Preparation of Arenesulphonyl Chlorides from Grignard Reagents

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Reaction of phenylmagnesium bromide with excess of sulphuryl chloride in ether–hexane at 0° gives benzenesulphonyl chloride and bromide in a combined yield of at least 58%. Substituted sulphonyl halides, $YC_6H_4{\cdot}SO_2X$ (Y = *o*-Me, *m*-Me, *m*-Cl, and *m*-CF_3), are produced similarly in comparable yields. Diphenylmagnesium, diphenylcadmium, or phenyl-lithium under similar conditions give somewhat smaller yields of benzenesulphonyl halides. Use of arylmagnesium chlorides, ArMgCl (Ar = Ph, *o*-$MeO{\cdot}C_6H_4$, *p*-$Me_3Si{\cdot}C_6H_4$, and C_6Cl_5), in tetrahydrofuran–hexane at 0° gives pure arenesulphonyl chlorides in yields of 53–64%.

Reactions of phenylethynylmagnesium chloride and of some benzylmagnesium chlorides with sulphuryl chloride in ether–hexane have also been studied.

Of the two standard methods for direct attachment of chlorosulphonyl groups to aromatic nuclei, *viz.* (*a*) chlorosulphonation of an aromatic compound,[1] and (*b*), treatment of the arenediazonium ion with sulphur dioxide in acetic acid in presence of cuprous chloride,[2] the first has the serious disadvantage that a mixture of isomers is usually formed, while the second is restricted to systems for which arenediazonium ions can be satisfactorily obtained.

Since alkanesulphonyl chlorides can be obtained in good yields from the reaction between alkylmagnesium halides and sulphuryl chloride,[3] one would expect that arenesulphonyl chlorides could be prepared analogously, but previous attempts have been unpromising. Thus, phenylmagnesium bromide reacted with an excess of sulphuryl chloride in ether at 10° to give a mixture of benzenesulphonyl chloride and bromide in a combined yield of 5% (determined as the sulphonamide).[3] We have now found that satisfactory yields of sulphonyl halides can be obtained from reactions in ether–hexane; for example, addition of an ethereal solution of phenylmagnesium bromide to excess of sulphuryl chloride in hexane at 0° gave a mixture of benzenesulphonyl chloride and bromide in a combined yield of 58% (determined as benzenesulphonamide). With a reaction temperature of −20 to −30°, only a 40% yield of benzenesulphonamide was obtained. A similar reaction at 0° gave

[1] R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, 1965, pp. 100—110.

[2] H. Meerwein, G. Dittmar, R. Göllner, K. Hafner, F. Mensch, and O. Steinfort, *Chem. Ber.*, 1957, **90**, 841.

[3] F. Cherbuliez and O. Schnauder, *Helv. Chim. Acta*, 1923. **6**, 249.

satisfactory results with substituted phenylmagnesium halides (*o*- and *m*-methyl, *m*-chloro-, and *m*-trifluoromethyl compounds); the highest yield of the sulphonamide, 60%, was obtained from *m*-bromochlorobenzene.

The use of arylmagnesium bromide is satisfactory for the preparation of sulphonamides (or sulphonic acids) but not for that of pure arenesulphonyl chlorides, since a mixture of chloride and bromide is formed, and, moreover, the bromides undergo substantial decomposition on distillation of the mixture. To avoid formation of the arenesulphonyl bromide we tried two approaches. The first involved precipitation of magnesium bromide from the ethereal solution with dioxan, and addition of the solution of diphenylmagnesium thus formed to sulphuryl chloride in hexane; a 42% yield of benzenesulphonyl chloride was thereby obtained. The second, and more satisfactory, approach involved preparation of the arylmagnesium chloride from the aryl chloride in tetrahydrofuran, and subsequent reaction as before; this gave pure benzenesulphonyl chloride in 64% yield, and *o*-methoxy-, *p*-trimethylsilyl-, and pentachloro-benzenesulphonyl chloride in yields of 53, 54, and 62%, respectively. (The *p*-trimethylsilyl compound is an example of a sulphonyl chloride which could probably not be made *via* the arenediazonium ion.)

We also briefly investigated the reaction of phenyllithium and of diphenylcadmium with sulphuryl chloride. Phenyl-lithium, made from bromobenzene in ether, was added to an excess of sulphuryl chloride in hexane at −20 to −30° to give mixed benzenesulphonyl halides in 44% yield, lower yields being obtained from reactions carried out at −60° or 0°. Diphenylcadmium, made from cadmium chloride and phenylmagnesium bromide in ether, was treated with sulphuryl chloride in hexane at 0° to give mixed benzenesulphonyl halides in 38% yield.

We attempted to extend our method to preparation of an alkynesulphonyl chloride but reaction of phenylethynylmagnesium chloride with 2 molar equivalents of sulphuryl chloride in ether–hexane at 0° unexpectedly gave αβ-dichlorostyrene-β-sulphonyl chloride as the major product. With a 1 : 1 molar ratio of reactants, phenylchloroacetylene was obtained in 48% yield; thus, of two plausible routes to αβ-dichlorostyrene-β-sulphonyl chloride in presence of excess of sulphuryl chloride [represented by equations (1) and (2)], the first seems the more likely. The possibility cannot be ruled out, however, that the compound $PhC{\equiv}C{\cdot}SO_2Cl$ is indeed first formed, but readily loses sulphur dioxide to give phenylchloroacetylene.

$$PhC{\equiv}C{\cdot}MgCl + SO_2Cl_2 \longrightarrow PhC{\equiv}C{\cdot}Cl \xrightarrow{SO_2Cl_2} PhCCl{=}CCl{\cdot}SO_2Cl \quad (1)$$

$$PhC{\equiv}C{\cdot}MgCl + SO_2Cl_2 \longrightarrow PhC{\equiv}C{\cdot}SO_2Cl \xrightarrow{SO_2Cl_2} PhCCl{=}CCl{\cdot}SO_2Cl + SO_2 \quad (2)$$

Use of ether–hexane for the reaction between sulphuryl chloride and benzylmagnesium chloride led to a better yield of phenylmethanesulphonyl chloride than was previously obtained with ether alone.[3] *p*-Chlorophenylmethanesulphonyl chloride was obtained analogously. For benzyl compounds, however, the method is effectively limited to sulphonyl halides which can be isolated by crystallization, since distillation results in extensive loss of sulphur dioxide and formation of the corresponding benzyl chloride. Thus, *p*-trimethylsilylbenzylmagnesium chloride appeared to react normally with sulphuryl chloride, but the product could not be be crystallized, and extensive decomposition occurred on distillation; only a very small amount of the desired product (characterized as the sulphonamide) was obtained, the major part of the distillate being *p*-trimethylsilylbenzyl chloride.

EXPERIMENTAL

Preparation of Arenesulphonyl Halides and Amides.—(a) *Use of arylmagnesium bromides.* The Grignard reagent prepared from bromobenzene (31 g., 0·20 mole) and magnesium turnings (5·3 g., 0·22 g.-atom) in ether (120 ml.) was added slowly to sulphuryl chloride (54 g., 0·40 mole) in hexane (120 ml.) kept at 0°. The reaction mixture was stirred for 8—10 hr. at room temperature and then treated with water. The organic layer was separated, dried (Na_2SO_4), and distilled to give material, b.p. 75—85°/1·0 mm., which was shown by v.p.c. to be mainly benzenesulphonyl bromide together with some benzenesulphonyl chloride. The combined yield of the halides, as measured by their conversion into benzenesulphonamide, was 58%.

When the reaction was carried out at −20° to −30° the mixed halides were obtained in 44% yield. Yields were not improved when the water treatment was omitted and work-up was carried out under anhydrous conditions.

Substituted benzenesulphonyl halides prepared by this method were not isolated, the solvents and excess of sulphuryl chloride being removed under reduced pressure after the coupling reactions and the residue being treated directly with aqueous ammonia to give *o*-methyl- (42%), m.p. 157° (lit.,[4] 153—154°), *m*-methyl- (58%), m.p. 109° (lit.,[5] 108°), *m*-chloro- (60%), m.p. 146° (lit.,[6] 147°), and *m*-trifluoromethyl-benzenesulphonamide (52%), m.p. 115—116° (lit.,[7] 111—112°).

(b) *Use of diphenylmagnesium.* Phenylmagnesium bromide (0·20 mole) in ether (120 ml.) was treated with anhydrous dioxan (40 ml.) and the mixture was stirred for 3 hr. at room temperature; the precipitated magnesium bromide–dioxan complex was then filtered off. The filtrate was added to sulphurylchloride (0·40 mole) in hexane at 0°, and the mixture was stirred for 2 hr. at 0°. Addition of water, followed by separation, drying, and fractional distillation of the organic layer gave benzenesulphonyl chloride (42%), b.p. 73—75°/2 mm.

(c) *Use of diphenylcadmium.* Anhydrous cadmium chloride (0·10 mole) was added to the Grignard reagent prepared from bromobenzene (0·20 mole) and magnesium

[4] R. Graf, *Chem. Ber.*, 1959, **92**, 509.
[5] A. A. Spryskov and T. I. Yakovleva, *Zhur. obshchei Khim.*, 1957, **27**, 239.
[6] C. Paal, Ber., 1901, **34**, 2748.
[7] H. L. Yale and F. Sowinski, *J. Org. Chem.*, 1960, **25**, 1824.

in ether, and the mixture was stirred under reflux for 0·5 hr. then cooled and added to sulphuryl chloride (0·40 mole) in hexane. Working up as in (*b*) gave a mixture of benzenesulphonyl chloride and bromide, b.p. 79—80°/3 mm., and hence the sulphonamide (38%).

(d) *Use of phenyl-lithium.* Phenyl-lithium (0·50 mole) prepared from bromobenzene and lithium in ether (300 ml.) was added to sulphuryl chloride (1·0 mole) in hexane kept at −20° to −30°. The mixture was stirred for 2 hr. at room temperature then treated with water. The organic layer was separated, dried, and fractionated to give a mixture of benzenesulphonyl chloride and bromide, b.p. 105—115°/10 mm., and hence the sulphonamide (43%).

Rather low yields were obtained when the reaction was carried out at a lower (−60° to −70°) or higher (0°) temperature, and the yield was not improved by working up under anhydrous conditions.

(e) *Use of arylmagnesium chlorides.* The Grignard reagent (0·20 mole) prepared from chlorobenzene and magnesium in tetrahydrofuran [8] (100 ml.) was added slowly to sulphuryl chloride (0·40 mole) in hexane kept at 0. The mixture was stirred for 2 hr. at room temperature, then worked up to give pure benzenesulphonyl chloride (64%), b.p. 73—75°/2 mm.

Prepared similarly were *o*-methoxy- (53%), m. p. 56° (lit., [9] 56°), *p*-trimethylsilyl- (54%), b.p. 112—115°/1 mm. (lit.,[10] 160—162°/11 mm.), and pentachloro-benzenesulphonyl chloride (62%), m.p. 78° (lit.,[11] 72°).

p-*Trimethylsilylbenzyl Chloride*.—Freshly distilled thionyl chloride (0·10 mole) in carbon tetrachloride (80 ml.) was added to *p*-trimethylsilylbenzyl alcohol [12] (0·10 mole). The mixture was heated under reflux and then distilled to give p-*trimethylsilylbenzyl chloride* (61%), b.p. 60—63°/0·7 mm. (Found: C, 60·3; H, 7·7. $C_{10}H_{15}ClSi$ requires C, 60·4; H, 7·6%).

Preparation of Arylmethanesulphonyl Chlorides.—(a) *Phenyl- and* p-*chlorophenyl-methanesulphonyl chloride.* The Grignard reagent (0·20 mole) prepared from benzyl chloride in ether (100 ml.) was added to sulphuryl chloride (0·40 mole) in hexane (100 ml.) at 0°. The mixture was stirred at room temperature for 2 hr. and then filtered. Solvents and excess of sulphuryl chloride were removed under reduced pressure from the filtrate, and the residue was recrystallised from light petroleum to give phenylmethanesulphonyl chloride (25·8 g., 68%), m.p. 94—95° (lit.,[3] m.p. 92°).

p-Chlorophenylmethanesulphonyl chloride (63%), m.p. 95° (lit.,[13] 93—94°), was prepared similarly.

(b) p-*Trimethylsilylphenylmethanesulphonyl chloride.* The Grignard reagent prepared from *p*-trimethylsilylbenzyl chloride (0·20 mole) in ether was added to sulphuryl chloride (0·40 mole) in hexane at 0°. The mixture was stirred at room temperature and filtered and then solvents and excess sulphuryl chloride were removed under reduced pressure from the filtrate; attempted crystallization was unsuccessful. On distillation, extensive decomposition occurred and the main product obtained was *p*-trimethylsilylbenzyl chloride (32 g., 80%), together with a small amount of higher boiling material, b.p. 115—117°/0·6 mm. The latter was treated with aqueous ammonia to give p-*trimethylsilylphenylmethanesulphonamide*, m.p. 132—134° (from hexane) (Found: C, 48·9; H, 6·9; N, 5·9. $C_{10}H_{17}NO_2SSi$ requires C, 49·3; H, 7·0; N, 5·75%).

Reactions between Phenylethynylmagnesium Chloride and Sulphuryl Chloride.—(a) Phenylethynylmagnesium chloride (0·10 mole) (prepared from phenylacetylene and one equivalent of butylmagnesium chloride) in tetrahydrofuran (80 ml.) and sulphuryl chloride (0·10 mole) were added simultaneously to ice-cold hexane (80 ml.). The mixture was subsequently stirred for 2 hr. and then treated with water. Working-up gave phenylchloroacetylene (48%) b.p. 60—62°/10 mm. (lit.,[14] b.p. 68°/12 mm.), the i.r. spectrum of which was identical with that of an authentic specimen.

(b) Phenylethynylmagnesium chloride (0·10 mole) in tetrahydrofuran (80 ml.) was added to sulphuryl chloride (0·20 mole) in hexane at 0°. The mixture was stirred for 5 hr., and then set aside overnight after which it was treated with water. Working-up gave material (6 g.), b.p. 135—140°/0·4 mm., which, in time, solidified and was recrystallized from light-petroleum (b.p. 40—60°) to give αβ-*dichlorostyrene*-β-*sulphonyl chloride*, m.p. 75° (Found: C, 35·5; H, 1·85; Cl, 39·1; S, 11·7. $C_8H_5Cl_3O_2S$ requires C, 35·3; H, 1·84; Cl, 39·2; S, 11·8%). The ^1H n.m.r. spectrum showed the expected pattern for the aromatic protons.

Treatment of the sulphonyl chloride with aqueous ammonia gave the corresponding *sulphonamide*, m.p. 174—176° (Found: C, 38·4; H, 2·7; Cl, 27·8; N, 5·6. $C_8H_7Cl_2NO_2S$ requires C, 38·4; H, 2·8; Cl, 28·4; N, 5·6%).

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