52. *Some Walden Inversion Reactions of the* p-*Toluenesulphonic and* p-*Toluenesulphinic Esters of* l-*Phenylmethylcarbinol.*

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THE *p*-toluenesulphonates of *d*-benzylmethylcarbinol and of *l*-menthol (Phillips, J., 1923, **123**, 44 ; 1925, **127**, 2566), of ethyl *d*-lactate (Kenyon, Phillips, and Turley, J., 1925, **127**, 399) and of the α- and β-methyl*cyclo*hexanols (Gough, Hunter, and Kenyon, J., 1926,

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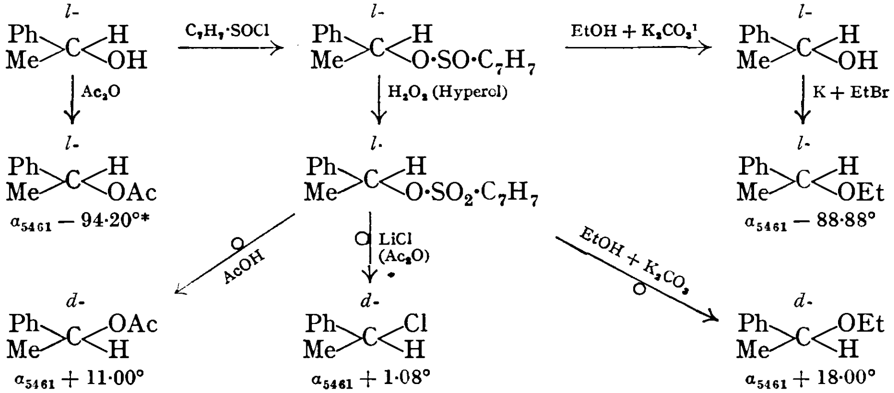
* 3 : 5-Dinitrobenzoyl chloride appears to crystallise from C_6H_6 with 1 mol. of solvent.

2052) have all been shown to react with ethyl alcohol and salts of carboxylic acids with inversion, the *p*-toluenesulphonoxy-anion being replaced by the entering anion :

$$\mathrm{RO{\cdot}SO_2{\cdot}C_7H_7} + \overset{+\,-}{\mathrm{HO}}\mathrm{Et} = \mathrm{ROEt} + \overset{+\,-}{\mathrm{HO}}\mathrm{{\cdot}SO_2{\cdot}C_7H_7}$$

A similar study has now been made of the reactions of a *p*-toluenesulphonate of an optically active α-hydroxy-compound containing a phenyl group directly attached to the asymmetric carbon atom, because McKenzie and Clough (J., 1910, **97**, 1016, 2564) have shown that the stereochemical changes which occur during the reactions of such compounds may differ from those which take place during the reactions of purely aliphatic compounds.

Considerable difficulty has been encountered in the preparation of a suitable *p*-toluenesulphinate, since both ethyl *l*-mandelate and *l*-phenylmethylcarbinol do not react smoothly with *p*-toluenesulphonyl chloride. Phenylmethylcarbinyl *p*-toluenesulphinate (Kenyon and Phillips, J., 1930, 1676), although relatively unstable, underwent oxidation with ease, but the resulting sulphonate was so reactive that its isolation in the pure state was not possible. In this respect it apparently resembles benzyl *p*-toluenesulphonate (Medvedev and Alexeeva, *Ber.*, 1932, **65**, 131), which can only be preserved in a vacuum over calcium chloride for a week, and decomposes within 20 minutes when sulphuric acid is used as the drying agent. The only feasible method of utilising phenylmethylcarbinyl *p*-toluenesulphinate was therefore to oxidise it with hyperol (urea perhydrate, an anhydrous oxidising agent which can be used in absence of water) in a solution of the reagent with which the sulphonate produced would react. The experimental results are given in the following scheme :



Since, during the preparation of the *l*-sulphinate from the *l*-alcohol, the four bonds of the asymmetric carbon atom can be assumed to remain undisturbed, the *l*-sulphinate has the same configuration as the *l*-alcohol. This assumption is in agreement with the recovery of the *l*-alcohol by alcoholysis of the ester without alteration in sign or magnitude of rotatory power. Further, the oxidation of the *l*-sulphinate involves merely the addition of an oxygen atom to the sulphur atom of the *p*-toluenesulphinoxy-group, a change which is unlikely to lead to inversion. The *l*-sulphonate obtained, therefore, has the same configuration as the *l*-alcohol. Other reactions in the above scheme, which for similar reasons can be considered to have been unattended by configurative change, are the esterification of the *l*-alcohol with acetic anhydride and the formation of the ethyl ether by the action of ethyl bromide on the potassio-derivative of the *l*-alcohol; lævo-phenylmethylcarbinyl acetate and lævo-α-phenyldiethyl ether have therefore the same configuration as the *l*-alcohol.

The interaction of the *l*-sulphonate with acetic acid and with ethyl alcohol led respectively to the formation of a dextro-acetate and a dextro-ethyl ether. Both of these reactions

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[1] Kenyon and Phillips, *loc. cit.*

* All observed rotations were actually determined in tubes of 25 mm. : they are recorded in the theoretical portion of this paper as for tubes of 100 mm.

must therefore have been accompanied by a Walden inversion; in addition they were accompanied by some racemisation, which was more pronounced than that occurring during similar reactions of the *p*-toluenesulphonates of the purely aliphatic alcohols (*loc. cit.*). *n*-Butyl alcohol and the *l*-sulphonate reacted also with inversion to give dextro-α-phenylethyl *n*-butyl ether, α_{5461} + 20·44°, since a lævo-*n*-butyl ether, α_{5461} − 76·80°, was obtained by the action of *n*-butyl bromide on the potassio-derivative of the *l*-alcohol.

When refluxed, in the presence of potassium carbonate, with an ethyl-alcoholic solution of lithium chloride, the *l*-sulphonate gave a lævo-ethyl ether, α_{5461} − 8·0°. Since the same reactants without lithium chloride gave a dextro-ether, the lævo-ether obtained arose from dextro-α-chloroethylbenzene, produced by the interaction of the *l*-sulphonate with lithium chloride. In this connection, Kenyon and Phillips (*loc. cit.*) have shown that a lævo-ethyl ether is produced when this dextro-chloride is heated under reflux with ethyl alcohol.

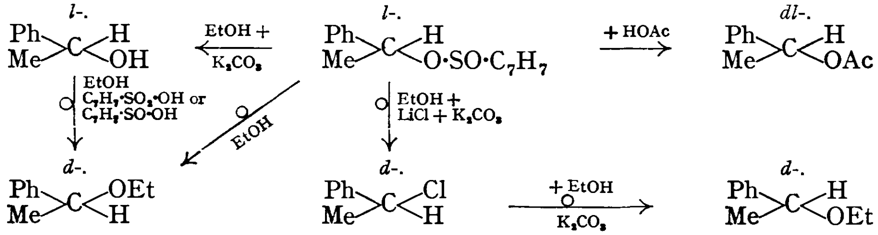
Dextro-α-chloroethylbenzene was also obtained, and in this case isolated, from the products of the interaction of the *l*-sulphonate with lithium chloride in acetic anhydride solution.

In the reaction scheme above, the production of the dextro-chloride from the *l*-sulphonate is assumed to occur with inversion for the following reasons. (*a*) The reaction between the *l*-sulphonate and acetic acid is essentially similar to that of the reaction between the ester and lithium chloride, because in both reactions the *p*-toluenesulphonoxy-anion is replaced by anions (acetate and chloride). Since it is known that the replacement by the acetate anion proceeds with inversion, it is likely that a similar replacement by the chloride anion also proceeds with inversion. (*b*) A dextrorotatory chloride is obtained by the interaction of the *l*-sulphinate with chlorine (Houssa and Phillips, J., 1932, 1232). There are reasons to suppose that this type of reaction is attended by inversion (Houssa, Kenyon, and Phillips, J., 1929, 1700). (*c*) The assumption agrees with the interpretation of the influence of pyridine on the interaction of the *l*-alcohol with thionyl chloride (Kenyon, Phillips, and Taylor, J., 1931, 382).

Provided the entering group is made available in the anionic state, the products of all the reactions studied thus show that *l*-phenylmethylcarbinyl *p*-toluenesulphonate undergoes replacement reactions in a similar manner to those sulphonic esters in which the asymmetric carbon atom is not directly linked to a phenyl group.

Walden Inversion Reactions of Phenylmethylcarbinyl p-*Toluenesulphinate.*—The *p*-toluenesulphinates of purely aliphatic and hydroaromatic alcohols do not yield ethers when heated with alcohols, or carboxylic esters when heated in solution with salts of carboxylic acids. Thus, ethyl *p*-toluenesulphinate yields only *d*-β-octyl and *l*-menthyl *p*-toluenesulphinates when heated respectively with *d*-β-octanol and *l*-menthol, and these two alcohols can be recovered when the *p*-toluenesulphinates are heated with excess of ethyl alcohol containing potassium acetate. Further, whereas the *p*-toluenesulphonates of these alcohols give carboxylic esters with inversion when heated with carboxylic acids, investigations at present in progress have shown that under the same conditions their *p*-toluenesulphinic esters yield carboxylic esters without either loss of rotatory power or change in configuration.

In contrast to the behaviour of these *p*-toluenesulphinic esters, *l*-phenylmethylcarbinyl *p*-toluenesulphinate was found to undergo inversion reactions, particularly with acidic reaction mixtures.



Thus, in the absence of potassium carbonate, which neutralises the acids liberated by side reactions during the alcoholysis of the ester, the *l*-sulphinate was converted by boiling ethyl alcohol into dextro-α-phenyldiethyl ether with α_{5461} + 2·08°. The production of a dextro-ether in this manner was not due to the atmospheric oxidation of the *l*-sulphinate to the *l*-sulphonate, since an ether of the same sign of rotation was produced when the air above the reaction mixture was replaced by nitrogen. A dextro-ether was obtained also when ethyl-alcoholic solutions of *l*-phenylmethylcarbinol containing either *p*-toluenesulphinic or -sulphonic acid were heated under reflux. In each case the ether probably arose from the ester of the secondary alcohol.

A lævo-ethyl ether was produced, however, when the *l*-sulphinate was heated under reflux with an ethyl-alcoholic solution of lithium chloride. Dextro-α-chloroethylbenzene was probably the initial product of this reaction and was converted by the ethyl alcohol into the lævo-ethyl ether. The production of the dextro-chloride from the *l*-ester in this manner is not inhibited by the presence of potassium carbonate. The interaction of the *l*-sulphinate with lithium chloride thus appears to be an inversion reaction which the ester will undergo in the absence of acids.

Since the potassio-derivative of the *l*-alcohol yields a lævo-ether when treated with ethyl bromide (*loc. cit.*), the dextro-ethers obtained in these reactions arise with inversion, and, for reasons already given, it is probable that the formation of the dextro-α-chloroethylbenzene and its conversion into the lævo-ether are both reactions attended by a change in configuration.

In acetic acid solution the *l*-sulphinate passed smoothly to the corresponding *dl*-acetate. Although the replacement reactions involving optically active radicals containing phenyl groups frequently occur with some racemisation, the cause of this total loss of rotatory power is obscure.

During its attempted oxidation the *l*-sulphinate isomerised to the sulphone more readily in solutions which may have contained acids than in those maintained neutral by potassium carbonate. This is in harmony with the greater readiness with which the *p*-toluenesulphonoxy-group is replaced under acid conditions and it would therefore appear likely that both the isomerism and the replacement reactions are catalysed by hydrogen ions.

EXPERIMENTAL.

d-Phenylmethylcarbinol [α_{5461} − 13·15° (l = 0·25)] was prepared by Houssa and Kenyon's method (J., 1930, 2260). In the description of the expts. the rotatory power of the alcohol used is only given when it was less than the above value.

Interaction of Optically Active Phenylmethylcarbinol with Ethyl-alcoholic Solutions of p-*Toluenesulphinic and* p-*Toluenesulphonic Acids*.—(i) p-*Toluenesulphinic acid*. EtOH was slowly distilled from a solution of the *l*-alcohol (12 g.) and *p*-toluenesulphinic acid (33 g.; 2 mols.) in EtOH (300 c.c.) into a flask, containing anhydr. K_2CO_3 and so heated that the dried EtOH was returned continuously to the reaction mixture, which, after 6 hr., was distilled in steam. From the steam distillate, dextro-α-phenyldiethyl ether (5 c.c.), b. p. 75—79°/18 mm., α_{5461} + 6·18° (l = 0·25), and *l*-phenylmethylcarbinol (5 c.c.) were isolated. The ether was freed from possible traces of the *l*-alcohol by treatment with phthalic anhydride. It then had b. p. 73°/19 mm. and α_{5461} + 7·53° (l = 0·25). A cryst. mass (16·3 g.) separated from the non-volatile portion of the reaction mixture. After recryst. it had m. p. 75°, alone or when mixed with di-*p*-tolyl disulphoxide.

(ii) p-*Toluenesulphonic acid*. The above expt. was repeated with a solution of the *d*-alcohol [10 g., α_{5461} + 5·03° (l = 0·25)] and *p*-toluenesulphonic acid (15 g.) in EtOH (300 c.c.). The main products were lævo-α-phenyldiethyl ether (6 c.c.), α_{5461} − 1·01° (l = 0·25), and *dl*-phenylmethylcarbinol (1·5 c.c.). No non-volatile products were obtained.

The Interaction of l-*Phenylmethylcarbinyl* dl-p-*Toluenesulphinate with Glacial Acetic Acid, Ethyl Alcohol, and Lithium Chloride*.—(i) *With glacial acetic acid*. *l*-Phenylmethylcarbinyl *dl*-*p*-toluenesulphinate (10 g.), prepared by the action of *p*-toluenesulphinyl chloride on the *l*-alcohol in the presence of pyridine (Kenyon and Phillips, *loc. cit.*), was dissolved in AcOH (40 c.c.) which had been dried by repeated fractional cryst. N was slowly passed through the flask containing the solution and, after 12 hr. at laboratory temp., the flask was heated on a steam-bath for 12 hr. The reaction mixture was poured into Na_2CO_3 aq., and the insol. oil extracted with Et_2O. From the dried extract, dl-*phenylmethylcarbinyl acetate* (3 g.) was isolated; b. p. 105°/15 mm., $n^{20°}$ 1·5045 (Found : C, 73·2; H, 7·3. $C_{10}H_{12}O_2$ requires C, 73·2; H, 7·3%). A small higher-boiling residue crystallised on cooling and was identified as *dl*-*p*-tolyl-α-phenylethylsulphone, m. p. and mixed m. p. 133—134° (Kenyon and Phillips, *loc. cit.*).

l-Phenylmethylcarbinyl acetate prepared by the action of Ac_2O (3 g.) on the *l*-alcohol [α_{5461} − 13·15° (l = 0·25); 5 g.] had b. p. 109°/18 mm., $n^{19°}$ 1·5048, $d_{4°}^{20°}$ 0·930, α_{5461} − 23·55° (l = 0·25), and $[\alpha]_{5893}$ − 58·4° in EtOH (c = 5·60; l = 2·0).

(ii) *With ethyl alcohol.* After the *l*-sulphinate (4·5 g.) had been heated under reflux for 50 hr. with EtOH (60 c.c.), the alcohol was removed by distillation, and the residue dissolved in Et_2O and washed with Na_2CO_3 aq. From the dried ethereal solution, α-phenyldiethyl ether (4 c.c.), b. p. 72—73°/18 mm., α_{5461} + 0·54° (l = 0·25), was obtained, the rotatory power of which was unchanged after it had been heated with phthalic anhydride and then redistilled.

When the above expt. was repeated with EtOH containing either KOAc or anhyd. K_2CO_3, α-phenyldiethyl ether was obtained in amount insufficient for isolation in the pure state, but detectable owing to its characteristic odour. Since traces of this ether were obtained whether the reaction flask contained air or N, it is probable that it arose from the sulphinate and not from the sulphonate produced therefrom by atmospheric oxidation. The main product of these reactions was the optically active alcohol, which was recovered without loss of rotatory power. In the presence of KOAc or K_2CO_3 the sulphinate thus undergoes alcoholysis.

(iii) *With lithium chloride in ethyl-alcoholic solution.* The *l*-sulphinate (10 g.) in EtOH (40 c.c.) containing LiCl (8 g.) and K_2CO_3 (25 g.) was heated under reflux for 48 hr. in a slow stream of N. The mixture was then poured into H_2O and the oily products were extracted with Et_2O. From the dried extract, lævo-α-phenyldiethyl ether (3·5 g.) was isolated, b. p. 80°/15 mm., $n^{18°}$ 1·4978, α_{5461} − 3·88° (l = 0·25) (Found : C, 79·8; H, 9·2. Calc. : C, 80·0; H, 9·3%).

When the above reaction was carried out in the presence of air instead of N, the α-phenyldiethyl ether obtained had b. p. 79°/14 mm., $n^{19°}$ 1·4976, and α_{5461} − 2·8° (l = 0·25).

According to Kenyon and Phillips (*loc. cit.*), optically pure α-phenyldiethyl ether prepared by the action of EtBr on the potassium derivative of the *l*-alcohol has α_{5461} − 22·22° (l = 0·25). It also has $[\alpha]_{5893}$ − 83·6° in EtOH (c = 6·4; l = 2·0).

The Attempted Preparation and Isolation of Phenylmethylcarbinyl p-*Toluenesulphonate and the Action of Air on the Corresponding Sulphinate.*—Below 50°, either in presence or absence of pyridine, phenylmethylcarbinol did not react with *p*-toluenesulphonyl chloride. At about 100°, reaction occurred with ease but, in the absence of pyridine, the sulphonate produced yielded phenylethylene, and in the presence of pyridine it reacted with the pyridine hydrochloride simultaneously produced with the formation of α-chloroethylbenzene. The potassio-derivative of the alcohol also reacted vigorously with *p*-toluenesulphonyl chloride, but again the main product was phenylethylene.

Quant. expts. showed that in C_6H_6 solution the sulphinate was oxidised by air at the ordinary temp., but also isomerised to sulphone. Dry air, saturated with C_6H_6 vapour, was drawn through (*a*) a solution obtained by making up the volume of 25 g. of the sulphinate to 50 c.c. with C_6H_6, (*b*) a similar solution containing K_2CO_3 (10 g.). The rates of conversion of sulphinate into sulphone and sulphonate were ascertained by determining, on definite vols. of the two solutions from time to time, (i) the amount of NaOH required to hydrolyse completely the sulphinate and the sulphonate, (ii) the amount of Br absorbed by the sulphinate. Since other expts. had shown that in C_6H_6 solution the sulphinate reacted with 1 mol. of Br, it was possible to calculate the required information, given in Table I, from the data thus obtained.

These results show clearly that the isomerisation of the sulphinate to the sulphone is retarded by K_2CO_3, but even in its presence 40% only of the ester is oxidised to sulphonate.

Although other expts. showed that the sulphinate at the ordinary temp. was oxidised by perhydrol almost quantitatively to the sulphonate, when the temp. of the sulphonate, in vac., was raised to remove phenylmethylcarbinol and other by-products, profound decomp. always occurred.

The above expts. having shown that the sulphonate was a very unstable compound, it was decided to prepare the sulphonate in the presence of the substances with which it could react by oxidising the sulphinate with hyperol.

The Interaction of l-*Phenylmethylcarbinol* p-*Toluenesulphonate with Ethyl and* n-*Butyl Alcohols, Lithium Chloride, and Acetic Acid.*—(i) *With potassium carbonate and ethyl alcohol.* A mixture of the *l*-sulphinic ester (10 g.; 1 mol.), hyperol (10 g.; 1 mol.), K_2CO_3 (20 g.), and EtOH

TABLE I.

The Conversion of dl-*Phenylmethylcarbinyl* dl-p-*Toluenesulphinate into the Corresponding Sulphonate and* p-*Tolyl-α-phenylethylsulphone.*

	With K_2CO_3.			Without K_2CO_3.		
Time, hrs.	Sulphinate.	Sulphonate.	Sulphone.	Sulphinate.	Sulphonate.	Sulphone.
			(Percentage of original sulphinate.)			
0	100	0	0	100	0	0
6	80	20	0	77·5	6	16·5
12	55	42·5	0·5	55	11	34
48	55	35	10	25	21	54
72	45	38·5	16·5	0	30	70
96	40	38·5	21·5	—	—	—

(50 c.c.) was kept for 12 hr., heated under reflux for 12 hr., and poured into H_2O, from which the dextro-α-phenyldiethyl ether produced was extracted, dried, and distilled. It (3 g.) had b. p. 80°/15 mm. n^{18° 1·4979, α_{5461} + 4·50° (l = 0·25).

(ii) *With potassium carbonate and* n-*butyl alcohol.* A mixture of the *l*-sulphinic ester (15 g.), hyperol (10 g.), K_2CO_3 (20 g.), and *n*-butyl alcohol (50 c.c.) was treated as described in (i) above. Most of the butyl alcohol was then removed and the less volatile residue was heated at 115° for 12 hr. with phthalic anhydride to convert any phenylmethylcarbinol or *n*-butyl alcohol it contained into the corresponding hydrogen phthalic esters. After these esters had been removed from the product by washing with dil. Na_2CO_3 aq., it was diluted with Et_2O, dried, and distilled. It (4 g.) proved to be *dextro*-n-*butyl α-phenylethyl ether*, b. p. 102°/23 mm. (Found: C, 81·1; H, 9·9. $C_{12}H_{18}O$ requires C, 81·0; H, 10·1%), n^{21° 1·4961, α_{5461} + 5·11° (l = 0·25).

l-*n*-Butyl α-phenylethyl ether was prepared as follows for comparison. Powdered K (1·6 g.) was dissolved in a solution of *l*-phenylmethylcarbinol (5 g.) in Et_2O (50 c.c.), *n*-butyl bromide (4 g.) added, and the mixture heated under reflux for ½ hr. The ether produced was isolated and purified in a similar manner to that described above. The *l*-*n*-butyl α-phenylethyl ether obtained had b. p. 100°/21 mm., n^{20} 1·4958, α_{5461} − 19·2° (l = 0·25), $[\alpha]_{5893}$ − 53·8° in EtOH (c = 7·20; l = 2·0).

(iii) *With lithium chloride and ethyl alcohol.* A mixture of the *l*-sulphinic ester (15 g.), hyperol (10 g.), K_2CO_3 (20 g.), LiCl (20 g.), and EtOH (50 c.c.) was treated as described in (i) above. The chief product isolated was lævo-α-phenyldiethyl ether, b. p. 79°/14 mm., n^{18° 1·4975, α_{5461} − 2·0° (l = 0·25).

(iv) *With lithium chloride and acetic anhydride.* LiCl (10 g.) was added to a solution of the *l*-sulphinate (8 g.) and hyperol (8 g.) in Ac_2O (30 c.c.). After 8 hr. the mixture was warmed for 4 hr. and then poured into dil. Na_2CO_3 aq.; the pptd. oil was extracted and distilled. After redistillation of the two products until subsequent distillation left their refractive indices unaltered, they proved to be dextro-α-chloroethylbenzene, b. p. 75°/15 mm., n^{18° 1·5297, α_{5461} + 0·27° (l = 0·25), and dextro-phenylmethylcarbinyl acetate, b. p. 105°/15 mm., n^{20° 1·5054, α_{5461} + 0·35° (l = 0·25).

In order to prove that the dextro-acetate thus obtained did not arise by the interaction of the α-chloroethylbenzene and Ac_2O, a solution of lævo-α-chloroethylbenzene [5 g., α_{5461} − 4·3° (l = 0·25)] and hyperol (1 g.) in Ac_2O (30 c.c.) was treated in a similar manner to the solution described above. The lævo-α-chloroethylbenzene (2·5 g.), b. p. 76°/16 mm., was recovered with α_{5461} − 3·7° (l = 0·25), together with a trace of phenylmethylcarbinyl acetate. It is probable, therefore, that the dextroacetate isolated in the main exp. was produced from the *l*-sulphonate.

(v) *With acetic acid.* Hyperol (10 g.) and the *l*-sulphinate (15 g.) were dissolved in AcOH (50 c.c.). After being kept for 12 hr. at laboratory temp., the solution was poured into dil. Na_2CO_3 aq., from which the product was extracted with CH_2Cl_2. It was dextro-phenylmethylcarbinyl acetate, with n^{18° 1·5047 and α_{5461} + 2·75° (l = 0·25).

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