An Easy, High-yield Synthesis of Highly Chlorinated Mono-, Di- and Triarylmethanes

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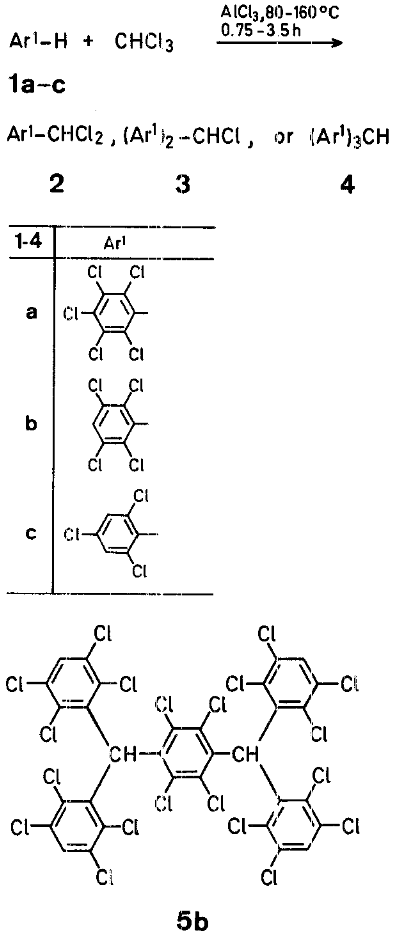
A simple, direct, high-yield Friedel-Crafts synthesis of highly chlorinated, overcrowded αH-aryl, αH-diaryl, and αH-triarylmethanes is described. The latter compounds are most valuable chemical precursors of inert free radicals, which are frequently obtained through otherwise cumbersome, medium-to-low-yield aromatic chlorination of triphenylmethane derivatives. The condensation is performed with aluminium chloride at temperatures ranging from 70 to 160 °C. The substrate is a benzene with all its hydrogens flanked by two *ortho* chlorines. The alkylating component is chloroform, αH-heptachlorotoluene (**2a**) or αH-undecachlorodiphenylmethane (**3a**). For comparison, the condensation with a few non-sterically-hindered substrates has also been performed.

It is generally believed that aromatic Friedel-Crafts alkylations take place through benzenium complexes[1]. When both the aromatic substrate and the alkylating (carbenium ion) agent are highly overcrowded polychloro compounds, the appropriate complex, in some cases, cannot even be constructed with the Stuart-Briegleb scale atomic models. Therefore it was assumed that this type of alkylation is highly hindered. Furthermore, the accumulation of chlorines with their negative inductive effects in both the substrate and the alkylating agent disfavours the condensation. For these reasons, although we have been engaged in perchloro-organic chemistry since 1948, this particular condensation has never been tried. We have synthesized a considerable number of highly chlorinated mono-, di-, and triarylmethanes[2-7], most of them as precursors of stable or inert carbon free radicals[2,4-7]. However, their synthesis are either medium-yield chlorinations of the parent hydrocarbons[2,4,7], or multistep procedures with very low overall yields[2,5].

We report here the first Friedel-Crafts condensation between polychlorobenzenes and highly chlorinated alkylating agents by means of aluminium chloride. This surprising condensation leads to highly overcrowded arylmethanes, and the relevant method is high-yielding, easy, and straightforward. In this connection it is mentioned that closely related chlorocarbons such as perchlorodiphenylmethane[4] and perchloro-9-phenylfluorene[7] react easily with aluminium chloride giving the corresponding stable carbenium ions. Consequently it is assumed that carbenium ions are intermediates in the condensations here described. Two basic procedures are used illustrated by the syntheses of mono- and symmetrical polyarylmethanes **2**, **3**, **4** (Procedure A, Scheme A) and unsymmetrical polyarylmethanes **6**, **7**, **8** (Procedure B, Scheme B).



Scheme A

Using chloroform as the alkylating agent in Procedure A, the ratio of polychlorobenzene **1** to chloroform is varied to obtain selectively the mono- (**2**), di- (**3**), or triarylmethane (**4**) as the main product (Table 1).

Table 1. Condensation of Polychlorobenzenes **1a–c** with Chloroform

Substrate	Ratio of **1**/$CHCl_3$	Product	Reaction Conditions Temperature [°C]/Time [h]	Yield [%] based on **1**	m.p.[a] [°C]	Molecular Formula[b] or Lit. m.p. [°C]
1a	1/1	**2a**[c]	80°/3	96	123–124°	119–121°[3]
1a	1.95/1	**3a**[d] (≡**6a**)	130°/3.5	89 (85)[e]	232–233.5°	231–233°[4]
1a	3.30/1	**4a**[c] (≡**8a**)	150°/2.5	80 (88)[e]	320° (dec)	320° (dec)[4]
1b	9.00/1	**4b**[d]	160°/0.75	22 (65)[e], (61)[b]	294–295°	$C_{19}H_4Cl_{12}$ (657.7)
1c	9.00/1	**4c**[c]	80°/2.5	28 (84)[e], (77)[f]	246–248°	$C_{19}H_7Cl_9$ (554.3)

[a] Not corrected.
[b] Satisfactory microanalyses obtained: C ±0.1, H ±0.0, Cl ±0.3.
[c] Product purified by digestion with pentane.
[d] Product purified by column chromatography (silica gel/hexane).
[e] Yield based on chloroform.
[f] Yield based on converted **1**.

Table 2. Condensation of Polychlorobenzenes **1a–e** with **2a** or **3a**

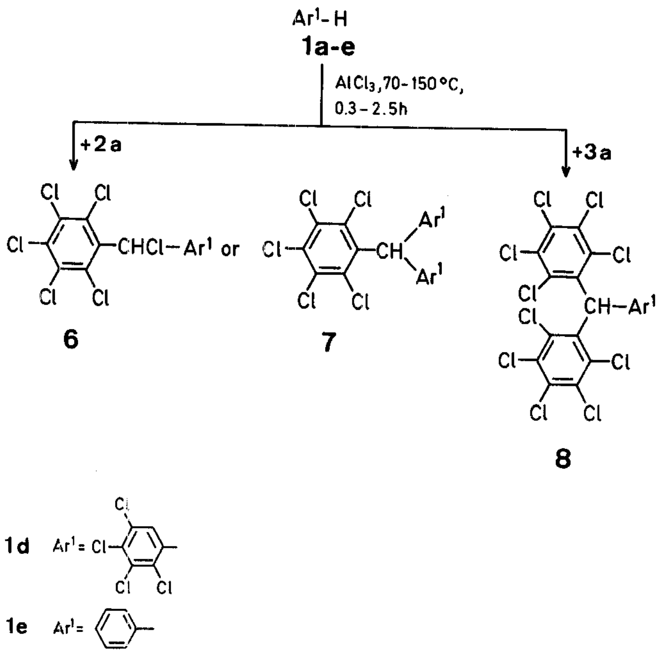
Substrate	Alkylating Agent	Ratio of **1**/**2a** or **3a**	Product	Reaction Conditions Temperature [°C]/Time [h]	Yield [%] based on **2a** or **3a**	m.p.[a] [°C]	Molecular Formula[b] or Lit. m.p. [°C]
1a	**2a**	1/1	**6a**[c] (≡**3a**)	140°/0.3	82	232–233.5°	231–233°[4]
1c	**2a**	1/1	**6c**[c]	120°/0.3	78	190–193°	$C_{13}H_3Cl_9$ (478.2)
1b	**2a**	3/1	**7b**[c]	140°/1.5	67 (74)[d]	234–235.5°	$C_{19}H_3Cl_{13}$ (692.1)
1a	**3a**	1/1	**8a**[e] (≡**4a**)	90°/2.5	85	320° (dec)	320° (dec)[4]
1b	**3a**	2/1	**8b**[c]	150°/1.5	71 (78)[d]	239–240.5°	238–240°[5]
1c	**3a**	1/1	**8c**[e]	85°/2.5	96	330–331°	$C_{19}H_3Cl_{13}$ (692.1)
1d	**3a**	1/1	**8d**[e]	90°/0.5	85	320–321°	$C_{19}H_2Cl_{14}$ (726.6)
1e	**3a**	≫1/1	**8e**[e]	70°/0.5	85	253–254°	$C_{19}H_6Cl_{10}$ (588.8)

[a] Not corrected.
[b] Satisfactory microanalyses obtained: C ±0.2, H ±0.2, Cl ±0.2.
[c] Product purified by digestion with pentane.
[d] Yield based on converted **1**.
[e] Product purified by column chromatography (silica gel/hexane).

Table 3. Spectral Data of New Compounds prepared

Product	I.R. (KBr)[a] ν [cm^{-1}]	^1H-N.M.R. (CCl_4/D_2O)[b] δ [ppm]	U.V. (c-C_6H_{12})[c] λ_{max} [nm] (ε)
4b	3120, 3075, 2930, 1545, 1410, 1388, 1350, 1320, 1164, 1098, 975, 865, 780, 707, 690, 647, 627, 490	6.95 (s, 1H, CH); 7.61 (s, 3H_{arom})	217 (110000); 241 (52500, sh); 284 (1650, sh); 291 (2450); 300 (2800)
4c	3120, 3080, 2905, 1570, 1540, 1430, 1420, 1365, 1245, 1185, 1170, 1140, 1130, 895, 854, 815, 800, 670, 570, 440	6.90 (s, 1H, CH); 7.09 (d, 3H_{arom}, J = 2 Hz)[d]; 7.22 (d, 3H_{arom}, J = 2 Hz)[d]	213 (93000); 230 (44500, sh); 243 (35500); 270 (590); 278 (725); 286 (565)
6c	3080, 2980, 1574, 1542, 1360, 1307, 860, 792, 675, 573	6.98 (s, 1H, CH); 7.31 (s, 2H_{arom})	218 (69200); 240 (23000, sh); 287 (570, sh); 294 (660); 305 (650)
7b	3110, 3060, 1545, 1390, 1350, 1292, 1162, 865, 805, 705, 640, 498	6.99 (s, 1H, CH); 7.61 (s, 2H_{arom})	220 (111600); 283 (1130, sh); 292 (2000); 302 (2250)
8c	3075, 1575, 1545, 1422, 1352, 1325, 1310, 1295, 1242, 860, 810, 800, 678, 577	6.90 (s, 1H, CH); 7.30 (d, 1H_{arom}, J = 2 Hz)[d]; 7.43 (d, 1H_{arom}, J = 2 Hz)[d]	218 (114000); 280 (710); 291 (790); 303 (705)
8d	3160, 1530, 1408, 1360, 1340, 1285, 867, 833, 800, 778, 732, 708, 678, 657, 640, 510	6.75 (s, 1H, CH); 6.85 (s, 1H_{arom})	220 (112900); 292 (1050); 302 (960, sh)
8e	3095, 3060, 3030, 2920, 1495, 1450, 1350, 1310, 1290, 855, 810, 790, 740, 695, 682, 663, 560, 550, 540	6.78 (s, 1H, CH); 7.31 (s, 6H_{arom})	213 (95500); 291 (620); 301 (570)

[a] Perkin-Elmer 682 spectrometer.
[b] Bruker FT 80 spectrometer.
[c] Beckman Acta M VI spectrometer.
[d] The two *meta*-hydrogens are not equivalent on account of the restricted rotation of the phenyl rings due to steric repulsions among the six *ortho*-chlorines.



Scheme **B**

In procedure B, the mono- (**2**) and diarylmethanes (**3**), described above, are in turn used as alkylating agents (instead of chloroform) for the synthesis of symmetrically and unsymmetrically substituted di- (**6**) and triarylmethanes (**7** and **8**; Table 2). Also in this case, the major products obtained depend on the stoichiometric proportions of the reactants.

It should be emphasized that the reaction temperatures must be high enough to melt at least one of the reactants. Except for the reaction of 1,2,4,5-tetrachlorobenzene (**1b**) with chloroform in a molar ratio of 9:1 to give **4b** + **5b**, polycondensation products have not been isolated. Moreover, highly pure products are easily obtained by column chromatography on silica gel, followed by recrystallization. The spectral data of the new compounds are given in Table 3.

Some general advantages of these Friedel-Crafts alkylations over other conventional syntheses are:

- possibility of synthesizing symmetrically or unsymmetrically substituted highly-chlorinated polyarylmethanes containing aromatic hydrogens via one- or two-step procedures;
- use of commercially or readily available starting materials;
- shorter reaction times;
- easier purification of the reaction mixture;
- much higher yields; and
- in contrast to the exhaustive chlorination methods, the use of non-corrosive reagents, and the absence of chlorinolysis and subchlorinated products.

Tris[2,3,5,6-tetrachlorophenyl]methane (4b); Typical Procedure A:

A mixture of 1,2,4,5-tetrachlorobenzene (**1b**; 9.6 g, 44 mmol), chloroform (0.40 ml, 4.9 mmol), and aluminium chloride (0.73 g, 5.2 mmol) is heated at 160 °C for 45 min in a glass pressure vessel. The mixture is then poured on to ice/1 normal hydrochloric acid (50 ml) and extracted with chloroform (3 × 100 ml). The organic layer is washed with water (3 × 50 ml), 2% aqueous sodium hydrogen carbonate (50 ml), dried with anhydrous sodium sulfate, and evaporated. The residue is subjected to column chromatography on silica gel (650 g) eluting with hexane to give firstly unreacted starting material **1b** (6.2 g), secondly the pure triarylmethane **4b** [yield: 2.1 g (61 %, based on unrecovered **1b**); m.p. 294–295 °C (from hexane), see Tables 1 and 3], and thirdly the polycondensation product 2,3,5,6-tetrachloro-$\alpha,\alpha,\alpha',\alpha'$-tetrakis[2,3,5,6-tetrachlorophenyl]-*p*-xylene (**5b**); yield: 0.4 g (11%, based on unrecovered **1b**); m.p. > 330 °C.

$C_{32}H_6Cl_{20}$	calc.	C 35.0	H 0.6	Cl 64.5
(1099.4)	found	34.9	0.7	64.4

I.R. (KBr): ν = 3120, 3065, 1550, 1400, 1365, 1350, 1295, 1163, 1098, 868, 700, 680, 658, 495, 486 cm^{-1}.

^{1}H-N.M.R. (CCl$_4$/D$_2$O$_{st}$): δ = 7.64 (s, 4H$_{arom}$); 7.00 ppm (s, 2H, 2CH). U.V. (CHCl$_3$): λ_{max} = 284 (sh), 291, 301 nm (ε = 2900, 3150, 4000).

Bis[pentachlorophenyl]-(2,4,6-trichlorophenyl)-methane (8c); Typical Procedure B:

A mixture of 1,3,5-trichlorobenzene (**1c**; 0.90 g, 5 mmol), bis[pentachlorophenyl]methane (**3a**; 2.74 g, 5 mmol), and aluminium chloride (1 g, 7 mmol) is heated at 85 °C for 2.5 h with stirring in a dry atmosphere. The mixture is worked up as described in Procedure A to give a residue which, on digestion with pentane, gives the pure product **8c**; yield: 3.31 g (96%); m.p. 330–331 °C (see Tables 2 and 3).

$C_{19}H_3Cl_{13}$	calc.	C 33.0	H 0.4	Cl 66.6
(692.1)	found	32.8	0.2	66.5

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