Silylaminyl Radicals. Part 2.[1] Free Radical Chain Halogenation of Hydrocarbons using *N*-Halogenobis(trialkylsilyl)amines

Malcolm D. Cook, Brian P. Roberts,* and Karamjit Singh
Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ

The liquid-phase halogenation of a number of hydrocarbons and of 1-chlorobutane by *N*-halogenobis(trialkylsilyl)amines has been studied using product analysis techniques. The reactions take place by free radical chain mechanisms which involve the propagation steps generalised in equations (A) and (B) (X = Br or Cl). At 353 K, the molar reactivities of toluene (benzylic C–H) and cyclohexane towards

$$(R_3Si)_2N\cdot + RH \longrightarrow (R_3Si)_2NH + R\cdot \qquad (A)$$

$$R\cdot + (R_3Si)_2NX \longrightarrow RX + (R_3Si)_2N\cdot \qquad (B)$$

$(Me_3Si)_2N\cdot$ are approximately equal and toluene is 5.2 times more reactive than perdeuteriotoluene. The relative rates of hydrogen abstraction by $(Me_3Si)_2N\cdot$ and $(Bu^tMe_2Si)_2N\cdot$ from the primary, secondary, and tertiary C–H groups in 2-methylbutane show that the silylaminyl radicals are not only highly reactive but also sterically demanding. Thus, at 333 K the average primary C–H reactivity is 0.6 times that of the tertiary C–H towards attack by $(Me_3Si)_2N\cdot$, but 4.2 times that of the tertiary C–H towards attack by the more bulky $(Bu^tMe_2Si)_2N\cdot$. Silylaminyl radicals are much more reactive in hydrogen abstraction than are analogous dialkylaminyl radicals and this difference is interpreted in terms of thermodynamic and polar effects which arise because of the σ-donor–π-acceptor nature of the trialkylsilyl substituent.

Although dialkylaminyl radicals $(R_3C)_2N\cdot$ abstract hydrogen very sluggishly from hydrocarbons,[2] replacement of one or both *N*-alkyl substituents by trialkylsilyl groups brings about a large increase in reactivity. For example, e.s.r. studies have shown that the bis(trimethylsilyl)aminyl radical $(Me_3Si)_2N\cdot$ (I) rapidly abstracts the strongly bound hydrogen from cyclopropane [*D*(C–H) 421 kJ mol^{-1}] even at 150 K,[1,3] while $Me_2N\cdot$ fails to react at this or higher temperatures. Dimethylaminyl radicals do abstract benzylic hydrogen from toluene at 407 K, but this reaction was not detected at *ca.* 290 K.[4]

In a preliminary communication[5] we reported that *N*-bromobis(trimethylsilyl)amine readily brominates hydrocarbons by a radical chain mechanism involving the propagation steps shown in equations (1) and (2). Norbornene or t-butylethylene was added to suppress the alternative reaction pathway propagated by bromine atoms [equations (3)—(5)].

The high reactivity of (I) was further evidenced by the photoinitiated reaction of *N*-bromobis(trimethylsilyl)amine with neopentane at 333 K, in the presence of t-butylethylene, to give neopentyl bromide [equation (6)].[5] Molecular bromine does not react to a significant extent with neopentane at the same temperature,[6] because bromine atoms abstract hydrogen much more slowly than (I) from the primary C–H groups.

A brief investigation of hydrocarbon (toluene and cyclohexene) bromination using $(Me_3Si)_2NBr$ was reported some years ago by Bailey and West.[7] However, the bromoamine was believed to act only as a source of molecular bromine [equations (3)—(5)] and the involvement of (I) was not considered. 3-Bromocyclohexene was the only reported product from the bromination of cyclohexene in refluxing carbon tetrachloride.[7]

The aim of the present work was to explore the potential of *N*-halogeno(trialkylsilyl)amines as halogenating agents and, in particular, to investigate the selectivities of trialkylsilylaminyl radicals in hydrogen abstraction from saturated aliphatic C–H groups.

$$\underset{(I)}{(Me_3Si)_2N\cdot} + RH \longrightarrow (Me_3Si)_2NH + R\cdot \qquad (1)$$

$$R\cdot + (Me_3Si)_2NBr \longrightarrow RBr + (Me_3Si)_2N\cdot \qquad (2)$$

$$Br\cdot + RH \rightleftharpoons HBr + R\cdot \qquad (3)$$

$$R\cdot + Br_2 \longrightarrow RBr + Br\cdot \qquad (4)$$

$$(Me_3Si)_2NBr + HBr \rightleftharpoons (Me_3Si)_2NH + Br_2 \qquad (5)$$

$$(Me_3Si)_2NBr + (CH_3)_4C \longrightarrow (Me_3Si)_2NH + (CH_3)_3CCH_2Br \qquad (6)$$

Results

General Techniques.—Reactions between hydrocarbons and the *N*-halogenosilylamines were carried out in sealed glass tubes (sample volume 0.8—0.9 ml) and were initiated by thermal decomposition (in darkness) of azobisisobutyronitrile (AIBN) or di-t-butyl hyponitrite (TBHN), or by photochemical decomposition of the halogenoamine during sample irradiation with light from a 125 W medium pressure mercury lamp or from a 400 W high pressure sodium lamp. The tubes were immersed in a thermostatted bath of liquid paraffin contained in an unsilvered Pyrex dewar flask which allowed penetration of light to the sample. Prior to initiation of the halogenation, reaction mixtures were kept in darkness at 0 °C.

The yields and isomeric compositions of the product halides were determined by g.l.c. analysis, using benzene or chlorobenzene as internal standards present during the reactions. Halides were identified by comparison with the authentic compounds and it was assumed that the flame ionisation detector was equally sensitive to isomeric halides derived from the same hydrocarbon. Relative response factors for other compounds were determined using mixtures of known compositions. Product halide mixtures of known composition, both close to and far removed from the observed molar ratios, were shown to be unaffected by the analytical techniques employed. The yields and isomeric compositions of product

$$(Me_3Si)_2N\cdot + cyclo\text{-}C_6H_{12} \xrightarrow{k_C} (Me_3Si)_2NH + cyclo\text{-}C_6H_{11}\cdot \quad (7)$$

$$(Me_3Si)_2N\cdot + PhCH_3 \xrightarrow{k_T} (Me_3Si)_2NH + PhCH_2\cdot \quad (8)$$

halides were essentially unaffected by heating samples for twice the normal reaction time before analysis, thus eliminating the possibility that selective reaction between the halides and the silylamine (also produced in the halogenation reaction) could influence the product distribution.

Before reaction, samples showed the red-brown or yellow-green colours of the *N*-bromo- or *N*-chloro-silylamines, respectively, and these colours were discharged after reaction.

Competitive Bromination of Toluene and Cyclohexane by $(Me_3Si)_2NBr$.—This competition has been studied previously:[5] in the present work the relative reactivities of toluene and perdeuteriotoluene were also measured. A deficiency of $(Me_3Si)_2NBr$ (*ca.* 7×10^{-4} mol) was caused to react with a mixture of toluene (*ca.* 4×10^{-3} mol) and cyclohexane (*ca.* 4×10^{-3} mol) containing norbornene or t-butylethylene as halogen scavenger and AIBN (2 mol % based on bromoamine) as initiator, in the dark at 353 K. The internal standard was chlorobenzene.

The relative molar reactivity (k_C/k_T) was calculated using the integrated rate equation (9), in which the subscripts 0 and ∞ refer to concentrations at the beginning and end of the reaction, respectively. The total yield of benzyl and cyclohexyl bromide was *ca.* 90% and, although the derivation of equation (9) assumes that all the hydrocarbon consumed is

$$(k_C/k_T) = \ln\{([C_6H_{12}]_0 - [C_6H_{11}Br]_\infty)/[C_6H_{12}]_0\} \\ /\ln\{([PhCH_3]_0 - [PhCH_2Br]_\infty)/[PhCH_3]_0\} \quad (9)$$

converted to bromide, any errors arising from its use should be negligible. The results are given in Table 1.

Table 1. Competitive bromination of cyclohexane and toluene by $(Me_3Si)_2NBr$ at 353 K[a]

Bromine scavanger (mol %)[b]	k_C/k_T
Norbornene (10)	1.04
Norbornene (10)	1.06
Norbornene (10)	5.42[c]
t-Butylethylene (5)	0.64
t-Butylethylene (25)	1.06
None[d]	0.20[d]

[a] Reaction time 90 min. [b] Based on bromoamine. [c] For the competitive reaction of cyclohexane and perdeuteriotoluene (≥99 atom % D). [d] From ref. 5; the low value is due to the incursion of a bromine atom chain reaction.

Halogenation of 2-*Methylbutane* (*Isopentane.*)—The reactions of isopentane with four *N*-halogenosilylamines were carried out over a range of temperatures under conditions similar to those used for the competitive experiments. Isopentane, which contains primary, secondary, and tertiary C–H groups, was present as the solvent in large molar excess (usually [alkane]/[halogenoamine] *ca.* 7—8) and reactions were initiated thermally, using TBHN (2 mol %), or photochemically. Norbornene was usually present as the halogen scavenger, and the internal standards were benzene or chlorobenzene. The yields and isomer distributions of the halogeno(methyl)butanes resulting from reactions with $(Me_3Si)_2NBr$, $(Me_3Si)_2NCl$, or $(Bu^tMe_2Si)_2NCl$ are given in Table 2.

In the presence of norbornene (5—20 mol %), the isomer distributions obtained from the reactions of $(Me_2Si)_2NBr$ and $(Me_3Si)_2NCl$ at a given temperature are the same within experimental error, indicating that (I) is responsible for abstraction of hydrogen from the isopentane and that the halide yields may be taken to reflect accurately the selectivity of this silylaminyl radical. In the absence of scavenger, incursion of halogen atom propagated pathways is evident from the shift of the halide isomer distribution towards that obtained from radical chain reactions of excess isopentane with the free halogens (see Table 2).

The product distribution was unaffected by doubling the initial concentration of the halogenoamine relative to that of isopentane, showing that polyhalogenation was not a complicating factor.

Although the red-brown colour of $Me_3Si(Bu^t)NBr$ was discharged slowly during photolysis in isopentane containing norbornene (20 mol %) at 353 K, only small amounts of bromopentanes (derived mainly from radical attack at the tertiary and secondary C–H groups) were produced and several unidentified products were formed.

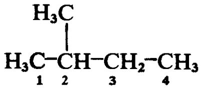
Halogenation of Other Hydrocarbons and of 1-*Chlorobutane*.—The halogenations of 2-methylpropane (isobutane), pentane, cyclohexene, and 1-chlorobutane (all present in molar excess as solvents) were also investigated, but in less detail. The isomeric compositions of the product halides are given in Tables 3—6. In the reactions of cyclohexene the relative yields of 3- and 4-bromocyclohexenes were the same with or without added norbornene. Cyclohexene would also be expected to function as a halogen scavenger, although a less effective one than norbornene, and it was present in large excess.

Competitive Bromination of Isopentane and Isobutane.—Mixtures of the two hydrocarbons ($[C_5H_{12}]/[C_4H_{10}] = 0.56$ and 1.19) were brominated with $(Me_3Si)_2NBr$ in the presence of 20 mol % norbornene. The reactions were initiated photochemically at 318 K and the isomeric compositions of the C_4 and C_5 bromides produced were essentially the same as those obtained with each hydrocarbon separately. The relative reactivities of the different C–H groups are given in Table 7.

In a number of the halogenations described above, a small amount of solid was precipitated during the reaction. Larger amounts of solid were formed if moisture was not rigorously excluded. Precipitation was most noticeable during chlorinations using $(Bu^tMe_2Si)_2NCl$, which also gave relatively low yields of alkyl chlorides, and the combined solid from several runs was isolated and shown to have an elemental composition very close to that calculated for ammonium chloride. This could be formed ultimately following cleavage of the Si–N bonds in $(Bu^tMe_2Si)_2NCl$ or $(Bu^tMe_2Si)_2NH$ by HCl, which would be formed if chlorine atoms are present in the system and abstract hydrogen (see above) or might arise from other side reactions. It has been noted previously that hydrogen halide can cleave either the Si–N or the N–Hal bonds in $(R_3Si)_2NHal$.[7]

The low yields obtained from chlorination reactions of $(Bu^tMe_2Si)_2NCl$ might also be a consequence of the rearrangement of $(Bu^tMe_2Si)_2N\cdot$ to (II) by 1,4-hydrogen transfer [equation (10)], which could compete with intermolecular hydrogen transfer from a hydrocarbon reactant. Other side reactions of $(Bu^tMe_2Si)_2N\cdot$ could occur because the reactivities of the C–H groups in $(Bu^tMe_2Si)_2NX$ (X = H or Cl) [*e.g.* equation (11)] would be expected to be at least as great as those of primary C–H groups in a simple hydrocarbon. Consistent with the incursion of such side reactions, the total yield of chloropentanes decreased from 14 to 6% as [iso-

Table 2. Halogenation of 2-methylbutane



$$\underset{1}{H_3C}-\underset{2}{CH}(CH_3)-\underset{3}{CH_2}-\underset{4}{CH_3}$$

Halogenating agent	T/K	Reaction time (min)	Norbornene (mol %)[a]	Initiation[b]	n-Halogeno-2-methylbutane isomer distribution (molar ratio) $n = 1$	2	3	4	Total halide yield (mol %)[a,c]
$(Me_3Si)_2NBr$	300	35	5	P	2.28	(1)	4.35	2.69	80
	300	35	10	P	2.25	(1)	4.38	2.60	79
	318	35	10	P	2.47	(1)	4.13	2.79	83
	318	35	10	TBHN	2.45	(1)	3.96	2.86	82
	318	70	10	TBHN	2.47	(1)	3.92	2.84	78
	318	35	20	P	2.50	(1)	4.11	2.82	83
	318	35	20	TBHN	2.49	(1)	3.97	2.82	85
	333	35	10	P	2.42	(1)	3.86	2.72	86
	333	70	10	P	2.46	(1)	3.90	2.69	89
	333	35	20	P	2.49	(1)	4.00	2.78	90
	333	70	20	P	2.48	(1)	4.00	2.80	93
	333	180	None	P	0.06[d]	(1)	0.10[d]	0.07[d]	73
	353	35	10	P	3.15	(1)	3.95	3.40	88
	353	70	10	P	3.16	(1)	4.00	3.40	87
	353	35	20	P	3.05	(1)	4.15	3.30	90
	353	70	20	P	3.11	(1)	4.21	3.29	91
Br_2[e]	333	5	None	P	<0.01	(1)	<0.01	<0.01	
$(Me_3Si)_2NCl$	318	120	20	TBHN	2.34	(1)	4.40	2.70	87
	318	210	20	TBHN	2.39	(1)	4.11	2.77	75
	318	120	None	TBHN	2.06	(1)	3.14	2.18	95
	333	120	20	TBHN	2.41	(1)	4.15	2.72	85
	333	240	20	TBHN	2.45	(1)	4.13	2.80	92
	333	120	20	P	2.45	(1)	4.28	2.83	88
	333	120	None	TBHN	1.98	(1)	2.73	2.00	85
	333	240	None	TBHN	1.95	(1)	2.76	1.93	88
$(Bu^tMe_2Si)_2NCl$	318	210	5	TBHN	6.09	(1)	1.57	16.3	15
	318	210	10	TBHN	8.87	(1)	2.16	24.3	15
	318	210	20	TBHN	10.5	(1)	2.19	29.9	14
	318[f]	210	20	TBHN	11.2[f]	(1)[f]	2.41[f]	31.0[f]	6[f]
	318[g]	210	20	TBHN	10.9[g]	(1)[g]	3.19[g]	30.8[g]	13[g]
	318	120	29[h]	TBHN	3.53	(1)	1.46	11.0	12
	333	210	20	TBHN	10.0	(1)	1.91	27.8	11
Cl_2[i]	318	20	None	P	1.41	(1)	1.45	0.74	75

[a] Based on halogenoamine. [b] P = photochemical; TBHN = thermal decomposition of TBHN (2 mol % based on halogenoamine). [c] The yields of silylamines were in the range 85—94%, except for reactions with $(Bu^tMe_2Si)_2NCl$ when the yields of $(Bu^tMe_2Si)_2NH$ were 15—20%. [d] Varies somewhat with the age of the halogenoamine. [e] Bromination with a deficiency of Br_2; the reaction mixture was analysed after about half the bromine had been consumed. [f] $[\text{Isopentane}]_0/[(Bu^tMe_2Si)_2NCl]_0$ was 2.8; in other experiments it was 9.2. [g] $(Bu^tMe_2Si)_2NH$ (23 mol %) was added before reaction. [h] $Bu^tCH{=}CH_2$ scavenger. [i] Chlorination with a deficiency of chlorine. To allow comparison of the results with those from halogenations using the *N*-chlorosilylamines, chlorobenzene (100 mol %) was present during the reaction as internal standard. Aromatic solvents are known to modify the reactivity of free chlorine atoms (see ref. 13).

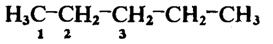
pentane]$_0$/[$(Bu^tMe_2Si)_2NCl$]$_0$ decreased from 9.2 to 2.8 (see Table 2).

Addition of Silylaminyl Radicals to Alkenes.—The effectiveness of norbornene in suppressing halogen atom chain reactions, whilst not seriously reducing alkyl halide yields, implies that silylaminyl radicals do not add readily to the reactive C=C bond in this alkene. Furthermore, the reaction of $(Me_3Si)_2NBr$ with cyclohexene gave good yields of bromocyclohexene and thus competitive addition of (I) to the double bond must be unimportant. However, addition of (I) to ethylene has been detected by e.s.r. spectroscopy during photolysis of tetrakis(trimethylsilyl)hydrazine (TTMH) in the liquid alkene as solvent [equations (12) and (13)].[1] This result implies that $(Me_3Si)_2NHal$ might undergo radical chain addition to excess of ethylene to give $(Me_3Si)_2NCH_2CH_2Hal$, since (III) should be capable of abstracting halogen from the *N*-halogenosilylamine.

Discussion

The isomeric compositions of the alkyl halides resulting from the reactions of *N*-halogenosilylamines with hydrocarbons clearly show that silylaminyl radicals are the chain carriers, provided that a scavenger of halogen atoms (and/or of molecular halogen and hydrogen halide) is present. The product distributions may be taken to reflect the selectivities of the silylaminyl radicals in hydrogen abstraction reactions. Whilst norbornene is highly reactive towards both homolytic and heterolytic addition,[8,9] the bridgehead allylic hydrogens are not readily abstracted and this alkene is evidently very appropriate for the suppression of halogen atom chain reactions propagated by either Br· or Cl·, without itself undergoing allylic halogenation. t-Butylethylene appears to be a less effective scavenger as expected. Although trichloroethylene efficiently suppresses chlorine atom chain pathways,[10,11] it appears to have almost no effect on reactions propagated by

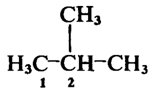
Table 3. Halogenation of pentane


$\underset{1}{H_3C}-\underset{2}{CH_2}-\underset{3}{CH_2}-CH_2-CH_3$

Halogenating agent	T/K	Reaction time (min)	Halogen scavenger [a] (mol %) [b]	Initiation [c]	*n*-Halogenopentane isomer distribution (molar ratios) [d] *n* = 1	2	3
$(Me_3Si)_2NBr$	303	60	N (10)	P	(1)	3.3	0.74
	323	60	N (10)	P	(1)	2.9	0.71
	323	95	N (10)	P	(1)	2.8	0.74
	323	95	B (5)	P	(1)	3.4	0.90
	323	95	B (10)	P	(1)	3.2	0.84
	323	95	B (20)	P	(1)	3.0	0.74
	323	95	T (10)	P	(1)	22.5	5.9
	323	95	T (20)	P	(1)	19.4	5.2
	353	60	N (10)	P	(1)	2.4	0.64
	353	60	N (15)	P	(1)	2.5	0.67
Br_2 [e]	323	32	None	P	(1)	215	58
$(Me_3Si)_2NCl$	318	80	N (20)	TBHN	(1)	2.81	0.78
	318	160	N (20)	TBHN	(1)	2.73	0.78
	323	80	N (20)	TBHN	(1)	2.61	0.73
$(Bu^tMe_2Si)_2NCl$	318	80	N (20)	TBHN	(1)	0.48	0.058
	318	160	N (20)	TBHN	(1)	0.49	0.063

[a] N = norbornene, B = t-butylethylene, T = 1,1,2-trichloroethylene. [b] Based on halogenoamine. [c] P = photochemical; TBHN = thermal decomposition of TBHN (2 mol %). [d] Total yields of halides 87—92 mol % based on halogenoamine, except for reactions with $(Bu^tMe_2Si)_2NCl$ when chloride yields were *ca.* 15%. [e] Molar ratio of pentane to Br_2 was 2.8 : 1; *ca.* 20% of the bromine was consumed in the reaction time.

Table 4. Bromination of 2-methylpropane with $(Me_3Si)_2NBr$


$\underset{1}{H_3C}-\underset{2}{\overset{CH_3}{\overset{|}{CH}}}-CH_3$

T/K	Reaction time (min)	Norbornene (mol %) [a]	Initiation [b]	*n*-Halogeno-2-methylpropane isomer distribution (molar ratios) *n* = 1	2	Total halide yield (mol %) [a,c]
275	120	20	P	1.48	(1)	82
318	80	20	TBHN	1.69	(1)	80
318	160	20	TBHN	1.65	(1)	74
318	20	20	P	1.62	(1)	78
318	120	20	P	1.58	(1)	86
329 [d]	180	5 [e]	P	1.05 [d]	(1)	87
333	90	20	TBHN	1.71	(1)	75
333	160	20	TBHN	1.70	(1)	85

[a] Based on bromoamine. [b] P = photochemical; TBHN = thermal decomposition of TBHN (2 mol %). [c] The yields of $(Me_3Si)_2NH$ were *ca.* 85%. [d] Data from ref. 5. The bromine scavenger was $Bu^tCH{=}CH_2$ (5 mol %) and there is clearly a small contribution from a bromine atom chain reaction under these conditions. [e] $Bu^tCH{=}CH_2$ scavenger.

Table 5. Bromination of cyclohexene with $(Me_3Si)_2NBr$ [a]

T/K	Reaction time (min)	Norbornene (mol%) [b]	*n*-Bromocyclohexene isomer distribution (molar ratios) [c] *n* = 3	4
300	90	10	36.3	(1)
318	90	None	32.8	(1)
318	90	10	34.4	(1)
333	80	None	30.7	(1)
333	90	5	30.2	(1)
333	90	10	31.9	(1)
333	180	10	31.4	(1)

[a] Initiated photochemically. [b] Based on bromoamine. [c] Total yield of bromides 77—86%.

the bromine atom, presumably because addition of Br· is less rapid or reversible and heterolytic addition of Br_2 or HBr is slow. Our result stands in contrast to the report[10] that trichloroethylene functions as a ' good bromine atom trap ' for halogenation by t-butyl hypobromite.

Subsequent to the appearance of our preliminary communication,[5] Konen *et al.*[12] reported that chlorination of methyl decanoate with $(Me_3Si)_2NCl$ occurred with surprisingly low selectivity. The reaction conditions used by these authors were not specified in detail; apparently, no halogen scavenger was present and the reactions may have been carried out under aqueous acidic conditions when the *N*-halogenosilylamine would have been hydrolysed. We conclude that a radical chain mechanism propagated by chlorine atoms was probably operative under the experimental conditions used by Konen *et al.* In the absence of a halogen scavenger, the product

Table 6. Chlorination of 1-chlorobutane at 318 K[a]

$$\underset{1}{ClCH_2}-\underset{2}{CH_2}-\underset{3}{CH_2}-\underset{4}{CH_3}$$

Chlorinating agent	Reaction time (min)	Norbornene (mol %)[b]	1,*n*-Dichlorobutane isomer distribution (molar ratios)				Total dichloride yield (mol %)[b]
			n = 1	2	3	4	
$(Me_3Si)_2NCl$	60	20	(1)	0.29	0.83	0.35	73
$(Bu^tMe_2Si)_2NCl$	60	20	(1)	0.16	0.58	1.43	26
	210	20	(1)	0.16	0.63	1.47	26

[a] Initiated by thermal decomposition of TBHN (2 mol % based on chloroamine). [b] Based on chloroamine.

Table 7. Competitive bromination of 2-methylbutane and 2-methylpropane with $(Me_3Si)_2NBr$ at 318 K[a]

	Relative C(*n*)–H reactivities[b]						Total bromide yield (mol %)[c]
	2-Methylbutane				2-Methylpropane		
$[C_5H_{12}]/[C_4H_{10}]$	*n* = 1	2	3	4	1	2	
0.56	2.35	(1)	3.91	2.86	3.31	2.02	86
1.19	2.41	(1)	4.12	2.88	3.55	2.19	75

[a] Reactions (duration 120 min) were initiated photochemically. [b] Calculated using an integrated rate expression analogous to equation (9). Not statistically corrected. [c] Based on bromoamine.

$$(Bu^tMe_2Si)_2N\cdot \longrightarrow \cdot CH_2CMe_2SiMe_2N(H)SiMe_2Bu^t \tag{10}$$

(II)

$$(Bu^tMe_2Si)_2N\cdot + (Bu^tMe_2Si)_2NX \longrightarrow (Bu^tMe_2Si)_2NH + \cdot CH_2CMe_2SiMe_2N(X)SiMe_2Bu^t \tag{11}$$

$$(Me_3Si)_2NN(SiMe_3)_2 \xrightarrow{h\nu} 2(Me_3Si)_2N\cdot \tag{12}$$

$$(Me_3Si)_2N\cdot + CH_2{=}CH_2 \longrightarrow (Me_3Si)_2NCH_2CH_2\cdot \tag{13}$$

(III)

distribution obtained from chlorination of isopentane by $(Me_3Si)_2NCl$ (Table 2) moves towards that characteristic of hydrogen abstraction by the chlorine atom.

At 353 K cyclohexane is *ca.* 1.1 times as reactive as toluene towards (I). For comparison, values of (k_C/k_T) for hydrogen abstraction by Br·, Cl·, and Bu^{t}O· are 0.06 (353 K), 7.6 (313 K), and 6.0 (313 K), respectively.[13] The bromine atom is much more selective than (I), in accord with the higher reactivity of the latter. The large difference in the selectivities of (I) and Bu^{t}O· is probably mainly steric in origin. Congestion in the transition state for hydrogen abstraction from the secondary C–H groups in cyclohexane is likely to be more severe for (I) than for the less bulky t-butoxyl radical.

The isotope effect (k_H/k_D 5.2 at 353 K) for benzylic hydrogen abstraction by (I) from toluene and from perdeuteriotoluene is somewhat greater than that for abstraction by $Me_2N\cdot$ (4.0 at 407 K) and similar to that for abstraction by Br· or by Bu^{t}O· (4.9 at 350 K and 5.5 at 313 K, respectively).[13] These values imply appreciable C–H stretching in the transition states for hydrogen abstraction and stand in contrast to the isotope effect for abstraction by Cl· (1.3 at 350 K)[13] which implies an unsymmetrical transition state with little C–H stretching for this rapid reaction.

The reactivities of the silylaminyl radicals in aliphatic hydrogen abstraction are summarised in Table 8 which also includes data, taken from the literature, for other types of attacking radical. After correction for statistical effects, tertiary and primary (3 H) C–H groups in isopentane are about equally reactive towards (I) and half as reactive as the secondary C–H groups. This change from the normal (thermodynamic) reactivity sequence, tertiary C–H > secondary C–H > primary C–H, for abstraction by relatively unhindered radicals such as Br·, Cl·, Bu^{t}O·, and $Me_2\dot{N}H^+$ may be attributed to the relatively large bulk of (I) which favours attack at less congested sites. Still greater deviation from the normal trend is found when $(Bu^tMe_2Si)_2N\cdot$ is the attacking radical and now the tertiary C–H groups are appreciably *less* reactive than the primary C–H groups. The trimethylsilyl(t-butyl)aminyl radical $Me_3Si\dot{N}Bu^t$ is less reactive than $(R_3Si)_2N\cdot$ but more reactive than $(R_3C)_2N\cdot$, as judged qualitatively from the rate of reaction of $Me_3Si(Bu^t)NBr$ with isopentane and from the yield and isomeric composition of product bromides.*

Although the reactivities of unhindered dialkylaminium radicals [*e.g.* $Me_2\dot{N}H^+$ and $\overline{CH_2(CH_2)_4\dot{N}}H^+$] follow the thermodynamic sequence, steric effects have been invoked to

---

* E.s.r. studies also show that $Me_3Si\dot{N}Bu^t$ is less reactive than $(Me_3Si)_2N\cdot$ and the e.s.r. spectrum of the former may be detected in fluid solution at low temperature.[14,15]

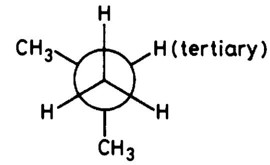
Table 8. Relative reactivities (per C–H bond) of hydrocarbons and of 1-chlorobutane towards hydrogen abstraction in the liquid phase

Abstracting radical	T/K	Hydrogen donor and relative reactivities for C–H group types					Ref.
		$(CH_3)_2$—	—CH—	—CH_2—	—CH_3		
$(Me_3Si)_2N\cdot$	300	0.38	(1)	2.19	0.87		This work
	318	0.41	(1)	2.04	0.93		
	333	0.41	(1)	2.02	0.92		
	353	0.52	(1)	2.04	1.12		
$(Bu^tMe_2Si)_2N\cdot$	318	1.81	(1)	1.13	10.2		This work
	333	1.67	(1)	0.96	9.27		
$Cl\cdot$	288	0.28	(1)	0.91	0.31		*a*
	318	0.24	(1)	0.73	0.25		This work
$Br\cdot$	333	$\leqslant$0.002	(1)	$\leqslant$0.01	$\leqslant$0.003		This work
$CH_2(CH_2)_3CH_2\dot{N}H^+$	278	0.002	(1)	0.11	0.002		*b*
$Pr^i_2\dot{N}H^+$ [c]	288	2.5	(1)	31.0	5.0		*a*
		CH_3—	—CH_2—	—CH_2—	—CH_2—	—CH_3	
$(Me_3Si)_2N\cdot$	303	(1)	4.95	2.22			This work
	323	(1)	4.32	2.18			
	353	(1)	3.68	1.97			
$(Bu^tMe_2Si)_2N\cdot$	318	(1)	0.73	0.18			This work
$Cl\cdot$	288	(1)	2.8	2.9			*a*
$Br\cdot$	323	(1)	323	174			This work
$Pr^i_2\dot{N}H^+$	288	(1)	28.0	17.0			*b*
		$(CH_3)_3$—	—CH				
$(Me_3Si)_2N\cdot$	275	0.16	(1)				This work
	318	0.18	(1)				
	333	0.19	(1)				
$(Me_3Si)_2N\cdot$	275	0.13	(1)				*d*
	333	0.11	(1)				
$Cl\cdot$	297	0.29	(1)				*e*
$Br\cdot$ [f]	419	<0.001	(1)				*g*
$Bu^tO\cdot$	170	*ca.* 0.002	(1)				*h*
		CH_2—	—CH_2—	—CH=CH—	—CH—	—CH_2	
$(Me_3Si)_2N\cdot$	300	(1)	36.3				This work
	318	(1)	33.6				
	333	(1)	31.1				
$Cl\cdot$	298	(1)	1.7				*i*
$Br\cdot$	350	(1)	$\geqslant$100 [j]				*i*
$Bu^tO\cdot$	298	(1)	21.2				*i*
$OCCH_2CH_2C(O)N\cdot$	298	(1)	5.6				*k*
		$ClCH_2$—	—CH_2—	—CH_2—	—CH_3		
$(Me_3Si)_2N\cdot$	318	(1)	0.29	0.83	0.23		This work
$(Bu^tMe_2Si)_2N\cdot$	318	(1)	0.16	0.59	0.97		This work
$Cl\cdot$	307	(1)	3.56	7.79	1.86		*l*
$Br\cdot$	303	(1)	1.12	2.10	0.014		*m*
$Bu^tO\cdot$	313	(1)	0.92	2.05	0.48		*n*
$Me_2\dot{N}H^+$	303	(1)	2.34	17.6	1.20		*m*

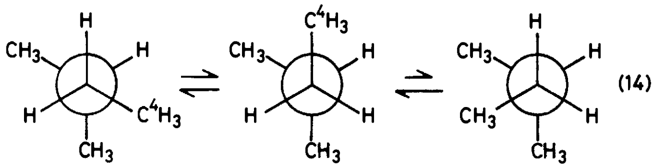
[a] N. C. Deno, D. G. Pohl, and H. J. Spinelli, *Bio-org. Chem.*, 1974, **3**, 66. [b] S. E. Fuller, J. R. Lindsay Smith, R. O. C. Norman, and R. Higgins, *J. Chem. Soc., Perkin Trans. 2*, 1981, 545. [c] Although the 2,2,6,6-tetramethylpiperidinium radical is undoubtedly even more selective than $Pr^i_2\dot{N}H^+$, conflicting results are reported in the literature (footnotes *a* and *b*). The discrepancy is probably due to the incursion of chlorine atom chain reactions (see also N. C. Deno, R. Fishbein, and J. C. Wyckoff, *J. Am. Chem. Soc.*, 1971, **93**, 2065). [d] Ref. 1; the radical (I) was generated by photolysis of TTMH. [e] E. M. Hodnett and P. S. Juneja, *J. Org. Chem.*, 1967, **32**, 4114. [f] In the gas phase. [g] P. C. Anson, P. S. Fredericks, and J. M. Tedder, *J. Chem. Soc.*, 1959, 918. [h] J. N. Winter and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1978, 545. [i] M. L. Poutsma, *J. Am. Chem. Soc.*, 1965, **87**, 2161. [j] 4-Bromocyclohexene was not detected. [k] Ref. 20 and J. C. Day, M. J. Lindstrom, and P. S. Skell, *J. Am. Chem. Soc.*, 1974, **96**, 5615. [l] C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, 1959, **81**, 1485. [m] Ref. 24. [n] C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, 1960, **82**, 6113.

explain the anomalous selectivities (primary C–H > tertiary C–H) of species with more bulky *N*-alkyl groups, for example $Pr^i_2\dot{N}H^+$ (see Table 8).[16] The bis(trialkylsilyl)aminyl radicals and $Pr^i_2\dot{N}H^+$ also attack the primary (3 H) C–H groups in isopentane more rapidly than the more hindered primary (6 H) groups. The use of *N*-halogenobis(trialkylsilyl)amines for hydrocarbon halogenation allows these unusual and potentially useful product selectivities to be achieved under neutral aprotic conditions.

The intramolecular selectivities of the bis(trialkylsilyl)-

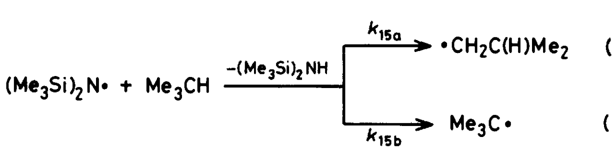


(IV)



(Va) (Vb) (VI)

(14)



(15a)

(15b)

aminyl radicals in hydrogen abstraction from pentane and from isobutane may also be understood in terms of a combination of the high reactivity and exacting steric demands of the attacking radicals. The reactivity of the terminal methyl groups in pentane increases relative to that of the secondary C–H groups as the bulk of the nitrogen radical increases on going from $(\mathrm{Me_3Si})_2\mathrm{N}\cdot$ to $(\mathrm{Bu^tMe_2Si})_2\mathrm{N}\cdot$.

Competition experiments show that the tertiary C–H group in isobutane (IV) is more reactive towards (I) than that in isopentane, presumably because the former is more accessible to radical attack. The most stable conformation of isopentane is (V) and, at 300 K, the concentration of (Va + b) is *ca.* 10 times that of the symmetrical conformer (VI) with a barrier of *ca.* 23 kJ mol^{-1} for conversion of (V) into (VI).[17]

Inspection of (V) suggests that the methyl group *gauche* to C-4 could be somewhat less reactive than that which is *anti*. The secondary C–H groups in (Va or b) are also non-equivalent and would be expected to exhibit different reactivities towards radical attack.

In view of these complexities, interpretation of the temperature dependence of the reactivities of primary, secondary, and tertiary C–H groups in isopentane is not straightforward, but nevertheless some general comments are worthwhile. The activation energy for hydrogen transfer to unhindered radicals generally increases on going from tertiary to primary C–H groups, as expected if the strength of the bond being broken is reflected in the energy of the transition state. However, inspection of Tables 2—4 shows that the selectivities of the silylaminyl radicals are relatively insensitive to changes of temperature, indicating that the activation energies for abstraction from primary, secondary, and tertiary C–H groups are rather similar. This similarity is probably related to the large bulk of the attacking radicals, since any decrease in the energy of the transition state associated with cleavage of a weaker bond would be offset by an increase in its energy as a result of unfavourable steric interactions.

The relative reactivity of primary and tertiary C–H groups in isobutane towards (I) has also been determined by an independent technique, using e.s.r. spectroscopy to monitor the relative concentrations of isobutyl and t-butyl radicals produced during continuous photolysis of TTMH in the hydrocarbon as solvent at temperatures between 170 and 280 K [equation (15)].[1] The value of (k_{15a}/k_{15b}) is given by equation (16) and the relative reactivity determined by the e.s.r. method is included in Table 8. Considering the substantial differences between the e.s.r. and halogenation-product analysis techniques, the selectivities determined by the two methods are in reasonable agreement. However, as shown by equation (16), the e.s.r. method indicates that the activation energy for abstraction from the tertiary C–H group is slightly *greater* than that for abstraction from a primary C–H group, whereas the results shown in Table 3 imply that E_a (tertiary C–H) is slightly *smaller* than E_a (primary C–H). This change in sign of E_a (primary C–H) − E_a (tertiary C–H) is difficult to explain, but both techniques do show that the difference in activation energies is rather small.

$$(k_{15a}/k_{15b}) = (0.37 \pm 0.05)\exp(2.66 \pm 0.50)/RT \text{ kJ mol}^{-1} \qquad (16)$$

$$\mathrm{Me_2\dot{N}H^+ + RH \longrightarrow Me_2\overset{+}{N}H_2 + R\cdot} \qquad (17)$$

$$\mathrm{R\cdot + Me_2\overset{+}{N}(H)Cl \longrightarrow RCl + Me_2\dot{N}H^+} \qquad (18)$$

The results described here and in Part 1 [1] show clearly that bis(trialkylsilyl)- and trialkylsilyl(alkyl)-aminyl radicals are significantly more reactive than dialkylaminyl radicals. We have attributed this difference to two effects, both consequences of the σ-donor–π-acceptor properties of the trialkylsilyl group. First, the N–H bond is evidently appreciably stronger in $(\mathrm{R_3Si})_2\mathrm{NH}$ and $\mathrm{R_3Si(R_3C)NH}$ than in $(\mathrm{R_3C})_2\mathrm{NH}$, making hydrogen abstraction more favourable thermodynamically. Secondly, the silylaminyl radicals are more electrophilic than $(\mathrm{R_3C})_2\mathrm{N}\cdot$, leading to more effective transition state stabilisation by charge transfer from the C–H σ bond under attack to the silylaminyl radical (SOMO–HOMO interaction [18]). Protonation of $(\mathrm{R_3C})_2\mathrm{N}\cdot$ brings about a similar increase in reactivity, probably for related reasons,[1] and *N*-halogenodialkylamines readily halogenate alkanes in acidic media by a radical chain pathway, as illustrated in equations (17) and (18).[16]

In parallel with other similarities in the substituent effects of trialkylsilyl and acyl groups (both π-acceptors), amidyl [19] $[\mathrm{R\dot{N}C(O)R}]$ and imidyl [20] $[\mathrm{RC(O)\dot{N}C(O)R}]$ radicals are also more reactive than neutral dialkylaminyl radicals. The N–H bond in succinimide is, like that in $(\mathrm{Me_3Si})_2\mathrm{NH}$, probably appreciably stronger than that in a dialkylamine.[21]

Abstraction of hydrogen from cyclohexene by bromine atoms takes place exclusively at the allylic position, whilst the highly reactive chlorine atom is relatively unselective. The succinimidyl radical (electronic configuration uncertain) abstracts hydrogen from C-3 5.6 times more rapidly than from C-4 and abstraction from C-4 is also observed for the reaction with (I), although allylic attack is strongly favoured. The selectivities of (I) and $\mathrm{Bu^tO}\cdot$ in hydrogen abstraction from cyclohexene are similar and, in general, the behaviour of these two radicals appears to be rather similar, provided that steric effects are not predominant in determining reactivity. Both these radicals also show little tendency to add to C=C bonds in competition with abstraction of hydrogen from saturated, in particular allylic, C–H groups.[22] Addition of (I) to ethylene can be detected when this alkene, which does not contain readily abstractable hydrogen, is present in high concentration as solvent.

Dialkylaminium radicals exhibit a marked preference for attack at the penultimate C–H groups of a normal alkyl chain

$$\mathrm{Me_2\overset{\bullet}{N}H^+ + CH_3CH_2CH_2CH_2Cl \longrightarrow Me_2\overset{+\bullet}{N}H_2 + CH_3\overset{\bullet}{C}HCH_2CH_2Cl} \qquad (19)$$

carrying an electronegative substituent at C-1 (leading to so-called $\omega - 1$ halogenation).[16] This selectivity, which results from a combination of polar and steric effects, increases with the bulk of the aminium radical.[23] In the chlorination of 1-chlorobutane with $Me_2\overset{+}{N}(H)Cl$, *ca.* 77% of the dichlorobutane produced originates from attack of $Me_2\overset{\bullet}{N}H^+$ on the hydrogen attached to C-3 [equation (19)].[24] The dimethylaminium radical is about as reactive as methyl in abstracting hydrogen from saturated C–H groups;[25] it is certainly less reactive than $Bu^tO\cdot$ and very probably also less reactive than (I). The bis(trialkylsilyl)aminyl radicals (I) and $(Bu^tMe_2Si)_2N\cdot$ do not show the same preference for attack at the $(\omega - 1)$ C–H group of 1-chlorobutane. In fact, the relative reactivity of the CH_2Cl group is surprisingly large and there is no apparent deactivation by the electron-withdrawing chlorine. We tentatively suggest that a transition state-stabilising interaction between the electropositive silicon atom in the attacking radical and the electron rich chlorine atom in 1-chlorobutane may be responsible for the unexpectedly high yields of 1,1-dichlorobutane. The relative reactivities of the other C–H groups in the molecule towards attack by (I), $Cl\cdot$, or $Bu^tO\cdot$ are similar. As expected the bulky $(Bu^tMe_2Si)_2N\cdot$ shows a greater tendency to attack the terminal methyl group than does (I).

Experimental

Materials.—All compounds containing Si–N bonds were handled under an atmosphere of dry nitrogen. *N*-Halogenosilylamines were prepared, handled, and stored in darkness or in subdued light.

N-Bromo- and *N*-chloro-bis(trimethylsilyl)amine and *N*-bromo(trimethylsilyl)-t-butylamine were prepared by the reaction of the appropriate silylamine with *N*-bromosuccinimide (*N*-bromo-compounds) or with t-butyl hypochlorite (*N*-chloro-compounds) as described by Wiberg and Raschig.[26]

N-*Chlorobis-(t-butyldimethylsilyl)amine*, b.p. 60 °C at 0.05 Torr, was a yellow-green liquid prepared by the reaction of t-butyl hypochlorite with bis-(t-butyldimethylsilyl)amine,[27] b.p. 72 °C at 0.3 Torr, in dichloromethane, using the method described by Wiberg and Raschig for preparation of $(Me_3Si)_2NCl$ (Found: C, 51.4; H, 10.9; N, 4.9; Cl, 12.8. $C_{12}H_{30}ClNSi_2$ requires C, 51.5; H, 10.8; N, 5.0; Cl, 12.7%), δ (C_6D_6) 0.18 (12 H, s) and 0.99 (18 H, s).

Di-t-butyl hyponitrite was prepared by the method of Kiefer and Traylor[28] and azobisisobutyronitrile (Aldrich) was recrystallised from acetone and dried under vacuum. Norbornene (Aldrich) was dissolved in isopentane and the solution was dried over P_2O_5. After filtration and removal of the solvent, norbornene was distilled at atmospheric pressure, b.p. 99 °C. t-Butylethylene (Aldrich, 95% pure) was distilled from calcium hydride, but g.l.c. analysis showed that impurities (presumably hydrocarbons) were still present. Trichloroethylene (B.D.H.) was purified[29] immediately before use.

Isopentane and pentane (both B.D.H.; AnalaR) were distilled from sodium wire and stored under nitrogen over activated molecular sieves. Cyclohexane (AnalaR), toluene (AnalaR), cyclohexene (G.P.R.), and 1-chlorobutane (G.P.R.) (all B.D.H.) were purified by standard methods.[29] Isobutane (Matheson Instrument Grade) and perdeuteriotoluene (Aldrich; 99 + atom %D) were used as received.

The authentic alkyl halides required as g.l.c. standards were obtained commercially (Aldrich or K and K Laboratories) and purified (if necessary) by standard methods[29] or were prepared by published procedures as described below. The structures of the alkyl halides were confirmed by ^1H and ^{13}C n.m.r. spectroscopic analysis.

2-Bromo- and 2-chloro-2-methylbutane were prepared by the action of aqueous hydrogen halide on the alcohol.[30] 2-Bromo- and 2-chloro-3-methylbutane (contaminated with the 2-halogeno-2-methylbutanes) were prepared by the reaction of 3-methylbutan-2-ol with triphenylphosphine dibromide in dimethylformamide (DMF)[31] or with thionyl chloride in hexamethylphosphoric triamide,[32] respectively. 1-Chloro-3-methylbutane was prepared from 3-methylbutan-1-ol and thionyl chloride in the presence of pyridinium chloride,[32] 1-bromo-2-methylbutane was prepared from 2-methylbutan-1-ol and Ph_3PBr_2 in DMF,[31,32] and 1-chloro-2-methylbutane was a gift from Dr. H. R. Hudson.[33]

3-Bromopentane and 3-chloropentane were prepared from pentan-3-ol by the reaction with Ph_3PBr_2 in DMF[32,34] or with chloromethylenedimethylammonium chloride in dioxan,[33] respectively.

3-Bromocyclohexene was obtained by allylic bromination of cyclohexene using *N*-bromosuccinimide under Ziegler conditions[35] and 4-bromocyclohexene from the reaction of cyclohexane-1,4-diol with phosphorus tribromide.[36]

1,1-Dichlorobutane was prepared from butanal and phosphorus pentachloride[37] and 1,2-dichlorobutane was prepared by addition of chlorine to but-1-ene in $CF_2ClCFCl_2$ solvent in the presence of air at *ca.* −20 °C.[38]

Procedure for Halogenation and Analysis of Products.—Reactions were carried out in cylindrical Pyrex tubes (5 mm i.d., 1.5 mm wall) which were constricted *ca.* 20 cm from the bottom, to facilitate sealing, and topped with B14 cones. Each tube was flamed while under vacuum, allowed to cool, and then filled with dry nitrogen. After removal from the vacuum line, it was stoppered with a self-sealing rubber cap through which the *N*-halogenosilylamine was injected, using a calibrated syringe, followed by a mixture containing the hydrocarbon(s) (or 1-chlorobutane), initiator, halogen scavenger, and internal standard. For reactions of molecular chlorine or bromine, the *N*-halogenosilylamine was replaced by a solution of the halogen in $CF_2ClCFCl_2$. The reaction tube was then re-attached to the vacuum line, the contents were freeze–thaw degassed, and the tubes were sealed at the constriction while under vacuum.* The contents were allowed to thaw and were mixed by shaking prior to immersion in a thermostatted oil- or water-bath. This procedure was modified slightly when isobutane, b.p. −1 °C, was a reactant. Using a calibrated vacuum line, a known weight of the gas was condensed into the reaction tube after all the other reagents had been added. To prevent injury in the event of possible explosion of tubes containing isobutane, the thermostat bath was surrounded by a heavy Perspex screen and reaction tubes were remotely introduced into and removed from the oil-bath.

After reaction, tubes were cooled with ice (solid CO_2 when isobutane was present), cracked open, and stoppered with self-sealing rubber caps. A cold-jacketted microsyringe was used to transfer samples containing isobutane to the chromatograph for analysis.

G.l.c. analysis was carried out using a Pye-Unicam Series 304 instrument equipped with a flame-ionisation detector and a temperature programable oven. Separation of all com-

---

* Reaction mixtures containing Cl_2 or Br_2 were sealed under an atmosphere of nitrogen.

ponents was accomplished readily using commercially available glass support coated open tubular (SCOT) capillary columns (55 m × 0.5 mm) and similar performance was obtained with SP 2100 or SE 30 stationary phases with nitrogen as carrier gas.

In general, two or more runs were carried out for each set of experimental conditions and the averaged data are presented in the Tables.

Acknowledgements
We are grateful to Mr. C. J. Cooksey for preparing a number of the alkyl halides and to Dr. H. R. Hudson for the gift of 1-chloro-2-methylbutane.

References

1 Part 1, J. C. Brand, B. P. Roberts, and J. N. Winter, *J. Chem. Soc., Perkin Trans. 2* 1983, 261.
2 J. R. Roberts and K. U. Ingold, *J. Am. Chem. Soc.*, 1973, **95**, 3228.
3 B. P. Roberts and J. N. Winter, *J. Chem. Soc., Chem. Commun.*, 1978, 545.
4 C. J. Michejda and W. P. Hoss, *J. Am. Chem. Soc.*, 1970, **92**, 6298.
5 B. P. Roberts and C. Wilson, *J. Chem. Soc., Chem. Commun.*, 1978, 752.
6 P. S. Skell and J. C. Day, *J. Am. Chem. Soc.*, 1978, **100**, 1951.
7 R. E. Bailey and R. West, *J. Organomet. Chem.*, 1965, **4**, 430.
8 J. Spanget-Larsen and R. Gleiter, *Tetrahedron Lett.*, 1982, **23**, 2435.
9 R. Huisgen, P. H. J. Ooms, M. Mingin, and N. L. Allinger, *J. Am. Chem. Soc.*, 1980, **102**, 3951.
10 C. Walling and J. A. McGuinness, *J. Am. Chem. Soc.*, 1969, **91**, 2053.
11 A. A. Zavitsas and J. D. Blank, *J. Am. Chem. Soc.*, 1972, **94**, 4603.
12 D. A. Konen, R. J. Maxwell, and L. S. Silbert, *J. Org. Chem.*, 1979, **44**, 3594.
13 G. A. Russell in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 1, ch. 7.
14 J. C. Brand, M. D. Cook, A. J. Price, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 1982, 151.
15 M. D. Cook, unpublished results.
16 (*a*) Y. L. Chow in 'Reactive Intermediates,' ed. R. A. Abramovitch, Plenum Press, New York, 1980, vol. 1, ch. 3; (*b*) Y. L. Chow, W. C. Danen, S. F. Nelsen, and D. H. Rosenblatt, *Chem. Rev.*, 1978, **78**, 243.
17 J. M. Young and A. A. Petrauskas, *J. Chem. Phys.*, 1956, **25**, 943; J. H. Chen and A. A. Petrauskas, *ibid.*, 1959, **30**, 304; D. J. Millen, *Prog. Stereochem.*, 1962, **3**, 138.
18 I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley-Interscience, London, 1976, ch. 5.
19 R. S. Neale, *Synthesis*, 1971, 1; A. Goosen, *S. Afr. J. Chem.*, 1979, **32**, 37 and references contained therein.
20 P. S. Skell and J. C. Day, *Acc. Chem. Res.*, 1978, **11**, 381.
21 E. Hedaya, R. L. Hinmann, V. Schomaker, S. Theodoropulos, and L. M. Kyle, *J. Am. Chem. Soc.*, 1967, **89**, 4875; Y. Apeloig and R. Schreiber, *ibid.*, 1980, **102**, 6144.
22 J. K. Kochi in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, vol. 2, ch. 23.
23 N. C. Deno, W. E. Billups, R. Fishbein, C. Pearson, R. Whalen, and J. C. Wyckoff, *J. Am. Chem. Soc.*, 1971, **93**, 438.
24 J. Spanswick and K. U. Ingold, *Can. J. Chem.*, 1970, **48**, 546.
25 V. Malatesta and K. U. Ingold, *J. Am. Chem. Soc.*, 1973, **95**, 6400.
26 N. Wiberg and F. Raschig, *J. Organomet. Chem.*, 1967, **10**, 15.
27 R. West and P. Boudjouk, *J. Am. Chem. Soc.*, 1973, **95**, 3983; J. R. Bowser, R. H. Neilson, and R. L. Wells, *Inorg. Chem.*, 1978, **17**, 1882.
28 H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, 1966, 6163.
29 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' Pergamon Press, Oxford, 1980, 2nd edn.
30 B. A. Chaudri, H. R. Hudson, and W. S. Murphy, *J. Chromatogr.*, 1967, **29**, 218.
31 R. A. Arain and M. K. Hargreaves, *J. Chem. Soc. C*, 1970, 67.
32 H. R. Hudson and G. Riga de Spinoza, *J. Chem. Soc., Perkin Trans. 1*, 1976, 104.
33 D. R. Hepburn and H. R. Hudson, *J. Chem. Soc., Perkin Trans. 1*, 1976, 754.
34 G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, 1964, **86**, 964.
35 B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith, and A. R. Tatchell, 'Vogel's Textbook of Practical Organic Chemistry,' Longman, London, 1978, p. 401, 4th edn.
36 F. R. Jensen and C. H. Bushweller, *J. Am. Chem. Soc.*, 1969, **91**, 5774.
37 A. L. Henne, M. W. Renoll, and H. M. Leicester, *J. Am. Chem. Soc.*, 1939, **61**, 938.
38 H. P. A. Groll, G. Hearne, F. F. Rust, and W. E. Vaughan, *Ind. Eng. Chem.*, 1939, **31**, 1239.

Received 26th *July* 1982; *Paper* 2/1277