referred to earlier. The crystalline di-*p*-nitrobenzoate, dimethanesulphonate, and ditoluene-*p*-sulphonate were also prepared.

Similar treatment of the *cis*-dibromide gave a liquid *cyclo*pentane-1 : 3-diol which also was free from any 1 : 2-isomer. It gave a bisphenylurethane, m. p. 172°, but in rather poor yield, and from the behaviour of the products isolated in the preparation of this and other derivatives it appeared that the diol was not stereochemically pure. This was confirmed by fractional crystallisation of the ditoluene-*p*-sulphonate, some of the *trans*-1 : 3-derivative being obtained. The pure *cis*-1 : 3-diol was isolated as a solid, m. p. 30—32°, by solvolysis of the purified *cis*-1 : 3-di-*p*-nitrobenzoate; it was also characterised as the dimethanesulphonate and ditoluene-*p*-sulphonate. The formation of a mixture of stereoisomers from the so-called *cis*-dibromide probably indicates that the latter, a liquid, always contains some *trans*-isomer in solution, and it is significant that Thiele (*loc. cit.*) in his studies on the configurations of the 3 : 5-dibromo*cyclo*pentenes obtained a good yield of 3 : 5-dibromo*cyclo*pentane-1 : 2-diol from the solid isomer, but reported that in the permanganate oxidation of the liquid dibromide the dibromoglycol obtained was contaminated with the stereoisomeric compound derived from the *trans*-dibromide.

It is of interest that, in those cases mentioned earlier when appreciable amounts of 1 : 2-diol were produced, the 1 : 3-diol formed usually contained both stereosiomers even when the pure *trans*-dibromide had been used. This suggests that the normal replacement reaction (without rearrangement) occurs partly by a S_N1 mechanism in the more highly ionising solvents.

One additional route to the *cyclo*pentane-1 : 3-diols was investigated, following the report of Mugdan and Young (*J.*, 1949, 2988) on the use of peracetic and pertungstic acids for the hydroxylation of unsaturated compounds. No experiments were described on conjugated dienes, and *cyclo*pentadiene was therefore treated with a solution of the appropriate peracid in acetic acid under various conditions, but after deacetylation and hydrogenation the resulting products contained 19—46% of 1 : 2-diol; furthermore, the 1 : 3-diol obtained was a mixture of stereoisomers. The method was therefore not of value for the present purpose.

The results of the various methods studied for the preparation of *cyclo*pentane-1 : 3-diol are summarised in Table 1.

In Table 2 the melting-points of the chief derivatives of the *cis*- and *trans*-forms of *cyclo*pentane-1 : 2- and -1 : 3-diol are given, and a consideration of these figures in the light of the evidence previously outlined makes it possible to account for most of the results of earlier investigators. The bisphenylurethane, m. p. 195°, of Dane *et al.* was clearly of the *cis*-1 : 2-diol. The two bisphenylurethanes, m. p.s 173° and 143°, of Criegee and Beucker, which were undoubtedly not 1 : 2-derivatives, were *cis*-1 : 3- and (*cis*- + *trans*-)1 : 3-compounds respectively. The derivatives prepared by Milas *et al.* (bisphenylurethane, m. p. 168—171°, and di-*p*-nitrobenzoate, m. p. 179—181°) and by Blomquist and Mayes (bisphenylurethane, m. p. 171°, and di-*p*-nitrobenzoate, m. p. 182°) were probably slightly impure *cis*-1 : 3-compounds, although derived from diol mixtures in each case. No explanation can be offered for the so-called *trans*-1 : 3-derivatives of Blomquist and Mayes (bisphenylurethane, m. p. 184°; di-*p*-nitrobenzoate, m. p. 207°).

TABLE 1.

Source	Reagent	Overall yield of *cyclo*pentanediol, % (1 : 2 + 1 : 3)	Proportion of 1 : 2-diol in product, %
*cyclo*Pentene	SeO_2–Ac_2O	11	64
*cyclo*Pentadiene	$PhI(OAc)_2$–AcOH	19 *	49 *
,,	H_2O_2–Bu^tOH–OsO_4	19	53
,,	$Me{\cdot}CO_3H$	9-28	19—46
,,	$Me{\cdot}CO_3H$–WO_3	10—17	*ca.* 40
cis-3 : 5-Dibromo*cyclo*pentene	AgOAc–AcOH (wet)	59	81
,,	KOAc–AcOH–Ac_2O	30	63
,,	NEt_4OAc–Me_2CO	48	0
trans-3 : 5-Dibromo*cyclo*pentene	AgOAc–AcOH (wet)	19	93
,,	AgOAc–AcOH (dry)	48	42
,,	KOAc–Ac_2O	56	26
,,	NEt_4OAc–Me_2CO	46	0

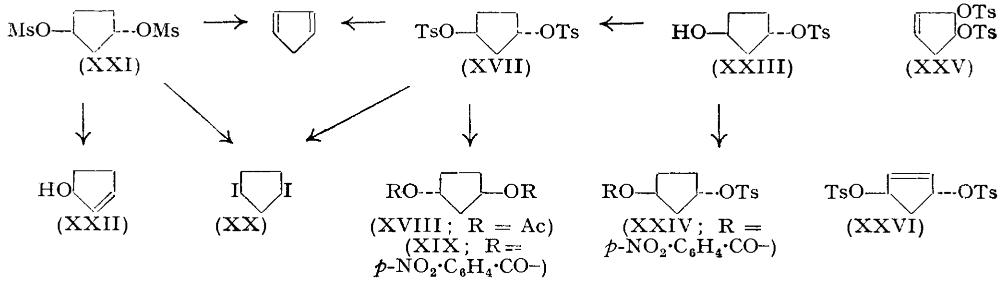
* Criegee and Beucker, *loc. cit.*

TABLE 2. *Melting points of derivatives of the* cyclo*pentane*-1 : 2- and -1 : 3-*diols.*

	cis-1 : 2	*trans*-1 : 2	*cis*-1 : 3	*trans*-1 : 3
Bisphenylurethane	197°	221°	173° *	163° *
Di-*p*-nitrobenzoate	117	143	186 *	153 *
Ditoluene-*p*-sulphonate	92	109	93	115—116
Dimethanesulphonate	82	82	92—94	89—90

* Crystallisation of a mixture of 1 : 3-stereoisomers gives a (*cis*- + *trans*-)1 : 3-bisphenylurethane, m. p. 142—144°; similarly a (*cis*- + *trans*-)1 : 3-di-*p*-nitrobenzoate has m. p. 135—140°. These mixtures are not readily separable by further recrystallisation.

Experiments on the replacement and elimination reactions of the toluene-*p*-sulphonates of the 1 : 3-diol were carried out on lines similar to those recorded in earlier papers in this series. The *trans*-ditoluene-*p*-sulphonate (XVII) with potassium acetate in boiling ethanol gave some *cyclo*pentadiene together with a liquid diacetate, which was shown to have the *trans*-structure (XVIII) by deacetylation, and characterisation of the resulting



(Ms = $Me{\cdot}SO_2$–; Ts = p-$C_6H_4Me{\cdot}SO_2$–)

trans-1 : 3-diol by reconversion into (XVII). Similarly, (XVII) with potassium *p*-nitrobenzoate in boiling ethanol gave *cyclo*pentadiene and the *trans*-1 : 3-di-*p*-nitrobenzoate (XIX). The *cis*-ditoluene-*p*-sulphonate on similar treatment gave *cyclo*pentadiene and *cis*-1 : 3-di-*p*-nitrobenzoate. The overall retention of configuration in these experiments shows that each toluene-*p*-sulphonate group, in the *cis*- and the *trans*-series, probably undergoes normal and independent S_N2 replacement with inversion.

Replacement of the toluene-*p*-sulphonyloxy-groups in (XVII) by iodine occurred readily on treatment with sodium iodide in boiling acetone; the reaction was complete in 2 hours and gave a 62% yield of distilled 1 : 3-di-iodo*cyclo*pentane (XX). The *trans*-dimethane sulphonate (XXI) also gave (XX), but in poorer yield. Reaction of (XVII) with lithium chloride in boiling ethanol was rapid; elimination, solvolysis, and replacement by halogen all occurred, to give *cyclo*pentadiene and a liquid mixture of halide and ether. With boiling methanolic potassium hydroxide, (XVII) gave *cyclo*pentadiene and an unsaturated product, which, although it could not be purified, was probably a methoxy*cyclo*pentene. The solubility of (XVII) in aqueous alkali was too low for hydrolysis to occur, but the *trans*-dimethanesulphonate (XXI) reacted smoothly with boiling 14% aqueous potassium hydroxide to give *cyclo*pentadiene and *cyclo*pent-2-en-1-ol (XXII).

These reactions of the 1 : 3-ditoluene-*p*-sulphonates took place much more readily than those of the 1 : 2-analogues (preceding paper), probably because the deactivating effect of vicinal toluene-*p*-sulphonyloxy-groups on one another does not arise. The reactivity, however, was also noticeably greater than with the ditoluene-*p*-sulphonates of *cyclo*hexane-1 : 3-diol (Clarke and Owen, *J.*, 1950, 2103), which provides further evidence that in substitution reactions *cyclo*pentane derivatives are more reactive than their *cyclo*hexane analogues (cf. Brown, Fletcher, and Johannesen, *J. Amer. Chem. Soc.*, 1951, **73**, 212; Brown and Borkowski, *ibid.*, 1952, **74**, 1894). It is also noteworthy that the proportion of substitution to elimination was generally higher with the ditoluene-*p*-sulphonates of *cyclo*pentane-1 : 3-diol than for any other alicyclic toluene-*p*-sulphonates yet investigated.

The monotoluene-*p*-sulphonate (XXIII) of *trans*-*cyclo*pentane-1 : 3-diol was prepared by treatment of a pyridine solution of the *trans*-diol with 1 mol. of toluene-*p*-sulphonyl chloride in chloroform, added over a period of 3 days at 0°. It was an oil, but it was characterised by conversion into a crystalline *trans*-1-*p*-nitrobenzoate 3-toluene-*p*-sulphonate (XXIV) and also into (XVII). In striking contrast to the monotoluene-*p*-sulphonates of *cyclo*pentane-1 : 2-diol (preceding paper), it reacted only slowly with cold 0·1N-methanolic potassium hydroxide, and after 4 days at 20° only 35% reaction had occurred; in the 1 : 2-series, even the *cis*-monotoluene-*p*-sulphonate under the same conditions required only an hour for a similar degree of change, whilst the *trans*-analogue reacted exceedingly rapidly. Nevertheless, the reactivity of (XXIII), although low, was greater than that of the monotoluene-*p*-sulphonate of *trans*-*cyclo*hexane-1 : 3-diol, which in a comparative experiment reacted to the extent of only 10% in 4 days at 20°.

In view of the high reactivity of the halogen atoms in 3 : 5-dibromo*cyclo*pentene towards substitution by acetate ions, the *trans*-dibromide (VIII) in benzene was treated with silver toluene-*p*-sulphonate at room temperature. A crystalline ditoluene-*p*-sulphonate of a *cyclo*pentenediol was obtained; this reacted with remarkable rapidity with sodium iodide in acetone, to the extent of 60% in an hour at room temperature, a rate unprecedented for any secondary toluene-*p*-sulphonate hitherto described. Of the two possible structures (XXV) and (XXVI), only the latter, with two allylic toluene-*p*-sulphonyloxy-groups, can reasonably account for this behaviour, and the compound is accordingly formulated as the ditoluene-*p*-sulphonate of *trans*-*cyclo*pent-2-ene-1 : 4-diol.

EXPERIMENTAL

cyclo*Pentadiene.*—Di*cyclo*pentadiene, contained in a flask surmounted by a Fenske fractionating column, was heated by an oil-bath at 180° so that only the monomer distilled over. The *cyclo*pentadiene was collected in a receiver at 0°, and was dried (Na_2SO_4) and distilled (b. p. 42°) just before use.

3 : 5-*Dibromo*cyclo*pentene.*—Bromine (160 g.) in chloroform (100 c.c.) was added to a stirred solution of *cyclo*pentadiene (65 g.) in chloroform (100 c.c.) at −25° to −30°. The solvent was

immediately distilled off under reduced pressure, and the green residue was quickly distilled, to give the *cis*-dibromide (182 g., 82%), b. p. 60—63°/0·5 mm., n_D^{18} 1·5855, as a colourless liquid. The *trans*-isomer was obtained by storage of this product at room temperature in the dark, under nitrogen, for 3 months (cf. Blomquist and Mayes, *loc. cit.*). When cooled to 0°, the dark liquid then deposited the solid *trans*-compound, which was collected just before use, and washed with light petroleum (b. p. 40—60°); it formed large colourless crystals, m. p. 45°.

Tetraethylammonium Acetate.—This was prepared as the monohydrate (crystallised from acetone at −80°) by Steigmann and Hammett's method (*loc. cit.*). Crystallisation of a product containing some residual water gave material, soluble in hot acetone but only sparingly in cold, which remained solid at room temperature and was a higher hydrate. When dried over phosphoric oxide it liquefied (Found: loss, 20·3%. Calc. for $NEt_4{\cdot}OAc,4H_2O \longrightarrow NEt_4{\cdot}OAc,H_2O$: loss, 20·7%), but on exposure to moist air it again crystallised.

Estimation of 1 : 2-*Diols.*—The saturated diol mixture (*ca.* 0·05 g.) was dissolved in 0·25M-sodium metaperiodate (5 c.c.) and made up to 25 c.c. with water. A similar solution, but containing no diol, was also prepared. At intervals, a 5-c.c. portion of solution was withdrawn, mixed with 10 c.c. of borax–boric acid buffer at pH 7·0 and an excess of potassium iodide, and titrated with aqueous sodium thiosulphate. In all cases the periodate consumed became constant within 24 hours. The method was checked with authentic specimens of *trans-cyclo*hexane-1 : 2-diol, and *cis*- and *trans-cyclo*pentane-1 : 2-diol.

Oxidation of cyclo*Pentene with Selenium Dioxide.*—*cyclo*Pentene (50 g.), selenium dioxide (80 g.), and acetic anhydride (144 g.) were warmed until the reaction set in; the heat produced was sufficient to maintain gentle refluxing, and selenium was deposited. The dark red reaction mixture was then heated at 100° for 6 hours, cooled, filtered from selenium, and concentrated. The residue on distillation gave a pale yellow liquid (25 g., 18%), b. p. *ca.* 113°/12 mm., which was redistilled, to give a diacetoxy*cyclo*pentene, b. p. 119—121°/13 mm., n_D^{17} 1·4620.

A portion of this product (2 g.) in ethanol (25 c.c.) was hydrogenated at atmospheric pressure in the presence of Raney nickel (only 0·64 mol. of hydrogen was absorbed) and gave a diacetoxy*cyclo*pentane (1·5 g.), b. p. 104°/14 mm., n_D^{17} 1·4480, which was dissolved in dry methanol (5 c.c.), containing a trace of sodium, and set aside for 16 hours. After neutralisation with carbon dioxide, the solution was concentrated and distilled to give a *cyclo*pentanediol (0·7 g.), b. p. 65—70°/1·5 mm., n_D^{21} 1·4780 (Found: 1 : 2-diol, 63·8%).

Hydroxylation of cyclo*Pentadiene.*—(i) *cyclo*Pentadiene (55 g.) was added to an anhydrous solution of hydrogen peroxide in *tert.*-butanol (0·055 g./c.c.; 520 c.c.) containing a 0·5% solution of osmic acid in anhydrous *tert.*-butanol (5 c.c.), at 0°. The solution was left at 0° for 3 days and worked up as described by Milas and Maloney (*loc. cit.*). The product was distilled to give a *cyclo*pentenediol (22 g., 26%), b. p. 118°/0·5 mm., n_D^{17} 1·5040.

Hydrogenation of the *cyclo*pentenediol in ethanol in the presence of Raney nickel gave a *cyclo*pentanediol, b. p. 69—73°/0·1 mm., n_D^{19} 1·4788 (Found: 1 : 2-diol, 52·6%).

(ii) A solution containing " pertungstic acid " (cf. Mugdan and Young, *loc. cit.*) was prepared by heating a mixture of 30% aqueous hydrogen peroxide (14·5 c.c.) and acetic acid (45 c.c.) to 80° for an hour and then adding tungsten trioxide (0·2 g.; freshly precipitated from alkaline solution by acid). The peracid solution was transferred to a pressure bottle, which also contained a test tube of *cyclo*pentadiene (6·6 g.). The bottle was closed, and the reactants mixed to give a homogeneous solution. Much heat was evolved, and after the initial reaction had subsided the bottle was kept at the appropriate temperature for the required time. When cold, the dark brown solution was made alkaline with 30% aqueous sodium hydroxide, and any acetylated material was hydrolysed by heating at 100° for an hour. The hydroxylated product was isolated by continuous ether-extraction of the alkaline solution for 2 days. The ethereal extract was dried (Na_2SO_4) and concentrated to an oil, which on distillation gave a *cyclo*pentenediol. This was hydrogenated in ethanol over Raney nickel, as described above, and the 1 : 2-diol in the saturated product was then estimated with sodium metaperiodate. Hydroxylations were carried out also with the peracetic solution in the absence of any added tungsten trioxide, and with anhydrous peracetic acid. The results are given below.

				Unsaturated diol		1 : 2-Diol (%) in saturated
Peracid	Temp.	Time, hr.	Yield, %	B. p.	*n*	diol
Pertungstic	60°	20	13	80—85°/0·2 mm.	1·5036/21°	40·7
,,	60	16	17	83—84°/0·1 mm.	1·5033/18°	39
Peracetic	60	20	28	80—85°/0·1 mm.	1·5055/14°	19
,,	70	96	13	82—84°/0·2 mm.	1·4982/21°	39
,, (anhyd.)	70	3	10	80—87°/0·3 mm.	1·5026/25°	46·5

Erroneous values were obtained when attempts were made to determine the 1 : 2-diol content directly on the *cyclo*pentenediol products with sodium metaperiodate; the figures ranged up to 200% of 1 : 2-diol, and the attack was evidently not restricted to the hydroxyl groups.

Reactions of cis-3 : 5-*Dibromo*cyclo*pentene with Acetates.*—(i) *With potassium acetate in dry acetic acid.* *cis*-3 : 5-Dibromo*cyclo*pentene (100 g.), freshly fused and finely ground potassium acetate (102 g.), and acetic acid (70 c.c.) containing acetic anhydride (10 c.c.) were heated at 100° for 18 hours. The dark liquid was poured into water (500 c.c.) and extracted with ether (4 × 100 c.c.). The extract was dried ($MgSO_4$) and worked up to give a diacetoxy*cyclo*pentene (43 g., 53%), b. p. 116—118°/2 mm., n_D^{20} 1·4652. The yield was the same as that recorded by Blomquist and Mayes. When the reaction was carried out using crude undistilled *cis*-dibromide, the overall yield of diacetate from *cyclo*pentadiene was increased to 63% (cf. 43% overall on the two stages, when distilled *cis*-dibromide was used).

The unsaturated diacetate (84 g.) was deacetylated by heating it under reflux for 5 hours with finely powdered barium hydroxide (310 g.) in ethanol (850 c.c.). The solution was cooled and filtered from precipitated barium salts, those remaining in solution being removed as carbonate by the passage of carbon dioxide. Evaporation and distillation gave a *cyclo*pentenediol (37 g., 81%), b. p. 103—105°/0·3 mm., n_D^{23} 1·5024.

The *cyclo*pentenediol (68 g.) was hydrogenated at room temp./20 atm. in ethanol (200 c.c.) in the presence of Raney nickel, to give a *cyclo*pentanediol (44·2 g., 70%), b. p. 115°/6 mm., n_D^{23} 1·4839 (Found : 1 : 2-diol, 62·8%). Its crude di-*p*-nitrobenzoate, prepared in pyridine, had m. p. 115—120° and was evidently a mixture; after several recrystallisations from ethanol and from ethyl acetate it gave a small quantity of the di-*p*-nitrobenzoate, m. p. 181—182°, of *cis-cyclo*pentane-1 : 3-diol (the authentic derivative is described below). The ditoluene-*p*-sulphonate of the saturated diol was an oil, which partly crystallised when kept. Several recrystallisations from methanol gave *trans-cyclo*pentane-1 : 2-diol ditoluene-*p*-sulphonate, m. p. 104—105°, not depressed on admixture with an authentic sample, m. p. 109° (Found : C, 55.7; H, 5·5; S, 15·4. Calc. for $C_{19}H_{22}O_6S_2$: C, 55·6; H, 5·4; S, 15·6%).

(ii) *With silver acetate in moist acetic acid.* A solution of the *cis*-dibromide (42 g.) in acetic acid (100 c.c.) was slowly added to a rapidly stirred suspension of freshly prepared silver acetate (from 100 g. of silver nitrate) in acetic acid (200 c.c.) containing small glass beads, so that the temperature did not exceed 30°. Stirring was maintained for a further 16 hours, and the silver salts were then filtered off and washed with acetic acid. Concentration of the filtrates and dilution with ether precipitated a further quantity of salts; evaporation of the filtered solution then gave an oil, which on distillation gave a diacetoxy*cyclo*pentene (24·3 g., 71%), b. p. 73—77°/0·5 mm., n_D^{27} 1·4639.

The product (24 g.) was dissolved in dry methanol (100 c.c.) containing sodium (*ca.* 50 mg.), and after 24 hours at room temperature the solution was neutralised with carbon dioxide and hydrogenated at room temperature and pressure over Raney nickel, the theoretical quantity of hydrogen being absorbed in 6 hours. Distillation of the product gave a *cyclo*pentanediol (11 g., 84%), b. p. 71—75°/0·5 mm. (Found : 1 : 2-diol, 81%). The ditoluene-*p*-sulphonate was obtained as a solid, which after one recrystallisation from methanol had m. p. 91—92°, undepressed on admixture with authentic *cis*-1 : 2-derivative of m. p. 92°, but depressed to *ca.* 80° with the *cis*-1 : 3-derivative of m. p. 93°. The product was therefore largely *cis-cyclo*pentane-1 : 2-diol.

(iii) *With tetraethylammonium acetate in acetone.* The *cis*-dibromide (165 g.) in pure acetone (200 c.c.) was added during an hour to a stirred solution of tetraethylammonium acetate (375 g.) in acetone (1300 c.c.) at <5°. Tetraethylammonium bromide began to separate almost from the beginning of the addition, and the solution became dark. The reaction mixture was kept at 0° for 16 hours, and the precipitated bromide was removed and washed with acetone until colourless. The filtrate and washings were concentrated under reduced pressure below 40°, diluted with water, and extracted with ether. The extracts were dried (Na_2SO_4) and evaporated to an oil, which on distillation gave 3 : 5-diacetoxy*cyclo*pentene (105 g., 78%), b. p. 90—95°/1·5 mm., 82—83°/0·5 mm., n_D^{25} 1·4575. Some diacetone alcohol, b. p. 63—64°/11 mm., n_D^{19} 1·4300, was isolated from the forerunnings of the distillation.

The unsaturated diacetate (104 g.) in ethanol (400 c.c.) was hydrogenated at room temp./5 atm. in the presence of Raney nickel, 1·03 mols. of hydrogen being absorbed. The resulting saturated *diacetate*, isolated by evaporation of the filtered solution, had b. p. 65°/0·3 mm., n_D^{17} 1·4492 (Found : C, 58·1; H, 7·4. $C_9H_{14}O_4$ requires C, 58·1; H, 7·6%). It was set aside in dry methanol (200 c.c.) containing sodium (0·5 g.) for 24 hours at room temperature. The solution was then neutralised and worked up as before, to give a *cyclo*pentane-1 : 3-diol (30·7 g.), b. p. 92°/0·8 mm., n_D^{21} 1·4835, which solidified on storage at 0° (Found : 1 : 2-diol, nil). De-acetylation was also carried out by boiling the crude saturated diacetate under reflux with an excess of barium hydroxide in ethanol for 20 hours; this method gave an overall yield of 62% from the unsaturated diacetate.

Treatment of the diol (0·5 g.) with *p*-nitrobenzoyl chloride (2·0 g.) in dry pyridine (5 c.c.) gave a solid (2 g.), m. p. 117—135°, which was recrystallised three times from ethyl acetate to give the *di*-p-*nitrobenzoate* of *cis-cyclo*pentane-1 : 3-diol (0·5 g.) as needles, m. p. 186° (Found : C, 57·0; H, 4·05; N, 7·1. $C_{19}H_{16}O_8N_2$ requires C, 57·0; H, 4·0; N, 7·0%). The m. p. was depressed to 135—140° on admixture with the *trans*-isomer of m. p. 153°, described below.

The *bisphenylurethane* of *cis-cyclo*pentane-1 : 3-diol was prepared by heating a solution of the diol (0·5 g.) in phenyl *iso*cyanate (3 c.c.) for 5 minutes under reflux. The solid which separated on cooling had m. p. 159—164°, raised by successive recrystallisations from acetic acid, toluene, and ethanol, to 172° (Found : N, 8·4. $C_{19}H_{20}O_4N_2$ requires N, 8·4%). A mixture with the *trans*-isomer of m. p. 162—163° had m. p. 142—144°.

The diol (4 g.) and toluene-*p*-sulphonyl chloride (16 g.) in dry pyridine (40 c.c.) gave a ditoluene-*p*-sulphonate (11 g.), m. p. 75—87°, after one recrystallisation from methanol. This material was fractionally crystallised successively from methanol, ethyl acetate–light petroleum (b. p. 40—60°), and acetone, and gave a less-soluble fraction (0·5 g.) of *trans-cyclo*pentane-1 : 3-diol ditoluene-*p*-sulphonate, m. p. and mixed m. p. 114—115°; further crystallisation of the more soluble material from chloroform–ether gave the *cis*-isomer, m. p. 92—93°, identical with the authentic derivative described below.

cis-cyclo*Pentane*-1 : 3-*diol*.—The above di-*p*-nitrobenzoate, m. p. 186° (5 g.), was heated in dry methanol (45 c.c.) containing sodium (*ca.* 20 mg.) under reflux for an hour. The cooled solution was filtered from methyl *p*-nitrobenzoate, concentrated to 10 c.c., and diluted with water (10 c.c.); a further small amount of the methyl ester was precipitated and removed. The solution was then carefully acidified with aqueous hydrochloric acid, filtered from a little *p*-nitrobenzoic acid, and evaporated under reduced pressure. The residue was extracted with boiling chloroform, and the extracts were dried (Na_2SO_4) and evaporated to an oil, which on distillation gave cis-cyclo*pentane*-1 : 3-*diol* (0·84 g., 67%) as a very hygroscopic solid, m. p. 30—32°, b. p. 90°/1 mm. (Found : C, 58·8; H, 9·9. $C_5H_{10}O_2$ requires C, 58·8; H, 9·9%). This regenerated the original di-*p*-nitrobenzoate, m. p. 186° (from chloroform). Reaction of the diol with boiling phenyl *iso*cyanate gave the bisphenylurethane, which after recrystallisation from acetic acid–light petroleum (b. p. 40—60°) was identical (m. p. and mixed m. p. 173°) with that previously isolated from the impure *cis*-diol. The *dimethanesulphonate* was prepared by treatment of the *cis*-1 : 3-diol (0·15 g.) with methanesulphonyl chloride (0·37 g.) in pyridine (1 c.c.) at 0° for 24 hours, and precipitation by the addition of crushed ice. It crystallised from methanol in small plates, m. p. 92—94° (Found : C, 32·4; H, 5·5; S, 24.6. $C_7H_{14}O_6S_2$ requires C, 32·6; H, 5·5; S, 24·8%), depressed to 80—83° on admixture with the *trans*-isomer of m. p. 89—90°. The *ditoluene*-p-*sulphonate*, similarly obtained, crystallised from methanol in plates, m. p. 93° (Found : C, 55·7; H, 5·5; S, 15·4. $C_{19}H_{22}O_6S_2$ requires C, 55·6; H, 5·4; S, 15·6%), depressed to 80—85° on admixture with the *trans*-isomer of m. p. 114—115°.

Reactions of trans-3 : 5-*Dibromo*cyclo*pentene with Acetates*.—(i) *With silver acetate in moist acetic acid.* A suspension of freshly prepared silver acetate (from silver nitrate, 100 g.) in acetic acid (200 c.c.), containing small glass beads, was rapidly stirred during the addition of a solution of *trans*-3 : 5-dibromo*cyclo*pentene (42 g.) in acetic acid (50 c.c.); the temperature rose to 30°. Stirring was continued for 16 hours, and the product was then isolated as described for the corresponding reaction with the *cis*-dibromide; distillation gave a diacetoxy*cyclo*pentene (19·2 g., 56%), b. p. 68—70°/0·2 mm., n_D^{16} 1·4677, which was hydrolysed by being boiled under reflux with barium hydroxide (73 g.) in ethanol (200 c.c.) for 5 hours. The solution was cooled and filtered, and barium salts remaining in solution were precipitated as carbonate by passage of carbon dioxide. Filtration, evaporation, and distillation of the residual oil gave a *cyclo*pentene-diol (5·1 g., 48%), b. p. 83—84°/0·5 mm., n_D^{18} 1·4957. This was dissolved in ethanol (30 c.c.) and hydrogenated at room temperature and pressure over Raney nickel; 0·97 mol. of hydrogen was absorbed. The catalyst was removed and the filtrate worked up to give a *cyclo*pentanediol (3·4 g., 68%), b. p. 60—66°/0·1 mm., which crystallised to a very hygroscopic solid (Found : 1 : 2-diol, 93%).

The diol (0·91 g.) with *p*-nitrobenzoyl chloride (3·55 g.) in pyridine (20 c.c.) gave a solid (4·1 g.), which after recrystallisation from ethanol gave *cis-cyclo*pentane-1 : 2-diol di-*p*-nitrobenzoate, m. p. and mixed m. p. 117°. The product was therefore almost pure *cis*-1 : 2-diol.

(ii) *With silver acetate in dry acetic acid.* The quantities used were identical with those in the preceding description, but the silver acetate was dried over phosphoric oxide under reduced pressure and the acetic acid was dehydrated by distillation from an excess of acetic anhydride. The unsaturated diacetate (27·8 g., 80%), b. p. 75—79°/0·5 mm., n_D^{21} 1·4510, was deacetylated by treatment with a catalytic amount of sodium in methanol and then hydrogenated as above, to give a *cyclo*pentanediol (9 g.), b. p. 80—81°/0·8 mm. (Found: 1 : 2-diol, 42%).

A portion (1 g.) of the diol was treated with toluene-*p*-sulphonyl chloride (5 g.) in pyridine (10 c.c.) at 0° for 24 hours. Addition of crushed ice precipitated an oil. A solution of this in chloroform was washed successively with water, dilute hydrochloric acid, and sodium hydrogen carbonate solution, dried ($CaCl_2$), and evaporated to a semi-solid residue, which furnished a solid, m. p. 90—95°, when recrystallised once from methanol (10 c.c.). Fractional crystallisation of this solid from chloroform–ether gave a less-soluble fraction (0·3 g.) of *trans-cyclo*pentane-1 : 2-diol ditoluene-*p*-sulphonate, m. p. and mixed m. p. 109°. Further crystallisations (from the same solvent) of the more soluble material gave *cis-cyclo*pentane-1 : 3-diol ditoluene-*p*-sulphonate, m. p. and mixed m. p. 91—92° (depressed to 70—75° by the *cis*-1 : 2-isomer). Evaporation of the original methanolic mother-liquors left a sticky solid which after 3 recrystallisations from chloroform–ether gave the *trans*-1 : 3-ester, m. p. and mixed m. p. 114°.

(iii) *With potassium acetate in acetic anhydride.* A mixture of the *trans*-dibromide (38 g.), anhydrous potassium acetate (60 g.), and acetic anhydride (200 c.c.) was heated gradually to the b. p.; a vigorous reaction occurred and the liquid continued to boil without further application of heat. When cold the dark brown mixture was cautiously diluted with water and extracted with ether. Evaporation of the dried (Na_2SO_4) extracts gave an oil which on distillation furnished a diacetoxy*cyclo*pentene (27·7 g., 89%), b. p. 90°/0·4 mm., n_D^{21} 1·4572. This was deacetylated by treatment in the usual way with dry methanol containing a small quantity of sodium, and then hydrogenated in the same solution (after neutralisation) over Raney nickel at room temperature and pressure to give a *cyclo*pentanediol (9·6 g.), b. p. 82°/0·3 mm. (Found: 1 : 2-diol, 26%).

The ditoluene-*p*-sulphonate, prepared from the diol (1 g.) as described above, on fractional crystallisation from methanol, followed by chloroform–ether, gave *trans-cyclo*pentane-1 : 3-diol ditoluene-*p*-sulphonate (0·3 g.), m. p. and mixed m. p. 114°.

(iv) *With tetraethylammonium acetate in acetone.* The *trans*-dibromide (50 g.) in acetone (100 c.c.) was added to a stirred solution of tetraethylammomium acetate (120 g.) in acetone (500 c.c.), cooled in an ice-bath, at such a rate that the temperature did not rise above 5°. Tetraethylammonium bromide began to separate immediately, and the solution became dark. After the addition was complete (1 hour), the mixture was kept at 0° for 16 hours and then filtered from tetraethylammonium bromide (90 g., 97%). The solid was washed with acetone until colourless, and the combined filtrate and washings were concentrated under reduced pressure and diluted with water (400 c.c.). The aqueous mixture was extracted with ether (3 × 100 c.c.) and the dried (Na_2SO_4) extracts were evaporated to a dark liquid, which on distillation gave *trans*-3 : 5-diacetoxy*cyclo*pentene (28·8 g., 70%), b. p. 75—76°/0·5 mm., n_D^{19} 1·4635, as a pale yellow liquid. Two further preparations gave yields of 73 and 83%.

The unsaturated diacetate (28·5 g.) was hydrogenated in ethanol (100 c.c.) at room temperature and atmospheric pressure in the presence of Raney nickel; 0·97 mol. of hydrogen was absorbed. The saturated diacetate was not isolated; the filtered ethanolic solution was directly hydrolysed under reflux with barium hydroxide (110 g.) for 5 hours. The barium salts were filtered off, and after removal of dissolved salts by passage of carbon dioxide, and further filtration, the solution was concentrated under reduced pressure to a viscous liquid which on distillation gave trans-cyclo*pentane*-1 : 3-*diol* (8·73 g., 55%), b. p. 80—85°/0·1 mm., as a colourless liquid, with a pleasant odour, which solidified to a crystalline, very hygroscopic solid, m. p. 40° (Found: 1 : 2-diol, nil; C, 58·8; H, 9·9. $C_5H_{10}O_2$ requires C, 58·8; H, 9·9%).

In further preparations, the saturated diacetate was isolated as an oil (by evaporation of the filtered hydrogenation product) and was deacetylated by treatment with dry methanol containing a catalytic amount of sodium. The yield of *trans*-1 : 3-diol was approximately the same as that obtained by hydrolysis with barium hydroxide.

Derivatives of trans-cyclo*Pentane*-1 : 3-*diol*.—Treatment of the diol (0·24 g.) with *p*-nitrobenzoyl chloride (0·96 g.) in pyridine (3 c.c.) for 24 hours at 0° gave, on precipitation in ice-water, a solid (0·9 g.), m. p. 140—148°, which after two recrystallisations from ethyl acetate gave needles of the trans-*di*-p-*nitrobenzoate*, m. p. 153° (Found: C, 56·9; H, 4·4; N, 7·3. $C_{19}H_{16}O_8N_2$ requires C, 57·0; H, 4·0; N, 7·0%).

The *trans*-1 : 3-diol (0·5 g.) was heated under reflux with phenyl *iso*cyanate (3 c.c.) for 5 minutes. On cooling, a solid separated, m. p. 145—155°, which was crystallised twice from acetic acid–light petroleum (b. p. 40—60°) to give fine needles of the trans-*bisphenylurethane*, m. p. 162—163 (Found : N, 8·7; $C_{19}H_{20}O_4N_2$ requires N, 8·4%).

A solution of methanesulphonyl chloride (6·0 g.) in pyridine (20 c.c.) was added slowly to a stirred solution of *cyclo*pentane-1 : 3-diol (2·4 g.) in pyridine (10 c.c.) cooled to −10°. The mixture was stored at 0° for 16 hours, and crushed ice was then added. The precipitated trans-*dimethanesulphonate* crystallised from methanol in needles, m. p. 89—90° (Found : C, 32·7; H, 5·7; S, 24·8. $C_7H_{14}O_6S_2$ requires C, 32·6; H, 5·5; S, 24·8%).

Similar treatment of the *trans*-1 : 3-diol (0·43 g.) in pyridine (2 c.c.) with toluene-*p*-sulphonyl chloride (1·72 g.) in pyridine (5 c.c.) followed by storage for 16 hours at 0° gave the trans-*ditoluene*-p-*sulphonate*, small nodules (from methanol), m. p. 114—115° (Found: C, 55·7; H, 5·5; S, 15·4. $C_{19}H_{22}O_6S_2$ requires C, 55·6; H, 5·4; S, 15·6%).

Reactions of the Ditoluene-p-*sulphonate of* trans-cyclo*Pentane*-1 : 3-*diol*.—(i) *With potassium acetate*. The ditoluene-*p*-sulphonate (3 g.) and fused potassium acetate (3·5 g.) were heated in dry ethanol (60 c.c.) under reflux, a slow current of nitrogen being passed through the apparatus and then through a wash-bottle containing a 1% solution of sodium nitroprusside in 1% methanolic potassium hydroxide. The latter became red in a few minutes, indicating the formation of *cyclo*pentadiene (Scagliarina and Lucchi, *Chem. Abs.*, 1940, **34**, 2287), and potassium toluene-*p*-sulphonate began to be precipitated from the reaction mixture. Boiling was maintained for 12 hours, and the salt was then removed by filtration (2·75 g., 90%). The filtrate was evaporated under reduced pressure and the residue was dissolved in water (50 c.c.) and extracted with ether. The ethereal solution was dried (Na_2SO_4) and evaporated to an oil, which on distillation gave the diacetate of *trans-cyclo*pentane-1 : 3-diol as a colourless mobile liquid (0·54 g., 43%), b. p. 65—68°/0·5 mm., n_D^{20} 1·4454.

The diacetate was deacetylated by treatment in dry methanol with a catalytic amount of sodium, and worked up as previously described, to give the *trans*-1 : 3-diol (0·24 g.), which was characterised by treatment with toluene-*p*-sulphonyl chloride (0·95 g.) in dry pyridine (3 c.c.) at 0° to give the *trans*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 114—115°.

(ii) *With potassium* p-*nitrobenzoate*. The ditoluene-*p*-sulphonate (1 g.) and potassium *p*-nitrobenzoate (2·5 g.) in dry ethanol (75 c.c.) were heated under reflux in a current of nitrogen for 8 hours; *cyclo*pentadiene was detected as in the previous experiment. The reaction mixture was cooled, diluted with water (30 c.c.), and distilled under reduced pressure to remove most of the alcohol. The residual solution was extracted with chloroform. Evaporation of the dried (Na_2SO_4) extracts gave a solid residue, which on recrystallisation from ethyl acetate–light petroleum (b. p. 40—60°) gave the *trans-cyclo*pentane-1 : 3-diol di-*p*-nitrobenzoate, m. p. and mixed m. p. 153°.

(iii) *With sodium iodide*. A solution of the ditoluene-*p*-sulphonate (1·5 g.) and sodium iodide (2·5 g.) in dry acetone (30 c.c.) was boiled under reflux for 2 hours in a slow stream of nitrogen, *cyclo*pentadiene being detected in the issuing gases as previously described. The precipitated sodium toluene-*p*-sulphonate was filtered off (1·38 g., 98%), and the solution was evaporated to a semi-solid residue. This was diluted with water, and the oil which separated was extracted with ether. The extracts were washed with aqueous sodium thiosulphate solution, dried (Na_2SO_4), and concentrated to an oil, which on distillation gave trans-1 : 3-*di-iodo*cyclo*pentane* (0·73 g., 62%), b. p. 55—60°/0·0005 mm., n_D^{19} 1·6490 (Found : I, 77·2. $C_5H_8I_2$ requires I, 78·8%), as a pale yellow liquid which did not wet glass.

(iv) *With lithium chloride*. The ditoluene-*p*-sulphonate (1·65 g.) and anhydrous lithium chloride (0·7 g.) were heated under reflux in ethanol (30 c.c.) under reflux in a current of nitrogen. After 6 hours no more *cyclo*pentadiene could be detected in the gas, and the solution, which was now acid, was neutralised with aqueous sodium hydroxide and concentrated to small volume. Extraction with ether gave a colourless liquid (0·14 g.), b. p. 58°/28 mm., n_D^{15} 1·4618, which showed no unsaturation towards bromine in carbon tetrachloride, and was probably a mixture of chloro- and ethoxy-compounds (Found : C, 54·4; H, 8·5; Cl, 29·0. Calc. for $C_5H_8Cl_2$: C, 43·2; H, 5·8; Cl, 51·0. Calc. for $C_9H_{18}O_2$: C, 68·3; H, 11·5%).

(v) *With methanolic potassium hydroxide*. A solution of the ditoluene-*p*-sulphonate (3 g.) in 5% methanolic potassium hydroxide (40 c.c.) was boiled under reflux in a current of nitrogen. A considerable quantity of *cyclo*pentadiene was formed, as judged from the rapid formation of a red precipitate in the nitroprusside trap, and after 1 hour the reaction was over. Potassium toluene-*p*-sulphonate (2 g.) was filtered from the cooled solution, and the filtrate was concentrated to small volume (1 atm.; Fenske column). The residue was diluted with water and extracted with pentane, but gave no product. The methanolic distillate was strongly unsaturated to bromine in carbon tetrachloride and to neutral aqueous potassium permanganate, but gave a negative reaction for *cyclo*pentadiene; it probably contained a methoxy*cyclo*pentene, since treatment with a slight excess of bromine and evaporation gave a colourless saturated oil (0·2 g.), b. p. 100°/20 mm., n_D^{20} 1·4972 (Found: C, 35·9; H, 5·5; Br, 47·7. Calc. for a bromodimethoxy*cyclo*pentane, $C_7H_{13}O_2Br$: C, 40·2; H, 6·3; Br, 38·3. Calc. for a dibromomethoxy*cyclo*pentane, $C_6H_{10}OBr_2$: C, 27·9; H, 3·9; Br, 62·0%).

Reactions of the Dimethanesulphonate of trans-cyclo*Pentane*-1 : 3-*diol*.—(i) *With sodium iodide.* The dimethanesulphonate (1·25 g.) and sodium iodide (3·1 g.) were boiled under reflux in acetone (35 c.c.), in a slow stream of nitrogen. The formation of *cyclo*pentadiene was detected as described above, and sodium methanesulphonate began to be precipitated within a few minutes. After 3 hours the solution was cooled, filtered, and worked up as for the similar reaction with the ditoluene-*p*-sulphonate, to give 1 : 3-di-iodo*cyclo*pentane (0·55 g., 35%), b. p. 65°/0·001 mm., n_D^{23} 1·6345, which was much darker than the product previously obtained.

(ii) *With aqueous potassium hydroxide.* A suspension of the dimethanesulphonate (4·7 g.) in a solution of potassium hydroxide (4·7 g.) in water (30 c.c.) was boiled under reflux in a current of nitrogen. After 1½ hours, when no more *cyclo*pentadiene was being evolved, the solution was steam-distilled. The distillate was continuously extracted with ether overnight; evaporation of the dried (Na_2SO_4) extracts gave an unsaturated oil which was distilled, to give *cyclo*pent-2-enol (0·71 g., 46%), b. p. 138—140°, n_D^{20} 1·4735, characterised as the phenylurethane, m. p. 127° (Dane *et al.*, *loc. cit.*, give m. p. 128—129°). The residue from the steam-distillation was neutralised with hydrochloric acid and continuously extracted with ether, to give a very small amount of oil (0·01 g.), identified as *trans-cyclo*pentane-1 : 3-diol by conversion into the di-*p*-nitrobenzoate; the amount available was insufficient for the m. p. to be raised above 147—150°, but a mixed m. p. with the authentic *trans*-derivative (m. p. 153°) was 150—153°.

Reaction of the Ditoluene-p-*sulphonate of* cis-cyclo*Pentane*-1 : 3-*diol with Potassium* p-*Nitrobenzoate*.—The ditoluene-*p*-sulphonate (1·05 g.) and potassium *p*-nitrobenzoate (2·5 g.) were boiled under reflux in dry ethanol (75 c.c.) for 8 hours under nitrogen; *cyclo*pentadiene was evolved and detected as previously described. The reaction mixture was worked up as for the similar reaction with the *trans*-ditoluene-*p*-sulphonate and gave a solid (0·15 g.), m. p. 175—182°, which after one recrystallisation from chloroform furnished the di-*p*-nitrobenzoate of *cis-cyclo*pentane-1 : 3-diol, m. p. and mixed m. p. 186°.

Monotoluene-p-*sulphonate of* trans-cyclo*Pentane*-1 : 3-diol.—A solution of toluene-*p*-sulphonyl chloride (9·8 g.) in chloroform (100 c.c.) was added in small portions, during 3 days, to a stirred solution of the *trans*-1 : 3-diol (5·0 g.) in dry pyridine (100 c.c.) at <0°. The mixture was stored for a further day at 0° and then concentrated under reduced pressure. The residue was diluted with water (250 c.c.), and the precipitated oil was taken up in chloroform and washed successively with dilute sulphuric acid, water, and aqueous sodium hydrogen carbonate; evaporation of the dried (Na_2SO_4) solution, finally at 0·0001 mm., gave the *monotoluene*-p-*sulphonate* (5·4 g., 43%) as a pale yellow viscous oil, n_D^{14} 1·5338 (Found: S, 12·7. $C_{12}H_{16}O_4S$ requires S, 12·5%). It was characterised by conversion of portions in pyridine into the *trans*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 114—115°, and the p-*nitrobenzoate toluene*-p-*sulphonate* of *trans-cyclo*pentane-1 : 3-diol, which after recrystallisation from methanol had m. p. 82—83° (Found: C, 56·3; H, 4·8; N, 3·3. $C_{19}H_{19}O_7NS$ requires C, 56·3; H, 4·7; N, 3·5%).

Rates of Reaction with Methanolic Potassium Hydroxide of the Monotoluene-p-*sulphonates of* trans-cyclo*Pentane- and* trans-cyclo*Hexane*-1 : 3-*diol*.—Solutions of the *cyclo*pentane compound (1·874 g.) in 0·0746N-methanolic potassium hydroxide (200 c.c.), and the *cyclo*hexane compound (prepared by the method of Clarke and Owen, *loc. cit.*) (1·992 g.) in 0·0748N-methanolic potassium hydroxide (200 c.c.) were kept at 20°, portions being withdrawn from time to time and titrated with standard aqueous sulphuric acid (phenolphthalein). The results are shown below:

Time, hr.		26	48	72	96
Reaction (%)	*cyclo*pentane deriv.	11	17	24	34
	*cyclo*hexane deriv.	2	—	—	10

Ditoluene-p-*sulphonate of* trans-cyclo*Pent*-2-*ene*-1 : 4-*diol*.—A solution of *trans*-3 : 5-dibromo*cyclo*pentene (5 g.) in dry benzene (25 c.c.) was slowly added to a stirred suspension of silver toluene-*p*-sulphonate (25 g.) in dry benzene (75 c.c.), containing glass beads. Stirring was maintained for 16 hours at room temperature, and the silver salts were then filtered off and washed with dry benzene. The solution was concentrated below 35° under reduced pressure to about 10 c.c., and then diluted with light petroleum (b. p. 40—60°) and cooled to 0°. A crystalline solid (3·2 g.), m. p. 63—65°, was thus obtained, and a further quantity (1·9 g.) with the same m. p. was precipitated on the addition of more light petroleum (total yield, 66%). A small quantity was recrystallised from carbon tetrachloride, to give trans-cyclo*pent-2-ene-1* : 4-*diol ditoluene*-p-*sulphonate*, m. p. 64—65° (Found : S, 15·2. $C_{19}H_{20}O_6S_2$ requires S, 15·7%), but an attempt to recrystallise the bulk of the material in this way resulted in gross decomposition, with formation of tar and acid.

Reaction with sodium iodide. The above ditoluene-*p*-sulphonate (0·14 g.) was added to a solution of sodium iodide (0·24 g.) in dry acetone (10 c.c.). The mixture became warm, sodium toluene-*p*-sulphonate began to be precipitated, and a brown colour developed in a few minutes. After 1 hour the salt was filtered off (0·08 g., 60%) and the free iodine (54%) was estimated by thiosulphate; *cyclo*pentadiene was detected in the solution with alkaline nitroprusside. Since the amount of free iodine almost corresponded to the quantity of sodium toluene-*p*-sulphonate formed, no appreciable amount of di-iodo*cyclo*pentene could be present.

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