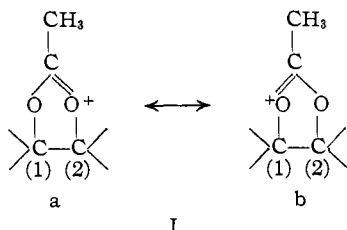


[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY No. 1315]

## Acetolysis of the *p*-Toluenesulfonates of the 2,3-Butanediols

BY H. J. LUCAS, F. W. MITCHELL, JR., AND H. K. GARNER

Previous studies on the acetolysis of the *p*-toluenesulfonates of glycols have been limited to *cis*- and *trans*-cyclohexanediols<sup>1</sup> where the six-membered ring prevents free rotation about the bond connecting the two hydroxyl-bearing carbon atoms. Winstein has shown that cyclic intermediate ions of the general type, I, play a part in these reactions.



It is evident, however, that when C-1 and C-2 are part of a cyclohexane ring, structures such as I are more stable in the *cis*-configuration. An acyclic glycol therefore, represents a more general case in that the *cis*- and *trans*-forms of I are more nearly equivalent in the energy required for their formation. This paper describes the acetolysis of the *p*-toluenesulfonates of *meso*- and D(-)-2,3-butanediol.<sup>2</sup>

The acetolysis reactions, shown in Fig. 1, have been carried out under (a) anhydrous conditions, and (b) with a limited amount of water present, for it has been noted that water influences the course of the reaction in the case of the cyclohexane derivatives.<sup>1</sup> The isomeric compositions of the reaction products, in terms of diacetate, are shown in Table I. Products from reactions when water was present were mixtures of monoacetates and diacetate with the former predominating. For analysis, these were converted to the diacetates, and the compositions of the product determined by means of melting points, refractive indices, and optical rotations. The compositions determined independently by the different constants were in good agreement.

The configurations shown for the optically active compounds are based on the known con-

figuration of D(-)-2,3-butanediol.<sup>3</sup> All except L(+)-*threo*-3-acetoxy-2-butanol, IX, were obtained from the active glycol by reactions not involving the asymmetric centers, and the configuration of this monoacetate was proved by conversion to L(-)-2,3-diacetoxybutane. The designation of any particular compound as D or L is based upon the configuration about carbon atom C-3 in conformity with carbohydrate nomenclature, where the configuration of the highest numbered asymmetric carbon atom determines the family.<sup>4</sup>

The formation from the *meso*- or D-ditosylate (II or III) of, respectively, the DL- or *meso*-diacetate of 2,3-butanediol (VI or VII), when heated with potassium acetate in anhydrous acetic acid, shows that an odd number of inversions has occurred. Although an intermediate acetate-tosylate was not isolated, it is reasonable to assume that the reaction proceeds in steps and that the tosylate groups are replaced one at a time.

When an acetate-tosylate ester is treated similarly, the number of inversions is either zero or even, since the ester of the *meso*-glycol, V, gives the *meso*-diacetate, VII, and that of the D-glycol, IV, gives the DL-diacetate, VI. However, the fact that DL-diacetate, VI, is formed from the D-acetate-tosylate shows that the number of inversions must be two, in going from IV to VI, or from V to VII, for one inversion of each asymmetric carbon atom is necessary for the formation of the L isomer in the DL mixture. Consequently three inversions are involved in the over-all change, ditosylate to diacetate (II to VI and III to VII). It will be shown later how the formation from D-acetate-tosylate, IV, of DL-diacetate, VI, instead of an active diacetate, points strongly to an intermediate cyclic ion.

When water is present the reaction takes a different course. This effect of water was first observed by Winstein and Buckles in the reaction of 2-acetoxy-3-bromobutane with silver acetate<sup>5</sup> and later by Winstein, Hess and Buckles in the acetolysis of 2-acetoxycyclohexyl-*p*-toluenesul-

(3) S. A. Morrell and A. H. Auernheimer, *THIS JOURNAL*, **66**, 792 (1944).

(4) Report of the Committee on Carbohydrate Nomenclature, Charles D. Hurd, Chairman, *Chem. Eng. News*, **26**, 1623 (1948).

(1) (a) S. Winstein, H. V. Hess and R. E. Buckles, *THIS JOURNAL*, **64**, 2796 (1942); (b) S. Winstein, C. Hanson and E. Grunwald, *ibid.*, **70**, 812 (1948); (c) S. Winstein, E. Grunwald, R. E. Buckles and C. Hansen, *ibid.*, **70**, 816 (1948).

(2) The phase of the work dealing with the *meso*-glycol was started in 1939 at the suggestion of Dr. Winstein. It was in progress at about the time he was working on the cyclohexane derivatives, but was interrupted by the war. Recently a supply of D(-)-2,3-butanediol was made available to us through the kindness of Dr. A. F. Langlykke, of the Northern Regional Research Laboratory, Peoria, Illinois, thus enabling us to complete our investigation. We wish to express our thanks to him and to the laboratory for this courtesy.

In some cases a compound could be assigned to either family. For example, it might seem logical to assign the monoacetate, IX, to the D family, since it is named as a derivative of D-2-butanol. However, introduction of the acetoxy group adds a new asymmetric center and changes the compound to a derivative of L-2,3-butanediol. Therefore, it is the opinion of the authors that the rules of carbohydrate nomenclature should be adhered to, and that assignment to the L family is the better choice.

(5) S. Winstein and R. E. Buckles, *THIS JOURNAL*, **64**, 2787 (1942).

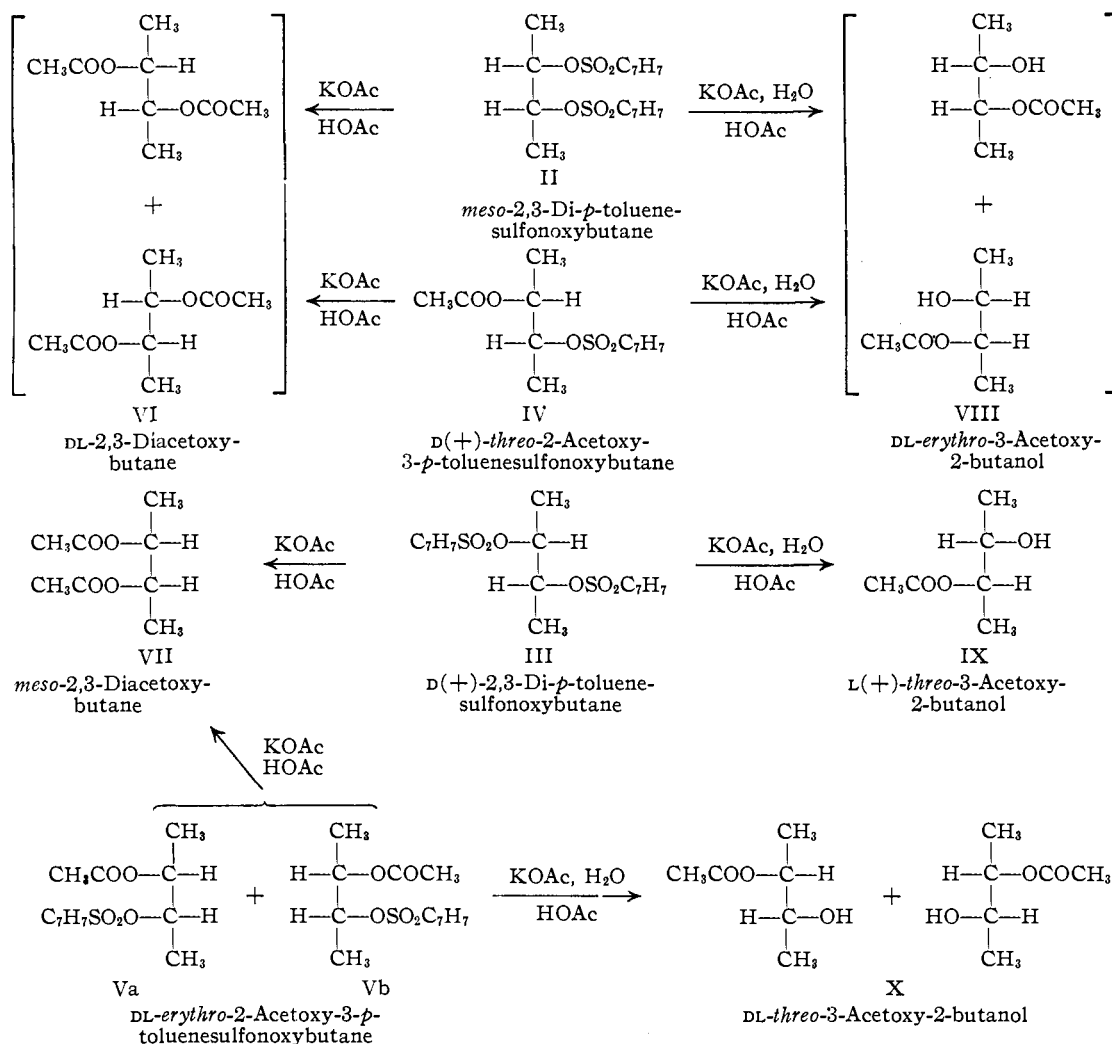


Fig. 1.—Acetolysis of ditosylates and acetate-tosylates of 2,3-butanediol.

fonate.<sup>1a</sup> The ditosylate of *meso*-2,3-butanediol, II, yields an *erythro*-monoacetate, VIII, while that of the *D*-glycol, III, yields a *threo*-monoacetate, IX, when an equivalent amount of water is present. The number of inversions involved in going to VIII is zero or two, and to IX is two. In the second step, acetate-tosylate to monoacetate, there is an odd number of inversions, since the acetate-tosylate of the *meso*-glycol, V, yields a *threo*-monoacetate, X, and that of the active glycol, IV, yields an *erythro*-monoacetate, VIII. On the assumption that there is just one inversion from acetate-tosylate to monoacetate, and that the acetate-tosylate is an intermediate in the acetolysis of the ditosylate, it follows that two inversions are involved in the over-all change (II to VIII and III to IX). The formation of inactive *erythro*-monoacetate, VIII, instead of an active monoacetate, from the active *threo*-acetate-tosylate, IV, is later shown to be additional evidence for a cyclic intermediate ion.

All of the phenomena described above are satisfactorily accounted for by the two mechanisms outlined in Figs. 2 and 3. Each of these involves the formation of a cyclic intermediate acetate ion, XI and XIII, respectively, of the type previously described by Winstein and co-workers as intermediates in similar changes.<sup>1,5,6</sup>

In Fig. 2, there are three steps in the change of *D*-ditosylate, III, to *meso*-diacetate, VII, in the absence of water. Step one is the S<sub>N</sub>2 displacement of the tosyloxy group by an acetoxy group with one inversion, similar to the well known behavior of derivatives of monohydric secondary alcohols.<sup>7</sup> Step two is the displacement of the second tosyloxy group by the carbonyl oxygen of the acetoxy group with one inversion, to form the

(6) The isolation of cyclohexene ethyl orthoacetate from the solvolysis of *trans*-2-acetoxycyclohexyl-*p*-toluenesulfonate in anhydrous ethanol substantiates the mechanism involving a cyclic intermediate; S. Winstein and R. E. Buckles, *THIS JOURNAL*, **65**, 613 (1943).

(7) H. Phillips, *J. Chem. Soc.*, **123**, 44 (1923).

TABLE I  
 COMPOSITION OF ACETATE MIXTURES FROM THE ACETOLYSIS EXPERIMENTS

Starting material	Water present, moles/ester	Method of isolation <sup>a</sup>	Properties of diacetate			Composition of diacetate, %		
			M. p., °C., cor.	$n_D^{25}$	$\alpha_D^{25}$	<i>meso</i>	DL	L(-)
D(+)-2,3-Di- <i>p</i> -toluenesulfonylbutane	0	I	0.7	1.4119	- 0.26	91.1	7.0	1.9
	0	I	0.3	1.4119	- 0.26	90.0	8.1	1.9
	0	II	0.8	1.4116	- 0.21	91.5	7.0	1.5
	2.7	I	18.5	1.4135	-11.64	15.9	0	84.1 <sup>d</sup>
	4.2	II	21.3	1.4135	-12.61	9.9	0	90.1 <sup>d</sup>
DL- <i>erythro</i> -2-Acetoxy-3- <i>p</i> -toluenesulfonylbutane	0	I	3.0	1.4117		98.2	1.8	0
	1.0	II	14 <sup>b</sup>			4.4	95.6	0
			41.5					
D(+)- <i>threo</i> -2-Acetoxy-3- <i>p</i> -toluenesulfonylbutane	0	II	41.2		+ 0.06	3.7	96.3	0
	3.4	II	1.4	1.4112	0.00	93.2	6.8	0
<i>meso</i> -2,3-Di- <i>p</i> -toluenesulfonylbutane	0	II	39.0	1.4120 <sup>c</sup>		10.0	90.0	0
	1.0	II		1.4117		>90	<10	0

<sup>a</sup> Method I. The reaction mixture was poured onto a mixture of sodium bicarbonate and ice, and the solution extracted with ether. Method II. Most of the solvent (acetic acid) was removed by distillation at reduced pressure until solid KOAc began to precipitate out. The mixture was then extracted directly with ether. <sup>b</sup> Three fractions from distillation. <sup>c</sup> Two fractions from distillation. <sup>d</sup> These values were obtained from the m. p.'s. Values from the rotations are 82.7 and 89.5%, respectively. The difference could arise either from the presence of a small amount of DL-diacetate which would raise the m.p., or from non-linearity of the rotation-composition curve.

cyclic intermediate, XI. This is comparable to similar changes in the cyclohexanediol series.<sup>1</sup> Step three is the conversion of the cyclic intermediate, XI, to the *meso* diacetate, VII, with one inversion at either carbon atom. Thus C-2 is inverted at step one, C-3 at step two and either C-2 or C-3 at step three. Therefore in the over-all change either C-2 is inverted twice and C-3 once, or else C-2 is inverted once and C-3 twice.

The cyclic intermediate, XI, Fig. 2, has the L-*threo* configuration and thus possesses optical activity. Activity is lost when this reacts with acetate ion since the resulting diacetate possesses the *meso* configuration. However, activity is retained when water is present, for then, instead of attack by acetate ion at either C-2 or C-3, the third step is reaction by water to open the ring without inversion. Probably it attacks the acetoxy carbon atom to form another intermediate, either XII, or an isomer with the positive charge on one of the other oxygen atoms. Then the ring opens to form L(+)-*threo*-3-acetoxy-2-butanol. Only one product is formed, since C-2 and C-3 have the same configuration. Configuration is retained in this ring-opening process when water is present. In the over-all change, III to IX, both C-2 and C-3 are inverted once, one at step one, the other at step two. Thus the formation of the L-monoacetate from the original D-ditosylate is strong evidence for the formation of the cyclic intermediate, XI.

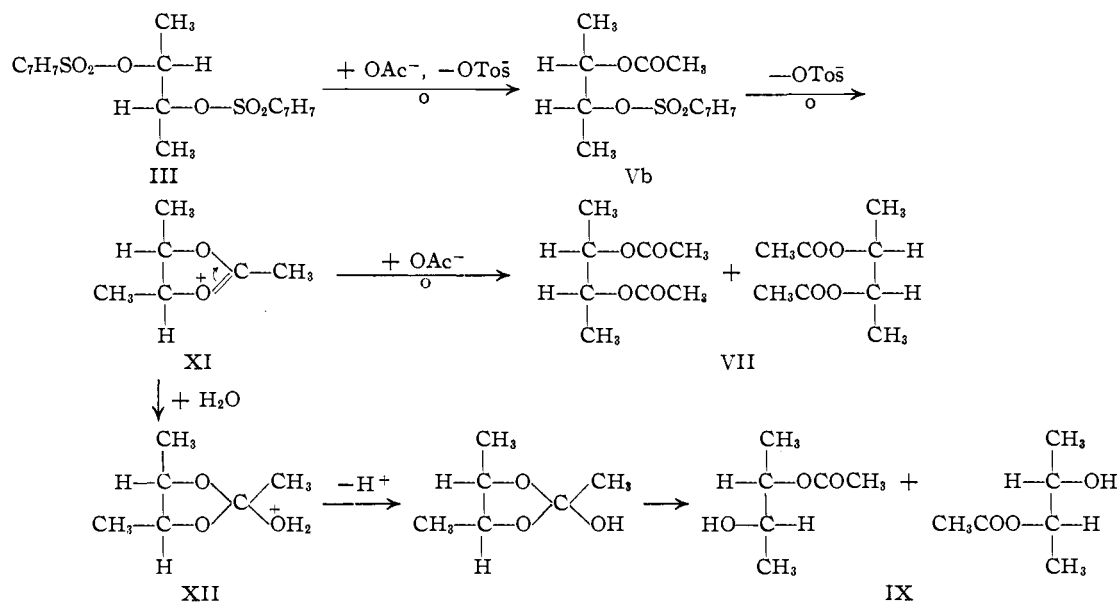
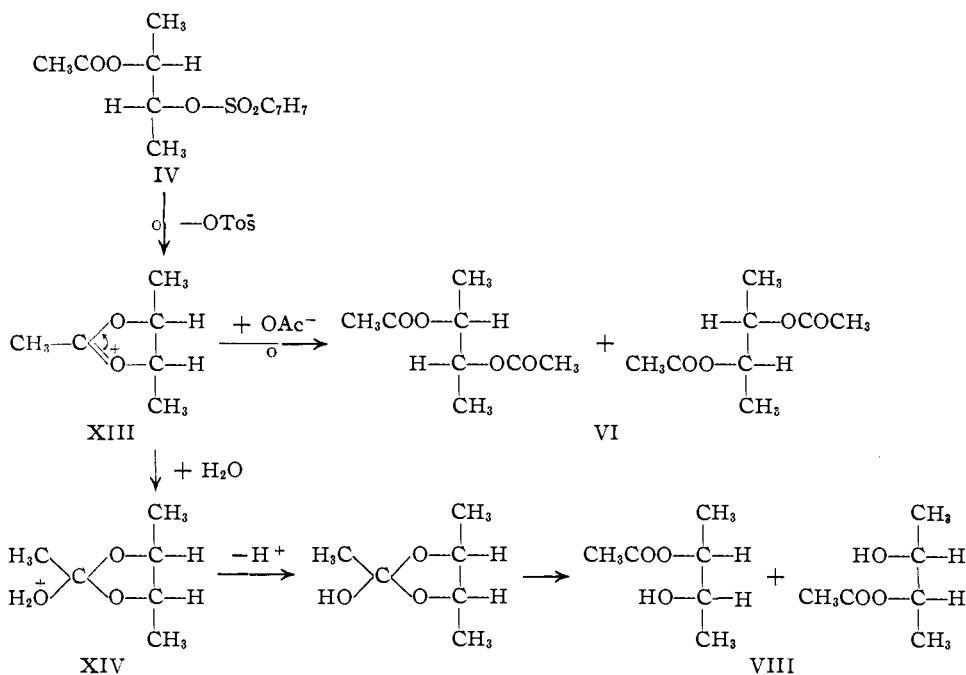
Similarly, the mechanism shown in Fig. 3 satisfactorily accounts for the results obtained from D-acetate-tosylate, IV. Here the first step, which is similar to step two in Fig. 2, is attack at C-3 by carbonyl oxygen with one inversion, to form the cyclic intermediate, XIII. This has the

*meso* configuration and thus is inactive. The second step is the conversion of this intermediate to the DL-diacetate, VI, with one inversion at either carbon atom. Thus either C-2 and C-3 are each inverted once, or else C-3 is inverted twice. The fact that the resulting diacetate has the *threo* configuration and yet is inactive is explained on the basis of these two configurational changes. The cyclic intermediate is necessary, therefore, in order for the D- and L-diacetates to be formed in equal amounts.

When water is present the ring of XIII is opened without an inversion, as in Fig. 2, probably going through XIV. Thus there is only one inversion, the one at C-3. The final product, VIII, therefore has the *erythro* configuration. The fact that it is a mixture of D and L forms, rather than the L form only, is an additional argument<sup>8</sup> for the formation of the inactive, cyclic intermediate, XIII or XIV.

The fact that the reaction product, when water is present, is mainly a monoacetate rather than a diacetate, is additional evidence that the reaction proceeds through the cyclic intermediate. The products formed in the reactions II to VIII, III to IX, IV to VIII, and V to X could be accounted for by assuming that the replacement of the second tosyloxy group took place similarly to the first, *viz.*, by a simple S<sub>N</sub>2 mechanism, and that the monoacetate arose from partial hydrolysis of the diacetate formed. However, pure D(+)-diacetate was only 7% hydrolyzed under the conditions of the acetolysis experiments, contrasted with the 60-70% monoacetate from the tosyl esters. Therefore, the monoacetate must

(8) However acyl migration could account for the inactivity of VIII.

Fig. 2.—Reaction steps in the acetolysis of *D*(+)-2,3-di-*p*-toluenesulfonybutane.Fig. 3.—Reaction steps in the acetolysis of *D*(+)-2-acetoxy-3-*p*-toluenesulfonybutane.

be the primary reaction product, and the presence of diacetate must be ascribed to partial acetylation of the monoacetate by the solvent, acetic acid.

A consideration of the relative rates of the possible reactions is also valuable evidence for the cyclic intermediate when water is present. Simple  $\text{S}_{\text{N}}2$  replacement of the second tosylate group by acetate ion occurs under anhydrous conditions to the extent of only about 2% as shown by the small amounts of *L*(-)-diacetate obtained from

III in addition to the *meso*-diacetate, VII. The reaction by way of the ion XI is therefore about fifty times faster than the  $\text{S}_{\text{N}}2$  attack by acetate ion. It does not seem reasonable that the addition of small amounts of water would completely reverse this order, as would be necessary for an  $\text{S}_{\text{N}}2$  replacement of the second tosylate to take place.

**Analysis of Reaction Products.**—The products obtained from the anhydrous solvolyses, and from the solvolyses in the presence of water,

after further acetylation, were mixtures of two or more of the following: *meso*-, DL-, D- and L-2,3-diacetoxybutane. Mixtures of two components could be analyzed satisfactorily by their melting points, taken by slowly melting the whole sample while the thermometer bulb was immersed directly in it, and noting the temperature at which the last of the solid disappeared. The refractive index, found to be a linear function of the composition, served as an auxiliary aid in determining the position on the melting point curve, in case this was necessary. The amount of optically active form was calculated from the rotation of the product. The rotation was assumed to be a linear function of the concentration, since the active form either was present in small amount or else it was the major constituent, comprising 90% of the mixture. In one case, the anhydrous solvolysis of D(+)-ditosylate, III, the product was a mixture of three components, and both the melting point and rotation were necessary to establish its composition.

Melting point curves were obtained for three systems of 2,3-diacetoxybutanes, *viz.*, *meso* and DL, *meso* and D, and D and L, Fig. 4. The curves were constructed from the data listed in Table II. The temperatures shown are the temperatures at which the last part of the solid disappears. It is interesting that whereas the first two curves are normal in having a eutectic, the last is unusual in that a racemic compound is indicated, and this forms solid solutions with the active forms.

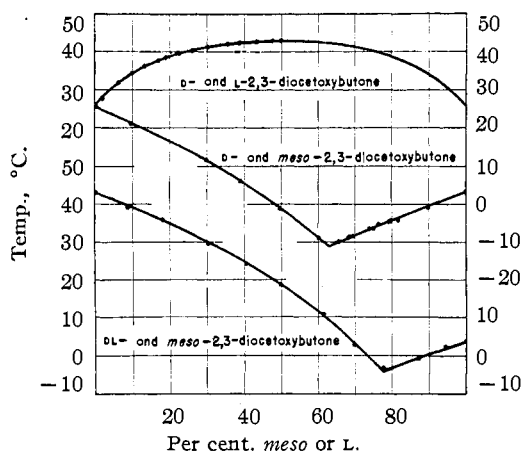


Fig. 4.

### Experimental<sup>9</sup>

***meso*-2,3-Butanediol.**—Crude 2,3-butanediol (Lucidol Co. by action of *Aerobacter aerogenes* on sugar) is about 90% *meso* and 10% DL plus L(+). The *meso* form, m. p. 30.4–32.0°, 96% pure,<sup>10</sup> was obtained with a minimum of manipulation by first allowing a 5-lb. bottle of the glycol to stand at room temperature, after seeding, for a month or so, then removing the liquid in a basket centrifuge or by allowing it to drain for several days protected from atmospheric moisture. A second, less pure crop can

(9) Microanalyses by G. Oppenheimer and G. A. Swinehart.

(10) C. E. Wilson and H. J. Lucas, *THIS JOURNAL*, **58**, 2396 (1936).

TABLE II  
MELTING POINTS OF DIACETATE MIXTURES

<i>meso</i> %	DL %	D %	M. p., °C., cor.
0.0	100.0		43.0
8.9	91.1		39.1
18.2	81.8		35.7
30.5	69.5		29.7
40.9	59.1		24.2
49.9	50.1		18.6
61.5	38.5		10.7
69.9	30.1		2.8
77.7	22.3		-3.5
87.2	12.8		-0.8
94.5	5.5		2.1
100.0	0.0		3.5
0.0		100.0	25.9
9.5		90.5	21.0
29.6		70.4	11.4
39.0		61.0	6.1
49.7		50.3	-1.0
60.2		39.8	-8.8
65.6		34.4	-9.7
68.1		31.9	-8.6
69.3		30.7	-8.1
74.9		25.1	-6.1
79.8		20.2	-4.0
89.9		10.1	-0.6
	3.9	96.1	27.8
	12.6	87.4	31.9
	19.8	80.2	34.3
	26.6	73.4	36.1
	33.8	66.2	37.7
	45.0	55.0	39.5
	52.0	48.0	40.3
	60.2	39.8	41.2
	71.4	28.6	42.1
	77.8	22.2	42.3
	86.8	15.2	42.7
	95.2	4.8	42.9

be obtained from the filtrate by cooling. Two crystallizations of the main crop of the glycol from isopropyl ether gave a 50% yield, m. p. 34.0°, 99.6% *meso*.

**DL-2,3-Butanediol.**—This was prepared from the *meso*-glycol, by methods previously described,<sup>10,11,12</sup> through the steps: *meso*-glycol → *meso*-diacetate → DL-*threo*-3-chloro-2-butanol → *cis*-2,3-epoxybutane → DL-2,3-butanediol. The last step, hydration of the oxide, was carried out using sulfuric acid rather than perchloric acid as a catalyst; yield, 50% from the *meso*-glycol, b. p. 75.3–75.6° at 10 mm.

**D(+)-2,3-Butanediol.**<sup>2</sup>—This isomer, from fermentation of starch by *Bacillus polymyxa*, had an observed rotation of -12.4°, which became -13.00°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -13.17°, after one distillation at reduced pressure, due to removal of a small amount of water.

**D(+)-2,3-Diacetoxybutane.**—This, prepared from the active glycol with acetic anhydride and pyridine,<sup>12</sup> had  $\alpha$ <sub>D</sub><sup>25</sup> +14.08°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +13.72°, m. p. 25.7–25.9° (cor.).

***meso*-2,3-Diacetoxybutane and DL-2,3-Diacetoxybutane.**—These were prepared from the respective glycol with acetic anhydride and a drop of sulfuric acid: b. p., *meso*, 76.0–76.5° at 10 mm.; m. p., *meso*, 3.5° (cor.), DL, 42.6–43.0° (cor.).

(11) H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941).(12) H. J. Lucas and H. K. Garner, *ibid.*, **70**, 990 (1948).

**Melting Point Curves of the Diacetates.**—The method of Collett and Johnston<sup>13</sup> was used. The samples (about 150 mg.) were weighed into thin-walled glass tubes about 8 mm. in diameter and sealed at the lower end. The upper end was then sealed off, and a section of 2 mm. glass rod sealed on for a handle. The melting points were taken in an electrically heated bath fitted with a mechanical stirrer. The samples were vigorously agitated while raising the bath temperature at a rate of about 0.1°/min. until they were about half melted. The rate of heating was then slowed to about 0.02°/min., and the temperature held stationary at 0.1° intervals for about five minutes to insure equilibrium. The melting point was taken as the temperature at which the last solid disappeared. Temperatures were read on a thermometer (immersed in the bath) which was graduated in 0.1° intervals and which had been calibrated by the Bureau of Standards.

**meso-2,3-Di-*p*-toluenesulfonylbutane.**—This was prepared from the *meso*-glycol and *p*-toluenesulfonyl chloride in pyridine solution, and purified by recrystallization from isopropyl ether; yield, 53%; m. p. 95.0–95.5° (cor.).<sup>14</sup>

*Anal.* Calcd. for C<sub>18</sub>H<sub>22</sub>O<sub>6</sub>S<sub>2</sub>: C, 54.25; H, 5.56; S, 16.09. Found: C, 54.60; H, 5.64; S, 16.09.

**D(+)-2,3-Di-*p*-toluenesulfonylbutane.**—This was prepared, in the same way as the *meso*-ditosylate, from the active glycol. After three recrystallizations, a 75% yield of pure ditosylate was obtained; m. p. 65.1–65.5° (cor.); [ $\alpha$ ]<sub>D</sub><sup>25</sup> +37.2° (0.9989 g. in 10.000 ml. of chloroform soln.). These values could not be raised by further recrystallization.

*Anal.* Calcd. for C<sub>18</sub>H<sub>22</sub>O<sub>6</sub>S<sub>2</sub>: C, 54.25; H, 5.56; S, 16.09. Found: C, 54.25; H, 5.65; S, 15.72.

**DL-erythro-2-Acetoxy-3-*p*-toluenesulfonylbutane.**—To 0.50 mole (45 g.) of *meso*-2,3-butanediol (m. p. 34.0°, 99.6% *meso*) was added 0.51 mole (40 g.) of redistilled pyridine and 0.50 mole (95.2 g.) of *p*-toluenesulfonyl chloride. After a few minutes the mixture heated strongly and cooling was necessary. After standing at room temperature for 12 hours, 0.50 mole (52 g.) of freshly distilled acetic anhydride and 3 drops of sulfuric acid were added. Cooling was again necessary. After standing for three hours the mixture was poured over a mixture of sodium bicarbonate (0.5 mole) and ice. The product separated as a white curd which was dissolved in ethyl ether. The ether solution was washed several times with water, dried with calcium sulfate, and cooled to 0°. After standing at 0° for twelve hours, a quantity of white crystals had formed. These were removed, and the mother liquors cooled to Dry Ice temperature. A second crop resulted. The two crops, yield 60%, melted at 39–45°. Several recrystallizations from anhydrous isopropyl ether gave a white crystalline product, m. p. 51.5–52.0° (cor.).

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>6</sub>S: C, 54.53; H, 6.33. Found: C, 54.95; H, 6.33.

Acetylation of the *meso*-glycol to 3-acetoxy-2-butanol, followed by tosylation, gave an identical product but the yield (25%) was much lower.

**D(+)-threo-2-Acetoxy-3-*p*-toluenesulfonylbutane.**—To 0.500 mole (45.0 g.) of active 2,3-butanediol, [ $\alpha$ ]<sub>D</sub><sup>25</sup>, –13.17°, dissolved in 5 moles (395 g.) of freshly distilled anhydrous pyridine was added, portionwise over a period of about an hour, 0.500 mole (95.2 g.) of *p*-toluenesulfonyl chloride. The temperature of the reaction mixture rose to about 40°, and after a short time pyridine hydrochloride began to separate. After standing at room temperature for three hours, 0.500 mole (51.0 g.) of freshly distilled acetic anhydride was run in slowly during a period of about thirty minutes. After standing overnight, the mixture was poured into 2 l. of 2.5 *N* hydrochloric acid. The oil layer was separated, the aqueous solution washed with ethyl ether, and the combined oil and washings, 500 ml., were washed twice with water and dried with anhydrous

potassium carbonate. On cooling to Dry Ice temperature for several days, 106 g. (74%) of white crystalline material was obtained. Six crystallizations from isopropyl ether and four from ethanol gave a 20% yield of material melting at 74.5–75.3° (cor.); [ $\alpha$ ]<sub>D</sub><sup>25</sup> +4.9° (1.0005 g. in 10.00 ml. of chloroform soln.). The melting point of a small sample was not changed by ten more recrystallizations from ethanol.

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>6</sub>S: C, 54.53; H, 6.33; S, 11.20; sapon. eq., 143. Found: C, 54.41; H, 6.31; S, 11.42; sapon. eq., 141.

Acetylation followed by tosylation without isolation of the monoacetate gave the same product but in much lower yield (crude yield, 20%) just as with the inactive isomer. However, the crude product, m. p., 71–73°, was much purer than that obtained by tosylation first. Better yields could probably be obtained if the monoacetate intermediate were isolated before treating with tosyl chloride.

**Solvolytic Experiments, Anhydrous Conditions; D(+)-2,3-Di-*p*-toluenesulfonylbutane.**—To a mixture of 0.20 mole (19.5 g.) of freshly fused potassium acetate and 50 ml. of glacial acetic acid (m. p. 15.5°, 0.5% water) was added 5 ml. of acetic anhydride. The flask was fitted with a reflux condenser and the solution brought to boiling for five minutes to remove the water. Then 0.050 mole (19.9 g.) of D(+)-2,3-di-*p*-toluenesulfonylbutane was added and the mixture was refluxed for four hours. Two methods of isolation were used on duplicate runs.

**Method I.**—The mixture was poured onto 1 mole (84 g.) of solid sodium bicarbonate and 400 g. of ice. The resulting solution was extracted four times with 50-ml. portions of isopropyl ether. The ether extracts were washed twice with 50-ml. portions of water, and then dried with anhydrous potassium carbonate. The ether was removed by distillation at atmospheric pressure, and the residues were distilled at reduced pressure to give 5.9 g. (68%) of colorless liquid boiling at 76.5–76.8° at 10 mm.; m. p., 0.7°; *n*<sub>D</sub><sup>25</sup> 1.4119;  $\alpha$ <sub>D</sub><sup>25</sup> –0.26. These constants indicate a composition of 91.1% *meso*-, 7.0% DL-, and 1.9% L-diacetate.

**Method II.**—The product was isolated by removing acetic acid from the reaction mixture through a fractionating column at reduced pressure until the excess potassium acetate began to separate out. On cooling, the entire mass solidified. The cake was broken up and extracted twice with 100-ml. portions of isopropyl ether. Distillation of the ether solution gave a product of approximately the same composition as that obtained by method I, 90.0% *meso*-, 8.1% DL and 1.9% L.

The results were also the same when the mixture of acetic anhydride, acetic acid, and potassium acetate was refluxed for two hours before adding the ditosylate, instead of five minutes as described above. This shows that the small amount of levorotatory diacetate present in the product did not arise as a result of small amounts of water remaining in the mixture.

**meso-2,3-Di-*p*-toluenesulfonylbutane.**—The acetylation was carried out as above. After refluxing for six hours, the product was isolated by method II, b. p. 73.5–74.5° at 10 mm.; m. p., 39°. The m. p. indicates a mixture of 90.0% DL and 10.0% *meso*-diacetates.

**D(+)-threo-2-Acetoxy-3-*p*-toluenesulfonylbutane.**—The acetylation was carried out as above. After refluxing for two and one-half hours, the product was isolated by method II, b. p. 81.1–82.6 at 10 mm. (cor.); m. p. 37.7–41.2° (cor.); [ $\alpha$ ]<sub>D</sub><sup>25</sup> +0.06° (0.9530 g. in 2.00 ml. of CHCl<sub>3</sub> soln.). The composition was therefore 96.3% DL-diacetate, 3.7% *meso*-diacetate, and possibly a trace of D(+)-diacetate.

**DL-erythro-2-Acetoxy-3-*p*-toluenesulfonylbutane.**—The same procedure was used, refluxing for two hours and isolating the product by method I, b. p. 75–76° at 10 mm., m. p. 3.0°, *n*<sub>D</sub><sup>25</sup> 1.4117. These constants indicate that the product was 96.0% *meso*-diacetate, and 4.0% DL.

**meso-2,3-Diacetoxybutane.**—Some pure *meso*-diacetate was put through exactly the same treatment, and was recovered with no change in physical constants.

(13) A. R. Collett and J. Johnston, *J. Phys. Chem.*, **50**, 70 (1926).

(14) F. C. Foster and L. P. Hammett, *THIS JOURNAL*, **68**, 1736 (1946), give the m. p. as 96°.

**Solvolysis Experiments in the Presence of Water:** *D*(+)-2,3-Di-*p*-toluenesulfonoxybutane.—In a 200-ml. flask fitted with a reflux condenser were placed 0.050 mole (19.9 g.) of *D*(+)-2,3-di-*p*-toluenesulfonoxybutane, 0.20 mole (19.5 g.) of fused potassium acetate, 50 g. of glacial acetic acid (m. p., 15.5°, 0.5% water), and 1.55 g. of water, bringing the total water in the solution to 0.10 mole (1.80 g.). The mixture was refluxed for four hours, another 2.0 g. of water being added in 0.5-g. portions at fifteen-minute intervals during the first hour of this period. The product was isolated by method II above; yield 4.6 g. (64%), b. p. 76.0–79.3° at 10 mm.;  $n_D^{25}$  1.4188;  $\alpha_D^{25}$  +4.75°. The saponification equivalent was 118.5, indicating that its composition was 70% monoacetate and 30% diacetate.

Five ml. of acetic anhydride and one drop of sulfuric acid were added to the mixture, and the resulting solution was fractionally distilled at reduced pressure. There was obtained 3.6 g. of liquid boiling at 81.1–81.5° at 10 mm.; m. p. 14.5–21.3;  $n_D^{25}$  1.4133,  $\alpha_D^{25}$  –12.61°. These constants indicate a composition of 90.1% L(–)-2,3-diacetoxybutane and 9.9% *meso*-isomer. Two recrystallizations from 30–60° petroleum ether raised the observed rotation to –14.08°, the value for pure L(–)-2,3-diacetoxybutane.

When isolation was carried out by method I, the yield was lower, and the saponification equivalent indicated that the original product was only 31% monoacetate with 69% diacetate. Since the monoacetate is miscible with water, it is probable that it was not all extracted from the aqueous solution. The composition of the diacetate prepared from the mixture, 84.1% L- and 15.9% *meso*-, was not far different from that of the diacetate isolated by method II, however.

A sample of *D*(+)-2,3-diacetoxybutane,  $[\alpha]_D^{25}$  +13.64, m. p. 24.5–25.6°, was put through the same procedure. The material recovered melted at 18.0–21.5° and had a saponification equivalent of 90.1, indicating the presence of only 7% of the monoacetate. On complete acetylation, the material melted at 26.2–27.1°;  $\alpha_D^{25}$  +13.91°;  $[\alpha]_D^{25}$  +13.57°, indicating a slight amount of racemization (2%) during the treatment.

***meso*-2,3-Di-*p*-toluenesulfonoxybutane.**—The acetylation was carried out in the same way as for the active ester. The mixture was refluxed for six hours, acetylated with acetic anhydride, and the product isolated by method II. Two fractions were obtained; 2.8 g., b. p. 75–76° at 10 mm.;  $n_D^{25}$  1.4120; and 3.03 g., b. p. 76–76.2° at 10 mm.;  $n_D^{25}$  1.4117. This represents a 58% yield of diacetate, composition, > 90% *meso*, < 10% DL.

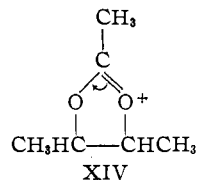
***D*(+)-*threo*-2-Acetoxy-3-*p*-toluenesulfonoxybutane.**—The solvolysis was carried out exactly as for the active ditosylate. The saponification equivalent of the primary product, 114, showed a composition of 60% monoacetate and 40% diacetate, yield, 65%. The diacetate had the

properties: b. p. 76.8–77.1° at 10 mm.; m. p. 1.4°;  $\alpha_D^{25}$  0.00°. The composition was therefore 93.2% *meso*- and 6.8% DL.

**DL-*erythro*-2-Acetoxy-3-*p*-toluenesulfonoxybutane.**—The solvolysis was carried out as above, heating for four hours, and isolating by method II. The primary product, b. p. 76–78.5° at 10 mm.,  $n_D^{25}$  1.4173, was about 50% monoacetate. The diacetate was collected in three fractions: (1) 0.27 g., b. p. 70–78.6° at 10 mm., m. p. 14°; (2) 2.55 g., b. p. 79–80° at 10 mm., m. p. 41.5°; (3) 2.65 g., b. p. 80° at 10 mm., m. p. 43°. The total yield was 60%, the over-all composition 96.0% DL and 4.0% *meso*.

### Summary

When the 2,3-di-*p*-toluenesulfonoxybutanes (*meso*, II and *D*, III) and the 2-acetoxy-3-*p*-toluenesulfonoxybutanes (*D-threo*, IV and DL-*erythro*, V) undergo acetolysis to form 2,3-diacetoxybutane under anhydrous conditions, or 3-acetoxy-2-butanol when water is present, the number of Walden inversions which take place are as follows: (a) three, in the case of II and III, under anhydrous conditions; (b) two, in the case of II and III, when water is present; (c) two, in the case of IV and V, under anhydrous conditions; (d) one, in the case of IV and V, when water is present. These results and other stereochemical relationships associated with some of the changes prove that a positively charged ion, XIV, is an intermediate.



Three melting point curves were obtained for three systems of 2,3-diacetoxybutane, *viz.*, (a) *meso* and DL; (b) *meso* and *D*; (c) *D* and L. Each of the first two curves shows a normal depression and a single eutectic point. The third indicates the existence of a racemic compound and a continuous series of solid solutions of this with the *D* and L forms.

PASADENA 4, CALIF.

RECEIVED AUGUST 8, 1949