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Preliminary communication

ANCHIMERIC ASSISTANCE IN SOLVOLYSIS OF AN ORGANOSILICON CHLORIDE AND ACETATE

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Summary

The compound $(Me_3Si)_3CSiMeClI$ reacts with $Hg(OAc)_2$ in AcOH to give $(Me_3Si)_2C(SiMe_2OAc)_2$, under conditions in which the chloride $(Me_3Si)_3CSiMe_2Cl$ is inert. Similarly, $(Me_3Si)_2C(SiMe_2OAc)_2$ reacts with CF_3CO_2H to give $(Me_3Si)_2$-$C[SiMe_2(O_2CCF_3)]_2$ under conditions in which $(Me_3Si)_3CSiMe_2OAc$ is inert. The results can be accounted for in terms of anchimeric assistance by the neighbouring acetoxy or trifluoroacetoxy group to the breaking of the Si—Cl or Si—OAc bond.

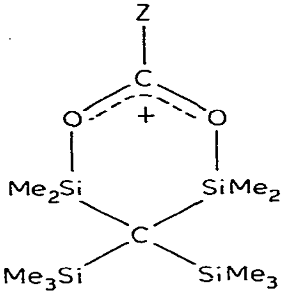
We recently reported the occurrence of 1,3-migrations of Me groups in reactions of the tris(trimethylsilyl)methyl ('trisyl') compounds $(Me_3Si)_3CSiRR'X$ (X = I or H) with electrophilic reagents, to give products of the type $(Me_3Si)_2$-$C(SiMe_2Y)(SiRR'Me)$, and suggested that a cation with an Me group bridging between Si(1) and Si(3) is formed, in an anchimerically assisted process, as X^- leaves [1]. We now present evidence for anchimeric assistance involving 1,3-bridging by an acetoxy or trifluoroacetoxy group. Neighbouring group effects of the type we propose have not previously been observed in organosilicon chemistry.

The relevant experimental observations are as follows:

(a) The compound $(Me_3Si)_3CSiMeClI$ (m.p. > 360°C; ^{1}H NMR, δ (ppm) 1.37 (s, 3H, SiMe) and 0.37 (s, 27H, Me_3Si)) reacts with 4 molar proportions of $Hg(OAc)_2$ in anhydrous AcOH during 2 h at 90°C to give $(Me_3Si)_2C(SiMe_2OAc)_2$ (m.p. > 360°C; ν(CO), 1750 cm^{-1}; ^{1}H NMR, δ (ppm) 2.02 (s, 6H, $COCH_3$), 0.55 (s, 12H, $SiMe_2$, and 0.28 (s, 18H, Me_3Si)). Under these conditions the iodide $(Me_3Si)_3CSiMe_2I$ reacts more readily, to give $(Me_3Si)_3CSiMe_2OAc$, while the chloride $(Me_3Si)_3CSiMe_2Cl$ is inert.

(b) The diacetate $(Me_3Si)_2C(SiMe_2OAc)_2$ reacts completely with CF_3CO_2H during 1 h at 90°C to give $(Me_3Si)_2C[SiMe_2(O_2CCF_3)]_2$ (m.p. 108—110°C, ν(CO), 1765 cm^{-1}; ^{1}H NMR, δ (ppm) 0.65 (s, 12H, $SiMe_2$) and 0.32 (s, 18H, Me_3Si)), whereas $(Me_3Si)_3CSiMe_2OAc$ is inert under these conditions.

(c) The compound $(Me_3Si)_3CSiMeClI$ reacts completely within a few minutes with an excess of AgO_2CCF_3 in CF_3CO_2H at room temperature to give $(Me_3Si)_2C[SiMe_2(O_2CCF_3)]_2$, whereas the chloride $(Me_3Si)_3CSiMe_2Cl$ requires 1 h at reflux for complete reaction. If an 0.5 molar proportion of AgO_2CCF_3 is used, the product mixture contains only $(Me_3Si)_2C[SiMe_2(O_2CCF_3)]_2$ along with unchanged $(Me_3Si)_3CSiMeClI$.



(Ia, Z = Me;
Ib, Z = CF_3)

The results can be very satisfactorily accounted for in terms of anchimeric assistance by acetoxy or trifluoroacetoxy groups. Thus for the reaction of $(Me_3Si)_3CSiMeClI$ with $Hg(OAc)_2$ in AcOH we suggest that the iodine is first replaced (rather more slowly than is the case with $(Me_3Si)_3CSiMe_2I$, because of the presence of the electron-withdrawing chlorine substituent) to give $(Me_3Si)_2C(SiMe_2OAc)(SiMe_2Cl)$, and the acetoxy group of the latter then assists the departure of Cl^-, to give the cation Ia. (A structure of this type can be readily constructed with accurately scaled molecular models.) The cation is then attacked by the solvent to give the observed product, $(Me_3Si)_2C(SiMe_2OAc)_2$. An analogous sequence, via the cation Ib, would occur in the reaction with AgO_2CCF_3 in CF_3CO_2H. Again, for the reaction of $(Me_3Si)_2C(SiMe_2OAc)_2$ with CF_3CO_2H, we suggest that the cation Ia is first formed, and is opened to give $(Me_3Si)_2C(SiMe_2OAc)[SiMe_2(O_2CCF_3)]$, which then loses acetate ion with anchimeric assistance by the trifluoroacetoxy group to give the cation Ib, which reacts with the solvent to give the observed $(Me_3Si)_2C[SiMe_2(O_2CCF_3)]_2$.

Work is continuing, and a full account will be presented later.

Acknowledgements

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Reference

1 C. Eaborn, D.A.R. Happer, S.P. Hopper and K.D. Safa, J. Organometal. Chem., (1979) in press. See also C. Eaborn, D.A.R. Happer, K.D. Safa and D.R.M. Walton, J. Organometal. Chem., 157 (1978) C50.