Easy Perchlorination of Nitrogen-, Oxygen-, Fluorine-, Silicon-, Sulphur-, and Tin-substituted Aryl Compounds

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Summary Aryl compounds containing a variety of heteroatomic substituents give good yields of the corresponding perchloro-derivatives when treated with a mixture of sulphur monochloride and anhydrous aluminium chloride in sulphuryl chloride solution; in aryl fluorides, such as hexafluorobenzene, considerable replacement of fluorine by chlorine takes place.

In 1922 Silberrad utilised a mixture of sulphur monochloride and anhydrous aluminium chloride in sulphuryl chloride solution to polychlorinate benzene.[1] Subsequently, Ballester and his co-workers discovered a different combination of S_2Cl_2–$AlCl_3$–SO_2Cl_2 (reagent BMC) which was more effective as a perchlorinating agent for aromatic hydrocarbons and related molecules under mild conditions.[2]

We have employed reagent BMC for the perchlorination of aryl derivatives of *p*-block elements; few pentachlorophenyl derivatives of these elements have previously been described, and the preparations of known derivatives are often lengthy or proceed in low yield.[3] By contrast, good yields are obtained in a single step using BMC, as shown in the Table; in most instances no cleavage to yield C_6Cl_6 occurred, and a single recrystallization ($CHCl_3$ or CCl_4) afforded analytically pure products.†

Table

Products of chlorination of aryl compounds with S_2Cl_2–$AlCl_3$–SO_2Cl_2

Compound	Reaction time/h	Products (yield/%)
Ph_3CH[a]	7	$(C_6Cl_5)_3CH$ (91), C_6Cl_6 (trace)
Ph_3SiH	4	$(C_6Cl_5)_2SiCl_2$[b] (35), $(C_6Cl_5)_3SiCl$[c] (trace) C_6Cl_6 (50)
Ph_3N	2	$(C_6Cl_5)_3N$ (60)
Carbazole	2	$(C_6Cl_4)_2NH$ (51)
Ph_3P	3	Ph_3PO (77)
Ph_3As	2	Ph_3AsO (94)
Ph_2O	2	$(C_6Cl_5)_2O$[d] (69)
PhSH	2·5	$(C_6Cl_5)SCl$[e] (90), C_6Cl_6 (trace)
Ph_2S	2	$(C_6Cl_5)_2S$ (59)
$Ph_2CHC_6H_4F$-*p*	5	$(C_6Cl_5)_2CHC_6Cl_4F$-*p* (91), C_6Cl_6 (trace)
$Ph_2CHC_6F_5$	12	$(C_6Cl_5)_2CHC_6F_5$ (15), C_6Cl_6 (trace)
(*p*-$FC_6H_4)_3CH$	3	C_6Cl_6 (28), $(C_6Cl_5)_2CHC_6H_4F$-*p* (22), C_6Cl_5F (5), (*p*-$FC_6Cl_4)_2CH(C_6H_2Cl_2$-F-*p*) (trace)
PhF	4	C_6Cl_5F (65), C_6Cl_6 (16)
C_6F_6	12	C_6Cl_6 (24), C_6Cl_5F (trace)

[a] Ref. 2. [b] Ref. 3a. [c] Identified by mass spectrometry: *m/e* 803·4697u; $^{12}C_{18}{}^{35}Cl_{16}{}^{28}Si$ requires *m/e* 803·4785u. [d] Ref. 3d. [e] Ref. 3c.

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† Satisfactory analytical and spectroscopic data were obtained for new compounds.

Ph_3M (M = P or As) underwent no nuclear chlorination but were oxidised to Ph_3MCl_2 which were hydrolysed to Ph_3MO during work-up, while Ph_3MO were recovered unchanged. Similarly, $PhSO_2Cl$, Ph_2SO, and Ph_2SO_2 (in contrast to PhSH and Ph_2S) were all recovered unchanged, as was $(p\text{-}O_2NC_6H_4)_3CH$. Both Ph_2SiH_2 and Ph_3SnCl yield, with reagent BMC, a chlorocarbon $C_{12}Cl_{12}$ [*m/e* 563·6275u {u = $(10^3N_A)^{-1}$ kg}; $^{12}C_{12}{}^{35}Cl_{12}$ requires 563·6262u] which has proved too insoluble for the determination of its ^{13}C n.m.r. spectrum, and which is at present structurally uncharacterised.

Triphenylmethane, *p*-fluorophenyldiphenylmethane, and pentafluorophenyldiphenylmethane all gave small yields of hexachlorobenzene in addition to the expected perchloroderivative. Unexpectedly, tris(*p*-fluorophenyl)methane gave hexachlorobenzene as the main product together with small amounts of pentachlorofluorobenzene and a mixture of compounds from incomplete chlorination of the reactant. This result implied that replacement of fluorine by chlorine had taken place and, accordingly, fluorobenzene and hexafluorobenzene were subjected to the same treatment. An excellent yield of a mixture of pentachlorofluorobenzene and hexachlorobenzene was obtained from the former, and in hexafluorobenzene all six fluorines were replaced by chlorine to give hexachlorobenzene. Complete replacement of fluorine was unexpected under the mild conditions of reagent BMC, but similar substitutions, effected by aluminium chloride, have previously been observed with fluoro-alkenes[4] and hexafluorobenzene.[5]

Perchlorination occurred with relative ease for aromatic compounds containing electron-releasing substituents. On the other hand, compounds containing electron-withdrawing substituents [$-NO_2$, $-P(O)R_2$, $-As(O)R_2$, $-SO_2R$, *etc.*] were recovered unchanged. This pattern of reactivity is akin to that found in many electrophilic aromatic substitutions, and suggests that the perchlorination by BMC may also be controlled by a step involving attack on the aromatic nucleus by an electrophile.

By contrast, only strongly deactivated species undergo perbromination by dibromoisocyanuric acid in sulphuric acid;[6] activated compounds suffer extensive cleavage and oxidation.

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