Free Radical Reactions of Bicyclo[2.1.1]hexane and Bicyclo[2.2.1]heptane

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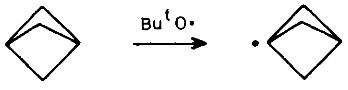
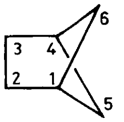
t-Butoxyl radicals abstract hydrogen from C(2) of bicyclo[2.1.1]hexane (**3**) to give bicyclo[2.1.1]hexan-2-yl radicals (**6**). At $T > 250$ K radicals (**6**) rearrange by β-scission to cyclopent-3-enylmethyl radicals; both species were observed by e.p.r. spectroscopy. In spite of the much greater ring strain the activation energy for rearrangement of (**6**) is about the same as that of cyclobutylmethyl radicals. Bromine atoms abstract hydrogen from C(2) of (**3**), but bis(trimethylsilyl)aminyl radicals abstract the bridgehead methine hydrogen at C(1) as well as the methylene hydrogens at C(2). There is very little abstraction of the bridgehead hydrogen in bicyclo[2.2.1]heptane by bis(trimethylsilyl)aminyl radicals. Thus, the greater bridgehead reactivity of (**3**) as compared with the bridge positions is not simply due to the lower selectivity of the bis(trimethylsilyl)aminyl radicals, but is an intrinsic property of the bicycloalkane.

Bicyclo[1.1.1]pentane (**1**) is an exceptional molecule in that both chlorine atoms[1] and t-butoxyl radicals[2] abstract one of the two bridgehead methine hydrogens much more readily than one of the six bridging methylene hydrogens. The e.p.r. spectrum of the bicyclo[1.1.1]pentan-1-yl radical (**2**) exhibited an enormous hyperfine splitting (h.f.s.) of 69.6 G† for the unique bridgehead γ-hydrogen.[2] This suggests that there is *ca.* 14% spin delocalisation onto the bridgehead γ-hydrogen which helps to explain the faster rate of hydrogen abstraction from the bridgehead position.[3]

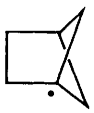


(**1**) (**2**)

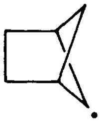
Hydrogen abstraction from bridgehead sites in bicycloalkanes is a rare phenomenon; bicyclo[2.2.0]hexane is the only other case where bridgehead attack is a major process.[4] We decided, therefore, to investigate the radical reactions of the next homologue of (**1**), *i.e.* bicyclo[2.1.1]hexane (**3**).



(**3**)



(**4**)



(**5**)

The bridgehead radical (**4**) had already been generated from the corresponding diacyl peroxide[5] and the e.p.r. spectrum shows a very large (22.5 G) h.f.s. for the unique γ-bridgehead hydrogen.[5] As judged by this criterion, the parent hydrocarbon (**3**) seemed a likely candidate for bridgehead reactivity towards free radicals. In the photochlorination of (**3**) the only detectable monochloride was 2-chlorobicyclo[2.1.1]hexane.[6] Although this study found no evidence of bridgehead chlorination it did show that the carbon skeleton does not rearrange and hence indicated that, in spite of its large strain energy, bicyclo[2.1.1]hexan-2-yl might be detectable by e.p.r. before rearrangement. A study of the reactions of t-butoxyl and bis(trimethylsilyl)aminyl radicals, and bromine atoms, with (**3**) is reported in this paper. For purposes of comparison some radical reactions of bicyclo[2.2.1]heptane (norbornane) were also investigated.

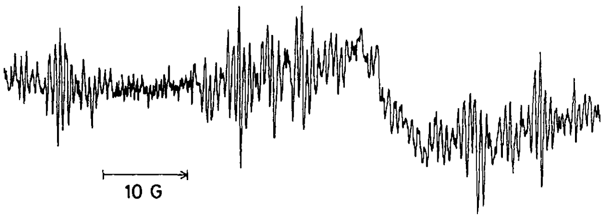


Figure. Low-field and central region of the 9.4 GHz e.p.r. spectrum of bicyclo[2.1.1]hexan-2-yl radicals (**6**) at 225 K in liquid di-t-butyl peroxide. Weak outer multiplet at high-field not shown

Results and Discussion

The hydrocarbon (**3**) was made in low yield by the mercury-photosensitised photolysis of hexa-1,5-diene,[7] and isolated from the product mixture by fractional distillation followed by preparative g.l.c.

Degassed solutions of (**3**) and di-t-butyl peroxide in cyclopropane were photolysed in the cavity of the e.p.r. spectrometer but only cyclopropyl radicals were detected. In neat peroxide, however, a weak and complex spectrum was obtained (Figure). The spectrum was compared with simulations of bicyclo[2.1.1]hexan-1-yl radicals[5] (**4**) and bicyclo[2.1.1]hexan-5-yl radicals (**5**);[8] the e.p.r. parameters being taken from the literature. Neither (**4**) nor (**5**) was present in detectable amounts. The spectrum was analysed as shown in Table 1, to give a doublet splitting of 20.3 G from H(2) and a triplet splitting of 27.7 G from the two equivalent H(3), together with small splittings from the six remaining hydrogens. This obviously corresponds to the bicyclo[2.1.1]hexan-2-yl radical (**6**). This identification was confirmed when an essentially identical spectrum was observed on photolysis of a mixture of 2-bromobicyclo[2.1.1]hexane (**7**), hexamethylditin, and di-t-butyl peroxide in t-butylbenzene.

The h.f.s. from H(2) is slightly lower than is normal for an α-hydrogen and the β-h.f.s. from H(3) and H(3′) are also lower than the values for β-hydrogens in cyclopentyl[9] (35.2 G) or cyclobutyl[9] (36.7 G) radicals. Either the radical centre is bent, or spin density is withdrawn from C(2) to other sites in the radical.

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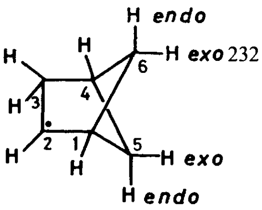
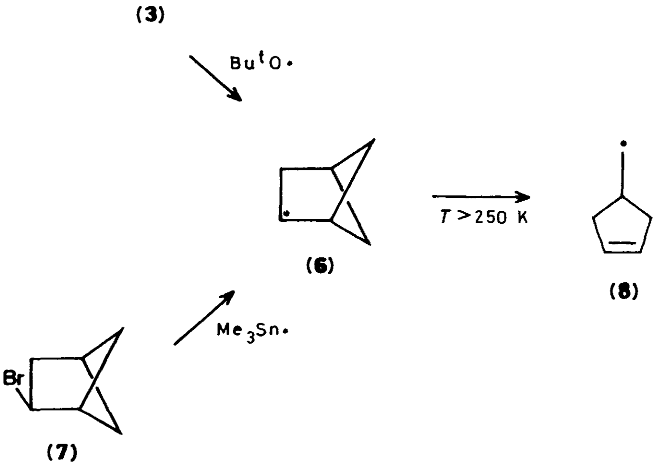
† 10 G ≡ 1 mT.

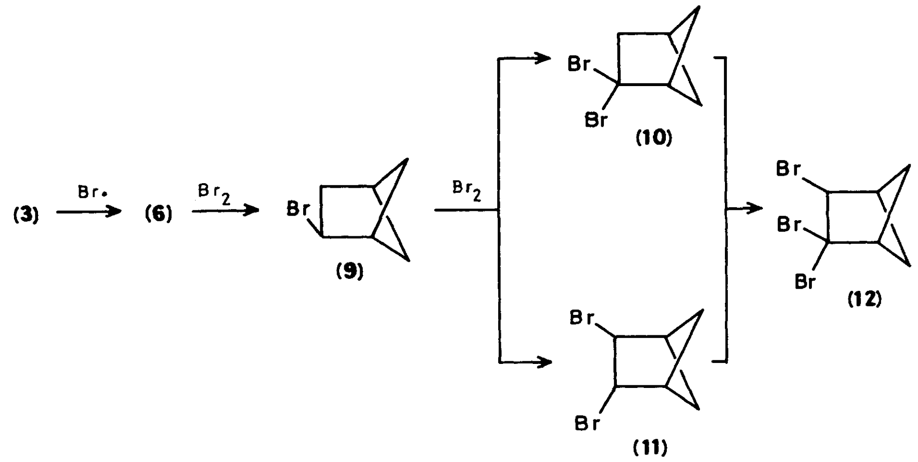
Table 1. E.p.r. parameters of bicyclo[2.1.1]hexan-2-yl radicals (**6**)

Radical	T/K	Exptl.[a] h.f.s./G		INDO[b]	INDO[c]
	232	20.3 (1 H)	H(2)	−18.8	−18.8
		27.7 (2 H)	H(3,3′)	33.2	36.9
		0.65 (1 H)	H(1)	0.0	−0.1
		0.65 (1 H)	H(4)	−0.9	−0.9
		3.9 (2 H)	H(5,6*exo*)	2.9	2.6
		1.3 (2 H)	H(5,6*endo*)	−1.3	−1.2

[a] Line width, $\Delta H_{pp} = 0.2$ G; $g = 2.003$. [b] MNDO optimised geometry, $\langle S^2 \rangle = 0.7580$. [c] MINDO/3 optimised geometry, $\langle S^2 \rangle = 0.7584$.



Scheme 1.



Scheme 2.

The six smaller h.f.s. cannot be assigned to specific hydrogens with certainty, but a tentative assignment is given in Table 1. The β-hydrogen at C(1) is in the nodal plane of the singly occupied *p*-orbital at the radical centre and is expected to have a small h.f.s.; in fact this h.f.s. must be ≤ 3.9 G and is probably only 0.65 G (Table 1). Similar very small h.f.s. have been observed from β-hydrogens at the bridgeheads in the bicyclo[3.1.1]hept-3-en-2-yl radical[10] and the related homobenzvalenyl radical.[11] If this is correct the γ-hydrogens, particularly H(5,6*exo*), show unusually large h.f.s. and this is consistent with the idea that significant spin density is transferred from C(2) to C(5) and C(6).

The intensity of the e.p.r. signal from (**6**) weakened above *ca.* 250 K and a new radical gradually replaced it in the range 270—310 K. On cooling the solution the process was reversed and the spectrum from (**6**) reappeared. The new radical had a four-line spectrum with a(3 H) = 22.6 G at 300 K. This spectrum is very similar to that of the cyclopentylmethyl radical [$a(2\ H_\alpha) = 21.3$, $a(H_\beta) = 21.3$ at 300 K][12] and we attribute it to the cyclopent-3-enylmethyl radical (**8**) (Scheme 1). Radical (**6**) is a cyclobutylmethyl type and such species are known to rearrange at about room temperature under e.p.r. conditions,[13–15] thus (**8**) is formed by rearrangement of (**6**) as shown in Scheme 1. The two radicals were approximately equal in concentration at 285 K. This is the same as the temperature marking the mid-point in the rearrangement of the cyclobutylmethyl radical[14] and it implies that the rate and activation energy for β-scission of (**6**) are very similar to those of the cyclobutylmethyl radical, *i.e.*[15] $(k/s^{-1}) = 4.7 \times 10^3$ at 25 °C and $(E/\text{kcal mol}^{-1})^* = 11.7$. The greater ring strain in (**6**), as compared with cyclobutylmethyl, evidently has no accelerating effect on the dynamics of the rearrangement.

The photobromination of (**3**) with a slight deficiency of bromine in CCl_4 solution was monitored as a function of time, see Table 2. In the early stages the only detectable product was 2-bromobicyclo[2.1.1]hexane (**9**) but the dibromides (**10**) and (**11**) (Scheme 2) became important at longer reaction times, as did a tribromide; probably (**12**). Retention time comparisons with authentic 1-bromobicyclo[2.1.1]hexane (**13**) showed that none was detectable, *i.e.* the mol % of (**13**) was ≤ 0.5. After 120 h photolysis a small amount of a second monobromide was observed. The mass spectrum was consistent with the molecular formula C_6H_9Br and this might have been the bromide derived from the rearranged radical, *i.e.* (**14**), but there was insufficient material for definite identification.

The reaction of (**3**) with bis(trimethylsilyl)-*N*-bromoamine under radical conditions[16] at 70 °C gave the 2-bromo derivative (**9**) together with a substantial amount of 1-bromobicyclo[2.1.1]hexane (**13**). Other products were 3-bromomethylenecyclopentane (**15**) and the same two dibromides as in the photobromination, see Table 3. None of bromide (**14**) could be detected, either on the chromatograms, or in the n.m.r. spectra of the isolated components; *i.e.* this rearrangement product was not obscured by having a retention time identical to that of any of the other components.

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* 1 cal ≡ 4.18 J.

Table 2. Products of the photobromination of bicyclo[2.1.1]hexane at 25 °C[a]

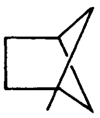
Time/h	2-Bromo **(9)**	C_6H_9Br	2,2-Dibromo **(10)**	2,3-Dibromo **(11)**	$C_6H_7Br_3$ **(12)**
24	100	—	—	—	—
31	90	—	7	3	—
48	86	—	8	4	2
120[b]	56	1	24	10	7

[a] (3) 1.5 mmol and Br_2 1.3 mmol in CCl_4 solution; products expressed as mol % total detectable product. [b] Several minor, unidentified products appeared on the chromatogram.

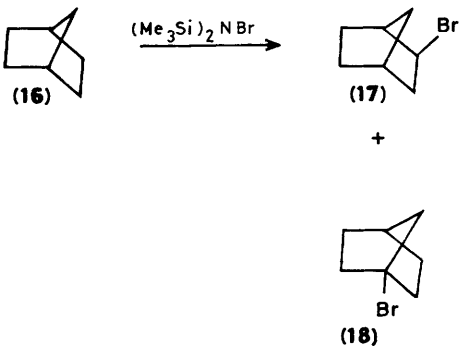
Table 3. Products of the reaction of (3) with bis(trimethylsilyl)-*N*-bromoamine at 70 °C[a]

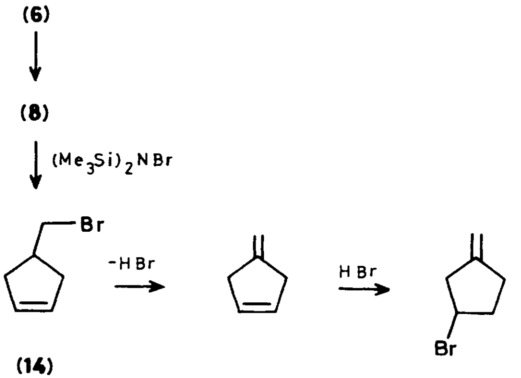
Time/h	1-Bromo **(13)**	2-Bromo **(9)**	3-Bromomethylene-cyclopentane **(15)**	2,2-Dibromo **(10)**	2,3-Dibromo **(11)**	Other[b]
21	25	45	6	6	6	12
26	25	43	6	5	7	12

[a] (3) 1.6 mmol with $(Me_3Si)_2NBr$ 1.6 mmol, $Bu^tCH{=}CH_2$ 0.06 mmol, and AIBN (5 mg) in C_6D_6; products given as mol % total detected products [excluding $(Me_3Si)_2NH$]. [b] Other products were: $Bu^tCHBrCH_2Br$ (*ca.* 10%), PhBr, and several minor unidentified components.



(13)





Scheme 3.

Compound (**15**) obviously results from a rearrangement; possibly by dehydrobromination and re-addition as shown in Scheme 3. The dehydrobromination seems a likely process in the presence of the bromoamine and its reaction product $(Me_3Si)_2NH$. The absence of (**14**) from the reaction products, and the small amount of (**15**) formed, support our earlier conclusion that radical (**6**) does not undergo β-scission rapidly in spite of its considerable ring strain.

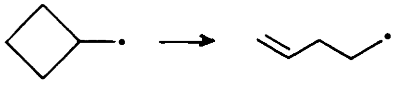
The formation of 25% of the 1-bromo derivative (**13**) (Table 3) suggests that the methine bridgehead hydrogen in (**3**) is activated towards abstraction. Alternatively, the $(Me_3Si)_2N^{\bullet}$ radical might be much less selective than $Bu^tO^{\bullet}$ and $Br^{\bullet}$ radicals.[16] To explore this latter possibility hydrogen abstraction from bicyclo[2.2.1]heptane (**16**) was also examined. This molecule is known to give a mixture of *exo*- and *endo*-2-halides in both photochlorination[17,18] and bromination[18] and to have approximately the same reactivity as cyclohexane.[18,19] There was no detectable bridgehead abstraction with either halogen. The reaction of (**16**) with *N*-bromobis(trimethylsilyl)amine, under the same conditions as above, gave a mixture containing 97% *exo*-2-bromide (**17**) and 3% of the 1-bromide (**18**). This result shows that the $(Me_3Si)_2N^{\bullet}$ radical *is less* selective than the halogen atoms. The quantity of (**18**) formed is rather small and hence it is unlikely that the low selectivity of $(Me_3Si)_2N^{\bullet}$ radicals alone can account for the significant amount of bridgehead attack observed with (**3**). Most probably, therefore, the bridgehead hydrogens in (**3**) are more reactive, relative to the bridge methylene hydrogens, as is suggested by the large h.f.s. and the analogy with bicyclo[1.1.1]pentane (**1**). Thus, the results are consistent with a small through-space interaction in (**4**), of much reduced magnitude compared with that in (**2**), as would be expected on the basis of their γ-h.f.s. At first sight the absence of any *endo*-2-bromide from (**16**) is surprising. However, the second step in the reaction involves abstraction of bromine from *N*-bromobis(trimethylsilyl)amine by norbornan-2-yl radicals. The bromoamine is much bulkier than either Br_2 or Cl_2 and hence the *exo*-product is greatly favoured.

The structures and heats of formation of radical (**6**) and its rearrangement product (**8**) were calculated using the semi-empirical MINDO/3[20,21] and MNDO[20,22] methods and also estimated from Benson's Group Contributions (GC).[23] The ring strain in (**6**) was taken as[24] 37 kcal mol^{-1}. The calculated enthalpies are compared with the corresponding values for cyclobutylmethyl radicals (**19**) and its rearrangement product (**20**) in Table 4. There are large differences in the ΔH_f values calculated by the semi-empirical methods, and the GC values are probably the most reliable. All three methods agree in making the β-scission of (**6**) much more exothermic than the β-

Table 4. Calculated heats of formation ΔH_f of bicyclo[2.1.1]hexan-2-yl and related radicals[a]

Method	ΔH_f(**6**)	ΔH_f(**8**)	$\Delta H^{0\,b}$	ΔH_f(**19**)[c]	ΔH_f(**20**)[c]	$\Delta H^{0\,c,d}$
MINDO/3	69.2	47.3	−22.0	31.6	38.7	7.1
MNDO	51.3	29.3	−22.0			
GC	55.8	47.5	−8.3	45.3	41.0	−4.3

[a] In kcal mol^{-1}. [b] Enthalpy of rearrangement (**6**) $\longrightarrow$ (**8**). [c] From Bews *et al.* (ref. 25). [d] Enthalpy of rearrangement (**19**) $\longrightarrow$ (**20**).



(19) **(20)**

scission of the archetype radical (**19**), as would be expected from the larger ring strain in (**6**). In line with the Hammond Postulate the activation energy for β-scission of (**6**) ought to be significantly *lower* than that of (**19**). However, the activation energies are about the same (see above). A β-scission is favoured if the SOMO can eclipse the bond to be broken.[26] In radical (**19**) rotation can occur about the $\dot{C}_\alpha$–C_β bond so that this most favourable orientation of the SOMO can be attained. In (**6**) the orientation of the SOMO, with respect to the bond to be broken, is fixed and although this orientation is favourable it is obviously not ideal. Thus, rearrangment of (**6**) is favoured, as compared with (**19**), by a greater exothermicity, but disfavoured by this stereoelectronic effect; it appears that these effects roughly cancel.

The structures of (**6**) calculated by the MINDO/3 and MNDO methods were rather similar, except that the C–H bonds were slightly longer in the MINDO/3 structure and the C–C bonds were slightly longer in the MNDO structure. These structures were used in INDO[27] calculations of the h.f.s. and the results are in Table 1. Both sets of calculated h.f.s. were in reasonable agreement with experiment and supported the proposed assignment to specific hydrogens. The very small calculated h.f.s. for the β-hydrogen H(1) are particularly noteworthy.

Experimental

E.p.r. spectra were recorded with a Bruker ER 200D spectrometer on degassed samples in Spectrosil tubes, irradiated with light from a 500 W super-pressure Hg arc. Unless otherwise noted, n.m.r. spectra were obtained with a Bruker WP 80 instrument for $CDCl_3$ solutions at ambient temperature with Me_4Si as internal standard. G.c.–m.s. analyses were carried out with a Finnegan Incos instrument. Preparative g.l.c. employed a Pye-Unicam 105 chromatograph with 5 m × 1 cm glass columns packed with Carbowax 20 M or FFAP.

Bicyclo[2.1.1]*hexane* (**3**). This was made by the mercury-photosensitised photolysis[7] of hexa-1,5-diene and separated by the same means as described previously for bicyclo[2.2.0]-hexane.[4]

Photobromination of (**3**).—To (**3**) (0.12 g) in CCl_4 (0.5 cm^3) was added bromine (0.20 g) and the solution was photolysed with light from two 60 W tungsten lamps at 25 °C for 120 h. The chromatogram showed five main products, together with unchanged (**3**). The individual components were separated by preparative g.l.c. The mass spectrum of the first eluted peak showed a fragmentation pattern consistent with a molecular formula C_6H_9Br; δ_H 0.95 (1 H, dd, 7 Hz, 10 Hz), 1.65 (4 H, m), 2.25 [1 H, dt, *J*(1 H) 6 Hz, *J*(2 H) 2 Hz], 2.6 (2 H, m), and 4.30 (1 H, d, *J* 6 Hz). This spectrum is very similar to that of 2-chlorobicyclo[2.1.1]hexane[6] and the compound can be identified as 2-bromobicyclo[2.1.1]hexane (**9**). The mass spectrum of the second peak showed it to be C_6H_9Br, but insufficient material was obtained for n.m.r. spectra. Peaks 3 and 4 were shown to be dibromides $C_6H_8Br_2$ by their mass spectra. The mass spectrum of peak 3 showed a much stronger ion for loss of HBr from the molecular ion; this is characteristic of 1,1-dihalogenocycloalkanes,[28] *i.e.* peak 3 is compound (**10**). This identification was confirmed by the 300 MHz ^1H n.m.r. spectrum, δ_H 1.69 (2 H, dd, *J* 5 and 2.5 Hz), 1.88 (2 H, m), 2.61 (1 H, m), 2.93 (2 H, q, *J* 1.6 Hz), and 3.25 [1 H, dt, *J* (2 H) 2.5, *J* (1 H) 6.5 Hz]. The 300 MHz ^1H n.m.r. spectrum of peak 4 showed this to be *trans*-2,3-dibromobicyclo[2.1.1]hexane (**11**), δ_H 1.69 (2 H, dd, *J* 5.2 and 2.2 Hz), 1.98 (2 H, m), 2.77 [2 H, dt, *J* (2 H) 3.0, *J* (1 H) 0.5 Hz], and 4.42 (2 H, m). The fifth peak was shown to be a tribromide $C_6H_7Br_3$ by its mass spectrum, but insufficient material was obtained for an n.m.r. spectrum. The proportions of these products are given in Table 2.

Reaction of (**3**) *with* N-*Bromobis*(*trimethylsilyl*)*amine*.—Compound (**3**) (0.137 g), $(Me_3Si)_2NBr$ (0.39 g), $Bu^tCH{=}CH_2$ (0.005 g), and AIBN (0.005 g) were dissolved in perdeuteriobenzene (0.4 cm^3) and heated at 70 °C for 26 h. The products were examined by g.c.–m.s. and separated by preparative g.l.c. Five main products were observed, together with unchanged (**3**) and $(Me_3Si)_2NH$. The mass spectrum of the first peak showed it to be a monobromide C_6H_9Br and the ^1H n.m.r. spectrum indicated that this is the 1-bromo derivative (**13**), δ_H (300 MHz) 1.62 (2 H, dd, *J* 4.5 and 2.0 Hz), 1.78 (2 H, m), 1.99 (4 H, m), and 2.61 (1 H, m). This identification was confirmed by the similarity of the n.m.r. spectrum to that of 1-chlorobicyclo[2.1.1]hexane.[29] The retention time, mass spectrum, and ^1H n.m.r. spectrum of peak 2 were all identical to that of the 2-bromo derivative (**9**). The ^1H n.m.r. spectrum of the separated material was examined at 300 MHz and showed no trace of the rearranged bromide (**14**). Compound (**9**) isolated in this experiment was used for the generation of radical (**6**) in the e.p.r. cavity. Peak 3 was shown to be a monobromide C_6H_9Br by its mass spectrum. The ^1H n.m.r. spectrum (300 MHz), δ_H 2.2—2.4 (4 H, m), 2.4—2.8 (2 H, m), 4.4 (1 H, m), 5.57 (1 H, m), and 5.75 (1 H, m) showed this to be 3-(bromo)methylenecyclopentane (**5**). Peaks 4 and 5 were dibromides and their mass spectra and retention times showed them to be (**10**) and (**11**). Several minor components were also present; the main one was $Bu^tCHBrCH_2Br$ as shown by its mass and ^1H n.m.r. spectra. The proportions of the products are given in Table 3.

Reaction of Norbornane (**16**) *with* N-*Bromobis*(*trimethylsilyl*)-*amine*.—(**16**) (1.0 g), $(Me_3Si)_2NBr$ (1.9 g), $Bu^tCH{=}CH_2$ (0.01 g), and AIBN (0.05 g) were dissolved in benzene (10 g) and heated at 75 °C for 43 h. The products were examined by g.c.–m.s. and separated by preparative g.l.c. The mixture contained unchanged (**16**) and $(Me_3Si)_2NH$ together with four main products. Peak 1: the mass spectrum showed this to be a monobromide $C_7H_{11}Br$; the ^{13}C and ^1H n.m.r. spectra were identical with those given in the literature[30] for 1-bromonorbornane (**18**). Peak 2 was shown to be bromobenzene. Peak 3 was shown by retention time comparisons with authentic material to be *exo*-2-bromonorbornane (**17**); the ^1H n.m.r. spectrum was also identical to that from authentic (**17**) and showed no evidence of the *endo* isomer. Peak 4 was identified as $Bu^tCHBrCH_2Br$ (see above).

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