Journal of Fluorine Chemistry, *42* (1989) 429–433

Received: June 29, 1988; accepted: September 12, 1988

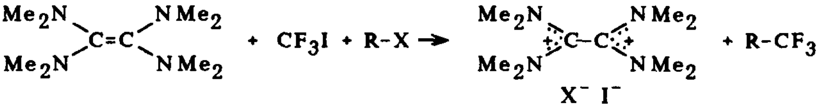
TETRAKIS(DIMETHYLAMINO)ETHYLENE/TRIFLUOROIODOMETHANE, A SPECIFIC NOVEL TRIFLUOROMETHYLATING AGENT

G. PAWELKE

Anorganische Chemie, FB 9, Universität-Gesamthochschule,
D-5600 Wuppertal (F.R.G.)

SUMMARY

At low temperatures tetrakis(dimethylamino)ethylene (I) and CF_3I form a charge transfer complex, which can act as a nucleophilic trifluoromethylating agent in polar solvents according to eqn. (1):



(1)

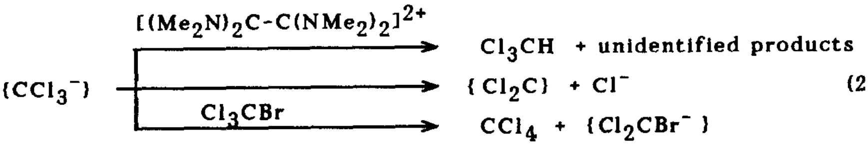
The applicability of eqn.(1) to various silicon and boron halides R-X was tested and the following trifluoromethyl-silicon and boron derivatives were obtained in reasonable yields: Me_3SiCF_3 (II), $Me_2Si(CF_3)_2$ (III), $(F_3C)_3BNHEt_2$ (IV).

INTRODUCTION

Tetrakis(dimethylamino)ethylene (I), first reported by PRUETT et al. [1], is a strong electron donor, and its chemistry has been reviewed [2]. Reactions of (I) with polyhalogenated compounds were studied by CARPENTER [3] and the reaction with Cl_3CBr was found to proceed according to eqn. (2):

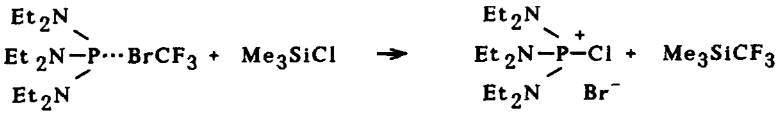
$$Cl_3CBr + (I) \longrightarrow [(Me_2N)_2C\text{-}C(NMe_2)_2]^{2+} + \{CCl_3^-\} + Br^- \qquad (2a)$$

0022-1139/89/$3.50



(2b)

The first step in the reaction of (I) with halogenated methanes is a nucleophilic attack on a positive halogen. A similar reaction occuring with electron rich phosphines, e.g. $P(NEt_2)_3$ and CF_3Br, was shown by RUPPERT <u>et al.</u> [4] to transfer F_3C groups onto silicon according to eqn. (3):

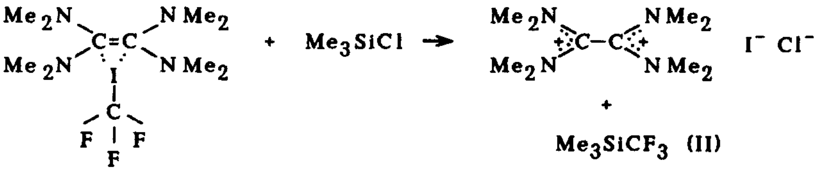


(3)

This analogy prompted us to investigate whether (I) reacts with CF_3Br in a similar manner.

RESULTS

When (I) was treated with CF_3Br in the presence of Me_3SiCl under conditions similar to those reported in [4], only traces of Me_3SiCF_3 were detected by ^{19}F-NMR spectroscopy. If however CF_3I was condensed onto (I) in polar solvents like CH_2Cl_2 or benzonitrile, formation of a deep red charge transfer complex was observed at low temperature. On raising the temperature to 0 °C the complex decomposed slowly to form $(F_3C)_2C(NMe_2)_2$ along with copious quantities of CF_3H and $[(Me_2N)_2C\text{-}C(NMe_2)_2]^{2+}$. In the presence of Me_3SiCl, however, trifluoromethylation at the silicon yielded 94 % of (II) according to eqn. (4):



(4)

Similar procedures were used to prepare $Me_2Si(CF_3)_2$ (III) from (I), CF_3I and Me_2SiCl_2 in 63 % yield. Furthermore $(F_3C)_3BNHEt_2$ (IV), which has been obtained recently by trifluoromethylation of Br_2BNEt_2 with $P(NEt_2)_3/CF_3Br$ [5], could be synthesized from Cl_2BNEt_2 according to eqn. (5) in CH_2Cl_2 as solvent with a yield of 34 % .

$$3(I) + 3\,CF_3I + Cl_2BNEt_2 \rightarrow (F_3C)_3BNEt_2^- + 3\,[(Me_2N)_2C\text{-}C(NMe_2)_2]^{2+} + \begin{matrix}3I^-\\2Cl^-\end{matrix}$$

$$(F_3C)_3BNEt_2^- + H^+ \rightarrow (F_3C)_3BNHEt_2 \quad (IV) \qquad (5)$$

These three examples, chosen to compare the novel trifluoromethylation reaction with RUPPERT'S method [4] , show, that the capability to transfer a trifluoromethyl group to silicon or to boron is about the same. In spite of the obvious disadvantage requiring CF_3I instead of the cheaper CF_3Br some important advantages should be noted.

1. The phosphonium salts, formed in the course of eqn. (3), are soluble in the required solvents ; therefore, isolation of nonvolatile trifluoromethyl derivatives from the reaction mixture is often difficult if not even impossible. The oxidation product of (I), however is a di cation, whose salts are only slightly soluble in solvents such as CH_2Cl_2 or benzonitrile. Thus they can be removed by simple filtration or, as for (IV), by extraction with water.

2. In the course of the trifluoromethylation using $P(NEt_2)_3$ as a reducing agent, transamination due to the reactivity of the phosphorus-nitrogen bond is often observed as a side reaction. They do not occur when (I) is employed since the stronger carbon-nitrogen and carbon-carbon bonds of (I) are less reactive.

The encouraging results obtained with the nucleophilic trifluoromethylating agent tetrakis(dimethylamino)ethylene /CF_3I give rise to the expectation that this reaction may be extended to elements other than boron or silicon and make hitherto unknown trifluoromethyl derivatives available.

EXPERIMENTAL

Materials

Tetrakis(dimethylamino)ethylene was obtained from Aldrich and redistilled before use, Cl_2BNEt_2 was prepared from BCl_3 and $B(NEt_2)_3$.

Trimethyl(trifluoromethyl) silane Me_3SiCF_3 (II) 6.1 g (31 mmol) CF_3I are condensed onto a solution of 1.7 g (16 mmol) Me_3SiCl in 50 ml dry benzonitrile at -196 °C . The solution is warmed to 0 °C and at that temperature 4.2 g (21 mmol) tetrakis(dimethylamino) ethylene (I) are added dropwise within 20 min. The reaction mixture is stirred for 1 h at 20 °C , (II) separated by fractional condensation and collected in a -95 °C trap. Yield 94 %. $\delta(^{19}F)$ = -66.1 [ppm], ^2J $(^{19}F^{29}Si)$ = 38.0 [Hz] .

Dimethyl-bis(trifluoromethyl)silane $Me_2Si(CF_3)_2$ (III) was prepared similarly from 2.8 g (22 mmol) Me_2SiCl_2 in 50 ml dry benzonitrile, 18.6 g (95 mmol) CF_3I and 12.8 g (64 mmol) (I) and obtained in 63 % yield.
δ (^{19}F) = -63.7 [ppm], ^2J $(^{19}F^{29}Si)$ = 43.6 [Hz] .

Tris(trifluoromethyl)borane-diethylamine $(F_3C)_3BNHEt_2$ (IV)
6.5 g (33 mmol) CF_3I are condensed onto a solution of 1.3 g (8.5 mmol) Cl_2BNEt_2 in 30 ml dry CH_2Cl_2 placed in a flask with a reflux condenser held at -78 °C. The solution is warmed to 0 °C and 5.2 g (26 mmol) (I) added dropwise within 20 min.. The reaction mixture is then stirred for 1 h at 20 °C and hydrolysed with 50 ml H_2O. The organic phase is shaken with dilute HCl and CH_2Cl_2 is removed in vacuo. The nonvolatile residue is sublimed at 70 °C/ 0.1 torr and (IV) recrystallized from Cl_3CH. Yield 32 %. mp. 137 °C.
$C_7H_{11}BF_9N$. Required/found; %C, 28.89/29.3; %H, 3.81/3.7; %F, 58.75/57.9
IR cm^{-1}: 3247 w ν NH, 3000 vw ν CH, 1140,1108 vs ν CF, 697 s δ_s CF_3,
Raman cm^{-1}: 3245 w ν NH, 2962 m ν CH, 725 vs δ_s CF_3, 308,283 s ρ CF_3.
δ (^{19}F) = -62 [ppm], δ (^{11}B) = -11.1 [ppm], ^2J $(^{11}B^{19}F)$ = 30 [Hz].
^1H δ CH_3 = 1.46 [ppm], δ CH_aH_b (H_a= 3.07 [ppm] H_b= 3.73 [ppm])
δ NH = 3.3 [ppm], ^3J HH = 7.2 [Hz], ^2J H_aH_b = 13.5 [Hz],
^3J H_aNH = 6.6 [Hz].

Physical measurements

^{19}F NMR : Varian EM 390, 84.67 MHz, internal $CFCl_3$.

^{11}B NMR : Varian CFT 80, 25.52 MHz, external $BF_3 \cdot O(C_2H_5)_2$.

^{1}H NMR : Bruker AC 250, 250 MHz, internal TMS, CD_3CN solution.

IR: Perkin-Elmer 580 B, KBr pellets.

Raman: Cary 82, Kr^+ 647.1 nm.

ACKNOWLEDGEMENT

The author wishes to thank Professor H. Bürger for support.

REFERENCES

1 R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., J. Am. Chem. Soc., 72 (1950) 3646.

2 N. Wiberg, Angew. Chem., 80 (1968) 809.

3 W. Carpenter, J. Org. Chemistry, 30 (1965) 3082.

4 I. Ruppert, K. Schlich, and W. Volbach, Tetrahedron Lett., 25 (1984) 2195.

5 D.J. Brauer, H. Bürger, F. Dörrenbach, G. Pawelke, and W. Weuter, to be published.