Tetrahedron Letters Vol. 21, pp 3979 - 3982
© Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/1008-3982$02.00/0

THE INTERACTION OF FLUORIDE ION WITH ORGANOSILANES: EQUILIBRATION OF THE EXO/ENDO ISOMERS OF 3-METHYL-3-SILABICYCLO[3.2.1]OCTANE

S.E. Cremer* and C. Blankenship

Department of Chemistry, Marquette University, Milwaukee, WI 53233

SUMMARY: The exo/endo isomers of the title compound can be obtained as an equilibrium mixture when treated with cesium fluoride in DMF; the observed equilibrium constant is in agreement with theoretical calculations.

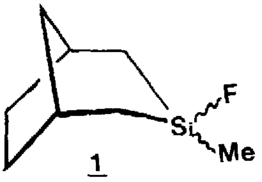
We wish to report a unique reaction in which the exo/endo isomers of 3-methyl-3-silabicyclo-[3.2.1]octane (MSBO),[1] are brought into thermodynamic equilibrium when treated with CsF in dimethylformamide (DMF) as shown in Eqn. 1.[2] Previous force field calculations[3] have indicated exo-MSBO to be the preferred isomer by 0.6 kcal/mole (K_{eq} = 2.3, 80°). When either pure isomer or a mixture was heated (80°) with CsF, a final 3:7 ratio of endo:exo-MSBO was obtained, which is in excellent agreement with that predicted.

Eqn 1

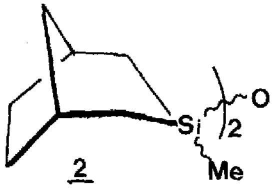
When CsF was replaced by KF, very little isomerization was observed at 80°. However, KF with 18-crown-6 at 80° produced the equilibrium mixture, The CsF/DMF medium caused a very slow isomerization at room temperature, but addition of 18-crown-6 increased this rate and gave the equilibrium ratio at ca. 25°. In several cases, reaction was allowed to proceed for various lengths of time after equilibrium had been attained with little or no change in the isomer ratio.

The two MSBO isomers are clearly distinguishable by a number of physical methods, and a tentative isomer assignment[4] was made from ^{1}H and ^{13}C NMR data. Less equivocally, the structure of endo-MSBO was confirmed by an electron diffraction study.[5] Isomer ratios were determined by GC and/or from the proton NMR spectrum (Table I, footnote *d*).

The results of a solvent study run in NMR tubes are shown in Table I. Polar, aprotic solvents favor isomerization. In addition, several reactions were run on a larger scale to allow a more complete product study. The MSBO isomers were normally the only "products", but varying amounts of 3-fluoro-MSBO 1 and isomers of siloxane 2 were also detected. The reaction was very sensitive to moisture, apparently giving siloxane 2. However, in CsF/DMF, there was evidence for a reaction of MSBO with solvent to give 2 and $(CH_3)_3N$. Even when 2 became the predominant product, the MSBO isomers were still at or near the equilibrium position. The isomeric fluorosilanes 1 were also detected in small amounts from several reactions. Most interestingly, in CCl_4 or $CDCl_3$, where no isomerization was detected, larger amounts of 1 were observed. On one occasion, 0.19g of MSBO was heated with 4 eq. CsF in CCl_4 (reflux) for 14 days; the isolated product (95% mass balance) consisted of nearly equal amounts of starting MSBO and 1. The starting MSBO isomer ratio changed little throughout reaction. In reactions where the isomers of 1 were observed, GC analyses indicated an approximate 7:13 endo:exo ratio,[6] regardless of the starting MSBO ratio. This result indicates that the fluorosilanes are rapidly isomerized under the reaction conditions.

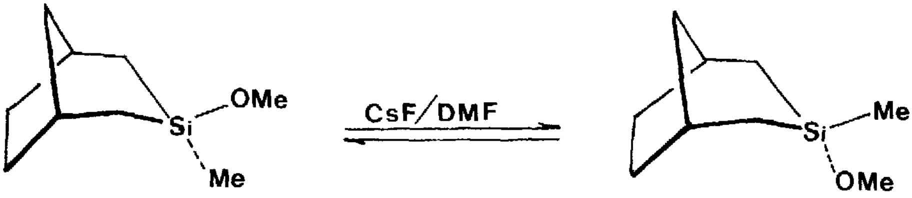


1



2

The CsF/DMF medium also promoted complete equilibration of exo-3-methoxy-MSBO within 2 hr. at room temperature (Eqn. 2).[7]



Eqn 2

start 93%
final 48%

start 7%
final 52%

TABLE I. REACTIONS OF MSBO WITH CESIUM FLUORIDE IN DIFFERENT SOLVENTS.[a]

Solvent	Reaction conditions[b] (eq. CsF, temp., time[c])	endo:exo MSBO isomer ratios[d] Starting	Final	Theory[e]
CD_3CN	2 eq., 100°, 18 da. (13 da.)	98:2	33:67	31:69
CD_3CN	2.5 eq., 85°, 17 da.	0:100	25:75	30:70
DMF	1 eq., 100°, 50hr. (24 hr.)	98:2	31:69	31:69
DMF	1 eq., 80°, 23 hr.	60:40	31:69	30:70
DMF	4 eq., 80°, 20 hr. (2 hr.)	0:100	30:70	30:70
C_6D_6	2 eq., 110°, 5 wk.	98:2	98:2	
CCl_4	2 eq., 110°, 5 wk.	98:2	98:2	
$CDCl_3$	1.1 eq., 110°, 4 wk.	98:2	98:2	
DME	2.5 eq., 85°, 2.5 mo.	98:2	94:6	
diglyme	2.5 eq., 85°, 2.5 mo.	98:2	69:31	

[a] Reactions were executed by combining the reagents, using 70-110 mg of silane, in dried NMR tubes under a nitrogen atmosphere. The tubes were sealed, heated in an oil bath, and periodically analyzed by proton NMR spectroscopy. Final reaction mixtures were also analyzed by GC and C-13 NMR spectroscopy.

[b] Control runs in CD_3CN or DMF without CsF showed no isomerization or side reactions at 100° for 2 weeks.

[c] The times in parentheses indicate when equilibrium was initially attained.

[d] Isomer ratios were determined by GC on a 6' x 1/8" 8%-FFAP column at 80° which gave near baseline resolution. Approximate retention times were 6 and 7 min. for the exo- and endo-isomers, respectively. Ratios were also determined by careful integration of the methyl resonances ($CDCl_3$) at δ = 0.18 (J = 4.3 Hz) and 0.03 (J = 3.4 Hz) for endo- and exo-MSBO, respectively.

[e] Calculated from ref. 3.

The methoxysilanes could also be equilibrated with KCN in DMF at 80°, but not at room temperature; these conditions caused no change in the MSBO isomer ratios even after prolonged heating at 120°.

A probable first step for the isomerization of MSBO involves formation of a pentacoordinate silicon intermediate with a fluoro subsituent. Such an intermediate was proposed in the CsF-catalyzed hydrosilation of carbonyl groups by triethylsilane in acetonitrile.[8] This intermediate was also proposed in the fluoride and other anion-induced alcoholyses of some silyl hydrides.[9] Subsequent events following the formation of such an intermediate under our conditions are uncertain, but a number of pathways are conceivable.[10] The generalization of our results to other cyclic and acylic silanes will be attempted in future investigations.

References and Notes

1. The synthesis of MSBO parallels that for 3-silabicyclo[3.2.1]octane by R. Carleer, N. Hosten, and M.J.O. Anteunis, Bull. Soc. Chim. Belg., 87, 709 (1978) and will be described elsewhere (ref. 5 below).
2. This is the first documented, quantitative example of epimerization of silanes; brief, qualitative mention of such a process in 1,2-dimethyl-1-silacyclobutane has been made: B.G. McKinnie, N.S. Bhacca, F.K. Cartledge, and J. Fayssoux, J. Org. Chem., 41, 1534 (1976).
3. R.J. Ouellette, J. Am. Chem. Soc., 96, 2421 (1974).
4. The observed chemical shifts of the endo (axial) and exo-methyl (equatorial) groups parallel those observed in 4-t-butyl-1-methyl-1-silacyclohexane: H. Sakurai and M. Murakami, Bull. Chem. Soc. Japan, 49, 3185 (1976).
5. Q. Shen, R.L. Hilderbrant, C.S. Blankenship, and S.E. Cremer, manuscript to be submitted to J. Organometal. Chem.
6. The tentative isomer assignment for 1 was based on proton NMR data (δ = 0.35, J = 7.6 H_z and 0.18, J = 8.2 H_z for the endo- and exo-methyl groups, respectively) and corresponds to the assignments in MSBO.
7. We have also established equilibrium in 4 mole % benzoic acid/$CDCl_3$.
8. M. Deneux, I.C. Akhrem, D.V. Avetissian, E.I. Myssoff and M.E. Vol'pin, Bull. Soc. Chim. Fr., 2638 (1973).
9. J. Boyer, R.J.P. Corriu, R. Perz, and C. Reye, J. Organometal. Chem., 157, 153 (1978).
10. R.J.P. Corriu, and M. Henner, J. Organometal. Chem., 74, 1 (1974).

(Received in USA 2 July 1980)