

UPPER EXCITED STATE PHOTOCHEMISTRY OF DI-TERT-BUTYL NITROXIDE

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(Received in USA 17 June 1977; received in UK for publication 7 July 1977)

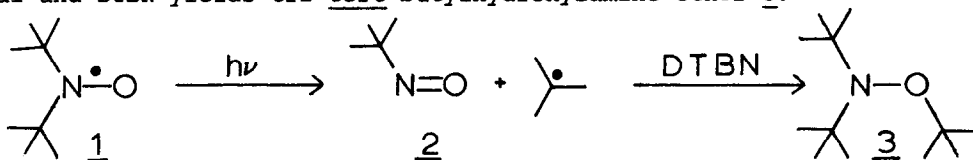
Over the past decade the paramagnetic compound di-tert-butyl nitroxide (DTBN, 1) has proved to be an interesting and surprisingly versatile quencher of electronically excited species.¹⁻¹⁴ DTBN quenches both singlet and triplet states at near diffusion controlled rates.¹⁻⁵ Efficient quenching of singlet excimers⁶ and exciplexes,⁷ triplet exciplexes,⁸⁻¹¹ and stilbene twisted triplet has also been reported.^{1,12} The mechanism of quenching is thought to be either electron exchange induced intersystem crossing or vibrational quenching where a complex deactivates directly to ground state.^{1,2}

There are, however, some potential problems which must be carefully considered before employing DTBN as a quencher of photoreactions. Nitroxides are excellent free radical scavengers,¹⁵⁻²⁰ and Schuster has reported that radical scavenging by DTBN can result in significant quenching of photoreactions, especially those involving a chain mechanism.²¹ A second problem is potential photochemical reactivity of DTBN. Presumably DTBN is not electronically excited when it quenches an excited species^{1,2} even though electronic energy transfer would generally be exothermic.²² However, direct excitation of DTBN is possible in the absence of judicious filtering of incident radiation. DTBN has a convenient window in its UV-visible absorption spectrum in the region of 320-380 nm ($\epsilon_{330}=0.5$), a weak $n-\pi^*$ band at 465 nm ($\epsilon=9$), and a strong $\pi-\pi^*$ band at 237 nm ($\epsilon=2580$) tailing to 320 nm. In this paper we report on the photoreactivity of the n,π^* and π,π^* doublet states of DTBN.

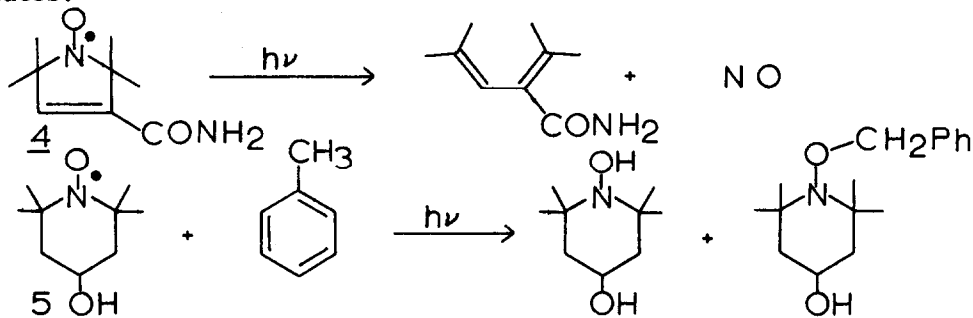
DTBN was prepared according to the method of Hoffman²⁰ and distilled through an annular spinning band column at 55° (11 torr) prior to use. A 2.8 ml sample of 0.10 M DTBN in spectro-grade pentane was placed in a quartz cuvette with a tight-fitting Teflon stopper and degassed with argon. The sample was irradiated at 254 nm with 1.32×10^{20} quanta using a linear quantum yield apparatus consisting of a Bausch and Lomb 250 mm monochromator, a 200 W super pressure mercury light source, and a thermostated cell compartment maintained at $20 \pm 0.5^\circ\text{C}$. The monochromator was adjusted for irradiation at 254 nm with a bandpass of 66 nm. The light intensity was monitored with potassium ferrioxalate actinometry.²³ DTBN was destroyed (16%, $\phi=0.21$) as measured by visible spectroscopy at 460 nm using a Beckman DU spectrometer. Analysis by

visible spectroscopy at 680 nm indicated a 70% yield based on DTBN destroyed ($\phi=0.072$) of tert-nitrosobutane (2). GLPC analysis using a 1.22 m by 0.635 cm column of 5% silicone vacuum grease on 60/80 mesh Chromosorb W at 60° (He 60 ml/min) with ethylbenzene as an internal standard showed an 85% yield based on DTBN destroyed ($\phi=0.087$) of tri-tert-butylhydroxylamine ether (3). Products 2²⁴ and 3²⁰ were isolated by comparison of IR, NMR, and/or UV-visible spectra with spectra of the known compounds. Irradiation of a similar sample of DTBN in spectrograde pentane at 448 nm with 1.32×10^{20} quanta resulted in no destruction of DTBN as shown by visible spectroscopy.

The photoreactivity of DTBN in its π, π^* doublet state is explained in terms of cleavage α to nitrogen to yield tert-nitrosobutane and tert-butyl radical as the primary photochemical process. Subsequent combination of the radical and DTBN yields tri-tert-butylhydroxylamine ether 3.



A possibly analogous α -cleavage of nitroxide 4 has been reported by Keana.²⁵ Nitroxide 5, however, only photoreacts inefficiently via an intermolecular hydrogen abstraction process.²⁶ Irradiations of 4 and 5 were performed under conditions which would populate both the n, π^* and π, π^* excited states.



Our photochemical results with DTBN suggest that nitroxide 5 also α -cleaves efficiently upon irradiation of its π, π^* band but that the resulting radical-nitroso compound efficiently, intramolecularly spin-traps itself. The cleavage-spin-trapping sequence then represents an energy wasting process. The hydrogen abstraction reaction of 5 is inefficient relative to the cleavage of 4²⁶ and DTBN, and nitrosocompounds 4 are well established spin-trapping agents.²⁷

In summary we have shown that DTBN is photoinert in its n, π^* doublet state and cleaves to tert-nitrosobutane and tert-butyl radical with relatively high quantum efficiency in its π, π^* doublet state. When using DTBN in quenching experiments, photodestruction will not occur if light of wavelength less than 320 nm is removed with appropriate filters or a monochromator.

Acknowledgments. Financial support from the National Institutes of Health under Grant GM-18349 is gratefully acknowledged. D.R.A. thanks the University of Colorado for a Graduate Fellowship, and T.H.K. the University of Colorado Council on Research and Creative Work for a Faculty Fellowship.

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