Tetrahedron Letters,Vol.30,No.29,pp 3825-3828,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Maxwell Pergamon Macmillan plc

NEW SYNTHESIS OF POLYCHLORO(TRIFLUOROMETHYL)BENZENES AND HIGHLY STRAINED POLYCHLORO(TRICHLOROMETHYL)BENZENES

Juan Riera,* Juan Castañer,* José Carilla and Ana Robert

Departamento de Materiales Orgánicos Halogenados, C.I.D.
(C.S.I.C.), Jorge Girona 18-26, 08034 Barcelona, Spain

SUMMARY: Several polycloro(trifluoromethyl)benzenes have been prepared by treatment of the corresponding polychlorobenzenes with CCl_3F and $AlCl_3$. The resulting trifluoromethyl derivatives, by reaction with the same inorganic halide in CS_2, give their trichloromethyl analogues.

While 2,3,4,5,6-pentachloro-1-(trifluoromethyl)benzene (II) can be prepared by $FeCl_3$-catalyzed chlorination of benzotrifluoride (IV) with Cl_2 at high temperatures,[1,2] strained perchlorotoluene (III) cannot be obtained either by ring chlorination of benzotrichloride (V)[3] or by photochlorination of 2,3,4,5,6-pentachlorotoluene[4,5] with Cl_2 since reaction stops before the replacement of the last hydrogen atom (<u>ortho</u> or <u>alpha</u>), or chlorinolysis to hexachlorobenzene takes place. However, chlorocarbon III can be prepared through a cumbersome aromatic chlorination of 2,3,4,5-tetrachloro-1-(trichloromethyl)benzene,[6] V[7] or IV[7] by means of the reagent BMC.[8]

We report now that II can be easely prepared (77% yield) by stirring at r.t. in a pressure vessel a CCl_3F solution of pentachlorobenzene (I) with a great excess of $AlCl_3$, and chlorocarbon III (96% yield) by stirring a mixture of II with an excess of $AlCl_3$ in CS_2 at room temperature.

$$\underset{(I)}{C_6HCl_5} \xrightarrow{CCl_3F,\ AlCl_3} \underset{(II)}{C_6Cl_5CF_3} \underset{AlCl_3,\ CCl_3F}{\overset{AlCl_3\ (CS_2)}{\rightleftarrows}} \underset{(III)}{C_6Cl_5CCl_3}$$

Since CCl_3F with $AlCl_3$ undergoes disproportionation under the preceding alkylation conditions giving CCl_4, CCl_2F_2 and $CClF_3$ (IR spectrum), and I does not react with CCl_4 in the presence of $AlCl_3$, even under stronger reaction conditions (reflux temperature), formation of II is regarded as due to the alkylation of I by CCl_3F, CCl_2F_2 and/or $CClF_3$, followed by replacement of chlorine by fluorine in the resulting perhalotoluene. Accordingly, it has also been found that III, treated with CCl_3F and $AlCl_3$ in a similar manner as I, reverts almost quantitatively to II.

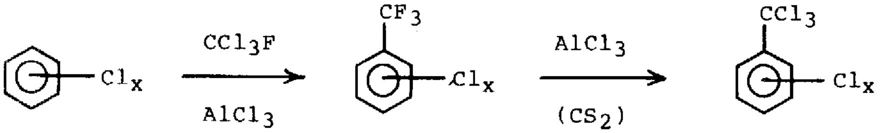
The high yield conversion of II into III can be explained by assuming that the equilibria of Scheme 1 are shifted toward the formation of III due to the presence of an excess of $AlCl_3$. The reversion of III to II, also in high yield, can be accounted for by assuming that in this case the equilibria are shifted toward the formation of II due to the disappearence of the $AlCl_3$ through its reaction with CCl_3F giving $AlCl_2F$.

$$\underset{(X,\ F\ or\ Cl)}{C_6Cl_5CX_2F} + AlCl_3 \rightleftharpoons C_6Cl_5CX_2^+\ AlCl_3F^- \rightleftharpoons C_6Cl_5CX_2Cl + AlCl_2F$$

Scheme 1

Related equilibria have been proposed to explain the conversion of $CCl_2{=}CClCClF_2$ into $CCl_2{=}CClCCl_3$ and $CCl_2{=}CClCF_3$ by the action of $AlCl_3$.[9]

Similarly to I, the treatment of polychlorobenzenes VI, IX, XII and XV with CCl_3F and $AlCl_3$ gives 2,3,4,5-tetrachloro- (VII, 92%), 2,3,4,6-tetrachloro- (X, 95%), 2,3,5,6-tetrachloro- (XIII, 77%) and 2,4,6-trichloro-1-(trifluoromethyl)benzene (XVI, 98%), respectively. These (trifluoromethyl)benzenes treated with $AlCl_3$, in a similar way as in II, are converted into their trichloromethyl analogues VIII, XI, XIV and XVII (90-96% yields).



1,2,3,4-Cl_4 (VI)	2,3,4,5-Cl_4 (VII)[10,11]	2,3,4,5-Cl_4 (VIII)[3,12,13]
1,2,3,5-Cl_4 (IX)	2,3,4,6-Cl_4 (X)	2,3,4,6-Cl_4 (XI)
1,2,4,5-Cl_4 (XII)	2,3,5,6-Cl_4 (XIII)[10]	2,3,5,6-Cl_4 (XIV)[6]
1,3,5-Cl_3 (XV)	2,4,6-Cl_3 (XVI)[14]	2,4,6-Cl_3 (XVII)[15]

Polyhalotoluenes VII, XIII and XIV had only been obtained in low yields as by-products. 2,3,4,6-Tetrachloro-1-(trifluoromethyl)benzene (X) and 2,3,4,6-tetrachloro-1-(trichloromethyl)benzene (XI) have been characterized by elemental analyses and IR, UV and ^{1}H NMR spectra.[16] In addition, X has also been characterized by ^{19}F NMR spectroscopy.[16] Furthermore, XI by treatment with 20% oleum and then with water gives 2,3,4,6-tetrachlorobenzoic acid (XVIII; 82%),[17] this confirming the structure of X.

Some general advantages of the methods here described for the synthesis of polychlorinated (trifluoromethyl)- and (trichloromethyl)-benzenes over other conventional syntheses are: 1) Possibility of synthesizing polychloro(trifluoromethyl)- and polychloro(trichloromethyl)-benzenes containing, or not aromatic hydrogens; 2) The use of commercial starting materials; 3) The use of milder reaction conditions; 4) An easier purification of the reaction mixture; 5) Much higher yields; and 6) In contrast with the exhaustive chlorination methods, the use of non-corrosive reagents, and the absence of chlorinolysis and subchlorinated products.

REFERENCES AND NOTES

1) Mc Bee, E.T.; Newcomer, J.S.; Burt, W.E.; Welch, Z.D., Natl. Nuclear Energy Ser. Div. VII, Preparative, Properties and Technol. of Fluorine and Organic Fluoro Compds., 1951 (Chem. Abstr. 1952, 46, 7987f)

2) Ligett, W.B., U.S. Pat. 2,654,789, 1953 (Chem. Abstr. 1954, 48, 12799d).

3) Harvey, P.G.; Smith, F.; Stacey, M.; Tatlow, J.C., J. Appl. Chem. (London) 1954, 4, 325.

4) Lock, G., Chem. Ber. 1933, 66, 1527; 1939, 72, 300.

5) Harvey, P.G.; Smith, F.; Stacey, M.; Tatlow, J.C., J. Appl. Chem. (London) 1954, 4, 319.

6) Ballester, M.; Molinet, J.; Castañer, J., J. Am. Chem. Soc. 1960, 82, 4254.

7) Ballester, M.; Castañer, J.; Riera, J., "Synthesis and Properties of Alkaromatic Chlorocarbons, Versatile Candidates for Thermostable Inert Materials"; A.R.L. Report 763125, U.S.A., 1973 (Chem. Abstr. 1973, 79, 136646d).

8) Fieser, L.F.; Fieser, M., "Reagents for Organic Synthesis"; Wiley; New York, 1967, p. 1131.

9) Burton, D.J.; Briney, G.C., *J. Org. Chem*. 1970, *35*, 3036.

10) Alikhanov, P.P.; Ushakov, A.A.; Kuznetsova, G.N.; Kalinachenco, V. R.; Motsarev, G.N., *Zh. Org. Khim*. 1985, *21*, 809.

11) Scott, J.A.; Tucker, A.C., *Eur. Pat. Appl*. 150,587, 1985 (*Chem. Abstr*. 1986, *104*, 68563g).

12) Ballester, M. *Anales Real Soc. Españ. Fis. Quim*. 1954, *50B*, 675.

13) Riera, J.; Castañer, J.; Armet, O.; Rovira, C., *An. Quim*. 1986, *50B*, 268.

14) Ushakov, A.A.; Motsarev, G.V.; Rozemberg, V.R.; Kolbasov, V.I.; Belova, L.V.; Chuvaeva, I.N. *Zh. Org. Khim*. 1974, *10*, 2183.

15) Tsujii, Y.; Awazu, T.; Murai, S.; Venishi, H., *Jpn. Kokai Tokkyo Koho* JP 60,142,950 (85,142,950), 1985 (*Chem. Abstr*. 1986, *104*, 50688s).

16) X: n_D^{20} 1.5380; IR (neat) ν 3080 (w), 1568 (m), 1533 (m), 1350 (s), 1270 (s), 1145 (s), 1060 (s), 815 (s), 668 (s) cm^{-1}; UV (C_6H_{12}) λ_{max} (ε) 209 (42500), 288 (1140), 297 (1330) nm; ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.60 (s); ^{19}F NMR (TFA 1% in $CDCl_3$ external standard) δ 19.88. Anal.: Calcd. for $C_7HCl_4F_3$: C, 29.6; H, 0.3; Cl, 50.0. Found: C, 29.6; H, 0.2; Cl, 50.1%.
XI: n_D^{20} 1.6338; IR (neat) ν 3120 (w), 3070 (w), 1555 (s), 1520 (s), 1400 (s), 1320 (s), 1105 (s), 930 (s), 800 (s), 768 (s), 698 (s), 625 (s) cm^{-1}; UV (C_6H_{12}) λ_{max} (ε) 212 (32500), 300 (1090 sh), 306 (1260); ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.60 (s). Anal.: Calcd. for C_7HCl_7: C, 25.3; H, 0.3; Cl, 74.7. Found: C, 25.5; H, 0.1; Cl, 74.3%.

17) XVIII: m.p. 143-4°; IR (KBr) ν 3400-2300 (broad abs.), 1720 (s), 1680 (s), 1570 (s), 1430 (m), 1330 (s), 1260 (s), 1165 (s), 870 (s), 820 (s), 615 (s) cm^{-1}. Anal.: Calcd. for $C_7H_2Cl_4O_2$: C, 32.3; H, 0.8; Cl, 54.6. Found: C, 32.3; H, 0.8; Cl, 54.5%.

(Received in UK 16 May 1989)