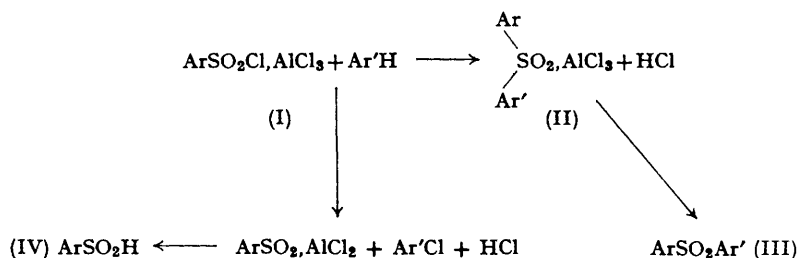


1085. *Interaction of Some Nitrobenzenesulphonyl Chlorides and Aromatic Hydrocarbons under the Influence of Aluminium Chloride.*

By E. C. DART, G. HOLT, and K. D. JEFFREYS.

In conditions where benzenesulphonyl chloride, aromatic hydrocarbons, and aluminium chloride provide the diaryl sulphones, the three mononitrobenzenesulphonyl chlorides and 2,4-dinitrobenzenesulphonyl chloride either do not react or are reduced (in order *o*- > *m*- > *p*-) to the sulphinic acid, with concomitant formation of aryl halide. The interaction of *o*-nitrobenzenesulphonyl chloride, aluminium chloride, and mesitylene, on a preparative scale, provides chloromesitylene (80%), and no product of side-chain halogenation can be detected. The mechanism of the reactions is discussed.

ETHYLENE DICHLORIDE is a most satisfactory solvent for Friedel-Crafts sulphonylations (I → II).¹ We therefore investigated the application of this procedure to sulphonylations



with nitrobenzenesulphonyl chlorides, since the few instances so far reported generally provide poor yields.²

Each of the three mononitrobenzenesulphonyl chlorides takes into ethylene dichloride solution two molecular proportions of aluminium chloride, but with the *ortho*-isomer a yellow complex (I; Ar = *o*-C₆H₄NO₂, AlCl₃) separates rapidly. The sulphonyl chlorides were recovered almost quantitatively when water was added to these solutions. Sulphonylation did not, however, proceed when a solution (or suspension) of the di(aluminium chloride) complex in ethylene dichloride was added to benzene in the same solvent. The formation of sulphinates indicated partial reduction of the sulphonyl chloride. Further, much 1,2-diphenylethane was produced, presumably because the aluminium chloride is not sufficiently "paralysed" to prevent its catalysing the interaction of benzene and ethylene dichloride. Clearly, ethylene dichloride is not a satisfactory solvent for these reactions.

¹ Holt and Padgin, *J.*, 1960, 2508.

² Olivier, *Rec. Trav. chim.*, 1916, **35**, 109.

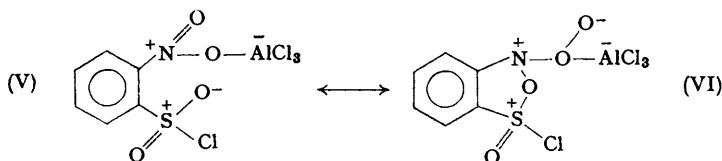
The influence of aluminium chloride on nitrobenzenesulphonyl chlorides in benzene depends both on the molar ratio of catalyst and on the orientation of the sulphonyl chloride. The sulphonyl chlorides were either recovered or partially reduced to sulphinic acid (I → IV) with concomitant formation of chlorobenzene; sulphone formation (I → II) was never the major reaction. Similar results were obtained in toluene or mesitylene (see Table). All reactions were at room temperature (18–24°).

Posn. of nitro-groups	Moles AlCl ₃	Solvent	Time (hr.)	Aryl halide (%)	Sulphone (%)	Sulphinic acid (%)	Sulphonyl chloride recovered (%)
2	1	Benzene	5	41	1.5	38	50
2	2	"	5	89	0.5	82	0
2	2	Toluene	5	80	0	91	0
2	2	Mesitylene	5	91	0	87	0
3	1	Benzene	19	15	7.0	20	67
3	2	"	19	75	5.0	72	15
4	1	Benzene	24	0	2.5	trace	94
4	2	"	24	41	4.0	43	45
4	2	Toluene	24	71	0	78	9
4	2	Mesitylene	24	86	0	88	0
2,4	1	Benzene	5	36	0	*	47
2,4	2	"	5	85	0	*	6
2,4	3	"	5	91	0	*	0
None	1	"	24	0	80	0	12.5

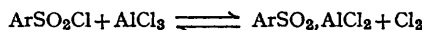
* Sulphinic acid too unstable to be isolated.³ In duplicate runs, the yields of sulphinic acid and of aryl halide were reproducible within 3–4%.

Where a sulphonyl chloride group has been reduced, sulphinic acid and aryl halide should be obtained in equimolecular amounts; the Table shows that this is substantially true.

The increase in yield of sulphinic acid and of aryl halide caused by using 2 mols. of aluminium chloride instead of 1 accords with H. C. Brown's suggestion⁴ that aluminium chloride more readily attaches itself to a nitro- than to a sulphonyl chloride group. Where the two groups are *ortho*- to one another it appears that the nitro-group, with its associated molecule of aluminium chloride, activates the -SO₂Cl group. One interpretation is annexed (V ↔ VI).



This "through space" interaction of the two groups inhibits formation of the ArSO₂⁺ ion which, either as such or as the ion-pair (ArSO₂⁺)(AlCl₄⁻), appears to be the effective species in the sulphonylation of benzene;⁵ instead, it renders the chlorine atom more positive and so more susceptible to nucleophilic attack by aromatic hydrocarbon or chloride ion. Each of these attacks will yield sulphinic acid and chlorinated hydrocarbon. Olivier suggested⁶ that the following equilibrium represents the interaction of sulphonyl and aluminium chlorides.



However, when dry nitrogen was passed slowly through the di(aluminium chloride) complex of 2,4-dinitrobenzenesulphonyl chloride in ethylene dichloride, chlorine was not detectably

³ Davies, Storrie, and Tucker, *J.*, 1931, 627.

⁴ Brown and Jensen, *J. Amer. Chem. Soc.*, 1958, **80**, 4038.

⁵ Brown and Jensen, *J. Amer. Chem. Soc.*, 1958, **80**, 4042.

⁶ Olivier, *Rec. Trav. chim.*, 1914, **33**, 91.

carried over. The addition of a second molecule of aluminium chloride yields more chlorobenzene and sulphinic acid because the positiveness of the halogen atom in the sulphonyl chloride group is further enhanced by oxonium-salt formation. Yields of chlorobenzene and sulphinic acid on passing from the *meta*- to the *para*-isomer may fall because the nitro-group (in combination with aluminium chloride) has a greater inductive effect from the *meta*- than from the *para*-position.⁷ This view accords with the substantially similar yields of chlorobenzene from 2-nitro- and 2,4-dinitro-benzenesulphonyl chlorides. A comparison of benzene- and 4-nitrobenzene-sulphonyl chlorides indicates, however, that a *para*-nitro-group is by no means uninfluential. Thus, where the former gives about 80% yield of diphenyl sulphone (presumably *via* PhSO₂⁺) and no detectable sulphinic acid, the latter gives much less sulphone (III; Ar = Ph, Ar' = *p*-C₆H₄NO₂) (4%) and is reduced to the extent of 43%. Apparently the *para*-nitro-group can make formation of *p*-O₂N·C₆H₄·SO₂⁺ difficult.

The influence of the nucleophilicity of aromatic hydrocarbon (mesitylene > toluene > benzene), as both solvent and reactant, is demonstrated by stirring *p*-nitrobenzenesulphonyl chloride with them; the yield of sulphinic acid and of aryl halide increases with nucleophilicity. No product of side-chain halogenation could be detected with toluene and mesitylene, and since, on a preparative scale, mesitylene gives chloromesitylene (80%) with *o*-nitrobenzenesulphonyl chloride and aluminium chloride, we are now determining whether our observations can lead to a general method for selective nuclear halogenation of alkylbenzenes.

EXPERIMENTAL

Interaction of Nitrobenzenesulphonyl Chlorides, Aluminium Chloride, and Aromatic Hydrocarbons.—General procedure. The requisite molecular proportion of finely-ground aluminium chloride was added rapidly to a stirred solution of the sulphonyl chloride (0.02 mole) in the aromatic hydrocarbon (100 ml.) at room temperature (18–24°). The cherry-red solution was protected from moisture while stirring was continued for the selected time. Reduction of the sulphonyl chloride was indicated by the evolution of hydrogen chloride and the separation of a viscous brown oil. The mixture was decomposed by the addition of ice-water (250 ml.). The organic layer (*A*) was separated and washed successively with dilute sodium carbonate (2 × 25 ml.) and water (2 × 50 ml.). The combined aqueous layer and alkali washings were adjusted to pH 7, the aluminium hydroxide was removed, and the filtrate was concentrated to about 50 ml. under reduced pressure. Acidification of the cooled (0°) solution by dropwise addition of 50% sulphuric acid liberated the sulphinic acid, which was filtered off or extracted with chloroform. The dried (MgSO₄) organic layer (*A*) was distilled (the last traces under reduced pressure) and the distillate was collected in a receiver at –70°. The residual sulphone and unchanged sulphonyl chloride were separated by converting the latter into the sulphonamide, which was removed by means of dilute alkali. The distillate, consisting of aromatic hydrocarbon and aryl halide, was analysed by gas-liquid chromatography on a 2 m. column of Silicone oil on Celite at 135° for benzene, 175° for toluene, and 215° for mesitylene. In each instance, the apparatus was calibrated against mixtures of known composition.

Chloromesitylene.—To a stirred solution of *o*-nitrobenzenesulphonyl chloride (22.1 g.) in mesitylene (120 ml.) kept at 15–20° by external cooling was added, in portions, finely-ground aluminium chloride (27 g.). After 5 hr., further sulphonyl chloride (22.1 g.) was added, followed by aluminium chloride (27 g.). After a further 5 hr. the mixture was treated with ice-water as described above; *o*-nitrobenzenesulphinic acid (76%) was isolated. The bulk of the mesitylene (b. p. 62–64°/15 mm.) was distilled from the washed and dried organic layer through a short column. Fractionation of the residue through a 5 cm. Vigreux column provided chloromesitylene (24.8 g., 80%; b. p. 90–94°/15 mm.; b. p. 204–206°;⁸ n_D^{20} 1.52138. Brown *et al.*⁹ give n_D^{30} 1.52119), whose infrared and ultraviolet spectra were identical with those of authentic^{10,11} chloromesitylene. The dinitro-derivative, obtained almost quantitatively by the procedure of Fittig and Hoogewerff,⁸ did not depress the m. p. of authentic dinitrochloromesitylene.

⁷ Gherseti, *Boll. sci. Fac. Chim. ind. Bologna*, 1963, **21** (4), 228.

⁸ Fittig and Hoogewerff, *Annalen*, 1869, **150**, 323.

⁹ Brown, Bruyne, and Gross, *J. Amer. Chem. Soc.*, 1934, **56**, 1291.

¹⁰ Wyman, Wang, and Freeman, *J. Org. Chem.*, 1963, **28**, 3173.

¹¹ McBee, *Ind. Eng. Chem.*, 1947, **39**, 393.

Sulphonyl chlorides,¹² sulphinic acids,^{13,14} and sulphones,^{2,15} prepared by standard procedures, had the physical characteristics ascribed in the literature. Aromatic hydrocarbons were of AnalarR grade.

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¹² Meerwein *et al.*, *Chem. Ber.*, 1957, **90**, 841.

¹³ Kharasch and Chalkey, *J. Amer. Chem. Soc.*, 1921, **43**, 612.

¹⁴ Limpricht, *Ber.*, 1892, **25**, 75; 3477.

¹⁵ Ullman and Pasdermadjian, *Ber.*, 1901, **34**, 1151.
