and/or to reversible formation of $\mathbf{9}^{2b}$ from its nonclassical counterparts **9x** and **9y** after trapping.

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Spectroscopy and Photolysis of a Ground-State Triplet Molecule, Diphenylmethylene

Sir:

Recent electron spin resonance (esr) studies of a number of aromatic methylenes[1,2] resulted in the assignment of a triplet ground state to these species. As part of a program designed to study the reactivity of these latter species, it was of interest to study their optical spectroscopy. The only methylenes which have been observed by ultraviolet and visible spectroscopy are methylene[3] and certain halogenated methylenes.[4] A previous attempt to obtain the electronic absorption spectrum of diphenylmethylene was unsuccessful.[5] We wish to report that we have obtained the emission and excitation spectra of diphenylmethylene in a variety of organic matrices at 77 °K.[6]

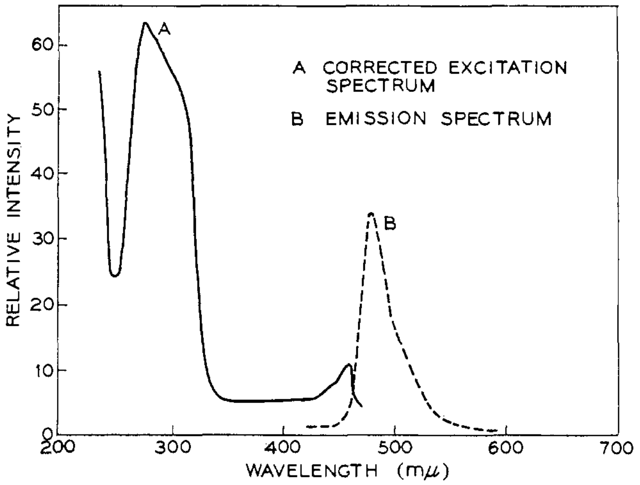

Figure 1. Electronic spectra of diphenylmethylene in methylcyclohexane at 77 °K.

The emission consists of a broad band in the region 470 to 600 mμ with $\lambda_{\max}$ 480 mμ (see Figure 1). The position and structure of this band are independent of the wavelength of the exciting light in the range 240 to 460 mμ. The corrected excitation spectrum corresponding to the 480-mμ emission shows that *diphenylmethylene absorbs in the range 240 to 470 mμ with principal maxima at 280 and 465 mμ* (see Figure 1). The position and structure of the excitation spectrum is independent of wavelength for emission in the range 470 to 600 mμ. When the phosphoroscope was placed in the spectrophotofluorometer,[6] both the excitation and emission spectra disappeared.

The emission is attributed to *fluorescence* arising from a radiative transition from the first excited triplet level of diphenylmethylene to the triplet ground level. This assignment is based upon the following evidence. (a) The emission is different from that of other possible products, *viz.*, tetraphenylethylene, benzophenone, benzophenone azine (which does not emit), alkyl-substituted diphenylmethanes, and the diphenylmethyl radical. (b) The intensity of the fluorescence band at 480 mμ correlates well with the intensity of the esr absorption at 1000 gauss of diphenylmethylene[1] obtained from the same sample tube. (c) The fluorescence disappears on warming and freezing indicative of the presence of a reactive intermediate. In the presence of dissolved oxygen a luminescent reaction occurs during warming giving rise to benzophenone phosphorescence. (d) The lifetime of the luminescence at 480 mμ is less than 1 msec. There is only one other published example of triplet–triplet emission from aromatic molecules.[7] Attempts to detect phosphorescence from diphenylmethylene have so far proven unsuccessful.

By studying the photolysis of diphenyldiazomethane as a function of exposure time in a rigid matrix, it should be possible to obtain some idea of the reactions of diphenylmethylene both in its ground state and in its excited state. Thus, at very low conversions, one could determine if free radicals were formed (with esr spectroscopy) and if molecular products were formed (identification by their luminescence spectra). These two types of products could arise by either abstraction or insertion reactions of diphenylmethylene or by photolysis of insertion products. Any major differences between the results at short exposure times and those at longer exposure times, when most of the incident light is being absorbed by diphenylmethylene, might be attributable to reactions of *excited* diphenylmethylene.

With light of wavelength 2537 A,[8] the only products initially detected in the photolysis of diphenyldiazomethane in methylcyclohexane at 77 °K were diphenylmethylene and tetraphenylethylene (by its fluorescence at 425 mμ). Neither free radicals (corresponding to abstraction reactions) nor phosphorescence at *ca.* 370 mμ (corresponding to alkyl-substituted diphenylmethanes, possible insertion products) were detected. However, on warming and freezing one of these solutions, a phosphorescence at 370 mμ was detected.[9]

At prolonged photolysis times, the intensity of the esr and fluorescence signals from diphenylmethylene decreased rapidly with concomitant appearance of solvent

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[1] R. W. Murray, A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962); R. W. Brandon, G. L. Closs, and C. A. Hutchison, Jr., *J. Chem. Phys.*, 37, 1878 (1962).

[2] A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, 87, 129 (1965), and references cited therein.

[3] G. Herzberg and J. Shoosmith, *Nature*, **183**, 1801 (1959); G. Herzberg, *Proc. Roy. Soc.* (London), **A262**, 291 (1961).

[4] P. Venkateswarlu, *Phys. Rev.*, 77, 79, 676 (1950); E. B. Andrews and R. F. Barrow, *Nature*, **165**, 890 (1950); R. K. Laird, E. B. Andrews, and R. F. Barrow, *Trans. Faraday Soc.*, **46**, 803 (1950); J. W. Johns, 7th International Symposium on Free Radicals, Padua, 1965.

[5] W. B. DeMore, H. O. Pritchard, and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959).

[6] The luminescence spectra were obtained on an Aminco-Bowman spectrophotofluorometer. Accurate fluorescence and excitation spectra were obtained with the assistance of Drs. J. W. Longworth and J. Ferguson.

[7] (a) F. Dupuy, G. Nouchi, and A. Rousset, *Compt. Rend.*, **256**, 2976 (1963). (b) A luminescence associated with diphenylmethylene has previously been observed: R. Harrell, unpublished results.

[8] A Rayonet photochemical reactor was used for all photolysis experiments. Unfiltered low-pressure mercury arcs were used for 2537-A irradiation and "Blaklite" lamps for irradiation at wavelengths >3100 A.

[9] A phosphorescence at *ca.* 370 mμ does not prove that an alkyl-substituted diphenylmethane is present. However, this is the most likely assignment to such a phosphorescence in the present case.

and diphenylmethyl radicals. The latter was identified by its fluorescence spectrum with λ_{max} at 535 mμ. A diphenylmethane[9] was also detected at longer exposure times. *We postulate that the products at long exposure times result from reactions of photoexcited diphenylmethylene or by photolysis of products formed by reaction of photoexcited diphenylmethylene with the matrix.*

Light of wavelength 3500 A[8] was also used to photolyze solutions of diphenyldiazomethane in methylcyclohexane at 77°K. The products at small exposure times were the same as those using 2537-A irradiation. At longer exposure times, diphenylmethylene disappearance was much slower than with 2537-A irradiation and was not accompanied by formation of detectable amounts of diphenylmethyl radicals. Phosphorescence of a substituted diphenylmethane was also observed.[9]

Diphenyldiazomethane photolysis was also studied as a function of exposure time and wavelength of incident light in a 2-methylpentene-2 glass at 77°K. The luminescence results coupled with the esr measurements show that *ground-state diphenylmethylene can be formed and is stable in a simple olefin glass* without serious complications from insertion, addition, or abstraction reactions. It is also stable in 2-methyltetrahydrofuran, methanol, ethanol, triethylamine, benzene, and fluorocarbon matrices at 77°K.

The photolysis of 9-diazofluorene, substituted phenyl- and diphenyldiazomethanes, and some aromatic azides (nitrene precursors) in organic glasses at 77°K have also been studied and will be reported later.[10]

Acknowledgments. The authors wish to thank Drs. R. W. Murray and E. Wasserman for several interesting discussions. W. A. Yager and R. M. R. Cramer are thanked for help with the esr measurements.

(10) NOTE ADDED IN PROOF. G. L. Closs, C. A. Hutchison, Jr., and B. E. Kohler, *J. Chem. Phys.*, in press, have observed the optical absorption spectrum of diphenylmethylene oriented in single crystals. Our absorption work *in glasses* indicates bands with λ_{max} 465, 290–300, and 240 mμ, the lower wavelength bands being much more intense than the 465 mμ band.

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Electron Spin Resonance Study of the Phenyldiazotate Free Radical, the Key Intermediate in Phenylations with Aromatic Diazo Compounds

Sir:

Recent evidence[1,2] strongly demanded a revised mechanism for the Gomberg reaction[3] and phenylations with N-nitrosoacetanilides,[3] according to which the diazoanhydride **1**[4] is formed as a common intermediate. This species was postulated to decompose into a phenyl radical, nitrogen, and the supposedly long-lived diazotate radical **2**. The occurrence of a paramagnetic intermediate in the course of these reactions has been confirmed by electron spin resonance spectroscopy and it will now be shown that the spectrum of this radical is consistent with the proposed structure **2**.

$$\underset{\mathbf{1}}{C_6H_5{-}N{=}N{-}O{-}N{=}N{-}C_6H_5} \longrightarrow C_6H_5\cdot + N_2 + \underset{\mathbf{2}}{C_6H_5{-}N{=}N{-}O\cdot}$$

When a freshly prepared solution of 400 mg of N-nitrosoacetanilide in 3 ml of benzene was placed into the microwave cavity of an AEG esr spectrometer, the spectrum shown in Figure 1a could be observed. A g value of 2.0055 was determined using DPPH for calibration. The deceptively simple spectrum, apparently caused by a high degree of accidental degeneracy, yielded only the largest and smallest hfs constants directly, together with the information that the other coupling constants involved must be approximately integral multiples of the smallest one. On rejection of all possibilities which are not consistent with the total width of the spectrum and the number of lines, or which give grossly wrong intensity ratios, one is left with two sets of approximate parameters differing by interchange of two splitting constants to two equivalent protons and a nitrogen nucleus, respectively. This ambiguity could be resolved by computer simulation.[5] Figure 1b shows the spectrum calculated with the parameters of Table I, column 2. From the sensitivity of the computed spectrum to changes in the parameters the standard deviations of the hfs constants can be estimated to ±0.03 gauss.

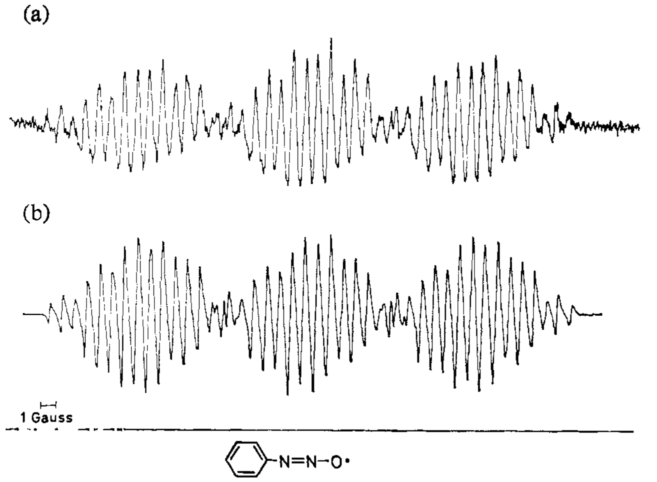

Figure 1. Electron spin resonance spectrum of the phenyldiazotate free radical. (a) Observed spectrum; magnetic field increases to the right. The decrease of intensity from right to left (downfield spectrum) is due to the decreasing radical concentration during the time of recording (20 min at 30°). (b) Calculated spectum with hfs constants of Table I, using Lorentzian line shape and a line width of 0.18 gauss.

To compute "experimental" spin densities, ρ_{exptl}, from the observed coupling constants is a straightforward problem for the aromatic carbon atoms. If one

(1) C. Rüchardt and E. Merz, *Tetrahedron Letters*, **36**, 2431 (1964); E. L. Eliel, J. G. Saha, and S. Meyerson, *J. Org. Chem.*, **30**, 2451 (1965).

(2) C. Rüchardt and B. Freudenberg, *Tetrahedron Letters*, **48**, 3623 (1964).

(3) *Cf.* ref 1 and 2 for a literature survey.

(4) T. Kauffmann, H. O. Friestad, and H. Henkeler, *Ann.*, **634**, 64 (1960).

(5) A Fortran II coded program was developed for an IBM 7090 computer equipped with a Mosley plotter and the necessary plotter routines on the system tape. Output is thereby directly obtained as a plot of the first derivative of the absorption spectrum in a predetermined scale. Part of the computational scheme is based on a program originally designed by E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963). We are indebted to Professor Maki, University of California, Riverside, Calif., who kindly provided us with a copy of his program.