753. *Aromatic Sulphonation. Part IV.** *Isomeric Ratios in the Sulphonation of Trimethyl-phenyl- and* -p-*tolyl-ammonium Methyl Sulphates.*

By J. C. D. Brand and A. Rutherford.

Sulphonation of the ion *p*-$CH_3{\cdot}C_6H_4{\cdot}NMe_3^+$ occurs quantitatively in the *m*-position with respect to the quaternary ammonium group. Sulphonation of $C_6H_5{\cdot}NMe_3^+$ yields an inhomogeneous mixture of at least three components, including the products of sulphonation in the *m*- and the *p*-position; quantitative analysis is attempted on the basis of solubility measurements.

Sulphonation of the trimethylphenylammonium and trimethyl-*p*-tolylammonium ions has not been examined previously. The ions react smoothly with fuming sulphuric acid, the consumption of sulphur trioxide is theoretical, and quantitative yields are obtained.

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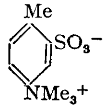
* Part III, preceding paper.

In the sulphonation of the trimethylphenylammonium ion, *m*-, *p*-, and (probably) *o*-isomerides are formed. The relevant observations may be summarised as follows.

(*a*) p-$CH_3{\cdot}C_6H_4{\cdot}NMe_3^+$.—The product is chemically homogeneous and has the empirical composition $C_{10\cdot0}H_{15\cdot9}O_{3\cdot1}N_{1\cdot01}S_{0\cdot98}$. The homogeneity follows from the fact that the first and the last fraction of a fractional crystallisation possess the same solubility, and further solubility measurements show that the substance is identical with the " betaine " (I).

(*b*) $C_6H_5{\cdot}NMe_3^+$.—The product has the empirical composition $C_{9\cdot0}H_{13\cdot0}O_{2\cdot8}N_{1\cdot03}S_{1\cdot02}$, but is not homogeneous because the solubility of successive fractions from a crystallisation rises continuously. The presence of trimethyl-*m*- and -*p*-sulphophenylammonium " betaines " (II) and (III) can be established by solubility measurements, but the product is not insoluble in a solution saturated simultaneously with both, and must therefore contain at least *three* components. Attempts to prepare the *o*-sulpho-compound were unsuccessful because mild methylating conditions were ineffective owing to the steric compression and vigorous conditions procured rearrangement. However, by assuming that the third constituent is the *o*-isomeride (which is consistent with the elemental analysis and the failure of the product to give any reactions of a tertiary amine or other likely decomposition product), the composition of the product can be shown semiquantitatively to be *o* 8, *m* 78, and *p* 14%. Details are given in the Experimental section.



(I)

m-$^+NMe_3{\cdot}C_6H_4{\cdot}SO_3^-$ (II)

p-$^+NMe_3{\cdot}C_6H_4{\cdot}SO_3^-$ (III)

It is interesting that the $C_6H_5{\cdot}NMe_3^+$ ion, which is nitrated exclusively in the *m*-position (Vorländer and Siebert, *Ber.*, 1919, **52**, 283; cf. Goss, Hanhart, and Ingold, *J.*, 1927, 250; Ingold, Shaw, and Wilson, *J.*, 1928, 1280), yields a mixture of isomerides on sulphonation. The sulphonating agent is apparently less powerfully electrophilic than the nitronium cation. Ostensibly this might mean that the reagent is uncharged, but the kinetics point strongly to the conclusion that the $SO_2{\cdot}OH^+$ cation is the effective sulphonating agent in oleum media (Part III, preceding paper); probably the explanation is that the formal charge on the large and polarisable sulphur atom is more effectively screened than is the case with NO_2^+.

EXPERIMENTAL

Materials.—Trimethyl-phenyl- and -*p*-tolyl-ammonium methyl sulphates were prepared by combination of the tertiary amine with methyl sulphate in acetone, recrystallised from alcohol–acetone, and dried *in vacuo* over phosphoric oxide. They had, respectively, m. p. 126° (Found: SO_4, 38·6. Calc. for $C_{10}H_{17}O_4NS$: S, 38·8%) and 144·5° (Found: SO_4, 36·7. Calc. for $C_{11}H_{19}O_4NS$: S, 36·7%), being analysed by estimation of $SO_4^=$ as barium sulphate after hydrolysis with concentrated hydrochloric acid at 100°.

*Trimethyl-2-sulpho-*p*-tolylammonium betaine* (Me = 1) (I) was obtained by methylation of 4-aminotoluene-2-sulphonic acid with methyl iodide and sodium carbonate in aqueous solution (Devoto and Ardissone, *Gazzetta*, 1934, **64**, 371). After evaporation, the betaine was separated from inorganic salts by extraction with 95% alcohol, and purified by further recrystallisations from aqueous alcohol. The *monohydrate* was obtained by drying *in vacuo* (Found: C, 48·8; H, 6·8; N, 5·9; S, 13·0; H_2O, 7·4. $C_{10}H_{15}O_3NS,H_2O$ requires C, 48·6; H, 6·9; N, 5·7; S, 13·0; H_2O, 7·3%), and the anhydrous betaine at 110° (Found: C, 52·2; H, 6·6; N, 6·3; S, 13·7. $C_{10}H_{15}O_3NS$ requires C, 52·4; H, 6·6; N, 6·1; S, 14·0%). Trimethyl-*m*-sulphophenyl ammonium betaine (II) (Found: C, 50·4; H, 6·1; N, 6·8; S, 14·7. Calc. for $C_9H_{13}O_3NS$: C, 50·2; H, 6·1; N, 6·5; S, 14·9%) and trimethyl-*p*-sulphophenyl ammonium betaine (III) (Found: C, 50·2; H, 5·9; N, 6·4; S, 15·2%) were readily prepared from metanilic and sulphanilic acid respectively by the same method.

Potassium *o*-dimethylaminobenzenesulphonate, prepared by methylation of *o*-aminobenzenesulphonic acid with methyl sulphate and potassium hydroxide, was converted through the barium salt into *o*-dimethylaminobenzenesulphonic acid (cf. Bamberger and Tschirner, *Ber.*, 1899, **32**, 1882) (Found: C, 47·6; H, 5·5; N, 7·3; S, 16·2%; *M*, 201·6. Calc. for $C_8H_{11}O_3NS$: C, 47·7; H, 5·5; N, 7·0; S, 15·9%; *M*, 201·3).

In an attempt to prepare trimethyl-*o*-sulphophenylammonium betaine, *o*-dimethylaminobenzenesulphonic acid was brought into solution in methyl sulphate (2 mols.) by refluxing for 1 hour. Dilution with alcohol yielded trimethyl-*p*-sulphophenyl-ammonium betaine, showing that "migration" of the sulpho-group had occurred. (Compare the conversion of *o*-aminobenzenesulphonic acid into sulphanilic acid by hot sulphuric acid; Bamberger and Kronig, *Ber.*, 1897, **30**, 2276.) The identity of the betaine was established by the fact that its co-solubility with (III) was zero.

Refluxing *o*-aminobenzenesulphonic acid (3·5 g.) with excess of methyl sulphate (13 ml.) also led to rearrangement and yielded 25—30% of methyl *p*-dimethylaminobenzenesulphonate, m. p. 91° (from benzene–light petroleum or aqueous methanol). Houben and Schreiber's assumption (*Ber.*, 1920, **53**, 2346) that the product of this experiment is methyl *o*-dimethylaminobenzenesulphonate is mistaken; that the ester formed belongs to the *p*-series is proved by the ultraviolet absorption spectrum (log $\varepsilon_{\text{max.}} = 4{\cdot}38$ at 2750 Å) in which there is no evidence of steric compression characteristic of *o*-compounds of this type. Methyl *p*-dimethylaminobenzenesulphonate can be prepared directly from sulphanilic acid and methyl sulphate, and is identical with the above product. Conversion of this ester into trimethyl-*p*-sulphophenylammonium betaine (III) occurs slowly at room temperature and rapidly above the m. p., as described also by Kuhn and Ruelius (*Chem. Ber.*, 1950, **83**, 244).

Heating *o*-dimethylaminobenzenesulphonic acid with methyl iodide and aqueous methanol at 110° led to hydrolysis of the sulphonate group. The difficulty of preparing the *o*-betaine by these methods is due as much to the ease of rearrangement and hydrolysis as to the steric hindrance to formation of the quaternary ammonium group.

Consumption of Sulphur Trioxide.—The sulphur trioxide consumed during sulphonation of trimethyl-*p*-tolylammonium methyl sulphate was determined by titrating the solution with water after complete reaction. Allowance was made for immobilisation of 0·5 mol. of sulphur trioxide by the betaine formed (*J.*, 1946, 880).

a = Moles of water added to 1000 g. of oleum.
b = Reduction in water-titre, moles per 1000 g. of oleum.

a	*b*	*b*/*a*	*a*	*b*	*b*/*a*
p-$C_7H_7{\cdot}NMe_3,SO_4Me$			1 : 2 : 4-$Me{\cdot}C_6H_3(SO_3^-)NMe_3^+$		
0·060	0·109	1·82	0·054	0·028	0·52
0·133	0·207	1·56	0·097	0·045	0·46
0·161	0·213	1·32	0·126	0·063	0·50
0·166	0·249	1·50	0·152	0·085	0·56
0·210	0·317	1·51	0·215	0·112	0·52
0·249	0·366	1·47	0·218	0·100	0·46
	r.m.s. av. :	1·49			0·50

The reaction consumes $1{\cdot}4_9 - 0{\cdot}5_0 = 0{\cdot}9_9$ mole of SO_3 per mole of reactant.

Isolation of the Products.—The product was separated from sulphuric acid by the usual methods. In a typical experiment (Expt. A, Table 1) trimethyl-*p*-tolylammonium methyl sulphate (12·02 g.) reacted with 15% fuming sulphuric acid (74 g.) for 24 hours at 25°. The mixture was then diluted to 12N-sulphuric acid and heated on the water-bath to hydrolyse the methyl hydrogen sulphate, then diluted further, neutralised with barium carbonate, filtered, and evaporated. The residue, after being washed with alcohol, was colourless and crystalline (10·63 g.), the only impurity being a little inorganic material (0·162 g., chiefly sodium sulphate) introduced with the barium carbonate; the yield of betaine (I) was 99·2%. The sodium sulphate was removed by one recrystallisation from aqueous alcohol (Found: C, 52·1; H, 6·9; N, 6·2%).

TABLE 1.

	Medium		Reactant			Recovery of product	
Expt.	Concn. of "free" SO_3, %	g.		g.	Time, hrs.	g.	%
A	15	74	$C_7H_7{\cdot}NMe_3,SO_4Me$	12·02	24	10·47	99·2
B	15	26	Betaine (I)	3·64	22	3·58	96·8
C	25	56	$Ph{\cdot}NMe_3,SO_4Me$	13·9	232	12·34	100·2
D	25	20	,,	5·00	15	2·68	(63·4) *

* Expt. D was interrupted before sulphonation was complete.

Other results are summarised in Table 1. Expt. B showed that the reaction product could be recovered unchanged from the sulphonating medium; migration of the sulphonate group does not occur in the systems with an NMe_3^+ substituent. Expt. D was interrupted at approximately two-thirds reaction to determine whether the product composition was the same as that found after complete reaction; this proved to be the case (Table 3).

Solubility Measurements.—The components were shaken mechanically in a stoppered flask in a thermostat for sufficient time to attain equilibrium (1—2 hours). Samples of the liquid phase were withdrawn through a filter by means of a pipette, and the solubility was determined by weighing the residue after evaporation. Aqueous ethanol was used as solvent. The results are in Tables 2 and 3. It was found that the product from the ion p-$C_7H_7{\cdot}NMe_3^+$ was entirely homogeneous, apart from the inorganic material introduced during the working up, and was (I). In the case of the $Ph{\cdot}NMe_3^+$ ion, however, formation of the betaines (II) and (III) was readily established (Table 3, lines 4—6), and in the following discussion the remainder, which was not identified directly, is assumed to be the *o*-isomeride.

TABLE 2. *Sulphonation of* p-$C_7H_7{\cdot}NMe_3^+$ *: co-solubility of the product with* (I) (65% *ethanol*; 20°).

Solid		Solubility (g./100 g. of soln.)		
	wt. (g.) equilibrated with 10 ml. of solvent	total	inorganic	organic
Betaine (I) alone	1·591	3·35	—	3·35
Betaine (I) + product of expt. A	>0·4 1·504 *	3·36	—	3·36
Betaine (I) + product of expt. A	>0·4 1·519	3·49	0·14	3·35
Betaine (I) + product of expt. B	>0·4 1·520	3·50	0·15	3·35

* After one recrystallisation.

Even if the assumption is granted that the *o*-isomeride completes the range of products from the $Ph{\cdot}NMe_3^+$ ion, the proportions still cannot be calculated from the co-solubility with (II) and (III) unless the mutual solubility effects are made the subject of a separate assumption. We assume (*a*) that in a solution saturated simultaneously with (II) and (III) the components are present in the ratio of their individual solubilities, and (*b*) that in computing the increment of the solubility of the *m*-isomeride in a ternary solution the *o*- and the *p*-isomeride can be counted together and the solution treated as binary. This is a crude argument, and the results can only be semi-quantitative. On the basis of these assumptions and by insertion of numerical values from Table 3 (lines 1—3), the solubility, S_m, of the *m*-isomeride in the presence of w g. of the $(o + p)$-isomerides is given by

$$S_m = 8{\cdot}25 + (8{\cdot}68 - 8{\cdot}25)w/(9{\cdot}45 - 8{\cdot}68) = 8{\cdot}25 + 0{\cdot}558w$$

The total solubility, S_t, is therefore

$$S_t = S_m + w = 8{\cdot}25 + 1{\cdot}558w$$

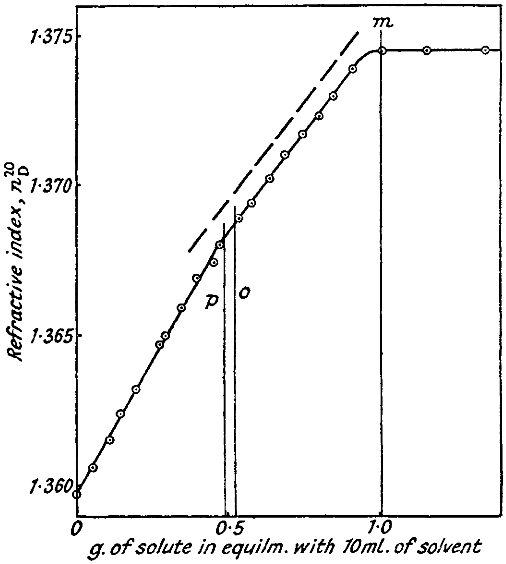
and by this equation we may calculate w from S_t, subject to the two previous assumptions. For the two solutions at the foot of Table 3 ($S_t = 9{\cdot}76$ and $9{\cdot}10$ g. per 100 g. of solvent), we obtain $w = 0{\cdot}97_0$ g. and $0{\cdot}54_7$ g.; S_m is, therefore, 8·79 and 8·55 g. per 100 g. of solvent, respectively. Hence, from the result in the last line of Table 3, the yield of $(o + p)$-isomers per 2·38 g. of reaction product is $9{\cdot}10 - 8{\cdot}55 = 0{\cdot}55$ g., or 23·1%. Similarly, from the penultimate line, the percentage yield of *o*-isomer is $100[9{\cdot}76—(8{\cdot}79 + 0{\cdot}77)]/2{\cdot}42 = 8{\cdot}3$. The percentage yield of *p*-isomer is $23{\cdot}1 - 8{\cdot}3 = 14{\cdot}8$.

The results of this calculation were tested for internal consistency in the following way. Successively increasing amounts of the reaction product were shaken with solvent and the refractive index of the solution determined at equilibrium after each addition (Figure). A change of slope of the curve relating refractive index to the total weight of solid occurred when the system became saturated with respect to one of the constituents. The points at which this should occur were also calculated from the product composition in Table 3, the location of the predicted alterations of slope being shown in the Figure. The solution appears to become saturated almost simultaneously with the *o*- and the *p*-isomeride. The gradient of the central

TABLE 3. *Sulphonation of* Ph·NMe$_3^+$ *: co-solubility of the product with* (II) *and* (III) (55% *ethanol*; 25°).

Solid	wt. (g.) equilibrated with 100 g. of solvent	Solubility * (g. per 100 g. of solvent)	Isomeric composition of product, % *m*	*p*	*o*
Betaine (III) alone	Excess †	0·735	—	—	—
Betaine (II) alone	Excess	8·25	—	—	—
Betaines (II) and (III)	,,	9·45	—	—	—
Betaine (II) + product of expt. C	,,	10·2	—	—	—
Betaines (II) & (III) + product of expt. C	,,	10·2	—	—	—
Product of expt. C	14·7 12·8	10·2$_3$ 10·2$_2$	— —	— —	— —
Betaines (II) & (III) + product of expt. C	Excess 2·45	9·77	78	14	8
Betaine (II) only + product of expt. C	Excess 2·45	9·08			
Betaines (II) & (III) + product of expt. D	Excess 2·42	9·76	77	15	8
Betaine (II) only + product of expt. D	Excess 2·38	9·10			

* Excluding inorganic material (cf. Table 2). † *I.e.*, sufficient to ensure saturation.



portion of the curve, where the solution is unsaturated only with respect to the *m*-isomeride, could be calculated from the refractive index of a saturated solution of the pure *m*-isomeride and the proportion of *m*-compound in the reaction product, and is shown in the Figure by a broken line displaced on the ordinate for the sake of clarity. The agreement is only approximate, but seems in both cases to be satisfactory.

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