can differentiate unequivocally between urea in tetragonal or hexagonal lattices, which correspond to free urea and the clathrate, respectively. According to this analysis, typical samples contained over 90% of the urea in the hexagonal form. Scanning electron micrographs revealed the presence of both types of crystals—predominantly those that were hexagonal—and was in qualitative agreement with the Raman data (which has been established to correlate with X-ray structures)[17] as was the elemental analysis.[18] The latter yielded an urea–ketone molar ratio of 8.6, to be compared with 7.6 that can be estimated on the basis of molecular dimensions. Irradiation of the 5-nonanone clathrate at room temperature under nitrogen[19] followed by addition of methanol led to Type II products, though, to our surprise, essentially *only one cyclobutanol isomer.*[20] This was characterized as the one having the methyl and hydroxyl groups in the cis configuration.[21] Neither Type I products, such as valeraldehyde or *n*-octane, nor products containing urea moieties were detected. This is consistent with laser flash photolysis experiments which show that urea is a very inefficient quencher of carbonyl triplets.[23]

Prolonged irradiation of the samples led to further photodecomposition of the 2-hexanone produced, affording acetone and, similarly, essentially only one cyclobutanol.[24] This, judging from its gas-chromatographic behavior, is also believed to be the cis isomer.

The cyclization to fragmentation ratio for 5-nonanone in urea was 0.67, compared with 0.32 in methanol, taking into account total cyclobutanol. The two ratios are 0.65 and 0.19, respectively, if only the cis isomer is taken into consideration. Product quantum yields for solid samples such as these are difficult to measure, although judging from the irradiation times required (by comparison with liquid samples), they must be only slightly lower.

The absence of Type I products is surprising in view of the fact that some Type I reaction usually takes place in solution[25] and that this is the only decay path available to the excited ketone that does not require the formation of a ring structure or transition state. Some Type I process may of course occur, provided the only reaction path of the germinate radical pair is its recombination to yield the parent ketone.

The Type II reaction involves a six-center transition state;[26] the steric demands of this transitional conformation, as well as those of the cyclobutanol produced, are such that the preparation of an inclusion product meeting such demands would be very difficult.[14] However, the geometry that can be attained by an included molecule may not necessarily be that permitting inclusion to occur. Examination of space filling models shows that the formation of the *cis*-cyclobutanol has less stringent rotational requirements, thus favoring the formation of this isomer. In fact, the cyclobutanol obtained, having both alkyl groups in pseudoequatorial positions, is expected to be more compact. Hydrogen bonding to the crystal lattice may help keep the biradical conformation quasi-frozen long enough for cyclization to occur (included molecules are known to have preferred orientations[15] in the urea channels). Related observations have been made in the irradiation of benzoin alkyl ethers adsorbed on silica gel,[27] where the formation of only one cyclobutanol was noted.

An obvious concern is whether the six-center abstraction required for the Type II reaction occurs at the expense of the integrity of the crystal lattice. This seems not to be the case for the 2-hexanone produced in the primary photodecomposition, since further photocyclizaton follows the same pattern, i.e., stereospecificity. Preliminary experiments with 2-undecanone show the same type of behavior, although in this case ~7% *trans*-cyclobutanol is also formed. These observations suggest, but do not completely confirm, that the cyclobutanols also remain included molecules.

Acknowledgment. We thank Dr. A. P. Roth for recording the electron micrographs.

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[18] The sample used in most studies gave C, 32.14%; N, 36.67%; H, 8.09%.

[19] Typically the 313-nm line for a mercury lamp was isolated with an interference filter. A few experiments using Rayonet RPR-3000 lamps did not show any difference with the 313-nm experiments.

[20] Only 3% of the trans isomer could be detected, even in an experiment exceeding 95% conversion.

[21] The two isomers were obtained in better than 90% purity by preparative gas chromatography of the reaction products in *tert*-butyl alcohol and characterized by ^{13}C and ^{1}H NMR spectroscopy. One isomer had ^{13}C chemical shifts (in ppm from Me$_4$Si) of 76.3 (C-1), 39.1 (C-2), 14.7 (Me at C-2), and 40.9 (CH$_2$ at C-1), consistent with the methyl being cis to the OH group. The other isomer showed the corresponding signals at 77.0, 43.8, 14.1, and 33.5, respectively, which is consistent with the methyl group being trans to the OH.[22] The ^{1}H chemical shift of the Me at C-2 were affected by successive additions of the shift reagent Pra-Resolve-II-d_{30} to a different extent for each isomer. The cis isomer was more affected, consistent with the above assignment. The isomer obtained in the urea complexes has the same mass spectra (GC-MS) as the authentic cis isomer.

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[23] These experiments were carried out by using benzophenone in wet acetonitrile and led to $k_q \ll 4 \times 10^4$ M^{-1} s^{-1}.

[24] This fragmentation may introduce some error in the cyclization–fragmentation ratios from 5-nonanone as a result of product photolysis. The cyclization product from 2-hexanone contains 5% of the trans isomer.

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[27] Benzoin methyl ether adsorbed on dry silica gel at −78 °C gives 40% Type I rearrangement product, 6% Type II cleavage (to deoxybenzoin), and 6% of a single oxetanol. The isopropyl ether under the same condition gives 50% Type I rearrangement product, 13% Type II cleavage, and 20% of a single oxetanol. The nature of the products is attributed to conformational control and restricted movement induced by the silica gel (Mayo, P. de; Nakamura, J.; Tsang, P. W. K.; Wong, S. K. *J. Am. Chem. Soc.* **1982**, *104*, 6824–6825. Nakamura, A., unpublished observations).

Determination of the Heat of Reaction for the Formation of Diphenylcarbene from Diphenyldiazomethane Using Photoacoustic Calorimetry

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In recent years, there has been a growing interest in elucidating the energetics of carbene reactions. In part, this growth has been stimulated by the use of these intermediates as a testing ground for molecular orbital theory.[1] To date, the central thrust of carbene research has been directed toward establishing both the spin multiplicity and the energy separation between the ground and excited states.[2] With the exception of methylene,[3] there has been no experimental determination of either the heats of formation of these reactive intermediates or the energetics for their reactions. In this communication, a direct measurement of the heat of reaction is reported for both the formation of diphenylcarbene from diphenyldiazomethane in degassed benzene and the formation of diphenylmethyl ethyl ether resulting from singlet carbene insertion into the O–H bond in ethanol.

Photoacoustic calorimetry is a method we have recently developed for determining the heat of reaction from ground-state

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Table I. Nonradiative Quantum Yields[4] and Normalized Photoacoustic Signal for the Calibration Compounds

compound	$\Phi_{nr}{}^a$	normalized photoacoustic signal
tetraphenylethylene	0.82	1.00
rhodamine-6G	0.47	0.67
anthracene	0.41	0.51
perylene	0.32	0.42
4-phenylbenzophenone	0.30	0.41

[a] Calculated as described in ref 4. For anthracene and 4-phenylbenzophenone, the reported triplet lifetimes indicate that no appreciable decay of the triplet state in degassed benzene is occurring on the order of the resonance frequency of the transducer. Data used for calculating the nonradiative quantum yield can be found in ref 9.

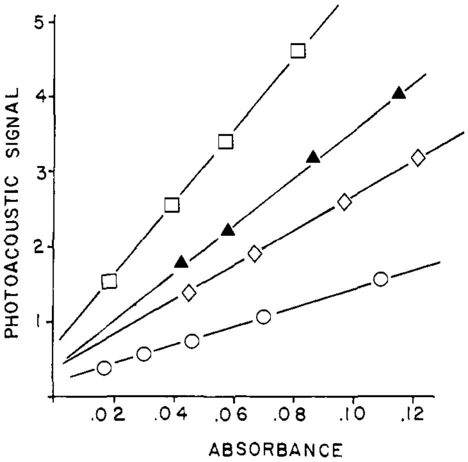


Figure 1. Photoacoustic signal vs. sample absorbance for diphenyldiazomethane and several of the calibration compounds. (□) Diphenyldiazomethane, (▲) tetraphenylethylene, (◇) rhodamine-6G, (○) 4-phenylbenzophenone.

molecules to photogenerated reactive intermediates.[4] In order to use this technique, the reaction being studied must satisfy the following two conditions: the reactive intermediate of interest must (1) be formed in less than 100 ns and (2) have a lifetime greater than 10 μs. The experiment involves the detection and integration of the photogenerated acoustic wave. The source of the acoustic wave is the heat released from the decay of the photoexcited species to the intermediate of interest. Photolysis is initiated by a Lambda Physic K600 nitrogen laser (5-ns pulse, 337 nm, 0.1 mJ); the pulse energy is measured by a Laser Precision Rj-7200 Ratiometer (RjP-735 pyroelectric probe). The photoacoustic wave is detected by a lead-zirconate, lead-titanate transducer, amplified by a PAR 113 preamplifier, and digitized with a LeCroy WD-8256 Waveform Digitizer. The laser power and digitized wave are inputed into a Digital MINC23 lab computer. The waveform is then normalized to the laser power and averaged for 20 laser shots. The resulting waveform is integrated for 1 μs around the first positive excursion. Diphenyldiazomethane was synthesized and purified by standard procedures.[5] For our studies, the solutions of the diazo compound did not exceed 10^{-5} M. The calibration of the instrument employing EtOH as the solvent has been thoroughly discussed in a previous report.[4] The calibration of degassed benzene was performed in a similar manner. The compounds used and their calculated nonradiative quantum yields are given in Table I. A plot of the photoacoustic signal vs. sample absorbance for several of the calibration compounds is given in Figure 1. The resulting calibration curve is shown in Figure 2.

Diphenyldiazomethane is an ideal chemical system to study using our calorimeter. Photolysis with 337-nm light produces singlet diphenylcarbene, which intersystem crosses (halflife ≈ 100 ps[2d]) to form triplet carbene (eq 1). The energy difference

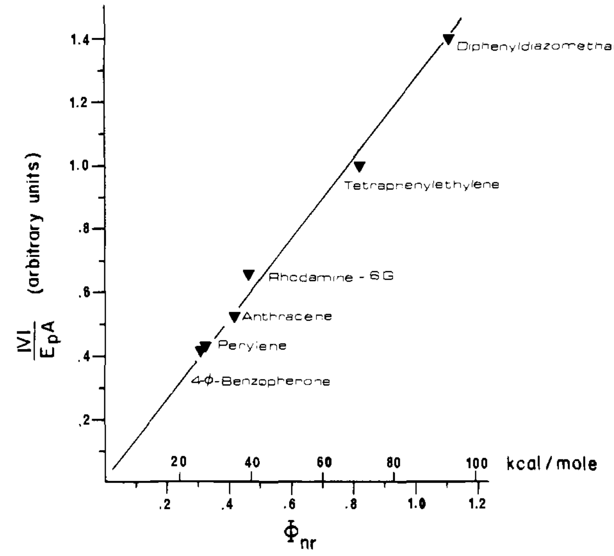
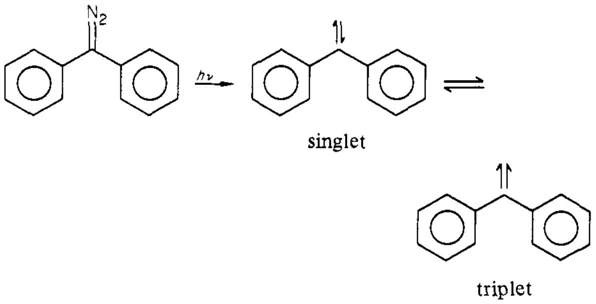


Figure 2. Instrument calibration curve for benzene.



(1)

between the singlet and triplet carbene has been determined to be 5.1 kcal/mol.[2d] Hence, at 1 ns following photolysis, greater than 99% of the carbene is in the triplet state. In degassed benzene solution at 25 °C, diphenylcarbene decays via dimerization and/or azine formation with a rate of $\sim 5 \times 10^9$ mol^{-1} s^{-1}.[5] Before we can determine the heat of reaction for eq 1, we must consider two additional points. First, if there was significant ground-state complexation between diphenyldiazomethane molecules, it would be possible for the initially formed singlet carbene to react with a ground-state diazo molecule. We would expect the percentage of complexed molecules to change in solutions of varying concentration of the diazo compound. This would be manifested by a nonlinear plot of sample absorbance vs. photoacoustic signal. However, the observed plot is linear (Figure 1) indicating that if ground-state complexation is occurring, the concentration is not large enough to contribute to the observed photoacoustic wave form. Secondly, the photoproduct, tetraphenylethylene, absorbs 337-nm light and could complicate the determination of the heat of reaction for the reaction of interest. For a typical accumulation of 20 laser shots, we have determined that less than 1% of the sample is photolyzed. Therefore, the photoproduct, tetraphenylethylene, is not formed in high enough concentration to contribute to the observed wave form. In conclusion, since triplet carbene is produced in high yield ($\Phi = 0.78$[6]) in less than a nanosecond and has a lifetime in degassed benzene of approximately 1 ms,[7] the above conditions for the application of photoacoustic calorimetry are satisfied. Assuming $\Phi = 0.78$, for the photoelimination of nitrogen,[8] the heat of reaction (Figure 2) for

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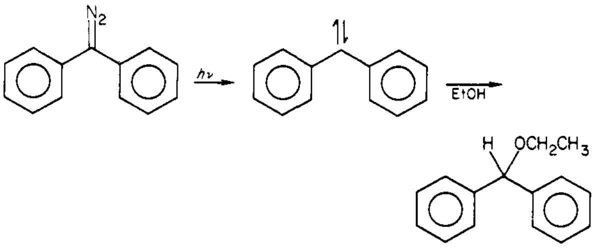
[8] If the quantum yield for dissociation were unity, the heat of reaction would be −9.8 kcal/mol. Therefore, for this particular reaction, the exothermicity is relatively insensitive to the quantum yield.

the formation of triplet diphenylcarbene from diphenyldiazomethane in benzene is $\Delta H = -12 \pm 2$ kcal/mol. This is to be contrasted with the endothermic heat of reaction of $\sim$33 kcal/mol for the formation of triplet methylene from diazomethane.[3]

In addition, this technique can be used to study reactions of carbenes. Examination of the photolysis of diphenyldiazomethane in neat ethanol results in the formation of diphenylmethyl ethyl ether (eq 2) with a quantum yield of $\Phi = 0.78$.[6] In neat ethanol,



(2)

the rate of insertion of the singlet carbene into the O–H bond, $k = 3.5 \times 10^{10}$ mol^{-1} s^{-1},[2d] will be approximately 2 orders of magnitude faster than the intersystem crossing rate of the carbene. Thus, the resulting ether will be formed on the picosecond time scale, satisfying the requirements for the application of photoacoustic calorimetry. We find that the heat of reaction from diphenyldiazomethane to diphenylmethyl ethyl ether is $\Delta H = -54 \pm 2$ kcal/mol. Assuming that the energy of the carbene is solvent independent, this result indicates a heat of reaction of -47 ± 2 kcal/mol for the formation of diphenylmethyl ethyl ether from singlet diphenylcarbene in ethanol.

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Registry No. Diphenyldiazomethane, 883-40-9; diphenylcarbene, 3129-17-7; ethanol, 64-17-5.

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Cation Radical Diels–Alder Reactions of Electron-Rich Dienophiles

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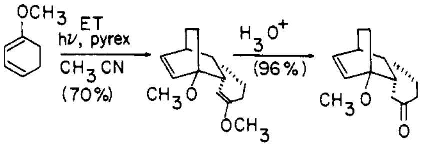
The exceptional reactivity and selectivity of cation radicals of hydrocarbon conjugated dienes as dienophilic components in Diels–Alder cycloadditions is now well documented.[1-5] The concept of cation radicals in general as highly electron deficient and therefore extremely reactive dienophiles is particularly significant in view of the strategic position of the Diels–Alder in organic synthesis and the inherent complementarity of the new Diels–Alder procedure to the classic one. Specifically, electron-rich π systems, which normally are ineffective as Diels–Alder dienophiles, are precisely the systems that are most readily converted to cation radicals. The extension of the cation radical catalyzed Diels–Alder procedure to a variety of electron rich dienophiles would thus qualify it as a significant adjunct to the conventional Diels–Alder synthetic strategy. The feasibility of the proposed extension to electron-rich dienophiles including dienes, alkenes, and styrenes is now reported, and a new and efficient alternative procedure for initiating the cation radical Diels–Alder is described.

Scheme I



1 **2** **3**

Triarylaminium salt catalyzed Diels–Alder cycloadditions of conjugated dienes bearing a directly attached electron-donating oxygen functionality (acetoxy, methoxy) were selected for initial investigation. The unreactivity of 1-acetoxy-1,3-butadiene toward dimerization suggested that the acetoxy group is insufficiently activating to permit cation radical formation in the simple diene system. More surprising was the unreactivity of 1-acetoxy-1,3-cyclohexadiene, which indicates the acetoxy group is actually sharply deactivating toward cation radical formation. In contrast, 1-methoxy-1,3-cyclohexadiene (**1**) instantly decolorizes the catalyst but apparently suffers polymerization, and no Diels–Alder dimer is formed. Similar discouraging results emerged from studies of other oxygenated dienes. Consequently, an alternate procedure for generating the requisite cation radicals, under conditions where polymerization is largely suppressed, was sought. An excellent procedure, modeled upon the well-known method of photosensitized electron transfer,[6,7] fortunately was developed and is illustrated in the Diels–Alder cyclodimerization of **1** (Scheme I): A solution of 7.7 g of **1**[8] dissolved in acetonitrile (140 mL) containing 25 mol % (3.2 g) of 1,4-dicyanobenzene (the electron transfer sensitizer = ET) was irradiated 32 h at room temperature by a 450W Hanovia medium-pressure mercury vapor lamp with Pyrex filter. The GC yield of dimer was determined to be 71%. Evaporation of the solvent, removal of the ET by extraction of the dimer into hexane, and distillation (bp 122–125 °C (2.75 torr)) yielded 3.8 g (50%) of dimer **2** as a 2:1 endo/exo pair. No other diastereomers were present in significant amounts. Hydrolysis of the dimer (methanol:water = 4.5:1, room temperature, 1.75 h, 10 mol % TsOH) gave 96% of ketone **3**. Diels–Alder additions and dimerizations of many of the hydrocarbon dienes previously studied[1,2] were repeated by using the new procedure, giving identical products in very similar proportions but generally more cleanly and often in slightly higher yields.[9] In each case a parallel blank reaction, omitting only ET, established the negligibility of direct photoreactions bypassing ET. Cross additions of **1** and these hydrocarbon dienes, either as diene or dienophile, were unfortunately unsuccessful. Apparently **1** is far more reactive in either Diels–Alder role than such dienes.

In addition to confirming the compatibility of the cation radical Diels–Alder with electron donor functionality, a second major goal of this work was to extend the reaction beyond the diene–diene format. The exploitation of electron-rich alkenes as dienophiles was considered a particularly important target. Not only are a variety of such systems readily available synthetically, but their cross additions to dienes should not be subject to competing Diels–Alder dimerization. Indeed, enol ethers and enamines were

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(8) This actually was 11.0 g of the 70% mixture available commercially. No products were observed to emanate from the minor isomer.

(9) All adducts were collected by preparative GC unless noted otherwise and characterized by GC/MS, high resolution MS, ^1H and ^{13}C NMR spectroscopy, and, where appropriate, proton decoupled ^1H NMR spectroscopy.

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