

REACTIONS OF GROUP IVB COMPOUNDS WITH ACYL FLUORIDES

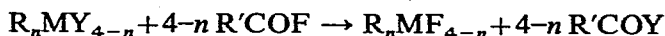
JOEL D. CITRON

Research Laboratory, Elastomer Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware (U.S.A.)

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SUMMARY

Derivatives of acyl fluorides can be readily prepared in high yields by reaction with Group IVB compounds. The reaction may be represented as



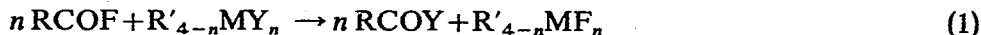
where $n=0-3$, and, when M is Si, Y may be nitrogen, oxygen, sulfur, or halogen. When M is Ge or Sn the scope of the reaction is more limited, but oxygen and nitrogen derivatives may be prepared. These results are discussed on the basis of the energies of the bonds involved.

INTRODUCTION

The reactions of acyl chlorides with compounds of the Group IVB elements are well known¹. However, it is also known that fluorocarbons often react with silicon compounds in a different manner than other organic halogen compounds; two of these anomalous reactions are the palladium catalyzed reduction of halocarbons by silicon hydrides² and the reaction of alkoxysilanes with fluoroketones³. Due to the unusual behavior of fluorocarbons in these cases, we decided to investigate the reactions of a wide range of Group IVB compounds with acyl fluorides.

RESULTS AND DISCUSSION

The results of these reactions are shown in Table 1. The obvious conclusion is that acyl fluorides do indeed react with a large variety of Group IVB compounds as generally described by eqn. 1. Using the appropriate organometallic compounds,



$$n = 1-4$$

$$M = \text{Si, Ge, Sn}$$

$$Y = \text{O, N, Cl, Br, I, S}$$

amides, esters, anhydrides, acid chlorides, etc., may be prepared from acyl fluorides, often in high yields. Furthermore, the use of difunctional (in the sense of this reaction) reactants leads to the formation of polymers, as exemplified by the preparation of

TABLE 1

REACTIONS OF ACYL FLUORIDES WITH GROUP IVB COMPOUNDS

Organometallic compound (mmoles)	Acyl fluoride (mmoles)	Time/temp. (°C)	Acyl fluoride derivative (%)	Organometallic product (%)
Me ₃ SiNEt ₂ (74)	n-C ₄ H ₉ COF (73)	1 min/25	n-C ₄ H ₉ CO(NEt ₂) (71)	
CH ₃ C(O)N(SiMe ₃) ₂ (52)	n-C ₄ H ₉ COF (100)	24 h/120	No reaction	
Me ₃ SiOMe (88)	n-C ₄ H ₉ COF (87)	72 h/70	n-C ₄ H ₉ CO ₂ Me (67)	Me ₃ SiF
Ph ₂ MeSiOC(Ph)HC(Ph)H ₂	n-C ₄ H ₉ COF (27)	19 h/110	n-C ₄ H ₉ CO ₂ C(Ph)HC(Ph)H ₂ (66)	Ph ₂ MeSiF (89)
(Me ₃ SiOCH ₂) ₂ (69)	p-C ₆ H ₄ COF ₂ (71)	72 h/160	tCOC ₆ H ₄ CO ₂ CH ₂ CH ₂ OT _n (95)	Me ₃ SiF (44)
Me ₂ Si(OEt) ₂ (43)	CF ₃ (CF ₂ COF) ₂ (42)	10 min/160	CF ₃ (CF ₂ CO ₂ Et) ₂ (87)	Me ₂ SiF ₂ (85)
Si(OCH ₂ CH=CH ₂) ₂ (98)	COF ₂ (150)	12 h/130	(CH ₂ =CHCH ₂ O) ₂ CO (91)	
Me ₃ SiOC ₆ H ₄ OCH ₃ -p (51)	PhCOF (51)	30 min/120	C ₆ H ₅ CO ₂ C ₆ H ₄ OCH ₃ -p (70)	Me ₃ SiF (59)
(PhMeSiO) _n (96)	p-C ₆ H ₄ COF ₂ (100)	8 h/300	tCOC ₆ H ₄ CO ₂ T _n (75)	PhMeSiF ₂ (16)
SiO ₂ ^a (25)	n-C ₄ H ₉ COF (100)	8 h/250	(n-C ₄ H ₉ CO) ₂ O (25)	
Me ₃ SiS-n-C ₈ H ₁₇ (80)	Me ₃ CCOF (79)	15 h/75	Me ₃ CCO(S-n-C ₈ H ₁₇) (74)	Me ₃ SiF (39)
Me ₃ SiCl (100)	n-C ₄ H ₉ COF (90)	19 h/25	n-C ₄ H ₉ COCl (81)	Me ₃ SiF (70)
Ge(OEt) ₄ (20)	n-C ₄ H ₉ COF (79)	20 min/25 ^b	n-C ₄ H ₉ CO ₂ Et (> 34 ^b)	
Ge(OEt) ₄ (20)	PhCOF (81)	2 min/120 ^c	PhCO ₂ Et (> 75 ^c)	GeF ₄ ^c
EtGeCl ₃ (48)	n-C ₄ H ₉ COF (150)	16 h/90	No Reaction	
Sn(NMe ₂) ₄ (17)	PhCOF (67)		PhCO(NMe ₂) (78)	SnF ₄ (85)
(n-Bu) ₃ SnOMe (75)	Me ₃ CCOF (76)	< 1 min/0	Me ₃ CCO ₂ Me (68)	(n-Bu) ₃ SnF (100)
Ph ₂ SnCl ₂ (44)	Me ₃ CCOF (87)	18 h/55	No Reaction	
Me ₃ SnCl (54)	n-C ₄ H ₉ COF (54)	15 h/90	No Reaction	

^a A colloidal silica (Hi-Sil® 233) was used. ^b See Experimental under analogous reaction of benzoyl fluoride with tetraethoxygermane. ^c See Experimental.

poly(ethelene terephthalate) and poly(terephthalic anhydride). Even COF_2 reacts to yield derivatives of carbonic acid.

An interesting facet is that the order of reactivity of the silicon compounds, $\text{SiN} > \text{SiCl} > \text{SiSR} > \text{SiOR} > \text{SiOSi}$, generally, follows the order of leaving group ability as described by Sommer and co-workers⁴, especially if one assumes the nitrogen of the silylamine is coordinated before bond breaking. The significance of this is not readily apparent. Even more intriguing however, is the failure of the chlorostannane and chlorogermane to react, while the chlorosilane reacts readily. Assuming the entropy change in these reactions is small (excluding phase changes), then the free energy (ΔG) of the reaction is approximately determined simply by the changes in energies (ΔH) of the bonds involved. Several of these are listed in Table 2. It is clear that

TABLE 2

BOND ENERGY CHANGES (ΔH) IN VARIOUS REACTIONS

Bond change		ΔH (kcal/bond mole)		
From	To	$-\text{NH}_2$	$-\text{OCH}_3$	$-\text{Cl}$
$\text{CH}_3\text{C}(\text{O})\text{F}$	$\text{CH}_3\text{C}(\text{O})\text{O}^a$	+34	+34	+34
$\equiv\text{Si}-^b$	$\equiv\text{SiF}$	-42	-46	-47
$\equiv\text{Ge}-^c$	$\equiv\text{GeF}$			-30

^a Values calculated from ref. 8. ^b Values calculated from ref. 9. ^c Ref. 1b.

the reaction is thermodynamically favored in all of the silicon cases, in accord with experimental observation*. For instance, the reaction of a silylamine with an acyl fluoride should have ΔH of ~ -8 kcal/mole. However, for chlorogermanes, ΔH is slightly positive; in view of the errors inherent in estimating bond energies this value could be as small as zero**. However, the small positive value indicates that the reaction is thermodynamically disfavored. Using this information, one may calculate limits on other bond energies. For instance, using a bond energy of 111 kcal/bond mole for $\text{Ge}-\text{F}$ ⁵, one may calculate that the germanium-oxygen bond energy is $< \sim 77$ kcal/bond mole.

EXPERIMENTAL

All reactions and distillations were run under nitrogen. All products were isolated (usually by distillation) and identified by physical constants and infrared spectra⁶. Acyl fluorides (except benzoyl fluoride, which was obtained from Aldrich

* The failure of *N,N*-bis(trimethylsilyl)acetamide to react is puzzling, and can be explained only by a kinetically very slow reaction. The same may be said of the silicon-carbon bonds that did not react.

** Note however, that the absolute values of bond energies in any of the individual sets (*i.e.*, acyl derivatives, silicon, or germanium compounds) do not have to be correct; only the *differences* must be accurate. Thus, for example, the silicon values, all determined by electron impact, would still be useful in this treatment if a constant absolute error had somehow been introduced into the experiments.

Chemical Company) were prepared by the method of Olah and Kuhn⁷. Silicon compounds were either purchased from Peninsular Chemresearch Corporation or prepared by standard procedures; the preparation of new compounds is described below. Tin and germanium compounds were obtained from Alfa Inorganic Chemicals. Physical constants and analyses of new compounds and polymers are listed in Table 3. Some representative procedures are given below. Reactions performed at temperatures considerably above the boiling point of one of the reactants were done in evacuated bombs.

TABLE 3

PROPERTIES OF NEW COMPOUNDS AND POLYMERS

Compound	B.p. (°C/mm)	n_D (°C)	Analyses, found (calcd.) (%)		
			C	H	S
$\text{Ph}_2\text{MeSiOC(Ph)HC(Ph)H}_2$	180–182.5/0.6	1.5907(22)	82.0 (82.2)	6.7 (6.6)	
$n\text{-C}_4\text{H}_9\text{CO}_2\text{C(Ph)HC(Ph)H}_2$	125.5/0.3	1.5305(22)	80.9 (80.8)	7.7 (7.7)	
$\text{-(COC}_6\text{H}_4\text{CO}_2\text{CH}_2\text{CH}_2\text{O)-}_n$			59.5 (62.5)	4.8 (4.2)	
$\text{-(COC}_6\text{H}_4\text{CO}_2\text{)-}_n$			66.7, 66.4 (64.9)	3.5, 3.2 (2.7)	
$\text{Me}_3\text{SiS-}n\text{-C}_6\text{H}_{13}$	208–211.5/760	1.4560(25)	56.7 (56.8)	11.2 (11.6)	16.9 (16.8)
$\text{Me}_3\text{CCO(S-}n\text{-C}_6\text{H}_{13}\text{)}$	119.5/12	1.4582(25)	65.4 (65.2)	10.8 (11.0)	15.9 (15.8)
$\text{Me}_3\text{SiOC}_6\text{H}_4\text{OCH}_3\text{-}p$	81.5/3.0	1.4887(22)	61.4 (61.2)	8.1 (8.2)	

(1,2-Diphenylethoxy)diphenylmethylsilane

In a 100 ml round-bottomed flask under nitrogen was mixed 12.5 g of 1,2-diphenylethanol, 40 ml of dry toluene, and a small piece (~0.1 g) of sodium. The mixture was refluxed until the sodium dissolved. About 10 ml of diphenylmethylsilane was added while refluxing but no gas was evolved, so two more small pieces of Na were added and the mixture refluxed for ~16 h. The solution was washed 4 times with water, dried over anhydrous Na_2SO_4 , and distilled to yield 12.0 g (62%) of the desired product. The physical constants are given in Table 3.

(p-Methoxyphenoxy)trimethylsilane

To a 100 ml round-bottomed flask under nitrogen was added 34 g of *p*-methoxyphenol and 50 ml of Me_3SiCl . The mixture was stirred and refluxed for 2.5 h, during which time HCl was evolved. The product was distilled to yield 34.2 g (70%) of (*p*-methoxyphenoxy)trimethylsilane, the physical constants of which are listed in Table 3.

(n-Hexylthio)trimethylsilane

Into a 500 ml round-bottomed flask was added 47 g of *n*-hexanethiol, 51 ml of Me_3SiCl , and 200 ml of heptane. Triethylamine (50 ml) was then added dropwise with

stirring and a copious white precipitate formed. After the solid was removed by filtration and the solvent vaporized under vacuum, distillation yielded 38.5 g (51 %) of (n-hexylthio)trimethylsilane the properties of which are given in Table 3.

Reaction of pentanoyl fluoride with (diethylamino)trimethylsilane

Into a 1.25 inch ID Teflon[®] tube containing a magnetic stirring bar was added 7.6 g of pentanoyl fluoride. Using a syringe, 14.0 ml of (diethylamino)trimethylsilane was added. During the addition much heat and a gas were generated. Upon distillation 8.1 g of *N,N*-diethylpentanamide was isolated.

Reaction of perfluoroglutaryl fluoride with dimethyldiethoxysilane

A mixture of 10.2 g of perfluoroglutaryl fluoride and 7.6 ml of dimethyldiethoxysilane was stirred and heated at 60° for 10 min in a 25 ml flask equipped with a magnetic stirrer and a gas vent leading to a dry ice trap. The 3.4 g of volatile material in the cold trap at the end of the reaction was identified as dimethyldifluorosilane. Distillation of the residue yielded 10.8 g of diethyl perfluoroglutarate.

Reaction of terephthaloyl fluoride with silicone oil

A Hastelloy bomb of 240 ml capacity was charged with 17.0 g of terephthaloyl fluoride and 13 g of a silicone fluid consisting of 90 mole percent phenylmethylsiloxy units and 10 mole percent dimethylsiloxy units. The bomb was evacuated and heated to 300° for 8 h. After cooling a mixture of solid and liquid was isolated. The material was evacuated to less than 1 mm pressure and heated at 100°. The distillate was 2.5 g of phenylmethyldifluorosilane, identified by its infrared spectrum. The 11.1 g of solid residue remaining was polymeric terephthalic anhydride.

Reaction of benzoyl fluoride with tetraethoxygermane

Five grams of tetraethoxygermane was added to a 50 ml flask equipped with condenser, magnetic stirring bar, and addition funnel, and containing a nitrogen atmosphere. Over a period of 20 min 10 g of benzoyl fluoride was added and then the solution was stirred at room temperature for an additional 10 min. The flask was slowly heated in an oil bath. Suddenly, at about 115°, and after 40 min since the start of heating, a violent reaction took place. A glass stopper was blown out and copious white fumes, as well as some liquid, were ejected from the flask. The reaction was heated an additional h at 120° while passing a nitrogen stream through the flask and a dry ice trap. A small amount of solid, subsequently identified from its mass spectrum as germanium tetrafluoride, was present in the trap. The nonvolatile material was distilled yielding 9.1 g of ethyl benzoate.

Reaction of benzoyl fluoride with tetrakis(dimethylamino)stannane

A 25 ml flask equipped with condenser, magnetic stirring bar and addition funnel was purged with nitrogen. Five grams of tetrakis(dimethylamino)stannane was added to the flask, and then 8.4 g of benzoyl fluoride was added to the addition funnel. Over a period of 20 min 4 ml of the acid fluoride was added, while the flask was cooled in a water ice bath. Each drop produced a vigorous reaction, and a white precipitate formed. The ice bath was removed, and 2 ml of acid fluoride was added over a 10 min period. The flask was warmed by the exothermic reaction. The rest of the acid fluoride

was added over a period of 10 min. The mixture was allowed to stir at room temperature overnight.

The mixture was distilled to give 7.8 g of *N,N*-dimethylbenzamide which crystallized to a low melting solid. The 2.8 g of solid, brown colored residue in the still pot was stirred and washed with ethyl ether. (Found: Sn, 61.6; F, 41.2. SnF_4 calcd.: Sn, 61.0; F, 39.0%.)

Reaction of 2,2-dimethylpropionyl fluoride with tri-n-butylmethoxystannane

Into a 1.25 inch ID Teflon[®] tube was added 7.9 g of 2,2-dimethylpropionyl fluoride. Tri-n-butylmethoxystannane was then added by syringe while stirring. After approximately 2 ml had been added, pressure was noted in the tube, and the reaction was obviously exothermic. The tube was cooled in a water ice bath and the remainder of the 21.5 ml of the tin compound was slowly added. A solid formed in the bottom of the tube. The magnetic stirring bar was inoperative, so the solid was broken up with a spatula, during which time it was evident further reaction was taking place.

After standing overnight, the volatiles were removed under vacuum and trapped in a dry ice trap. This material was virtually pure methyl 2,2-dimethylpropionate.

The solid white residue remaining was washed with hexane and dried overnight under vacuum at approximately 90°. It weighed 23.5 g and its elemental analysis indicated it was tri-n-butylfluorostannane. (Found: C, 47.1, H, 8.8; F, 4.8; Sn, 38.0. $\text{C}_{12}\text{H}_{27}\text{FSn}$ calcd.: C, 46.7; H, 8.8; F, 6.1; Sn, 38.4%.)

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