

## Spin Trap Study on the Photochemical Reaction between *trans*-Stilbene and Triethylamine

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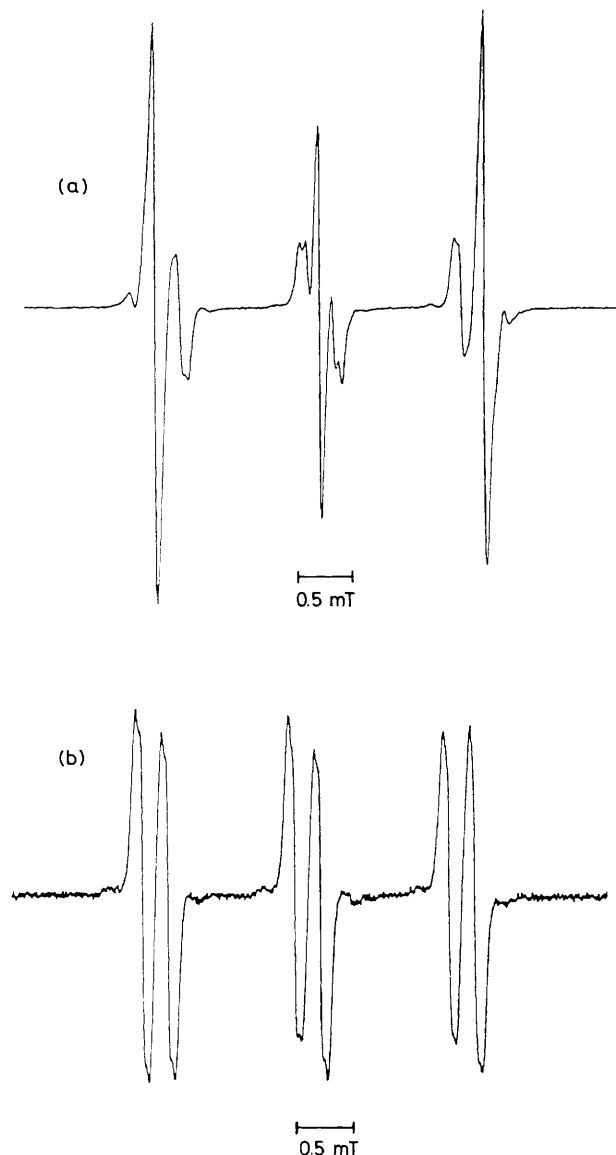
1,2-Diphenylethyl radical trapped by 2-methyl-2-nitrosopropane during the photolysis of *trans*-stilbene and triethylamine has been studied by resolution-enhanced e.s.r. spectroscopy.

The reactive intermediates identified in the photochemical reaction between *trans*-stilbene (TS) and triethylamine include the singlet state of TS, an exciplex, and radical cations and anions.<sup>1-3</sup> Radicals were also proposed to be involved in the reaction from product analysis but so far have escaped identification. We have applied the recently developed technique of spin trap-radical chromato-e.s.r. (s.t.-r.c.-e.s.r.) spectroscopy<sup>4</sup> and microcomputer-assisted numerical analysis<sup>5</sup> (e.g. resolution enhancement) to the identification and determination of the structure of the radicals formed for the TS-amine system.

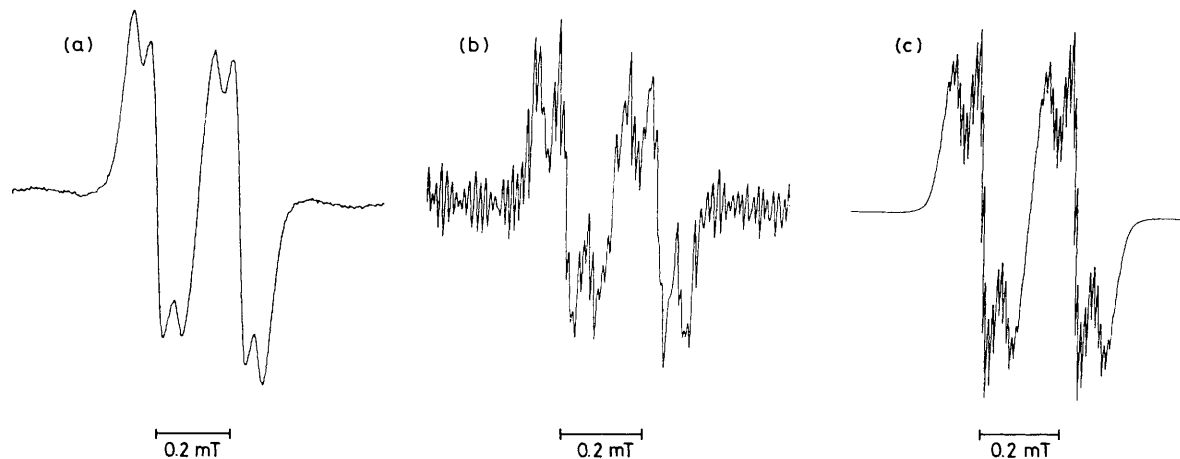
2-Methyl-2-nitrosopropane (MNP) was used as a spin trap reagent in order to identify the trapped radicals. MNP has

been used extensively for trapping and identification of free radicals produced in photochemical reactions.<sup>6</sup>

Degassed acetonitrile solutions containing concentrations of 0.05 M TS, 1.5 M triethylamine, and 0.3 M MNP were irradiated with a medium-pressure mercury lamp for 3 h. The acetonitrile solvent was removed, the residue was dissolved in benzene, and the e.s.r. spectrum was recorded (Figure 1a). The spectrum indicates that at least two chemically different radicals were trapped by the MNP. Chromatographic separation of the mixture led to two pure radicals. Besides the self-trapped di-*t*-butylaminoxyl radical (Bu<sub>2</sub>NO•), a pure spin-adduct (**1**) [radical (**1a**),  $g$  2.0066,  $a_N$  1.44 mT] was also obtained (Figure 1b). Figure 2a indicates the  $m_I = +1$  part

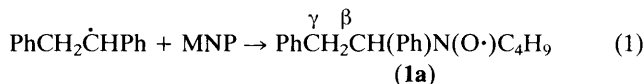


**Figure 1.** E.s.r. spectra of (a) the spin adducts before chromatographic separation, and (b) the radical (**1a**) after chromatographic separation.

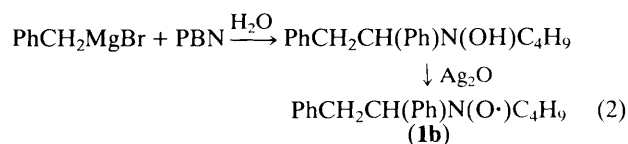


**Figure 2.** (a) The  $m_s = +1$  part lowest field peak of the radical (**1a**) measured in toluene at  $-60^\circ\text{C}$ ; (b) resolution enhanced spectrum from (a); (c) simulated spectrum of (b).

(lowest field) of the radical (**1a**) measured in toluene at  $-60^\circ\text{C}$  to get better resolution. Application of a resolution enhancement technique using Fourier transform deconvolution<sup>7</sup> led to the e.s.r. spectrum shown in Figure 2b. Since hyperfine structure due to long-range interaction was observed, simulation of the e.s.r. spectrum was possible, keeping in mind the fact that the most probable short-lived radicals in this system are thought to be either  $\text{PhCH}_2\dot{\text{C}}\text{HPh}$  or  $\text{Et}_2\text{NCHMe}$ .<sup>1</sup> The best fit simulated spectrum (shown in Figure 2c) was obtained for the spin adduct of the former radical [see reaction (1)] and the hyperfine splitting constants (mT) are  $a_{\text{N}}$  1.437,  $a_{\text{H}}(\beta)$  0.217 (1H),  $a_{\text{H}}(\gamma)$  0.056 (2H),  $a_{\text{H}}(o,\beta\text{-phenyl})$  0.015 (2H),  $a_{\text{H}}(p,\beta\text{-phenyl})$  0.026 (1H),  $a_{\text{H}}(\text{t-butyl})$  0.009 (9H). The hyperfine splitting constants for the  $\gamma$ -phenyl protons and the *meta* protons of the  $\beta$ -phenyl group could not be determined. Thus we conclude that the isolated radical (**1a**) is obtained by trapping of the 1,2-diphenylethyl radical with MNP [reaction (1)].



To be certain of the structure of the radical (**1a**), we have also prepared the radical (**1b**) by the Grignard reaction of benzylmagnesium bromide with  $\alpha$ -phenyl-*t*-butylnitrone (PBN) [reaction (2)].



The e.s.r. spectrum of the radical (**1b**) prepared as in reaction (2) was identical with that of the radical (**1a**). This also supports the trapping of the 1,2-diphenylethyl radical by the MNP.

Furthermore, long-range hyperfine splitting constants (mT) for the radical (**1b**) were determined to be  $a_{\text{H}}(o,\beta\text{-phenyl}) + 0.0130$  (2H),  $a_{\text{H}}(p,\beta\text{-phenyl}) + 0.0288$  (1H), and  $a_{\text{H}}(\text{t-butyl}) - 0.0087$  (9H) by analysis of the n.m.r. spectrum of a concentrated solution of the radical. These values were in good agreement with those obtained by the analysis of the resolution-enhanced e.s.r. spectrum of radical (**1a**).

The radical (**1a,b**) has also been prepared by several other methods<sup>8</sup> by using PBN as a trapping agent though reports on the e.s.r. parameters are rather contradictory.

We have thus demonstrated for the first time that the 1,2-diphenylethyl radical was trapped by MNP to give the radical (**1a**) and the long-range hyperfine splitting constants from  $\gamma$ -H and the phenyl ring at  $\beta$ -C of the radical (**1a**) are also reported for the first time by using the combined s.t.-r.c.-e.s.r. and resolution enhancement methods. Although an  $\alpha$ -amino-alkyl radical was expected to be trapped, it was not detected in this experiment by using MNP as a trapping reagent. It is clear that combination of the s.t.-r.c.-e.s.r. and the resolution enhancement methods can be applied to the studies of other photochemical systems.

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