Tetrahedron Letters No.32, pp. 3553-3555, 1968. Pergamon Press. Printed in Great Britain.

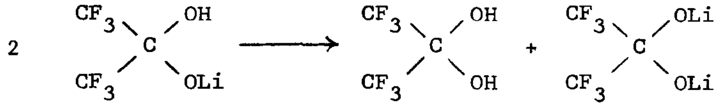
THE DI-LITHIUM SALT OF HEXAFLUOROPROPANE-2,2-DIOL

Paul H. Ogden and Geoffrey C. Nicholson
Central Research Laboratories
3M Company
3M Center
St. Paul, Minnesota 55101

(Received in USA 14 March 1968; received in UK for publication 13 May 1968)

The strongly acidic properties of fluorinated gem-diols have been recorded (1) and metal derivatives of these compounds possessing the formula $(CF_3)_2C(OH)OM$, wherein M is an alkali metal have been reported recently (2). Since these salts have been shown to be unstable in the presence of base it is clearly not possible to prepare compounds of the formula $(CF_3)_2C(OM)_2$ by the addition of a stoichiometric quantity of base to the gem-diol.

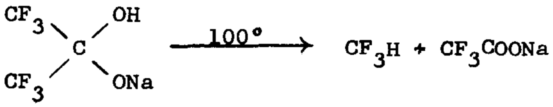
During our thermogravimetric analysis studies on salts of fluorinated gem-diols it was noted that whereas the sodium, potassium and cesium (rubidium was not studied) salts of hexafluoropropane-2,2-diol decompose at ca 100° producing fluoroform, hexafluoroacetone or its hydrate, and metal trifluoroacetate, the lithium salt disproportionates above 50° in vacuo producing hexafluoropropane-2,2-diol and its di-lithium salt quantitatively (I).

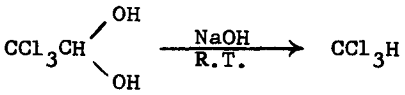


(I)

The di-lithium salt is the first reported organic compound of this type. Since it is prepared from a class of compounds of which very few members can be isolated, and under conditions in which other members of its class are unstable, it is probable that it is the only organic compound containing a gem-di(O-metal) group that can be isolated in a pure state at this time.

That it should be stable is quite surprising in view of the ease with which mono-metal derivatives of gem-diols undergo haloform type reactions, i.e.,

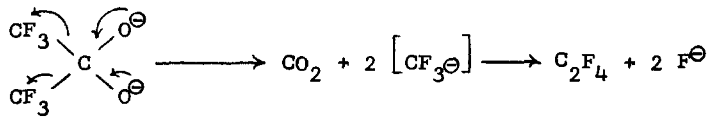




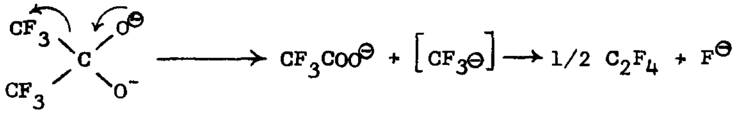
The di-lithium salt was identified by its infrared and F^{19} n.m.r. spectra, its x-ray diffraction powder photograph, and its elemental analysis. Calcd. for $C_3F_6O_2Li_2$: C, 18.3; Li, 7.2. Found: C, 18.2: Li, 7.01. Its infrared spectrum possesses many bands in common with the mono-lithium salt (2) but most significant is the absence of bands in the 2.95µ region corresponding to OH stretching and 9.5µ region corresponding to OH bending.

At 150° the di-lithium salt decomposes vigorously (3), 1 mole of salt producing about 1.5 moles of the gases tetrafluoroethylene, carbon dioxide, hexafluoroacetone and trifluoroacety fluoride in the ratios 4:4:2:1 respectively. The resultant solid consisted mainly of lithium fluoride with a trace of lithium trifluoroacetate.

Such products indicate that decomposition of the salt occurs by elimination of either one or both trifluoromethyl groups as trifluoromethyl anions (IIa and IIb). Loss of fluoride ion followed by dimerization of the resultant difluorocarbene then produces tetrafluoroethylene and lithium fluoride. The ratio of tetrafluoroethylene to trifluoroacetyl fluoride indicates that decomposition predominantly involves simultaneous elimination of both fluoroalkyl groups (IIa).

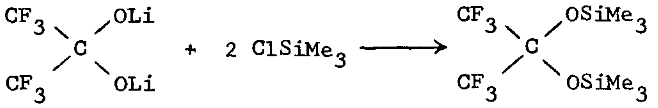


(IIa)



(IIb)

A salt of a weak acid, pKa_2 of $(CF_3)_2C(OH)_2 > 10.0$, the di-lithium salt is an extremely strong organic base, it is soluble in organic solvents such as acetone and is a highly reactive chemical intermediate. When treated with trimethyl chlorosilane in acetone at 0° it was converted to the disiloxy compound $(CF_3)_2C(OSiMe_3)_2$ in 35% yield.



(III)

The siloxy compound was identified by its infrared, mass, F^{19} and H^1 n.m.r. spectra and elemental analysis, Found: C, 25.7; H, 2.1; F, 54.5; M.W., 333. Calcd. for $C_5H_{18}F_6O_2Si_2$: C, 25.8; H, 2.2; F, 54.6; M.W., 328.

Careful pyrolysis of the mono-lithium salt of chloropentafluoropropane-2,2-diol, which was identified by elemental analysis and its infrared spectrum, produced the corresponding lithium salt together with a small amount of lithium chlorodifluoroacetate. The infrared spectrum of this di-lithium salt possessed bands in common with that of the mono-lithium salt together with one at 5.9µ corresponding to the carbonyl absorbtion of the chlorodifluoroacetate. Absorbtions at 2.77µ and 9.53µ assigned to OH stretching and bending were greatly reduced. This di-lithium is thermally less stable than the derivative of hexafluoropropane-2,2-diol and was found by T.G.A. to decompose at 115°. When the pyrolysis is conducted on a large sample, the di-lithium salt obtained is contaminated with lithium trifluoroacetate (4). The decreased stability of the salt containing chlorine is presumably due to the improved leaving properties of either $CF_2Cl^{\ominus}$ from the salt, or $Cl^{\ominus}$ from $CF_2Cl^{\ominus}$.

REFERENCES

(1) W. J. Middleton and R. V. Lindsay, Jr., *J. Am. Chem. Soc.*, **86**, 4948 (1964).

(2) J. H. Prager and P. H. Ogden, *J. Org. Chem.*, in the press.

(3) Care should be taken not to exceed *ca* 120° when preparing the di-lithium salt since large samples of the di-lithium salt decompose extremely violently if heated to 150°.

(4) We are grateful to Dr. P. G. Thompson of these laboratories for this experiment.