Interaction of the Isomeric Chlorosulphonylbenzoyl Chlorides and Benzene, under the Influence of Aluminium Chloride

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Acylation rather than sulphonylation is the major primary reaction when the isomeric chlorosulphonylbenzoyl chlorides (I) are stirred with aluminium chloride (1 or 2 mol. equiv.) and benzene at room temperature. The *ortho*-isomer (I) also yielded *o*-benzoylbenzenesulphinic acid (V) and chlorobenzene by reduction of the first-formed *o*-benzoylbenzenesulphonyl chloride. When ethylene dichloride is used as solvent, sulphonylation is almost completely inhibited and there is no reduction of the *ortho*-isomer. This provides a convenient synthesis for *o*-, *p*-, and the previously unknown *m*-benzoylbenzenesulphonyl chlorides. Electron-attracting groups in the nucleus of benzenesulphonyl chloride retard sulphonylation whereas the same substituents in benzoyl chloride accelerate acylation.

WHILST benzene- and simple alkylbenzene-sulphonyl chlorides react with aromatic hydrocarbons under the influence of aluminium chloride in ethylene dichloride solution to provide high yields of diaryl sulphones,[1] benzenesulphonyl chlorides containing electron-attracting groups behave in a more complex manner. For example, *o*-nitrobenzenesulphonyl chloride apparently does not sufficiently ' paralyse ' the aluminium chloride (2 mol. equiv.) to prevent it catalysing the interaction of the aromatic hydrocarbon and the ethylene dichloride used as solvent since considerable quantities of 1,2-diphenylethane are produced.[2] When benzene is used as both solvent and reactant, the isomeric nitrobenzene-sulphonyl chlorides either do not react or suffer reduction to the sulphinic acid (in the order $o > m > p$) with concomitant formation of chlorobenzene. The isomeric phenylsulphonylbenzenesulphonyl chlorides and benzene-disulphonyl chlorides show somewhat similar behaviour.[3]

We now report that, as detailed in the Table, when the isomeric chlorosulphonylbenzoyl chlorides (I) were stirred with aluminium chloride and benzene, acylation proceeded much faster than sulphonylation and that reduction of the sulphonyl chloride group is only important with the *o*-isomer. When, with the *m*- and *p*-isomers (I) the aluminium chloride was restricted to 1 mol. equiv. (expt. 5 and 10), no products of sulphonyl-ation could be isolated. Presumably the catalyst is associated almost exclusively with the more basic carbonyl oxygen of the reactant (I) and of the product (II). The fact that *o*-benzoylbenzenesulphonyl chloride and *o*-chlorosulphonylbenzoyl chloride react with benzene to furnish identical amounts of *o*-benzoylbenzene-sulphinic acid (expt. 3 and 4) suggests that, in the latter reaction the sulphinic acid has completely arisen from reduction of *o*-benzoylbenzenesulphonyl chloride [(II) *o*-isomer ⟶ (V) *o*-isomer]. Apparently, therefore the products listed in expt. 3 arise almost exclusively from primary acylation, the extent of which was about 89%. In no instance was any primary product of sulphonyl-ation isolated. Apparently slow initial sulphonylation (I) ⟶ (III) is followed by rapid acylation (III) ⟶ (VI) since when *meta*- and *para*-phenylsulphonylbenzoyl chlorides were stirred with benzene and aluminium chloride under conditions similar to those employed in

the foregoing, *meta*- and *para*-benzoylphenyl phenyl sulphones (VI) were obtained in 85 and 90% yields respectively.
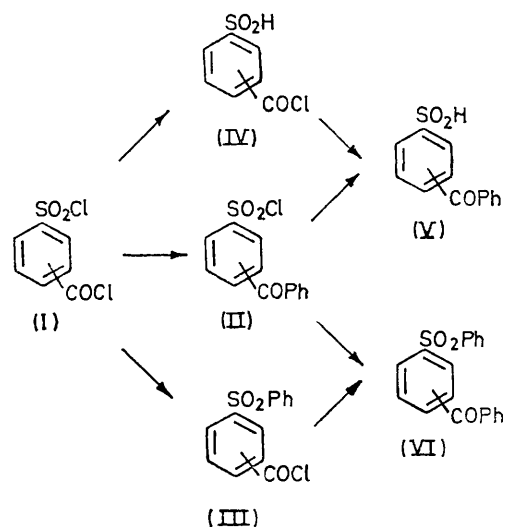
The interaction of *o*-chlorosulphonylbenzoyl chloride, aluminium chloride (*ca.* 2 mol. equiv.), and benzene was studied by Remsen and Saunders[4] who isolated *o*-benzoylbenzenesulphonyl chloride and *o*-benzoylphenyl phenyl sulphone in proportions which depended on temperature and reaction time. Presumably *o*-benzoyl-benzenesulphinic acid was not isolated because of the work-up procedure they adopted.

When the interaction of the chlorosulphonylbenzoyl chlorides (I), benzene, and aluminium chloride were investigated in ethylene dichloride solution, there was no participation by the solvent, and in no instance was any sulphinic acid detected. Acylation (I) ⟶ (II) proceeded much more rapidly than sulphonylation and advantage was taken of this fact to develop a procedure for the preparation of the *m*- and *p*-benzoylbenzene-sulphonyl chlorides (II) (see Experimental section).

It has been suggested that the halogenating power of a sulphonyl chloride increases with increasing ' positivity ' of its chlorine atom.[2,3] Clearly, the depression in electronegativity in passing from the nitro to the

[1] G. Holt and B. Pagdin, *J. Chem. Soc.*, 1960, 2508.

[2] E. C. Dart, G. Holt, and K. D. Jeffreys, *J. Chem. Soc.*, 1964, 5663.

[3] E. C. Dart, G. Holt, and K. D. Jeffreys, *J. Chem. Soc. (C)*, 1966, 1284.

[4] I. Remsen and A. P. Saunders, *Amer. Chem. J.*, 1895, **17**, 347.

benzoyl substituent is sufficient to cause a significant drop in the yields of chlorobenzene and sulphinic acid. However, since in the corresponding reactions of the m- and p-benzoylbenzenesulphonyl chlorides, no products of reduction were isolated, it is probable that the chlorinating properties of the *ortho*-isomer are not wholly related to the electronegativity of the benzoyl substituent, but are due, to some degree, to its proximity

hibits acylation. Semi-quantitative results showing the percentage of acylation when a number of substituted aroyl chlorides are allowed to react with benzene under comparable conditions (see Experimental section) are as follows: m-Cl·O$_2$S– (51), p-Cl·O$_2$S– (68), p-Ph·SO$_2$– (48), m-NO$_2$– (48), p-NO$_2$– (65), and H– (1·5%). It is noteworthy that all these groups retard the sulphonylation of benzene and that the effect is particularly

Interaction of the chlorosulphonylbenzoyl chlorides, benzene, and aluminium chloride

| Expt.	Reactant	AlCl$_3$ (mol. equiv.)	Reaction time (h)	Benzoyl-phenyl-phenyl sulphone (%)	Benzoyl-benzene-sulphonyl chloride (%)	Benzoyl-benzene-sulphinic acid (%)	Chloro-benzene (%)	Recovered reactant (%)
1	o-Cl·O$_2$SC$_6$H$_4$COCl	2	1	4, 5	79	11·5		0
2		2	5	20	56	20	10	0
3		2	24	45	9	35	21	0
4	o-Cl·O$_2$SC$_6$H$_4$COPh	2	24	40		35	29	20
5		1	24	0	66	0	0	
6	m-Cl·O$_2$SC$_6$H$_4$COCl	2	1	6	69	0	0	
7		2	5	28	60	0	0	
8		2	24	61	33	Trace	0	
9	m-Cl·O$_2$SC$_6$H$_4$COPh	2	24	41	0	0	0	48
10		1	24	0	68	0	0	16
11	p-Cl·O$_2$SC$_6$H$_4$COCl	2	1	25	72	0	0	0
12		2	5	47	52	0	0	0
13		2	24	70	28	0	0	0
14	p-Cl·O$_2$SC$_6$H$_4$COPh	2	24	60	0	0	0	37

to the uncomplexed sulphonyl oxygen (VII). Such an interaction would intensify the positive character of the sulphonyl chloride chlorine atom, thus creating a more potent halogenating species.

(VII)
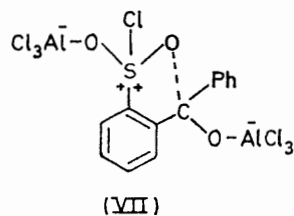
Whereas a drop in electronegativity depresses halogenation, it clearly facilitates sulphonylation. If, as H. C. Brown suggests,[5] the active species in the sulphonylation of benzene is the ArSO$_2$$^+$ ion, the increased yields of sulphone observed with o-benzoylbenzenesulphonyl chloride (II) over o-nitrobenzenesulphonyl chloride might be attributed to the greater stability of the o-benzoylbenzenesulphonylium ion over that of its nitro-counterpart. Such a suggestion does not, however, accord with the observation that a greater yield of sulphone is obtained from p-benzoylbenzenesulphonyl chloride than from its *meta*-isomer. It must be considered however that the greater the stability of the ion, the less will be its reactivity, but the data in hand are insufficient to quantify the two opposing effects.

The observation that the chloro- and the phenylsulphonylbenzoyl chlorides acylate benzene much more rapidly than does benzoyl chloride indicates that the presence of electron-attracting groups in the aromatic nucleus of an aroyl halide accelerates rather than in-

marked when the substituent is in the p-position. These results accord with Slootmaeker's[6] observations that ρ for benzoylation is positive. The fact that sulphonylation, which proceeds through ArSO$_2$$^+$, has a negative ρ value does not necessarily signify that acylation proceeds through the oxonium complex rather than ArCO$^+$. Considering the two step process, if the positive value of ρ for the second step is greater in magnitude than the negative value for the first step then, as observed, the overall value will be positive.
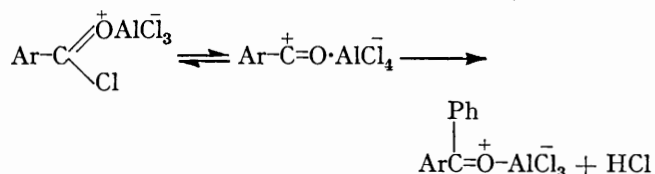
All the known compounds gave satisfactory analytical and i.r. data.

Interaction of Chlorosulphonylbenzoyl Chlorides, Benzoyl-benzenesulphonyl Chlorides, or Phenylsulphonylbenzoyl Chlorides, Aluminium Chloride, and Benzene. General Procedure.—(a) *In benzene.* The selected molecular proportion of finely-ground aluminium chloride was added rapidly to a stirred solution of the chloride (0·02 mol) in benzene (100 ml) at room temperature (18—24°). The resulting straw-coloured liquid was protected from atmospheric moisture whilst stirring was continued for the selected period of time. Reduction of sulphonyl chloride was indicated by the separation of a heavy viscous brown oil, otherwise the solution slowly darkened to become deep red or brown. The mixture was decomposed by the addition of ice–water (250 ml). The organic layer (A) was

[5] H. C. Brown and F. R. Jensen, *J. Amer. Chem. Soc.*, 1958, **80**, 4042.

[6] P. J. Slootmaekers and R. Verbeerst, *Bull. Soc. chim. belges*, 1968, **77**, 273; see also P. J. Slootmaekers, R. Roosen, and J. Verhulst, *ibid.*, 1962, **71**, 446.

separated and washed successively with dilute sodium carbonate (2 × 25 ml) and water (2 × 50 ml). The combined aqueous layer and alkali washings on acidification gave o-*benzoylbenzenesulphinic acid*, the only sulphinic acid to be isolated.

The dried benzene layer (A) was distilled (the last traces under reduced pressure) and the distillate was collected in a receiver cooled at −70°. The residue (B) was treated as described below. The distillate, consisting of benzene and possibly chlorobenzene, was analysed by g.l.c., using a 2 m column of silicone oil on Celite, at 135°, the apparatus being calibrated against mixtures of known composition.

The residue (B) possibly containing chlorosulphonyl-benzoyl chloride and benzoylphenyl phenyl sulphone had to be treated in different ways according to its origin. That from the *ortho*-isomer was boiled gently under reflux for 1 h with ether containing an excess of aniline. Water was added and the ether layer was washed with dilute hydrochloric acid and then with water. Removal of the ether left an off-white solid which was boiled for 0·5 h with N-sodium hydroxide solution. The base-insoluble material on recrystallisation from ethanol gave o-benzoylphenyl phenyl sulphone, m.p. and mixed m.p.[4] 186—187°.

The pale yellow sodium hydroxide solution was cooled (0°) and made just acid with 10% hydrochloric acid. The precipitated solid on crystallisation from ethanol provided o-benzoylbenzenesulphonanilide, m.p. and mixed m.p.[4] 144—145°. Under the foregoing conditions, o-phenyl-sulphonylbenzoyl chloride and o-chlorosulphonylbenzoyl chloride would have yielded o-phenylsulphonylbenzanilide, and o-sulphobenzoic acid dianilide respectively, but these compounds were not detected.

Residue (B) from the *meta*- and *para*-isomers was heated with an excess of ammonia (s.g. 0·880) to convert acid chlorides into amides. The mixture was evaporated to dryness, sulphonamides were removed by means of N-sodium hydroxide, and the alkaline extract (C) was treated as indicated below. The alkali-insoluble residue consisting of benzoylphenyl phenyl sulphone and phenylsulphonyl-benzamide was boiled with dilute sodium hydroxide until ammonia was no longer evolved and the benzoylphenyl phenyl sulphone was separated from the cooled solution. Acidification of the filtrate provided the phenylsulphonyl-benzoic acid.

Solution (C) was acidified to precipitate a mixture of benzoylbenzenesulphonamide and sulphonamidobenzamide. The latter was removed by refluxing the mixture with dilute alkali, acidifying the cooled solution, and extracting the resulting sulphonamidobenzoic acid from the benzoyl-benzenesulphonamide with dilute sodium hydrogen carbonate solution.

The foregoing procedure involves isolation not of the reaction products themselves, but their derivatives. To enable a more accurate assessment of yield to be obtained, each of these conversions was carried out with separate samples of the pure material. For example, in the investigation above the benzoylsulphonyl chlorides are isolated as benzoylbenzenesulphonamides. The yields of the latter were adjusted to accord with the observation

that under the conditions used, pure benzoylbenzene-sulphonyl chlorides are converted into the amides in 91% yield.

(b) *In ethylene dichloride.* The procedure was essentially that described by Holt and Pagdin,[1] and the crude organic product of reaction was worked up as described in (a) above.

Benzoylbenzenesulphonyl Chlorides.—*p*-Chlorosulphonyl-benzoyl chloride (14·34 g, 0·06 mol) and aluminium chloride (16·6 g, 0·125 mol) in ethylene dichloride (400 ml) containing benzene (9·36 g, 0·12 mol) was kept for 24 h at room temperature (18—24°). The mixture was decomposed by the addition of ice-water, and removal of the solvent from the washed and dried organic layer gave a pale yellow product which was dissolved in the minimum volume of boiling light petroleum (b.p. 60—80°) (charcoal). The cooling solution was decanted from the first trace of solid and on cooling to 0° deposited the crude sulphonyl chloride (80%), m.p. 88—90°. The material was sufficiently pure for most purposes but its m.p. could be raised to 95—96° by repeated recrystallisation from light petroleum. The *meta*-isomer (80%) was obtained by the same procedure.

The compounds obtained by the above procedures are given below.

From o-*chlorosulphonylbenzoyl chloride*, m.p.[7] 40°. o-Benzoylphenyl phenyl sulphone, m.p.[4] 186—187°; o-benzoylbenzenesulphonyl chloride, m.p.[4] 98—99°; o-benzoylbenzenesulphonanilide, m.p.[4] 144—145°; o-*benzoyl-benzenesulphinic acid*, m.p. 92—94° (Found: C, 63·3; H, 4·2; S, 12·9. $C_{13}H_{10}O_3S$ requires C, 63·5; H, 4·2; S, 13·0%); S-*benzylisothiouronium* o-*benzoylbenzenesulphinate*, m.p. 188—190° (Found: C, 61·2; H, 4·7; N, 6·8; S, 15·3. $C_{20}H_{20}N_2O_3S_2$ requires C, 61·1; H, 4·9; N, 6·8; S, 15·5%).

From m-*chlorosulphonylbenzoyl chloride*, b.p.[8] 116—119° at 0·5 mmHg. m-*Benzoylphenyl phenyl sulphone*, m.p. 114—115° (Found: C, 70·8; H, 4·5; S, 10·2. $C_{18}H_{10}O_3S$ requires C, 70·8; H, 4·4; S, 9·9%), $v_{max.}$ 710s and 755s (monosubstitution), 788s (*m*-disubstitution), 1140 (sym. str.) (SO_2), 1330 (asym. str.), and 1650s cm⁻¹ (diaryl C=O); m-*benzoylbenzenesulphonyl chloride*, m.p. 36—38° (Found: C, 55·5; H, 3·2; Cl, 12·6; S, 11·2. $C_{13}H_9ClO_3S$ requires C, 55·6; H, 3·3; Cl, 12·65; S, 11·4%), $v_{max.}$ 699 and 770 (monosubstitution), 816m (*m*-disubstitution), 1170 (sym. str.) (SO_2), 1320 (asym. str.) (SO_2), and 1660s cm⁻¹ (C=O); m-benzoylbenzenesulphonamide, m.p. 151—152° (lit.,[9] 144°) (Found: C, 60·0; H, 4·2; N, 5·4; S, 12·3. Calc. for $C_{13}H_{11}NO_3S$: C, 60·0; H, 4·2; N, 5·4; S, 12·3%).

From p-*chlorosulphonylbenzoyl chloride*, m.p.[10] 56—57°. *p*-Benzoylphenyl phenyl sulphone, m.p. 142—143° (lit.,[11] 133°, lit.,[12] 144°) (Found: C, 70·6; H, 4·3; S, 9·8. Calc. for $C_{18}H_{10}O_3S$: C, 70·8; H, 4·4; S, 9·9%); *p*-benzoyl-benzenesulphonyl chloride, m.p. 95—96° (lit.,[13] 86—88°) (Found: C, 55·4; H, 3·2; Cl, 12·7; S, 11·5. Calc. for $C_{13}H_9ClO_3S$: C, 55·6; H, 3·3; Cl, 12·65; S, 11·4%); *p*-benzoylbenzenesulphonamide, m.p.[14] 172—173°; *p*-sulphonamidobenzamide, m.p. and mixed m.p.[10] 236—237°; *p*-sulphonamidobenzoic acid, m.p. and mixed m.p.[15] 280°.

Phenylsulphonylbenzoyl Chlorides.—m-Phenylsulphonyl-benzoic acid, m.p.[16] 186—187° (79%), obtained by the

[7] D. Sh. Rozina, L. T. Nesterenko and Yu. I. Vainshtein, *Zhur. obshchei Khim.*, 1958, **28**, 2878 (*Chem. Abs.*, 1959, **53**, 9128).
[8] R. Delaby, J. V. Harispe, ans J. Paris, *Bull. Soc. chim. France*, 1945, 954 (*Chem. Abs.*, 1946, **40**, 5033).
[9] P. Ruggli and F. Grün, *Helv. Chim. Acta*, 1941, **24**, 197.
[10] J. Maarse, *Rec. Trav. chim.*, 1914, **33**, 209.
[11] L. C. Newell, *Amer. Chem. J.*, 1897, **20**, 310.

[12] H. Burton and P. F. Hu, *J. Chem. Soc.*, 1948, 601.
[13] G. Manecke, J. Beier, and G. Wehr, *Makromol. Chem.*, 1970, **134**, 231.
[14] F. G. Bordwell and G. W. Crosby, *J. Amer. Chem. Soc.*, 1956, **78**, 5367.
[15] H. J. Taverne, *Rec. Trav. chim.*, 1914, **25**, 56.
[16] W. E. Truce and M. F. Amos, *J. Amer. Chem. Soc.*, 1951, **73**, 3013.

interaction of *m*-chlorosulphonylbenzoic acid, aluminium chloride, and benzene, yielded, with thionyl chloride, m-*phenylsulphonylbenzoyl chloride*, m.p. 78—79° (57%) (Found: C, 55·8; H, 3·3; Cl, 12·6; S, 11·2. $C_{13}H_9ClO_3S$ requires C, 55·6; H, 3·3; Cl, 12·65; S, 11·4%), $v_{max.}$ 690s and 760s (monosubstitution), 780s (*m*-disubstitution), 1160 and 1310 (SO_2), and 1550s cm^{-1} (C=O in CO·Cl). With ammonia the chloride gave m-*phenylsulphonylbenzamide*, m.p. 155—157° (78%) (Found: C, 60·0; H, 4·3; N, 5·6; S, 12·4. $C_{13}H_{11}NO_3S$ requires C, 60·0; H, 4·2; N, 5·4; S, 12·3%). *p*-Phenylsulphonylbenzoyl chloride, m.p.[17] 145—146: was readily obtained by the action of thionyl chloride on the corresponding acid.

The identity of some of the new compounds described above was confirmed by comparison (mixed m.p. and/or i.r. spectra) with authentic specimens prepared as follows: *o*-benzoylbenzenesulphinic acid, 67%, was obtained by reducing *o*-benzoylbenzenesulphonyl chloride with sodium sulphite. It gave the expected *S*-benzylisothiouronium salt. *m*- and *p*-Benzoylbenzenesulphonamides were obtained from the corresponding chlorides which were prepared (58 and 80% respectively) from the diazotised *m*-[18] and *p*-aminobenzophenone [19] by Meerwein's procedure.[20]

Microanalyses were carried out by Mr. B. Manohin.

[17] W. S. Weedon and H. W. Doughty, *Amer. Chem. J.*, 1905, **33**, 427.
[18] R. Geigy and W. Koenigs, *Ber.*, 1885, **18**, 2401.

[19] P. J. Montagne, *Rec. Trav. chim.*, 1923, **43**, 506.
[20] H. Meerwein, G. Dittmar, R. Gollner, K. Hafner, F. Mench, and O. Steinfort, *Chem. Ber.*, 1957, **90**, 841.