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TIME-RESOLVED AND LOW-TEMPERATURE ABSORPTION SPECTROSCOPIC STUDIES ON 10-SILAANTHRACEN-9(10H)-YLIDENE

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Laser-photolysis studies have been carried out on a solution of 9-diazo-10,10-dimethyl-10-sila-9(10H)-anthracene in cyclohexane to obtain a series of UV absorptions due to transient species. The spectral assignment was corroborated by absorption spectra and ESR studies of the photolyses in an EPA matrix at 77 K.

Irradiation of diazo compounds leads to loss of nitrogen and consequent formation of products due to the corresponding carbenes in the singlet and/or triplet electronic states. Time-resolved studies of these processes are the subjects of current interest.1) Some controversies are occasioned however as to the correct assignment of absorptions and time constants obtained in these studies. We wish to report here a time-resolved spectroscopic study on the photolysis 9-diazo-10,10-dimethyl-10-sila-9(10H)-anthracene (1a).2) To avoid ambiguity in the absorption spectral assignment, the stationary photolysis of 1a in an EPA matrix at 77 K has been monitored by absorption and ESR spectroscopy.

Laser-photolysis measurement was carried out by using the fourth harmonic (266 nm) of a Quanta-Ray DCR-1 Nd:YAG laser (pulse width of 5 ns) as the exciting light source.3) A degassed cyclohexane solution of 1a (8.9×10^{-4} M) was used at room temperature. The transient absorption spectra obtained 20 ns, 100 ns, 2 μs, and 8 μs after the laser pulse are shown in Fig. 1. A very fast rise of a peak at 343 nm was observed after the excitation. This may correspond to intersystem crossing from the singlet 10,10-dimethyl-10-silaanthracen-9(10H)-ylidene (1b) to the triplet 1b. The absorption peaks for the former are considered not to be obtained with the time resolution of our system. The rate of intersystem crossing of 1b was measured from the rise curve of the absorption at 343 nm to give the value of 4.4×10^7 s^{-1}. The spectral features obtained 100 ns after the pulse are a strong absorption at 343 nm and a weak absorption extending from 450 to 520 nm. This spectrum is quite similar to that measured during the photolysis of 1a in EPA

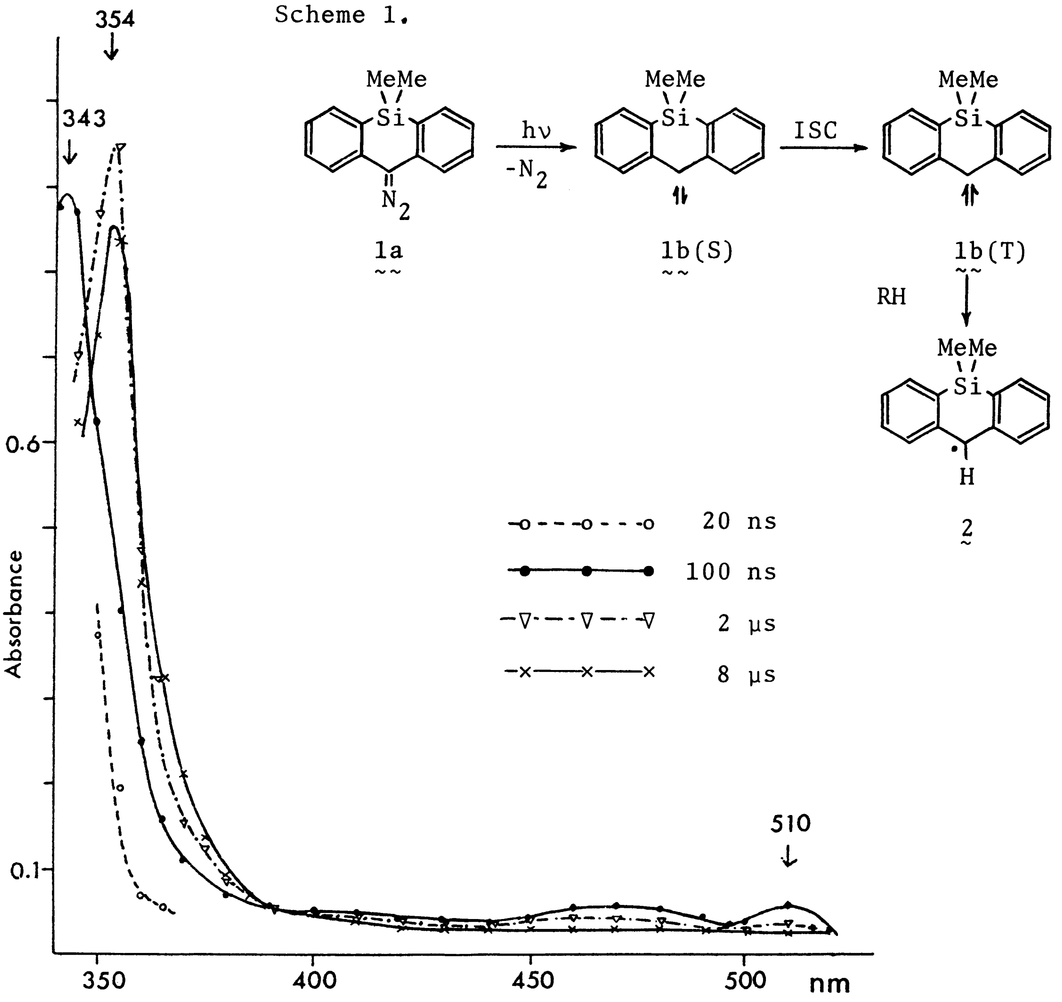


Fig. 1. Absorption spectra of the transient products formed during the irradiation of 1a in degassed cyclohexane. The curves were recorded at the given delay times. The maxima at 343 and 510 nm are due to triplet 1b and the maximum at 354 nm is due to radical 2.

matrices at 77 K as shown in Fig. 2. The latter spectrum is safely assigned to triplet carbene 1b, since intense triplet signals were obtained by ESR spectroscopy under these conditions.[2)] Triplet 1b appeared to be stable at temperatures lower than 100 K. No appreciable formation of a doublet species was detected at these temperatures. The intensity of the peak at 343 nm in the time-resolved spectra reached a maximum at ca. 100 ns, and then started to decrease. At its expense, new absorptions appeared with a sharp peak at 354 nm which reached a maximum intensity 2 μs after the pulse and then decayed slowly. The 354 nm peak can be assigned to the corresponding radical 2 resulting from hydrogen abstraction by triplet carbene 1b (Scheme 1). The pattern of absorptions of triplet carbene 1b and radical 2 parallels those of 10,11-dihydrodibenzo[a,d]cyclohepten-5-ylidene 3 for which absorption maxima are reported to be at 340 and 510 nm and that of the

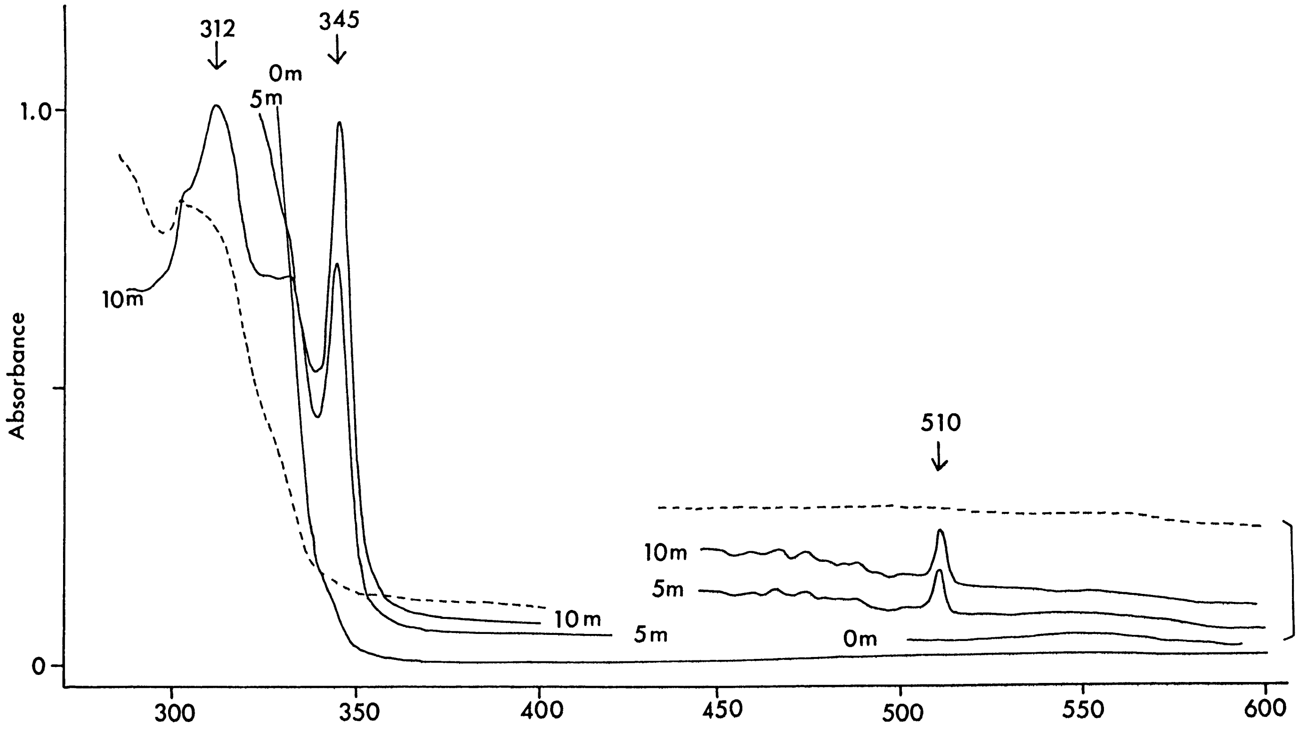
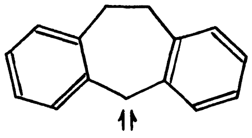


Fig. 2. Absorption spectra measured in EPA matrices at 77 K. An absorption of 1a having a weak maximum at 550 nm was recorded at 0 min. The spectra due to 1b with maxima at 312, 345, and 510 nm were recorded at irradiation times of 5 and 10 min.7)

corresponding radical is at 350 nm.4) The assignment of the absorptions of triplet 1b and radical 2 was further confirmed by quenching experiments. Although the lifetime of singlet 1b appeared to decrease significantly by the addition of methanol, those shorter than 20 ns could not be measured precisely with the present instrumental system. Thus the reaction rate of singlet 1b with methanol was deduced from quenching of the amount of triplet 1b formed as judged by the decrease in absorbance at 355 nm observed at 100 ns after the light pulse. The absorptions were normalized by those of 20 ns after the pulse.5) When 1.48×10^{-1} M of methanol were added, about 30% of singlet 1b was quenched and the rest underwent intersystem crossing to give triplet 1b. In this way, the rate constant for the reaction of singlet 1b with methanol was evaluated to be 1.5×10^{8} $M^{-1}s^{-1}$. Addition of 2-methyl-2-butene (1.17×10^{-1} M) had no effect on singlet 1b, reasoning for the lack of cyclopropane derivatives in preparative photolyses.2) Quenching rate constants for triplet 1b were determined from the change in its lifetime in the presence of additives. The results are summarized in Table 1. They are qualitatively similar to those of hydrogen abstraction by t-butoxy radical in which relative reactivities per hydrogen atom are 2 : 1 : 8 for methanol, 2-methyl-2-butene, and 2-methyltetrahydrofuran, respectively.6) The decay of radical 2 was almost independent of the solvent; the lifetime of 29 ± 3 μs was obtained when its absorbance was assumed to follow the first order decay.

Table 1. Reactivity of Triplet 1b with Hydrogen Donating Quenchers

quencher	$k_q/M^{-1}s^{-1}$
methanol	6.9×10^6
2-methyl-2-butene	4.2×10^6
2-methyltetrahydrofuran	2.8×10^7



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In conclusion, the absorption spectra and the pertinent rate constants for the triplet 9-anthracenylidene 1b and the corresponding radical 2 have been obtained. The rate constants are mostly smaller than those of diphenylcarbene and 9-fluorenylidene.$^{1)}$ Critical comparison of these data will be given in a full paper.

References

1) G. L. Closs, C. A. Hutchison, Jr., and B. Kohler, J. Chem. Phys., 44, 413 (1966); G. L. Closs and B. E. Rabinow, J. Am. Chem. Soc., 98, 8190 (1976); J. J. Zupancic and G. B. Schuster, ibid., 102, 5958 (1980); 103, 944, 2423 (1981); K. B. Eisenthal, N. J. Turro, M. Aikawa, J. A. Butcher, Jr., C. DePuy, G. Hefferson, W. Hetherington, G. M. Korenowski, and M. J. McAuliffe, ibid., 102, 6563 (1980); P. C. Wong, D. Griller, and J. C. Scaiano, ibid., 103, 5934 (1981); 104, 5106 (1982); D. Griller, C. R. Montgomery, J. C. Scaiano, M. S. Platz, and L. Hadel, ibid., 104, 6813 (1982); B.-E. Brauer, P. B. Grasse, K. J. Kaufmann, and G. B. Schuster, ibid., 104, 6814 (1982).

2) A. Sekiguchi and W. Ando, Bull. Chem. Soc. Jpn., 55, 1675 (1982); A. Sekiguchi, W. Ando, T. Sugawara, H. Iwamura, and M. T. H. Liu, Tetrahedron Lett., 23, 4095 (1982)

3) H. Hayashi and S. Nagakura, Bull. Chem. Soc. Jpn., 53, 1519 (1980).

4) I. Moritani, S. Murahashi, H. Ashitaka, K. Kimura, and H. Tsubomura, J. Am. Chem. Soc., 90, 5918 (1968). For further spectroscopic analogies, see: H. Masuhara, M. Okuda, and M. Koizumi, Bull. Chem. Soc. Jpn., 41, 2319 (1968); 44, 38 (1971).

5) Since an accurate determination of the weakened absorbanceat 343 nm was difficult owing to the compensation problem of background absorptions, the measurement was carried out at longer wavelength. Absorptions due to radical 2 at 355 nm were negligible in the 100 ns period.

6) A. Richie, M. Schulz, and D. Becker, Chem. Ber., 98, 3627 (1965); R. M. Carman and D. E. Cowley, Tetrahedron Lett., 1968, 2723.

7) The observed 2 nm bathochromic shift of the 345 nm band and the sharpening of the 510 nm absorption relative to those in cyclohexane at room temperature (Fig. 1) are considered to be due to the medium and/or temperature effects.

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