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ANION-CONTROLLED REDISTRIBUTION REACTIONS IN THE SYSTEM $C_3Cl_3{}^+A^-/(CH_3)_3SiN(CH_3)_2$[1]

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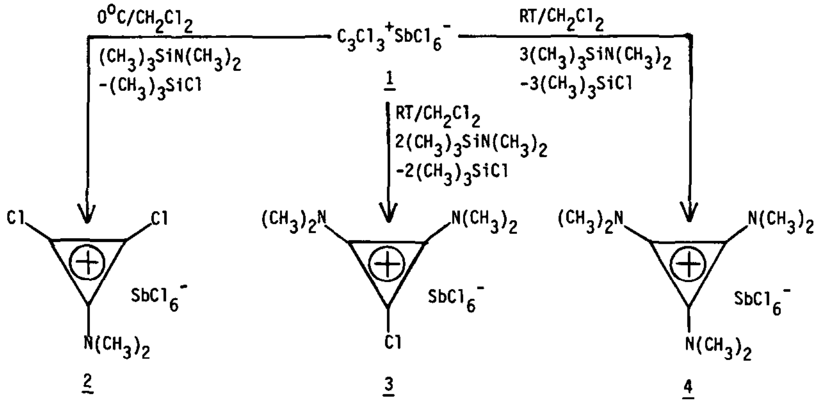
Summary: Transamination reactions of the 4z-exchange type between $C_3Cl_3{}^+A^-$ and $(CH_3)_3SiN(CH_3)_2$ are introduced as a novel mode of aromatic substitution at the $C_3{}^+$-core. The extent of transamination can be controlled by appropiate choice of counterion A^-.

While many ligand redistribution reactions of the 4z-exchange type are known for trigonal boron systems[2], virtually nothing is known about comparable reactions of isoelectronic carbeniumions. As a model case we have examined the reaction of silylamines with chlorocyclopropeniumsystems as their hexachloroantimonate-V salts and we now wish to report on some remarkable observations which we have made in the course of this study.

Thus we have found that $C_3Cl_3{}^+SbCl_6{}^-$ [3] undergoes very clean transamination reactions with $(CH_3)_3SiN(CH_3)_2$, the extent of which can be controlled by simple variation of temperature and stoichiometry, according to the following scheme:



Under the reaction conditions given in the scheme partially aminated cyclopropenium systems 2 and 3 can be obtained in reasonable to good yield. It is noteworthy, that 2 and 3 are both inaccessible by the more conventional transamination technique of reacting C_3Cl_4 with $(CH_3)_2NH$ [4].

2 represents the first monodialkylamino-dihalogeno-$C_3{}^+$-system. In view of its two exchangeable Cl-substituents it is of potential value for generating new substitution patterns of the $C_3{}^+$-core. 2 is colorless and readily soluble in CH_2Cl_2, from which it must be precipitated immediately after formation with n-hexane (yield: 50%; mp.: 180°C (dec.); ^1H-NMR ($CDCl_3$): τ= 6.67 (s); IR (KBr): 1930 (m), 1613 (s), 1428 (s), 1354 (s) cm^{-1}). Gradually in CH_2Cl_2-solution and almost instantanously in CH_3CN 2 reacts with itself in what seems to be a disproportionation reaction (1) which produces bright yellow insoluble 3 in 80% yield

(mp.: 252°C (dec.); ^{1}H-NMR (CD_3CN): τ = 6.78 (s, 6H), 6.81 (s, 6H); IR (KBr): 1955 (m), 1635 (s), 1409 (s), 1390 (s) cm^{-1}):

$$\underline{2} \xrightarrow[\text{solution}]{\text{in}} 0.5\ \underline{3}\downarrow + 0.5\ \underline{1}$$

The mechanism of this unprecedented ligandredistribution which formally takes place between two positively charged species is unclear at present. 3 is also abtained as bright yellow needles in 65% yield by reacting 1 with 2 moles of silylamine (cf. scheme) at room temperature and subsequent recrystallization of the crude product from CH_3CN.

So far synthesis of bisdialkylamino-chloro-C_3^+-systems via C_3Cl_4/R_2NH has been restricted to such cases, where bulky groups R prevented triple amination[4]. 3 contains the hitherto inaccessible parent of the series, with a reactivity pattern quite different from the sterically hindered homologues[5].

Further reaction of 3 as a suspension in CH_2Cl_2 with excess $(CH_3)_3SiN(CH_3)_2$ gave the peraminated salt 4 as highly insoluble dark violet cristals in virtually quantitative yield (mp.: 182°C (dec.); ^{1}H-NMR (CD_3CN): τ = 6.94 (s); IR (KBr): 1560 (s), 1403 (s) cm^{-1}). As colour and solubility of this material differed so dramatically from the corresponding known perchlorate[4] (which is colourless and very well soluble in CH_2Cl_2) a single crystal X-ray determination of 4 was undertaken[6]. The results of this study fully confirmed the assumed structure and allowed to attribute the abovementioned properties of 4 to a new kind of CT-interaction between cation and anion of this salt. A detailed discussion will be presented in a forthcoming full paper[7].

Comparison of the ^{1}H-NMR data of salts 2-4 reveals a progressive down-field shift of methyl resonances in the sequence 4 - 3 - 2 as an indication of the increasing electron demand of the C_3^+-core along this series. In addition, 3 exhibits rotational hindrance around the C-N bonds, as is expected of a bisdialkylamino-C_3^+-system. The infrared data of 2-4 are characteristic of cyclopropeniumions of C_{2v} and D_{3h} symmetry, respectively[4].

Remarkably, replacement of $SbCl_6^-$ in 1 by Cl^-, BF_4^- or $CF_3SO_3^-$ [8,9] resulted in exclusive triple amination upon reaction with $(CH_3)_3SiN(CH_3)_2$. Thus, the selective mono- and disubstitution processes reported above are due to a novel type of counterion control[10], the precise nature of which is under further investigation.

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