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Electronic Excited States of Small Ring Compounds 3: Cyclopropene, Vinylcarbene, and Vinylmethylene[1]

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Abstract: The 3,3-isopyrazoles IIa–e have been prepared. Irradiation of IIa–e produces the vinyl diazo compounds IXa–e. When the vinyl diazo compounds IXa–e are irradiated at 10 °C the cyclopropenes Xa–d result in high yields. When the irradiation of the vinyl diazo compounds IXa–d is carried out at ca. 5 K in rigid medium (MCIP), the ESR spectrum indicates a stable triplet species is produced. The vinylmethylene structure Ia–d has been assigned to these triplet species. The temperature dependence (5–30 K) of the ESR signal due to Ia–d indicates the triplet is the ground state and that the singlet is not thermally populated within this temperature range. In contrast, no triplet signal was detected upon irradiation of IIe under these conditions and it is proposed that Ie is a ground-state singlet species. The involvement of vinylcarbene and/or vinylmethylene as intermediates in the preparation and photochemical reaction of cyclopropenes is discussed. Some limitations of the temperature-dependent ESR signal intensity approach for the determination of the energy separation of equilibrating singlet and triplet states are pointed out.

Introduction

We have a continuing interest in the mechanism(s) for the interconversion and the relative energies of three-membered rings and the corresponding heterolytic and homolytic bond-cleaved species.[4] Vinylmethylene and/or vinylcarbene have frequently been proposed as intermediates in the preparation and photochemical and thermal reactions of cyclopropenes. However, direct evidence of their involvement, insight into the structure and nature of these species, and even knowledge as to which is the ground state was not available at the onset of this work. In this regard, the theoreticians were several years ahead of the experimentalists; at least two groups have discussed the problem in some detail.[5]

In this paper, we will report the details of our preliminary account of the preparation and characterization of the vinylmethylenes Ia and Id and vinylcarbene Ie.[6] In addition we have prepared the 4-methoxy (Ib) and 4-cyano (Ic) derivatives and can now report the effect of these electron-donating and electron-withdrawing substituents on the vinylmethylene. Since

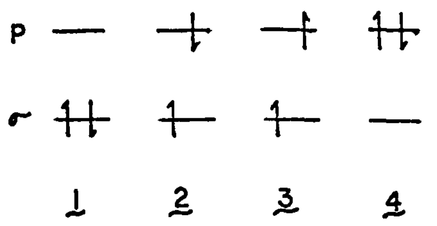
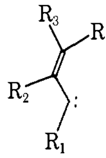


Figure 1. The four possible electronic configurations of the parent divalent carbon species. The states can be labeled as follows: **1** (σ^2); **2** and **3** (σp); **4** (p^2). The actual ground state is **3**, triplet σp. Neglecting electronic interactions, the calculated (extended Hückel) lowest-energy state is **1**, σ^2 singlet.

our initial report, the parent vinylmethylene (Ig) has been characterized and can be compared to those reported in this paper.[7,8] We begin with a brief summary of the theoretical considerations so that the experimental results can be compared with predictions made more than five years ago.[5a,b]



Ia, $R_1 = R_2 = C_6H_5$; $R_3 = R_4 = CH_3$
b, $R_1 = 4\text{-}CH_3OC_6H_4$; $R_2 = C_6H_5$; $R_3 = R_4 = CH_3$
c, $R_1 = 4\text{-}CNC_6H_4$; $R_2 = C_6H_5$; $R_3 = R_4 = CH_3$
d, $R_1 = C_6H_5$; $R_2 = CO_2CH_3$; $R_3 = R_4 = CH_3$
e, $R_1 = CO_2CH_3$; $R_2 = C_6H_5$; $R_3 = R_4 = CH_3$
f, $R_1 = C_6H_5$; $R_2 = H$; $R_3 = R_4 = CH_3$
g, $R_1 = R_2 = R_3 = R_4 = H$

The linear divalent parent carbon species would have two half-filled degenerate p orbitals. By bending the H-C-H angle from linearity, these two orbitals become nondegenerate. The orbital in the plane of the system is stabilized by mixing with the 2s carbon orbital and is referred to as σ. The orbital perpendicular to the plane of the atoms retains its pure p character. Four possible configurations result from the population of two nondegenerate orbitals with two electrons (Figure 1).

Extended Hückel calculations carried out on the parent vinyl system (Ig) indicated that the difference in energy between the lowest state (σ^2) and the next highest state (σp) is less than 0.5 eV. Although these calculations do not distinguish between singlet and triplet of a given configuration, Hoffmann suggested a "rough empirical criterion": if the extended Hückel energy for the doubly occupied lowest-energy orbital (σ^2) in the most favorable conformation is less than 1.5 eV below the next highest state consisting of two half-filled orbitals containing electrons of unpaired spin (σp triplet), then the ground state will in fact be the triplet (σp) state. Thus, it was predicted that the vinyl system (Ig) would be a ground-state triplet.[5a,b]

Salem and Stohrer have discussed in some detail the various states available to the vinyl species based on a combination of valence-bond arguments and ab initio calculations.[4d] Geometries **1** and **2** were considered (Figure 2) and it was concluded that the ground state was the triplet diradical-type structure **2a** associated with geometry **2**. The triplet state of **2a** was calculated to be approximately 7 kcal mol^{-1} below the first excited-singlet state **2b**, which has a certain amount of zwitterionic character in a valence-bond representation.

Based on the above models (**2a** and **2b**) for the ground-state and first-excited states, it is possible that substituents could stabilize the zwitterionic singlet state **2b**. While it is not immediately obvious (to us at least) to what extent substituents would stabilize **2b**, our rationale was that appropriate substitution would certainly stabilize **2b** relative to **2a**. Substituents should have a small effect on the stability of **2a**, based on both benzyl and allyl radical models for this triplet-diradical state. Therefore, we prepared systems with substituents which should greatly stabilize the zwitterionic valence-bond contributors to **2b**, such as *p*-cyanophenyl, *p*-methoxyphenyl, and carbomethoxy at C(1) and a pair of methyls at C(3).

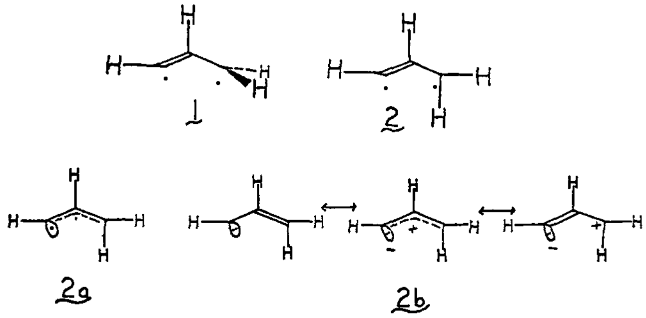


Figure 2. The geometries of the vinyl species in the ground and first excited states: **2a** is the ground-state triplet diradical; **2b** is the first excited-singlet state; **1** and **2** differ only by a rotation by 90° around the C-C bond.

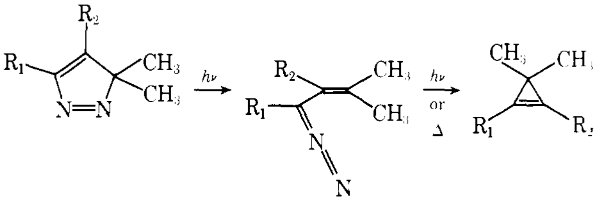
The experimental determination of the lowest-state multiplicity of these species can be a relatively simple matter. If the triplet can be detected by electron spin resonance (ESR) spectroscopy, analysis of the temperature dependence of the signal intensity will reveal if the concentration of the triplet is changing. If the concentration of the triplet species is not affected by temperature, the triplet is the lowest state and the temperature is not high enough to allow significant population of the upper singlet; or, the singlet is the lowest state and the difference in the energy between the singlet and triplet is so small that the triplet is in statistical equilibrium with it. We conclude from this study that Ia-d are ground-state triplet species and with less certainty that Ie is a ground-state singlet. We have included in the discussion some general comments regarding the limitations of this method for determining the energy separation of equilibrating singlet and triplet states.

Results

Key intermediates in the synthesis of Ia-e were the substituted 3,3-isopyrazoles (IIa-e). Two general methods were used to prepare these compounds: the 1,3-dipolar cycloaddition of diazoisopropane to the appropriate acetylene; the cyclization of hydrazine and an α,β-unsaturated ketone followed by oxidation, a procedure which followed rather closely that used by Williams and Dolbier for the preparation of the parent system Ia.[9] The reactions that were used are summarized in sequences I and II in Scheme I. Derivatives Ia[4,9] and Id,e[6,10] have been reported previously. Details of the procedures used are given in the Experimental Section.

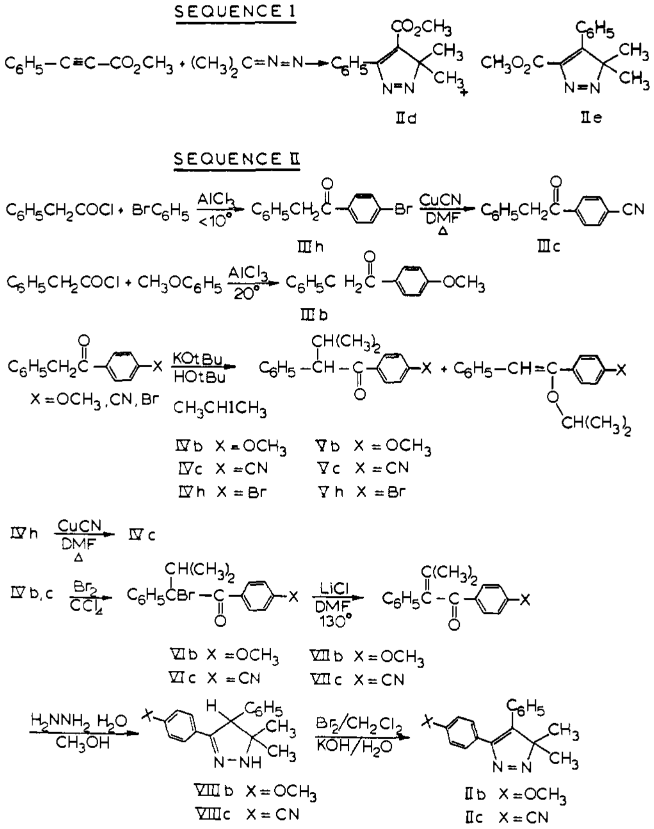
Irradiation of the isopyrazoles (IIa-e) in solution (benzene or carbon tetrachloride) at 10 °C leads to formation of the vinyl diazo compounds (IXa-e).[11] These vinyl diazo compounds were stable in solution at room temperature. They were not isolated, but were characterized by NMR, ir, and visible spectroscopy.

Further irradiation of the vinyl diazo compounds (IXa-e) at 10 °C in solution yields the cyclopropenes (Xa-d) in good yield. Care must be taken not to simultaneously irradiate the



IIa-e IXa-e Xa-d

Scheme I.



cyclopropenes because they are photochemically labile and give dienes on irradiation. In the case of cyclopropene Xa, the highest yields of this compound are realized when the irradiation of the isopyrazole is carried out in two steps. The isopyrazole is irradiated through a filter system which does not allow the vinyl diazo compound to be irradiated and the vinyl diazo compound is then irradiated at longer wavelengths through a filter system which prevents irradiation of the cyclopropene. In this way it can be shown that in the preparation of cyclopropene Xa: (1) little or no cyclopropene is formed directly, in one step, from the isopyrazole; and (2) irradiation of the vinyl diazo compound gives little or no isopyrazole, the exclusive product being the cyclopropene.

When the irradiation of the isopyrazoles IIa-d was carried out in a methylcyclohexane/isopentane (4:1) matrix (MCIP) at ca. 5 K in the ESR cavity, signals assigned to triplet species were observed (along with a strong signal in the $g = 2$ region due to the formation of free-radicals). Frequently, however, the triplet signal generated in this way was not intense enough to allow accurate intensity measurements to be made at the very low microwave power levels which must be used at low temperature to avoid saturation phenomena. Signals of much greater intensity could be obtained by preparing the vinyl diazo compound first, by irradiation of the isopyrazole through the proper filters at 10 °C. The solution of the vinyl diazo compound could then be transferred to the ESR cavity, cooled, and irradiated. Once generated, the triplet appeared to be stable to further irradiation (i.e., no noticeable decrease in signal intensity with further irradiation). These results are taken to mean that while photochemical ring opening of the isopyrazoles (IIa-d) can occur at 5 K, one of the products (perhaps the triplet species) absorbs in the same region as the isopyrazole and that this inhibits the further generation of the vinyl diazo compound and ultimately the triplet species.

The irradiation of IIe at 10 °C seemed identical with that of the other isopyrazoles. The vinyl diazo compound IXe was produced and further irradiations yielded the cyclopropene Xd. However, no triplet signal was detected on irradiation of either IIe or IXe when the irradiation was carried out at ca. 5 K, even though the color due to IXe disappeared under these conditions. The solutions which had been irradiated at ca. 5 K were warmed to ca. 30 K slowly, but no triplet signal was detected.

The signals due to the triplet species can be assigned in terms of the hamiltonian $\mathcal{H} = g\beta H\hat{S} + D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2)$. The zero-field splitting parameters,[12] obtained from the observed spectra by employing an iterative computer program, are summarized in Table I.[13]

At constant temperature, the intensity of the signal (any of the six theoretically observable $\Delta M_s = 1$ lines and the half-field line) due to the triplet species is directly proportional to the concentration. For a constant concentration of triplets, the signal intensity will vary with temperature in the same way as will the signal intensity of a doublet (free radical); that is, the signal intensity will follow the Curie law.[14] Thus, if the concentration of the triplet species is independent of temperature, a plot of signal intensity vs. temperature^{-1} will be linear and extrapolate to zero at infinite temperature.

Figures 3a-c show the effect of temperature on the triplet signal intensity for the species generated on irradiation of IXa-c. These results were typical. The points in Figure 3 are experimental values and the linear relationship indicates that the concentration of the triplet species is not a function of temperature.

We have made several attempts to detect a triplet species (Ia) from irradiation of the cyclopropene (Xa). Neither direct irradiation of Xa nor sensitized (benzophenone, ~0.1 M) irradiation in MCIP at ca. 5 K have led to formation of any observed signal due to a triplet species.

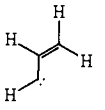
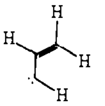
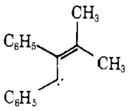
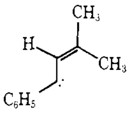
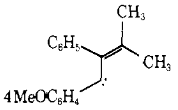
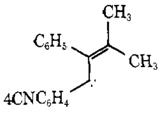
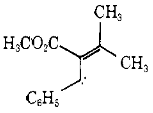
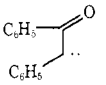
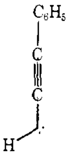
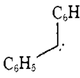
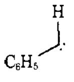
Discussion

We assign the structures Ia-d to the triplet species generated by irradiation of IXa-d. This assignment is made partially by analogy with the preparation of other methylenes which have been studied in detail after irradiation of the corresponding diazo precursers[15] and is reasonable in view of the observed zero-field splitting parameters. These are shown in Table I along with data from some model systems for comparison. In particular, the parent system (Ig *cis* and *trans*) has been characterized since our preliminary report.

The D value for Ia is considerably smaller than that for Ig (*cis* and *trans*). This is consistent with increased delocalization of the electrons by the phenyl substitution at the divalent carbon and the methyl groups in Ia. The presence of the phenyl group on the central carbon in Ia has very little effect on the D value (compare Ia and If). This may reflect the nodal character of this position.

In contrast to Ig, for which two planar isomers are observed (*cis* and *trans*), only one triplet species has been detected for the more heavily substituted cases (Ia-d). The magnitude of the D values observed for these carbenes (Ia-g) is consistent with a model in which one electron is largely localized at the divalent carbon and the other electron is delocalized through an extended π system composed of both the vinyl and phenyl π orbitals. This model is supported by the observed change in D on going from Ig (trans) to Ia or If. If one singly occupied p orbital was conjugated with one substituent and the other orbital with the other substituent, both electrons would be delocalized considerably and one might expect D values closer to those observed for excited aromatic triplets such as naphthalene or fluorene (ca. 0.1 cm^{-1}) or, at least, considerably smaller than observed here. This model for the divalent center in phenyl vinylmethylene is analogous to that proposed for diphenylmethylene and fluorenylidene.[16] Examination of the ^{13}C hyperfine interactions for diphenylmethylene oriented in

Table I. Zero-field Splitting Parameters for Some Vinyl Methylenes and Model Compounds

Methylene	D/hc, cm^{-1}	E/hc, cm^{-1}	Ref.
 Ig (*trans*)	0.4093 (0.4090) (N_2 matrix)	0.0224 (0.0233)	*a* (*b*)
 Ig (*cis*)	0.4578 (0.4130)	0.0193 (0.0176)	*a* (*b*)
 Ia	0.3580	0.0206	*c*
 If	0.357	0.0194	*d*
 Ib	0.3336	0.0179	*e*
 Ic	0.3368	0.0182	*e*
 Id	0.3643	0.0166	*c*
	0.3815	0.0489	*f*
	0.541	0.0035	*g*
	0.4050	0.0194	*h*
	0.5098	0.0249	*i*

[a] Reference 7. [b] O. L. Chapman, unpublished results. [c] Reference 6. [d] J. L. Riemenschneider, Ph.D. Thesis, University of Chicago, 1969. [e] This work. [f] A. M. Trozzolo and S. R. Fahrenholtz, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., 1966, No. K23. [g] R. A. Bernheim, R. J. Hempf, J. V. Gramas, and P. S. Skell, *J. Chem. Phys.*, 43, 196 (1965). [h] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, 41, 1763 (1964). [i] A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, 84, 4990 (1962).

a benzophenone crystal lattice indicates that the phenyl groups are approximately coplanar and the delocalization of the p_x orbital of the divalent carbon is much greater than that of the p_y orbital.[16] The results for fluorenylidene (in which the phenyl rings must be coplanar) were similar.

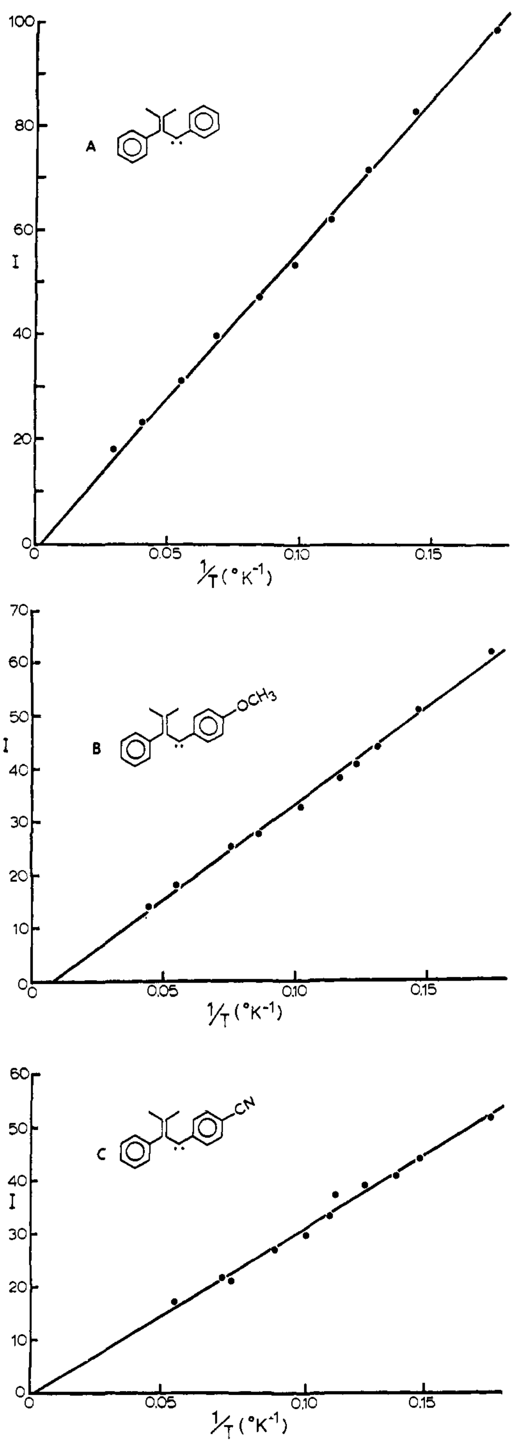


Figure 3. Experimental I vs. $1/T$ plots for species generated on irradiation of (a) IXa, (b) IXb, and (c) IXc.

The substitution by p-methoxy (Ib) and p-cyano (Ic) on the parent system (Ia) results in a further decrease in the value of D, consistent with increased delocalization. Comparison of the D value for Ia with that for the keto analogue XI indicates a larger average electron-separation distance in the former. Hyperconjugation involving the allylic methyl groups and/or a greater contribution of allylic relative to enolic delocalization[17] of the unpaired electron can explain this observation.

The effect of temperature on the intensity of the signals from the triplets Ia-d follows Curie law dependence, which indicates that the concentration of the triplet species is not changing significantly as a function of temperature. These results indicate one of the following: (1) the singlet is the ground state of these species and is separated by such a small energy from the

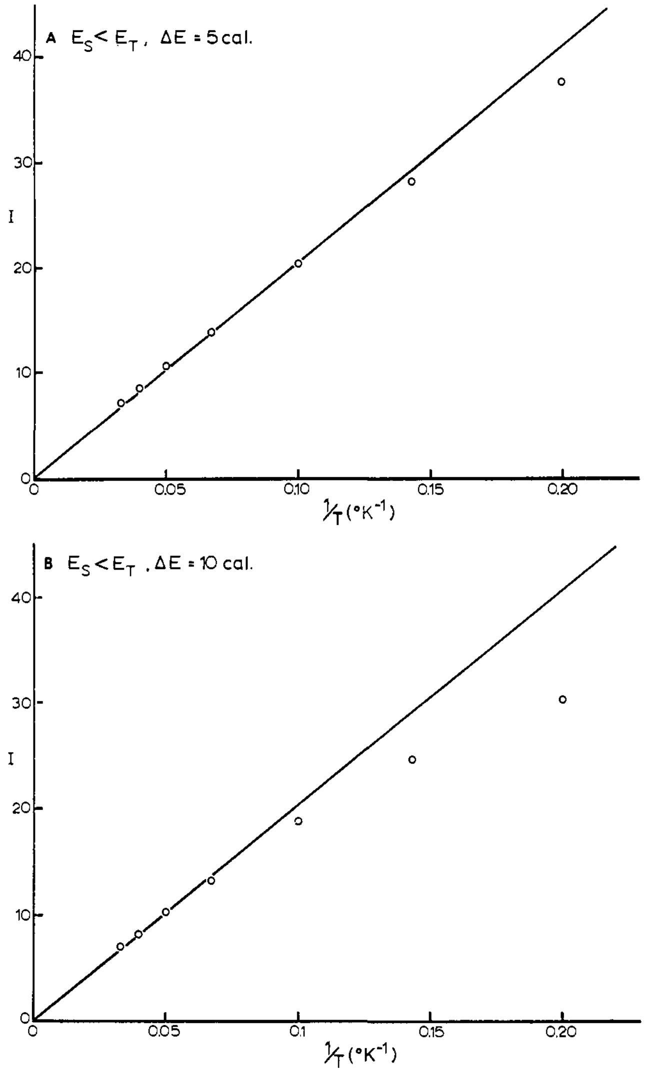


Figure 4. Calculated I vs. $1/T$ plots, $E_s < E_T$: (a) $\Delta E = 5$ cal mol^{-1}; (b) $\Delta E = 10$ cal mol^{-1}.

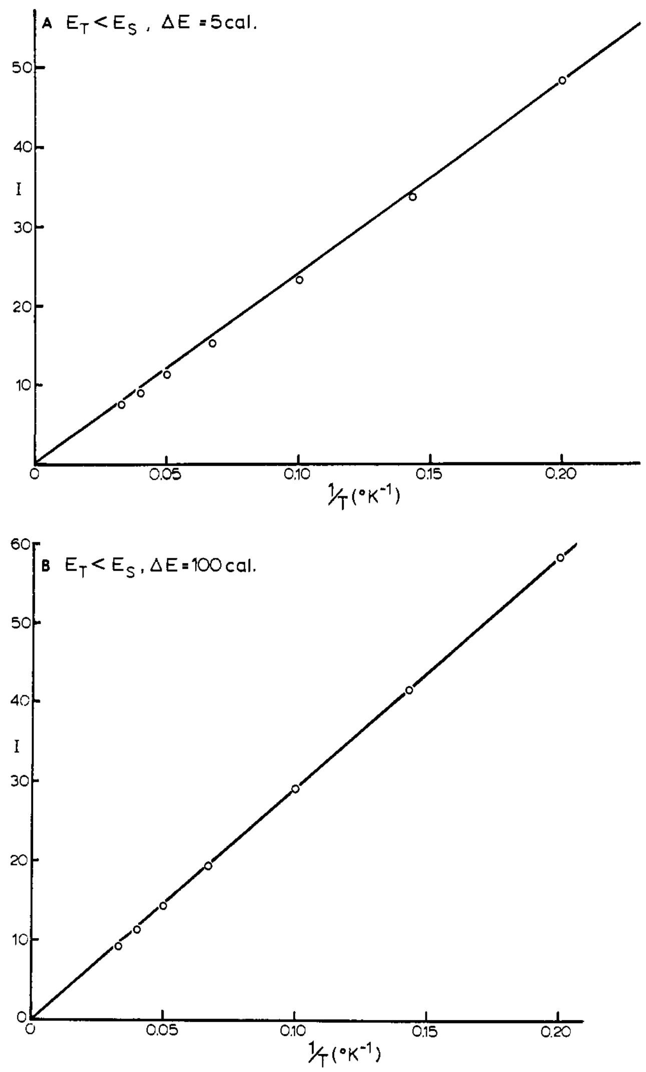


Figure 5. Calculated I vs. $1/T$ plots, $E_T < E_s$: (a) $\Delta E = 5$ cal mol^{-1}; (b) $\Delta E = 100$ cal mol^{-1}.

upper triplet as to be in thermal equilibrium with this upper state even at these low temperatures; or (2) the triplet is the ground state and the singlet is too far above the ground triplet state in energy to be significantly populated at the highest temperature studied.

The expected behavior of the intensity vs. temperature profile for these two possibilities as a function of the energy separating the two states can be calculated from the expression

$$I = \frac{a}{T}\,\frac{3e^{-\Delta E/RT}}{1 + 3e^{-\Delta E/RT}}$$

where "a" is a constant. This equation is based on the Boltzmann distribution between a singlet and a triplet species (note that there are three triplets and one singlet).

For the case in which a triplet state is in thermal equilibrium with a ground-state singlet, an estimate of the energy difference required to cause observable deviation from Curie law dependence can be made by considering Figure 4. The expected behavior of the I vs. $1/T$ plots for the cases in which the singlet state lies at (A) 5 cal mol^{-1} and (B) 10 cal mol^{-1} below the triplet state are shown. If the singlet state lies at lower energy than the triplet state, it must be lower by somewhat less than 5 cal mol^{-1} if Curie law dependence is observed. We view this as a remote possibility for all the examples studied, and consider it likely that the vinyl species Ia–d are ground-state triplets.

Figure 5 illustrates the expected deviation from Curie law dependence if the triplet state is the ground state and the singlet state lies at (A) 5 cal mol^{-1} and (B) 100 cal mol^{-1} above the triplet state over the temperature range studied. In this case, it should be noted that the maximum possible deviation from linearity due to the population of an upper singlet state is 25%. The practical limit for the observation of deviations from Curie law dependence, from a graphical standpoint at least, seems to be in the neighborhood of 100 cal mol^{-1} for the case in which the triplet is the ground state and the temperature range is as reported here. The problem, of course, is that the deviation from linearity increases with temperature (to a maximum of 25%), but $1/T$ decreases the intensity as temperature increases.

The lack of a triplet signal on irradiation of either IIe or IXe is unique among the derivatives studied. As with most "negative" results, there are several possible explanations for failure to observe a signal. In view of its similarity, in the higher temperature solution irradiations, to the other derivatives, we favor a singlet ground state for Ie with a singlet–triplet separation that is large enough that the triplet state is not significantly populated at 20 K. Hence, a signal would not be observed at the low temperatures studied.

Along the same line, it is perhaps speculation to attempt to attach any significance to the lack of a triplet signal on direct and triplet–triplet transfer-sensitized irradiation of the cyclopropene Xa. It is known that direct irradiation of Xa in solution at room temperature leads to the formation of dienes. There is reason to believe that different intermediates (if there are any) are involved between the vinyl diazo compound and the cyclopropene and the cyclopropene and the dienes. The cyclopropene to diene reaction involves the cyclopropene singlet (the cyclopropene triplet does not lead to the dienes). Therefore, it may be that the singlet intermediate is involved here. The cyclopropene singlet is known to have a very inefficient ($<10^{-3}$) intersystem crossing process;[18,19] in fact, we have observed intense fluorescence from the cyclopropene (Xa) at low temperatures.[19] This lack of intersystem crossing may also contribute to the lack of formation of Ia on direct irradiation of Xa. The triplet–triplet transfer-sensitized irradiation was designed to populate the cyclopropene triplet, but no signal was observed which could be assigned to Ia. This result is consistent with the observation that the triplet of the cyclopropene Xa does not give the dienes at room temperature. Recent experiments with an optically active cyclopropene also support the argument that the cyclopropene triplet does not open.[20]

Experimental Section

General. Preparative irradiations were carried out using a GE 1-kW medium-pressure mercury-arc lamp with a quartz cooling jacket which was immersed in a constant-temperature bath at 10 °C. Degassing was not carried out unless stated otherwise. Melting points were not corrected.

The filter systems used were prepared as follows.

Filter System A. A 2 × 15 cm test tube was filled with a 0.4 M solution of $SnCl_2 \cdot 2H_2O$ in 10% HCl. The test tube was placed in a 250-ml beaker containing a solution of 1.0 M $CoSO_4 \cdot 7H_2O$ and 0.1 M $NiSO_4 \cdot 6H_2O$ in 5% H_2SO_4 (path length ≥2 cm).

Filter System B. $BiCl_3$ (200 mg) was dissolved in 10% HCl (150 ml) and this solution was placed in a container such that there was at least 1 cm of filter solution shielding the irradiation vessel used.

^{1}H NMR spectra were obtained from a Varian HA-100 spectrometer (unless noted otherwise) using deuteriochloroform as a solvent and tetramethylsilane as an internal standard. Infrared spectra were obtained on a Beckman IR-5A spectrometer either neat, on sodium chloride plates, or as a solution in carbon tetrachloride in KBr cells.

ESR spectra were obtained from and temperature dependence studies were performed on a Varian E-12 ESR spectrometer using an Air Products Model LTD-3-110 "Helitran" liquid He Dewar and transfer system. Samples were placed in Supersil ESR tubes and were irradiated with a Schoeffel 1-kW high-pressure mercury-arc lamp.

ESR samples were generally prepared by dissolving approximately 6 mg of the isopyrazole in 1 ml of 4:1 methylcyclohexane/isopentane (MCIP) followed by irradiation in a Pyrex NMR tube through filter system A to give the vinyl diazo compound. The sample (usually pink) was then transferred to an ESR tube. For samples used in the temperature dependence studies, approximately 6 mg of phenylazide was added to the sample after transfer to the ESR tube. Irradiations in the ESR cavity were generally carried out through a Corning G53-75 filter (≥370 nm), through which both the vinyl diazo compound and the phenylazide could be irradiated. It was generally found that the methylene signals obtained by direct irradiation of the isopyrazole were much too weak for temperature dependence studies. Therefore, the vinyl diazo compound was prepared before the sample was transferred to the ESR cavity, as stated above.

Temperature readings at liquid He temperatures were obtained using two chromel vs. gold–0.07% iron thermocouples, one imbedded in the liquid He dewar near the sample cavity and one used as a standard at ice-water temperature. The voltage readings were obtained from a Hewlett-Packard 3420B DC differential voltmeter. The inclusion of the phenylazide provided an internal check on the temperature readings, since the triplet signals from phenylnitrene are known to follow the Curie law.

Temperature Dependence Studies. Initial ESR signals were obtained at 10-mW rf power, at which time signals as intense as possible were obtained for both the vinyl methylene and the phenylnitrene. The signal intensity was checked periodically at a power of 1 μW (53 dB). The sample was irradiated until an intense signal was obtained at 1-μW power for the methylene and nitrene. All temperature studies were carried out at full liquid He flow, varying the temperature with a heater imbedded in the liquid He Dewar.

The correction factors required for both the thermocouples and the temperature difference between the liquid He Dewar and the sample cavity are easily measured. At full liquid He flow, the Dewar temperature must be 4.2 K. The difference between the Dewar temperature (4.2 K) in microvolts and that given by the voltmeter gives the thermocouple correction in microvolts. At full He flow, the Dewar temperature in microvolts can be obtained. Then, by removing the standard thermocouple from the Dewar at ice-water temperature and placing it in the sample cavity, the difference between the sample cavity and He Dewar temperatures can be obtained in microvolts. This difference remains constant over the temperature range studied here as long as the liquid He flow is kept at maximum. The sum of the thermocouple correction and the sample cavity correction gives the overall correction used. A check on the corrections made is possible because the phenylnitrene used as an internal standard must give a linear I vs. $1/T$ plot.

Two sets of intensity measurements, from low to high temperature, were made for each sample. After the first set of measurements, the heater was turned off and the temperature was allowed to return to that at full liquid He flow. A new intensity reading for the methylene was obtained and compared to the value obtained from the first run at that temperature. These intensities were the same, within experimental error. A significant difference in these intensities would indicate that the methylene had disappeared irreversibly (i.e., reacted) during the temperature studies and, thus, the I vs. $1/T$ relationship would not be applicable. The signal intensity was determined by measuring the height (peak-to-peak) of one of the distinct derivative peaks of the spectrum (usually the high-field Mx_2).

The intensity relationship assumes that the zero-field splitting parameters and line-broadening factors are temperature independent. This assumption is supported by the observation that the positions and shapes of the lines in the spectrum were not noticeably affected by variation of the temperature.

Attempts to Detect Triplet Species from Cyclopropene Xa by ESR. Neither direct irradiation of the cyclopropene Xa nor triplet–triplet transfer-sensitized irradiation in the presence of benzophenone led to signals which could be assigned to a triplet species. The direct irradiation was carried out on a solution of 4.5 mg of Xa in 1 ml of MCIP at ca 5 K. The solution was irradiated through Corning filter 7-51 (300–420 nm) for 10 min, but no signals which could be assigned to a triplet species were observed. Direct irradiation of the solution without the filter for 1 min produced similar results, with a strong signal in the $g = 2$ region appearing.

The sensitized irradiation was carried out on a solution of Xa (5 mg) and approximately 0.1 M benzophenone (18 mg) in 1 ml of MCIP at ca 5 K. The solution was irradiated for 20 min through Corning filter 7-51, but no triplet signal was observed. Irradiation of the solution without a filter for 1 min produced similar results.

Preparation of Compounds. *p*′-Bromodeoxybenzoin. Anhydrous aluminum chloride (63 g, 0.47 mol) and bromobenzene (400 ml) were placed in a 1000-ml three-neck round-bottom flask equipped with a mechanical stirrer, a 125 ml addition funnel, an HCl trap, and a thermometer extending below the surface of the reaction mixture. The above mixture was cooled to below 10 °C with an ice-water bath, at which time phenylacetyl chloride (66 g, 0.425 mol) in bromobenzene (150 ml) was added through the addition funnel at such a rate that the temperature of the reaction mixture did not rise above 10 °C. The reaction mixture was allowed to stir at less than 10 °C for 2 h and was then poured onto ice (1500 g) in a beaker. This mixture was heated on a steam bath, giving a yellow organic layer and a colorless aqueous layer. The organic layer was separated, extracted with water (2 × 1 l.), and dried over magnesium sulfate (anhydrous). After filtration, the excess bromobenzene was removed under vacuum, leaving a yellow solid in the distillation pot. This solid was recrystallized from methanol, giving colorless crystals (70 g, 60%), mp 115–115.5 °C: NMR δ 4.16 (2 H, s), 7.20 (5 H, s), and 7.62 (4 H, m); ir 3.50 (w), 5.95 (s), 6.30 (s), 7.82 (m), 9.24 (s), 9.82 (s), and 10.01 (s) μm.

Anal. Calcd for $C_{14}H_{11}BrO$: C, 61.13; H, 4.00. Found: C, 61.07; H, 3.96.

***p*′-Cyanodeoxybenzoin.** *p*′-Bromodeoxybenzoin (50 g, 0.18 mol), cuprous cyanide (18.7 g, 0.21 mol), and *N*,*N*-dimethylformamide (150 ml) were placed in a 250-ml round-bottom flask equipped with a magnetic stirring bar, condenser, and drying tube. The mixture was heated to reflux using an oil bath and was kept at reflux for 5 h with vigorous stirring. During the reaction time, the mixture slowly turned a deep red-brown color. After 5 h, the hot reaction mixture was poured into hot 10% aqueous sodium cyanide (500 ml) and was kept for 30 min on the steam bath. An orange oil separated from the aqueous layer. The mixture was extracted with benzene (2 × 500 ml). The benzene layer was extracted with 10% aqueous sodium cyanide (1 × 500 ml) and water (3 × 500 ml) and dried over magnesium sulfate (anhydrous). After filtration and removal of the benzene, an orange solid remained which was crystallized from 95% alcohol. The crystals obtained were yellow (25 g, 63%) and complete removal of the yellow color required column chromatography. The pure compound was colorless, mp 113.5–114.5 °C: NMR δ 4.25 (2 H, s), 7.24 (5 H, m), and 7.82 (4 H, m); ir 3.44 (w), 4.53 (m), 5.92 (s), 7.83 (s), and 9.98 (s) μm.

Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.37; H, 4.89; N, 6.48.

1-(*p*-Bromophenyl)-3-methyl-2-phenyl-1-butanone. *tert*-Butyl alcohol (1000 ml) and freshly cut potassium metal (24.5 g, 0.625 mol) were placed in a dry 2000-ml three-neck round-bottom flask equipped with a condenser, drying tube, stopper, magnetic stirring bar, and under a nitrogen atmosphere. The mixture was heated to reflux using an oil bath and after all but a small amount of the potassium had reacted, the oil bath was removed and *p*′-bromodeoxybenzoin (142 g, 0.516 mol) was added with stirring. The solution immediately turned a deep orange color. The oil bath was replaced and the mixture was brought to reflux again. After 5 min, 2-iodopropane (82.2 ml, 140 g, 0.82 mol) was added slowly through the top of the condenser. A colorless precipitate formed almost immediately and the color of the solution became yellow. The reaction was allowed to stir at reflux for 24 h, at which time it was almost colorless. The solvent was removed by distillation until ca. 200 ml remained. Chloroform (300 ml) was added and potassium bromide was removed by filtration. The solvents were evaporated, leaving a yellow oil which slowly crystallized. The product was recrystallized from 95% alcohol, giving colorless crystals (122 g, 75%), mp 98–98.5 °C. Removal of the solvent from the mother liquors yielded an oily mixture of *C*- and *O*-alkylated products which was discarded. Spectral data: NMR δ 0.73 (3 H, d), 0.99 (3 H, d), 2.52 (1 H, m), 4.08 (1 H, d), 7.22 (5 H, m), and 7.63 (4 H, m); ir 3.50 (m), 5.95 (s), 6.32 (s), 7.74 (m), 8.22 (m), 9.25 (s), and 9.85 (s) μm.

Anal. Calcd for $C_{17}H_{17}BrO$: C, 64.37; H, 5.40. Found: C, 64.22; H, 5.27.

1-(*p*-Cyanophenyl)-3-methyl-2-phenyl-1-butanone. 1-(*p*-Bromophenyl)-3-methyl-2-phenyl-1-butanone (121 g, 0.382 mol), cuprous cyanide (39.6 g, 0.443 mol), and *N*,*N*-dimethylformamide (121 ml) were placed in a 250-ml round-bottom flask equipped with a condenser, drying tube, and magnetic stirring bar. The mixture was stirred vigorously and heated at reflux for 7 h. The color of the reaction slowly changed to deep red brown. The hot mixture was poured into hot 10% aqueous sodium cyanide (1 l.) and heated on a steam bath for 1 h. An orange, oily layer separated from the aqueous layer and was extracted with benzene (2 × 750 ml). The benzene layer was washed with hot 10% aqueous sodium cyanide (1 × 500 ml) and water (2 × 500 ml) and was dried over magnesium sulfate (anhydrous). After filtration, the benzene was evaporated, leaving an orange oil which would not solidify. The ir spectrum of the neat oil showed a strong nitrile band at 4.53 μm. This product was used in the next reaction without further purification. Spectral analysis was obtained and a sample (oil) purified further: NMR δ 0.75 (3 H, d), 1.02 (3 H, d), 2.58 (1 H, m), 4.22 (1 H, d), 7.22 (5 H, m), and 7.76 (4 H, m); ir 3.48 (m), 4.53 (m), 5.92 (s), 7.70 (m), 8.18 (s), 8.45 (m), 9.78 (m), and 10.54 (m) μm.

Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 81.56; H, 6.74; N, 5.01.

1-(*p*-Cyanophenyl)-3-methyl-2-phenyl-2-buten-1-one. 1-(*p*-Cyanophenyl)-3-methyl-2-phenyl-1-butanone (91.3 g, 0.347 mol), bromine (17.9 ml, 55.5 g, 0.347 mol), and carbon tetrachloride (900 ml) were placed in a 2-l. round-bottom flask equipped with a magnetic stirring bar and HBr trap. The mixture was allowed to stir at room temperature for 24 h, at which time the orange color of the bromine had disappeared and a yellow solution remained. The NMR spectrum of the reaction mixture indicated that all the starting material was gone and 2-bromo-1-(*p*-cyanophenyl)-3-methyl-2-phenyl-1-butanone was present as the only observable product. The carbon tetrachloride was removed on the rotary evaporator and *N*,*N*-dimethylformamide (900 ml) and lithium chloride (59.1 g, 1.39 mol) were added. The mixture was heated to 130 °C, stirred, and allowed to react for 3 h. The reaction mixture was then poured into water (2 l.) and extracted with diethyl ether (2 × 1 l.). The ether layer was dried over magnesium sulfate (anhydrous). After filtration, the ether was evaporated and a brown oil remained. This oil was distilled under vacuum (197 °C, 0.45 mm) to give the desired product (80 g, 88%): NMR (δ) 1.80 (3 H, s), 1.89 (3 H, s), 7.24 (5 H, m), and 7.80 (4 H, m); ir 3.36 (m), 3.51 (m), 4.51 (m), 5.99 (s), 6.89 (m), 7.65 (m), and 8.08 (s) μm.

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.65; H, 5.93; N, 5.17.

3-(*p*-Cyanophenyl)-5,5-dimethyl-4-phenyl-Δ^2-pyrazoline. A 2-l. three-neck round-bottom flask was equipped with a nitrogen inlet tube, a drying tube, a magnetic stirring bar, and covered with aluminum foil to keep out light. Under a nitrogen atmosphere, 1-(*p*-cyanophenyl)-3-methyl-2-phenyl-2-buten-1-one (70 g, 0.268 mol), hydrazine hydrate (94 ml, 2.41 mol), and methanol (1775 ml) were added and the mixture was allowed to stir at room temperature for 36 h. After evaporation of the methanol, diethyl ether was added to give an upper organic layer and a lower hydrazine layer. The hydrazine layer was separated, extracted with diethyl ether (1 × 500 ml), and discarded. The combined ether layers were dried over magnesium sulfate (anhydrous). After filtration, the ether was evaporated, leaving a yellow oil (62 g) which crystallized on standing. The compound was used without further purification. The crude yield was 84%: T-60 NMR δ 0.88 (3 H, s), 1.47 (3 H, s), 3.96 (1 H, s), 6.37 (1 H, s, br), 7.03 (5 H, m), and 7.44 (4 H, m); ir 2.96 (m), 3.34 (m), 4.44 (m), 6.16 (m), 6.28 (m), 6.76 (m), 7.14 (m), and 7.41 (m) μm.

3-(*p*-Cyanophenyl)-5,5-dimethyl-4-phenyl-5*H*-pyrazole. 3-(*p*-Cyanophenyl)-5,5-dimethyl-4-phenyl-Δ^2-pyrazoline (20 g, 0.073 mol), aqueous potassium hydroxide (10.8 g KOH in 162 ml of H_2O), and methylene chloride (270 ml) were placed in a 500-ml three-neck round-bottom flask under a nitrogen atmosphere and equipped with a magnetic stirring bar and 50-ml addition funnel. The apparatus was covered with aluminum foil to exclude light. With vigorous stirring, bromine (8.1 ml, 0.146 mol) in methylene chloride (32 ml) was added through the addition funnel over about 10 min. The reaction was kept at room temperature with a water bath and allowed to stir for 26 h. The reaction mixture was poured into a 500-ml separatory funnel and the orange methylene chloride layer was separated and extracted with water (1 × 200 ml), 10% aqueous sodium thiosulfate (1 × 200 ml), and water again (1 × 200 ml). After drying over magnesium sulfate (anhydrous) and filtration, the methylene chloride was evaporated and a brown oil was obtained, which crystallized when methanol was added. The product was recrystallized from methanol (150 ml), yielding dark orange needles (8 g, 40%). Complete removal of the orange color required column chromatography on aluminum oxide, eluting with benzene. The pure product had a mp 183–184 °C: NMR δ 1.52 (6 H, s) and 7.5 (9 H, m); ir 3.25 (w), 3.33 (m), 3.38 (w), 4.42 (m), 6.15 (m), and 6.76 (m) μm.

Anal. Calcd for $C_{18}H_{15}N_3$: C, 79.09; H, 5.53; N, 15.38. Found: C, 78.88, H, 5.78; N, 15.50.

1-(*p*-Cyanophenyl)-3-methyl-2-phenyl-1-diazobut-2-ene. 3-(*p*-Cyanophenyl)-5,5-dimethyl-4-phenyl-5*H*-pyrazole (20 mg) was dissolved in warm carbon tetrachloride (0.5 ml) and the warm solution was transferred as quickly as possible to a Pyrex NMR tube. The solution was irradiated through filter system A. After 2 h of irradiation, the solution had turned pink-orange and the NMR spectrum of the mixture showed a small doublet at δ 1.90. The ir spectrum of the mixture showed a diazo stretching band at 4.80 μm. The intensity of the doublet in the NMR spectrum did not increase after 3.5 h of irradiation and after 14 h of irradiation, all the vinyl diazo compound had disappeared. The NMR spectrum of the solution indicated the presence of 1-(*p*-cyanophenyl)-3,3-dimethyl-2-phenylcyclopropene and complete disappearance of both the pyrazole and the vinyl diazo compound.

The long-wavelength absorption band of the 1-(*p*-cyanophenyl)-3-methyl-2-phenyl-1-diazobut-2-ene was obtained from a solution prepared by irradiating 3-(*p*-cyanophenyl)-5,5-dimethyl-4-phenyl-5*H*-pyrazole (20 mg) in benzene for 1 h through filter system A. Spectral data: T-60 NMR δ 1.90 (d); ir 4.80 (w) μm; uv 491 nm.

1-(*p*-Cyanophenyl)-3,3-dimethyl-2-phenylcyclopropene. 3-(*p*-Cyanophenyl)-5,5-dimethyl-4-phenyl-5*H*-pyrazole (1.009 g, 0.0037 mol) was dissolved in benzene (30 ml) and this solution was placed in a Pyrex vessel and irradiated through filter system **B**. After 1 h, the solution was a definite orange color and nitrogen gas bubbles could be seen. After a total of 7 h of irradiation, the orange color had disappeared and the bubbling had ceased. The irradiation was stopped and the benzene evaporated. An orange oil was obtained, which gave the expected NMR spectrum for 1-(*p*-cyanophenyl)-3,3-dimethyl-2-phenylcyclopropene. Purification was carried out by column chromatography on aluminum oxide. The cyclopropene was obtained as a colorless oil (0.816 g, 90%) and remained as an oil after bulb-to-bulb distillation: NMR δ 1.47 (6 H, s) and 7.45 (9 H, m); ir 3.39 (w), 3.53 (m), 4.55 (s), 5.57 (m), 6.25 (s), 6.65 (m), and 6.89 (m) μm.

Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 87.94; H, 6.32; N, 5.99.

***p*′-Methoxydeoxybenzoin.** Phenylacetic acid (136.1 g, 1 mol) and phosphorus trichloride (45 ml, 0.5 mol) were placed in a 2-l. round-bottom flask fitted with a condenser and HCl trap. The mixture was heated on a steam bath for 1.5 h, at which time the heating was stopped and anisole (750 ml) was added. The solution of anisole and acid chloride was slowly poured into a 2-l. round-bottom flask fitted with a condenser and containing aluminum trichloride (150 g, 1.12 mol). The flask was cooled in an ice bath during the addition. When the addition was complete, the deep red mixture was stirred at room temperature until all of the aluminum trichloride had disappeared (approximately 10 min) and the reaction had slowed. The reaction was heated on the steam bath for 1.5 h, at which time HCl evolution had stopped. The reaction mixture was allowed to cool and poured into a beaker containing 1 kg of ice and 400 ml of concentrated HCl, giving a green two-layered solution. The layers were separated, the aqueous layer was washed with 1:1 benzene/diethyl ether (2 × 300 ml), and the combined organic layers were washed with water (1 × 200 ml). The emulsion resulting from the water extraction was broken up by the addition of 4 N aqueous sodium hydroxide. After drying over anhydrous magnesium sulfate and filtering, solvent was removed until about 300 ml of anisole remained. Product crystallized from the anisole and was collected by vacuum filtration and washed with 95% alcohol. Further removal of solvent from the mother liquors and subsequent cooling gave more crystals, a total of 161 g (71%) of the desired product was collected (mp. 69–72 °C): T60 NMR δ 3.83 (3 H, s), 4.22 (2 H, s), 7.28 (5 H, s), and 7.50 (4 H, m); ir 3.42 (w), 5.97 (s), 6.25 (s), 7.94 (s), and 8.52 (s) μm.

1-(*p*-Methoxyphenyl)-3-methyl-2-phenyl-1-butanone. *p*′-Methoxydeoxybenzoin (94.5 g, 0.42 mol) was added to a solution, at reflux, of potassium *tert*-butoxide prepared by adding freshly cut potassium metal (19.3 g, 0.49 mol) to *tert*-butyl alcohol (500 ml) in a 1 l. round-bottom flask equipped with a condenser. The *p*′-methoxydeoxybenzoin dissolved to give a yellow-brown solution to which 2-iodopropane (100 g, 0.59 mol) was added slowly (rapid addition causes a very vigorous reaction which must be cooled in an ice bath). A precipitate formed immediately and the solution turned yellow. The reaction mixture was heated at reflux for 24 h. After cooling and filtration to remove the KI precipitate, the solvent was removed and a yellow oil was obtained. The NMR spectrum of the oil indicated the presence of a small amount of *O*-alkylated product as an impurity. On addition of methanol, the oil crystallized, giving crystalline product (105.6 g, 94%) melting at 75–78 °C. Recrystallization from 95% alcohol gave a pure product (mp 76–77 °C); NMR δ 0.076 (3 H, d), 1.02 (3 H, d), 2.66 (1 H, m), 3.89 (3 H, s), 4.27 (1 H, d), 7.48 (5 H, m), and 7.62 (4 H, m); ir 3.39 (m), 5.96 (s), 6.24 (s), 7.92 (s), 8.53 (s), and 9.61 (m) μm.

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.80; H, 7.67.

1-(*p*-Methoxyphenyl)-3-methyl-2-phenyl-2-buten-1-one. 1-(*p*-Methoxyphenyl)-3-methyl-2-phenyl-1-butanone)45.3 g, 0.169 mol) carbon tetrachloride (375 ml), bromine (31.3 g, 0.195 mol), and a catalytic amount of aluminum trichloride was placed in a 500-ml round-bottom flask equipped with an HBr trap and a magnetic stirring bar. The mixture was allowed to stir for 18 h, at which time an NMR spectrum of the reaction mixture indicated complete disappearance of the starting material and formation of the brominated product. Evaporation of the solvent afforded a dark red oil which was not further characterized.

The oil was dissolved in *N,N*-dimethylformamide (300 ml) in a 500-ml round-bottom flask fitted with a condenser. Anhydrous lithium chloride (28.6 g, 0.676 mol) was added and the mixture was stirred at 130 °C for 2 h. The dark yellow solution was poured into 1 l. of distilled water and extracted with diethyl ether (3 × 400 ml). The combined ether extracts were dried over magnesium sulfate (anhydrous). Filtration and evaporation of the ether afforded a dark green oil (42.6 g). Distillation under reduced pressure (148 °C (0.2 mm)) gave a pure product (39.1 g, 87%) as a colorless oil which crystallized, mp 86–87 °C: NMR δ 1.81 (3 H, s), 1.90 (3 H, s), 3.88 (3 H, s), 7.50 (5 H, m), and 7.62 (4 H, m); ir 3.44 (m), 6.02 (s), 6.25 (s), 7.93 (s), 8.54 (s), and 9.63 (m) μm.

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.94; H, 6.88.

5,5-Dimethyl-3-(*p*-methoxyphenyl)-4-phenyl-5*H*-pyrazole. 1-(*p*-Methoxyphenyl)-3-methyl-2-phenyl-2-buten-1-one (30 g, 0.113 mol), hydrazine hydrate (59.8 g, 1.20 mol), and methanol (600 ml) were placed in a 1-l. three-neck round-bottom flask covered with aluminum foil and allowed to stir at room temperature for 36 h. Removal of the methanol on a rotary evaporator afforded 5,5-dimethyl-3-(*p*-methoxyphenyl)-4-phenyl-Δ^2-pyrazoline as a colorless oil.

The crude oil was dissolved in methylene chloride (400 ml) and the resulting solution was washed with water (2 × 200 ml), dried over magnesium sulfate (anhydrous), and filtered. The solution was placed in a three-neck round-bottom flask equipped with a 100-ml addition funnel, a magnetic stirring bar, and under a nitrogen atmosphere. A solution of potassium hydroxide (16 g, 0.286 mol) in water (220 ml) was added and the entire apparatus was covered with aluminum foil. With vigorous stirring, a solution of bromine (18.1 g, 0.113 mol) in methylene chloride (55 ml) was added dropwise over 30 min and the resulting solution was stirred at room temperature for 2 h. The yellow organic layer was separated and extracted with water (2 × 100 ml). The aqueous layer was extracted with methylene chloride (1 × 100 ml) and the combined organic layers were dried over magnesium sulfate (anhydrous). After filtration, the organic layer was treated with decolorizing carbon, followed by another filtration. The methylene chloride was removed on the rotary evaporator and the yellow solid which remained was washed once with hexane. Recrystallization of the product (three times) from hexane gave colorless crystals of the desired product, mp 128–128.5 °C (overall yield 11.95 g, 38%): NMR δ 1.53 (6 H, s), 3.87 (3 H, s), and 7.59 (9 H, m); ir 3.40 (w), 6.23 (m), 6.63 (s), 6.85 (m), 8.00 (s), and 8.52 (s) μm.

Anal. Calcd for $C_{18}H_{18}N_2$: C, 77.67; H, 6.52; N, 10.07. Found: C, 77.38; H, 6.51; N, 9.95.

3-Methyl-1-(*p*-methoxyphenyl)-2-phenyl-1-diazobut-2-ene. 5,5-Dimethyl-3-(*p*-methoxyphenyl)-4-phenyl-5*H*-pyrazole (16.8 mg) was dissolved in carbon tetrachloride (0.5 ml) and placed in a Pyrex NMR tube. The solution was irradiated for 75 min through filter solution A. The irradiation was stopped and the NMR and ir spectra of the pink solution were obtained.

The visible absorption spectrum of the vinyl diazo compound was obtained from a solution prepared by irradiating 5,5-dimethyl-3-(*p*-methoxyphenyl)-4-phenyl-5*H*-pyrazole (15.8 mg) in benzene (1.0 ml) in a Pyrex NMR tube using filter solution A. Spectral data: T-60 NMR δ 1.88 (d); ir 4.91 (s); vis λ_{max} 524 nm.

3,3-Dimethyl-1-(*p*-methoxyphenyl)-2-phenylcyclopropene. A solution of 5,5-dimethyl-3-(*p*-methoxyphenyl)-4-phenyl-5*H*-pyrazole (1.020 g, 0.0037 mol) and 2 drops of pyridine in benzene (8 ml) was irradiated through filter solution B. After 5.5 h, the red color of the vinyl diazo compound had disappeared and all nitrogen evolution had ceased. Evaporation of the solvent gave the crude cyclopropene (0.928 g), which was chromatographed on an aluminum oxide column, eluting with 5:1 benzene/diethyl ether. After one recrystallization from hexane, the cyclopropene was obtained as colorless needles, mp 77–78 °C: NMR δ 1.49 (6 H, s), 3.92 (3 H, s), and 7.46 (9 H, m); ir 3.53 (m), 5.56 (w), 6.25 (m), 6.62 (s), 6.90 (m), 7.89 (s), and 9.64 (m) μm.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.07; H, 7.32.

2-Carbomethoxy-3-methyl-1-phenyl-1-diazobut-2-ene (IXd) and 1-Carbomethoxy-3-methyl-2-phenyl-1-diazobut-2-ene (IXe). The ir and NMR spectra of these compounds were obtained by irradiating a solution of the appropriate isopyrazole (16 mg) in carbon tetrachloride (0.5 ml) through filter system A until the solution was a definite pink color.

The visible absorption spectra of these vinyl diazo compounds were obtained from solutions prepared by irradiating the appropriate isopyrazole (16 mg) in benzene (1.0 ml) through filter system A. Spectral data for IXd: T-60 NMR δ 2.07 (d); ir 4.89 μm; vis λ_{max} 510 nm (ϵ 75). For IXe: T-60 NMR δ 1.87 (d); ir 4.80 μm; vis λ_{max} 420 nm (ϵ 115).

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Photochemistry of Quaternary Salts of 1,2-Bispyridylethylenes. Heavy Atom Induced Singlet–Triplet Intersystem Crossing as a Path for Decay in Charge-Transfer Exciplexes[1,2]

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Abstract: An investigation of the effect of heavy-atom-containing quenchers on the photochemistry of quaternary salts of 1,2-bispyridylethylenes is reported. Haloaromatics as well as non-halogen-containing aromatics quench the fluorescence of the electron-deficient olefins; the former induce trans → cis isomerization presumably via the olefin triplet. The quenching mechanism can be demonstrated to be formation of a charge-transfer exciplex with all of the quenchers studied; with non-halogen-containing quenchers the exciplex evidently decays rapidly without the occurrence of isomerization. For most of the halogen-containing quenchers, the "heavy-atom effect" involves quenching of the localized singlet to the exciplex followed by quantitative decay to the localized olefin triplet; this mechanism occurs provided the quencher oxidation potential is greater than 1.38 V, such that the exciplex lies energetically between the olefin excited singlet and triplet states. When the exciplex lies lower in energy than the triplet no isomerization is observed.

An area of interest to both photochemists and spectroscopists has been the induction of singlet–triplet intersystem crossing by external and internal heavy atoms.[3-11] Both the internal and external effects are believed to involve enhanced spin–orbit coupling, which occurs when electrons involved in the transition are subjected to the enhanced electric field in the vicinity of the heavy atom.[3] A major question concerning the external heavy-atom effect has been the nature of binding interactions between the heavy-atom-containing molecule and the excited substrate. McGlynn and co-workers have suggested that a charge-transfer interaction in the excited state is a prerequisite to the operation of the external heavy-atom effect.[4,5] Giachino and Kearns found, however, that the magnitude of the heavy-atom effect did not increase when heavy-atom perturbers were used with increased capabilities of forming charge-transfer complexes.[6] Until recently most examples where charge-transfer interactions were believed involved in external heavy-atom effects involved systems where the heavy-atom quencher, usually an alkyl halide, was the electron acceptor and the excited substrate was an aromatic hydrocarbon. In recent work, however, Herman and Schulte-Frohlinde found that intersystem crossing in 9-cyanoanthracene and 9,10-dicyanoanthracene could be induced by a series of heavy-atom quenchers having varying electron-donating abilities.[7] For these systems the quencher giving the highest fraction of triplet formation was *p*-bromoanisole, the best electron donor in the series studied. Although McGlynn and co-workers have suggested that donor–acceptor charge-transfer interactions contribute to the field of the heavy atom and give rise to enhanced spin–orbit coupling in the substrate,[8] the latter results suggest that donor–acceptor interactions may play their major role simply in bringing and holding the heavy atom into the vicinity of the excited substrate.

In the present paper we report results of an investigation of the effect of heavy-atom-containing quenchers on the photochemistry of quaternary salts of some 1,2-bispyridylethylenes. These electron-deficient olefins are attractive candidates for investigation of external heavy-atom effects, since in several instances both inefficient triplet formation and rather efficient, intense fluorescence is observed;[12,13] in addition, sensitization studies have indicated that triplets, once formed, undergo efficient isomerization such that triplet counting is easily accomplished.[14] In previous investigations we have found that these electron-deficient molecules react readily from their excited singlet states in processes involving nucleophilic attack as well as formation of charge-transfer exciplexes.[12,13,15] In