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MECHANISM OF THE REACTION OF TRIALKYLBORANES WITH α-AZIDOSTYRENE

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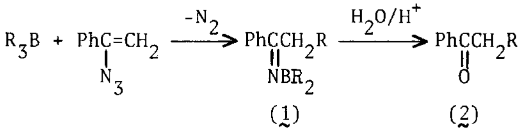
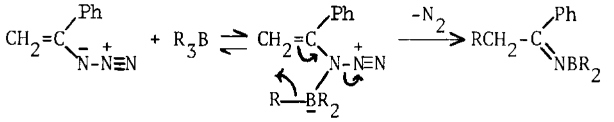
Trialkylboranes and α-azidostyrene react, with evolution of nitrogen, to give iminoboranes $R_2BN{=}C(CH_2R)Ph$ *by a free radical chain mechanism involving intermediate α-azidoalkyl and iminyl radicals.*

In 1975, Susuki *et al.*[1] reported that the reaction of α-azidostyrene with a trialkylborane in tetrahydrofuran at room temperature gives the iminoborane (1), which yields the ketone (2) after hydrolysis. The overall transformation provides a useful preparative route to alkyl



$$R_3B + \underset{\substack{|\\N_3}}{PhC}{=}CH_2 \xrightarrow{-N_2} \underset{\substack{\|\\NBR_2\\(1)}}{PhC}CH_2R \xrightarrow{H_2O/H^+} \underset{\substack{\|\\O\\(2)}}{PhC}CH_2R \qquad (1)$$

phenyl ketones. Susuki was interested primarily in the synthetic utility of this reaction and did not investigate its mechanism, although the heterolytic pathway shown in equation (2) was considered to be reasonable.[1,2] This pathway is certainly possible, but a homolytic



$$CH_2{=}C(Ph)\overset{-}{N}{-}\overset{+}{N}{\equiv}N + R_3B \rightleftharpoons CH_2{=}C(Ph)N(\overset{-}{B}R_3){-}\overset{+}{N}{\equiv}N \xrightarrow{-N_2} RCH_2{-}C(Ph){=}NBR_2 \qquad (2)$$

mechanism appeared more likely to us in view of the ease with which trialkylboranes undergo S_H2 dealkylation reactions with many types of radicals, including nitrogen-centred species [reaction (3)].[3,4]

$$Me_2N\cdot + R_3B \longrightarrow Me_2NBR_2 + R\cdot \qquad (3)$$

The reactions of tri-n-, tri-iso-, and tri-sec-butylboranes with α-azidostyrene (AS)[5] under nitrogen in benzene at 45 °C were monitored using ^1H n.m.r. spectroscopy to follow the decay of the vinylic proton resonances of AS at δ 4.66 and 5.13. The methyl resonance of anisole was used as an internal concentration standard. In a typical experiment, a dry, nitrogen filled n.m.r. tube was charged through a self-sealing rubber cap with tri-n-butylborane (0.81 mmol) followed by benzene (330 μl) and anisole (15 μl), the latter two compounds having been deaerated by purging with dry nitrogen. After mixing and thermal equilibration in a water bath at 45 °C, deaerated AS (0.81 mmol) was added using a calibrated microsyringe. If air was rigorously excluded no reaction occurred on mixing, whereas if traces of air had been admitted the reaction began immediately, as evidenced by the progressive reduction in the size of the vinylic proton resonances and by the appearance and growth of a distorted 1:2:1 triplet (J 7.3 Hz) centred at δ 2.48, which we assign to the CH_2 protons α to the C=N group in (1; R = Bu^n).[6,7]

Reactions which did not begin immediately after mixing the reagents could be initiated by addition of air or 1 mol% di-t-butyl hyponitrite (TBHN) as a solution in benzene. The TBHN decomposes thermally at 45 °C to give t-butoxyl radicals[8] which would react very rapidly with the trialkylborane,[9] as shown in equations (4) and (5). Even in the presence of small

$$Bu^tON{=}NOBu^t \xrightarrow{\text{heat}} 2Bu^tO\bullet + N_2 \qquad (4)$$

$$Bu^tO\bullet + R_3B \longrightarrow Bu^tOBR_2 + R\bullet \qquad (5)$$

amounts of air, the reactions did not start if the stable free radical galvinoxyl[10] (1 mol%) was added before the AS, and an initiated reaction could be stopped immediately by addition of a similar quantity of galvinoxyl. The results of experiments with $Bu^n{}_3B$ are summarized in Figure 1 and similar results were obtained for $Bu^i{}_3B$ and $Bu^s{}_3B$.

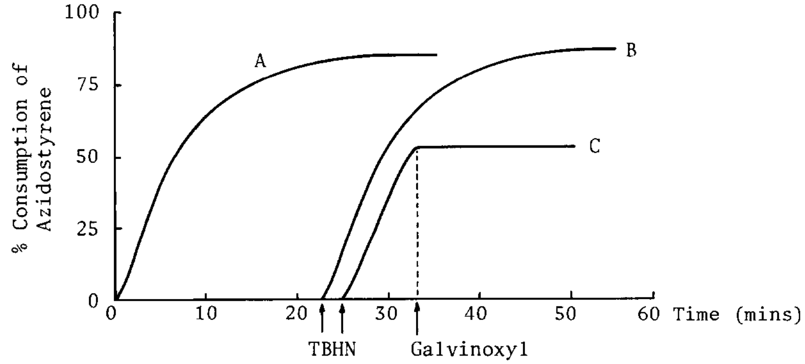


Figure 1: Progress of the reaction of $Bu^n{}_3B$ (0.80 mmol) with AS (0.80 mmol) in benzene at 45 °C. Curve A; 1 mol% TBHN present initially. Curve B; 1 mol% TBHN added at time indicated. Curve C; similar to B, but 1 mol% galvinoxyl added at time indicated.

For initial borane concentrations of 1.22 M and in the presence of 1 mol% TBHN, the rate of reaction of AS (1.24 M) with $Bu^n{}_3B$ was faster ($t_{1/2}$ *ca.* 5 min) than with $Bu^i{}_3B$ or $Bu^s{}_3B$ which reacted at similar rates ($t_{1/2}$ *ca.* 7 min). For all three boranes, reaction ceased after consumption of *ca.* 85% of the AS (see Figure 1) and the reason for this behaviour is not clear at present.

These observations prove conclusively that the reaction of AS with trialkylboranes is a free radical chain process and the most likely mechanism for the formation of the iminoborane (1) is shown in equations (6)-(10).

Initiation

$$\longrightarrow R\bullet \qquad (6)$$

Propagation

$$R\bullet + PhC(N_3){=}CH_2 \longrightarrow Ph\dot{C}(N_3)CH_2R \qquad (7)$$

(3)

$$Ph\dot{C}(N_3)CH_2R \longrightarrow Ph(RCH_2)C{=}N\bullet + N_2 \qquad (8)$$

(4)

$$Ph(RCH_2)C{=}N\bullet + R_3B \longrightarrow Ph(RCH_2)C{=}NBR_2 + R\bullet \qquad (9)$$

(1)

Termination

$$\left.\begin{array}{l} 2R\cdot \longrightarrow \\ R\cdot + Ph(RCH_2)C{=}N\cdot \longrightarrow \\ 2Ph(RCH_2)C{=}N\cdot \longrightarrow \end{array}\right\} \text{Non-radical products} \qquad (10)$$

The sequence of borane reactivities $Bu^n_3B > Bu^i_3B \simeq Bu^s_3B$ for a fixed rate of initiation suggests that the S_H2 step (9) is at least partially rate-limiting under these conditions, since S_H2 reactions at boron in R_3B are generally subject to steric control and their rates decrease in the order $Bu^n_3B > Bu^i_3B > Bu^s_3B$. For example, the rate constants for t-butoxydealkylation of Bu^n_3B, Bu^i_3B, and Bu^s_3B [reaction (5)] at 30 °C are 3×10^7, 1×10^6 and 3×10^5 $l\ mol^{-1}s^{-1}$, respectively.[9] The iminoborane (**1**) is expected to be much less reactive than R_3B towards iminodealkylation, because π bonding between boron and nitrogen, as represented by the allene-like canonical structure $R_2\bar{B}{=}\overset{+}{N}{=}C(CH_2R)Ph$, would have to be disrupted in the transition state for S_H2 attack at boron.

Addition of alkyl radicals to the electron deficient C=C bond in AS to give the resonance stabilised α-azidoalkyl radical (**3**) is expected to be very rapid and its rate, like that of the analogous addition[11] to $(EtO)_2P(O)CH{=}CH_2$, may be governed by polar effects such that a secondary alkyl radical could add more rapidly than a primary one. Loss of nitrogen from the α-azidoalkyl radical to give the alkyl phenyl iminyl radical (**4**) should also be very rapid at room temperature and above.[12-14]

The reaction of trialkylboranes with AS is efficiently initiated by air because the autoxidation of R_3B to give R_2BOOR is a self-initiated free radical chain process, involving R• and ROO• as chain carriers.[3] The subsequent reaction of R_3B with R_2BOOR to give R_2BOR also involves free radicals[3,15] and would provide a second source of initiation for the borane-AS reaction.

E.s.r. spectroscopic studies have provided independent evidence for the occurrence of reactions (7) and (8). Thus, when a benzene solution containing AS (*ca.* 1 M) and diisovaleryl peroxide[16] (*ca.* 0.7 M) was heated at temperatures between 40 and 60 °C in the spectrometer cavity, an e.s.r. spectrum which we assign to the iminyl radical (**4**; R = Bu^i) was observed [*a*(N) 9.90 G, *g* 2.0031]. The spectrum appeared as three broad lines, although there were indications of additional fine structure, and an essentially indistinguishable spectrum, assigned to [**4**; R = $Me_2C(CN)$-] was obtained at 75 °C when the diacyl peroxide was replaced by azobis(isobutyronitrile) [eqns. (11) and (12)].[17]

$$Bu^iC(O)OOC(O)Bu^i \longrightarrow 2Bu^i\cdot + 2CO_2 \qquad (11)$$

$$Me_2C(CN)N{=}NC(CN)Me_2 \longrightarrow 2Me_2\dot{C}CN + N_2 \qquad (12)$$

When TBHN (*ca.*0.5 M) was heated in benzene in the presence of AS (*ca.* 1 M) the spectrum shown in Figure 2 was observed [*a*(N) 9.85 G, *g* 2.0031] and for this iminyl radical additional fine structure, probably resulting from hyperfine coupling of *ca.* 0.4 G from four protons, was well resolved under optimum instrumental conditions. It is very likely that (**4**; R = Bu^tO) is responsible for this spectrum, but at this stage we cannot eliminate the possibility that a carbon-centred radical (perhaps Me•), formed by secondary reactions of $Bu^tO\cdot$, has been trapped by AS. When the benzene solvent was replaced by tetrahydrofuran, the small splittings were barely resolvable although *a*(N) and *g* were virtually unchanged and we propose that the

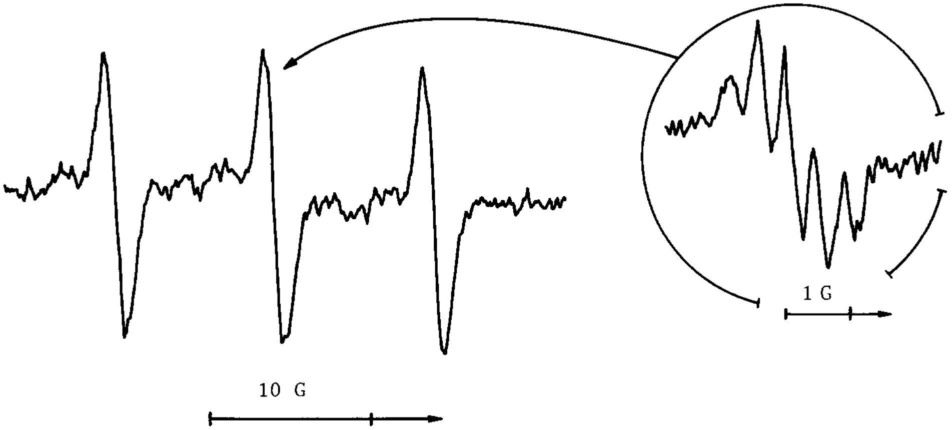


Figure 2: E.s.r. spectrum of $Ph(Bu^tOCH_2)C{=}N\cdot$ in benzene at 56 °C. The central line is shown inset under higher resolution.

radical $\overline{O(CH_2)_3\dot{C}H}$, rather than $Bu^tO\cdot$, is trapped by AS under these conditions.

By comparison with $PhCH{=}N\cdot$,[14] we would expect a splitting of *ca.*0.4 G from three ring protons in (4; R = Bu^tO) and the observed pattern of five lines would result if *one* of the α-methylene protons gives a splitting of similar magnitude, a situation which could arise if rotation about the RCH_2-C bond is not free. Alternatively, *both* methylene protons could give rise to splitting of *ca.*0.4 G and the benzene ring could be twisted with respect to its conformation in $PhCH{=}N\cdot$, such that only two ring protons give rise to resolvable splitting.

Extension of this work to aliphatic vinylic azides and detailed kinetic studies of the reaction of vinylic azides with trialkylboranes are clearly warranted.

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[6] The α-methylene protons of 1-phenylhexanone (2; R = Bu^n) in C_6D_6 solvent appear as a similar triplet (*J* 7.3 Hz) centred at δ 2.65.
[7] Nitrogen gas was evolved during the reaction and the pressure in the n.m.r. tube was maintained at slightly above atmospheric by allowing the gas to escape through a slit in the self-sealing rubber cap. After acidic hydrolysis and treatment with alkaline hydrogen peroxide (as described by Susuki *et al.*[1]) of the reaction product from Bu^i_3B and AS in benzene, 4-methyl-1-phenylpentanone was isolated by distillation.
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