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FIRST σ-COMPLEXES OBTAINED FROM AROMATIC SULFONES

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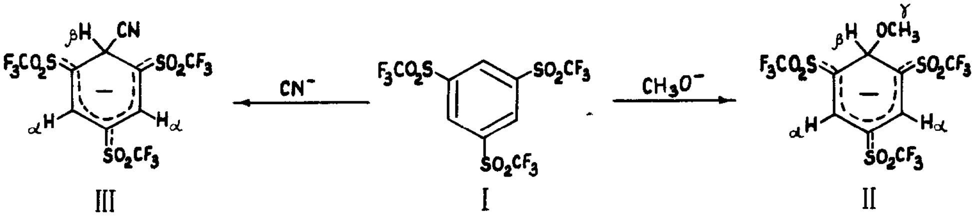
Anionic σ-complexes produced by nucleophilic addition (Meisenheimer type) have been until recently known only for nitro-aromatics. As for other strong electron-withdrawing groups, there are rare cases of formation of relatively low-stable σ-complexes affected by CN groups.[1] Any attempts to determine the formation of any intermediates in the reaction of nucleophilic agents with substituted benzenes containing CF_3-, SO_2CH_3- and SO_2CF_3 groups were unsuccessful.[2]

We have obtained stable σ-complexes II and III as a result of 1, 3, 5-tris (trifluoromethylsulfonyl)benzene I[3] interaction with sodium methoxide and NaCN.



When one equivalent of sodium methoxide (3 M solution) in methanol or of cristalline NaCN is added to sulfone I (0.05 g) mixed with methanol (0.3 ml) or acetonitrile, instead of sulfone I singlet (δ 8.87 ppm in acetone relative to GMDS) two signals appear in the NMR spectrum at a higher field (δ 7.87 and 5.67 ppm for II in CH_3OH and 7.55 and 4.98 ppm for III in CH_3CN) with intensity ratio 2 : 1 which may be attributed to two benzene ring protons Hα and hydrogen Hβ of the sp^3-hybridized carbon atom. Similar changes are also observed in the NMR ^{19}F spectra. In contrast with the singlet of initial compound (δ 13.92 ppm in CH_3CN, 14.68 ppm in CH_3COCH_3 and 15.07 ppm in CH_3OH upfield relative to $C_6H_5CF_3$), the products of reaction with sodium methoxide and NaCN exhibit two signals (2 : 1) in a higher field at δ 17.65 and 18.00 ppm for II in CH_3OH and at δ 16.46 and 17.37 ppm for III in CH_3CN which correspond to fluor atoms of SO_2CF_3 groups in ortho- and para-positions.

After almost complete evaporation of solvents in vacuo complexes II and III are precipitated with absolute ether. The obtained species are yellow (λ_{max} of II is 225, 263 and 362 nm in CH_3OH and that of III - 230, 264 and 390 nm in CH_3CN), decompose at 270-280° and are quite stable being stored in the air. Dissolved in acetone-D_6, they exhibit the PMR and NMR ^{19}F spectra similar to those obtained *in situ* : PMR for I - 8.88; for II - H_α7.54(2), H_β5.35(1), H_γ2.55(3); for III - H_α7.37(2), H_β4.75(1) ppm. NMR ^{19}F for I - 14.41; for II - 17.10(2), 17.50(1); for III - 16.85(2), 17.59(1) ppm. σ-Complexes II and III do not decompose when their solutions are diluted even to 10^{-4} M concentration - the UV-spectra of their 10^{-2} and 10^{-4} M solutions are identical. It should be emphasized, that the UV-spectrum of sulfone I in methanol does not differ from that of complex II, whereas in CH_3CN it has a single absorption band at λ_{max}<200 nm. Perhaps, due to high electron-withdrawing ability of SO_2CF_3 groups sulfone I, unlike sim-trinitrobenzene, can form some associates with methanol similar to σ-complex II.

The elemental analyses of the obtained complexes are consistent with their compositions. Their decomposition with hydrochloric acid leads to formation of practically pure sulfone I.

Thus, it has been established, that aromatic compounds activated with trifluoromethylsulfonylic groups are able to form stable anionic σ-complexes of the Meisenheimer compound type.

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