Journal of Fluorine Chemistry
Elsevier Sequoia S.A., Lausanne — Printed in Switzerland

Short Communication

Insertion of SO_2 and CO_2 into $(CF_3)_2C{=}NLi$

RICHARD F. SWINDELL * AND JEAN'NE M. SHREEVE †

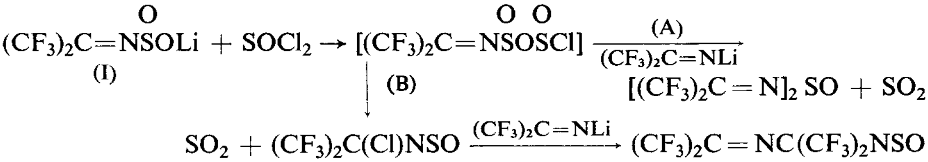
Department of Chemistry, University of Idaho, Moscow, Idaho 83843 (U.S.A.)

(Received March 6, 1972)

Recently[1] we reported the facile introduction of the hexafluoroisopropylidenimino group into a series of compounds from reactions of $(CF_3)_2C{=}NLi$ with inorganic halides. On the basis of these results, and results from reaction[2] of SF_4 with $(CF_3)_2C{=}NLi$, we proposed that the reactions proceed in an irreversible series of steps although it was not possible to isolate intermediates for other than the SF_4 reactions.

When $(CF_3)_2C{=}NLi$ reacts with $SOCl_2$ or $COCl_2$, even with the co-reactants in large excess, the major products observed are $(CF_3)_2C{=}NC(CF_3)_2NSO$ or $(CF_3)_2C{=}NC(CF_3)_2NCO$, with no trace of the symmetrical sulfoxide $[(CF_3)_2C{=}N]_2SO$ or substituted urea $[(CF_3)_2C{=}N]_2CO$. In an attempt to prepare the latter compounds and further substantiate the step-wise mechanism, a different synthetic technique was devised which might eliminate the formation of the postulated but unisolated intermediate $(CF_3)_2C(Cl)N{=}E{=}O$ (where E = S or C).

We have observed that SO_2 and CO_2 insert quantitatively into $(CF_3)_2C{=}NLi$ giving new lithium salts ((I) and (II) respectively), which are stable in glass at 25° for extended periods. Reaction of these with $SOCl_2$ or $COCl_2$ were expected to form intermediates which, if stable to loss of SO_2 or CO_2 respectively, would react further to form the symmetrical compounds (alternative A). On the other hand, if the intermediates were unstable, they should react further giving rise to rearranged compounds (alternative B). Thus for $SOCl_2$:



$$\underset{\text{(I)}}{(CF_3)_2C{=}N\overset{O}{S}OLi} + SOCl_2 \rightarrow [(CF_3)_2C{=}N\overset{O}{S}O\overset{O}{S}Cl] \xrightarrow[(CF_3)_2C{=}NLi]{(A)} [(CF_3)_2C{=}N]_2SO + SO_2$$

$$\downarrow \text{(B)}$$

$$SO_2 + (CF_3)_2C(Cl)NSO \xrightarrow{(CF_3)_2C{=}NLi} (CF_3)_2C{=}NC(CF_3)_2NSO$$

Experimental

Insertion of SO_2 into $(CF_3)_2C{=}NLi$

SO_2 (10 mmole) was condensed on to $(CF_3)_2C{=}NLi$ (7.2 mmole) at −196° and allowed to warm slowly to 25°. After 2 h, excess SO_2 (2.7 mmole) was removed under vacuum leaving a finely divided cream colored solid (I).

---

* NDEA Fellow.

† Alfred P. Sloan Foundation Fellow.

Reaction of (I) and $SOCl_2$

$SOCl_2$ (6.45 mmole) was condensed on to (I) (2.7 mmole) at −196° and warmed slowly to 25°. After 12 h, the products were separated by gas chromatography using a 50 cm 20% Kel-F on Chromosorb P column to give $(CF_3)_2C(Cl)$-$N{=}S{=}O$ (73% yield) and $(CF)_2C{=}NC(CF_3)_2N{=}S{=}O$[1] (16% yield).

$(CF_3)_2C(Cl)NSO$ (nc) is a colorless liquid with a boiling point of 90.2° obtained from the equation $\log P_{torr} = 8.26 - 1954/T$. The molar heat of vaporization is 8.94 kcal mole^{-1} and the Trouton constant is 24.6 e.u. The ^{19}F NMR spectrum shows a singlet at 76.3 φ. The infrared spectrum is as follows: 1328 (m), 1282 (vs), 1248 (vs), 1198 (m), 965 (m), 932 (m), 752 (w), 725 (m) cm^{-1}. Principal peaks in the mass spectrum correspond to the ions (relative intensity): $M{-}F^+$(4), $M{-}Cl^+$(25), $C_3F_6ClN^+$(2), $C_3F_5NCl^+$(37), $M{-}CF_3^+$(100), C_2F_4NSO(13), $SOCl^+$(26), CF_3^+(93), SCl^+(25), SO_2^+(33), CF_2^+(13), SO^+(73). (Calcd. for C_3ClF_6NS: C, 14.54; Cl, 14.33; F, 46.1; N, 5.67; S, 12.92%. Found: C, 14.56; Cl, 14.03; F, 45.8; N, 5.71; S, 12.96%.)

$(CF_3)_2C(Cl)NSO$ is also formed when (II) and $SOCl_2$ react.

Insertion of CO_2 into $(CF_3)_2C{=}NLi$

CO_2 (10 mmole) and 5 ml of 2-methylbutane were condensed on to $(CF_3)_2$-$C{=}NLi$ (7 mmole) at −196° and allowed to warm slowly to 25°. A vigorous exothermic reaction occurred while still cold which resulted in a detonation when no 2-methylbutane was used. The latter presumably acts as a heat sink. After 1 h, excess CO_2 (2.8 mmole) and the heat sink were removed under vacuum leaving a finely divided cream colored solid (II).

Reaction of (II) and $COCl_2$

$COCl_2$ (8 mmole) was condensed on to (II) (3.8 mmole) at −196° and warmed slowly to 25°. After 8 h, the products were separated by gas chromatography using a 50 cm 20% Kel-F on Chromasorb P column to give $(CF_3)_2C(Cl)N{=}C{=}O$ (50% yield) and $(CF_3)_2C{=}NC(CF_3)_2N{=}C{=}O$[1] (9% yield).

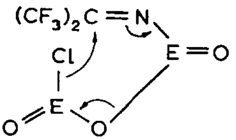
$(CF_3)_2C(Cl)NCO$ (nc) is a colorless liquid with a boiling point of 50.3° obtained from the equation $\log P_{torr} = 7.81 - 1594/T$. The molar heat of vaporization is 7.35 kcal mole^{-1} and the Trouton constant is 22.7 e.u. The ^{19}F NMR spectrum shows a singlet at 77.4 φ. The infrared spectrum is as follows: 2275 (vs), 1520 (m), 1292 (vs), 1248 (vs), 1190 (m), 1028 (s), 962 (s), 932 (s), 755 (m), 722 (m) cm^{-1}. Principal peaks in the mass spectrum correspond to the ions (relative intensity): $M{-}F^+$(7), $M{-}Cl^+$(34), $M{-}CF_3^+$(100), $M{-}CF_2Cl^+$(26), $CFClNCO^+$(31), CF_2NCO^+(70), CF_2CN^+(9), CF_3^+(61), CF_2N^+(57), CF_2^+(9). (Calcd. for C_4ClF_6N: C, 21.12; Cl, 15.60; F, 50.03; N, 6.17%. Found: C, 21.00; Cl, 15.42; F, 50.3; N, 6.23%.)

$(CF_3)_2C(Cl)NCO$ is also formed when (II) and $[ClC(O)]_2$ or $SOCl_2$ react.

Results and discussion

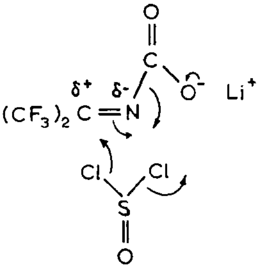
The synthesis of $(CF_3)_2C(Cl)NSO$ and $(CF_3)_2C(Cl)NCO$ indicates that these products were indeed the postulated intermediates in the formation of $(CF_3)_2C{=}NC(CF_3)_2NSO$ and $(CF_3)_2C{=}NC(CF_3)_2NCO$ since reaction of the intermediates with $(CF_3)_2C{=}NLi$ gives the latter compounds.

No trace of $[(CF_3)_2C{=}N]_2SO$ or $[(CF_3)_2C{=}N]_2CO$ was observed in the above reactions. The products obtained indicate that the proposed intermediates $(CF_3)_2C{=}N\overset{O}{S}O\overset{O}{S}Cl$ and $(CF_3)_2C{=}N\overset{O}{C}O\overset{O}{C}Cl$ are short lived since SO_2 and CO_2 are eliminated at temperatures as low as −30°. The migration of chloride and formation of SO_2 or CO_2 can be rationalized from the pseudo six-membered ring



E = S or C

However, if this intermediate does form, a competing mechanism is probably operative also since reaction of $SOCl_2$ and (II) gives primarily $(CF_3)_2C(Cl)NSO$ with $(CF_3)_2C(Cl)NCO$ as a minor product. Reaction of $COCl_2$ with (I) gives traces of these compounds also, but little reaction occurs after 12 h at 25°. The formation of these products indicates that nucleophilic attack at the electron-deficient double bond may occur,



but the lack of reactivity between $COCl_2$ and (I) is puzzling. Isotopic labelling experiments would be of help in resolving this problem.

Fluorine research at the University of Idaho is supported by the Office of Naval Research and the National Science Foundation. We thank Dr. R. A. De Marco for mass spectra.

REFERENCES

1 R. F. Swindell, D. P. Babb, T. J. Ouellette and J. M. Shreeve, *Inorg. Chem.*, *11* (1972) 242.
2 R. F. Swindell and J. M. Shreeve, *Chem. Comm.*, (1971) 1272.