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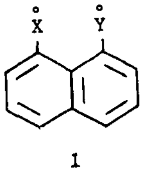
Heteroatomic Biradicals. Electron Spin Resonance Spectroscopy of a Nitrogen Analogue of 1,8-Naphthoquinodimethane

Sir:

Biradical[1] intermediates play an important role in many thermal[2] and photochemical[3] processes. Over the last 15 years, low temperature ESR spectroscopy has become a powerful, direct probe of these otherwise transient species.[4] It appeared that an ESR study of variously functionalized perinaphthalene diyls (**1**) might provide insight into structure reactivity relationships in biradical chemistry. Previous work in this laboratory has shown that the known 1,8-naphthoquinodimethane[5] biradical (**3**) could be prepared from a diazo precursor.[6] We herein report the use of this technique to prepare a nitrogen-centered biradical by photolysis of an azide.



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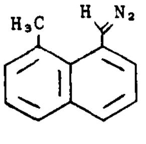

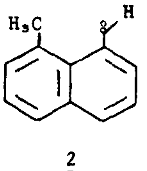

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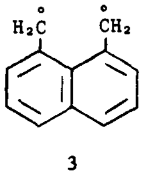
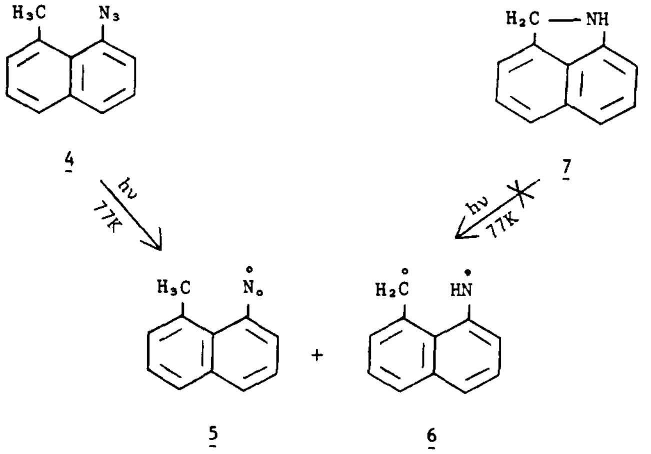


3

Treatment of an acetone solution of 8-methyl-1-naphthoyl chloride[6] with aqueous sodium azide, at 25 °C, produces 8-methyl-1-naphthyl isocyanate. Only trace amounts of the intermediate acyl azide could be observed.[7] The isocyanate was hydrolyzed to 1-amino-8-methylnaphthalene with aqueous acid. Diazotization of the amine, followed by treatment with sodium azide, yields 1-azido-8-methylnaphthalene (**4**).[8]

Photolysis of **4** in 2-methyltetrahydrofuran (2MTHF) at 77 K produces ESR absorptions centered at 6100, 3300, and 1588 G (see Figures 1 and 2). The resonance absorptions are characteristic of randomly oriented triplet states[9] and are assigned to 1-methyl-8-nitrenonaphthalene **5** ($|D/\hbar c| = 0.79 \pm 0.02$ cm^{-1}, $|E/\hbar c| < 0.003$ cm^{-1}) and 1-imino-8-naphthoquinomethane ($|D/\hbar c| = 0.0255 \pm 0.0002$ cm^{-1}, $|E/\hbar c| = 0.0008 \pm 0.0002$ cm^{-1}). Control experiments with cyclic amine **7**[10] demonstrate that it is not photochemically converted into **5** or **6**. The spectrum of **6** is consistent with a single conformation;[11] however, the spectra of the syn and anti forms of the biradical may not be appreciably different.



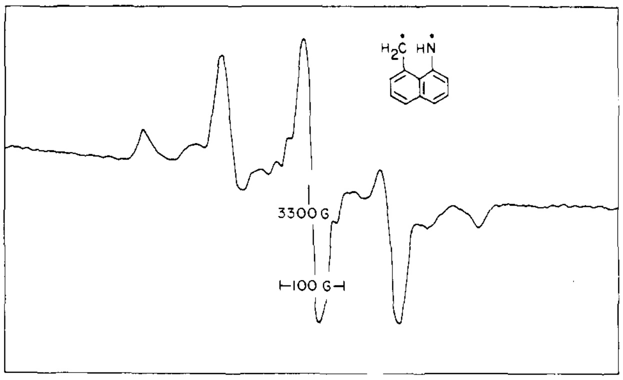


Figure 1. The ESR spectrum of biradical **6** in 2MTHF (77 K).

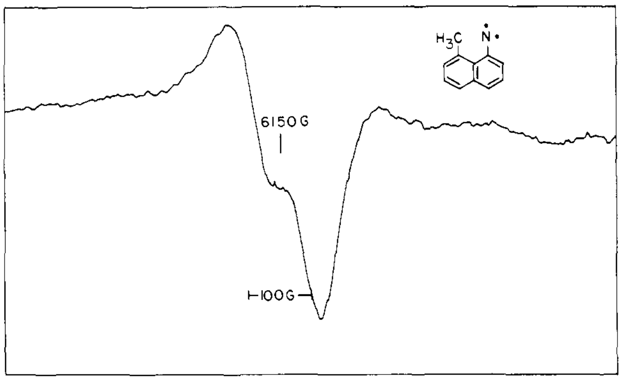


Figure 2. The ESR spectrum of nitrene **5** in 2MTHF (20 K).

The $|D/\hbar c|$ value of **6** is 17% larger than that of **3**,[5,6] indicating an average, closer proximity of the two unpaired electrons in the aza diyl.[12] This is similar to tris(imino)trimethylenemethane[13] which has a larger $|D/\hbar c|$ value than trimethylenemethane itself.[4a] The heteroatomic biradical **6** strictly obeys the Curie–Weiss Law over the temperature range 17 to 83.5 K.[14] Therefore the nitrogen-centered diyl has a triplet ground state, in agreement with 1,8-naphthoquinodimethane.[5d,6,15]

At 77 K the nitrene ESR spectrum does not interconvert into that of the biradical; both species are indefinitely stable at this temperature. The heteroatomic triplet biradical is, in fact, more thermally labile than the triplet nitrene. Warming of the sample to 98 K results in the rapid and complete dissipation of the ESR spectrum of **6**, but very little diminution of the nitrene signal intensity. Clearly **6** is not formed from triplet **5** in a thermally activated process at 77 K.

To test whether the triplet biradical arises via secondary photolysis of the triplet nitrene, the signal intensities of **5** and **6** were studied as a function of irradiation time (Figure 3). The ratio of **5**/**6** was invariant with the duration of photolysis ($230 < \lambda < 449$ nm). At 77 K the nitrene and the biradical are both formed simultaneously; secondary photolysis of the triplet nitrene is not a major source of the biradical. The hydrogen atom transfer may occur from an excited state (electronic or vibrational) of the azide, an azacycloheptatetraene,[16] or singlet 1-methyl-8-nitrenonaphthalene.

There are significant differences between the nitrene–heteroatomic biradical system (**5** and **6**) and the hydrocarbon case (**2** and **3**). The lifetime of 1,8-naphthoquinodimethane at 98 K is at least an order of magnitude longer than that of the aza

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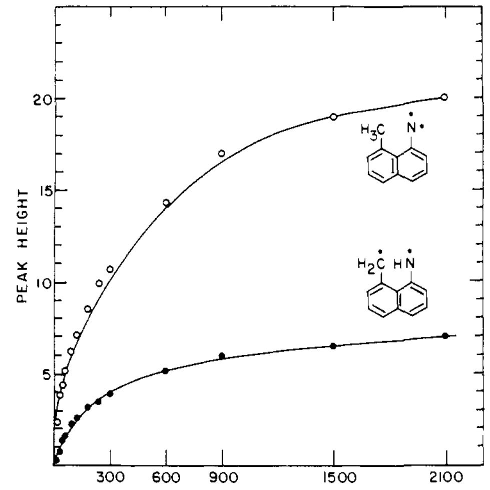

Figure 3. The intensities of **5** and **6** as a function of irradiation time (77 K). The lower curve can be converted into the upper by multiplying by a constant numerical factor of 3.0 ± 0.3. 1-Azido-8-methylnaphthalene does not partition into equal amounts of **5** and **6**.

diyl. Even more striking is a comparison of **2** and **5**. The triplet nitrene is indefinitely stable at 77 K, whereas the triplet carbene could not be detected even at 4 K. If the discrete carbene intermediate is, in fact, on the reaction pathway to **3**, there must be a very large reactivity difference between the triplet states of **2** and **5**.

A complete kinetic analysis of the triplet species described herein is in progress.

Acknowledgments. The authors thank Professor John Swenton for valuable discussions, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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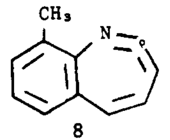
(16) Chapman and co-workers have shown that phenylnitrene and pyridylmethylenes photochemically interconvert via aza cycloheptatetraenes. It is conceivable that the hydrogen atom transfer may occur via an intermediate such as **8**. See: Chapman, O. L.; Le Roux, J. P. *J. Am. Chem. Soc.* **1978,** *100*, 282. Chapman, O. L.; Sheridan, R. S.; Le Roux, J. P. *ibid.* **1978,** *100*, 6245.



8

(17) This treatment assumes that the integrated signal intensity is proportional to peak height, and that the triplet concentration is proportional to the integrated signal intensity.

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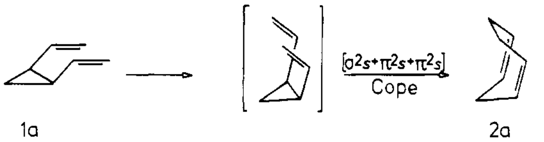
Synthesis and Cope Rearrangement of *cis*-1,2-Dialkenylcyclopropanes

Sir:

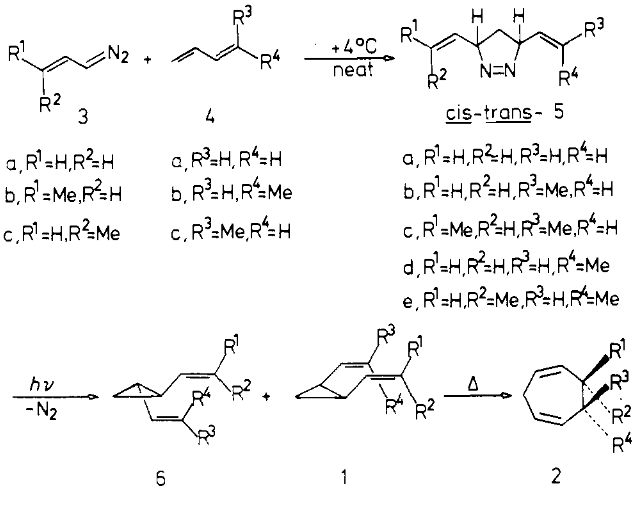
Attempts to synthesize *cis*-1,2-divinylcyclopropane (**1a**) were largely unsuccessful in the past[1,2] owing to its rapid Cope rearrangement[3] to 1,4-cycloheptadiene (**2a**) (eq 1). They have, however, contributed much to the development and application of fluxional tautomerism which led to studies of several systems with a **1a** skeleton.[2,4] The rearrangement has recently become of additional interest, since derivatives of **1a** were implied as possible precursors in the biosynthesis of natural products (with a **2a** moiety) from marine brown algae (*Dictyopteris* and *Ectocarpus siliculosus*).[5]



1a 2a (1)

Since **1a** and most of its derivatives were inaccessible until a few years ago,[6] it is not surprising that only few kinetic data for their rearrangements are known so far. We report here a general and convenient synthesis for *cis*-1,2-dialkenylcyclopropanes (and the corresponding trans isomers) and kinetic data for their Cope rearrangements. We had shown before[6b] that low-temperature photolysis of the *cis*- and *trans*-3,5-divinyl-1-pyrazolines (**5a**), obtained via 1,3-dipolar cycloaddition of 3-diazo-1-propene (**3a**) to 1,3-butadiene (**4a**) (Scheme I), provides a simple route to **1a**.[6c] Frontier orbital considerations[7] predict the addition of diazo compounds (**3**) to occur exclusively at the terminal double bonds of conjugated dienes (**4**). This is indeed observed and, since **3** and **4** can be prepared easily in great variety, a large number of derivatives (**1**) becomes accessible this way in a very short synthetic sequence (Scheme I).[8] Moreover, as a further advantage, the stereo-

Scheme I



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