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ELECTRONIC ABSORPTION SPECTRA OF THE PRODUCTS FORMED BY THE PHOTOLYSIS OF DIAZO COMPOUNDS AT 77°K, POSSIBLY IDENTIFIED TO CARBENES

by Ichiro Moritani, Shun-Ichi Murahashi, Masaki Nishino,
Katsumi Kimura, and Hiroshi Tsubomura
Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka, Japan

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Extensive investigations have been made on the chemical properties of carbenes as interesting transient intermediates. Special attention has been paid to the fact that the carbenes show different chemical behavior according to their spin states (triplet or singlet)[1,2].

As far as spectroscopic studies of carbenes are concerned, rather little work has been done except difluorocarbene and methylene.* For these carbenes, spectroscopic observations have been made by the vapor-phase flash photolysis[3] and by the matrix isolation technique[4,5]. Recently the electron spin

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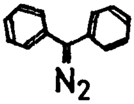
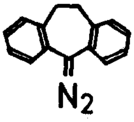
*DeMore et al. photolyzed diazomethane, diazocyclopentadiene, and diphenyldiazomethane in nitrogen or perfluoroether matrices at 20°K. Some interesting spectra were obtained but none that could be assigned to the desired carbenes. W. B. DeMore, H. D. Pritchard and N. Davidson, J. Am. Chem. Soc., 81, 5874 (1959).

resonance spectra have been studied on some substituted carbenes; diphenylmethylene, phenylmethylene, biphenylenemethylene, etc., and it was found that these carbenes have the triplet ground states[6,7].

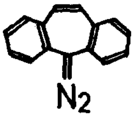
We wish to report here some interesting spectra obtained from the photolysis of the three following compounds in organic matrices at 77°K; diphenyldiazomethane (I), 1-diazo-2,3;6,7-dibenzocycloheptadiene (II)*, and 1-diazo-2,3;6,7-dibenzocycloheptatriene (III)*.



(I)



(II)



(III)

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*Relatively stable diazo compounds II and III were prepared by Bamford-Stevens method from corresponding tosylhydrazones, II_a and III_a (W. R. Bamford and T. S. Stevens, J. Chem. Soc., 4735 (1952), D. G. Farnum, J. Org. Chem., 28, 870 (1963).) Decomposition points for these compounds were: II, 71°C; III, 62°C; II_a, 175°C; III_a, 204°C. All of these compounds showed satisfactory elemental analysis, infrared and ultraviolet spectra.

FIG. 1

Absorption spectra observed by the photolysis of diphenyldiazomethane in rigid media at 77°K; (——) before irradiation (-·-·-) after irradiation, and (····) after warming up to 25°C.

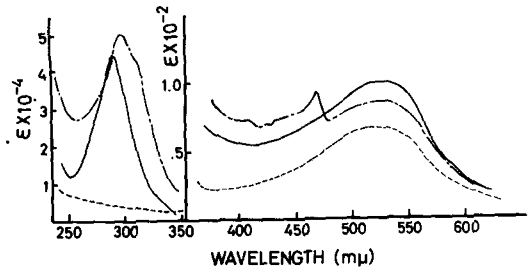
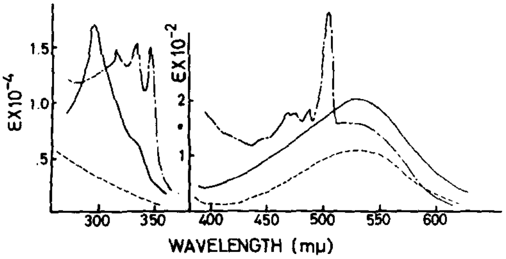


FIG. 2

Absorption spectra observed by the photolysis of 1-diazo-2,3; 6,7-dibenzocycloheptadiene in rigid media at 77°K; (——) before irradiation, (-·-·-) after irradiation, and (····) after warming up to 25°C.



Organic matrices used were a mixture of ethanol and methanol, a mixture of methylcyclohexane and isopentane, and polychlorotrifluoroethylene (Daifloil #10)*. About 10^{-4}mol./l solutions were used for the absorption measurement in the ultraviolet region and 5×10^{-3} mol./l solutions for the measurement in the visible region. A quartz cell of 1 cm path length was used. The Daifloil solutions were sandwiched by two quartz plates using a spacer of 0.1 mm thickness in order to make the samples more transparent at 77°K. The sample cells were immersed in the liquid nitrogen contained in a quartz Dewar, and photolyzed by using a 250w high pressure mercury lamp through a Pyrex filter. Absorption spectra were then measured with a Cary spectrophotometer Model 15.

As shown in Figs. 1 and 2, two absorption bands appeared in the ultraviolet and visible regions after irradiating I and II for a few minutes. With different solvents the same spectra were obtained and the absorption intensities increased with the irradiation period. The spectra thus obtained were stable at this temperature, but disappeared at higher temperature. Hence the transient substances thus produced must react rapidly to form more stable substances at higher temperature. Under the present experimental conditions, the most reasonable conclusion seems to be that these spectra are attributed to the carbenes. The forma-

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*Granted by Daikin Kogyo Co., Ltd., Osaka, Japan, to whom the authors thanks are due.

tion of diphenylmethylene by the photolysis of I under the condition similar to the present experiment has already been shown by the ESR studies[7]. It is to be noted that the same transient spectra were obtained in the Daifloil solutions as well as in the hydrocarbons or alcohols. This reasonably exclude the possibility that the transient spectra are due to free radicals produced by the hydrogen abstraction of the photolyzed species. It is interesting that the similar absorption features were obtained from the photolysis of two diazo compounds, I and II, which were expected to lead to radicals having similar π-electronic configurations. In order to check the effect of oxygen on the transient spectra, we also photolyzed deaerated solutions under the same experimental condition. However, no spectral differences were observed.

No transient species was found by the photolysis of III at 77°K. In this case the absorption spectrum of III changed by the photolysis, but it remained unchanged after warming up to the room temperature. This indicates that the carbene from III reacts rapidly producing some stable material even in the rigid media at 77°K.

We have also investigated the photochemical reactions of II and III in the presence of *cis*- and *trans*-2-butene at about 0°C. All reaction products clearly indicated that the carbenes are the intermediates. The chemical evidences for the intermediates will be reported in a separate communication.

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