to Prof. Louis Bellon on his 70th birthday.

Registry No. **1**(O), 67-56-1; **2**(O), 64-17-5; **3**(O), 71-36-3; **4**(O), 67-63-0; **5**(O), 75-65-0; **6**(S), 75-08-1; **7**(S), 107-03-9; **8**(S), 75-33-2; **9**(S), 75-66-1; **10**(S), 352-93-2; **11**(S), 110-01-0; **12**(S), 758-16-7; **13**(S), 2782-91-4; **14**(S), 631-67-4; **15**(S), 16703-45-0; **16**(S), 3735-92-0; **17**(S), 597-51-3; **18**(O), 3553-80-8; **19**(O), 37174-63-3; **20**(S), 544-40-1; **21**(S), 822-38-8; **22**(O), 76-22-2; **23**(S), 13461-16-0; **24**(S), 6596-81-2; **25**(S), 25433-07-2; **26**(S), 3418-46-0; **27**(S), 25444-93-3; **28**(S), 13673-63-7; **29**(O), 21892-80-8; **30**(S), 1908-87-8; **31**(S), 5685-07-4; **32**(S), 21364-38-5; **33**(S), 2254-94-6; **34**(O), 694-32-6; **35**(O), 497-25-6; **36**(O), 2682-49-7; **37**(O), 59167-68-9; **38**(O), 25444-99-9; **39**(O), 1849-01-0; **40**(O), 59-49-4; **41**(O), 934-34-9; **42**(S), 13431-10-2; **43**(S), 29704-02-7; **44**(S), 20406-60-4; **45**(S), 61406-12-0; **46**(S), 24421-05-4; **47**(S), 29228-88-4; **48**(S), 5840-81-3; **49**(S), 96-53-7; **50**(S), 25433-05-0; **51**(S), 6670-14-0; **52**(S), 5351-51-9; **53**(S), 2360-22-7; **54**(S), 2382-96-9; **55**(S), 149-30-4.

Supplementary Material Available: A more detailed version of this paper, containing a discussion of β_{cyc} values, tables of the experimental dipole moments and equilibrium constants used for the calculation of the coefficients *a*, *b*, and *c*, as well as tables of these parameters, the dipole moments and equilibrium constants used for the determination of the β_m values for the bases studied in this work, β values for cyclic and acyclic bases of closely related structures, and β_{cyc} values for amphiprotic oxygen and sulfur bases (37 pages). Ordering information is given on any current masthead page.

Reaction of Diphenylcarbene with Diphenyldiazomethane[†]

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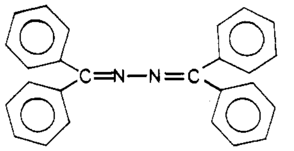
The reaction of diphenylcarbene with diphenyldiazomethane, which leads to the corresponding azine, has been examined by a combination of laser flash photolysis techniques and product studies. In acetonitrile at room temperature, the apparent rate constants for carbene plus diazo compound are 2.3×10^{10} and 3.4×10^7 M^{-1} s^{-1} for the singlet and triplet species, respectively.

A wealth of kinetic data now exists on the reactions of singlet and triplet arylcarbenes with various substrates.[1,2] However, there appears to be virtually no data concerning one of their most common reactions, that of the carbene with its parent diazo compound. Product studies on the thermolysis of diphenyldiazomethane in hydrocarbon solvents show that substantial amounts of benzophenone azine (I)[3,4] are formed.


(1)

I

Experimentally, the reaction belongs to a general class where a triplet ground-state species appears to react with a singlet substrate to yield molecular products in apparent contravention of the Skell–Woodworth rules.[5] Thus, alcohols,[3,6-8] nitriles,[9,10] ketones,[11] and thioketones[12] all quench the optical absorption spectra of the triplet carbene. The usual explanation for this type of observation has been the proposal, originally advanced by Bethell,[4] that the singlet and triplet states of the carbene are in equilibrium; the reactivity is then attributed to the singlet population present. An alternative explanation, which we have suggested for the reactions of alcohols,[6] amines,[13] and carbon tetrachloride[14] with diphenylcarbene is that the triplet may not simply function as a reservoir for the singlet carbene through an equilibrium mechanism but may be directly involved in the above reactions. The direct reaction of the triplet carbene with the substrate has been definitely established in some cases of carbene addition to thioketones.[12] For example triplet fluorenylidene reacts with adamanthanethione with a rate constant of 6.4×10^9 M^{-1} s^{-1} in Freon 113 at room temperature. Since the reaction is essentially diffusion controlled, it cannot be explained in terms of a small population of an upper (i.e., singlet) state.

In this paper we report the results of product and laser flash photolysis studies which lead to rate constants for the reactions of singlet and triplet diphenylcarbene with diphenyldiazomethane in acetonitrile solution.

Experimental Section

Materials. Diphenyldiazomethane was prepared by the literature method[15] and purified by vacuum sublimation. Methanol and acetonitrile (Aldrich) were spectroscopic grade and were purified by distillation from calcium hydride. Authentic samples

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[†] Issued as NRCC-28638.

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of diphenylmethyl ether and benzophenone azine were obtained from the reaction of diphenylcarbene in the presence and absence of methanol, respectively.[6]

Product Studies. Product studies related to the singlet reaction were carried out on thoroughly degassed acetonitrile solutions of diphenyldiazomethane containing methanol (usually 3.0 M). Photolyses were carried out at room temperature with a tungsten filament lamp. Products were analyzed by GC–MS and quantified by GC using authentic materials as calibrants.

Product studies were also carried out on acetonitrile solutions of diphenyldiazomethane (10 mM) in the absence of methanol. Two methods of irradiation were used. In one experiment, solutions were irradiated with a tungsten filament lamp (~1 min, ~20% conversion). In a second experiment, the pulses from a Molectron UV-24 nitrogen laser (337.1 nm; ~8 ns; 10 mJ/pulse) were employed.

Laser Flash Photolysis. The laser flash photolysis system used in these experiments has been described in detail elsewhere.[16] Samples were irradiated by the pulses (337 nm) from a nitrogen laser; the kinetic experiments described in this work required the use of relatively high concentrations of diphenyldiazomethane. Fortunately, the extinction coefficient of diphenyldiazomethane (ϵ_{337} = 330 M^{-1} cm^{-1}) is low at the laser wavelength. However, in order to attain the concentrations necessary for this work and at the same time to sustain reasonable optical properties for the sample cell, a special cuvette (0.3-mm path length) was required.

The optical absorption of triplet diphenylcarbene (λ_{max} ~310 nm)[7] is normally detected readily when dilute, nitrogen-purged solutions of diphenyldiazomethane are used. However, at the concentrations required for some of the experiments described herein, the solutions were not sufficiently transparent at this wavelength. Accordingly, benzophenone oxide[17] (λ_{max} = 410 nm), which is produced by reaction of the carbene with oxygen, was used as a kinetic probe. In our experiments, the solutions were purged by a gas mixture (Matheson) containing 1% oxygen in nitrogen, which provided enough oxygen to generate a suitable signal from the carbonyl oxide (vide infra), while allowing the carbene–diazo reaction to be the dominant process.

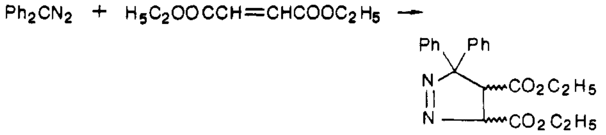
Results

Reactions of Singlet Diphenylcarbene. Photolysis of diphenyldiazomethane (0.056 and 0.198 M) at room temperature and in the absence of a quencher gave substantial yields of benzophenone azine. In principle, the azine should arise from the reaction of singlet carbene with the parent diazo compound. The rate constant for this reaction can be determined by using a concentration of methanol high enough to trap nearly all the singlet before it can intersystem cross to the triplet. Under these conditions, there is a competition between methanol and diazo compound for singlet carbene.

Kinetic analysis then gives eq 2. This analysis is valid when the reaction is carried out to low conversion and

$$\frac{k_{\mathrm{MeOH}}{}^{s}[\mathrm{MeOH}]}{k_{\mathrm{diazo}}{}^{s}[\mathrm{diazo}]} = \frac{[\text{diphenyl methyl ether}]}{[\text{benzophenone azine}]} \qquad (2)$$

when the unreacted diazo compound is destroyed without the intermediacy of the carbene. A quantitative analysis of the products coupled with the value of $k_{\mathrm{MeOH}}{}^{s}$, previously determined,[19] yields the desired rate constant $k_{\mathrm{diazo}}{}^{s}$. Thoroughly degassed solutions of diphenyldiazomethane in acetonitrile containing methanol (3.0 M) were photolyzed at room temperature with a tungsten filament lamp. The photolysis was monitored by UV–vis spectroscopy and was carried out to ~10% conversion. Unreacted diazo was then destroyed in the dark using the known 1,3-dipolar cycloaddition of dialkyl fumarate to diazo compounds[20] (eq 3).



(3)

The yields of ether and azine were then corrected for the amount of product obtained in a parallel experiment in which the solution was not irradiated. The corrected molar ratios of ether-to-azine were 28.9 and 8.1 for initial diazo concentrations of 0.056 and 0.198 M, respectively. Introducing $k_{\mathrm{MeOH}}{}^{s} = 1.24 \times 10^{10}$ M^{-1} s^{-1} [21] leads to $k_{\mathrm{diazo}}{}^{s} = 2.3 \times 10^{10}$ M^{-1} s^{-1}, independent of the diazo concentration. The fact that $k_{\mathrm{diazo}}{}^{s}$ was independent of the concentration of diazo precursor supports that both products arise from the same state of the carbene. It follows that this state must be the singlet state of the carbene, since at 3.0 M methanol the singlet reaction with methanol is ~12 times more rapid than intersystem crossing to the triplet ground state.[23]

Reactions of Triplet Diphenylcarbene. In order to characterize the reaction of triplet diphenylcarbene, product studies were carried out at 295 K in deaerated solutions, using both laser and lamp irradiation. In the laser experiment, solutions of diazo compound (10 mM) were exposed to 600 nitrogen laser pulses, leading to about 20% conversion. GC–MS analysis indicated two major products: tetraphenylethylene, resulting from carbene self-reaction, and benzophenone azine (I). Carbene self-reaction is expected to be an important product under conditions of pulsed irradiation.[7] By contrast, continuous irradiation using a tungsten lamp yielded azine but only traces of tetraphenylethylene. A few other minor products were detected by GC, but their detailed characterization was not pursued. Our results under laser irradiation differ from those of Turro et al.,[24] who obtained a greater variety of products in the laser irradiation of diphenyldiazomethane than in the lamp irradiation. Most likely this difference is the result of the use of a different laser wavelength and power (249 nm, ~180 mJ/pulse) than that used in our experiments.

In the time-resolved experiments, the concentrations of diazo precursor required to achieve a suitable degree of carbene–diazo reaction are such that the solutions are not transparent at λ ~310 nm, where the carbene absorbs strongly. Under these conditions, it is not possible to examine the reaction directly by monitoring the carbene decay. The problem was readily circumvented by using an appropriate probe molecule, which yields an easily detectable signal upon reaction with the carbene. After testing various substrates we found that oxygen, which yields the transient benzophenone oxide (λ_{max} = 410

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(21) The value of $k_{\mathrm{ST}}/k_{\mathrm{MeOH}}{}^{s}$ has been reported as 0.26 ± 0.04 M, where k_{ST} is the rate constant for singlet-to-triplet intersystem crossing,[19] from which the authors estimated $k_{\mathrm{MeOH}}{}^{s} = 3.5 \times 10^{10}$ M^{-1} s^{-1}, based on $k_{\mathrm{ST}} = 9.1 \times 10^{9}$ s^{-1}. The value of k_{ST} in acetonitrile at room temperature has been revised to $k_{\mathrm{ST}} = (3.23 \pm 0.19) \times 10^{9}$ s^{-1}.[22] Using this corrected value and the original ratio of $k_{\mathrm{ST}}/k_{\mathrm{MeOH}}{}^{s}$, we calculate $k_{\mathrm{MeOH}}{}^{s} = 1.24 \times 10^{10}$ M^{-1} s^{-1}.

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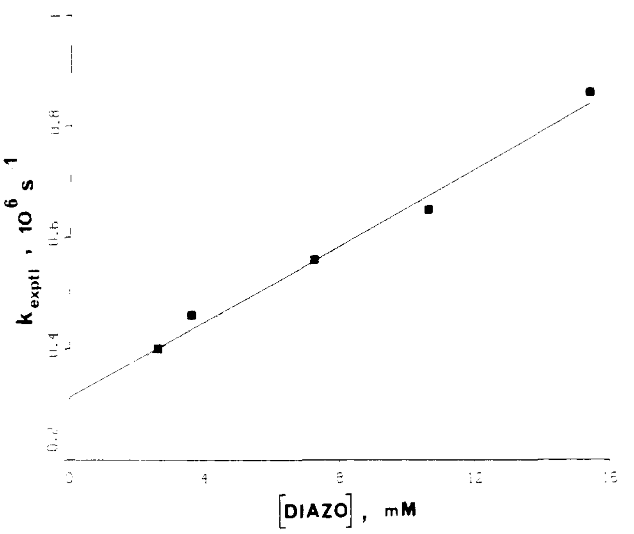


Figure 1. Plot of k_{exptl} values extrapolated to zero laser dose vs concentration of diphenyldiazomethane in acetonitrile at 295 K, according to eq 4.

nm),[17,18] was a convenient probe. At low laser doses, the buildup of the probe signal approaches pseudo-first-order kinetics; the experimental rate constant, k_{exptl}, was related to those of interest via eq 4. In this equation, k_0 is the

$$k_{exptl} = k_0 + k_{O_2}{}^{T}[O_2] + k_{diazo}{}^{T}[diazo] \qquad (4)$$

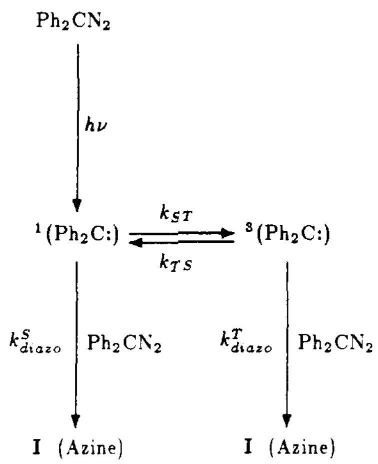
rate constant for carbene decay in the absence of oxygen and at "zero" diazo concentration, $k_{O_2}{}^{T}$ is the rate constant for the scavenging of carbene by oxygen ($k_{O_2}{}^{T} = 5 \times 10^9$ M^{-1} s^{-1}),[17,18] and $k_{diazo}{}^{T}$ is the bimolecular rate constant for carbene reaction with the diazo compound.

At high laser powers, the decay of the carbene incorporates second-order processes resulting from carbene self-reaction; under these conditions the behavior deviates from that represented by eq 4. In order to avoid these complications, the growth kinetics of the probe signal were determined each diazo concentration for five different laser doses (adjusted with calibrated neutral density filters covering the 11–100% transmittance range). The value of k_{exptl} was then extrapolated to zero laser dose, where eq 4 provides a full description of the system. Figure 1 shows a plot of k_{exptl} values (extrapolated to zero laser dose) as a function of [diazo]; from the slope we obtain $k_{diazo}{}^{T} = (3.4 \pm 0.5) \times 10^7$ M^{-1} s^{-1} (errors as $\pm 2\sigma$) in acetonitrile at 295 K. These experiments were carried out at constant oxygen concentration, as indicated in the Experimental Section. The carbonyl oxide lifetimes exceeded 100 μs. No other signal that could be identified as an absorbing product or intermediate in the carbene–diazo reaction was detected.

Discussion

The competition experiments described above demonstrate that the singlet state of diphenylcarbene was scavenged by diphenyldiazomethane at a rate which was essentially diffusion controlled. The conclusion is unequivocal, since the rapid reaction between the singlet carbene and the kinetic standard, methanol, has been investigated by picosecond spectroscopy which showed that there were no complications with the reaction mechanism.[19] It was therefore a simple matter to establish conditions for a competition experiment in which the singlet state of the carbene was scavenged by methanol and diazo compound before it underwent singlet-to-triplet intersystem crossing. The rate constant, $k_{diazo}{}^{s} = 2.3 \times 10^{10}$ M^{-1} s^{-1}, therefore represents an accurate kinetic description of the singlet carbene–diazo reaction.[25]

Scheme I



The interpretation of the data for the reaction of the triplet carbene with diazo compound is not as straightforward. The measured rate constant offers a true description of the lifetime of the triplet carbene in the presence of diazo compound. However, several mechanistic interpretations are possible.

A direct reaction between the triplet carbene and its diazo precursor is undoubtedly the simplest interpretation of these results. Similar interpretations have been questioned in the past because of the spin-forbidden nature of the overall process. Instead, a frequently invoked mechanism that explains reactions of this type involves reaction of a singlet carbene that is in thermal equilibrium with the ground-state triplet. The triplet carbene thus behaves as a reservoir for the highly reactive singlet species.[4]

We have already reported evidence that in the cases of methanol,[6] amines,[13] carbon tetrachloride,[14] and thioketones[12] the reaction with diphenylcarbene is best interpreted in terms of a direct reaction of the triplet carbene involving a surface crossing.

Under the experimental conditions employed to study the kinetics of the triplet carbene reaction $k_{ST} \gg k_{diazo}{}^{S}$[diazo] and the overall triplet reaction will be given by eq 5, which takes into account both possible mechanisms (Scheme I), where $K = k_{TS}/k_{ST}$. If the first term after the

$$k_{diazo}{}^{T}(\text{observed}) = k_{diazo}{}^{T}(\text{true}) + Kk_{diazo}{}^{S} \qquad (5)$$

equal sign is negligible, i.e., if all the observed triplet reactivity is due to the equilibrium concentration of singlet carbene, then the ratio

$$k_{diazo}{}^{T}(\text{observed})/k_{diazo}{}^{S} = K$$

should be a constant, independent of the nature of the substrate, since it should only reflect the intrinsic properties of the carbene. We have demonstrated earlier[6,13] that this is not the case; thus, such ratios are 2×10^{-3}, $\leq 7.2 \times 10^{-4}$, and $\leq 2.2 \times 10^{-4}$ for methanol, *n*-butylamine, and *tert*-butylamine, respectively. The experimental value for diphenyldiazomethane derived from our work is 1.5×10^{-3}. We suggest that the mechanism for the reaction of triplet diphenylcarbene with its parent diazo is analogous to that proposed for methanol and amines, i.e., direct reaction from the triplet manifold via a surface crossing. We base

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(25) One referee has suggested the possibility of a carbene–methanol ylide as the reactive species in the singlet azine formation. While we cannot entirely rule out this possibility, it is clear that azine formation does not require methanol and that our kinetic data does not require that we invoke an additional intermediate.

this conclusion on the fact that the smallest of the ratios mentioned above (i.e., $\leq 2.2 \times 10^{-4}$ for *tert*-butylamine) effectively sets an upper limit for the fraction of reaction that can take place from an equilibrated singlet state. Given the fact that the observed reactivity is approximately an order of magnitude higher than could be expected from such a model, we believe that the simplest explanation for the observed triplet reactivity is a direct triplet–diazo reaction leading to the product ground state, since there is no evidence for excited product (azine) formation. It should be noted however, that our conclusion in this case is based on the comparison with other systems reported earlier,[6,12–14] rather than on entirely independent evidence.

To the best of our knowledge, the rate constants reported here are the first values reported for carbene–diazo reactions.[26] Both singlet and triplet carbene states were found to react with the parent diphenyldiazomethane with rate constants of 2.3×10^{10} and 3.4×10^{7} M^{-1} s^{-2}, respectively, in acetonitrile at room temperature. The partition between singlet and triplet processes will be largely determined within the singlet manifold; i.e., at sufficiently high diazo concentrations or in the presence of other scavengers (such as the experiments using 3 M methanol discussed above) the carbenes will be trapped before they have an opportunity to undergo intersystem crossing to the triplet state.

Registry No. $PhC(=N_2)Ph$, 883-40-9; $Ph_2C=NN=CPh_2$, 983-79-9; $Ph_2C=CPh_2$, 632-51-9; $PhCH_2Ph$, 3129-17-7.

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[26] A rough estimate of 3×10^{7} M^{-1} s^{-1} for $k_{diazo}{}^{T}$ was reported earlier[27] on the basis of a lifetime determination using dielectric loss techniques.

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Quaternary Ammonium Tetrakis(diperoxotungsto)phosphates(3–) as a New Class of Catalysts for Efficient Alkene Epoxidation with Hydrogen Peroxide

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The use of quaternary ammonium tetrakis(diperoxotungsto)phosphates(3–) in conjunction with hydrogen peroxide as the primary oxidant in an aqueous/organic biphase system provides an efficient, versatile, and synthetically valuable catalytic method for olefin epoxidation. By this method, a variety of water-insoluble unactivated alkenes, internal or terminal, open-chain or cyclic, isolated or carrying diversified functionalities, were epoxidized in high yields under mild conditions and after relatively short reaction times.

In connection with our works on the oxidation of organic substrates with hydrogen peroxide catalyzed by the tungstate–phosphate ion association,[1,2] we recently succeeded in isolating and structurally characterizing by X-ray diffraction analysis a novel tungsten peroxo complex, tetrahexylammonium tetrakis(diperoxotungsto)phosphate(3–) (**1a**).[3] Interestingly, we observed that this

$$Q^{+}{}_{3}\left\{PO_4\left[W(O)(O_2)_2\right]_4\right\}^{3-}$$

1

a ; $Q^{+} = \left[(C_6H_{13})_4N\right]^{+}$

b ; $Q^{+} = \left[(C_8H_{17})_3NCH_3\right]^{+}$

c ; $Q^{+} = \left\{\left[C_{18}H_{37}(76\%) + C_{16}H_{33}(24\%)\right]_2N(CH_3)_2\right\}^{+}$

complex, besides being a good stoichiometric reagent for olefin epoxidation in nonprotic solvents, also acted as a catalyst for the same reaction when used in conjunction with hydrogen peroxide as the primary oxidant in an aqueous/organic biphasic system.

Examples of well-defined early transition metal peroxo species displaying catalytic activity are scanty in the literature,[4] despite the number of such complexes known.[5] This prompted us to try out whether a general method for the synthesis of epoxides might be worked out, based on the above oxidizing system. In the course of this study, we had to face two main problems, the first one related to the efficiency of the catalyst complex involved and the second one concerned with the control of undesired side effects caused by the oxidizing system itself.

It is known from the phase-transfer technique that the organic structure of the catalyst cation not only influences its ability to transport an anion from the aqueous to the organic phase but also strongly affects the rate of the organic phase reaction.[6] Therefore, various onium moieties of suitable lipophilic character (other than tetrahexylammonium) were preliminarily tested as a counterion in the synthesis of **1**, in the hope of isolating some complex that might exhibit an efficiency higher than **1a** as an oxidation catalyst. This led us to single out two new terms of **1**, **1b** and **1c**, which actually appeared to fulfill our expectations.

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