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Short Communication

Interaction of carbonyl compounds with organometallic azides
IV. Perfluoroalkyl isocyanates*

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Although isocyanates have classically been prepared by treatment of the carboxylic acid chlorides containing one carbon atom more in the alkyl chain with an ammonium or alkali metal azide, *i.e.* the Curtius rearrangement[2], this method has been fraught with difficulties, particularly in the case of perfluoroalkanoyl chlorides. The Curtius rearrangement proceeds through the intermediacy of an acyl azide, which usually must be isolated in a pure form before being subjected to thermal decomposition. The explosive nature of acyl azides is well documented[3] and sensitivity appears to be inversely proportional to boiling point, *e.g.* acetyl azide, CH_3CON_3, having never been isolated as a pure compound[4]. It is thus not surprising that perfluoroacyl azides would be quite shock-sensitive[5].

We sought a simple procedure amenable to ready preparation of the isocyanates, which are valued precursors to fluorinated amines, ureas, carbamates and thiocarbamates. A one-pot reaction in which the sensitive azide was generated *in situ* and thermolysed at low concentration and in which the product isocyanate was recoverable by distillation was the ideal.

Preparations utilizing trimethylsilyl azide

The recently reported trimethylsilyl azide (TMSA) modification of the Curtius degradation[6] appeared to offer a feasible method. In this procedure, TMSA is added dropwise to a solution of acid chloride in toluene or xylene, heated at *ca.* 100° until nitrogen evolution ceases and worked up by distilling out trimethylchlorosilane and solvent, followed by fractionation of the residue.

This procedure worked well for perfluorohexanoyl chloride (I), a solution of which was treated with TMSA in mesitylene. After 18 h heating at 100°, nitrogen evolution was nearly quantitative and fractionation of the reaction mixture gave 89% of trimethylchlorosilane and 79% of perfluoropentyl isocyanate (IV). An analogous

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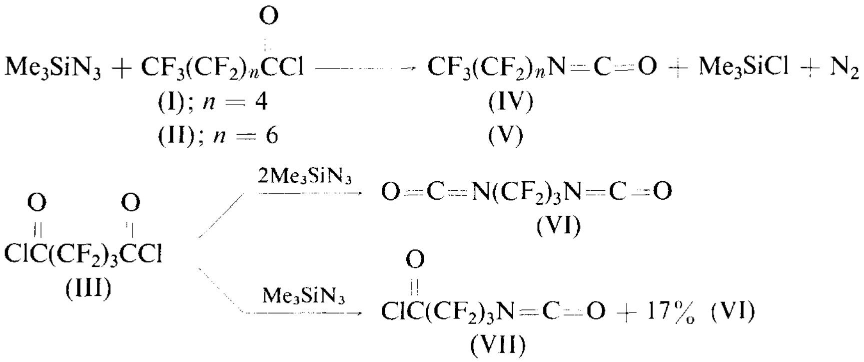
preparation with perfluorooctanoyl chloride (II) and TMSA without solvent gave 82% of perfluoroheptyl isocyanate (V). The IR spectra of the products showed the absence of Si–C absorption at 850 cm^{-1} and intense C–F absorption around 1120 cm^{-1}.

Hexafluoroglutaroyl chloride (III) upon reaction with two equivalents of TMSA in the absence of solvent gave 78% of 1,3-di-isocyanatoperfluoropropane (VI), while equimolar quantities of TMSA and (III) afforded 34% of 3-chlorocarbonylperfluoropropyl isocyanate (VII) together with 17% of (VI). Separation of (VI) (b.p. 65°) and (VII) (b.p. 80°) from each other and from trimethylchlorosilane (b.p. 57°) was difficult and the actual yields were much higher. Those reported represent pure material obtained after two successive fractionations. Figure 1 summarizes these results.



$$Me_3SiN_3 + CF_3(CF_2)_n\overset{O}{\overset{\|}{C}}Cl \longrightarrow CF_3(CF_2)_nN{=}C{=}O + Me_3SiCl + N_2$$

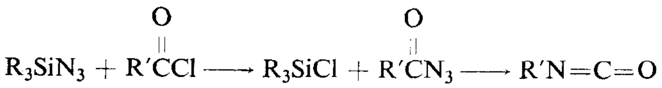
(I); $n = 4$ → (IV)
(II); $n = 6$ → (V)

$$Cl\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}Cl \text{ (III)} \xrightarrow{2Me_3SiN_3} O{=}C{=}N(CF_2)_3N{=}C{=}O \text{ (VI)}$$

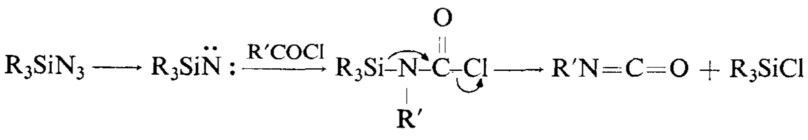
$$Cl\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}Cl \text{ (III)} \xrightarrow{Me_3SiN_3} Cl\overset{O}{\overset{\|}{C}}(CF_2)_3N{=}C{=}O \text{ (VII)} + 17\% \text{ (VI)}$$

Fig. 1. Reactions of trimethylsilyl azide with acid chlorides.

We infer that perfluoroalkanoyl azides are formed as intermediates in the reaction of TMSA with acid chlorides and that they undergo smooth thermolytic decomposition, being formed at temperatures above their decomposition points. As TMSA is known to be thermally stable up to 450°[7]—but not photochemically stable[8]—it appears that the reaction mechanism can be expressed by a two-step sequence: metathesis of $-SiN_3$ and $-\overset{O}{\overset{\|}{C}}Cl$, followed by thermolysis of $-\overset{O}{\overset{\|}{C}}N_3$ (eqn. (1)). The alternative pathway of TMSA decomposition, nitrene insertion and desilylation (eqn. (2)) seems less likely since $R_3Si\ddot{N}:$ undergoes self-insertion in preference to reaction with a substrate[8].



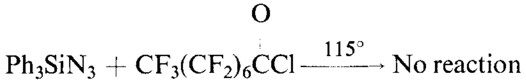
$$R_3SiN_3 + R'\overset{O}{\overset{\|}{C}}Cl \longrightarrow R_3SiCl + R'\overset{O}{\overset{\|}{C}}N_3 \longrightarrow R'N{=}C{=}O \tag{1}$$



$$R_3SiN_3 \longrightarrow R_3Si\ddot{N}: \xrightarrow{R'COCl} R_3Si{-}\underset{R'}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}Cl \longrightarrow R'N{=}C{=}O + R_3SiCl \tag{2}$$

Reaction with triphenylsilyl azide

In the hope of developing a system in which the perfluoroalkyl isocyanate would be the lowest boiling component of the reaction mixture and hence easily separable, we attempted a reaction with Ph_3SiN_3 as the azide-delivering component. Equimolar quantities of (II) and Ph_3SiN_3 were heated in mesitylene for 24 h. Work-up afforded a 92% recovery of the chloride and 99% of the azide (eq. (3)). No isocyanate or acyl azide was isolated.



$$Ph_3SiN_3 + CF_3(CF_2)_6\overset{O}{C}Cl \xrightarrow{115^\circ} \text{No reaction} \qquad (3)$$

This was puzzling, for if Ph_3SiN_3 was acting merely as a source of azide ion it should have been more active than Me_3SiN_3, since the Si–N bond in the former will be weakened by inductive donation of the phenyl groups[9]. As the TMSA–acyl chloride reaction proceeds in non-polar media, it is probable that the transition state for transfer of the N_3 moiety from silicon to acyl carbon is relatively non-polar and in all probability quite different from the transition state of the reaction of NaN_3 with RCOCl, which is usually carried out in polar media[2]. Hence we infer that the N_3^- ion is not involved in the present reaction.

Mechanism of azide transfer from silicon to carbon

Both the S_N2–Si mechanism for reactions involving silicon–heteroatom bond formation[10] and the necessity of electrophilic catalysis in nucleophilic acyl substitution reactions are well documented. Electrophilic catalysis requires[11] that azide transfer from Si to C involve an intermediate such as (VIII), where R_3SiN_3 acts as electrophile. Other than another molecule of RCOCl, R_3SiN_3 is the best electrophile in the system. Collapse to acyl azide could occur by several pathways, *e.g.* *via* (IX) and (X).

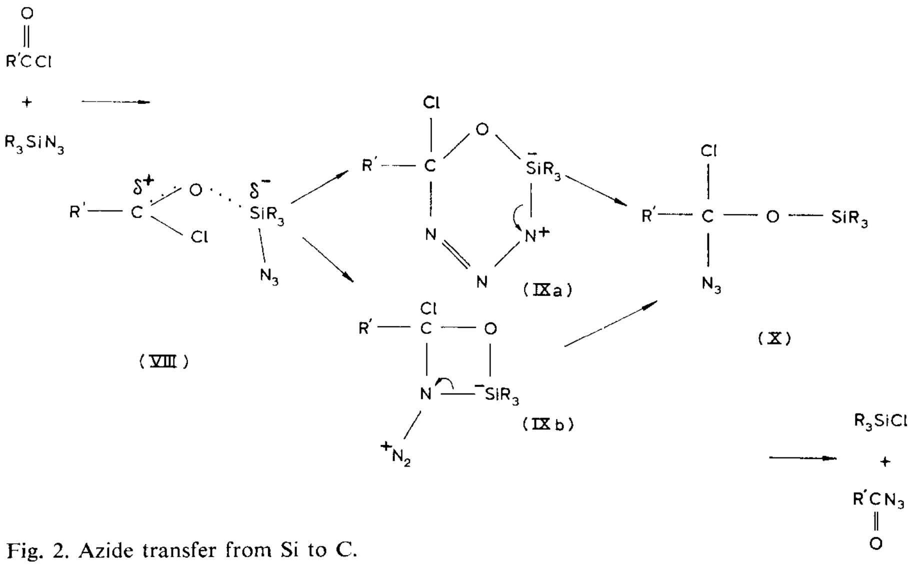


Fig. 2. Azide transfer from Si to C.

But why does Ph_3SiN_3 fail to react? Steric hindrance is seldom a great factor in reactions at a silicon center[10], but electronic factors often are. Ph_3SiN_3 shows the normal reactivity for an Si–N bond in its sensitivity to hydrolysis and forms a phosphinimine derivative readily, a characteristic of silyl azides[7]. But the Ph_3Si group is a much poorer Lewis acid than the Me_3Si group chiefly because of the electron-releasing phenyl groups. Hence the non-reactivity of Ph_3SiN_3 towards acyl halides can be ascribed to electronic factors, specifically the poor Lewis acid character of the Ph_3Si group. As formation of complex (VIII) is not favored, so is the reaction of Ph_3SiN_3 with fluoroacyl chlorides.

Conclusions

The trimethylsilyl azide modification of the Curtius degradation afforded yields of fluorinated isocyanates in the area of 80% when the reactants were mixed in equimolar proportions. Use of an excess of silyl azide is not advisable, as a reaction takes place between silyl azides and isocyanates. Details on this reaction, which is much slower than the azide–acid halide reaction, will be reported at a later time.

Experimental

General comments

All reactions with silyl azides were carried out under purified nitrogen in an efficient fume hood. IR spectra were determined on a Perkin–Elmer Model 21 spectrophotometer. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, N. Y. Silyl azides, prepared as described by us earlier[12], and perfluoroacyl halides, obtained from either Pierce Chemical Co. or Petrarch Systems, Inc., were redistilled before use. Both classes of compounds are extremely irritating to nasal mucous membranes and care in their use should be exercised.

Perfluoropentyl isocyanate (IV)

A solution of 5.8 g (0.05 mole) of TMSA in 30 ml of mesitylene was added over a 30 min period to 16.6 g (0.05 mole) of perfluorohexanoyl chloride (I). The mixture, which began to evolve N_2 toward the end of the addition, was heated in an oil bath maintained at 100° for 18 h, then fractionated with a 35 cm jacketed Widmer column. After removal of 4.8 g (89%) of trimethylchlorosilane, b.p. 56–58°, isocyanate (IV)[5] was collected as a colorless liquid, b.p. 77–79°. The yield was 12.3 g (79%); IR (neat): 2245 (vs), 1315, 1252 (sh) and 1120 cm^{-1}.

Perfluoroheptyl isocyanate (V)

In a procedure identical with the above with the exception that no solvent was employed, 43.3 g (0.10 mole) of perfluoro-octanoyl chloride (II) and 15.0 g (0.13 mole) of TMSA gave 35.7 g (82%) of the isocyanate, b.p. 118–120°; IR (neat): 2250, 1450, 1310, 1250 and 1115 cm^{-1}.

Reaction of hexafluoroglutaryl chloride (III) with TMSA

(a) 1:2 Ratio — A reaction using the above procedure between 13.8 g (0.05 mole) of (III) and 11.5 g (0.10 mole) of TMSA gave, after distillation through a 30 cm heated and jacketed, helices-packed column, 9.1 g (78%) of di-isocyanate (VI) b.p. 64–65°; IR: 2260, 1282, 1217, 1170 and 1140 cm^{-1}. (Found: C, 25.60; H, 48.50; N, 12.21%. $C_5F_6N_2O_2$ requires C, 25.77; F, 48.91; N, 12.02%.)

(b) 1:1 Ratio — The same procedure was followed with 0.1 mole each of (III) and TMSA. The distillation fractions boiling at 60–70° and 70–87° were collected individually and re-distilled through a 35 cm jacketed Widmer column with a flexopulse head giving a 20:1 reflux ratio. After traces of Me_3SiCl had been removed, 4.0 g (17%) of (VI), b.p. 65°, was collected. Following a small intermediate fraction, chlorocarbonyl isocyanate (VII) (8.7 g, 34%) was collected at 80–83° as a colorless, air-sensitive liquid. IR (neat): 2255, 1788, 1312 and 1245–1125 cm^{-1}. (Found: C, 23.40; F, 44.19; N, 5.60%. $C_5F_6NO_2Cl$ requires C, 23.51; F, 44.61; N, 5.48%.)

Reaction of (II) with triphenylazidosilane

A solution of 15.2 g (0.05 mole) of triphenylazidosilane (Petrarch Systems) in 20 ml of mesitylene was added to 21.6 g (0.05 mole) of perfluoro-octanoyl chloride. The mixture was stirred in a bath at 115–120° for 24 h. Distillation afforded 19.8 g (92%) of unreacted (II). After removal of mesitylene from the residue by evaporation at reduced pressure, hexane extraction of the remaining crystalline mass, concentration and cooling gave colorless crystals, which, after drying *in vacuo,* weighed 15.0 g. They were identified as triphenylazidosilane by IR and mixed melting point analysis.

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