An Electron Spin Resonance Study of Trialkylsilyl Radical Addition to Alkyl Isocyanates

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Addition of photochemically-generated trialkylsilyl radicals to alkyl isocyanates to give imidoyl radicals (A) has been studied in cyclopropane solution using e.s.r. spectroscopy. The rate of addition of trimethylsilyl radicals to

$$R^1{}_3Si^{\bullet} + R^2N{=}C{=}O \xrightarrow{k_{add}} \underset{(A)}{R^2N{=}COSiR^1{}_3}$$

alkyl isocyanates has been determined relative to that of addition to methyl trifluoroacetate or ethylene and k_{add} (R^1 = Me) was found to decrease in the order R^2 = Me > Et > Pr^i > Bu^t at 164 K. It is proposed that this trend is steric in origin and that the Me_3Si group is closer to the *N*-alkyl group in the transition state for addition than in the product imidoyl radical. The palladium chloride catalysed addition of triethylsilane to n-butyl isocyanate gives the imidate $Bu^nN{=}C(H)OSiEt_3$ rather than the isomeric *C*-silylamide $Bu^nN(H)C({=}O)SiEt_3$, as previously reported.

PREVIOUS e.s.r.[1] and product analysis[2] studies have established that alkoxyl or siloxyl radicals add rapidly to alkyl isocyanides to form imidoyl radicals [for example, equation (1; M = C or Si)]. When M = C the imidoyl radical (I) undergoes irreversible β-scission above 220 K [equation (2)] to give t-butyl radicals and the alkyl isocyanate and the kinetics of this fragmentation have been examined using e.s.r. spectroscopy.[1]

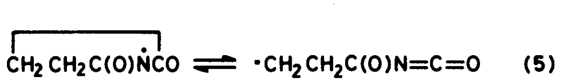
However, no e.s.r. evidence was found for an analogous β-scission of (I; M = Si) at temperatures up to 273 K and the difference in behaviour was attributed to the greater strength of the Si–O bond compared with that of the C–O bond.[1] These results suggested to us that the reverse reaction, namely addition of trialkylsilyl radicals, to alkyl isocyanates [equation (3; M = Si)] to form imidoyl radicals, might proceed at a convenient rate for study in solution using e.s.r. spectroscopy, and in this paper we report the results of such a study.

$$Me_3MO^{\bullet} + RN{=}C \longrightarrow \underset{(I)}{RN{=}\dot{C}OMMe_3} \quad (1)$$

$$RN{=}\dot{C}OMMe_3 \longrightarrow RN{=}C{=}O + Me_3M^{\bullet} \quad (2)$$

$$Me_3M^{\bullet} + RN{=}C{=}O \longrightarrow RN{=}\dot{C}OMMe_3 \quad (3)$$

$$R^1OH + R^2N{=}C{=}O \longrightarrow R^2N(H)C(O)OR^1 \quad (4)$$



$$\overline{CH_2CH_2C(O)\dot{N}CO} \rightleftharpoons {}^{\bullet}CH_2CH_2C(O)N{=}C{=}O \quad (5)$$

Heterolytic (nucleophilic) addition to isocyanates is well established, for example, alcohols add readily to give urethanes [equation (4)]. By contrast, very little is known about homolytic addition to isocyanates, although interest in such reactions has been aroused by the recent results of Skell *et al.*[3] which have been interpreted in terms of rapid *reversible* ring-opening of the σ, but not the π, electronic state of the succinimidyl radical [equation (5)].

RESULTS

E.s.r. spectra of the transient free radicals reported in this paper were recorded during continuous u.v. irradiation of appropriate liquid samples in the spectrometer cavity. Trimethylsilyl radicals were generated by photolysis of di-t-butyl peroxide (DTBP) in the presence of trimethylsilane [equations (6) and (7)].[4] The solvent was cyclopropane.

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^{\bullet} \quad (6)$$

$$Bu^tO^{\bullet} + Me_3SiH \longrightarrow Me_3Si^{\bullet} + Bu^tOH \quad (7)$$

At *ca.* 167 K when methyl isocyanate (*ca.* 2M) was also present, the e.s.r. spectrum of $Me_3Si^{\bullet}$ was replaced by that shown in Figure 1(a). Replacement of the trimethylsilane by $(CD_3)_3SiH$ gave rise to the simplified spectrum, shown in Figure 1(c), which may be readily analysed in terms of *a*(1N) 0.82, *a*(3H) 0.28 G, *g* 2.0013 at 167 K. Comparison of these e.s.r. parameters with those reported[1] for the imidoyl radical $MeN{=}\dot{C}OBu^t$ [*a*(1N) ≤ 0.2, *a*(3H) 0.75, *a*(9H) 0.13 G, *g* 2.0013 at 190 K] leads us to assign the spectrum to the adduct $MeN{=}\dot{C}OSi(CD_3)_3$ [equation (8)]. The spectrum of the protio analogue (Figure 1a) was also observed during photolysis of bis(trimethylsilyl) peroxide in the presence of methyl isocyanide [equations (9) and (10; R = Me)].[1] A computer simulation using *a*(1N) 0.78, *a*(3H) 0.29, *a*(9H) 0.15 G is shown in Figure 1(b).

A number of other imidoyl radicals (II) were generated in a similar fashion by addition of trimethylsilyl radicals to alkyl isocyanates [equation (1; R = Me, Et, Bu^n, Pr^i)] and the spectroscopic parameters are listed in Table 1.

The spectrum assigned to (II; R = Bu^n) was identical with that obtained during photolysis of bis(trimethylsilyl) peroxide in the presence of n-butyl isocyanide [equation (10; R = Bu^n)]. The spectrum of (II; R = Et) was analysed with the aid of deuterium substitution and that of $EtN{=}\dot{C}OSi(CD_3)_3$, shown in Figure 2(a), was computer simulated using *a*(1N) 0.74, *a*(2H) 0.69, and *a*(3H) 0.21 G

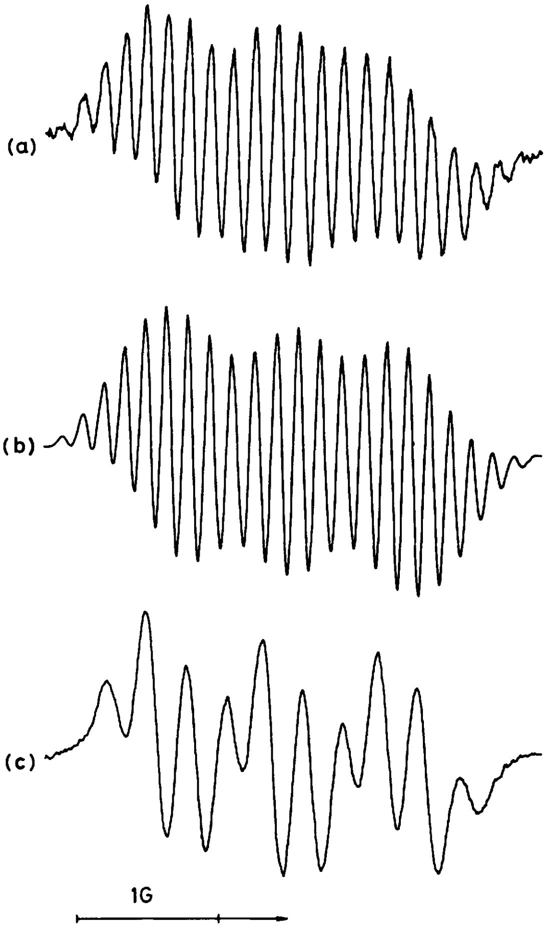


FIGURE 1 (a) E.s.r. spectrum of $CH_3N{=}\dot{C}OSiMe_3$ generated by photolysis at 167 K of a cyclopropane solution containing MeNCO, Me_3SiH, and Bu^tOOBu^t. (b) Computer simulation of the spectrum shown in (a) obtained using the parameters given in the text. (c) E.s.r. spectrum of $CH_3N{=}\dot{C}OSi(CD_3)_3$ at 167 K

[see Figure 2(b)]. The imidoyl adducts were also detectable above the range 150—180 K, but at higher temperatures the very long-lived radical[5] $(Me_3Si)_2N\dot{C}(SiMe_3)_2$ (formed by secondary reactions) increased rapidly in concentration as the photolysis progressed (see Experimental section).

$$(CD_3)_3Si\cdot + MeN{=}C{=}O \longrightarrow MeN{=}\dot{C}OSi(CD_3)_3 \qquad (8)$$

$$Me_3SiOOSiMe_3 \xrightarrow{h\nu} 2Me_3SiO\cdot \qquad (9)$$

$$Me_3SiO\cdot + RN{=}C \longrightarrow RN{=}\dot{C}OSiMe_3 \qquad (10)$$

In contrast, we found no e.s.r. evidence for addition of trimethylsilyl radicals to either Bu^tNCO or Me_3SiNCO. Thus, initially only the spectrum of $Me_3Si\cdot$ was detected when a cyclopropane solution containing DTBP (14% v/v), Me_3SiH (28% v/v), and Bu^tNCO (2.4M) was photolysed at temperatures between 172 and 243 K, although the spectra of long-lived secondary radicals rapidly appeared as the photolysis progressed. However, the imidoyl radical (II; R = Bu^t) has been generated previously[1] by addition of trimethylsiloxyl radicals to t-butyl isocyanide [equation (10; R = Bu^t)] and its e.s.r. spectrum appears as a single line of width (ΔB_{p-p}) *ca.* 1.6 G at 188 K (*g* 2.0013).*

TABLE 1

E.s.r. parameters of the imidoyl radicals $R^1N{=}\dot{C}OSiR^2_3$ in cyclopropane

			Hyperfine splittings (G)[a]			
R^1	R^2	T/K	a(N)	$a(H_\gamma)$[b]	$a(H_\delta)$[b]	a(9H)[c]
Me	Me	167	0.78	0.29 (3)		0.15
Me	CD_3	167	0.82	0.28 (3)		
Et	Me	175	0.74	0.66 (2)	0.23 (3)	0.15
Et	CD_3	175	0.74	0.69 (2)	0.21 (3)	
Bu^n	Me	172	0.75[d]	0.75 (2)[d]	[e]	[e]
Pr^i	Me	175	0.74	0.78 (1)	0.27 (6)	0.15
Me	Et	160	0.91	0.23 (3)		
Et	Et	169	0.75	0.75 (2)	[e]	
Bu^n	Et	172	0.80	0.80 (2)	[e]	

[a] The *g*-factors of all radicals were 2.0013 ± 0.0001. [b] Number of equivalent protons shown in parentheses. [c] Nine equivalent protons of the Me_3Si group. [d] Values obtained from a spectrum of better quality than that reported in ref. 1 for the radical generated by addition of $Me_3SiO^\cdot$ to Bu^nNC. More precise spectroscopic parameters could be obtained from the spectrum obtained in the present work. [e] Not resolved.

Imidoyl radicals were also generated by addition of triethylsilyl radicals to methyl, ethyl, n-butyl, and isopropyl isocyanates. Thus, the spectrum [Figure 2(c)] of the imidoyl radical $Bu^nN{=}\dot{C}OSiEt_3$ was observed during photolysis of a cyclopropane solution containing DTBP, triethylsilane, and n-butyl isocyanate. In general, the spectra of $RN{=}\dot{C}OSiEt_3$ were less well resolved than those of the trimethylsilyl analogues and splitting from the silylmethylene protons was not detected. The spectroscopic parameters of the triethylsilyl adducts are included in Table 1.

$$Me_3Si\cdot + RN{=}C{=}O \xrightarrow{k_1} \underset{\text{(II)}}{RN{=}\dot{C}OSiMe_3} \qquad (11)$$

Photolysis of solutions containing DTBP and an alkyl isocyanate $R^1R^2C(H)NCO$ in the absence of trialkylsilane gave rise to e.s.r. spectra of the α-isocyanatoalkyl radicals (III), produced by hydrogen abstraction [equation (12)].

No well defined spectra were obtained in similar experiments with t-butyl or trimethylsilyl isocyanates. The e.s.r. parameters for (III), given in Table 2, are in accord with those of the matrix isolated α-isocyanatoalkyl radicals detected by Wood *et al.*[6] after *X*-irradiation of solid solutions of primary or secondary alkyl isocyanates in adamantane.

Photochemical generation of methyl (from MeN=NMe) or t-butyl (from $Bu^t_2C{=}O$) radicals in the presence of methyl, n-butyl, t-butyl, or trimethylsilyl isocyanate resulted in the detection of the e.s.r. spectrum of only $Me^\cdot$ or $Bu^{t\cdot}$ respectively, between 172 and 250 K. Thus, these alkyl radicals do not add sufficiently rapidly to any of the isocyanates to yield detectable concentrations of adduct radicals.

Photolysis of a cyclopropane solution containing DTBP, Me_3SiH, and acetyl isocyanate afforded an e.s.r. spectrum [a(N) 1.6, $a(3H_\beta)$ 16.3 G, *g* 2.0029 at 160 K] which we assign to the radical (IV), produced by addition of trimethylsilyl radicals to the oxygen of the acetyl group [equation (13)], and no imidoyl radical was detected.

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* Repetition of this experiment has afforded *g* 2.0015 between 170 and 287 K in cyclopropane–CF_2ClCCl_2F (5 : 2 v/v).

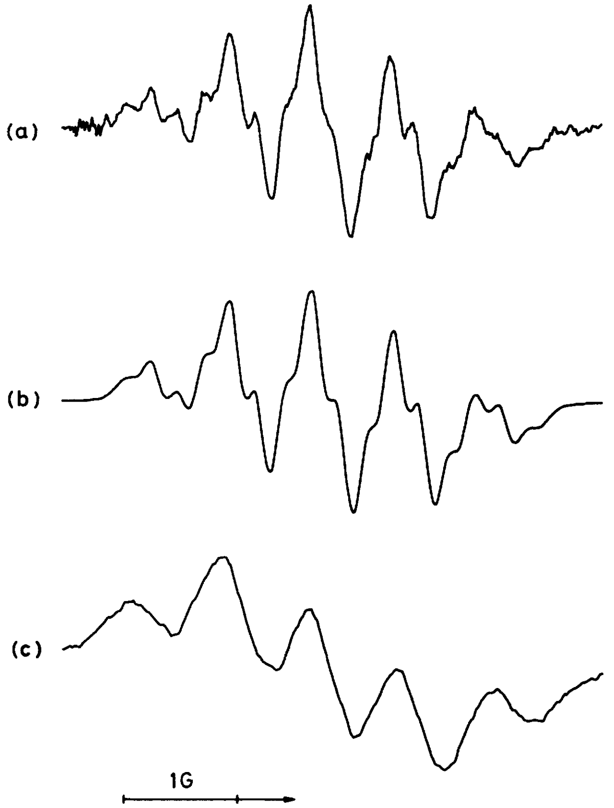


FIGURE 2 (a) E.s.r. spectrum of $\mathrm{EtN{=}\dot{C}OSi(CD_3)_3}$ generated by photolysis at 175 K of a cyclopropane solution containing EtNCO, $\mathrm{(CD_3)_3SiH}$, and $\mathrm{Bu^tOOBu^t}$. (b) Computer simulation of the spectrum shown in (a) using the parameters given in the text. (c) E.s.r. spectrum of $\mathrm{Bu^nN{=}\dot{C}OSiEt_3}$ generated by photolysis at 172 K of a cyclopropane solution containing $\mathrm{Bu^nNCO}$, $\mathrm{Et_3SiH}$, and $\mathrm{Bu^tOOBu^t}$

Relative Rates of Addition of $\mathrm{Me_3Si^{\bullet}}$ *to* RNCO. Rates of the addition reaction (11) were determined relative to the rate of addition of $\mathrm{Me_3Si\cdot}$ to methyl trifluoroacetate [equation (14)].[7] Reaction (14) was chosen as competitor because it proceeded at a convenient rate and because the e.s.r. spectrum of the adduct (V) did not overlap with the spectra of the imidoyl radicals. At 219 K the spectrum of (V) appeared as a quartet of quartets [a(3F) 16.8, a(3H) 1.8 G, g 2.0033], but as the temperature was lowered the central pair of quartets, corresponding to $M_I(3F_\beta) \pm \frac{1}{2}$, broadened whilst the outer pair of quartets [$M_I(3F_\beta) \pm \frac{3}{2}$] remained sharp. We attribute this line shape effect to restriction of rotation about the $\mathrm{CF_3{-}C}$ bond and consequent modulation of the β-fluorine splittings on the e.s.r. time scale.[8,9]

$$\mathrm{Bu^tO\cdot + R^1R^2C(H)N{=}C{=}O \longrightarrow Bu^tOH + R^1R^2\dot{C}N{=}C{=}O} \quad (12)$$

(III)

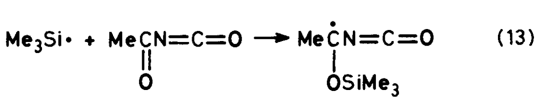
TABLE 2

E.s.r. parameters of the α-isocyanatoalkyl radicals $\mathrm{R^1(R^2)\dot{C}N{=}C{=}O}$ in cyclopropane

R^1	R^2	T/K	g Factor	Hyperfine splittings (G) a(N)	$a(\mathrm{H}_\alpha)$ [a]	$a(\mathrm{H}_\beta)$ [a]
H	H	156	2.0029	4.6	20.6 (2)	
Me	H	158	2.0028	4.8	21.0 (1)	22.2 (3)
Me	Me	167	2.0030	4.7		20.4 (6)

[a] Number of equivalent protons shown in parentheses.

Cyclopropane solutions containing known weights of methyl isocyanate (1.1—3.2M) and methyl trifluoroacetate (0.6—1.6M) in addition to DTBP (20% v/v) and $\mathrm{Me_3SiH}$ (25% v/v) were photolysed at 164 K. Spectra of both (II; R = Me) and (V) were observed (see Figure 3) and the concentration ratio of these two radicals was obtained by double integration of the derivative spectra. When $\mathrm{[MeNCO]/[CF_3CO_2Me]}$ was kept constant at 1.74, the radical concentration ratio was independent of $\mathrm{[Me_3SiH]}$ (12—38% v/v). Similar competition experiments were carried out with the other isocyanates and maximum limits for [(II)]/[(V)] were estimated in runs with t-butyl isocyanate. When samples containing RNCO, trifluoroacetate, and $\mathrm{Me_3SiH}$, in which the DTBP had been replaced by an equal volume of cyclopropane, were photolysed in control experiments the e.s.r. signals [of (V) and/or of $\mathrm{CF_3\dot{C}(OH)OMe}$] obtained were negligibly weak in comparison with the spectra observed in the presence of DTBP.



$$\mathrm{Me_3Si\cdot + Me\underset{\underset{O}{\|}}{C}N{=}C{=}O \longrightarrow Me\underset{\underset{OSiMe_3}{|}}{\dot{C}}N{=}C{=}O} \quad (13)$$

(IV)

$$\mathrm{Me_3Si\cdot + CF_3C(O)OMe \xrightarrow{k_2} CF_3\dot{C}(OSiMe_3)OMe} \quad (14)$$

(V)

FIGURE 3 E.s.r. spectra of $\mathrm{CH_3N{=}\dot{C}OSiMe_3}$ and $\mathrm{CF_3\dot{C}(OMe)OSiMe_3}$ generated by photolysis at 163 K of a cyclopropane solution containing MeNCO (2.1M), $\mathrm{CF_3C(O)OMe}$ (1.3M), $\mathrm{Me_3SiH}$, and $\mathrm{Bu^tOOBu^t}$. The lines of $\mathrm{CF_3\dot{C}(OMe)OSiMe_3}$ corresponding to $M_I(3F) \pm 1/2$ are broadened beyond the limit of detectability (see text)

Assuming that the radicals (II) and (V) are formed only by reactions (11) and (13), respectively, and destroyed by reactions (15)—(17), it may be shown [10] that equation (18) holds where r is equal to [(II)]/[(V)]. Taking [11] k_x as equal to $(4k_t^{II}k_t^{V})^{\frac{1}{2}}$ allows (k_1/k_2) to be calculated if $2k_t^{II}$ and $2k_t^{V}$ are known. The rate constants for self-reaction of $\mathrm{MeN{=}\dot{C}OSiMe_3}$ (II; R = Me) and (V) were measured in separate experiments by kinetic e.s.r. spectroscopy using the rotating sector technique.[12,13] At 164 K the values obtained were 3.7×10^9 and 5.6×10^8 l mol^{-1} s^{-1}, respectively, when the radicals were generated by photolysis of cyclopropane solu-

$$\left.\begin{array}{l}(\mathrm{II})+(\mathrm{II})\xrightarrow{2k_t^{\mathrm{II}}}\\[1em] (\mathrm{II})+(\mathrm{V})\xrightarrow{k_x}\\[1em] (\mathrm{V})+(\mathrm{V})\xrightarrow{2k_t^{\mathrm{V}}}\end{array}\right\}\text{non-radical products}\qquad\begin{array}{r}(15)\\[1em](16)\\[1em](17)\end{array}$$

$$\frac{k_1}{k_2}=\frac{r[\mathrm{CF_3CO_2Me}](2k_t^{\mathrm{II}}r+k_x)}{[\mathrm{RNCO}](2k_t^{\mathrm{V}}+k_xr)}\qquad(18)$$

tions containing DTBP (20% v/v), Me_3SiH (25% v/v), and MeNCO or CF_3CO_2Me (13% v/v). Because of difficulties in measuring $2k_t^{II}$ for the imidoyl radicals (II; R = Et or Pr^i), we were forced to assume that these rate constants are the same as that for (II; R = Me). The values of (k_1/k_2) obtained at 164 K are given in Table 3. It is possible that $2k_t^{II}$ might decrease somewhat as R increases in bulk but, if this is so, the decrease in reactivity towards $Me_3Si^{\bullet}$ on going from MeNCO to Bu^tNCO would be emphasized still further.*

TABLE 3

Relative rate constants for addition of trimethylsilyl radicals to alkyl isocyanates and to methyl trifluoroacetate or ethylene at 164 K in cyclopropane solvent

Reactant A	Reactant B	[A]/[B]	k_A/k_B
MeNCO	CF_3CO_2Me	0.52—1.0	0.54 ± 0.02
EtNCO	CF_3CO_2Me	2.3	0.23 ± 0.01
Pr^iNCO	CF_3CO_2Me	4.0	0.021 [a]
Bu^tNCO	CF_3CO_2Me	6.3	$\leqslant 0.006$ [b]
MeNCO	$CH_2=CH_2$	2.8	0.68
CF_3CO_2Me	$CH_2=CH_2$	1.4	1.19

[a] Approximate value; the concentration of persistent radicals increased very rapidly with the duration of photolysis. [b] Imidoyl adduct from Bu^tNCO was not detected.

Similar competition experiments were carried out with mixtures of methyl isocyanate and ethylene and, making assumptions analogous to those described above, the value of k_1 (R = Me) was obtained relative to k_3 [equation (19)] [14,15] by measuring the relative concentrations of (II; R = Me) and (VI). The value of $2k_t^{VI}$ was determined using kinetic

$$\mathrm{Me_3Si\cdot}+\mathrm{CH_2{=}CH_2}\xrightarrow{k_3}\underset{(\mathrm{VI})}{\mathrm{Me_3SiCH_2\dot{C}H_2}}\qquad(19)$$

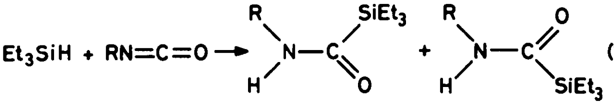
e.s.r. spectroscopy and found to be 1.4×10^9 l mol^{-1} s^{-1} when the radical was generated by photolysis of a cyclopropane solution containing DTBP (25% v/v), Me_3SiH (25% v/v), and $CH_2=CH_2$ (5% v/v) at 164 K. The cycle was completed by measuring k_2 relative to k_3 during competitive addition of $Me_3Si\cdot$ to CF_3CO_2Me and ethylene. The results of these experiments, which are internally consistent within experimental error, are included in Table 3.

Addition of Trialkylsilanes to Alkyl Isocyanates.—Trialkylsilanes are said not to undergo addition to alkyl isocyanates in the absence of palladium catalysts, even at elevated temperatures.[16] However, if the imidoyl radicals were to abstract hydrogen from a trialkylsilane at a sufficient rate, a chain reaction, with propagation steps shown (for Et_3SiH) in equations (20) and (21), could be established leading to the imidate (VII).

$$\mathrm{Et_3Si\cdot}+\mathrm{RN{=}C{=}O}\longrightarrow\mathrm{RN{=}\dot{C}OSiEt_3}\qquad(20)$$

$$\mathrm{RN{=}\dot{C}OSiEt_3}+\mathrm{Et_3SiH}\longrightarrow\underset{(\mathrm{VII})}{\mathrm{RN{=}C(H)OSiEt_3}}+\mathrm{Et_3Si\cdot}\qquad(21)$$

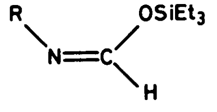
We thus attempted to initiate, by thermal decomposition of di-t-butyl hyponitrite [17] (4 mol%), the radical chain addition of triethylsilane to ethyl isocyanate (*ca.* 2M in triethylsilane as solvent) at temperatures up to 328 K. However, no evidence for addition was detected by ^1H n.m.r. spectroscopy. We conclude that reaction (21) is probably too slow under these conditions to maintain the chain and we note that triethylsilane does not undergo radical chain addition to hex-1-ene during 38 h at 313 K in the presence of a source of initiating t-butoxyl radicals, implying that β-trialkylsilylalkyl radicals also do not rapidly abstract hydrogen from Et_3SiH under these conditions.[18]



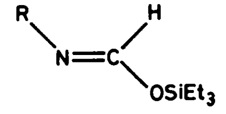
(22)

(VIIIa) (VIIIb)

Ojima and Inaba [16] have reported that $PdCl_2$ catalyses the addition of Et_3SiH to n-butyl or cyclohexyl isocyanate at 353—403 K to give the *C*-silylamide (VIII; R = Bu^n or cyclo-C_6H_{11}).† Two isomers were obtained from n-butyl isocyanate and it was thought that these were (VIIIa) and (VIIIb). The single product obtained from cyclohexyl isocyanate was assigned the *trans*-structure (VIIIb) on steric grounds. Since we considered that the imidate structure (VII) was much more reasonable for these adducts, we have repeated Ojima and Inaba's synthesis with n-butyl isocyanate.



(VIIa)



(VIIb)

The ^1H n.m.r. spectrum of the product in C_6D_6 showed two singlets at δ 8.21 and 8.29 (relative integrals 1 : 2.3), assigned by Ojima and Inaba to the N–H protons in (VIIIa) and (VIIIb), but which we now assign to the imidoyl C–H protons in (VIIa) and (VIIb). The proton-coupled ^{13}C n.m.r. spectrum of the product in C_6D_6 showed a pair (relative integrals *ca.* 1 : 2.5) of doublets of triplets at δ 170.3 ($^1J_{C-H}$ 187.5, $^3J_{C-H}$ 8.0 Hz) and 164.4 p.p.m. ($^1J_{C-H}$ 189.5, $^3J_{C-H}$ 5.5 Hz) which we assign to the imidoyl carbons of (VIIa and b). The values of $^1J_{C-H}$ are typical for hydrogen

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* We have reported previously [1] that $2k_t^{II}$ for (II; R = Bu^t), generated by addition of $Me_3SiO^{\cdot}$ to Bu^tNC, is 3×10^8 l mol^{-1} s^{-1} at 200 K. Repetition of these measurements has afforded more reliable values of 1.1×10^9 l mol^{-1} s^{-1} at 200 K for a reaction mixture containing $Me_3SiOOSiMe_3$ and Bu^tNC in cyclopropane–benzene (1 : 1 : 10 : 4 v/v) or cyclopropane–CF_2ClCCl_2F (1 : 1 : 10 : 4 v/v), and 2.2×10^8 l mol^{-1} s^{-1} at 164 K in the cyclopropane–CF_2ClCCl_2F solvent system. Thus, $2k_t^{II}$ for (II; R = Bu^t) does appear to be somewhat smaller than that for (II; R = Me).

† The mechanism of the palladium-catalysed addition (22) is not known. Both heterolytic and homolytic pathways can be envisaged.

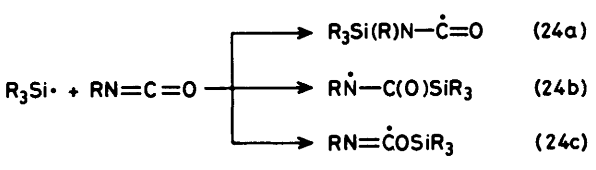
which is *directly bound* to sp^2-hybridised carbon and coupling constants of this magnitude are not consistent with the *C*-silylamide structure (VIII).[19]

Photolysis of DTBP in the presence of (VII; R = Bu^n) at 170—270 K afforded e.s.r. spectra of more than one radical, but the spectrum of $Bu^nN{=}\dot{C}OSiEt_3$ [*cf.* Figure 2(c)] was probably present. It is possible that rotation about the C–O or C=N bonds in the imidoyl radicals (II) may not be sufficiently rapid to bring about configurational equilibration (see Discussion section) within the lifetime of (II) and thus the isomeric composition of (II) derived by addition of silyl radicals to RNCO and by abstraction of hydrogen from (VII) could differ.

DISCUSSION

Addition of trialkylsilyl radicals to ketones [equation (23)] is a well known reaction that has been studied extensively using e.s.r. spectroscopy.[20] The rate of similar addition to carboxylic acid derivatives has been shown to depend markedly on the nature of the carbonyl substituents.[7,20]

$$R_3Si\cdot + R_2C{=}O \longrightarrow R_2\dot{C}OSiR_3 \qquad (23)$$

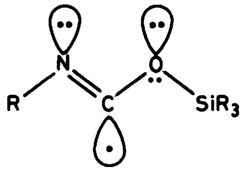


$$R_3Si\cdot + RN{=}C{=}O \longrightarrow R_3Si(R)N{-}\dot{C}{=}O \qquad (24a)$$
$$\longrightarrow R\dot{N}{-}C(O)SiR_3 \qquad (24b)$$
$$\longrightarrow RN{=}\dot{C}OSiR_3 \qquad (24c)$$

There are three possible sites for addition of trialkylsilyl radicals to alkyl isocyanates, as shown in equations (24a—c). Formation of the imidoyl radical would be expected to be the most exothermic reaction, because of the appreciably greater strength of the Si–O bond [D(Me$_3$Si–OH) 536 kJ mol^{-1}][21] compared with the strengths of the Si–N and Si–C bonds. Addition of alkyl radicals to alkyl isocyanates was not detected and imidoyl radical formation by addition of t-butyl radicals [*cf.* reaction (24c)] would be less favourable by *ca.* 155 kJ mol^{-1}.[21] In fact, the reverse reaction, β-scission of $RN{=}\dot{C}OCMe_3$, proceeds readily.[1]

Addition of $Me_3Si^{\cdot}$ to acetyl isocyanate gives the α-isocyanatoalkyl radical (IV) rather than an imidoyl adduct. Addition to the acetyl carbonyl group is faster and probably more exothermic then addition to the C=O fragment of the isocyanate function.

The e.s.r. parameters of the imidoyl radicals (II) clearly establish them to be σ radicals strongly bent at C_α [$a(^{13}C_\alpha)$ for $Bu^tN{=}\dot{C}OSiMe_3$ is 116 G[1]]. Semi-empirical (INDO) molecular orbital calculations[22] for planar $HN{=}\dot{C}OH$ suggest a *trans*-configuration about the N=C bond since, although *cis*- and *trans*-configurations did not differ greatly in energy, only for *trans*-configurations was a small nitrogen splitting (−2 to +3 G) predicted and much larger splittings (+5 to +30 G) were calculated for *cis*-configurations.* The most stable conformation about the C–O bond is less certain, but it is likely that the atoms comprising the SiOC=N system are coplanar in order to maximise conjugation between a lone pair of electrons on oxygen and the C=N group. The *s-trans* conformation about the C–O bond will probably be preferred for steric reasons and thus we consider that the imidoyl radicals probably adopt the W structure (IX) with a planar SiOCNC skeleton. There will, of course,



(IX)

be conjugative delocalisation of the unpaired electron onto nitrogen and oxygen.

The differences in rates of addition of trimethylsilyl radicals to the alkyl isocyanates are surprisingly large. The rate of addition to RNCO decreases along the series R = Me > Et > Pr^i > Bu^t such that addition to Bu^tNCO could not be detected by e.s.r. spectroscopy. At 164 K addition of $Me_3Si^{\cdot}$ to MeNCO is about 1.5 times slower than its addition to ethylene [reaction (19)] and an absolute value for k_3 (4.7×10^3 l mol^{-1} s^{-1} extrapolated to 164 K) has been obtained previously using flash photolysis–e.s.r. spectroscopy.[23] However, we prefer to regard the reported value of k_3 as a lower limit † and conclude that k_1 (R = Me) is $>3 \times 10^3$ l mol^{-1} s^{-1} at 164 K. Furthermore, since only $MeN{=}\dot{C}OSiMe_3$ was detectable when $Me_3Si^{\cdot}$ was generated in the presence of MeNCO (*ca.* 1M) at 164 K we again conclude[24] that k_1 is $>$*ca.* 3×10^3 l mol^{-1} s^{-1}.

Addition of trimethylsilyl radicals to alkyl isocyanates must be significantly exothermic and it seems likely that a reactant-like transition state is involved. Interaction of the nucleophilic trialkylsilyl radical with the electrophilic isocyanate would be expected to involve charge transfer from the addendum to the acceptor and this polar effect may be represented in valence bond terms by inclusion of structures (Xb and c) in a description of the transition state. It is unlikely that changing R from Me to Bu^t would result in significant destabilisation of the isocyanate radical anion $[RN{=}C{=}O]^{-\cdot}$ because of any difference in the electronic effects of the alkyl groups. Equally, the relatively large distance between the groups R and Me_3Si in the imidoyl radical (II) might suggest that

$$Me_3Si\cdot\ \ RN{=}C{=}O \longleftrightarrow Me_3Si^{+}\ \ RN{=}\dot{C}{-}\bar{O} \longleftrightarrow Me_3Si^{+}\ \ R\bar{N}{-}\dot{C}{=}O$$

(Xa) (Xb) (Xc)

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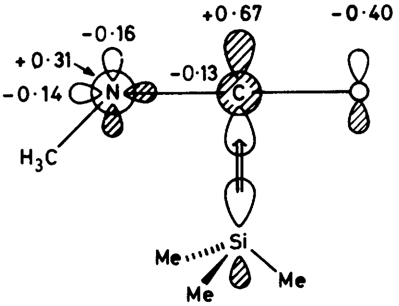
* The following standard bond lengths were used in these calculations: N–H, 1.01; N=C, 1.32; C–O, 1.36; O–H, 0.96 Å. Calculations were performed for all combinations of the following bond angles: $\widehat{NCO}$, 115—145° (10° steps); $\widehat{HNC}$ and $\widehat{COH}$, 90—270° (45° steps).

† The reported[15,23] lifetimes of $Me_3Si^{\cdot}$ in the presence and absence of ethylene are remarkably similar. Furthermore, with the low concentrations of ethylene employed, it appears likely that the alkene could have been rapidly consumed in the area of the sample where $Me_3Si^{\cdot}$ was generated photochemically.

steric effects would have little influence on the rate of addition. However, closer examination of this reaction using the perturbational molecular orbital approach[25] indicates that the trimethylsilyl and *N*-alkyl groups may be closer in the transition state for addition than in the imidoyl radical produced.

The alkyl isocyanates are bent at nitrogen ($\mathrm{C\hat{N}C}$ is 140° in MeNCO[26]) and the NCO group is probably close to linear, although bending at carbon appears to require little energy.[26,27] The most favourable direction of approach of the trimethylsilyl radical is probably with the silicon atom in the CNCO plane of the isocyanate, since the unpaired electron of the final imidoyl radical resides in a σ orbital.[28] The dominant frontier orbital interaction should be between the SOMO of the nucleophilic $\mathrm{Me_3Si^{\bullet}}$ and the LUMO of the electrophilic isocyanate. Simple considerations suggest and MO calculations confirm that the LUMO of an alkyl isocyanate is a σ orbital, primarily antibonding between the two-coordinate carbon atom and both nitrogen and oxygen. The principal relevant contributions to the LUMO, as predicted by CNDO calculations[22] employing the geometry of MeNCO obtained from electron diffraction studies,[26] are indicated in the Scheme (orbitals with coefficients <0.1 are omitted).



SCHEME

The trimethylsilyl radical is pyramidal at silicon[29] and the SOMO is a hybrid of Si-3*s* and -3*p* orbitals. In the absence of steric constraints, the lowest energy approach of $\mathrm{Me_3Si^{\bullet}}$ could be in a direction such as to permit appreciable overlap between the SOMO and the LUMO of the isocyanate in the region of the two-coordinate carbon, since the $2p_\sigma$ atomic orbital of this atom is the principal contributor to the LUMO (see Scheme). Thus, the *N*-alkyl and trimethylsilyl groups could be significantly closer in the transition state for addition than in the product imidoyl radical. Steric compression, which would be particularly severe for addition to $\mathrm{Bu^tNCO}$, could prevent adoption of the electronically favoured transition state geometry and result in the observed low rate of addition to this isocyanate. This explanation requires that the trialkylsilyl radical and the *N*-alkyl group are on the same side of the N=C=O group, as shown in the Scheme, and this is reasonable if the final configuration of the imidoyl radical is the W structure (IX).

EXPERIMENTAL

Materials.—The alkyl isocyanates were commercial products (Aldrich) and were purified by distillation before use. Trimethylsilane (PCR), triethylsilane (Fluka), and cyclopropane (Cambrian) were used as received. Di-t-butyl hyponitrite,[17] methyl trifluoroacetate,[30] trimethylsilyl,[31] and acetyl isocyanates[32] were prepared by published methods. Tris(trideuteriomethyl)silane was prepared by reduction of $\mathrm{(CD_3)_3SiCl}$ using lithium aluminium hydride in diethyldigol.

Triethylsilyl (*N*-n-butyl)formimidate (VII; R = $\mathrm{Bu^n}$) was prepared by reaction of triethylsilane with n-butyl isocyanate.[16] Triethylsilane (4.7 g, 40 mmol), n-butyl isocyanate (4.0 g, 40 mmol), and palladium dichloride (70 mg) were heated under nitrogen at 130 °C for 12 h. Distillation of the reaction mixture gave the *product*, b.p. 80 °C at 1 Torr (lit.[16] 82 °C at 1.0 Torr). The ^{1}H and ^{13}C n.m.r. spectra were measured in $\mathrm{C_6D_6}$ ($\mathrm{Me_4Si}$ internal standard) using a Varian XL-200 spectrometer. Two isomers A and B were detected, and [A]/[B] was 2.3 (lit.,[16] 3). The ^{1}H spectrum showed (isomer A values given first) δ 8.30, 8.20 (s, N=C*H*) and 3.12, 2.78 (t, *J* 7.6, 7.6 Hz, C*H*$_2$N). The proton-decoupled ^{13}C spectrum showed (isomer A first) δ 164.4, 170.3 (N=*C*H); 41.3, 44.7 (*C*H$_2$N); 32.5, 35.9 (*C*H$_2$CH$_2$N); 20.8, 19.9 [*C*H$_2$(CH$_2$)$_2$N]; and 14.8, 13.8 [*C*H$_3$(CH$_2$)$_3$N].

E.s.r. Spectroscopy.—The techniques employed for the detection of photochemically generated radicals in solution have been described previously.[24] Suprasil quartz sample tubes were sealed under vacuum and radical concentration ratios were extrapolated to zero photolysis time to avoid complications arising from reagent consumption and/or the build-up of persistent secondary radicals. Photolysis of solutions containing $\mathrm{Bu^tOOBu^t}$, $\mathrm{Me_3SiH}$, and RNCO gave rise to the spectrum of a very long-lived radical identified as $\mathrm{(Me_3Si)_2\dot{C}N(SiMe_3)_2}$ by comparison with the authentic species[5] generated by photolysis of $\mathrm{Bu^tOOBu^t}$, $\mathrm{Me_3SiH}$, and $\mathrm{Bu^tCN}$ in cyclopropane. The concentration of this persistent radical increased very rapidly with the duration of photolysis in experiments with $\mathrm{Pr^iNCO}$ and $\mathrm{Bu^tNCO}$.

Photolysis of cyclopropane solutions containing alkyl or trimethylsilyl isocyanates, with or without trialkylsilane, did not give rise to any e.s.r. signals.

Molecular Orbital Calculations.—Calculations were performed using a version of QCPE program 141 modified by Dr. A. R. Gregory (see A. R. Gregory, *J. Chem. Phys.*, 1974, **60**, 3713). We employed the INDO (*K* = 1) option in our calculations for radicals. Closed shell INDO calculations for MeNCO failed to converge for the geometry obtained from electron diffraction studies; however, CNDO/2 calculations did converge satisfactorily.

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