Acknowledgment. The support of the National Institute of Health under Grant No. GM 08521 and the National Science Foundation under Grant No. GP 30743X is gratefully acknowledged.

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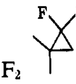
Received October 23, 1971

Metal Atom Reactions with Fluorocarbons. I. Nonsolvated Fluoroorganic Zinc Compounds

Sir:

A new technique for the direct synthesis of nonsolvated fluoroorganic zinc compounds has been employed in our laboratories. Zinc atoms have been cocondensed with fluoroalkyl iodides on a liquid nitrogen cooled surface in the manner previously described by Skell and coworkers[1] for the study of carbon atoms and some metallic substances.[2] We have found evidence that zinc atoms (by vaporization of zinc from a hot tungsten crucible under vacuum) insert into C–I bonds and that the resultant organometallic compounds have vastly different properties than those generated by normal solution-phase techniques.

Table I. Product Yields from Reactions of Zinc Atoms with Various Fluorinated Substrates[a]

Substrate	Products[f]							
	CF_3H	CF_3CF_3	$CF_2{=}CF_2$[b]	CF_3CFHCF_3	$CF_3CF{=}CF_2$	 F F[g]	F^-	I^-
CF_3I	0.81	1.7	6.6				8	25
$CF_3I(H_2O)$[c]	23	6.6	8.2				8	30
$CF_3I(CHBr_3)$[d]	1.7	0.81	9.1				13	27
$CF_3I((CH_3)_2C{=}O)$[e]	19	7.4	6.7				70	90
$CF_3I((CH_3)_2C{=}CH_2)$[e]	2.5	2.5	1.3			1.7	7	31
$CF_3I((CH_3)_3CHO)$[e]	17	2.5	0.0				90	92
$CF_3I((CF_3)_2C{=}O)$[e]	1.7	3.3	14		0.0		25	*j*
$CF_3CFICF_3(H_2O)$[c]				31	5.8[h]		0	63

[a] Yields based on zinc vaporized and corrected for the fact that only about 60% of the zinc reaches the reaction zone because of a widespread deposition and obstruction by electrode supports. [b] TFE polymer is also formed. [c] Vapor of fluoroalkyl iodide saturated with water vapor. [d] Vapor of fluoroalkyl iodide saturated with bromoform vapor. [e] An 85:15 mixture of iodide–additive. [f] Volatile products were identified by comparison of ir with those published (D. G. Weiblen, *Fluorine Chem.*, **2,** 449 (1954)). Iodide was determined by washing the residue out with dilute acid and then precipitating as silver salt. Fluoride was determined by precipitation as thorium salt. [g] This product was identified by mass spectroscopy and comparison of nmr spectra with that published (R. A. Mitsch, *J. Amer. Chem. Soc.*, **87,** 758 1965)). [h] Most of this product (65%) was formed on residue pyrolysis at *ca.* 100°. Some heptafluoroisopropyl radical dimer (2%) was detected by mass spectroscopy and glpc. [i] Apparently a very small amount of water was present which had a scavenging effect. [j] The residue was hydrolyzed with concentrated nitric acid which destroyed the iodide.

When zinc atoms reacted with CF_3I, a dark grey matrix was formed that decomposed vigorously on warming to *ca.* −80°. Hexafluoroethane and tetrafluoroethylene (TFE) were the only volatile products (*cf.* Table I), while both fluoride and iodide ions and a fluorine and iodine containing polymer remained in the reactor after distillation. Much of the polymer was formed in the vacuum apparatus above the reactor. Pyrolysis of the residue at 100° yielded only trace quantities of the same volatile products. If water was added to the residue (without pyrolysis) trace quantities of fluoroform and TFE were formed. If the CF_3I vapor was saturated with water vapor before deposition, a good yield of fluoroform resulted, but hexafluoroethane and TFE were still formed.

These results indicate that the fluoroorganic zinc compound formed is unstable at well below room temperature and can be hydrolyzed by water while quite cold. Similar and more striking results were found upon the reaction of zinc atoms with heptafluoroisopropyl iodide saturated with water vapor. The hydrolysis product, 2-hydroheptafluoropropane, was formed in large yield compared to hexafluoropropene. Therefore, the organozinc compound was efficiently hydrolyzed at well below room temperature. This observation is interesting in light of the fact that heptafluoroisopropyl zinc iodide formed in solution is very stable and not very easily hydrolyzed.[3] Furthermore, zinc atoms with heptafluoro-*n*-propyl iodide yielded a large amount of hexafluoropropene on warming to only room temperature. This observation also indicates that these nonsolvated organozinc compounds are much more reactive and less stable than those formed in solution.[4]

Fluoroform is an important product when either acetone or pivalaldehyde is used as an additive. The hydrogen uptake by CF_3 must be free radical in nature for the following reasons. Pivalaldehyde is a good hydrogen atom source, but a poor proton source since it has no enolizable hydrogens. Also, with bromoform as additive (possible proton source but poor hydrogen atom source by bond strength considerations) little fluoroform was detected. Note also the low yield of all products when isobutylene, a good radical scavenger, was the additive. These results are consistent with known free-radical decompositions of fluoroorganic zinc compounds.[4] However, with the nonsolvated

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(1) P. S. Skell, L. D. Wescott, Jr., J. P. Goldstein, and R. R. Engel, *J. Amer. Chem. Soc.*, **87,** 2829 (1965).

(2) See for example: P. S. Skell and J. E. Girard, Abstracts, 162nd National Meeting of the American Chemical Society, Sept 1971, No. ORGN 6; P. S. Skell and J. Havel, *J. Amer. Chem. Soc.*, **93,** 6687 (1971).

(3) R. D. Chambers, W. K. R. Musgrave, and J. Savory, *J. Chem. Soc.*, 1993 (1962).

(4) W. T. Miller, Jr., E. Bergman, and A. H. Fainberg, *J. Amer. Chem. Soc.*, **79,** 4159 (1957).

species the decompositions occur at least 150° lower than in the solution phase.

Difluorocarbene (CF_2) is also a decomposition product as shown by the presence of TFE, and trapping by isobutylene. The CF_2 is not formed by disproportionation of CF_3 radicals since tetrafluoromethane is not a product while fluoride ion is. It is interesting that no TFE or polymer was formed in the pivalaldehyde experiment, and yet a large yield of fluoride was found. Perhaps the aldehyde scavenges the CF_2 formed. At this time we have no good explanation as to why the fluoride and iodide yields are so high when carbonyl compounds are used as additives.

The following scheme explains the major pathways.

$$CF_3I + Zn \longrightarrow \underset{\text{I}}{CF_3ZnI}$$

$$\text{I} + H_2O \xrightarrow{-50\text{ to }-100°} CF_3H + Zn(OH)I$$

$$\text{I} \xrightarrow{-80°} :CF_2 + ZnFI$$

or

$$\text{I} \xrightarrow{-80°} \cdot CF_3 + \cdot ZnI$$

$$2CF_3 \longrightarrow CF_3CF_3$$

$$\cdot ZnI + CF_3I \longrightarrow ZnI_2 + \cdot CF_3$$

$$2CF_2 \longrightarrow \text{TFE}$$

$$\cdot CF_3 + \text{TFE} \longrightarrow \text{polymer}$$

$$\cdot CF_3 + RH \longrightarrow CF_3H + R\cdot$$

After appropriate hydrolysis techniques, we determined that I did not add to the carbonyl bonds of the additives to yield alcohols.

Both CH_3I and CF_3Br were much less reactive with zinc atoms than CF_3I.

Further investigations of other metal atoms with saturated and unsaturated fluorocarbons are in progress.

Acknowledgment. We acknowledge with gratitude the support of the Research Corporation, and a University of North Dakota Faculty Research Grant.

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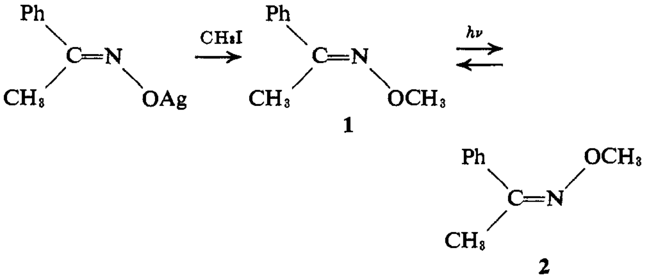
Received October 9, 1971

Photoisomerization about the Carbon–Nitrogen Double Bond of an Oxime Ether

Sir:

While photochemical reactions have been observed with several systems possessing a C–N double bond,[1–12] a more frequently encountered phenomenon for simple imines is a high rate and efficiency of radiationless decay of the excited state.[13] The facile deactivation of the imine chromophore can be attributed to rotation about the π bond in the excited state, thereby allowing for dissipation of electronic energy.[14] The photo[15–20] and thermal[21–23] interconversions of the syn and anti isomers of imines are a subject of long-standing interest. Recent investigations into the factors influencing the ease of isomerization about the C–N double bond have shown that the inversion barrier is remarkably sensitive to attached substituent groups.[21–23] The great configurational stability of oxime ethers stands in striking contrast to the behavior of *N*-aryl- and alkylimines.[21] These oxime ethers are attractive candidates for mechanistic photostudies since the presence of the methoxyl group drastically reduces the rate of thermal interconversion ($k < 10^{-13}$ at 60°). In the present communication we report on some aspects of the direct and sensitized isomerization of the syn and anti isomers of acetophenone oxime *O*-methyl ether.

The *anti-O*-methyl ether of acetophenone oxime (**1**) was synthesized by O-methylation of the silver salt of acetophenone oxime (nmr (CCl_4) τ 7.91 (s, 3 H), 6.08 (s, 3 H)). The corresponding syn isomer **2** was prepared by irradiation of **1** in pentane using a 2537-Å source (nmr (CCl_4) τ 7.88 (s, 3 H), 6.25 (s, 3 H)). The two isomers could be readily separated by vapor phase chromatography and their thermal stability was established by heating each isomer separately at 150° for 168 hr (in benzene) and noting the absence of isomerization. The ultraviolet absorption spectra of both the syn and anti forms resembled that of α-methylstyrene. The 0–0 band of the syn isomer appears at 2850 Å (100 kcal/mol), while that of the anti form appears at 2900 Å (98 kcal/mol). These absorptions can be attributed to a π–π^* transition; no absorption corresponding to a lower energy n–π^* transition was observed.



1

2

The photostationary state ratio obtained by direct irradiation in a pentane solution at 2537 Å (syn/anti) was 2.21 ± 0.03. The quantum yield for syn → anti isomerization at 2537 Å was 0.43 ± 0.02 in the 4–5% reaction range, while that for anti → syn was 0.48 ±

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