CCXIX.—*The Optical Instability of Tercovalent Carbonium Kations. The Transformation of* l-*Phenylmethylcarbinyl* dl-p-*Toluenesulphinate into Optically Inactive* p-*Tolyl-α-phenylethylsulphone.*

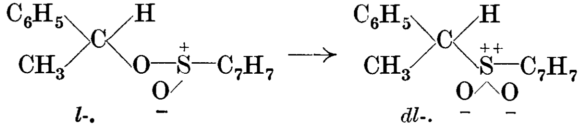
By Joseph Kenyon and Henry Phillips.

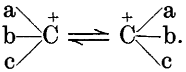
It has always been assumed that an atom or group attached to an asymmetric carbon atom can be directly replaced by another atom or group without the occurrence of a change in configuration. Since, however, in studies of the Walden inversion, the replacement of groups usually involves an exchange of anions, it would appear to follow that, at some stage of the reaction, two electrons are withdrawn from the octet of the asymmetric carbon atom and that a carbonium ion is momentarily formed. The assumption that replacement can occur without change in configuration implies, therefore, that the structure of a carbonium kation is sufficiently rigid to enable it to maintain its configuration unchanged.

Such an assumption was made by Biilmann (*Annalen*, 1912, **388**, 330), who considered that the interaction of silver oxide, water, and α-bromopropionic acid took place between the silver kation and the acid anion: $CH_3\cdot CHBr\cdot CO\cdot\overset{-}{O} + \overset{+}{Ag} \longrightarrow CH_3\cdot\overset{+}{C}H\cdot CO\cdot\overset{-}{O} + AgBr$. The "Zwitterion" produced then combined with the hydroxyl ion from the water, the net result of these two changes being that hydroxylation occurred without change of configuration: $CH_3\cdot\overset{+}{C}H\cdot CO\cdot\overset{-}{O} + \overset{-}{O}H \longrightarrow CH_3\cdot CH(OH)\cdot CO\cdot\overset{-}{O}$.

McKenzie and Clough (J., 1913, **103**, 687), in a criticism of Biilmann's hypothesis, suggested that the configuration of the "Zwitterion" was possibly stabilised by the free electric charge playing the part of the necessary fourth grouping. More recently, McKenzie, Roger, and Wills (J., 1926, 779) have brought forward experimental evidence from which they conclude (compare, however, Kenyon, Lipscomb, and Phillips, this vol., p. 415) that a free electric charge can stabilise the configuration of a tercovalent carbonium kation. They also draw attention to the fact that the tercovalent sulphur atoms in both the optically active methylethylthetine ion (Pope and Peachey, J., 1900, **37**, 1072) and the optically active ethyl *p*-toluenesulphinate of Phillips (J., 1925, **127**, 2552) are associated with free electrical charges. It must be admitted, however, that the sulphur atoms in these two forms of combination possess complete octets of valency electrons, whereas the carbon atom of Biilmann's "Zwitterion" has only a sextet of valency electrons. The "Zwitterion" might, therefore, be a far less rigid structure than the stable ester molecule or than the thetine ion.

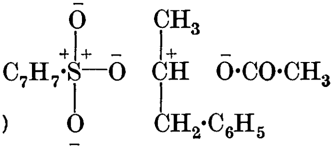
In the present communication, the spontaneous conversion of l-*phenylmethylcarbinyl* p-*toluenesulphinate* into optically inactive *p*-tolyl-α-phenylethylsulphone is described:



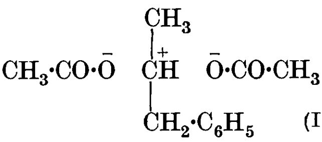
This change is closely analogous to an exchange of anions by an asymmetric carbon atom, since the optically active phenylmethylcarbinyl kation migrates from an oxygen atom (which it leaves negatively charged) to the vacant valency electrons of the sulphur atom. The experimental result that the sulphone thus produced is optically inactive is strong evidence in support of the view that a tercovalent carbonium kation cannot maintain its configuration unchanged, but oscillates between two forms of opposite configuration  In the absence of the special mechanism which leads to a Walden inversion, it would therefore appear that the replacement of a group attached to an asymmetric carbon atom must inevitably yield an optically inactive or racemised product.

A further hypothesis, however, has been put forward to explain the supposed occurrence of direct displacement without complete racemisation. From evidence derived from the *X*-ray analysis of the crystal structure of calcite (Bragg, *Proc. Roy. Soc.*, 1914, *A*, **89**, 486) and basic beryllium acetate (Bragg and Morgan, *ibid.*, 1923, *A*, **104**, 437), Lowry (Deuxième Conseil de Chimie Solvay, 1925, 40) concluded that a carbonium kation adopts a stable planar configuration, and postulated the formation of the complex (I) during the interaction of potassium acetate and *d*-benzylmethylcarbinyl *p*-toluenesulphonate in alcoholic solution (Phillips, J., 1923, **123**, 44).

(I.)



$$C_7H_7\cdot\overset{+}{S}(\bar{O})_2\overset{+}{—}\bar{O}\quad \overset{+}{C}H(CH_3)(CH_2\cdot C_6H_5)\quad \bar{O}\cdot CO\cdot CH_3$$

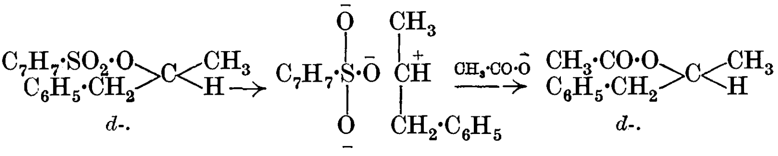


$$CH_3\cdot CO\cdot\bar{O}\quad \overset{+}{C}H(CH_3)(CH_2\cdot C_6H_5)\quad \bar{O}\cdot CO\cdot CH_3$$

(II.)

Direct replacement of the *p*-toluenesulphonoxy-ion was then assumed to lead to an optically active benzylmethylcarbinyl acetate without inversion. Since, however, direct replacement would apparently lead to the formation of the complex (II), which, on dissociation, would be equally capable of yielding either enantiomorphous form of the acetate, it would appear more probable that this hypothesis predicts also that direct replacement is accompanied by complete racemisation.

It is possible that Lowry's mechanism of supposed direct replacement without racemisation is more accurately represented by the scheme :



$$\underset{d\text{-.}}{\begin{matrix}C_7H_7\cdot SO_2\cdot O\\ C_6H_5\cdot CH_2\end{matrix}\!>C<\!\begin{matrix}CH_3\\ H\end{matrix}} \longrightarrow C_7H_7\cdot S(\bar{O})_2\cdot\bar{O}\ \overset{+}{C}H(CH_3)(CH_2\cdot C_6H_5) \xrightarrow{CH_3\cdot CO\cdot\bar{O}} \underset{d\text{-.}}{\begin{matrix}CH_3\cdot CO\cdot O\\ C_6H_5\cdot CH_2\end{matrix}\!>C<\!\begin{matrix}CH_3\\ H\end{matrix}}$$

On the basis of this scheme, however, *d*-phenylmethylcarbinyl *dl*-*p*-toluenesulphinate should, on isomerisation, produce an optically active sulphone, which is contrary to the observed experimental result. It is therefore improbable that, in the liquid state, a carbonium kation adopts a stable planar configuration and so enables direct replacement to occur without complete racemisation.

The conclusion that direct replacement cannot yield an optically active product is supported by recent experimental work which has emphasised that either a Walden inversion or complete racemisation occurs during the replacement of groups attached to an asymmetric carbon atom (Kenyon, Phillips, and Turley, J., 1925, **125**, 399; Freudenberg and Lux, *Ber.*, 1927, **60**, 2447; Kuhn and Wagner-Jauregg, *ibid.*, 1928, **61**, 504; Houssa, Kenyon, and Phillips, J., 1929, 1700). The exceptions to this rule are to be found amongst the reactions of compounds containing a phenyl group attached to the asymmetric carbon atom and those containing a carboxyl group. A special mechanism, involving the conversion of the optically active group into a carbonium anion, has been suggested to account for the behaviour of compounds containing phenyl groups (Kenyon, Lipscomb, and Phillips, *loc. cit.*), whilst the unforeseen participation of the carboxyl group in replacement reactions has been advanced as the cause of the supposed departure of the reactions of carboxylic acids from the above rule (Kenyon and Phillips, *Trans. Faraday Soc.*, 1930, **26**, 451).

p-*Tolyl-α-phenylethylsulphone.*—*l*-Phenylmethylcarbinyl *dl-p*-toluenesulphinate can be prepared by the interaction of *l*-phenylmethylcarbinol and *p*-toluenesulphinyl chloride in the presence of pyridine, but unlike the β-octyl ester (Phillips, *loc. cit.*), it decomposes when heated and cannot be distilled even at pressures lower than 0·1 mm. It can, nevertheless, be obtained as an almost colourless liquid, with $[\alpha]_{5461} -91°$ in ethyl-alcoholic solution, and when heated under reflux with ethyl alcohol containing potassium carbonate, it undergoes alcoholysis and yields *l*-phenylmethylcarbinol unchanged in rotatory power. On standing in a closed glass vessel for a few days at the ordinary temperature, *l*-phenylmethylcarbinyl *dl-p*-toluenesulphinate deposits crystals of *p*-tolyl-α-phenylethylsulphone which are optically inactive. The rate of change differs from sample to sample, suggesting that the transformation is favoured by the presence of unrecognised catalysts.

Although *d*-β-octyl *dl-p*-toluenesulphinate can be prepared by warming a mixture of equimolecular quantities of *d*-β-octanol and ethyl *dl-p*-toluenesulphinate under reduced pressure (Phillips, *loc. cit.*), when attempts are made to prepare *l*-phenylmethylcarbinyl *dl-p*-toluenesulphinate by a similar method, a further change occurs and the ester produced is largely converted into optically inactive *p*-tolyl-α-phenylethylsulphone.

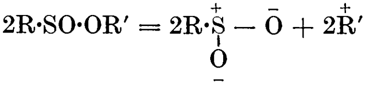
That the optical inactivity of the sulphone, obtained from the sulphinic ester, is not due to the chemical instability of the phenylmethylcarbinyl radical is evident, since dextrorotatory *p*-tolyl-α-phenylethylsulphone and dextrorotatory α-phenyldiethyl ether can be readily prepared by the interaction of *l*-α-chloroethylbenzene and sodium *p*-toluenesulphinate in ethyl-alcoholic solution. When thus prepared, the sulphone is not optically pure and can be separated by recrystallisation into fractions with $[\alpha]_{5461} + 29°$, $+ 35·5°$, $+ 96°$, $+103°$, in chloroform solution. This reaction is considered to be an inversion reaction on the assumption that *l*-α-chloroethylbenzene reacts with salts by a mechanism similar to that which enables *l*-β-chloro-octane to react with potassium acetate with inversion (Pickard and Kenyon, J., 1914, **105**, 830; Houssa, Kenyon, and Phillips, *loc. cit.*).

The Isomerisation of Sulphinic Acids and their Esters.—Under the experimental conditions employed, *l*-phenylmethylcarbinyl *p*-toluenesulphinate does not pass quantitatively to the corresponding *dl*-sulphone, but gives rise also to di-*p*-tolyl disulphoxide and αα′-diphenyldiethyl ether. The conversion of the sulphinic ester to the sulphone is therefore only one of several changes slowly undergone by this ester at ordinary temperatures, but more rapidly at higher temperatures.

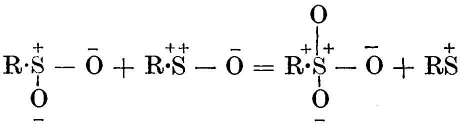
The formation of the disulphoxide and di-ether during the isomerisation of the sulphinic ester recalls the well-known transformation of sulphinic acids, which proceeds according to the equation (Fromm and Palma, *Ber.*, 1906, **39**, 3308; Hilditch, J., 1910, **97**, 2580), $3R{\cdot}SO{\cdot}OH = R{\cdot}SO_2{\cdot}OH + R{\cdot}SO_2{\cdot}SR + H_2O$, and suggests that sulphinic esters undergo a similar transformation indicated in the general equation $3R{\cdot}SO{\cdot}OR' = R{\cdot}SO_2OR' + R{\cdot}SO_2SR' + R_2'O$ or R_2'.

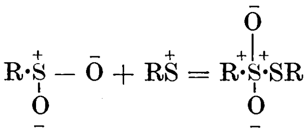
These equations summarise a series of changes undergone by sulphinic acids and their esters which probably take place according to the following equations, in which R′ is either an alkyl radical or a hydrogen atom :

(i) $R{\cdot}SO{\cdot}OR' = R{\cdot}\overset{++}{S} - \overset{-}{O} + \overset{-}{O}R'$

(ii) 
$2R{\cdot}SO{\cdot}OR' = 2R{\cdot}\underset{\underset{-}{O}}{\overset{+}{S}} - \overset{-}{O} + 2\overset{+}{R}'$

(iii) $R{\cdot}SO{\cdot}OR' = R{\cdot}SO_2{\cdot}R'$

(iv) 
$R{\cdot}\underset{\underset{-}{O}}{\overset{+}{S}} - \overset{-}{O} + R{\cdot}\overset{++}{S} - \overset{-}{O} = R{\cdot}\underset{\underset{-}{O}}{\overset{\overset{O}{+|+}}{S}} - \overset{-}{O} + R\overset{+}{S}$

(v) 
$R{\cdot}\underset{\underset{-}{O}}{\overset{+}{S}} - \overset{-}{O} + R\overset{+}{S} = R{\cdot}\underset{\underset{-}{O}}{\overset{\overset{\overset{-}{O}}{+|+}}{S}}{\cdot}SR$

The transformation of a sulphinic ester into a sulphone may be considered to be an abortive attempt by the sulphinic ester to dissociate as in equation (ii). In the case of the acids, the change shown in (iii) is reversible, since R′ then represents a proton, and $R{\cdot}SO_2{\cdot}R'$ the alternative formula for sulphinic acids (Hilditch, J., 1908, **93**, 1620). When R′ is an alkyl radical, the sulphone produced is stable and the change is then irreversible. Of the possible products predicted by these equations, *dl*-*p*-tolyl-α-phenylethylsulphone, *di-p*-tolyl disulphoxide, and $\alpha\alpha'$-diphenyldiethyl ether have been isolated from the products of the isomerisation of *l*-phenylmethylcarbinyl *dl-p*-toluenesulphinate. The formation of phenylmethylcarbinyl *p*-toluenesulphonate has not so far been detected.

It is probable that the mutarotation of *d*-β-octyl *d* + *dl-p*-toluenesulphinate and *d*-β-octyl *l* + *dl-p*-toluenesulphinate (Phillips, *loc. cit.*) is due to these esters undergoing some or all of the changes given in the above equations. Although the rotatory powers of these esters were of opposite sign, they eventually reached a common equilibrium value indicating that the asymmetry of the sulphur atom had been destroyed. Further, several specimens of *d*-β-octyl *p*-toluenesulphinate which have been preserved in closed vessels for two or more years have deposited crystals of di-*p*-tolyl disulphoxide. Similarly, specimens of ethyl *d* + *dl-p*-toluenesulphinate, also preserved in closed vessels, have since become optically inactive and have deposited crystals of the disulphoxide. The presence of the corresponding sulphone or *p*-toluenesulphonic ester amongst the decomposition products of these two esters has not been proved.

It is permissible, however, to conclude from this brief consideration of the transformations undergone by sulphinic acids and their esters, that the formation of *dl-p*-tolyl-α-phenylethylsulphone from *l*-phenylmethylcarbinyl *p*-toluenesulphinate is not a result of the interaction of the normal products of the transformation of this ester, but is due to a modification of one of the reactions by which these products arise. $\alpha\alpha'$-Diphenyldiethyl ether has been prepared from *l*-phenylmethylcarbinol and from *l*-α-phenylchloroethane by using Ward's methods (J., 1927, 454) which would be likely to cause some racemisation. From *l*-α-phenylchloroethane an optically inactive product was obtained, whilst the ether obtained from *l*-phenylmethylcarbinol had $\alpha_{5461} - 2{\cdot}0 (l = 1{\cdot}0)$. The $\alpha\alpha'$-diphenyldiethyl ether obtained during the transformation of the sulphinic ester had $\alpha_{5461} - 0{\cdot}64° (l = 1{\cdot}0)$, which is therefore another possible indication that some racemisation of the phenylmethylcarbinyl radical occurs during the change.

EXPERIMENTAL.

The Preparation and Alcoholysis of l-*Phenylmethylcarbinyl* p-*Toluenesulphinate.*—*p*-Toluenesulphinyl chloride (12·4 g.) was added slowly to an ice-cold solution of *l*-phenylmethylcarbinol (8·5 g.; $\alpha_{5461} - 12{\cdot}95°, l = 0{\cdot}25$) in pyridine (6·2 g.). The resulting mixture was triturated with ether (25 c.c.) in order to facilitate the reaction, more ether was then added, and the ethereal solution washed with dilute hydrochloric acid and then repeatedly with aqueous potassium carbonate. The ether was removed from the dried extract partly by distillation at ordinary pressure and subsequently at 15 mm. The l-*phenylmethylcarbinyl* dl-p-*toluenesulphinate* was thus obtained as a colourless, viscous liquid, which was freed from traces of *l*-phenylmethylcarbinol by gently heating it at less than 0·1 mm.; yield 93% of theory (Found : S, 12·2. $C_{15}H_{16}O_2S$ requires S, 12·3%); it had α_{5461} − 10·60°, α_{4358} − 18·50° in ethyl-alcoholic solution ($c = 5·839$; $l = 2·0$), whence $[\alpha]_{5461}$ − 90·8°, $[\alpha]_{4358}$ − 159°.

This ester (16·4 g.) was heated under reflux with ethyl alcohol (150 c.c.) and anhydrous potassium carbonate (18 g.) for several hours. The alcohol was then removed by distillation, and the residue distilled in a current of steam. From the ethereal extract of the aqueous distillate, *l*-phenylmethylcarbinol (6·5 c.c.), b. p. 92—93°/14 mm., α_{5461} − 12·89° ($l = 0·25$), was obtained. *l*-Phenylmethylcarbinol can therefore be regained from its *p*-toluenesulphinic ester, prepared as described above, without loss of rotatory power.

p-*Tolyl*-α-*phenylethylsulphone*.—*l*-α-Chloroethylbenzene [4·2 g.; α_{5461} − 14·2° ($l = 0·25$)], prepared by McKenzie and Clough's method (*loc. cit.*), sodium *p*-toluenesulphinate (9·5 g., 1·5 mols.), anhydrous potassium carbonate (4·0 g.), and ethyl alcohol (70 c.c.) were heated under reflux for 45 mins. The resulting mixture was distilled in a current of steam, and from the distillate dextrorotatory α-phenyldiethyl ether, b. p. 73—74°/16 mm. (Holmberg, *Ber.*, 1912, **45**, 1002; Ward, *loc. cit.*), with α_{5461} + 4·41° ($l = 0·25$) was isolated. The non-volatile portion of the mixture contained a granular powder (1·2 g.), m. p. 126—128°, $[\alpha]_{5461}$ + 35·5° in chloroform solution, and when it was cooled deposited crystalline needles (0·15 g.), m. p. 134—135°, α_{5461} + 40° in chloroform solution ($c = 0·60$; $l = 2·0$). These two solid products were both dextrorotatory *p*-tolyl-α-phenylethylsulphone and differ in rotatory power and m. p. because the *d*-sulphone is more soluble in solvents and possesses a lower m. p. than the *dl*-sulphone. Thus a solution of these two products in hot ethyl alcohol (15 c.c.), when cooled, deposited *dextrorotatory* p-*tolyl*-α-*phenylethylsulphone* (1·0 g.), m. p. 134—135°, $[\alpha]_{5461}$ + 29·0° in chloroform solution ($c = 3·55$; $l = 2·0$) (Found : C, 69·4; H, 6·0. $C_{15}H_{16}O_2S$ requires C, 69·3; H, 6·2%). The ethyl-alcoholic filtrate, when concentrated, deposited a dextrorotatory sulphone (0·15 g.), m. p. 124—125°, α_{5461} + 103° in chloroform solution ($c = 0·60$; $l = 2·0$). During the reaction between α-chloroethylbenzene and sodium *p*-toluenesulphinate in ethyl alcohol, the presence of potassium carbonate is necessary, since the formation of α-phenyldiethyl ether leads to the production of hydrochloric acid, in the presence of which the sodium *p*-toluenesulphinate is partly converted into di-*p*-tolyl disulphoxide, and it is difficult to separate *p*-tolyl-α-phenylethylsulphone completely from this disulphoxide by fractional crystallisation.

dl-p-*Tolyl-α-phenylethylsulphone.*—(i) *By the interaction of* dl-α-*chloroethylbenzene and sodium* p-*toluenesulphinate. dl*-Chloroethylbenzene (7·8 g.), sodium *p*-toluenesulphinate (15 g.), and ethyl alcohol (150 c.c.) were heated together under reflux for 30 mins. The alcohol was then removed by distillation, and the residue distilled in a current of steam. The non-volatile portion (4·15 g.) was recrystallised from aqueous alcohol and was finally separated into *dl*-*p*-tolyl-α-phenylethylsulphone (1·5 g.), m. p. 131—132°, and di-*p*-tolyl disulphoxide (1·1 g.), m. p. and mixed m. p. 75—76°.

(ii) *By heating a mixture of* dl-*phenylmethylcarbinol and ethyl* dl-p-*toluenesulphinate.* A mixture of the *dl*-alcohol (22 g.) and the sulphinic ester (31 g.), prepared by the method of Houssa, Kenyon, and Phillips (*loc. cit.*), was heated at 50—60°/20 mm. for 30 hours. The product, a mixture of crystals and a viscous oil, was triturated with ethyl alcohol (60 c.c.) and then filtered. The crystals, *dl*-*p*-tolyl-α-phenylethylsulphone, had m. p. 123—125°, and by recrystallisation from ethyl alcohol were obtained with m. p. and mixed m. p. 133—134°.

(iii) *By heating a mixture of* l-*phenylmethylcarbinol and ethyl* dl-p-*toluenesulphinate.* A mixture of ethyl *dl*-*p*-toluenesulphinate (18·5 g.) and *l*-phenylmethylcarbinol (12·2 g.) was heated at 60—80°/18 mm. for 20 hours. The viscous mass produced was triturated with ether, whereupon impure *d*-*p*-tolyl-α-phenylethylsulphone (6·9 g.), m. p. 133—134°, separated. It was contaminated by a trace of an optically active impurity and had $[\alpha]_{5461}$ $-$ 0·64° (c = 12·5; l = 2·0) in chloroform solution. It was recrystallised from ethyl alcohol–chloroform and obtained (4·3 g.) with m. p. 137° (Found : C, 69·3; H, 6·2%); it was optically inactive in chloroform solution (c = 21·5; l = 2·0) to light of λ5461 and 4359. The ethereal filtrate from this *dl*-sulphone was evaporated, and a current of steam passed through the resulting oily residue. Only a few drops of this residue were volatile in steam, and the non-volatile portion set to a thick paste on cooling. This paste was dissolved in chloroform, and the solution washed with aqueous sodium carbonate and then dried. After removal of the chloroform and dilution of the residual oil with ether, di-*p*-tolyl disulphoxide crystallised and had m. p. and mixed m. p. 73—75° after being washed with a mixture of ether and light petroleum. The ethereal filtrate from the disulphoxide was evaporated, and from the residue (13·6 g.) a fraction was obtained which distilled almost completely at 92°/0·1 mm. It consisted of αα′-diphenyldiethyl ether (compare Ward, *loc. cit.*), and after redistillation (b. p. 160—161°/18 mm.) had α_{5461} $-$ 0·16° (l = 0·25).

Similar results were obtained (*a*) by heating *d*-phenylmethylcarbinol (3·9 g.) and ethyl *dl*-*p*-toluenesulphinate (5·8 g.) for 48 hrs. at 40—50°/18 mm., and then, since no obvious change took place, for 1·5 hrs. at 70°/18 mm., whereupon a vigorous ebullition occurred; and (*b*) by heating *d*-phenylmethylcarbinol (3·1 g.) and ethyl *dl*-*p*-toluenesulphinate (4·7 g.) at 50—90°/18 mm. for 8 hrs.

(iv) *By the transformation, at ordinary temperatures, of* d + dl-*phenylmethylcarbinyl* p-*toluenesulphinate.* The *d* + *dl*-sulphinic ester was prepared from *d* + *dl*-phenylmethylcarbinol (α_{5461} + 5·03°, $l = 0{\cdot}25$) and *p*-toluenesulphinyl chloride by the method previously described. When freshly prepared, it had $[\alpha]_{5461}$ + 33·2° in chloroform solution ($c = 4{\cdot}55$; $l = 2{\cdot}0$), falling after 9 days at the ordinary temperature to $[\alpha]_{5461}$ + 30·4°, and after a further 29 days, to $[\alpha]_{5461}$ + 24·5°.

The *d* + *dl*-ester (4·4 g.) when kept in a closed glass vessel for 20 days became a mass of crystals, which, after trituration with light petroleum, had m. p. 69—74°. They were optically inactive in chloroform solution ($c = 15{\cdot}0$; $l = 2{\cdot}0$). By recrystallisation from ethyl alcohol, the di-*p*-tolyl disulphoxide was removed from the crystals, leaving *dl*-*p*-tolyl-α-phenylethylsulphone (1·4 g.), m. p. and mixed m. p. 133—134°.

Optically Active α-Phenyldiethyl Ether.—(i) *From* l-*phenylmethylcarbinol.* Ethyl bromide (6·0 g.) in ether (15 c.c.) was gradually added to a solution obtained by the action of powdered potassium (2·0 g.) on the *l*-alcohol (6·1 g.) dissolved in ether (50 c.c.). The ethereal mixture was washed three times with water, dried, and then distilled. The fraction (4·0 c.c.) of b. p. 71—73°/15 mm. consisted almost entirely of *l*-α-phenyldiethyl ether and had α_{5461} − 21·17° ($l = 0{\cdot}25$). It was freed from traces of the *l*-alcohol by heating it with an excess of phthalic anhydride in pyridine for 2 hours. The pure *l*-α-phenyldiethyl ether recovered from this reaction mixture had b. p. 67°/14 mm. and α_{5780} − 19·50°, α_{5461} − 22·22°, α_{4358} − 37·88° ($l = 0{\cdot}25$).

(ii) *From* l-α-*chloroethylbenzene.* A mixture of *l*-α-chloroethylbenzene [1·5 g., α_{5461} − 11·67° ($l = 0{\cdot}25$)], potassium carbonate (5 g.), and ethyl alcohol (15 c.c.) was heated under reflux for 1½ hrs. The reaction mixture was then poured into water, and the oily product extracted and heated under reflux with an alcoholic solution of potassium hydroxide to free it from unchanged chloro-compound. The recovered *d* + *dl*-α-phenyldiethyl ether had b. p. 72°/20 mm. and α_{5461} + 3·14° ($l = 0{\cdot}25$).

αα′-Diphenyldiethyl Ether.—(i) *From* l-*phenylmethylcarbinol.* The *l*-alcohol [5 g., α_{5461} − 50·4° ($l = 1{\cdot}0$)] was gently boiled under reflux with 0·5*N*-aqueous hydrochloric acid (80 c.c.) for 8 hours (compare

Ward, *loc. cit.*). The reaction mixture was then cooled, extracted with ether, and the ethereal extract dried and distilled. Below 154°/15 mm. a mixture of styrene and phenylmethylcarbinol (1·5 c.c.) was obtained, the main product, lævorotatory $\alpha\alpha'$-diphenyldiethyl ether, had b. p. 154—155°/15 mm., and $\alpha_{5461} - 0{\cdot}50°$ ($l = 0{\cdot}25$).

(ii) *From* l-α-*chloroethylbenzene.* A mixture of *l*-α-chloroethylbenzene [5 g., $\alpha_{5461} - 64{\cdot}0°$ ($l = 1{\cdot}0$)] and water (75 c.c.) was gently boiled under reflux for 2 hrs. (Ward, *loc. cit.*). The product isolated from the cold reaction mixture was separated by distillation into styrene (3·9 c.c.), *dl*-phenylmethylcarbinol, b. p. 99—101°/18 mm., and *dl*-$\alpha\alpha'$-diphenyldiethyl ether (1·0 c.c.), b. p. 159—160°/18 mm.

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