Radical Chain Bromination of Hydrocarbons Using Bis(trimethylsilyl)bromamine

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Summary Bis(trimethylsilyl)bromamine, $(\mathrm{Me_3Si})_2\mathrm{NBr}$, reacts with hydrocarbons to bring about bromination by a free radical chain mechanism in which the radical $(\mathrm{Me_3Si})_2\mathrm{N}\cdot$ is responsible for hydrogen abstraction.

WE have shown recently that the bis(trimethylsilyl)aminyl radical (**2**) is much more reactive than a dialkylaminyl radical.[1] Using e.s.r. spectroscopy it was demonstrated that (**2**) readily abstracts hydrogen from hydrocarbons at low temperature, even from cyclopropane at 140 K, and in this sense the reactivity of (**2**) is similar to that of an alkoxyl radical[2] or the succinimidyl radical.[3] We now report that bis(trimethylsilyl)bromamine (**1**), which is readily prepared,[4] reacts with a variety of hydrocarbons to yield the corresponding alkyl bromide and hexamethyldisilazane in good yield [equation (1)].

$$\underset{(\mathbf{1})}{(\mathrm{Me_3Si})_2\mathrm{NBr}} + \mathrm{RH} \longrightarrow \mathrm{RBr} + (\mathrm{Me_3Si})_2\mathrm{NH} \qquad (1)$$

For example, the bromination of an excess of toluene in benzene solution takes place readily in the dark during 1 h at 353 K in the presence of azobisisobutyronitrile [AIBN; 2 mol% based on (**1**)], but not in the absence of initiator, to give benzyl bromide (*ca.* 90% yield by g.l.c.). Norbornene or t-butylethylene† [5 mol% based on (**1**)] was also added to scavenge any bromine present adventitiously in the system. Thus, the reaction follows a free radical chain mechanism and the species responsible for hydrogen abstraction was shown to be (**2**), rather than the bromine atom, by studying the competitive bromination of mixtures of toluene and cyclohexane at 353 K. In the absence of added alkene, the molar reactivity of cyclohexane was found to be 0·2 times that of toluene. This relative reactivity ($k_{\mathrm{C}}/k_{\mathrm{T}}$) increased when norbornene was present, but reached a limiting value of 1·0 for *ca.* 3 mol% alkene, with no further increase up to 25 mol%. At 353 K ($k_{\mathrm{C}}/k_{\mathrm{T}}$) for attack by the bromine atom[5] is 0·017, and hence bromination by (**1**) in the presence of > 3 mol% alkene probably involves the propagation sequence shown in equations (2) and (3).

$$\underset{(\mathbf{2})}{(\mathrm{Me_3Si})_2\mathrm{N}\cdot} + \mathrm{RH} \longrightarrow (\mathrm{Me_3Si})_2\mathrm{NH} + \mathrm{R}\cdot \qquad (2)$$

$$\mathrm{R}\cdot + (\mathrm{Me_3Si})_2\mathrm{NBr} \longrightarrow (\mathrm{Me_3Si})_2\mathrm{N}\cdot + \mathrm{RBr} \qquad (3)$$

In the absence of alkene, bromination occurs more slowly and it is likely that part of the product is formed by a bromine atom chain mechanism [equations (4)—(6)].

$$\mathrm{Br}\cdot + \mathrm{RH} \longrightarrow \mathrm{HBr} + \mathrm{R}\cdot \qquad (4)$$

$$\mathrm{HBr} + (\mathrm{Me_3Si})_2\mathrm{NBr} \rightleftharpoons (\mathrm{Me_3Si})_2\mathrm{NH} + \mathrm{Br_2} \qquad (5)$$

$$\mathrm{R}\cdot + \mathrm{Br_2} \longrightarrow \mathrm{RBr} + \mathrm{Br}\cdot \qquad (6)$$

In order to characterise further the radical (**2**) we investigated (using ^{1}H n.m.r. spectroscopy) the competitive bromination by (**1**) of toluene and a series of substituted toluenes (*p*-Me, *p*-Bu^t, *p*-F, *p*-Br, *p*-Cl, *m*-F, and *p*-CN) at 353 K in the presence of AIBN (2 mol%) and norbornene (5 mol%). The results were plotted according to the Hammett equation and yielded a ρ-value of $-0{\cdot}62$ (against σ^+). This reaction constant may be compared with previously determined ρ-values of $-1{\cdot}36$, $-1{\cdot}08$, and $-0{\cdot}35$ for Br• (353 K),[6] Me$_2$N• (409 K),[7] and Bu^{t}O• (313 K),[8] respectively. The negative ρ-value obtained for (**2**), quite different from that determined for Br•, probably reflects in part the importance of contributions to the transition state for hydrogen abstraction in which the silylamino group carries a negative charge.‡

E.s.r. studies[1] have shown that the regioselectivity of (**2**) can be very different from that of the t-butoxyl radical. For example, photochemical generation of (**2**) in liquid isobutane results in detection of e.s.r. spectra of isobutyl and t-butyl radicals and the concentration ratio [Bu^i•]:

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† These alkenes do not contain readily abstractable allylic hydrogens.

‡ The magnitude and sign of the ρ-value depend upon the polar character of the attacking radical, changes in the strength of the benzylic C–H bonds as a function of ring substituents, and the position of the transition state along the reaction co-ordinate. A negative value is usually taken as indicative of an electrophilic attacking radical.

[$Bu^t\cdot$] was given by 0·28exp($-3830/RT$ J mol^{-1}). At 329 K this ratio is 1·1 : 1 and corresponds to the relative rates of alkyl radical formation, if the rate constants describing removal of these species are assumed to be similar. Photolysis (tungsten filament lamp) at 329 K of a solution of (**1**) (0·8 M) in isobutane containing t-butylethylene (0·15 M) afforded isobutyl and t-butyl bromides in the molar ratio 1·05 : 1 (total yield 85%).§

The ability of (**2**) to abstract hydrogen from strong C–H bonds means that (**1**) may be employed for bromination of relatively unreactive hydrocarbons. For example, neopentane reacts readily with (**1**) at 333 K after a short induction period (photochemical initiation) to give neopentyl bromide.

Bis(trimethylsilyl)bromamine should prove a useful brominating agent for organic compounds, complementing halogenation by dialkylhalogenoamines in acidic solution when R_2NH^{+} is the chain carrier.[9] The aminium radical cation is also much more reactive in hydrogen abstraction reactions than is the neutral dialkylaminyl radical, and protonation effects in an intermolecular sense what the trimethylsilyl ligands in (**2**) do intramolecularly, that is reduce the energy of the nitrogen lone pair and thereby increase the electrophilicity and reactivity of the aminyl radicals.

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§ Solutions of (**1**) are reddish-brown before reaction but colourless after (**1**) has been consumed. All reactions were carried out under dry nitrogen or in glass tubes sealed *in vacuo*.

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