**102.** *The Molecular Rearrangement of* (−)*Phenylmethylcarbinyl* dl-p-*Toluenesulphinate.*

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A further study has been made of the molecular rearrangement of (−)phenylmethyl-carbinyl *dl-p*-toluenesulphinate to *dl-p*-tolyl-α-phenylethylsulphone (Kenyon and Phillips, J., 1930, 1676). Experiments upon *dl*-phenylmethylcarbinyl *p*-toluenesulphinate show that the rearrangement is facilitated in formic acid solution. The rearrangement of the (−)ester in formic acid solution gives the *dl*-sulphone in 75% yield. The hypothesis of Kenyon and Phillips (*loc. cit.*) that the rearrangement occurs *via* ionisation is confirmed with respect to the greater proportion of the sulphone produced, and is elaborated in the light of the results of experiments on the mutarot-ation of the ester in solvents. In formic acid solution containing sodium formate a mixture of (−) and *dl*-sulphone is produced, but the yield is only 10%, the main product being a mixture of (−) and *dl*-phenylmethylcarbinyl formate. Both these products have the same relative configuration as the original sulphinic ester. Evidence is adduced that the formate arises (i) as a result of formolysis of the sulphinate, giving the (−)formate, (ii) by combination of α-phenylethyl kations with formate anions, giving the *dl*-formate. It is suggested that the (−)sulphone is formed by intramolecular rearrangement; in the presence of an added anion rearrangement *via* ionisation is diverted and only the small proportion of lævorotatory sulphone formed by the intra-molecular process is obtained.

It was suggested (Kenyon and Phillips, *Trans. Faraday Soc.*, 1930, **26**, 451; Kenyon, Phillips, and Taylor, J., 1931, 384) that reactions which result in Walden inversion take place by way of intermediate complex formation whereby the entering anion becomes associated with the asymmetric carbon atom before detachment of the replaced anion is effected, whilst fission of the optically active molecule into a carbonium kation and an anion before the entering anion becomes associated with it results in racemisation. Subse-quently, these suggestions were put forward in more precise forms by Polanyi and co-workers (*Z. physikal. Chem.*, 1932, *B*, **19**, 164; 1933, *B*, **20**, 161) and by Hughes, Ingold, and co-workers (J., 1937, 1252).

The second part of this hypothesis, *i.e.*, preliminary fission of the molecule, has been contested on the ground that it would require more energy than is available under the usual conditions of replacement reactions (Wallis and Moyer, *J. Amer. Chem. Soc.*, 1933, **55**, 2598; Olson, *J. Chem. Physics*, 1933, **1**, 418; Olson and Halford, *J. Amer. Chem. Soc.*, 1937, **59**, 2644; Steigman and Hammett, *ibid.*, p. 2540). Hughes and Ingold (J., 1935, 244) considered that solvation of the molecule may provide the energy required for ionisation, whereas Kenyon and Phillips (J., 1930, 1676) concluded that the spontaneous transformation of (−)phenylmethylcarbinyl *p*-toluenesulphinate (I) into *dl-p*-tolyl-α-phenylethylsulphone (II) provided experimental evidence of ionisation during the course of

$$\text{(I.)} \quad \text{CHPhMe-O-}\overset{\overset{\displaystyle O}{\uparrow}}{\text{S}}\text{-C}_7\text{H}_7 \qquad\qquad \text{CHPhMe-}\overset{\overset{\displaystyle O}{\uparrow}}{\underset{\underset{\displaystyle O}{\downarrow}}{\text{S}}}\text{-C}_7\text{H}_7 \quad \text{(II.)}$$

the rearrangement. This ionic fission and the racemisation of the liberated kation may be expected to occur more readily in derivatives of α-phenylethane than in those of purely aliphatic secondary alcohols (Hughes, Ingold, and co-workers, *loc. cit.*); it is likely, however, that molecular rearrangement through the intermediate formation of ions is exceptional. For example, Kenyon, Partridge, and Phillips (J., 1937, 207) have provided evidence which suggests that the anionotropic rearrangement of the hydrogen phthalate of α-phenyl-γ-methylallyl alcohol is an intramolecular process. Other investigations (reviewed by Waters, "Physical Aspects of Organic Chemistry," 1935, p. 346 *et seq.*, and by Watson, "Modern Theories of Organic Chemistry," 1937, p. 132 *et seq.*) indicate that intramolecular rearrangement is more common than rearrangement *via* ionisation. If the migrating

radical is optically active and its asymmetric carbon atom retains its octet of electrons during the rearrangement, asymmetry is completely maintained (Jones and Wallis, *J. Amer. Chem. Soc.*, 1926, **48**, 169; Wallis and Nagel, *ibid.*, 1931, 53, 2787; Wallis and Dripps, *ibid.*, 1933, **55**, 1701); intramolecular migration of an optically active radical containing an asymmetric carbon atom carrying a sextet of electrons results in an optically active product with retention of configuration and partial racemisation (Sprung and Wallis, *ibid.*, p. 3838; Wallis and Bowman, *J. Org. Chem.*, 1936, **1**, 383).

In view of its significance and its unique character, the rearrangement of (—)phenyl-methylcarbinyl *dl-p*-toluenesulphinate has been submitted to further study. The rearrangement has also been examined of the homogeneous ester, prepared from (—)phenyl-methylcarbinol having $\alpha_{5461} - 11.9°$ ($l$, 0·25); the ester used by Kenyon and Phillips (*loc. cit.*) was prepared from carbinol of $\alpha_{5461} + 5.03°$ ($l$, 0·25). The solid product of the rearrangement, recrystallised once from aqueous ethyl alcohol, gives optically inactive *p*-tolyl-α-phenylethylsulphone in 22% yield.

Table I records the results of experiments using approximately 5 g. of *dl*-sulphinate in 20 c.c. of each of a variety of solvents at laboratory and at elevated temperatures. Col. 2 gives ε, the dielectric constant of the solvent at 20°. The yields recorded are percentages of those obtainable if all the sulphinate had been converted into the derivative in question.

The data in Table I show that decomposition occurs at elevated temperatures. The formation of di-*p*-tolyl disulphoxide during the rearrangement has been discussed by Kenyon and Phillips (*loc. cit.*); an alternative mode of formation of the disulphoxide is by the usual decomposition of *p*-toluenesulphinic acid formed, together with styrene, by thermal decomposition of the ester. *p*-Tolyl-α-phenylethylsulphone is stable at 80°, being recovered unchanged after heating at that temperature for 24 hours in the homogeneous state or in nitrobenzene solution. The results of the experiments at room temperature

TABLE I.

*Transformation of* dl-*phenylmethylcarbinyl* dl-p-*toluenesulphinate in solvents and in the presence of sodium formate and sodium* p-*toluenesulphinate.*

| | | Reaction at room temp. | | | Reaction at elevated temp. | | |
|---|---|---|---|---|---|---|---|
| Solvent. | $\epsilon_{20°}$. | Dur-ation, days. | Isolated products.* | Temp. | Dur-ation, hours. | Isolated products. | |
| (None) | — | 23 | Sulphone, 27%; styrene, trace | 80° | 3 | Sulphone, 10% (profound decomp.) | |
| Ethyl ether satd. with HCl † | — | 18 | Disulphoxide, 22% | — | — | — | |
| Benzene | 2·3 | 21 | Sulphone, 9% | 80 | 24 | Disulphoxide, 23% | |
| Pyridine | 12·4 | 18 | Unchanged sulphinate | — | — | — | |
| Acetone | 21·5 | — | — | 56 | 24 | Unchanged sulphinate | |
| Nitrobenzene | 34·1 | 25 | Sulphone, 30% | 80 | 2·5 | Sulphone, 9% (profound decomp.) | |
| Acetonitrile | 37·5 | 22 | Unchanged sulphinate | 80 | 20 | Disulphoxide, 21% | |
| Formic acid | 57·0 | 22 | Sulphone, 72; formate, 13% | 80 | 2·5 | Sulphone, 54%; formate, trace | |
| Sodium formate ‡ in formic acid | — | 23 | Sulphone, 11; formate, 75; sulphinic acid, 12% | — | — | — | |
| Sodium *p*-toluenesulphinate § in formic acid | — | 18 | Sulphone, 6; formate, 62% | — | — | — | |

\* Sulphone, disulphoxide, formate, and sulphinic acid signify respectively *p*-tolyl-α-phenylethyl-sulphone, di-*p*-tolyl disulphoxide, phenylmethylcarbinyl formate, and *p*-toluenesulphinic acid.

† The sulphinate was recovered unchanged after 20 days from solution in ethyl ether in the presence of anhydrous potassium carbonate, and from ethereal ammonia and ethereal hydrogen chloride.

‡ 2·5 Mols. per mol. of sulphinate.   § 1·25 Mols. per mol. of sulphinate

indicate that the rearrangement is favoured in solvents of high dielectric constant, and may be diverted in the presence of added anions; these conclusions are in harmony with the suggestion that the rearrangement occurs *via* ionisation. The comparatively high yield

of sulphone obtained from the rearrangement of the homogeneous sulphinate may be ascribed to the fact that the sulphinate is itself likely to have a high dielectric constant. The difference between the results obtained in nitrobenzene and in acetonitrile solution indicate an unexpected difference in the degree of solvation of the sulphinate in these two solvents, and the facile rearrangement in formic acid solution may be due, not only to the high dielectric constant of this solvent, but also to the ability to solvate both anion and kation, which is peculiar to hydroxylic solvents. If solvation of the kation by formic acid occurs, it must be by electrostatic attraction similar to the hydration of inorganic kations (Day, Hughes, Ingold, and Wilson, J., 1934, 1593), since solvation by co-ordination would result in the formation of phenylmethylcarbinyl formate.

Table II records the products of the rearrangement of the (—)sulphinate, solutions of the same concentrations being used as those described in Table I. The high yield of optically inactive sulphone produced by the rearrangement of the (—)sulphinate in formic acid solution is a convincing confirmation of Kenyon and Phillips's observation that the reaction is accompanied by racemisation.

(—)Phenylmethylcarbinyl formate has the same configuration as the (—)carbinol, because it is converted into this by saponification, a process which does not disturb the bonds of the asymmetric carbon atom (Holmberg, *Ber.*, 1912, **45**, 2997; Ingold and Ingold, J., 1932, 756; Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, **30**, 508). The (—)formate therefore has the same configuration as the (—)sulphinate, which is formed from the (—)carbinol by a reaction in which the bonds of the asymmetric carbon atom are not disturbed. The formation of a mixture of (—) and dl-*phenylmethylcarbinyl formate* during the re-arrangement of (—)phenylmethylcarbinyl *p*-toluenesulphinate in the presence of sodium formate cannot be accounted for by any of the hypotheses previously advanced to explain retention of configuration during replacement reactions, *viz.*, occurrence of an even number of consecutive inversion reactions, or the retention by the carbon atom of its electron octet (Kenyon and Phillips, *Trans. Faraday Soc.*, loc. cit.), or an intramolecular replacement in which the entering atom and the atom which it replaces are held on the same side of the

TABLE II.

*Rearrangement of* (—)*phenylmethylcarbinyl* dl-p-*toluenesulphinate in formic acid solution and in the presence of sodium formate and sodium* p-*toluenesulphinate.*

(Optically active products all formed with retention of configuration.)

| Solvent. | | Formic acid. | | H·CO₂Na in H·CO₂H. | | Sodium *p*-toluene-sulphinate in H·CO₂H.* |
|---|---|---|---|---|---|---|
| | Product. | Sulphone.† | Formate. | Sulphone.† | Formate.‡ | Formate. |
| Crude product | Yield, % ............... | 75 | trace | 13 | — | — |
| | M. p. ..................... | 127—130° | — | 110—115° | — | — |
| Purified product | Yield, % ............... | 60 | — | 10 | 75 | 62 |
| | M. p. ..................... | 134° | — | 127—128° | — | — |
| | Rotatory power § ...... | nil | — | −65·6° | −9·5° | −0·47° |
| | % of max. recorded rotatory power ...... | nil | — | 63 | 20 | 1 |

\* (—) + dl-Sulphinate having 75% of maximum rotatory power was used in this experiment. The solid reaction product contained a high proportion of disulphoxide, which made purification of the sulphone difficult.

† The dl-sulphone has m. p. 134°, and sulphone of $[a]_{5461}$ +103° in chloroform (*l*, 2·0; *c*, 0·6) has m. p. 124—125° (Kenyon and Phillips, *loc. cit.*).

‡ (—)Phenylmethylcarbinyl formate has $a_{5461}$ −48·90° (*l*, 0·236).

§ $[a]_{5461}$ of the sulphone in chloroform (*l*, 2·0; *c*, 2·65); $a_{5461}$ of the formate (*l*, 0·236).

asymmetric carbon atom (Hughes, Ingold, and co-workers, *loc. cit.*). Sulphinic esters of optically active alcohols, however, undergo reactions analogous to the saponification or alcoholysis of carboxylic esters, in which the bonds of the asymmetric carbon atom are not disturbed. For example, (—)phenylmethylcarbinyl *p*-toluenesulphinate undergoes alcoholysis in ethyl-alcoholic solution (Kenyon and Phillips, J., 1930, *loc. cit.*) with complete retention of configuration. Like sodium acetate in acetic acid solution (Steigman and Hammett, *loc. cit.*), a solution of sodium formate in formic acid is basic, resembling aqueous

sodium hydroxide in that it contains sodium ions, anions in equivalent amount, and the undissociated acid corresponding to these anions. It can therefore react with the sulphinic ester in the same way that aqueous sodium hydroxide reacts with ethyl $(+)\alpha$-$p$-toluene-sulphinoxypropionate (Gerrard, Kenyon, and Phillips, J., 1937, 153) yielding $(-)$phenyl-methylcarbinyl formate without disturbance of the bonds of the asymmetric carbon atom and therefore uncontaminated by the $(+)$ester. At the same time the *dl*-formate is produced by the interaction of liberated phenylmethylcarbinyl kations with formate anions. The sum of these two processes is the formation of the mixture of $(-)$ and *dl*-formate with $\alpha_{5461} - 9.52°$ $(l, 0.236)$. Since the optically pure ester has $\alpha_{5461} - 48.90°$ $(l, 0.236)$, it is concluded that approximately 20% of the formate is optically active and produced by " formolysis," and the remainder is produced from the liberated and immediately racemised carbonium kations. This suggestion is supported by the results of the experiment in formic acid solution in the presence of sodium $p$-toluenesulphinate (Table II). Formate ions are present in this solution, as is shown by the high yield of formate (62%) compared with the low yield of formate in formic acid alone (Tables I and II). The formate produced, however, is almost entirely racemic, because the reaction (formolysis) which results in the formation of optically active formate is repressed by the presence of its products, $p$-toluene-sulphinyl ion or $p$-toluenesulphinic acid.

The observations described above support the suggestion that the rearrangement occurs to a preponderating extent *via* ionisation, but the formation of lævorotatory, instead of racemic, $p$-tolyl-$\alpha$-phenylethylsulphone in 10% yield during the rearrangement of the sulphinate in the presence of sodium formate shows that a small part of the rearrangement can occur by an alternative route. The $(-)$sulphone has the same relative configuration as $(-)$phenylmethylcarbinol, because it can be obtained from the latter by two successive reactions, each of which involves inversion of configuration, *viz.*, conversion of the $(-)$car-binol into the $(+)$chloride (Kenyon, Phillips, and Taylor, *loc. cit.*) and conversion of this into the $(-)$sulphone (Kenyon and Phillips, J., 1930, *loc. cit.*). The $(-)$sulphone has therefore the same configuration as the $(-)$sulphinate, which is prepared from the $(-)$carbinol by esterification with $p$-toluenesulphinyl chloride. Like the $(-)$formate, described above, the $(-)$sulphone cannot be derived from the $(-)$sulphinate by replacement reactions. It is therefore concluded that the mixture of $(-)$ and *dl*-sulphone is formed by intramole-cular rearrangement, with retention of configuration and partial racemisation, like the rearrangements described by Sprung and Wallis (*loc. cit.*) and Wallis and Bowman (*loc. cit.*). In this type of rearrangement, an optically active product is obtained because the carbonium kation does not become free; fission of the carbon–oxygen bond and formation of the carbon–sulphur bond occur simultaneously. This process was suggested by Wallis and Moyer (*J. Amer. Chem. Soc.*, 1933, **55**, 2598) as the mechanism of the Hofmann re-arrangement. If all the $(-) + dl$-sulphone obtained in formic acid–sodium formate solution is produced by intramolecular rearrangement, approximately 15% of the $(-)$sulphinate undergoes the intramolecular process under these conditions; the racemic fraction of the sulphone obtained may, however, be derived in part from $\alpha$-phenylethyl kations which fail to react with formate ions.

It is likely that the rearrangement of the sulphinate *via* ionisation is usually accompanied by a minor intramolecular rearrangement. The optically active sulphone is more soluble than the racemic form (Kenyon and Phillips, *loc. cit.*) and, by recrystallisation, a racemic product would therefore be obtained from a sulphone of very low rotatory power. The original explanation of the rearrangement may now be extended as follows :
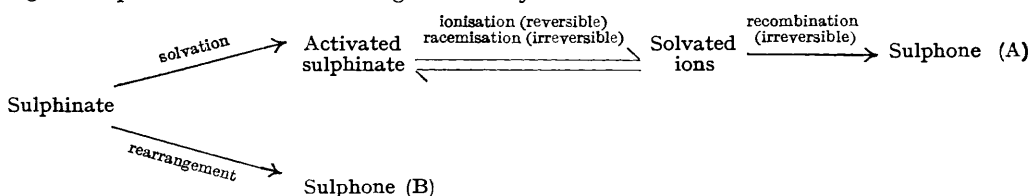


A = Major reaction, ionic, with racemisation. B = Minor reaction, intramolecular, with retention of configuration.

Support for the above scheme is given by observations of the mutarotation of solutions of the (—)sulphinate in formic acid solution, in which the rearrangement takes place most readily, and in acetonitrile solution, in which it does not occur. The results are given in Table III. The rotatory power of the solution in formic acid $(l, 0\cdot5)$ falls from $\alpha_{5461}$ — $3\cdot92°$, 20 minutes after dissolution ($\alpha_{5461}$ — $6\cdot7°$ extrapolated to zero time), to $\alpha_{5461}$ — $0\cdot90°$ after 75 minutes, but only a small amount (approximately $10\%$ yield) of phenylmethyl-carbinyl formate is formed during this time, the rest of the sulphinate being recovered and having, after isolation from the solution, $[\alpha]_{5461}^{17°}$ — $61\cdot7°$ in ethyl alcohol $(l, 2\cdot0; c, 1\cdot2)$; the original sulphinate had $[\alpha]_{5461}^{20°}$ — $84\cdot3°$ $(l, 2\cdot0; c, 5\cdot13)$. The mutarotation, which is therefore not due to racemisation or to reaction of the sulphinate, and is too rapid to be reasonably ascribed to variation of the specific rotatory power of the sulphinate as a result of its diminished concentration, must be caused by a reversible modification in the environ-ment of the asymmetric carbon or sulphur atoms of the sulphinate molecule, occurring in solution. It can therefore be ascribed to an incipient disturbance of the molecule, prior to ionisation, corresponding to the stage described as solvation in the above scheme. Solvation in this sense implies, not only the attraction of solvent molecules by the solute, but also enhanced reactivity of the solute and formation of a new structure. Evidence of the second stage of the ionic mechanism, reversible ionisation accompanied by racemisation, is given by the observation that the sulphinate recovered from solution in formic acid after 75 minutes has lost $25\%$ of its rotatory power. The third stage of this mechanism is established by the formation of *dl*-sulphone.

The solution of the (—)+ *dl*-sulphinate in acetonitrile, on the other hand, remains unchanged in rotatory power, $\alpha_{5893}$ — $9\cdot46°$ $(l, 2\cdot0; c, 18\cdot6)$, during 88 hours. The sulphinate recovered from this solution after $23\cdot5$ hours has $[\alpha]_{5461}^{17\cdot5°}$ — $70\cdot3°$ in ethyl alcohol $(l, 2\cdot0; c, 4\cdot88)$; the original sulphinate had $[\alpha]_{5461}^{20°}$ — $70\cdot5°$ in ethyl alcohol $(l, 2\cdot0; c, 5\cdot02)$. These observations are in harmony with the fact that in this solvent the rearrangement does not take place. The subsequent decrease in rotation is due to the general instability of sulphinic esters, resulting in decomposition and racemisation. After 256 hours the rotatory power of the solution falls to $\alpha_{5893}$ — $4\cdot24°$ and the sulphinate recovered from the solution at that time has $[\alpha]_{5461}$ — $43\cdot6°$ in ethyl alcohol $(l, 2\cdot0; c, 4\cdot88)$.

In ethereal solution in the presence of potassium carbonate the sulphinate shows even greater stability. A solution of the (—)+ *dl*-ester in ether, having $\alpha_{5461}^{17°}$ — $21\cdot52°$ $(l, 2\cdot0; c, 11\cdot4)$ when freshly prepared, undergoes little change in rotatory power when kept over anhydrous potassium carbonate during 20 days, $\alpha_{5461}^{17°}$ being then — $21\cdot26°$. The sul-phinate is recovered from this solution with undiminished rotatory power. The lævorot-atory sulphinate undergoes mutarotation in formic acid solution in the presence of sodium formate and sodium *p*-toluenesulphinate, and in nitrobenzene solution (Table IV), but the results cannot be precisely interpreted because certain of the products formed under these conditions are optically active.

TABLE III.

*Mutarotation of solutions of lævorotatory phenylmethylcarbinyl* dl-p-*toluenesulphinate in formic acid and in acetonitrile.*

In $H\cdot CO_2H$ $(l, 0\cdot5; c, 23\cdot9)$. | | In $CH_3\cdot CN$ $(l, 2; c, 18\cdot6)$. | | | | | |
|---|---|---|---|---|---|---|---|
| Mins. after dissolution. | $\alpha_{5461}^{18°}$. | Hours after dissolution. | $\alpha_{5893}^{17°}$. | Hours after dissolution. | $\alpha_{5893}^{17°}$. | Hours after dissolution. | $\alpha_{5893}^{17°}$. |
| 20 | $-3\cdot92°$ | 0 | $-9\cdot46°$ | $42\cdot5$ | $-9\cdot45°$ | 160 | $-7\cdot62°$ |
| 40 | $-2\cdot41$ | $1\cdot5$ | $-9\cdot44$ | 88 | $-9\cdot50$ | 193 | $-5\cdot91$ |
| 75 | $-0\cdot90$ | $11\cdot25$ | $-9\cdot46$ | 112 | $-9\cdot25$ | $208\cdot5$ | $-5\cdot34$ |
| | | $23\cdot5$ | $-9\cdot44$ | $136\cdot75$ | $-8\cdot57$ | 256 | $-4\cdot24$ |

EXPERIMENTAL

(—)Phenylmethylcarbinol was prepared by the method of Houssa and Kenyon (J., 1930, 2260), and *dl*- and (—)-phenylmethylcarbinyl *p*-toluenesulphinates by that of Kenyon and Phillips (*loc. cit.*). The (—)sulphinate had $n_D^{17°}$ $1\cdot5745$; $[\alpha]_{5461}^{20°}$ — $87\cdot0°$, $[\alpha]_{4358}^{20°}$ — $150\cdot2°$ $(l, 2\cdot0; c, 4\cdot725)$ in ethyl alcohol.

*Transformation of* dl-*Phenylmethylcarbinyl* dl-p-*Toluenesulphinate.*—(i) *In the homogeneous state.* (a) At room temperature. The *dl*-ester (15·4 g.) after 26 days at room temperature was converted into a crystalline mass which was washed with light petroleum and ethyl alcohol. The residue (5·7 g.), m. p. 110—115°, was twice recrystallised from aqueous ethyl alcohol; the *p*-tolyl-*dl*-α-phenylethylsulphone (2·7 g.) obtained had m. p. 133—134°, alone or mixed with an authentic specimen. From the concentrated light petroleum and alcoholic wash-liquors, an oil (0·5 c.c.), b. p. 45—60°/16 mm., $n_D^{20°}$ 1·518, was isolated, which resinified on addition of a drop of concentrated sulphuric acid and was presumably styrene.

From another specimen of the sulphinate (0·63 g.) the sulphone (0·17 g.) was isolated after 23 days, with m. p. and mixed m. p. 131—133°.

(b) At 80°. The sulphinate (8 g.), when heated on the steam-bath for 3 hours, was converted into a brown crystalline mass from which, by the method described above, 0·8 g. of sulphone, m. p. and mixed m. p. 134°, was obtained.

(ii) *In ethereal solution.* (a) In ethyl ether saturated with hydrogen chloride. A solution of the *dl*-ester (5 g.) in 17 g. of ether saturated with hydrogen chloride, after standing at laboratory temperature for 18 days, was washed with aqueous sodium bicarbonate and with water and dried. The solid residue left after removal of the ether was washed with ethyl alcohol. The solid product (0·6 g.), after recrystallisation from ethyl alcohol, gave di-*p*-tolyl disulphoxide, m. p. and mixed m. p. 78°. From the alcoholic wash-liquor a fraction (2 c.c.), b. p. 76°/22 mm., was obtained, which was presumably α-phenyldiethyl ether (b. p. 67°/14 mm.) formed by inter-action of α-phenyl-α-chloroethane with ethyl alcohol.

(b) In ether containing hydrogen chloride (0·7%). A solution of the *dl*-ester (4·4 g.; $n_D^{17°}$ 1·5753) in 25 c.c. of ether containing 0·18 g. of hydrogen chloride was washed as above, after standing at room temperature for 21 days. The residue left after removal of the ether consisted of unchanged ester ($n_D$ 1·564).

(c) In ether containing ammonia (0·1%). A solution of the *dl*-ester (5 g.; $n_D^{17°}$ 1·5753) in 25 c.c. of ether containing anhydrous ammonia (0·025 g.), after standing at laboratory temper-ature for 21 days, was washed with water and dried. The sulphinate ($n_D^{16°}$ 1·5713) was recovered on removal of the ether.

(d) In ether in the presence of anhydrous potassium carbonate. The *dl*-ester (5 g.; $n_D^{16°}$ 1·5756), after standing for 18 days in ether (20 c.c.) with anhydrous potassium carbonate, was recovered unchanged ($n_D^{16°}$ 1·5740).

(iii) *In benzene solution.* (a) At room temperature. The sulphinate (5 g.; $n_D^{17°}$ 1·5736) was dissolved in benzene (25 c.c.). After 21 days, the benzene was removed and the pasty residue washed with a mixture of light petroleum and ethyl alcohol and recrystallised from aqueous ethyl alcohol. The product (0·45 g., m. p. 132—133°), recrystallised from aqueous ethyl alcohol, gave the *dl*-sulphone, m. p. and mixed m. p. 134°. The light petroleum–ethyl alcohol washings contained 3·8 g. of an oil, which could not be distilled and was presumably sulphinate.

(b) At 80°. The *dl*-ester (6 g.) in benzene (20 c.c.) was heated under reflux for 24 hours, and the benzene then removed by distillation. The solid product was filtered off from the liquid product, and after recrystallisation from alcohol, had m. p. 70—75° (yield 0·75 g.); a second recrystallisation gave di-*p*-tolyl disulphoxide, m. p. (and mixed m. p. with an authentic specimen) 76—77°. From the liquid product (2 c.c.) a few drops were obtained on distillation at 12 mm., bath temp. 150° (αα'-diphenyldiethyl ether has b. p. 154—155°/15 mm.).

(iv) *In pyridine solution.* A solution of the sulphinate (5 g.; $n_D^{16°}$ 1·5756) in pyridine (20 g.), after standing at room temperature for 18 days, was diluted with benzene, washed with dilute hydrochloric acid and with water, and dried (calcium chloride). The benzene was removed by distillation (finally at 15 mm.); the residual oil was unchanged sulphinate, $n_D^{16°}$ 1·570.

(v) *In acetone solution at* 56°. A solution of the *dl*-sulphinate (9·8 g.; $n_D^{15°}$ 1·5761) in acetone (33 g.) was heated under reflux for 24 hours. After removal of the acetone by distillation (finally at 15 mm.), the unchanged ester was recovered, $n_D^{16°}$ 1·562.

(vi) *In nitrobenzene solution.* (a) At room temperature. A solution of the *dl*-ester (5 g.) in nitrobenzene (20 g.), after standing at room temperature for 25 days, was heated at 90°/12 mm. until the solvent was removed. The solid residue was washed with alcohol, leaving a crystalline solid (1·85 g., m. p. 121—128°) from which the *dl*-sulphone (1·5 g.; m. p. and mixed m. p. 134°) was obtained by recrystallisation as described above.

(b) At 80°. A solution of the *dl*-sulphinate (5 g.) in nitrobenzene (20 g.) darkened when heated on the steam-bath for 2·5 hours. The nitrobenzene was removed at 130°/65 mm.; from the dark viscous residue the sulphone (0·4 g., m. p. and mixed m. p. 132—134°) was obtained by recrystallisation from aqueous ethyl alcohol.

(vii) *In acetonitrile solution*. (a) At room temperature. A solution of the sulphinate (5 g.; $n_D^{17°}$ 1·5736) in acetonitrile (15 g.), after standing at room temperature for 22 days, was diluted with ether–benzene, washed with sodium bicarbonate solution and water, and dried, and the solvents removed by distillation (finally at 15 mm.). The residue of unchanged ester had $n_D^{18°}$ 1·568 : it remained liquid after standing for 24 hours at − 2°, and after inoculation with sulphone and sulphoxide.

(b) At 80°. A solution of the sulphinate (5 g.) in acetonitrile (20 g.) was heated on the steam-bath for 20 hours, and the solvent removed by distillation at 30 mm. The residual oil after two days deposited crystals of di-*p*-tolyl disulphoxide (0·55 g.), m. p. 80°, which after recrystallisation from alcohol had m. p. and mixed m. p. 79°.

(viii) *In formic acid solution*. (a) At room temperature. A solution of the sulphinate (10 g.) in anhydrous formic acid (40 g.), after standing at room temperature for 22 days, was diluted with ether–benzene (1 : 1) and washed with aqueous sodium bicarbonate (no precipitate was formed on acidifying the wash-liquors). The solvents were removed by distillation; the solid residue (7·2 g., m. p. 129—132°), recrystallised from aqueous alcohol, gave the sulphone (6·1 g), m. p. and mixed m. p. 134°. The wash-liquors yielded *dl*-phenylmethylcarbinyl formate, b. p. 94—95°/20 mm., $n_D^{18°}$ 1·5054 (0·7 c.c. approx.).

(b) At 80°. A solution of the sulphinate (7·4 g.) in formic acid (21 g.) was heated on the steam-bath for 2·5 hours, then poured into water and extracted with ether–benzene. The extract was washed with sodium carbonate solution, dried (calcium chloride), and concentrated. The crystalline residue (4·0 g.), recrystallised from aqueous alcohol, gave the sulphone (3·5 g.), m. p. and mixed m. p. 134°. Distillation of a small amount of oil separated from the solid product gave a few drops, b. p. 90°/20 mm. (phenylmethylcarbinyl formate has b. p. 87°/13 mm.).

(ix) *In formic acid solution in the presence of sodium formate*. A solution of the sulphinate (15 g., 1 mol.) and anhydrous sodium formate (10 g., 2·5 mols.) in anhydrous formic acid (78 g., 30 mols.), after standing at room temperature for 23 days, was diluted with ether–benzene (1 : 1), washed with aqueous sodium bicarbonate, dried (sodium sulphate), and the solvents removed. The residue was separated into a crystalline and a liquid fraction. The former (1·6 g., m. p. 133°), recrystallised from aqueous alcohol, gave the sulphone (1·4 g.), m. p. and mixed m. p. 134—135° ; and the latter on distillation gave 6·2 c.c. of material, b. p. 90—91°/16 mm., $n_D^{19°}$ 1·5048, from which on redistillation, dl-*phenylmethylcarbinyl formate*, b. p. 88—88·5°/16 mm., $n_D^{18°}$ 1·5056, $d_4^{13°}$ 1·058, was obtained (Found : C, 72·1; H, 6·7. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%).

Acidification of the sodium bicarbonate wash-liquor precipitated *p*-toluenesulphinic acid (1·1 g.), m. p. 86—87° (Found : equiv., by titration with N-aqueous sodium hydroxide, 158. Calc. for $C_7H_7 \cdot SO_2H$ : equiv., 156). Recrystallised from hot water, the acid had m. p. 87—88°, alone or mixed with an authentic specimen.

(x) *In formic acid solution in the presence of sodium* p-*toluenesulphinate*. A solution of the *dl*-ester (7·0 g., 1 mol.) and sodium *p*-toluenesulphinate (dried at 110° ; 6·0 g., 1·25 mols.) in anhydrous formic acid (36 g.), after standing at laboratory temperature for 18 days, was diluted with ethyl ether, washed with water and with aqueous sodium carbonate, and dried. After removal of the ether and being washed with light petroleum, the solid residue (1·8 g., m. p. 100—105°) was recrystallised from ether–light petroleum. Two crystal forms which were deposited were separated mechanically and recrystallised separately, giving (*a*) di-*p*-tolyl disulphoxide, which after two crystallisations from ether–light petroleum had m. p. and mixed m. p. 77° (yield, 0·3 g.) ; (*b*) impure *p*-tolyl-α-phenylethylsulphone, which after two recrystallisations from aqueous alcohol had m. p. 130° (yield, 0·35 g.). From the light petroleum wash-liquor above, *dl*-phenylmethylcarbinyl formate was obtained, which after redistillation had b. p. 94·5°/17 mm., $n_D^{21°}$ 1·5075 (yield 2·5 g.). From the sodium carbonate wash-liquor above, *p*-toluenesulphinic acid (1·8 g.) was obtained on acidification (m. p. 87°).

*Thermal Stability of* p-*Tolyl-α-phenylethylsulphone*.—The sulphone was not discoloured by heating on the steam-bath for 24 hours and its m. p. (133—135°) remained unchanged. The sulphone (0·5 g.) in nitrobenzene (5 c.c.) solution was heated on the steam-bath for 24 hours without discoloration and recovered with unchanged m. p. after removal of the solvent.

*Transformation of* (−) *and* (−) + dl-*Phenylmethylcarbinyl* dl-p-*Toluenesulphinates*.—(i) *Homogeneous*. The (−)ester (2·05 g.), after standing for 27 days at room temperature, was converted into a solid mass, which was washed with ethyl alcohol and with light petroleum. The residue (0·75 g., m. p. 113—117°), recrystallised from aqueous alcohol, gave *dl*-*p*-tolyl-α-phenylethylsulphone (0·45 g.), m. p. 129—131°, optically inactive in chloroform solution (*l*, 2 ; *c*, 2·07) ; recrystallised from aqueous alcohol, the sulphone had m. p. 132—133°, mixed m. p. with authentic sulphone 134°.

(ii) *In formic acid solution.* A solution of the (−)ester (4 g.) in anhydrous formic acid (16 g.), after standing at room temperature for 9 days, was diluted with ether–benzene (1 : 1), washed with aqueous sodium bicarbonate, and dried (sodium sulphate), and the solvents removed. The residue was washed with light petroleum. From the crystalline product (3·0 g., m. p. 127—130°), recrystallised from aqueous alcohol, dl-p-tolyl-α-phenylethylsulphone (2·4 g.) was obtained, m. p. and mixed m. p. 134°, optically inactive in chloroform solution (l, 2·0; c, 5·04). From the light petroleum wash-liquor, one drop, b. p. 83°/12 mm. (phenylmethylcarbinyl formate), was obtained.

(iii) *In formic acid solution in the presence of sodium formate.* A solution of the (−)sulphinate (10·4 g., 1 mol.) and anhydrous sodium formate (6·7 g., 2·5 mols.) in anhydrous formic acid (50 g., 27 mols.), after standing for 19 days at room temperature, was diluted, washed, and concentrated as in (ii) above. From the residual oil, on fractional distillation, a fraction (4·3 c.c.) was obtained with b. p. 88·5°/13 mm., $n_D^{16°}$ 1·5066, $\alpha_{5893}^{17°}$ − 7·92°, $\alpha_{5461}^{17°}$ − 9·53° (l, 0·236). Redistilled, this fraction was identified as (−) + dl-phenylmethylcarbinyl formate, b. p. 91°/15 mm.; $n_D^{17°}$ 1·5056, $\alpha_{5893}^{17°}$ − 8·03; $\alpha_{5461}^{17°}$ − 9·52 (l, 0·236). The solid undistillable residue was washed with aqueous alcohol, and the crystalline product (1·4 g., m. p. 110—115°) was twice recrystallised from aqueous alcohol, yielding (−) + dl-p-tolyl-α-phenylethylsulphone, m. p. 127—128°, $[\alpha]_{5461}^{18°}$ − 65·6° in chloroform solution (l, 2·0; c, 2·65). Acidification of the sodium bicarbonate wash-liquor from this preparation precipitated p-toluenesulphinic acid (0·7 g.), m. p. and mixed m. p. 86° (Found : equiv., 159).

(iv) *In formic acid solution in the presence of sodium p-toluenesulphinate.* A solution of 7·0 g. (1 mol.) of (−) + dl-phenylmethylcarbinyl p-toluenesulphinate {$[\alpha]_{5461}^{21°}$ − 70·3° in ethyl alcohol (l, 1; c, 5·1); prepared from (−) + dl-carbinol having $\alpha_{5461}^{19°}$ − 19·66° (l, 0·5)} and 6 g. (1·25 mols.) of sodium p-toluenesulphinate (dried to constant weight at 110°) in anhydrous formic acid (36 g., 27 mols.) was kept at room temperature for 18 days. Table IV records the variation in rotatory power of this solution. At the end of 18 days it was diluted with ethyl ether, washed with aqueous sodium carbonate and with water, and dried (calcium chloride). The solid residue left after removal of the solvent was extracted with light petroleum; the crystalline residue {2·2 g., m. p. 79—105°, $[\alpha]_{5461}^{17°}$ − 5·4° in chloroform (l, 2; c, 5·01)}, after three recrystallations from aqueous ethyl alcohol, had m. p. 100—110°, and was optically inactive in chloroform solution. After two further recrystallisations dl-p-tolyl-α-phenylethylsulphone (0·15 g.) was obtained, m. p. and mixed m. p. 135°. From the light petroleum extract, (−) + dl-phenylmethylcarbinyl formate was obtained, b. p. 90·5—91°/14 mm., $n_D^{22°}$ 1·5050, $\alpha_{5461}^{21°}$ − 0·47° (l, 0·236). Acidification of the sodium carbonate wash-liquor precipitated p-toluenesulphinic acid (2·4 g.), m. p. 86°.

(−)*Phenylmethylcarbinyl Formate.*—A solution of (−)phenylmethylcarbinol [4 g., $\alpha_{5461}$ − 11·88° (l, 0·25)] in mixed formic–acetic anhydride (7 g.), after heating on the steam-bath for 90 minutes, was diluted with ether, and the solution washed with sodium bicarbonate, with water, and dried over sodium sulphate. After removal of the ether, (−)phenylmethylcarbinyl formate, b. p. 88·5—89·5°/14 mm., was obtained. After redistillation, it had b. p. 87—87·5°/14 mm., $n_D^{18°}$ 1·5048, $d_4^{18°}$ 1·057, $\alpha_{6438}^{20°}$ − 33·04°, $\alpha_{5893}^{20°}$ − 40·57°, $\alpha_{5780}^{20°}$ − 42·66°, $\alpha_{5461}^{20°}$ − 48·90°, $\alpha_{4358}^{20°}$ − 88·6° (l, 0·236), whence $[\alpha]_{6438}^{20°}$ − 132·8°, $[\alpha]_{5893}^{20°}$ − 163·0°, $[\alpha]_{5780}^{20°}$ − 171·6, $[\alpha]_{5461}^{20°}$ − 196·5°, $[\alpha]_{4358}^{20°}$ − 356·0°, yield, 4·2 g.

After standing for 11 months in a closed vessel, this formate, which then had $[\alpha]_{5461}^{20°}$ − 185·0° (l, 0·236), was saponified by heating on the steam-bath with potassium hydroxide (1·25 mols.) in ethyl alcohol for 30 minutes. The solution was extracted with ether, and the extract washed with aqueous potassium carbonate and dried (potassium carbonate), yielding (−)phenylmethylcarbinol, b. p. 95·5—96°/15 mm., $n_D^{20°}$ 1·5271, $\alpha_{5461}^{20°}$ − 10·90°, (l, 0·236).

*Mutarotation of* (−) *and* (−)+dl-*Phenylmethylcarbinyl* dl-p-*Toluenesulphinate in Solution.*—(i) *In formic acid.* The (−)+dl-ester of $[\alpha]_{5461}^{20°}$ − 84·3° (l, 2·0; c, 5·13 in ethyl alcohol), $n_D^{19°}$ 1·5703, was used. The observations of rotatory power of a solution of this ester (1·5 g.) in formic acid (5·8 g.) are given in Table III. After the last observation had been made, the solution was poured into water and extracted with ether. The extract was dried, and the ether removed. From the residue, phenylmethylcarbinyl formate (0·2 c.c.) was obtained, b. p. 86°/12 mm., $n_D^{15°}$ 1·5058, leaving (−)+dl-phenylmethylcarbinyl p-toluenesulphinate, $n_D^{16°}$ 1·5672, $[\alpha]_{5461}^{17°}$ − 61·7° in ethyl alcohol (l, 2·0; c, 1·20).

(ii) *In acetonitrile.* (−)+dl-Ester of $[\alpha]_{5461}^{20°}$ − 70·5° in ethyl alcohol (l, 2·0; c, 5·02), $n_D^{20·5°}$ 1·5740, was used. The observations of rotatory power of a solution of this ester (8·7 g.) in acetonitrile (30·2 g.) are given in Table III. 23·5 Hours after the solution was made, a portion was withdrawn, and the solvent removed by distillation, finally at 0·1 mm. The residual ester

## TABLE IV.

*Mutarotation of solutions of* (−) *and* (−) + dl-*phenylmethylcarbinyl* p-*toluenesulphinate in nitrobenzene, and in formic acid containing sodium formate and sodium* p-*toluenesulphinate.*

[$l$ = 2·0 except where otherwise indicated.  $t$ = Time (hours) after dissolution.]

| (−)Ester in nitrobenzene. | | | | (−)Ester (3·09 g.) in H CO$_2$H (16·4 g.) with H·CO$_2$Na (2·0 g.). | | (−)Ester (1·96 g.) in H·CO$_2$H (15·2 g.) and H·CO$_2$Na (1·83 g.). | | (−) + dl-Ester (7·0 g.) in H·CO$_2$H (36 g.) and sodium p-toluenesulphinate (6·0 g.). | |
| Solution kept at 31°. (c, 4·80.) | | (c, 17·3.) | | | | | | | |
| $t$. | $\alpha_{5893}^{17°}$. | $t$. | $\alpha_{5893}^{17°}$.* | $t$. | $\alpha_{5461}^{17°}$. | $t$. | $\alpha_{5461}^{19°}$. | $t$. | $\alpha_{5461}^{18°}$. |
|---|---|---|---|---|---|---|---|---|---|
| 0·5 | −4·90° | 1 | −2·20° | 0·5 | −16·79° | 0·1 | −12·16° | 45 | −8·70° |
| 20 | −4·59 | 18 | −2·33 | 2·5 | −16·57 | 2·0 | −11·84 | 69 | −7·44 |
| 43 | −0·63 | 66 | −2·34 | 3·75 | −16·46 | 19·5 | −10·76 | 95 | −6·31 |
| 47 | −0·46 | 74 | −2·31 | | | 67·5 | − 9·45 | 118 | −5·60 |
| 66·5 | −0·18 | 90 | −2·27 | | | 75 | − 9·26 | 165 | −4·46 |
| 71·5 | −0·15 | 120 | −2·20 | | | 92 | − 8·93 | 218 | −3·79 |
| | | 140 | −2·15 | | | 122 | − 8·46 | 310 | −2·82 |
| | | 165 | −1·93 | | | 143 | − 8·19 | 381 | −2·47 |
| | | 186 | −1·65 | | | 167 | − 7·90 | 434 | −2·21 |
| | | 234 | −1·31 | | | 188 | − 7·58 | | |
| | | 288 | −0·82 | | | 236 | − 7·32 | | |
| | | | | | | 289 | − 7·00 | | |

\* $l$ = 0·25.

had $n_D^{17·5°}$ 1·5752, and $[\alpha]_{5461}^{18°}$ − 70·3° in ethyl alcohol ($l$, 2·0; $c$, 4·88). The ester recovered in the same way after 256 hours had $n_D^{17·5°}$ 1·5740, $[\alpha]_{5461}^{18°}$ − 43·6° in ethyl alcohol ($l$, 2·0; $c$, 4·88); it remained liquid when kept for 24 hours at − 2°.

(iii) *In nitrobenzene.* The observations are given in Table IV. Darkening of the solution prevented observation after 288 hours. The specific rotatory power of the ester in nitrobenzene solution does not vary with concentration sufficiently to affect these results: $[\alpha]_{5893}^{17°}$ − 51·1° ($l$, 2·0; $c$, 4·80), $[\alpha]_{5893}^{17°}$ − 50·5° ($l$, 2·0; $c$, 1·02).

(iv) *In formic acid solution containing sodium formate.* The changes in rotatory power of a solution of the (−)ester in formic acid in presence of 2·5 and of 3·6 molar proportions of sodium formate are given respectively in the third and fourth sections of Table IV. The first solution after 3·75 hours was poured into water and extracted with ether, the extract washed with aqueous sodium bicarbonate, dried, (sodium sulphate), and the ether removed. The residual sulphinate gave no distillate at 130°/13 mm. It had $n_D^{19°}$ 1·5703, and $[\alpha]_{5461}^{20°}$ − 84·3° in ethyl alcohol ($l$, 2·0; $c$, 5·130).

(v) *In formic acid containing sodium* p-*toluenesulphinate.* Table IV gives the change in rotatory power of the solution, the preparation of which is described above.

(vi) *In ether containing potassium carbonate.* The (−) + dl-ester {1·76 g., $[\alpha]_{5461}^{20°}$ − 70·5° in ethyl alcohol ($l$, 2·0; $c$, 5·02); $n_D^{20·5°}$ 1·5740} in solution in ether (9·8 g.) with potassium carbonate (0·7 g.) was observed polarimetrically ($l$, 2·0). The original rotation, $\alpha_{5461}^{17°}$ − 21·52°, was maintained, the value after 20 days being $\alpha_{5461}^{18°}$ − 21·26°. Ether was then removed from the filtered solution, finally at 0·1 mm., yielding (−) + dl-ester having $n_D^{19°}$ 1·5753, $[\alpha]_{5461}^{19°}$ − 70·8° in ethyl alcohol ($l$, 2·0; $c$, 4·775).

The formic acid used in these experiments was prepared from the 98—100% acid by repeated solidification and partial liquefaction, the fluid being rejected.