

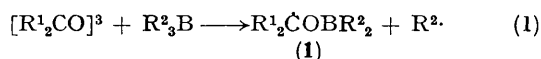
## Photochemical Reaction of 2,2,4,4-Tetramethylpentan-3-imine [Bu<sup>t</sup><sub>2</sub>C=NH] with Triethylborane: a Photo-reaction Sensitized by Conjugated Dienes

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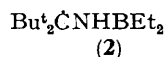
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**Summary** Photolysis in the cavity of an e.s.r. spectrometer of hydrocarbon solutions of Bu<sup>t</sup><sub>2</sub>C=NH and BEt<sub>3</sub> at temperatures below -10 °C gives ethyl radicals and the radical Bu<sup>t</sup><sub>2</sub>ĊNHBEt<sub>3</sub> (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<sub>H</sub>2*)<sup>1</sup> at boron [reaction (1)].<sup>2,4</sup> When the ketone and



borane are photolysed in the cavity of an e.s.r. spectrometer the e.s.r. spectra of radical (1) and R<sup>2</sup>· can generally be observed.<sup>2,3</sup> Since imines and ketones are isoelectronic it was not surprising to find that u.v. photolysis of an n-pentane solution of Bu<sup>t</sup><sub>2</sub>C=NH and BEt<sub>3</sub> gave, at < -10 °C, the superimposed e.s.r. spectra of the ethyl radical and a radical with *g* 2.0027, *a<sup>N</sup>* 2.81, *a<sup>11B</sup>* + 10.22, † and *a<sup>H</sup>*(NH) + 33.45 G, to which we assign structure (2) For steric reasons, the boron will eclipse the C<sub>α</sub>-2*p<sub>z</sub>* orbital.<sup>5</sup>



If (2) were formed *via* the imine in its triplet state (triplet energy 75–85 kcal mol<sup>-1</sup>)<sup>6</sup> it should be possible to quench the reaction with a conjugated diene.<sup>7</sup> To our

† At -95 °C, Me<sub>2</sub>ĊOBPr<sup>n</sup>, has *a<sup>11B</sup>* 8.3 G.<sup>2</sup> This coupling is probably -8.3 G because delocalization of the electron on to oxygen will cause the boron to lie close to the C<sub>α</sub>-2*p<sub>z</sub>* nodal plane.

‡ The ethyl e.s.r. signal produced by photolysis of Me<sub>3</sub>COOCMe<sub>3</sub> and Et<sub>3</sub>B is also decreased by the addition of these dienes.

§ This is supported by our observations that 0.05 mol l<sup>-1</sup> Bu<sup>t</sup><sub>2</sub>C=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<sup>-1</sup>), and (ii) formation of acetophenone by photolysis of butyrophenone (triplet energy 74 kcal mol<sup>-1</sup>).

surprise, the e.s.r. signal from (2) was enhanced<sup>8</sup> 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<sub>2</sub>Cl<sub>2</sub> (in which the signal was very weak without added diene). No e.s.r. signals were detected in tetrahydrofuran (with which the Et<sub>3</sub>B 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,<sup>5,9</sup> *e.g.* at -80 °C, *k* = 3 × 10<sup>8</sup> l mol<sup>-1</sup> s<sup>-1</sup> 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.<sup>6§</sup> 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 <sup>11</sup>B n.m.r. spectroscopy in cyclopentane. Between 40 and -60 °C (lower temperatures made the signal too broad) the <sup>11</sup>B signal shifted from 2220 Hz (downfield from BF<sub>3</sub>·Et<sub>2</sub>O; 25.14

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<sub>3</sub>B concentrations in the range 0.2—1.0 mol l<sup>-1</sup> 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<sub>R</sub>2 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<sup>-1</sup> butadiene, remains uncertain. The quantum yield for radical formation at -80 °C in the absence of dienes is *ca.* 10<sup>-2</sup>, and in neat diene, *ca.* 10<sup>-1</sup>. 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<sup>t</sup><sub>2</sub>C=NH (0.5 mol l<sup>-1</sup> and Et<sub>3</sub>B (0.5 mol l<sup>-1</sup>) in cyclopentane. This reaction is complete in *ca.* 1 day at room temperature.

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