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$AlCl_3$ - Catalyzed Regiospecific Alkylation of Aromatics with Chlorobenzotrifluorides : A High Yield Preparation of 1,1 - Dichlorodiphenylmethanes

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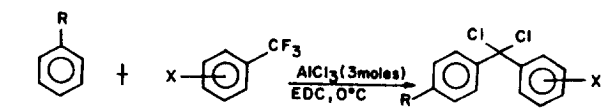
Abstract : *Chlorobenzotrifluorides (2/3), under typical Friedel - Crafts reaction conditions, react efficiently with aromatic compounds (1) to afford 1,1-dichlorodiphenylmethanes, (4) in excellent yield and purity.* Copyright © 1996 Elsevier Science Ltd

Friedel - Crafts alkylations allow C-C bond formation in both aromatic and aliphatic systems and are of substantial synthetic and industrial importance. Benzotrichloride has been extensively used by us as a benzoylating agent under Friedel - Crafts reaction conditions to prepare a variety of benzophenones.[1] Subsequently, we found it possible to isolate the intermediate Ph_2CCl_2 (90% yield), presumably formed in such reactions, by simply carrying out the aqueous work-up without any further heating. Promoted by this finding, we became interested in preparing Ar_2CF_2, the fluorine analogue, by subjecting the corresponding $ArCF_3$ to Friedel - Crafts conditions. Enigmatically, the reaction took altogether a different course in furnishing the halogen - exchanged product, 1,1-dichlorodiphenylmethanes, **4**, the results of which are presented in this communication (Scheme 1).



1, R = H, Me
X, OMe

2, X = 2-Cl
3, X = 4-Cl

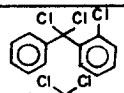
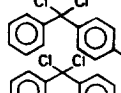
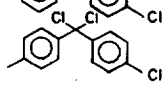
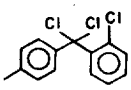
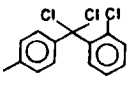
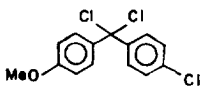
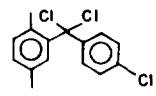
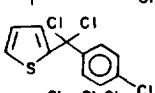
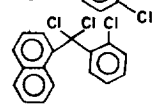
4
Yield : >90%

SCHEME - 1

The synthesis of perchloro compounds has received extensive interest in pharmaceutical and agrochemical (as pesticides) industry.[2] Generally, these compounds are synthesized by the chlorination of the corresponding carbonyl compounds.[3]

In order to gauge the scope and generality, we have subjected a variety of aromatic substrates to Friedel - Crafts alkylation with $ArCF_3$ to produce the perchloro compounds, **4**, in excellent yields (Table 1). All the perchloro compounds thus synthesized[4] exhibit a characteristic signal around δ 91 in their ^{13}C NMR spectra confirming the presence of *gem-* dichloro carbon moiety. Further, attempts to purify the bromo perchloro compound (ENTRY 4) (m.p. 58°C) through column chromatography (SiO_2 and neutral Al_2O_3) resulted in the formation of the corresponding ketone (m.p. 139°C). It is notable that the alkylation proceeds in a highly regiospecific manner *(para-* selectivity) as no *ortho-* isomer is obtained (^{13}C NMR). However, phenolic and anilinic substrates gave mixtures of products difficult to separate. The reaction possibly proceeds in two steps: (1) C-F bond of $ArCF_3$ being extremely reactive undergoes a facile exchange[5] with $AlCl_3$ to produce $ArCCl_3$, (2) $ArCCl_3$ on reaction with $AlCl_3$ generates ArC^+Cl_2 which in turn alkylates arenes. In summary, this study provides a convenient and efficient method for the preparation of *gem-* dichloro compounds, **4**, in excellent yields.

Table I : $AlCl_3$ catalyzed reaction of benzotrifluoride with aromatic compounds.

Entry	Substrate 1	$ArCF_3$ 2/3	Product[a] 4	Yield[b] (%)
1		2		96
		3		98
2		3		97
3		2		92
4		2		91
5		3		97
6		3		94
7		3		95
8		2		90

a : Characterized by IR, ^1H & ^{13}C NMR, MS and elemental analysis ; b : isolated.

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References and Notes :

1. Paul, V., Sudalai, A., Daniel, T. and Srinivasan, K.V. *Tetrahedron Lett.*, 1994, **35**, 2601; and references cited therein.

2. T. Chivers, in *The Chemistry of Carbon-Halogen bond*, ed. by S. Patai, J. Wiley & Sons, Chichester, New York, 1973, p.918.

3. Newman, M.S. and Sujeeth, P.K., *J. Org. Chem.* 1978, **43**, 4367 and references cited therein.

4. To a cooled (0°C) and stirred solution of anhyd. $AlCl_3$ (0.033 mol) in 1,2-dichloroethane (15 ml) was added 4-chlorobenzotrifluoride (0.011 mol) upon which a red-colored complex was formed. To this complex was added p-xylene (0.011 mol) and it was stirred for 3h at 0°C. It was then poured into ice, stirred for 5 min. and extracted with dichloromethane. Distillation of the solvent gave the pure perchloro p-xylene product (94%); m.p. 84°C; ^1H NMR (90 MHz, $CDCl_3$) : δ 1.9 (3H, s, CH_3), 2.5 (3H, s, CH_3), 7.0 (2H, br.s, ArH), 7.25 (2H, d, J = 8 Hz, ArH), 7.5 (2H, d, J = 8 Hz, ArH) and 7.9 (1H, br.s., ArH); ^{13}C NMR (50.3 MHz, $CDCl_3$) : δ 21.4, 21.7, 91.5, 127.9, 128.7, 128.8, 130.5, 133.0, 133.4, 135.0, 135.5, 139.8 and 143.5; MS : m/z (% rel. intensity) : 300 (M^+, 5), 263 (100), 227 (40), 212 (12), 192 (98), 178 (43), 165 (14), 152 (8), 114 (18), 106 (15), 94 (28) and 82 (20).

5. Henne, A.L. and Newman, M.S. *J. Am. Chem. Soc.*, 1938, **60**, 1697.

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