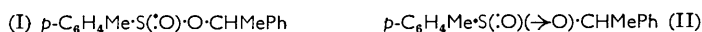


719. *The Rearrangement of Sulphinic Esters.*

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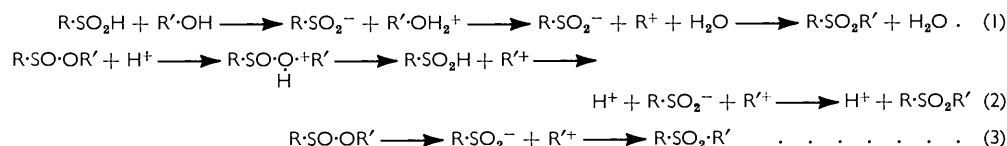
Further observations support the view that the isomerisation of certain sulphinic esters to the corresponding sulphones is mainly an intermolecular process involving ionisation of the ester.

ARCUS, BALFE, and KENYON¹ studied the conversion of α -methylbenzyl toluene-*p*-sulphinic acid (I) into α -methylbenzyl *p*-tolyl sulphone (II) and concluded that the process was in part intramolecular, but mainly dependent on ionisation of the ester. Later, COPE, MORRISON, and FIELD² effected the rearrangement of allyl benzenesulphinic acid and related compounds, without reaching a final decision on the mechanism. The results now reported emphasise the intermolecular and no doubt ionic character of the change.



Sulphones were prepared from the related sulphinic acid and alcohol ($\text{R}\cdot\text{SO}_2\text{H} + \text{HOR}' \longrightarrow \text{R}\cdot\text{SO}_2\text{R}'$) in three ways: (1) by heating the acid and alcohol in acetic acid-hydrochloric acid,³ (2) by heating the related sulphinic ester in the same medium; and (3) by thermal rearrangement of the ester alone or in an inert solvent. None of these processes is of general application and in each individual case they give substantially the same result (Table 1).

Experiments with diphenylmethyl compounds support the formulations:



The synthesis of sulphone from alcohol and sulphinic acid proceeds easily in acetic acid, nitromethane, acetonitrile, benzene, or toluene; but rearrangement of the ester takes place only in the first two solvents. Rearrangement, however, is observed in the remaining solvents in presence of a little toluene-*p*-sulphinic acid; it does not proceed in acetonitrile in presence of sodium toluene-*p*-sulphinic acid. It would appear that rearrangement is favoured by ionising solvents (including the homogeneous ester itself) and availability of protons. The sulphone is also produced from diphenylmethyl methyl ether and toluene-*p*-sulphinic acid in nitromethane or toluene, but not from diphenylmethanol and methyl toluene-*p*-sulphinic acid.

The intermolecular character of the reaction was further shown by "mixing experiments." When diphenylmethyl toluene-*p*-sulphinic acid was heated in acetic acid containing

¹ Arcus, Balfe, and Kenyon, *J.*, 1938, 485.

² Cope, Morrison, and Field, *J. Amer. Chem. Soc.*, 1950, **72**, 59.

³ Hinsberg, *Ber.*, 1917, **50**, 468.

TABLE I.

R	R'	Yield (%) of sulphone by method		
		(1)	(2)	(3)
<i>p</i> -Tolyl	Methyl	0	0	0
"	Phenyl	0	0	0
"	Benzyl	0	0	0
"	<i>o</i> -Nitrobenzyl	0	0	0
"	α -Methylbenzyl	20	20	20-30
"	$\alpha\alpha$ -Dimethylbenzyl	90	86	87
"	Diphenylmethyl	90	93	100
"	<i>p</i> -Chlorodiphenylmethyl	80	89	95
"	Phenyl- <i>o</i> -tolylmethyl	90	90	95
"	Phenyl- <i>p</i> -tolylmethyl	80	82	80
<i>p</i> -Chlorophenyl	Diphenylmethyl	90	93	100

p-chlorobenzenesulphonic acid, some *p*-chlorophenyl diphenylmethyl sulphone was produced; the same ester and *p*-chlorodiphenylmethanol gave a mixture of sulphones which contained chlorine but from which no *p*-chlorodiphenylmethyl *p*-tolyl sulphone could be isolated. Clear evidence was obtained of the formation of dichlorinated and chlorine-free sulphones when a mixture of *p*-chlorodiphenylmethyl toluene-*p*-sulphinic acid and phenyl-*p*-tolylmethyl *p*-chlorobenzenesulphinate was heated without a solvent.

The following inequalities in the rates of rearrangement of homogeneous esters were observed qualitatively; $\alpha\alpha$ -dimethylbenzyl toluene-*p*-sulphinic acid > α -methylbenzyl toluene-*p*-sulphinic acid; phenyl-*o*-tolylmethyl toluene-*p*-sulphinic acid > diphenylmethyl toluene-*p*-sulphinic acid; diphenylmethyl *p*-chlorobenzenesulphinate > diphenylmethyl toluene-*p*-sulphinic acid. A rate-determining ionisation is consistent with these observations.

EXPERIMENTAL

All identifications of known solids were supported by mixed melting points.

Alcohols.—*p*-Chlorodiphenylmethanol⁴ and phenyl-*o*-tolylmethanol⁵ were prepared by published methods and phenyl-*p*-tolylmethanol⁶ (12.5 g.; m. p. 58°) from benzaldehyde (14.7 g.) and the Grignard reagent from *p*-bromotoluene (25 g.) and magnesium (3.35 g.).

Toluene-p-sulphinic Esters.—Toluene-*p*-sulphinyl chloride⁷ was freed from solvents and thionyl chloride at 0.05 mm. at room temperature and used at once without distillation. The chloride (1.03 mol.), in a little dry ether, was added slowly to the alcohol (1 mol.) in pyridine (1.15 mol.) at 0° with shaking and addition of more ether as required to facilitate mixing. After additions of ether and 2*N*-hydrochloric acid the separated ether layer was washed thoroughly with dilute hydrochloric acid, sodium hydrogen carbonate solution, and water, and dried (12 hr.; Na₂SO₄). Removal of the ether *in vacuo* left the ester in good yield; see Table 2.

TABLE 2. *Toluene-p-sulphinic esters.*

Ester	Description	M. p.	Formula	Found, S %	Reqd., S %
Methyl ⁸	Oil	(b. p. 129-130°/ 14 mm.)	C ₈ H ₁₀ O ₂ S	—	—
Phenyl	Unstable needles	51-52°	C ₁₃ H ₁₂ O ₂ S	—	—
Benzyl	Needles	22-24	C ₁₄ H ₁₄ O ₂ S	13.1	13.0
<i>o</i> -Nitrobenzyl	Needles	58-59	C ₁₄ H ₁₃ O ₄ NS	10.8	11.0
$\alpha\alpha$ -Dimethylbenzyl	Oil	—	C ₁₆ H ₁₈ O ₂ S	11.5	11.7
Diphenylmethyl	Needles from EtOH	84	C ₂₀ H ₁₆ O ₂ S	9.9	9.9
Phenyl- <i>o</i> -tolylmethyl	Needles from EtOH	68-70	C ₂₁ H ₂₀ O ₂ S	9.4	9.5
<i>p</i> -Chlorodiphenylmethyl	Oil	—	C ₂₀ H ₁₇ O ₂ SCl	9.4	9.0
9-Fluorenyl	Prisms from Et ₂ O	107-108	C ₂₀ H ₁₆ O ₂ S	9.8	10.0

p-Chlorobenzenesulphinyl chloride was prepared by adding the sulphonic acid⁹ (3 g.) to thionyl chloride (1.35 mol.) in ether (2 ml.). After the vigorous reaction, solvent and excess of

⁴ Tschitschibabin and Schesler, *Chem. Zentr.*, 1926, I, 919.

⁵ Tschitschibabin, *Chem. Zentr.*, 1910, I, 30.

⁶ Cf. Marshall *et al.*, *J.*, 1915, **107**, 516, 894.

⁷ Phillips, *J.*, 1925, 2569.

⁸ Cf. Arndt and Scholtz, *Annalen*, 1934, **510**, 62.

⁹ Knoevenagel and Kenner, *Ber.*, 1908, **41**, 3320.

thionyl chloride were removed at 0.2 mm. pressure, and the residual oil was kept for 6 hr. over potassium hydroxide in a vacuum desiccator (Found: Cl, 36.9. $C_6H_4OSCl_2$ requires Cl, 36.4%). It yielded in the usual way *diphenylmethyl p-chlorobenzenesulphinic acid*, needles, m. p. 83–84° from ether–ligroin (Found: S, 9.2. $C_{19}H_{15}O_2S$ requires S, 9.3%); and *phenyl-p-tolylmethyl p-chlorobenzenesulphinic acid*, a slightly yellow oil (Found: S, 8.6. $C_{20}H_{17}O_2S$ requires S, 9.0%).

Methyl, phenyl, benzyl, and *o*-nitrobenzyl *p*-toluenesulphinate did not give sulphone at temperatures below those leading to gross decomposition; the fluorenyl ester changed above 120° into an amorphous solid from which no homogeneous substance was isolated. Sulphones were formed from the α -methylbenzyl and $\alpha\alpha$ -dimethylbenzyl esters slowly in the cold, more rapidly when heated, purer specimens being more stable. Rearrangement of the diarylmethyl esters took place, more reproducibly, above 100°. In a typical experiment α -methylbenzyl toluene-*p*-sulphinate (1.7 g.), acetic acid (4 ml.), and concentrated hydrochloric acid (0.15 ml.) were boiled for 1 hr. The product was dissolved in benzene and washed with alkali; the neutral material recovered by evaporation gave α -methylbenzyl *p*-tolyl sulphone (0.32 g.) from methanol–benzene. The same sulphone was synthesised by boiling α -methylbenzyl alcohol (1 g.), toluene-*p*-sulphinic acid (0.7 g.), acetic acid (4 ml.), and concentrated hydrochloric acid (0.15 ml.) for 1 hr. and isolating the product in the same way.

Diphenylmethyl *p*-tolyl sulphone was also prepared by heating diphenylchloromethane (5 g.) and sodium toluene-*p*-sulphinate (5 g.) in alcohol (40 ml.) under reflux for 3 hr.; the sulphone crystallised on cooling.

"*Mixing Experiments.*"—(1) Diphenylmethyl toluene-*p*-sulphinate (1 g.) and *p*-chlorobenzenesulphinic acid (0.1 g.) in acetic acid (2.5 ml.) were boiled for 15 min. The first crop of needles (0.85 g.), m. p. 186°, containing a trace of chlorine, was diphenylmethyl *p*-tolyl sulphone: the second crop gave, after four crystallisations from ethanol–acetone, *p*-chlorophenyl diphenylmethyl sulphone, m. p. 176–179° (Found: C, 67.0; H, 4.8; S, 8.8; Cl, 9.9. Calc. for $C_{19}H_{15}O_2S$: C, 66.5; H, 4.4; S, 9.3; Cl, 10.4%).

(2) Diphenylmethyl toluene-*p*-sulphinate (1 g.), *p*-chlorodiphenylmethanol (0.1 g.), and acetic acid (2.5 ml.) were boiled for 15 min.; successive crops of crystals were substantially diphenylmethyl *p*-tolyl sulphone containing a little chlorine; no *p*-chlorodiphenylmethyl *p*-tolyl sulphone could be isolated.

TABLE 3. Sulphones, $R \cdot SO_2 \cdot R'$.

R	R'	Crystalln. solvent	M. p.	Formula	Found, S (%)	Reqd., S (%)
$\alpha\alpha$ -Dimethylbenzyl	<i>p</i> -Tolyl	EtOH	144–145°	$C_{16}H_{18}O_2S$	11.5	11.7
Diphenylmethyl	<i>p</i> -Tolyl	EtOH	188–189	$C_{20}H_{18}O_2S$	9.7	9.9
Phenyl- <i>o</i> -tolylmethyl	<i>p</i> -Tolyl	EtOH	127–128	$C_{21}H_{20}O_2S$	9.3	9.5
Phenyl- <i>p</i> -tolylmethyl	<i>p</i> -Tolyl	MeOH–COMe ₂	157	$C_{21}H_{20}O_2S^a$	9.5	9.5
<i>p</i> -Chlorodiphenylmethyl	<i>p</i> -Tolyl	MeOH–COMe ₂	142	$C_{20}H_{17}O_2S$	9.3	9.0
Diphenylmethyl	<i>p</i> -Chlorophenyl	MeOH–COMe ₂	177	$C_{19}H_{15}O_2S$	9.7	9.3
Phenyl- <i>p</i> -tolylmethyl	<i>p</i> -Chlorophenyl	MeOH–COMe ₂	173	$C_{20}H_{17}O_2S$	9.2	9.0
<i>p</i> -Chlorodiphenylmethyl	<i>p</i> -Chlorophenyl	MeOH	126	$C_{19}H_{14}O_2S$	9.0	8.5

Additional analyses: ^a Found: C, 74.8; H, 5.8. Required: C, 75.0; H, 6.0%. ^b Found: C, 67.5; H, 4.75; Cl, 9.9. Required: C, 67.4; H, 4.8; Cl, 10.0%. ^c Found: C, 66.1; H, 4.3; Cl, 10.8. Required: C, 66.5; H, 4.4; Cl, 10.4%. ^d Found: C, 67.3; H, 4.8; Cl, 10.4. Required: C, 67.4; H, 4.8; Cl, 10.0%. ^e Found: C, 60.4; H, 3.5. Required: C, 60.5; H, 3.7%.

(3) Phenyl-*p*-tolylmethyl *p*-chlorobenzenesulphinic acid (0.6 g.) and *p*-chlorodiphenylmethyl toluene-*p*-sulphinate (0.6 g.) were heated for 12 min. at 160°. The pale green melt crystallised when rubbed with ether, and was recrystallised from acetone–methanol. The second crop (A) had m. p. 142–143° (Found: C, 71.5; H, 5.6; S, 9.2; Cl, 2.7%). The mother liquors were evaporated and the residue crystallised successively from acetone–methanol, ligroin, and methanol, the more soluble fraction being retained in each case; the final mixture (B) had m. p. 110–120° (Found: C, 64.5; H, 4.4; S, 8.8; Cl, 13.2%). The carbon : sulphur ratios show that no significant quantities of disulphoxides were present; the chlorine values demonstrate the presence of chlorine-free sulphone in (A) and dichlorinated sulphone in (B).

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