acetate solution of the compound. The crystals were of rather poor quality and did not diffract strongly. That selected for intensity data collection was developed on {100} and {011} and measured 0.21 × 0.14 × 0.28 mm. Unit-cell constants were derived from a least-squares fit to the setting angles of 25 widely dispersed reflections on a Nonius CAD-4 diffractometer. Intensity data were collected by a variable width, variable speed $2\theta/\omega$ scan to the practical diffraction limit of $\theta = 22°$. There were no nonstatistical variations in the intensities of three standard reflections monitored throughout the data collection, and no reflection was sufficiently intense to warrant the use of attenuators. The data were corrected for Lorentz and polarization effects, but absorption corrections were not required. After averaging equivalent measurements, the data set consisted of 3320 unique reflections of which 1452 were classed as observed ($I > 2.5\sigma(I)$).[9]

Structure determination was undertaken by using direct methods. Since the crystal space group has four general equivalent positions but the unit cell contains eight molecules there are two crystallographically distinct molecules to be located (56 nonhydrogen atoms). The two independent molecules are labeled A and B. In the first *E* map, 49 atoms were correctly positioned, and the remainder were located from subsequent difference electron density maps. A least-squares refinement cycle in which all atoms were assigned the atomic scattering factor of carbon returned relatively low isotropic temperature factors for those atoms expected to be oxygens and nitrogens on the basis of chemical reasoning. With all atoms correctly assigned, two refinement cycles were computed. The temperature factors of some atoms at the extremities of the side chains became comparatively high, and accordingly these atoms were removed from the structure-factor calculation and a difference map computed. All atoms reappeared as single (albeit somewhat diffuse) peaks, and it was concluded that high thermal vibrations and not disorder were responsible for the high temperature factor values. The nonrigidity of packing would also be a contributory cause of the relatively peak weak diffraction by the crystals.

For the final least-squares cycles, hydrogen atoms were included in fixed calculated positions with isotropic temperature factors set approximately 10% higher than those of the atoms to which they were attached. no attempt has been made to assign anisotropic thermal parameters to any atoms as this would not be justified on the basis of the limited number of observations. Final residuals were $R = 0.103$ and $R_w = 0.110$.

**Acknowledgment.** This work was supported by the Auckland Division of the Cancer Society of New Zealand and by the Medical Research Council of New Zealand.

**Registry No.** **3**, 5519-42-6; **4**, 19551-66-7; **5**, 20544-67-6; **6**, 98688-29-0; **7**, 98688-21-2; **7** (acid chloride), 98688-22-3; **8**, 98688-23-4; **9**, 98688-24-5; **9** (acid chloride), 98688-25-6; **10**, 98688-26-7; **11**, 98688-27-8; **12**, 98688-28-9; $H_3CCOCH_2COCH_3$, 123-54-6; $H_3CCOCH(CH_3)COCH_3$, 815-57-6.

**Supplementary Material Available:** Atomic coordinates, bond lengths, and bond angles for **12** (4 pages). Ordering information is given on any current masthead page.

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[9] Programs used for unit cell determinations and initial data processing were part of the CAD-4 SDP structure determination package by B. Frenz. The direct methods structure solution and least-squares refinement were carried out with SHELX on the University of Auckland IBM 4341 computer.

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# Structures of Diarylcarbenes and Their Effect on the Energy Separation between Singlet and Triplet States[1]

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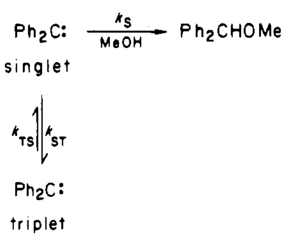
Theory indicates that expansion of the central C–C–C angle in a diarylcarbene should lead to an enhancement of its triplet–singlet energy gap. The series of carbenes diphenyl, mesitylphenyl, mesityl-*o*-tolyl, and dimesityl was used to test this hypothesis. Electron paramagnetic resonance (EPR) spectra of the triplet states of these carbenes showed that increasing ortho substitution at the aryl groups led to an expansion of the C–C–C angle. Product and kinetic studies, on reactions which reflected the singlet–triplet energy gap, showed that this expansion led to an enhanced triplet–singlet energy separation thus substantiating the theoretical prediction. The results establish a relationship between structure and the energy separation between the triplet and singlet states of simple diarylcarbenes.

Electron nuclear double resonance (ENDOR) studies[3,4] of diphenylcarbene (I) in matrices have shown that the carbene has a triplet ground state with a central C–C–C angle of 148° and a dihedral angle of 35° between the phenyl rings. Theoretical calculations[5–7] support this conclusion and further suggest[6] that the energy separation between the triplet and singlet states is very sensitive to structural distortions such as expansion of the central C–C–C angle or rotation of the phenyl rings. In fact, theory suggests[6,7] that expansion of the central C–C–C angle causes a slight destabilization of the triplet state but at the same time strongly destabilizes the singlet state in

**Scheme I**



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[3] Hutchison, C. A., Jr.; Kohler, B. E. *J. Chem. Phys.* **1969**, *51*, 3327. Doetschman, D. C.; Hutchison, C. A., Jr. *J. Chem. Phys.* **1972**, *56*, 3964.

[4] For studies of diphenylcarbenes in glasses, see; Trozzolo, A. M.; Wasserman, E. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1973; Vol. II, Chapter 5. Humphreys, R. W. R.; Arnold, D. R. *Can. J. Chem.* **1979**, *57*, 2652.

[5] Higuchi, J. *J. Chem. Phys.* **1963**, *39*, 1339.

[6] Metcalfe, J.; Halevi, E. A. *J. Chem. Soc., Perkin Trans. 2* **1977**, 364.

[7] Hoffman, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.

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**Table I. Values of *D* and *E* for Diarylcarbenes II and III in Various Matrices**

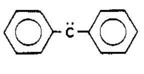
| | | II | | III | |
|---|---|---|---|---|---|
| matrix | temp, K | *D*, MHz | *E*, MHz | *D*, MHz | *E*, MHz |
| | | Before Annealing | | | |
| isopentane/ether | 4 | 11 500 ± 60 | 475 ± 20 | 11 700 ± 50 | 490 ± 30 |
| 2-methyltetrahydrofuran | 4 | 11 580 ± 40 | 495 ± 20 | 11 750 ± 70 | 450 ± 20 |
| 1,1-diphenylethylene | 4 | 11 520 ± 50 | 465 ± 15 | 11 800 ± 100 | 450 ± 20 |
| | | After Annealing | | | |
| isoptentane/ether | 68 | 11 500 ± 40 | 475 ± 20 | 11 100 ± 60 | 400 ± 20 |
| 2-methyltetrahydrofuran | 68 | 11 560 ± 40 | 480 ± 20 | 11 300 ± 60 | 400 ± 20 |
| 1,1-diphenylethylene | 68 | 11 520 ± 35 | 465 ± 15 | | |

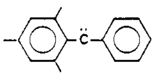
which both electrons occupy the same molecular orbital.

While approximate molecular orbital calculations can outline broad trends of the kind described above, they are unlikely to lead to accurate estimates of the singlet–triplet gap for even the minimum energy geometry. The main sources of such evidence are mechanistic and kinetic studies. These show that triplet diphenylcarbene often carries out singlet-like reactions, such as insertion into alcohols[8,14] (eq 1), in apparent contravention of the rules of spin-selection for carbene reactions.[14] Such observations have been rationalized in terms of an equilibrium mechanism in which the triplet state of the carbene thermally populates the singlet manifold to a limited extent, (Scheme I).[8,14] Although the precise mechanistic details are quite controversial,[13,14] the fact that such reactions can occur implies that the triplet–singlet gap is relatively small.

$$Ph_2C\colon + MeOH \rightarrow Ph_2C(OMe)H \qquad (1)$$

The reactions of dimesitylcarbene (IV) are strikingly different, there being no evidence for any singletlike behavior of the triplet ground state.[16,17] Indeed, the chemistries of both its singlet and triplet states follow the rules of spin-selection as delineated by Skell and Woodworth,[14] suggesting that the triplet–singlet gap is relatively large.


I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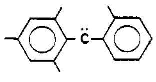
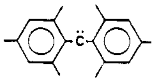

III


IV

Electron paramagnetic resonance (EPR) studies of IV in glasses[18] and in single crystals of its parent diazo compound,[19] support this view. They show that the triplet carbene has a structure in which the aryl groups are orthogonal and in which the central C–C–C angle is much larger than that in diphenylcarbene. The carbene presumably adopts this geometry in order to minimize steric interactions between the *o*-methyl groups, and in so doing adopts a structure in which the triplet–singlet energy separation is enhanced.

In this work, we have carried out EPR and chemical studies of mesitylphenylcarbene (II) and mesityl-*o*-tolylcarbene (III) in order to investigate the relationships between structure, the triplet–singlet energy gap and the chemistry of the series I–IV of diarylcarbenes, all of which have triplet ground states.

## Experimental Section

**Materials.** Diphenyldiazomethane[20] (V) and dimesityldiazomethane[21] (VI) were prepared by literature methods. Mesitylphenyldiazomethane (VII) and mesityl-*o*-tolyldiazomethane (VIII) were synthesized by nitrosation of the corresponding benzophenone imines followed by reduction with lithium aluminium hydride using the method described for V.[21] They have the following spectroscopic properties. NMR ($CCl_4/Me_4Si$): VII, $\delta$ 2.2 (s, 6 H), 2.3 (s, 3 H), 6.7–7.5 (m, 7 H); VIII, $\delta$ 2.1 (s, 6 H), 2.3 (s, 3 H), 2.6 (s, 3 H), 6.7–7.5 (m, 6 H). Visible spectra in cyclohexane: VII, $\lambda_{max}$ 518 nm ($\epsilon$ 85 $M^{-1}$ $cm^{-1}$); VIII, $\lambda_{max}$ 508 nm ($\epsilon$ 154 $M^{-1}$ $cm^{-1}$); values for IV and V were within experimental error of the literature data.[20,21]

All other materials were commercially available and were generally purified by distillation with the exception of 1,1-diphenylethylene which was used as received.

**EPR Experiments.** EPR measurements were made on a Varian E12 x-band spectrometer using a microwave power of 30 mW and a modulation amplitude of 4 G. Samples were prepared from solutions of diazo compounds ($10^{-3}$–$10^{-5}$ M) in an appropriate solvent and were deoxygenated using at least three freeze–pump–thaw cycles. They were then quickly frozen in the cavity of the spectrometer to form glasses and were briefly irradiated with a mercury–xenon lamp in order to generate the carbenes. Field positions were measured with a Varian gaussmeter, and the microwave frequency was determined with a Hewlett-Packard 5246L frequency counter.

**Product Studies.** Isooctane solutions of the diazo compounds (0.03 M) in soda glass tubes were purged with nitrogen and were then irradiated under identical conditions ($\lambda > 320$ nm) until the starting materials had been destroyed. Products were analyzed qualitatively by GC/mass spectrometry. (Hewlett-Packard 5995) and quantitatively by GC (Varian 3700). Both analytical instruments were fitted with capillary columns.

## Results and Discussion

The EPR spectra of triplet states are characterized by two parameters, *D* and *E*.[22,23] The *D* value is related to the separation between the unpaired electrons and varies considerably with the nature of the triplet, e.g., carbene, nitrene, etc. While the overall magnitude of *D* is characteristic of a particular class of triplets, smaller variations in this parameter are seen within a given class and reflect structural differences between the triplets concerned. The *E* value, when weighted by *D*, is a measure of the deviation from axial symmetry and, for diarylcarbenes, will therefore

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(8) Bethell, D.; Stevens, G.; Tickle, P. *Chem. Commun.* **1970**, 792.

(9) Bethell, D.; Newall, A. R.; Whittaker, D. *J. Chem. Soc. B* **1971**, *23*.

(10) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

(11) Eisenthal, K. B. Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr.; DuPuy, C. L.; Hefferon, G.; Hetherington, W.; Korenowski, G. M.; McAuliffe, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 6563.

(12) Turro, N. J. *Tetrahedron* **1982**, *38*, 809.

(13) Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198.

(14) For a review, see: Griller, D.; Nazran, A. S.; Scaiano, J. C. *Ac. Chem. Res.* **1984**, *17*, 283.

(15) See, for example: Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549.

(16) Nazran, A. S.; Griller, D. *Chem. Commun.* **1983**, 850.

(17) Nazran, A. S.; Griller, D. *J. Am. Chem. Soc.* **1984**, *106*, 543.

(18) Nazran, A. S.; Gabe, E. J.; LePage, Y.; Northcott, D. J.; Park, J. M.; Griller, D. *J. Am. Chem. Soc.* **1983**, *105*, 2912.

(19) Nazran, A. S.; Gabe, E. J.; LePage, Y.; Northcott, D. J.; Park, J. M.; Griller, D. *J. Phys. Chem.* **1984**, *88*, 5251.

(20) Smith, L. I.; Howard, K. L. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 351.

(21) Zimmerman, H. E.; Paskovich, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 2149.

(22) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1976.

(23) Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance"; McGraw Hill: New York, 1972; Chapter 10.

**Table II. Values of *D* and *E* for Some Diarylcarbenes in Glasses at ~77 K**

| carbene | *D*, MHz | *E*, MHz | carbene | *D*, MHz | *E*, MHz |
|---|---|---|---|---|---|
| I | 12 200[a] | 570[a] | III | 11 200[b,c] | 400[b,c] |
| II | 11 530[b] | 470[b] | IV | 10 440[c,d] | 440[c,d] |

[a] Average of values reported for a variety of glasses: Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Chim. Phys.* **1964**, *61*, 1003.

[b] Average of values obtained in this work.

[c] After annealing.

[d] Average of values from ref 18 and 19.

depend upon the magnitude of the central C–C–C angle.

EPR spectra of carbenes II and III were obtained in glasses at 4 and 77 K by subjecting frozen solutions of their parent diazocompounds to short periods of photolysis. The spectra were both strong and persistent at these temperatures and were analyzed in terms of *D* and *E* values, which are reported in Table I.

Perhaps the most striking difference between II and III was in the temperature dependences of their spectra. The *E* value for III showed a marked and irreversible reduction as the temperature was increased from 4 to ca. 70 K. This behavior has been observed for dimesitylcarbene[18,19] and to a lesser extent for dianthrylcarbene.[24] It indicates that, on warming, the carbene relaxes to a structure with an expanded C–C–C angle.

After the initial photolysis of the diazocompound, VII at 4 K, the motion of the newly formed carbene must be restricted by the rigidity of the matrix. Warming and thus softening the matrix allows the carbene to assume its minimum energy geometry. Although the change in *E* is relatively small compared to the experimental error, it is accompanied by a clear reduction in *D*. This indicates that the electrons are becoming more delocalized and is consistent with the concept of angular expansion on relaxation.

The *D* and *E* values for II show no change with temperature and are similar to those of III before annealing. We therefore conclude, that the minimum energy geometry of II has a somewhat smaller C–C–C angle than that in III and that the matrix provides sufficient space for it to achieve that geometry at all temperatures.

Representative values of *D* and *E* for diphenylcarbene and dimesitylcarbene are compared with values of II and III in Table II. Both of these parameters decrease with increasing steric crowding in the carbenes and reflect the steric influence of *o*-methyl groups which force an expansion of the central angle. However, for the more hindered carbenes, the experimental errors for *E* are similar to the differences between the *E* values. Accordingly values of *D*, which could be measured to much greater precision, are probably a more reliable guide to structure and the relative triplet–singlet energy separation.

Theory indicates that the triplet–singlet energy gap will increase as the central C–C–C angle is increased.[6,7] Comparison between the chemistries of diphenylcarbene[8–14] and dimesitylcarbene[6,17] shows that, for these extremes, the concept is valid. What remains at issue is whether there is a smooth gradation in chemistry as the central angle is increased. That is, are II and III intermediate in their behavior between diphenyl- and dimesitylcarbenes? The best approach to this problem would seem to be to choose reactions which reflect differences in the equilibrium populations of the singlet and triplet diarylcarbenes. However, making appropriate choices is somewhat more difficult than would, at first, appear.

Photolysis of a diaryldiazomethane in solution at 25 °C leads initially to the formation of the carbene in its singlet state. However, intersystem crossing to the ground-state triplet typically takes place in ca. $10^{-9}$ s.[25,26] Thus, in the absence of high concentrations of singlet quenchers, essentially all of the singlet carbenes will cross to the triplet ground state. However, if the singlet–triplet gap is not large, small concentrations of the singlet may persist in thermal equilibrium with the triplet (Scheme I).[8,9] While the concept is simple the choice of a reaction that accurately probes the magnitude of the singlet–triplet separation remains controversial.

Flash photolysis studies,[10–14] for example, have shown that the optical spectrum of triplet diphenylcarbene can be quenched by methanol, a typical singlet quencher, to give the insertion product (reaction 1). However, the precise details of the mechanism are disputed. On one hand, Eisenthal, Turro, and their collaborators[11,25] favor the mechanism described above, in which the singlet and triplet states are in thermal equilibrium. The triplet state therefore merely furnishes a small quantity of the singlet which reacts with the alcohol (Scheme I). Interpretation of their data led to a triplet–singlet energy gap of ca. 4 kcal mol$^{-1}$ for diphenylcarbene.[11,12] However, this conclusion was reached at by combining data obtained in various solvent systems. We have presented kinetic data which dispute this conclusion and which are only consistent with Scheme I if the triplet–singlet energy gap shows a strong solvent dependence.[27,28]

As a whole, the data for the methanol reaction are equally consistent with other possible mechanisms.[13] For example, an alternative mechanism which is consistent with all of the published data would be formation of a complex between the triplet carbene and methanol which can then access the singlet manifold more readily than the free carbene. While it is not surprising that solvent or substrates can perturb an energy gap of a few kilocalories, it nevertheless represents a significant complication in the choice of reactions which reflect the magnitude of the triplet–singlet energy gap.

In view of these complexities, we chose two reactions to test the relationship between the triplet and singlet states of the carbenes described herein. The first was the methanol reaction. Here, one can take the view that the process reflects the ease with which the carbene ultimately accesses the singlet manifold, no matter which mechanism applies. In this instance, we used laser flash photolysis to probe the reaction kinetics. The second reaction studied was that between the carbenes and their parent diazo compounds in hydrocarbon solvent. The reaction of the carbene with diazo compound yields azine and represents a singlet pathway, whereas other reactions that occur in this system, such as attack by the carbene at solvent molecules or carbene dimerization, represent competitive pathways for decay of the triplet carbene. Thus, the distribution of products should serve as a guide to the relative importance of singlet and triplet processes.

**Reaction of Carbenes I–IV with Methanol.** Rate constants for the reactions of carbenes II and III with methanol were investigated by using laser flash photolysis techniques (literature data for I and IV are available).[13,17] Thus, laser flash photolysis (308 nm) of diazocompounds

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(24) Wasserman, E.; Kuck, V. J.; Yager, W. A.; Hutton, R. S.; Green, F. D.; Abegg, V. P.; Weinshenker, N. M. *J. Am. Chem. Soc.* **1971**, *93*, 6335.

(25) Wang, Y.; Sitzmann, E. V.; Novak, F.; DuPuy, C.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 3238.

(26) Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868.

(27) Such effects have recently been detected[26] and offer a partial but incomplete explanation for this problem.

(28) Solvent effects have also been detected in the reaction of fluorenylidene and 1,2-dichloroethylenes.[29]

(29) Gaspar, P. P.; Lin, C.-T.; Whitsel Dunbar, B. L.; Mack, D. P.; Balasubramanian, P. *J. Am. Chem. Soc.* **1984**, *106*, 2128.

**Table III. Rate Constants ($k_1$) for the Reactions of Carbenes I–IV with Methanol in Isooctane at 298 K**

| carbene | $k_1$, $M^{-1}$ $s^{-1}$ | carbene | $k_1$, $M^{-1}$ $s^{-1}$ |
|---|---|---|---|
| I | $6.4 \times 10^{6}$ [a] | III | $2.1 \times 10^{4}$ |
| II | $8.2 \times 10^{4}$ | IV | $<2 \times 10^{3}$ [b] |

[a] Reference 13. [b] Reference 17; cyclopentane solvent.

VII and VIII (ca. $5 \times 10^{-5}$ M), in cyclopentane as solvent, gave rise to the optical absorption spectra of the corresponding carbenes within the lifetime of the laser flash. The spectra themselves were quite similar to that observed for I[10,13] and consisted of a sharp band with $\lambda_{max} = 320$ nm.

The absorption spectra of the triplet carbenes were quenched by addition of methanol and the observed rate constant for the reaction, $k_{obsd}$ was related to that of interest, $k_1$, via eq 2, where $k_0$ is the rate constant for the

$$k_{obsd} = k_0 + k_1[CH_3OH] \qquad (2)$$

decay of the carbene in the absence of methanol. Values of $k_{obsd}$ were linearly dependent on the methanol concentration and showed no sign of a dependence on the extent to which the methanol was oligomerized. Values of $k_1$ are reported in Table III.

The data quite clearly show that the rate constants for methanol quenching decrease as values of the spectroscopic $E$ and $D$ parameters decrease. This correlation suggests that the methanol reaction becomes more facile as the triplet–singlet energy gap becomes smaller. However, this is a rather superficial interpretation since the possibility of a steric effect on the reaction and the precise details of the reaction mechanism have to be considered.

A steric effect on the reaction, between the carbenes in question and methanol, would obviously affect the rate constants in the direction observed. We cannot assess the significance of this steric contribution if the reaction mechanism involves formation of a complex, between the triplet carbene and methanol, which ultimately undergoes intersystem crossing to give the reaction products. However, if the equilibrium mechanism (Scheme I) applies, it is possible to separate the steric contribution from the enthalpy difference between the singlet and triplet states of carbenes.

According to the mechanism of Scheme I, $k_1 = k_S/K$, where $K = k_{ST}/k_{TS}$.[13] For carbenes I and IV, values of $k_S$ are $(1.3 \pm 0.6) \times 10^{11}$ and $(1.4 \pm 0.3) \times 10^{9}$ $M^{-1}$ $s^{-1}$, respectively,[30] in nonpolar solvents at 298 K. We presume that the lower rate constant observed for IV is due to a steric effect which lowers the efficiency of its reaction with methanol. Combination of the values for $k_1$ and $k_S$ leads to the following values of $K$, $2.0 \times 10^{4}$ (I) and $>7.0 \times 10^{5}$ (IV) and hence to free-energy differences of 5.9 (I) and >8.0 (IV) kcal $mol^{-1}$ between the singlet states of these carbenes and their triplet ground states.

Entropy differences, between singlet and triplet states of carbenes, are generally believed to be small since they are thought to reflect the differences in the multiplicities of the spin states. We therefore conclude that the singlet triplet *enthalpy* gap for IV is greater than that for I by at least 2 kcal $mol^{-1}$. This result is clearly in accord with the prediction, based on EPR and theoretical studies, that the singlet–triplet energy gap becomes greater as the central C–C–C angle of the carbene is expanded. While data for $k_{ST}$ are not available for II and III, the trends in $k_1$ and in the spectroscopic $D$ and $E$ values suggest that they conform to this general picture.

**Reactions of Carbenes I–IV with Their Parent Diazo Compounds.** Carbenes react with their parent diazo compounds to give the corresponding ketazines, eq 3. If Scheme I applies, spin conservation dictates that this reaction must be exclusively confined to the singlet carbene. Accordingly, we studied systems where competing reactions of the triplet carbene were possible, so that the distribution of ketazine to triplet derived products represented a measure of the triplet–singlet energy gap.

An alternative mechanism for azine formation is one in which a triplet carbene complexes with diazo compound to give an ylide which ultimately accesses the singlet manifold. In this case the product distribution still reflects the singlet–triplet separation so long as access to the singlet manifold diminishes as the gap becomes greater.

Solutions of the diazo compounds of interest (0.03 M in isooctane) were photolyzed under identical conditions with a flood lamp ($\lambda > 320$ nm). Quantum yields for the photolysis of diaryldiazomethanes are high (0.8–1.0),[31] and the optical densities of the solutions were such that the rate of carbene generation was effectively the same for all of the diazo compounds examined.

For all of the carbenes under study, the reaction of the carbene with diazo compound was in competition with the self-reaction of the carbene which gave olefin and with the reaction of the carbene with the solvent which gave the diarylmethyl radical (reactions 4 and 5). The radical ultimately formed diarylmethane and tetraphenylethane (reactions 6 and 7).

$$Ar\ddot{C}Ar' + Ar(Ar')CN_2 \rightarrow Ar(Ar')C{=}NN{=}C(Ar')Ar \qquad (3)$$

$$2Ar\ddot{C}Ar' \rightarrow Ar(Ar')C{=}C(Ar')Ar \qquad (4)$$

$$Ar\ddot{C}Ar' + RH \rightarrow Ar\dot{C}HAr' + R\cdot \qquad (5)$$

$$Ar\dot{C}HAr + RH \rightarrow ArCH_2Ar' + R\cdot \qquad (6)$$

$$2Ar\dot{C}HAr' \rightarrow Ar(Ar')CHCH(Ar')Ar \qquad (7)$$

$$RH = \text{isooctane}$$

Reaction 4 is a spin-allowed reaction of the triplet carbene, since there is a $^1/_9$ probability that the encounter of two triplet carbenes will lead to the tetrarylethane in its singlet state. In addition, reaction 5 is spin allowed because the reaction of the carbene with solvent leads to a triplet radical pair as the primary product.

The yields of products are given in Table IV. Clearly, the ratio of singlet–triplet derived products is highest for diphenylcarbene and decreases with increasing substitution at the ortho positions of the aryl groups. It should be noted that steric effects cannot account for the result since they would tend to affect the product distribution in the opposite sense. That is, azine formation[32] for dimesitylcarbene would be more facile than olefin formation, since the former reaction would have led to the less congested compound. Equally, it cannot be argued that the effect is due to a much higher reactivity toward the solvent for dimesitylcarbene vs. diphenylcarbene, since the lifetimes of the carbenes in hydrocarbon solvents show the reverse trend.[17,33] We therefore conclude that the product distribution reflects an increase in the singlet–triplet gap in going from diphenyl- to dimesitylcarbene. The result corroborates the trend observed in the EPR spectra of the carbenes (vide supra) which led to the same conclusion.

Finally, we note that the relative yields of products formed in reactions of the triplet carbenes, i.e., dimerization (reaction 4) and hydrogen abstraction (reaction 5), are

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(30) For I, $k_s$ was obtained by combining $k_S/k_{ST} = 12 \pm 5$ $M^{-1}$[13] with $k_{ST} = (1.1 \pm 0.1) \times 10^{10}$ $s^{-1}$[26]; for IV, $k_S/k_{ST} = (0.14 \pm 0.03)$ $M^{-1}$[17] and $k_{ST} = (1.05 \pm 0.07) \times 10^{10}$ $s^{-1}$.[31]

(31) Sitzmann, E. V., unpublished results.

(32) The azine has been shown to be quite stable under the reaction conditions.[21]

**Table IV. Percentage Yields of Carbene-Derived Products Obtained by Photolysis of Diaryldiazomethanes (0.03 M) in Isooctane at 298 K**

| $Ar(Ar')CN_2$ | $Ar(Ar')CH_2$<br>A | $(Ar(Ar')C)_2$<br>B | $(Ar(Ar')C{=}N)_2$<br>C | $Ar(Ar')CH_2$<br>D | yield of C/yield of (A + B + D) |
|---|---|---|---|---|---|
| $(I)N_2$ | 39 | <1 | 39 | 29 | 0.64 |
| $(II)N_2$ | 47 | 4 | 19 | 30 | 0.23 |
| $(III)N_2$ | 57 | 14 | 5 | 24 | 0.05 |
| $(IV)N_2$ | 15 | 85 | | | 0.00 |

a sensitive function of carbene structure (Table IV). The product yields show that diphenylcarbene readily abstracts hydrogen from the solvent, there being no detectable yields of the dimeric product tetraphenylethylene. By contrast, dimesitylcarbene gives high yields of olefin. As expected, the ratios for mesitylphenyl- and mesityl-*o*-tolycarbenes fall between these extremes. Clearly, the difference in activation energies for the hydrogen abstraction vs. dimerization reactions increases substantially with steric crowding in the carbene itself. Presumably, the dimerization reaction has a low activation energy for all of the carbenes investigated. The reduction in the rate of hydrogen abstraction for the more crowded carbenes may reflect a steric effect and/or an electronic stabilization. However, we are unable to discriminate between these possibilities or the strength of the available data.

## Summary

The triplet–singlet energy gap in diarylcarbenes can be enhanced by substitution of methyl groups at the ortho positions of the aromatic rings. Substitution of this kind forces an expansion of the central C–C–C angle of the carbene which, in turn, leads to an increase in the triplet–singlet energy gap. The effect is manifest in both the EPR spectra of the carbenes and in their chemistry.

**Registry No.** I, 3129-17-7; II, 98678-48-9; III, 98678-49-0; IV, 85236-86-8; V, 883-40-9; VI, 61080-14-6; VII, 65231-75-6; VIII, 98678-50-3; MeOH, 67-56-1.

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[33] Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2831.

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# Development of a Solar Energy Storage Process. Photoisomerization of a Norbornadiene Derivative to a Quadricyclane Derivative in an Aqueous Alkaline Solution

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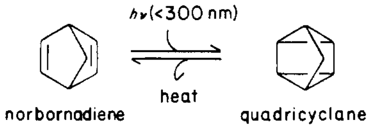
In an aqueous alkaline solution, the photoisomerization of norbornadiene derivatives 1 to quadricyclane derivatives 2 was investigated. Upon irradiation with sunlight, **1a–g** isomerized quantitatively to **2a–g** even in the presence of air, although the reaction medium was water which was usually reactive toward cyclopropane and cyclobutane rings of quadricyclane. In fact, **1h–j** gave undesirable compounds on irradiation under the same conditions. In order to increase solubility and the amount of heat being stored, we synthesized compounds **3** which had two norbornadiene chromophores in the same molecule. From analyses of the spectral data and the photoreactivities of **3**, we confirmed the same behavior as those of **1**, i.e., the two neighboring chromophores did not interfere. Since the reaction medium is water and the photoisomerization by sunlight is clean, these water-soluble norbornadiene derivatives **1a–g**, **1k–m**, and **3a–c** are promising for solar energy storage.[1]

Solar energy storage has received much attention from the viewpoint of solving today's energy problem.[2] Valence isomerization of norbornadiene and quadricyclane is one of the most promising systems for solar energy storage, and many chemists have studied it for the last decade.[2,3] This system has an inherent disadvantage that norbornadiene cannot absorb sunlight by itself. To solve this problem, many improvements have been investigated; these are mainly classified into two categories: (i) use of sensitizers and (ii) introduction of chromophores. In the former, Kutal et al.[4] proposed an iridium complex ($\pi\pi^*$ exitation) as the sensitizer rather than acetophenone or benzophenone ($n\pi^*$ exitation) which easily reacted with norbornadiene and quadricyclane to give undesired adducts.[5]



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[1] In the system, sunlight conversion efficiency is much lower than a solar battery in actual use. However, the system has merits in the points that energy of sunlight is converted to the chemical energy and the chemical energy is able to be stored for future use.

[2] (a) Sasse, W. H. F. "Solar Power and Fuels"; Bolton, J. R., Ed.; Academic Press: New York, 1977; Chapter 8. (b) Laird, T. *Chem. Ind. (London)* **1978**, 186. (c) Jones, G., II; Chiang, S.; Xuan, P. T. *J. Photochem.* **1979**, *10*, 1. (d) Scharf, H.-D.; Fleischhauer, J.; Leismann, H.; Ressler, I.; Schlenker, W.; Weitz, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 652.

[3] (a) Hautala, R. R.; King, R. B.; Kutal, C. "Solar Energy; Chemical Conversion and Storage", The Humana Press: Clifton, NJ; 1979. (b) Philippopoulos, C.; Marangozis, J. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 458. (c) Maruyama, K.; Tamiaki, H. *Kagaku Kogyo* (*Osaka*) **1984**, *58*, 319.

[4] (a) Kutal, C. *Adv. Chem. Ser.* **1978**, *168*, 158. (b) Grutsch, P. A.; Kutal, C. *J. Chem. Soc., Chem. Commun.* **1982**, 893.

[5] (a) Hammond, G. S.; Turro, N. J.; Feisher, A. *J. Am. Chem. Soc.* **1961**, *83*, 4674. (b) Hammond, G. S.; Wyatt, P.; DeBore, C. D.; Turro, N. J. *J. Am. Chem. Soc.* **1964**, *86*, 2532. (c) Gorman, A. A.; Leyland, R. L.; Rodgers, M. A. J.; Smith, P. G. *Tetrahedron Lett.* **1973**, 5085. (d) Hautala, R. R.; Little, J. *Adv. Chem. Ser.* **1978**, *184*, 1. (e) Hautala, R. R.; King, R. B.; Sweet, E. M.; Little, J. L.; Shields, A. W. *J. Organomet. Chem.* **1981**, *216*, 281.

0022-3263/85/1950-4742$01.50/0