entropic in nature and have been discussed by several authors;[48] however they do not appear sufficient to account for the high rates associated with enzyme catalysis.

A possible explanation for the macromolecular nature and unusual catalytic efficiency of enzymes is based on the *conformational adaptability* of enzymes. An enzyme can divide the catalytic process into a number of discrete steps, and the structure can be optimized for each step by small alterations in the macromolecular structure. The possibility that conformational changes increase proton-transfer rates has been mentioned earlier. The large number of intermediate states observed with relaxation methods is consistent with this sort of mechanism. Conformational changes may play a more dynamic role in catalysis by lowering the free energy of activation *via* a "compensation effect."[49] For example, the activation energy for decomposition of H_2 by an inert gas is greater than 100 kcal/mol, whereas that for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is only about 40 kcal/mol. In both reactions an H_2 bond is

broken, but the activation energy is lower in the second case because two H–I bonds are also formed. In an enzyme reaction the formation of protein side-chain bonds (*e.g.*, hydrogen bonding and hydrophobic interactions) might lower the free energy of activation for the making and breaking of substrate bonds. This type of compensation could alter both the enthalpy and the entropy of activation.[50]

Although the *conformational adaptability* of the protein appears to be a reasonable explanation of the catalytic efficiency of enzymes, direct verification by experiments is currently not possible. However, the combination of detailed kinetic studies of enzymes with fast reaction techniques and structural information about enzymes obtained by X-ray techniques promises to yield an increasingly detailed picture of the mechanism of enzyme catalysis.

(48) D. E. Koshland, Jr., *J. Theoret. Biol.*, **2**, 75 (1962); T. C. Bruice and V. K. Pandit, *J. Am. Chem. Soc.*, **82**, 5858 (1960); T. C. Bruice and S. L. Benkovic, *ibid.*, **86**, 418 (1964); F. Westheimer, *Advan. Enzymol.*, **24**, 441 (1962); M. L. Bender, F. J. Kézdy, and C. R. Gunter, *J. Am. Chem. Soc.*, **86**, 3714 (1964).
(49) G. G. Hammes, *Nature*, **204**, 342 (1964).

(50) For some other proposed models of enzyme action see: D. E. Koshland, Jr., *Proc. Natl. Acad. Sci. U. S.*, **44**, 98 (1958); R. Lumry and H. Eyring, *J. Phys. Chem.*, **58**, 110 (1954); W. P. Jencks in "Current Aspects of Biochemical Energetics," N. V. Kaplan and E. P. Kennedy, Ed., Academic Press, New York, N. Y., 1966, p 273

# Electronic Spectroscopy of Arylmethylenes

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The tetravalency of carbon lies at the very foundation of the structural theory of organic chemistry. However, the most important reaction intermediates in organic chemistry are those in which at least one carbon atom is in a valence state other than the normal tetravalent one. Three types of such intermediates are *trivalent* carbon derivatives, namely, carbonium ions, carbanions, and free radicals.

The study of *divalent* carbon species, RĊR′, has received considerable attention in recent years.[1] Of particular interest is the assignment of the spin multiplicity of these intermediates since, unlike carbonium ions, carbanions, or free radicals, where the spin state is usually obvious, there are two possible electronic configurations which can occur readily in divalent carbon species: (a) a singlet configuration (1) in which the unshared electrons are paired in an sp^2 orbital, leaving an empty p orbital, or (b) a triplet configuration (2) in which the two unshared electrons are unpaired,

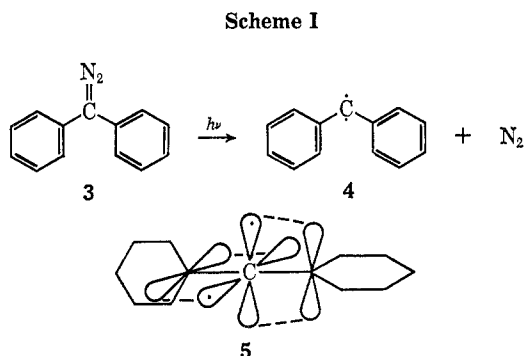each in a p orbital, and in which the RĊR′ angle is
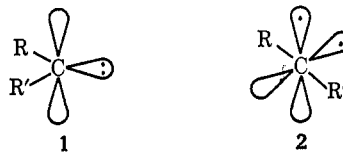
more nearly linear than when the molecule is in configuration 1.

A number of chemical criteria have been developed to assist in the assignment of the spin state.[2] The application of these criteria is logically an inductive process in which the spin state is inferred from chemical evidence. For example, Skell, *et al.*,[3] studied the photolysis of diphenyldiazomethane (3) in *cis*- and *trans*-2-butene. From the fact that the addition was not completely stereospecific, they concluded that diphenyl-

(1) (a) J. Hine, "Divalent Carbon," Ronald Press, Inc., New York, N. Y., 1964; (b) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964; (c) G. G. Rozantsev, A. A. Fainzil'berg, and S. S. Novikov, *Usp. Khim.*, **34**, 177 (1965); *Russ. Chem. Rev.*, 69 (1965).

(2) (a) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956); (b) R. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959); W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956). For a review, see P. P. Gaspar and G. S. Hammond, Chapter 12 of ref 1b.
(3) R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Amer. Chem. Soc.*, **81**, 1009 (1959).

Scheme I

Figure 1. Electron paramagnetic resonance spectrum of diphenylmethylene in benzophenone.

methylene (4), which was formed as an intermediate, was a triplet molecule, and the electronic configuration 5 was suggested to account for its stability. Although subsequent electron spin resonance experiments have shown this precise representation to be incorrect for the ground state, the Etter, Skovronek, and Skell[3] experiments did much to stimulate interest in the assignment of the electron configuration of divalent carbon species.

Recently it has become possible to study some divalent carbon intermediates directly by observing their epr, absorption, and emission spectra.[4] In order to obtain these measurements it is convenient to use the matrix-isolation technique.[5] The intermediates are prepared by the low-temperature photolysis of the appropriate precursor (usually the diazo compound) in a suitable inert matrix. Although several aliphatic methylene[6] derivatives have been studied spectroscopically[7] in condensed phases, the arylmethylenes provide structural features which are more amenable to observation, and this article will deal with them exclusively.

Assignment of Triplet Ground State

Diphenylmethylene (4) was the first arylmethylene to be studied in any detail by physical methods. It was identified[8,9] as a ground-state triplet molecule by its epr spectrum (Figure 1). This spectrum may be analyzed in terms of two zero-field parameters,[10]
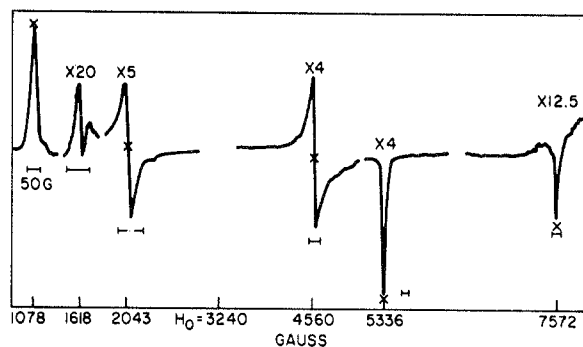
D and E, with $D = 0.4055 \text{ cm}^{-1}$ and $E = 0.0194 \text{ cm}^{-1}$. Although a detailed account of the epr results and their correlation with molecular orbital calculations will not be given here, several qualitative comments are relevant. The value of D is related to the average $\langle 1/r^3 \rangle$ where r is the distance between the two spins, so that a high value of D implies a large spin–spin interaction and a close proximity of the two spins. The value of E indicates qualitatively the magnitude of the deviation of the spin–spin interaction from cylindrical symmetry.

The values of the zero-field parameters, D and E, for 4 may be compared with those of the phosphorescent triplet state of naphthalene (6).[11]

6, $D = 0.0992 \text{ cm}^{-1}$ 4, $D = 0.4055 \text{ cm}^{-1}$
    $E = 0.0143 \text{ cm}^{-1}$ $E = 0.0194 \text{ cm}^{-1}$
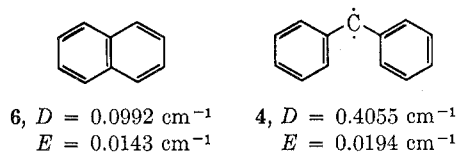
The higher D value of 4 shows that the two unpaired electrons are largely localized on the divalent carbon atom. The ground-state triplet assignment is based on the fact that the epr absorptions can be detected days after the photolysis has been carried out, in contrast to the phosphorescent states, where the epr absorptions disappear quickly after irradiation ceases. An orbital representation comparing a triplet ground-state molecule with a phosphorescent (excited) triplet state is given in Scheme II. Other typical arylmethylenes which have been assigned a triplet ground state by epr experiments are given in Table I.

Scheme II

singlet   phos-   triplet
ground   phorescent   ground
state   triplet   state
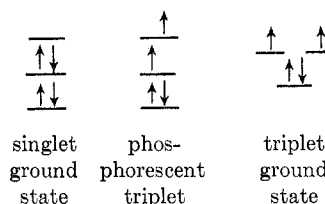
The effect of matrix has been studied by epr tech-

(4) A. M. Trozzolo and W. A. Gibbons, *J. Amer. Chem. Soc.*, **89**, 239 (1967).

(5) (a) E. Whittle, D. A. Dows, and G. C. Pimentel, *J. Chem. Phys.*, **22**, 1943 (1954); (b) I. Norman and G. Porter, *Nature*, **174**, 108 1954; *Proc. Roy. Soc.*, **A230**, 399 (1955). See also G. C. Pimentel in "Formation and Trapping of Free Radicals," A. M. Bass and H. P. Broida, Ed., Academic Press Inc., New York, N. Y., 1960, Chapter 4.

(6) The author prefers to consider all divalent carbon intermediates as methylene derivatives, although he has faltered on occasion, reverting to the apparently more popular "carbene."

(7) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **44**, 2850 (1966); D. E. Milligan and G. C. Pimentel, *ibid.*, **29**, 1405 (1958); C. M. Moore and G. C. Pimentel, *ibid.*, **41**, 3504 (1964); G. W. Robinson and M. McCarty, Jr., *J. Am. Chem. Soc.*, **82**, 1859 (1960); T. D. Goldfarb and G. C. Pimentel, *ibid.*, **82**, 1865 (1960); W. B. DeMore, H. O. Pritchard, and H. Davidson, *ibid.*, **81**, 5874 (1959).

(8) R. W. Brandon, G. L. Closs, and C. A. Hutchison, Jr., *J. Chem. Phys.*, **37**, 1878 (1962).

(9) R. W. Murray, A. M., Trozzolo, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, **84**, 3213 (1962).

(10) E. Wasserman, L. C. Snyder and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964). For other reviews of epr detection of triplet states, see M. Bersohn and J. C. Baird, "An Introduction to Electron Paramagnetic Resonance," W. A. Benjamin, Inc., New York, N. Y., 1966; A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967.

(11) C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958); W. A. Yager, E. Wasserman, and R. M. R. Cramer, *ibid.*, **37**, 1148 (1962).

niques,[12] and by using ^{13}C-labeled diazo compounds ($R_2{}^{13}C{=}N_2$) the structures of several arylmethylenes were determined.[13] Also, electron nuclear double resonance (endor) techniques have been applied to the structure determination of fluorenylidene (11).[14]

Other interesting aspects of the epr experiments were the detection of geometrical isomerism in 8 and 9, the assignment of a quintet ground state (four unpaired electrons) to 12 and 13, and the correlation of D with the π spin density at the divalent carbon atom.[15]

In addition to the diazo compounds, other precursors have been used in the epr detection of arylmethylenes. Among these are gem-diazides,[16] aryloxiranes,[17] diazirines,[18] and p-toluenesulfonylhydrazones.[19]

Absorption and Emission Spectra of Arylmethylenes

Although the epr experiments allow the detection of arylmethylenes, other nonradical products of the photolysis of diazo compounds cannot be determined by this technique. In order to apply the epr results in a program designed to study the reactivity of the arylmethylenes, it became necessary to study the optical spectroscopy of these species.
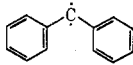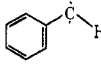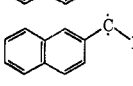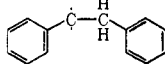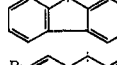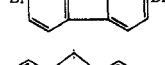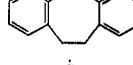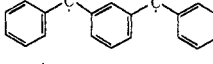
Earlier, Schüler and Michel[20] had observed the behavior of toluene in the positive column of a glow discharge, and they obtained a spectrum which was assigned to the benzal radical or phenylmethylene (7). DeMore, et al.,[21] photolyzed diphenyldiazomethane in rigid media, but the spectrum of 4 was not assigned.

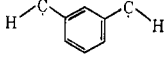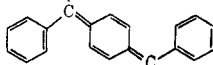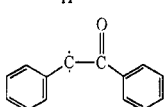Almost simultaneously, three papers appeared describing the optical absorption of 4. Closs, et al.,[22] reported the long-wavelength absorption band of 4 oriented in single crystals of 1,1-diphenylethylene. Moritani, et al.,[23] found two new absorption bands in photolyzed solutions of diphenyldiazomethane, and by correlating esr studies, fluorescence, fluorescence excitation, and absorption spectroscopy Gibbons and Trozzolo[24] reported the luminescence, excitation, and

absorption spectrum of 4. This led to the assignment of at least two and possibly three absorption bands of 4 as well as its fluorescence spectrum.

Table I

Arylmethylenes with Triplet Ground State

Methylene	Compd	$\lvert D/hc\rvert$, cm^{-1}	$\lvert E/hc\rvert$, cm^{-1}	Ref
	4	0.4050	0.0194	8, 9
	7	0.5098	0.0249	a
	8	$\begin{cases}0.4555\\0.4347\end{cases}$	$\begin{cases}0.0202\\0.0208\end{cases}$	b
	9	$\begin{cases}0.4711\\0.4926\end{cases}$	$\begin{cases}0.0243\\0.0209\end{cases}$	b
	10	0.493	0.0289	c
		0.3777	0.0160	d
	11	0.4078	0.0283	a
		0.3991	0.0279	e
		0.3932	0.0170	f
	12	0.0701	0.020	g
		0.07131	0.01902	h
	13	0.0844	0.0233	g
	14	0.0521	<0.002	i
	15	0.38	0.03	j
	21	0.3815	0.0489	k

a A. M. Trozzolo, R. W. Murray, and E. Wasserman, J. Amer. Chem. Soc., 84, 4990 (1962). *b* A. M. Trozzolo, E. Wasserman, and W. A. Yager, ibid., 87, 129 (1965). *c* A. M. Trozzolo and S. R. Fahrenholtz, Abstracts of Papers, 2nd Middle Atlantic Regional Meeting, New York, N. Y., Feb 1967, p 62. *d* E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, J. Amer. Chem. Soc., 86, 2304 (1964). *e* S. Murahashi, I. Moritani, and T. Nagai, Bull. Chem. Soc. Jap., 40, 1655 (1967). *f* I. Moritani, S. Murahashi, M. Nishino, Y. Yamanoto, K. Itoh, and N. Mataga, J. Amer. Chem. Soc., 89, 1259 (1967). *g* E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, and G. Smolinsky, ibid., 89, 5076 (1967). *h* K. Itoh, Chem. Phys. Lett., 1, 235 (1967). *i* A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, J. Amer. Chem. Soc., 85, 2526 (1963). *j* E. Wasserman, quoted in E. J. Moriconi and J. T. Murray, J. Org. Chem., 29, 3577 (1964). *k* A. M. Trozzolo and S. R. Fahrenholtz, Abstracts of Papers, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, No. K23.

(12) A. M. Trozzolo, E. Wasserman, and W. A. Yager, J. Chim. Phys., 61, 1663 (1964).

(13) (a) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, J. Chem. Phys., 40, 2408 (1964); (b) R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchison, Jr., B. E. Kohler, and R. Silbey, ibid., 43, 2006 (1965).

(14) C. A. Hutchison, Jr. and G. A. Pearson, ibid., 43, 2545 (1965); 47, 520 (1967).

(15) E. Wasserman, W. A. Yager, and A. M. Trozzolo, unpublished results. The correlation had been carried out earlier with a series of ground-state nitrenes [G. Smolinsky, L. C. Snyder, and E. Wasserman, Rev. Mod. Phys., 35, 576 (1963)].

(16) L. Barash, E. Wasserman, and W. A. Yager, J. Amer. Chem. Soc., 89, 3931 (1967).

(17) A. M. Trozzolo, W. A. Yager, G. W. Griffin, H. Kristinnsson, and I. Sarkar, ibid., 89, 3357 (1967).

(18) E. Wasserman and V. J. Kuck, unpublished results.

(19) R. E. Moser, J. M. Fritsch, and C. N. Matthews, Chem. Commun., 770 (1967).

(20) H. Schüler and A. Michel, Z. Naturforsch., 10a, 459 (1955).

(21) W. B. DeMore, H. O. Pritchard, and N. Davidson, J. Amer. Chem. Soc., 81, 5874 (1959).

(22) G. L. Closs, C. A. Hutchison, Jr., and B. Kohler, J. Chem. Phys., 44, 413 (1966).

(23) I. Moritani, S. Murihashi, N. Nishino, K. Kimura, and H. Tsubimora, Tetrahedron Lett., 373 (1966).

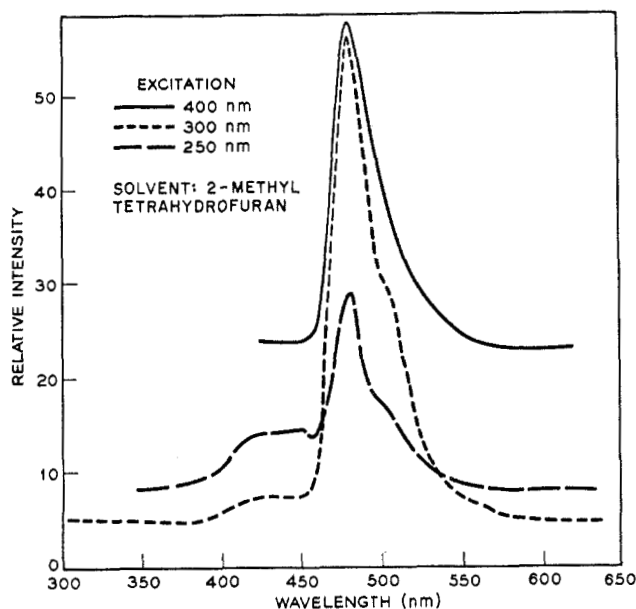(24) W. A. Gibbons and A. M. Trozzolo, J. Amer. Chem. Soc., 88, 172 (1966).

Figure 2. Luminescence of diphenylmethylene.[4]

1. Emission Spectrum of Diphenylmethylene (4).

The emission of **4** consists of a broad band (λ_{max} 480 nm) with a shoulder at longer wavelength (Figure 2). The same spectrum was obtained for all excitation wavelengths in the range 230–470 nm.

The emission was identified as the *fluorescence* of **4**, a triplet ground-state molecule, from the following evidence. (a) A plot of the intensity of the known low-field esr absorption of diphenylmethylene[12] against the intensity of the 480-nm emission gave a linear correlation which passed through the origin.[4] Since at short irradiation times no monoradical esr signal nor any other luminescent product was detected, it was concluded that the luminescence is in fact due to excited **4**.[24] (b) The emission at 480 nm is completely different from that of other possible products of the photolysis of diphenyldiazomethane (benzophenone, tetraphenylethane, tetraphenylethylene, diphenylmethyl radical, and benzophenone azine). (c) Upon warming the photolyzed solutions from 77°K, the fluorescence at 480 nm disappeared with the concomitant appearance of a new emission spectrum, which was identified as the phosphorescence of benzophenone. When the solution was thoroughly degassed, the phosphorescence was not observed. This chemiluminescent reaction had been reported previously, and it involves the reaction of **4** with oxygen.[25] (d) The lifetime[26] of the species emitting at 480 nm is 70–100 nsec, and the spectrum is the mirror image of the long-wavelength band in the absorption spectrum attributed to **4**. (e) The absorption spectrum and the fluorescence excitation spectrum are identical within experimental error, and they are qualitatively similar to the corresponding spectra of the diphenylmethyl radical (see Table II).

2. The Absorption and Excitation Spectra of Diphenylmethylene.

Provided that one species is responsible for a given emission, that quenchers are absent, that the quantum yield is independent of wavelength, and that one is using a properly calibrated light source and detector, the excitation spectrum should correspond to the absorption spectrum of the emitting species.

The excitation spectrum which corresponds to the 480-nm fluorescence is shown in Figure 3. This spectrum was independent of emission wavelengths in the range 475–550 nm, thus showing again that the emission is that of only one species—diphenylmethylene. These results indicated that **4** absorbs in the range 240–470 nm with principal maxima at 465 and 280–300 nm. (There also appeared to be another band at approximately 240 nm.)

The absorption spectrum[4] of a photolyzed sample of **3** showed the same bands as the fluorescence excitation spectrum of **4**, and it disappeared on warming the frozen solutions. In some absorption experiments, **4** was produced "quantitatively," *i.e.*, a known concentration of diphenyldiazomethane was destroyed. Under these conditions, the following minimum extinction coefficients were calculated: ϵ 25,000 (λ_{max} 301 nm) and 300 (λ_{max} 465 nm).

3. Spectral Assignments.

Diphenylmethylene, in contrast to the vast majority of organic molecules, has a triplet ground state. The absorptions at 465, 300, and 240 nm must therefore correspond to electronic transitions from the ground state to higher levels in the triplet manifold. Previous esr studies[13] have shown that **4** is essentially a planar molecule, the Ar–C–Ar angle being approximately 140–150°. The unpaired electrons are largely localized in each of the two unshared orbitals of the methylene carbon atom. The nodal plane of one of these orbitals corresponds to the molecular plane and is designated p_y, and the other, in-plane orbital is designated p_x. A diagram is shown in Figure 4.

The following observations are considered in assigning the electronic transitions of diphenylmethylene.

(a) There is a qualitative resemblance between the spectra (absorption and emission) of **4** and those of the diphenylmethyl radical (see Table II). If it is assumed that the p_x electron is not involved in the transitions, then the π system of **4** can be considered (like the di-

Table II
Comparison of Diphenylmethylene with Odd-Alternant Radicals

Species	Absorption maxima, nm	Emission maximum, nm
$C_6H_5\dot{C}H_2$	319, 450[a–c]	462[c]
$(C_6H_5)_2\dot{C}H$	336, 515[b,d]	535[d]
$(C_6H_5)_2\dot{C}\cdot$	300, 465[d]	480[d]

[a] I. Norman and G. Porter, *Proc. Roy. Soc.* (London), **A230**, 399 (1955). [b] G. Porter and E. Strachan, *Trans. Faraday Soc.*, **54**, 431 (1958). [c] S. Leach and L. Grajcar, 5th International Symposium on Free Radicals, Uppsala, 1961. [d] Reference 4.
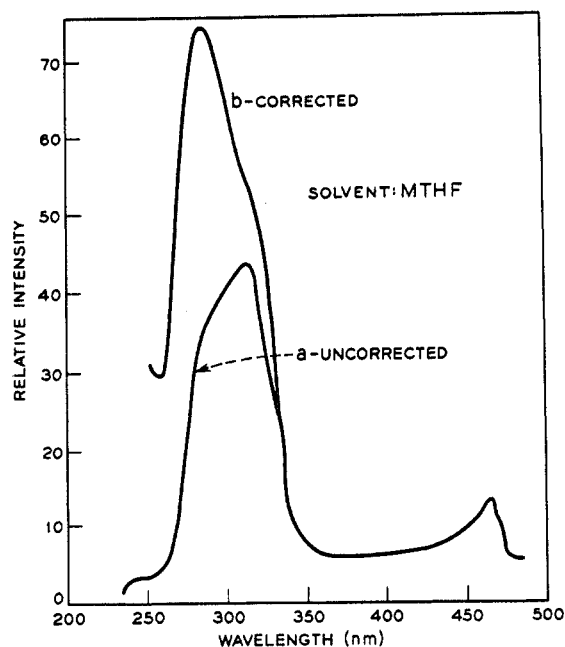
(25) Reference *a* of Table I.
(26) W. R. Ware and P. J. Sullivan, *J. Chem. Phys.*, in press. The author thanks Professor Ware for a preprint of this work.

Figure 3. Excitation spectrum of diphenylmethylene fluorescence at 77°K.[4]
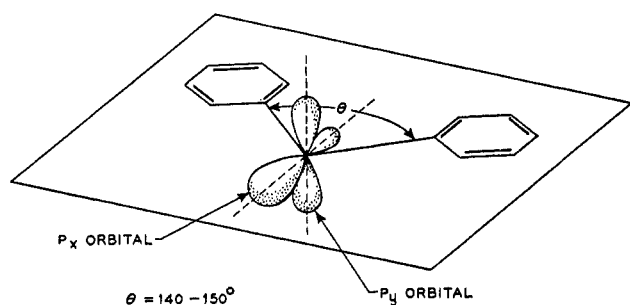

Figure 4. Structure of diphenylmethylene.[18]

phenylmethyl radical) as that of an odd-alternant hydrocarbon radical having 13 π electrons. It has been shown previously[27] that in systems of this type, a strong absorption band in the ultraviolet region and a weak band in the visible region should be expected. This is exactly what has been found for the benzyl, diphenylmethyl, and triphenylmethyl radicals,[28] and it suggests that the finding of two similar bands in **4** is consistent with a $\pi-\pi^*$ assignment for the absorptions. There are indications that **4** has still a third absorption band at $\sim$240 nm which would agree with the recent finding of an analogous band in the benzyl radical spectrum.[29]

(b) Polarization studies are of interest. If the above assignments are correct, then both the high-energy (300 nm) and the low-energy (465 nm) absorption bands

(27) M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc.*, **67A**, 795 (1955); H. C. Longuet-Higgins and J. A. Pople, *ibid.*, **68A**, 591 (1955).

(28) E. J. Land, "Progress in Reaction Kinetics," Vol. III, G. Porter, Ed., Pergamon Press, Oxford, 1965, Chapter 8.

(29) G. Porter and M. I. Savadatti, *Spectrochim. Acta*, **22**, 803 (1966).

should be polarized in the molecular plane. The fluorescence spectrum should be polarized similarly. Only the polarization of the long-wavelength absorption band has been reported,[22] and it was found that only light which was polarized parallel to the line of the phenyl ring centers was absorbed.

Attempts to detect phosphorescence from **4** were unsuccessful. This was unfortunate since this phosphorescence could have arisen from radiative processes involving either an excited singlet state or an excited quintet state. It thus might have been possible to obtain directly triplet–singlet energy level differences which would be useful in the field of carbene chemistry.

4. Spectra of Substituted Diphenylmethylenes. The photolysis of other diaryldiazomethanes gave almost exclusively the corresponding substituted diphenylmethylenes, which, in each case, esr studies have shown to be ground-state triplet molecules. The maxima of both the absorption and the emission bands were shifted to longer wavelengths from those of **4**; the short-wavelength bands were more intense than the visible-range bands. Again, the absorptions are considered to involve $\pi-\pi^*$ transitions (Table III).

Table III

Spectra of Diphenylmethylenes in 2-Methyltetrahydrofuran (MTHF)[4]

$$R\langle\overline{}\rangle-\overset{\cdot}{C}-\langle\overline{}\rangle R'$$

R, R'	Absorption maxima, nm	Emission maximum, nm
H, H	300, 465	480
Cl, H	311, 475	487
Br, H	316, 475	488
CH₃, H	301, 472	487
OCH₃, H	335, 345[a]	495
NO₂, H	265, 370, 555	No emission
C₆H₅, H	355[a]	555
OCH₃, OCH₃	335–345[a]	507

[a] Obtained from the fluorescence excitation spectrum rather than the absorption spectrum.

Application of Spectroscopic Measurements

By combining epr, luminescence, and absorption spectroscopy, it is possible to detect reactive methylene intermediates in rigid media and to follow their rates of formation and disappearance. In addition, it is possible to study the reactions of ground-state triplet molecules with minimal interference from singlet reactions. It was mentioned earlier that in carbene chemistry the electronic configuration **1** or **2** is inferred from the reaction products by using the criteria cited previously.[2] The room-temperature reactions may involve both configurations (see Scheme III). However, by performing the photolysis of the diazo compound at 77°K, it is possible to form the ground-state triplet methylene almost exclusively, even in relatively reactive matrices, such as olefins.[24] The experiments require only very small amounts of material, and both the epr and luminescence experiments can be made with one sample.

Scheme III
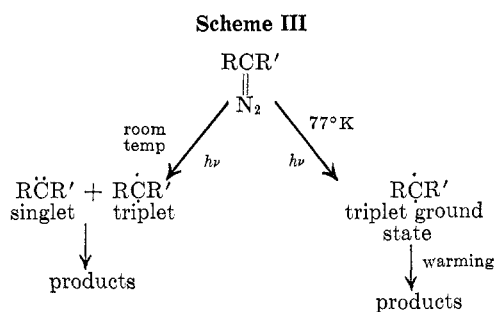
By employing analytical glpc, it is also possible to identify the products after warm-up. Several examples of this technique will be discussed.

1. Reaction of Arylmethylenes with Oxygen. When a solution containing diphenylmethylene **4** and dissolved oxygen is warmed from 77°K, a chemiluminescent reaction occurs with the formation of benzophenone.[25] The emission was identified as the phosphorescence of benzophenone.

Although the mechanism of this reaction is not known, it may involve bimolecular reaction of two peroxy biradicals, **16** (Scheme IV). Other arylmethy-

Scheme IV
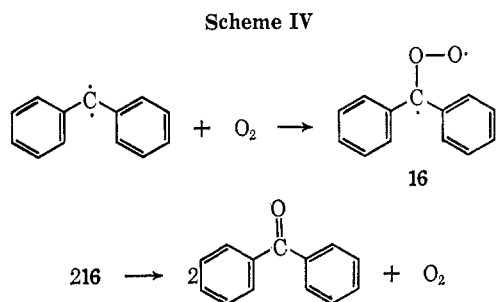
lenes behave similarly, and the luminescent reaction upon warm-up may be used to detect the presence of the triplet methylene in the low-temperature photolysis of diazo compounds.

2. Warm-up in Hydrocarbon Solvent. When the warming of **4** in a hydrocarbon matrix from 77°K is followed spectrofluorometrically, the fluorescence of **4** is replaced by that of the diphenylmethyl radical **17** (see Table II).[30] After warming to room temperature and recooling to 77°K, the luminescence (now phosphorescence) closely resembles that of diphenylmethane. Since the reactivity of **4** should be that of a biradical, a reasonable interpretation of the results is given by Scheme V.

Scheme V
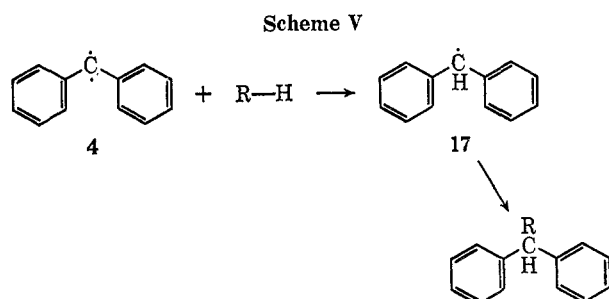
The abstraction reaction also seems to predominate when an olefin is used as the matrix. Photolysis of **3** in cis- and trans-4-methyl-2-pentene, respectively, at

77°K yield **4** as the exclusive product. On warming, a number of products are formed, but the cyclopropane fraction is a minor constituent.[30] The stereospecificity of this addition has not been determined and is currently under study.

3. Photochemical Wolff Rearrangement. The photochemical Wolff rearrangement of azibenzil (**18**) has been observed previously,[31] and the major product is diphenylketene (**19**). The ketomethylene **20** which is
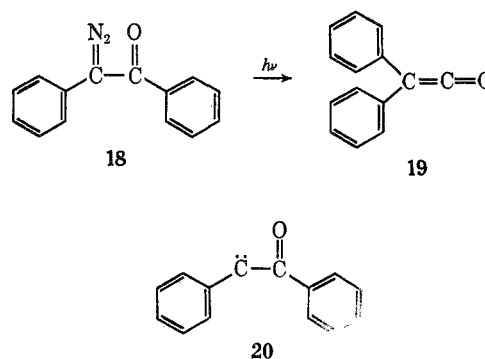

believed to be the reactive intermediate presumably may be present in either the singlet or the triplet state. The available evidence[1,32] is consistent with the presence of the singlet species, although attempts to trap the intermediate with 1,3 dipolarophiles failed.[33]

Padwa and Layton[32a] have shown that rearrangement predominates over hydrogen abstraction in the photochemical reaction of α-diazoacetophenone in a variety of alcohols. However, when a triplet sensitizer was added and selectively activated, the product of hydrogen abstraction, acetophenone, became more prominent. It was concluded that the singlet ketomethylene is the probable reactive intermediate in the Wolff rearrangement. However, these results also are consistent with a concerted process for the rearrangement (with no ketomethylene being present) in the unsensitized reaction and a *triplet diazo compound* as the reactive intermediate in the photosensitized reaction.[34] The possibility[35] that induced decomposition of the diazo compound proceeds *via* a free-radical chain has not been eliminated.

When azibenzil was photolyzed in a variety of organic glasses at 77°K using 3500-Å irradiation, the principal product was benzoylphenylmethylene (**21**). The epr spectrum of this species was obtained,[36] and a triplet ground state was assigned (Table I).

(30) A. M. Trozzolo and W. A. Gibbons, unpublished results.
(31) L. Horner, E. Spietschka, and A. Cross, *Ann.*, **573**, 17 (1951).
(32) (a) A. Padwa and R. Layton, *Tetrahedron Letters*, 2167 (1965); (b) D. W. Cowan, M. M. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964).
(33) R. Huisgen, H. König, G. Binsch, and H. J. Sturm, *Angew. Chem.*, **73**, 368 (1961).
(34) L. Friedman, private communication.
(35) (a) L. Horner, G. Bauer, and J. Dörges, *Chem. Ber.*, **98**, 2631 (1965); (b) L. Horner and G. Bauer, *Tetrahedron Letters*, 3573 (1966); (c) L. Horner and H. Schwarz, *ibid.*, 3579 (1966).
(36) Reference k of Table I.

Scheme VI
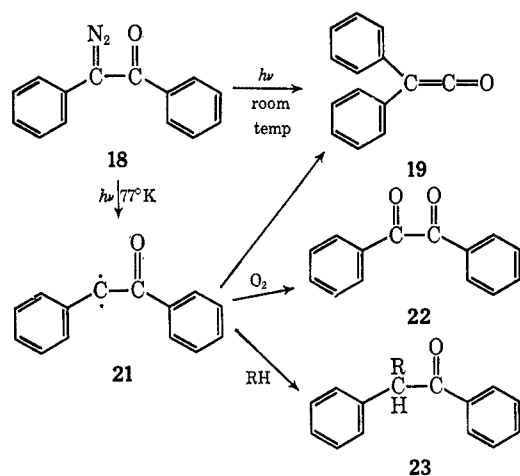
When the glass was warmed, the benzoylphenylmethylene was free to react. The products obtained from warming an irradiated solution in methylcyclohexane or tetrahydro-2-methylfuran were benzil (**22**) (0–12%), deoxybenzoin (**23**) (74–80%) (or solvent-substituted deoxybenzoin), and only a very small amount of diphenylketene (0–12%), the Wolff rearrangement product (Scheme VI). These compounds were observed by their characteristic phosphorescence spectrum[36] and gas chromatographic retention time. The amount of benzil which was found depended upon how much oxygen was initially present. The formation of benzil from the ground-state **21** is analogous to the

formation of benzophenone from diphenylmethylene.[25] The formation of **23** probably occurs by hydrogen abstraction from the solvent.

When the photolyses of azibenzil were performed at room temperature, the product distributions were quite different from those obtained in the low-temperature experiments. Diphenylketene (**19**), the usual Wolff rearrangement product, was the major component (85–90%), as judged from phosphorescence and gas chromatographic analysis.

The results obtained indicate that the triplet ground-state species **21** does not undergo the Wolff rearrangement efficiently, if at all, but that it does behave as a free-radical species (hydrogen abstraction, reaction with oxygen). Further extrapolation would suggest that, since **21** does not rearrange to **19** upon warming from 77°K, it is probably not the reactive intermediate in the room-temperature Wolff rearrangement of **18** to **19**.
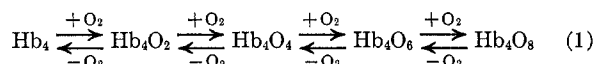
Reversible Activation of Covalent Molecules by Transition Metal Complexes. The Role of the Covalent Molecule[1]

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Received June 7, 1968

The reactions of metals or their compounds with small gaseous[2] molecules play a vital role in life and industry. Oxygen transport by hemoglobin (Hb) (eq 1) and the catalytic hydrogenation of olefins over
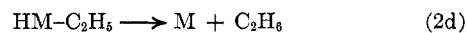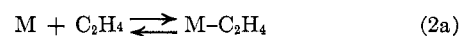
$$Hb_4 \underset{-O_2}{\overset{+O_2}{\rightleftarrows}} Hb_4O_2 \underset{-O_2}{\overset{+O_2}{\rightleftarrows}} Hb_4O_4 \underset{-O_2}{\overset{+O_2}{\rightleftarrows}} Hb_4O_6 \underset{-O_2}{\overset{+O_2}{\rightleftarrows}} Hb_4O_8 \quad (1)$$

metal surfaces (eq 2) are two prominent examples

(2) The work reviewed here deals with the activation of small covalent molecules, most of which are gases at ordinary temperatures, thus the brief and convenient synonyms "gas" and "gaseous molecule," although most of the reactions described are those of solutions of gases in liquids. It should be also noted that the types of reactions which are presented and interpreted are not limited to "small" or "gaseous" molecules (see, *e.g.*, Table III).

among a vast variety of these reactions. A fundamental step in these chemical processes is the initial com-

$$\underline{M} + C_2H_4 \rightleftarrows \underline{M}\text{–}C_2H_4 \qquad (2a)$$

$$\underline{M} + H_2 \rightleftarrows H\underline{M}H \qquad (2b)$$

$$H\underline{M}H + \underline{M}\text{–}C_2H_4 \rightleftarrows H\underline{M}\text{–}C_2H_5 \qquad (2c)$$

$$H\underline{M}\text{–}C_2H_5 \longrightarrow \underline{M} + C_2H_6 \qquad (2d)$$

($\underline{M}$ = metal surface, not necessarily an individual surface atom)

bination of the reacting molecule with the metal. The step is usually reversible; it is called the *activation* of the reactant (eq 1, 2a, 2b). *An understanding of the over-all reaction requires a knowledge of this primary interaction: its stoichiometry, mechanism, energetics, and the nature of the bonding in and the structure of the activated*