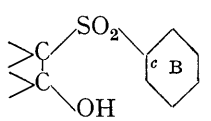
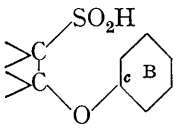
292. *The Rearrangement of o-Hydroxysulphones. Part V.*

By Frederick Galbraith and Samuel Smiles.

Previous experiments suggested that a positive character of the carbon atom *c* in B (I) is one of the more important conditions determining the rearrangement of this type of sulphone (I ⟶ II), and it has been shown that, if the hydroxyl group is attached to an aromatic nucleus, rearrangement succeeds when B is *o*- or *p*-nitrophenyl, 2-hydroxy-1-naphthyl, or *p*-methanesulphonylphenyl. The study of this condition has now been continued. In one series of experiments the behaviour of sulphones in which the positive character of *c* is established by the presence of carbonyl groups in B has been examined. Oxidation of the sulphides obtained from the reaction of anthraquinone-1-bromothiol with *p*-cresol, 2-naphthol or its 6-bromo-derivative yielded the *sulphones* (III) and (V). In presence of alkali, these undergo rearrangement, but the process is not so easily accomplished as with the *o*- or *p*-nitrophenylsulphones [*e.g.*, (III), where $C_{14}H_7O_2$ is $C_6H_4{\cdot}NO_2$], and in accordance with previous observations (Kent and Smiles, J., 1934, 422) the rearrangement of (III) requires more intense conditions than that of (V). The sulphinic *acid* (VI) was characterised by conversion into a disulphide, and its structure was further determined by hydrolysis of the corresponding sulphonic acid, yielding 2-naphthyl-1-


(I.)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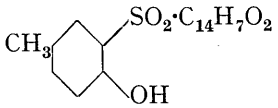
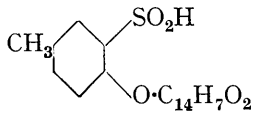

(III.)

anthraquinonyl oxide, identical with synthetic material. The ease with which the sulphone (V) suffered rearrangement led to the examination of the *sulphone* (VII); this was quickly converted by warm *N*-aqueous alkali hydroxide into the *sulphinic acid* (VI), which was characterised by its *methylsulphone* and conversion into the *disulphide*. Moreover, the *sulphoxide* corresponding to (VII) under similar conditions yielded a mixture of the sulphinic acid (VIII) and the related *disulphide*, the behaviour being similar to that observed with the 2-nitrophenyl derivative (Kent and Smiles, *loc. cit.*).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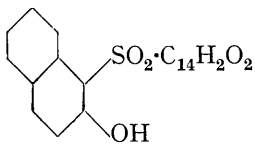
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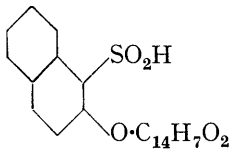
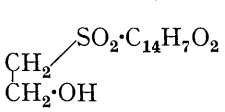

(VI.)

The behaviour of these sulphones thus accords with the explanation previously given to this type of rearrangement, and also with the character of α-substituents in the anthraquinone nucleus. In this connection it is noteworthy that attempts to effect, under usual conditions, the rearrangement of (IX) or the corresponding *sulphoxide* failed, apparently owing to the weak influence of the carboxylic ion on the *o*-carbon atom (compare Hurtley, J., 1929, 1870). The same reason may be given to account for the stability of the 2-amino-sulphone (X) in presence of warm aqueous alkali hydroxide (compare Evans and Smiles, this vol., p. 181).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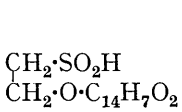
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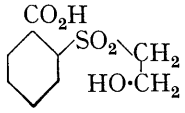
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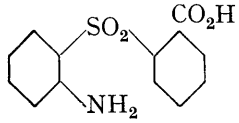

(X.)

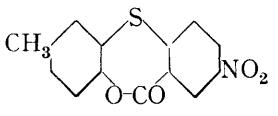
With the object of gaining further information concerning the influence exerted by the presence of this type of substituent in the nucleus B (I), further experiments were made by the colorimetric method developed by Kent and Smiles (*loc. cit.*) in examining the

influence of changing character of the *o*-hydroxyl. All the sulphones examined are derivatives of *p*-cresol [compare (IV)], and were obtained from this by known methods; their behaviour is summarised in the table, the position of the substituents in B with respect to *c* being indicated in the column headed B. The rearrangement of the sulphones 1, 5, 6, and 8 has already been qualitatively studied, and the products arising therefrom examined (J., 1931, 3264; 1932, 1488; 1934, 422); that of the sulphones 2, 3, 4, and 7 is now described for the first time. In cases 2, 3, and 4, the diphenyl ether 2-sulphinic acids [compare (IV)] have been characterised in the usual way and the sulphinic group has been eliminated by treatment with mercuric chloride (this vol., p. 181), the resulting derivatives of diphenyl ether being identified by comparison with synthetic materials. The chemistry of the derivatives encountered presented no unusual features, but it is noteworthy that the sulphide corresponding to No. 7 was converted by hot acetic anhydride into the *lactone* (XI).

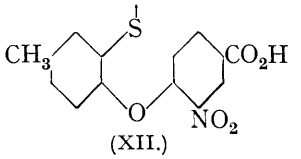
The data quoted in the table represent the approximate times (in minutes) required for completing the rearrangement of equivalent amounts of the various sulphones; they were obtained in methyl-alcoholic or aqueous solutions at the stated temperatures, the molecular concentrations of the reagents and their relative molecular proportions being the same as those previously adopted (J., 1934, 422).

		1·25 Mols. MeONa in MeOH.		1·25 Mols. NaOH in water.	
	B.	0°.	50°.	50°.	100°.
1.	2 : 4-Dinitro-	6—8	very rapid	—	—
2.	2-Nitro-4-benzoyl-	40	<0·5	—	—
3.	4-Nitro-2-benzoyl-	—	12	—	—
4.	2-Nitro-4-carboxy- (Na salt)	—	50	70	2
5.	4-Chloro-2-nitro-	—	70	(125)	3
6.	2-Nitro-	—	255 (270)	310 (315)	7 (7)
7.	4-Nitro-2-carboxy- (Na salt)	—	450	550	15
8.	4-Nitro-	—	very slow	very slow	70

The figures given in parentheses are those obtained formerly. In spite of the errors inherent in the method, the behaviour of these sulphones is sufficiently divergent to justify their arrangement in order of activity. Consideration of the general character of the rearrangement (J., 1934, 422) led to the conclusion that this should be favoured by an increase in the positive character of the carbon atom in B from which sulphonyl is displaced; comparison of the activities of sulphones 1, 5, 6, and 8 fully confirms this conclusion. This relationship being assumed to be established, the behaviour of the other sulphones may be used as a source of information concerning the carboxylic ion and the benzoyl group. Comparison of 6 with 2 and 4, and of 8 with 3 and 7, clearly shows the positive effect exerted by both these substituents at the *o*- and *p*-carbon atoms; moreover, the positive character of the benzoyl group is evidently stronger than that of the carboxylic ion and weaker than that of the nitro-group.



(XI.)



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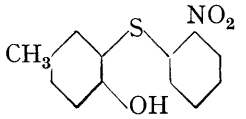

(XIII.)

In conclusion, attention is directed to the behaviour of the carboxy-disulphides encountered during these experiments. These substances were obtained by reduction of the sulphinic acids produced by rearrangement of the sulphones 4 and 7; they are rapidly converted by aqueous alkali hydroxide into the sulphides (*e.g.*, XIII) from which the sulphones were prepared. The process evidently consists of a preliminary hydrolysis of the disulphide system similar to that observed (J., 1921, 1792) in the case of *m*-dithiobenzoic acid, followed by rearrangement of the thiol then formed (XII ⟶ XIII). Further illustration of the *o*-thiol-oxide type of rearrangement (J., 1932, 1040) is thus afforded.

Experimental.

1-*Anthraquinonyl* 4-*hydroxy*-m-*tolyl sulphide* was obtained by heating (150°, 5—6 hrs.) anthraquinone-1-bromothiol with excess of *p*-cresol in chlorobenzene until liberation of hydrogen

bromide had ceased. The residue, after removal of *p*-cresol and chlorobenzene, was boiled with excess of dilute aqueous sodium hydroxide; the desired sulphide was liberated from the alkaline solution, and after purification from acetic acid and benzene, formed yellow needles, m. p. 228° (Found : C, 72·9; H, 4·0. $C_{21}H_{14}O_3S$ requires C, 72·8; H, 4·0%). This sulphide (5 g.) was converted into *1′-anthraquinonyl-4-hydroxy*-m-*tolylsulphone* (III) by oxidation with hydrogen peroxide (10 c.c., 30%) in acetic acid (50 c.c.) at 100°; from acetic acid this formed needles, m. p. 220° (Found : C, 67·0; H, 3·7; S, 8·5. $C_{21}H_{14}O_5S$ requires C, 66·7; H, 3·7; S, 8·5%). The sulphone was recovered unchanged after it had been boiled for 5 hrs. in 2*N*-aqueous alkali solution; its methyl ether, obtained by reaction with methyl iodide in alkaline solution, had m. p. 225°.

1-Anthraquinonyl 3-sulphino-p-*tolyl ether* (IV) was formed when the sulphone was heated (130°, 3 hrs.) with aqueous sodium hydroxide (2*N*, 2 mols.). After being liberated from the alkaline solution and purified by solution in aqueous sodium carbonate, it formed needles, m. p. 174°, from aqueous alcohol (Found : C, 66·5; H, 4·0. $C_{21}H_{14}O_5S$ requires C, 66·7; H, 3·7%).

1-Anthraquinonyl 2-acetoxy-1-naphthyl sulphide (compare V) was obtained from the hydroxy-sulphide described by Fries (*Ber.*, 1912, **45**, 2967). It formed yellow needles, m. p. 208°, from acetic acid (Found : C, 73·5; H, 4·2. $C_{26}H_{16}O_4S$ requires C, 73·6; H, 3·8%). Oxidation (4 hrs., 100°) of this (15 g.) with hydrogen peroxide (20 c.c., 30%) in acetic acid (100 c.c.) yielded the sulphone, which separated from the cooled mixture. *1′-Anthraquinonyl-2-acetoxy-1-naphthylsulphone* formed pale yellow needles, m. p. 264—265°, from acetic acid (Found : C, 68·4; H, 3·4; S, 7·0. $C_{26}H_{16}O_6S$ requires C, 68·4; H, 3·5; S, 7·0%). Hydrolysis of this with hot alcoholic sulphuric acid yielded *1′-anthraquinonyl-2-hydroxy-1-naphthylsulphone* (V), interlaced needles, m. p. 210°, from acetic acid (Found : C, 69·7; H, 3·4. $C_{24}H_{14}O_5S$ requires C, 69·6; H, 3·4%).

1-Anthraquinonyl 1-sulphino-2-naphthyl ether (VI) was formed when a solution of the sulphone (V) in 2*N*-aqueous sodium hydroxide was boiled (30 mins.). From benzene and light petroleum it formed pale yellow needles, m. p. 160° (decomp.) (Found : C, 69·8; H, 3·5; S, 7·4. $C_{24}H_{14}O_5S$ requires C, 69·6; H, 3·4; S, 7·4%).

2-α-Anthraquinonyloxy-1-naphthyl disulphide, obtained from the sulphinic acid by the usual method, formed yellow plates, m. p. 238°, from acetic acid (Found : C, 75·4; H, 3·4; S, 8·2. $C_{48}H_{26}O_6S_2$ requires C, 75·6; H, 3·4; S, 8·4%).

1-Anthraquinonyl 2-Naphthyl Ether, $C_{10}H_7{\cdot}O{\cdot}C_{14}H_7O_2$.—The sodium sulphinate (as VI) was oxidised in aqueous solution with the theoretical quantity of permanganate; after removal of oxides of manganese and the solvent, the residue was warmed (100°, 30 mins.) with sulphuric acid (20%). The ether separated from the mixture, and after purification had m. p. 170°; it was identical with a synthetic specimen (m. p. 170°) prepared from the reaction of 1-chloroanthraquinone with potassium 2-naphthoxide at 150° (2 hrs.) (Found : C, 82·5; H, 4·2. Calc. : C, 82·3; H, 4·0%). Laube (*Ber.*, 1906, **39**, 2246) gives m. p. 180°.

1-Anthraquinonyl 6-bromo-2-hydroxy-1-naphthyl sulphide, prepared by the interaction of 6-bromo-2-naphthol and anthraquinone-1-bromothiol at 110° (4 hrs.), formed yellow needles, m. p. 280—281°, from acetic acid (Found : C, 62·7; H, 3·1. $C_{24}H_{13}O_3BrS$ requires C, 62·5; H, 2·8%); its *acetyl* derivative, m. p. 240° (Found : C, 62·1; H, 3·1; Br, 15·7. $C_{26}H_{15}O_4BrS$ requires C, 62·0; H, 2·9; Br, 15·9%), was oxidised (5 g.) with hydrogen peroxide (20 c.c., 30%) in acetic acid (100° c.c., 4 hrs., 100°), and on dilution of the mixture, *1′-anthraquinonyl-6-bromo-2-acetoxy-1-naphthylsulphone* (compare V) was obtained; pale yellow needles from acetic acid, m. p. 223° (Found : C, 58·0; H, 2·7; Br, 15·0; S, 6·0. $C_{26}H_{15}O_6BrS$ requires C, 58·3; H, 2·8; Br, 15·0; S, 6·0%).

1-Anthraquinonyl 1-Sulphino-6-bromo-2-naphthyl Ether (compare VI).—The acetoxy-sulphone was hydrolysed in the usual manner with alcoholic sulphuric acid, and a solution of the resulting hydroxy-sulphone in 2*N*-alkali was boiled (30 mins.). The *sulphinic acid*, liberated from the resulting solution as usual, was purified from benzene; m. p. 170° (decomp.) (Found : C, 58·1; H, 2·6. $C_{24}H_{13}O_5BrS$ requires C, 58·4; H, 2·6%).

2-α-Anthraquinonyloxy-6-bromo-1-naphthyl disulphide, prepared by reducing the sulphinic acid, formed yellow needles from acetic acid, m. p. 283—284° (Found : C, 62·4; H, 2·8. $C_{48}H_{24}O_6Br_2S_2$ requires C, 62·6; H, 2·6%).

1-Anthraquinonyl-β-acetoxyethylsulphone (compare VII) was prepared by warming (100°, 1·5 hrs.) a solution of the corresponding sulphide (Gattermann, *Annalen*, 1912, **393**, 113) in acetic acid (1 g. in 5 c.c.) containing hydrogen peroxide (1·1 c.c., 30%). It separated from the cold diluted mixture, and was purified from acetic acid; m. p. 162—163° (Found : C, 60·4; H, 3·8. $C_{18}H_{14}O_6S$ requires C, 60·3; H, 3·9%). Hydrolysis in acid media yielded *1-anthra-*

quinonyl-β-*hydroxyethylsulphone* (VII), which, purified from alcohol, had m. p. 198° (Found: C, 60·4; H, 3·8. $C_{16}H_{12}O_5S$ requires C, 60·7; H, 3·8%).

1-*Anthraquinonyl* β-*Acetoxyethyl Sulphoxide*.—A solution of the sulphide (2 g.) in acetic acid (20 c.c.) containing hydrogen peroxide (1 c.c., 30%) was warmed (100°, 1 hr.), and water was added to the cooled liquid to produce turbidity; the required product separated slowly and was purified from alcohol; m. p. 168° (Found: C, 63·1; H, 4·2; S, 9·2. $C_{18}H_{14}O_5S$ requires C, 63·1; H, 4·1; S, 9·3%).

1-*Anthraquinonyl* β-*hydroxyethyl sulphoxide* was obtained from the acetyl derivative and purified from xylene; m. p. 220° (Found: C, 64·0; H, 4·0. $C_{16}H_{12}O_4S$ requires C, 64·0; H, 4·0%).

Methyl-β-1-*anthraquinonyloxyethylsulphone* (compare VIII).—Rearrangement of the sulphone (VII) was effected by suspending it or the acetyl derivative in boiling alcohol containing *N*-sodium hydroxide. Methyl iodide was added to the red solution of the sulphinate (VIII) thus obtained; the colour faded whilst the desired *sulphone* separated (60% yield); this formed plates from alcohol and had m. p. 145—146° (Found: C, 62·1; H, 4·4; S, 9·7. $C_{17}H_{14}O_5S$ requires C, 61·8; H, 4·2; S, 9·7%).

Di-(β-1-*anthraquinonyloxyethyl*) *Disulphide* (compare VIII).—Rearrangement of the sulphoxide took place rapidly when a solution of the substance in alcohol containing sodium hydroxide was boiled. A solution of the sulphinate (VII) was formed, and the disulphide separated; this formed needles, m. p. 223°, from benzene (Found: C, 67·7; H, 3·9; S, 11·0. $C_{32}H_{22}O_6S_2$ requires C, 67·7; H, 3·8; S, 11·3%). Methylation of the solution of the sulphinate formed during this rearrangement yielded the methyl-sulphone described above. The disulphide was also obtained by reducing the sulphinic acid provided by rearrangement of the sulphone (VII).

2-*Carboxyphenyl* β-*hydroxyethyl sulphide*.—An aqueous solution of potassium 2-thiolbenzoate and ethylene chlorohydrin was heated (100°, 1 hr.). The required *sulphide*, liberated from the solution and purified from water, had m. p. 127° (Found: C, 54·3; H, 5·0. $C_9H_{10}O_3S$ requires C, 54·5; H, 5·0%). The *sulphoxide* separated from the reacting mixture when an aqueous solution (20 c.c.) of the sulphide (2 g.) containing hydrogen peroxide (5 c.c.) was warmed (90°, 2 hrs.). Purified from water, it had m. p. 179° (Found: C, 50·1; H, 4·7; S, 14·8. $C_9H_{10}O_4S$ requires C, 50·4; H, 4·7; S, 14·9%).

2-*Carboxyphenyl*-β-*hydroxyethylsulphone* (IX) was obtained by further oxidation of the sulphoxide with hydrogen peroxide in aqueous solution. It was isolated by addition of brine to the mixture, and formed needles from water, m. p. 195° (Found: C, 47·2; H, 4·4. $C_9H_{10}O_5S$ requires C, 46·9; H, 4·3%). This substance and the corresponding sulphoxide were recovered unchanged after being heated (100°, 2 hrs.) with *N*-aqueous sodium hydroxide.

2-*Acetamido*-2′-*carboxydiphenylsulphone* (as X).—The acetyl derivative of the corresponding sulphide (Mayer, *Ber.*, 1909, **42**, 3046) was oxidised in acetic acid as usual with hydrogen peroxide. It formed needles from this solvent, m. p. 282° (Found: C, 56·3; H, 4·2; N, 4·5. $C_{15}H_{13}O_5NS$ requires C, 56·4; H, 4·1; N, 4·4%). Neither this substance nor the amine suffered rearrangement when their solutions in excess of 2*N*-aqueous sodium hydroxide were heated (100°, 3 hrs.).

Derivatives of Phenyl 4-*Hydroxy*-m-*tolyl Sulphide and Sulphone*.—The potassium salt of 4-hydroxy-*m*-tolylthiol (1 mol.) was liberated in alcoholic solution by hydrolysis of the carbonate (Zincke and Arnold, *Ber.*, 1917, **50**, 116) with the requisite amount of alkali. The appropriate halogen derivative (1 mol.) in alcoholic or aqueous solution was then added to the mixture, which was boiled until reaction was complete (1—2 hrs.); the required sulphide was finally liberated from the solution by 2*N*-hydrochloric acid at 0°. The sulphones were obtained from the sulphides by oxidation with excess of hydrogen peroxide (30%) in acetic acid (90—100°), the process usually requiring 1—2 hours for completion. In some cases (*e.g.*, sulphone No. 7) the sulphoxide separated during the oxidation, but it dissolved as conversion into the sulphone proceeded.

4-*Carboxy*-2-*nitrophenyl* 4-*Hydroxy*-m-*tolyl Sulphide* (No. 4).—The 4-bromo-3-nitrobenzoic acid used in the preparation of this sulphide was obtained by nitration of *p*-bromobenzoic acid with cold stirred nitric acid (*d* 1·5); it had m. p. 199° (Hübner, *Ber.*, 1875, **8**, 558). The *sulphide* formed yellow needles from acetic acid, m. p. 215° (Found: C, 54·8; H, 3·7. $C_{14}H_{11}O_5NS$ requires C, 55·1; H, 3·6%). The *acetyl* derivative had m. p. 163° (Found: N, 4·1. $C_{16}H_{13}O_6NS$ requires N, 4·0%).

4′-*Carboxy*-2′-*nitrophenyl*-4-*hydroxy*-m-*tolylsulphone* (No. 4), needles from acetic acid, m. p. 265—266° (Found: C, 49·7; H, 3·4; N, 4·1; S, 9·1. $C_{14}H_{11}O_7NS$ requires C, 49·8; H, 3·2; N, 4·1; S, 9·5%).

2-*Carboxy*-4-*nitrophenyl* 4-*Hydroxy*-m-*tolyl Sulphide*.—Nitration of *o*-bromobenzoic acid as

above yielded 2-bromo-5-nitrobenzoic acid, m. p. 180° (Hübner, *loc. cit.*). The *sulphide*, bright yellow needles from acetic acid, had m. p. 237° (Found : C, 55·1; H, 3·9; N, 4·7; S, 10·1. $C_{14}H_{11}O_5NS$ requires C, 55·1; H, 3·6; N, 4·6; S, 10·5%). The acetyl derivative, m. p. 230—231°, was obtained with acetic anhydride and pyridine. Hot acetic anhydride (1·5 hrs., 100°) gave the *lactone* (XI), m. p. 178° (Found : C, 58·6; H, 3·1; N, 5·1. $C_{14}H_9O_4NS$ requires C, 58·5; H, 3·1; N, 4·9%).

2′-Carboxy-4′-nitrophenyl-4-hydroxy-m-*tolylsulphone* (No. 7), needles from acetic acid, m. p. 245° (Found : C, 50·0; H, 3·3; N, 4·1. $C_{14}H_{11}O_7NS$ requires C, 49·8; H, 3·2; N, 4·1%).

4-Benzoyl-2-nitrophenyl 4-Hydroxy-m-*tolyl Sulphide.*—The 4-bromo-3-nitrobenzophenone required was obtained by the method of Schopff (*Ber.*, 1891, **24**, 3771). The *sulphide* had m. p. 165° (Found : C, 65·4; H, 4·2. $C_{20}H_{15}O_4NS$ requires C, 65·7; H, 4·1%).

4′-Benzoyl-2′-nitrophenyl-4-hydroxy-m-*tolylsulphone* (No. 2), needles from acetic acid, m. p. 154° (Found : C, 60·4; H, 3·9; N, 3·5; S, 8·0. $C_{20}H_{15}O_6NS$ requires C, 60·4; H, 3·8; N, 3·5; S, 8·0%).

2-Benzoyl-4-nitrophenyl 4-Hydroxy-m-*tolyl Sulphide.*—*2-Bromo-5-nitrobenzophenone*, prepared from 2-bromo-5-nitrobenzoic acid by the method used by Schopff for the 4-bromo-3-nitro-derivative, had m. p. 122° (Found : C, 50·9; H, 2·8. $C_{13}H_8O_3NBr$ requires C, 50·9; H, 2·6%). The related *sulphide* formed yellow needles, m. p. 139° (Found : C, 66·0; H, 4·4; N, 3·8. $C_{20}H_{15}O_4NS$ requires C, 65·7; H, 4·1; N, 3·8%).

2′-Benzoyl-4′-nitrophenyl-4-hydroxy-m-*tolylsulphone* (No. 3) had m. p. 209° (Found : C, 60·1; H, 4·0; N, 3·5. $C_{20}H_{15}O_6NS$ requires C, 60·4; H, 3·8; N, 3·5%). 4-Nitrophenyl 4-hydroxy-*m*-tolyl sulphide was more readily (compare J., 1932, 1491) obtained in a pure state by the present method. The sulphone (No. 8) (m. p. 158°) previously described (*loc. cit.*) contained a small amount of sulphoxide; in the pure condition it had m. p. 162°.

Sulphinic Acids and Disulphides derived from Diphenyl Ether.—The sulphinic acids were formed by rearrangement of the hydroxysulphones and were isolated and converted into disulphides in the usual manner (J., 1934, 426). The sulphinic group was eliminated from the acids by successive treatment with mercuric chloride and hydrochloric acid (this vol., p. 181).

4-Carboxy-2-nitrophenyl 3-Methanesulphonyl-p-*tolyl Ether.*—The sulphinic acid formed by rearrangement of No. 4 was not isolated in a pure state, but was characterised as the *methylsulphone*, m. p. 233° (Found : C, 50·9; H, 3·8; N, 3·7. $C_{15}H_{13}O_7NS$ requires C, 51·2; H, 3·7; N, 3·9%), and as *di*-(*p′-carboxy-o′-nitrophenoxy*-m-*tolyl*) *disulphide*, m. p. 241° (Found : C, 55·0; H, 3·7. $C_{28}H_{20}O_{10}N_2S_2$ requires C, 55·3; H, 3·3%), which was rapidly converted by warm alcoholic sodium hydroxide into the red sodium salt of the hydroxy-sulphide (m. p. 215°).

4-Carboxy-2-nitrophenyl p-*Tolyl Ether.*—The usual method of degradation applied to the above sulphinic acid yielded the ethyl ester (m. p. 78°) of this ether after treatment of the mercury derivative with hydrochloric acid in alcohol. The *ether* formed pale yellow needles from alcohol, m. p. 212°, and was identical with the ether synthesised from *p*-cresol and 4-bromo-3-nitrobenzoic acid by the usual method (Found : C, 61·5; H, 4·3; N, 5·4. $C_{14}H_{11}O_5NS$ requires C, 61·5; H, 4·0; N, 5·1%).

Di-(*o′-carboxy*-p′-*nitrophenoxy*-m-*tolyl*) *Disulphide.*—The sulphone No. 7 was converted by rearrangement as usual into the sulphinic acid; this was characterised by the disulphide, m. p. 257° (Found : C, 55·0; H, 3·4; N, 4·4. $C_{28}H_{20}O_{10}N_2S$ requires C, 55·3; H, 3·3; N, 4·6%), which was converted by warm alcoholic sodium hydroxide into the sulphide, m. p. 237°, used for the preparation of the sulphone concerned.

4-Nitro-2-benzoylphenyl p-*Tolyl Ether.*—The sulphone No. 3 gave by rearrangement a sulphinic acid which was not isolated in the pure condition but was converted by degradation into the *ether*. This formed plates from alcohol, had m. p. 129°, and was identical with the ether prepared from *p*-cresol and 2-bromo-5-nitrobenzophenone (Found : C, 71·9; H, 4·5. $C_{20}H_{15}O_4N$ requires C, 72·1; H, 4·5%).

2-Nitro-4-benzoylphenyl p-*tolyl ether*, obtained from sulphone No. 2 in a similar manner, was identical with the ether (m. p. 100°) synthesised from *p*-cresol and 4-bromo-5-nitrobenzophenone (Found : C, 71·9; H, 4·5. $C_{20}H_{15}O_4N$ requires C, 72·1; H, 4·5%).

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