Photochemical Reaction of 2,2,4,4-Tetramethylpentan-3-imine [$Bu^t_2C{=}NH$) with Triethylborane: a Photo-reaction Sensitized by Conjugated Dienes

By Juan C. Scaiano and Keith U. Ingold*

(*Division of Chemistry, National Research Council of Canada, Ottawa, Canada* K1A OR9)

Summary Photolysis in the cavity of an e.s.r. spectrometer of hydrocarbon solutions of $Bu^t_2C{=}NH$ and BEt_3 at temperatures below -10 °C gives ethyl radicals and the radical $Bu^t_2\dot{C}NHBEt_2$ (**2**); the formation of (**2**) is sensitized by the addition of conjugated dienes.

Ketones in their triplet state (n,π^* or π,π^*) react with organoboranes *via* a bimolecular homolytic substitution (S_H2)[1] at boron [reaction (1)].[2,4] When the ketone and

$$[R^1_2CO]^3 + R^2_3B \longrightarrow \underset{(\mathbf{1})}{R^1_2\dot{C}OBR^2_2} + R^{2}\cdot \qquad (1)$$

borane are photolysed in the cavity of an e.s.r. spectrometer the e.s.r. spectra of radical (**1**) and $R^2\cdot$ can generally be observed.[2,3] Since imines and ketones are isoelectronic it was not surprising to find that u.v. photolysis of an n-pentane solution of $Bu^t_2C{=}NH$ and BEt_3 gave, at <-10 °C, the superimposed e.s.r. spectra of the ethyl radical and a radical with g $2{\cdot}0027_3$, a^N $2{\cdot}81$, a^{11B} $+$ $10{\cdot}22$,† and $a^H(NH)$ $+$ $33{\cdot}45$ G, to which we assign structure (**2**) For steric reasons, the boron will eclipse the C_α-$2p_z$ orbital.[5]

$$\underset{(\mathbf{2})}{Bu^t_2\dot{C}NHBEt_2}$$

If (**2**) were formed *via* the imine in its triplet state (triplet energy 75—85 kcal mol^{-1})[6] it should be possible to quench the reaction with a conjugated diene.[7] To our surprise, the e.s.r. signal from (**2**) was enhanced[8] by the addition of butadiene or *trans*-penta-1,3-diene while the ethyl signal decreased (probably because Et· adds to the diene).‡ In fact, the cleanest and most intense e.s.r. spectrum of (**2**) was obtained using butadiene as solvent. The signal-enhancing effect of the dienes occurred in n-pentane, cyclopentane, toluene, and CH_2Cl_2 (in which the signal was very weak without added diene). No e.s.r. signals were detected in tetrahydrofuran (with which the Et_3B would complex) even with added diene.

Radical (**2**) decays with second-order kinetics and is very much shorter lived than the majority of 1,1-di-t-butylalkyl radicals,[5,9] *e.g.* at -80 °C, $k = 3 \times 10^3$ l mol^{-1} s^{-1} in toluene, cyclopentane, and 8:1 (v/v) cyclopentane–*trans*-penta-1,3-diene [which gave 300% more of (**2**) during photolysis than cyclopentane alone].

It is clear that the formation of (**2**) is, in some way, sensitized by the dienes. Triplet sensitization of free imine seems ruled out by the fact that imines have higher triplet energies than the dienes.[6]§ The u.v. spectrum of imine–borane mixtures showed a red shift of the 237 nm imine band. Inversion of triplet states is unlikely since this shift is only *ca.* 5 nm at 25 °C. The formation of a complex seemed more likely and was confirmed by ^{11}B n.m.r. spectroscopy in cyclopentane. Between 40 and -60 °C (lower temperatures made the signal too broad) the ^{11}B signal shifted from 2220 Hz (downfield from $BF_3{\cdot}Et_2O$; 25·14

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† At -95 °C, $Me_2\dot{C}OBPr^n_2$ has a^{11B} 8·3 G.[2] This coupling is probably $-8{\cdot}3$ G because delocalization of the electron on to oxygen will cause the boron to lie close to the C_α-$2p_z$ nodal plane.

‡ The ethyl e.s.r. signal produced by photolysis of $Me_3COOCMe_3$ and Et_3B is also decreased by the addition of these dienes.

§ This is supported by our observations that 0·05 mol l^{-1} $Bu^t_2C{=}NH$ did not affect the quantum yields for: (i) *trans–cis* isomerization of penta-1,3-diene sensitized by benzophenone (triplet energy 69 kcal mol^{-1}), and (ii) formation of acetophenone by photolysis of butyrophenone (triplet energy 74 kcal mol^{-1}).

MHz) towards a limiting value of *ca.* 1100 Hz as the imine concentration was increased or as the temperature was lowered. The results suggest that with imine and Et_3B concentrations in the range 0·2—1·0 mol l^{-1} essentially all the minor component will be complexed at −90 °C and that there will be very little complex at room temperature.

The formation of (**2**) probably involves electronic excitation of the complex, rather than an intermolecular S_H2 reaction, since in all systems where (**2**) could be detected its initial rate of formation upon photolysis and its steady-state concentration increased markedly as the temperature was lowered. The sensitizing effect of the conjugated dienes must, we believe, be attributed to their ability to transfer *singlet* energy to the imine–triethylborane complex. Whether reaction then occurs directly from the excited singlet state, or after intersystem crossing to a triplet complex which is so short lived that it cannot be quenched even by 10 mol l^{-1} butadiene, remains uncertain. The quantum yield for radical formation at −80 °C in the absence of dienes is *ca.* 10^{-2}, and in neat diene, *ca.* 10^{-1}. These low values must result from energy 'wasting' processes including cage reactions (which could be particularly important if a singlet radical pair is produced in the cage).

Finally, we note that ethane is formed essentially quantitatively in a slow, thermal, reaction between $Bu^t_2C{=}NH$ (0·5 mol l^{-1} and Et_3B (0·5 mol l^{-1}) in cyclopentane. This reaction is complete in *ca.* 1 day at room temperature.

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