Tetrahedron Letters, Vol. 33, No. 41, pp. 6191-6192, 1992
Printed in Great Britain

0040-4039/92 \$5.00 + .00
Pergamon Press Ltd

Tris(dimethylamino)sulfonium 1,1,2,4,5-Pentakis(trifluoromethyl)- 2,5-cyclohexadienide - A New Stable Fluorinated Carbanion Salt Prepared by Anionic Trifluoromethylation of 1,2,4,5-Tetrakis(trifluoromethyl)benzene

Alexander A. Kolomeitsev, Valerie N. Movchun, Yurii L. Yagupolskii*

Institute of Organic Chemistry, Academy of Sciences of Ukraine, 253660, Kiev-94, Ukraine

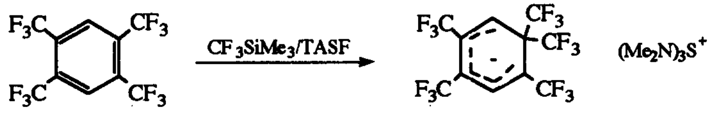
Jacek Porwisiak and Wojciech Dmowski

Institute of Organic Chemistry, Polish Academy of Sciences, 01-224, Warsaw 44, Poland

Abstract: An interaction of the 1,2,4,5-tetrakis(trifluoromethyl)benzene with the pseudometallorganic system CF_3SiMe_3/TASF results in addition of $TAS^+CF_3^-$ to the benzene ring and formation of $TAS^+(CF_3)_5C_6H_2^-$ - a new stable tertiary fluorinated delocalized carbanion salt.

The accumulation of electronegative fluorinated substituents in a benzene ring leads to enhanced reactivity of the nucleus towards nucleophiles and influences the course of its metallation.[1,2] Whereas the lithiation of 1,3-bis(trifluoromethyl)- and 1,3,5-tris(trifluoromethyl)benzenes gives stable aryllithium derivatives,[3,4] the introduction of a fourth electronegative CF_3-group changes the character of reactivity of CF_3-substituted benzene. It has been shown that the reaction of 1,2,4,5-tetrakis(trifluoromethyl)benzene with RLi results in the formation of fluoromethyl derivatives of the 2,5-cyclohexadiene-1-ylidene.[5]

During the course of our studies on the reactivity of polysubstituted fluorinated compounds we have investigated the interaction of 1,2,4,5-tetrakis(trifluoromethyl)benzene (1) with pseudometallorganic system CF_3SiMe_3/TASF, presenting a masked form of highly nucleophilic CF_3-anion.[6-8] We have found that compound (1) gently reacts with the CF_3SiMe_3/TASF (1:1) at -30°C in THF to form stable carbanion salt (2).



(1) (2)

Thus, the ipso-attack of the CF_3-anion on the CF_3-substituted aromatic carbon-atom of (1) occurs, as was previously observed for the reaction with RLi. The presence of TAS^+-cation stabilizes the generated carbanion and prevents its decomposition with elimination of F-anion and following transformations according to addition-elimination scheme. All spectral[10] and analytical data of the compound (2) are consistent with the assigned structure.

It should be noted that the known stable F-carbanion TAS-salts contain perfluorinated tertiary alkyl anions, $^{-}C(R_f)_3$.[9] The salt (**2**) represents a new type of stable partially fluorinated carbanion salts, stabilized by CF_3-groups and two vinylic moieties.

References and Notes

1. Yagupolskii,L.M.; Lukmanov,V.G.; Alekseeva,L.A. *Zh.Org.Khim.*, **1976**, *12*, 470.
2. Yagupolskii,L.M.; Kolomeitsev,A.A.; Kondratenko,N.V.; Ignat'ev,N.V.; Popov,V.I. *Zh.Org.Khim.*, **1986**, *22*, 2559-2563.
3. Heuer,L.; Jones,R.G.; Schmutzler,R. *J.Fluorine Chem.*, **1990**, *46*, 243-254.
4. Carr,G.E.; Chambers,R.D.; Holmes,T.F.; Parker,D.G. *J.Organomet.Chem.*, **1987**, *325*, 13-23.
5. Dmowski,W.; Porwisiak,E. *J.Fluorine Chem.*, **1991**, *54*, 120.
6. Surya Prakash,G.K.; Krishnamuti,R.; Olah,G.A. *J.Am.Chem.Soc.*, **1989**, *111*, 393-395.
7. Bardin,V.V.; Kolomeitsev,A.A.; Furin,G.G.; Yagupolskii,Yu.L. *Izv.A.N ..SSSR, Ser.Khim.*, **1990**, 1693.
8. Kolomeitsev,A.A.; Movchun,V.N.; Kondratenko,N.V.; Yagupolskii,Yu.L. *Synthesis.*, **1990**, 1151-1152.
9. Smart,B.E.; Middleton,W.J.; Farnham,W.B. *J.Am.Chem.Soc.*, **1986**, *108*, 4905-4907.

10. Preparation of (**2**): 1.38g(5mmol) TASF was gradually added to a solution of 1.75g(5mmol) of 1,2,4,5-tetrakis(trifluoromethyl)benzene and 0.71g(5mmol) Me_3SiCF_3 in anhydrous THF (30 ml) at 30ºC over 1.5-2 hours. The cold mixture was filtered to remove unreacted TASF and the solvent was evaporated. The residue was washed twice with petroleum ether/ether (1:1 mixture) (30 ml) and evacuated to afford 1.75g (60%) of (**2**), a dark yellow oil, m.p. 19ºC.
    ^{1}H NMR(CD_3CN): 7.03(1Hs,H-6), 4.78(1Hs,H-3), 2.85(18Hs,CH_3).
    ^{19}F NMR(C_6D_6/THF): 53.00(3Fqq, J=11.0Hz, J=2.3Hz, CF_3-4), 54.10(3Fstq, J=9.6Hz, J=2.3 Hz, CF_3-2), 63.40(3Fq, J=11.0Hz, CF_3-5), 73.10(6Fq, J=9.6Hz, CF_3-1).

(Received in UK 29 June 1992)