Reaction of Diphenylcarbene with Amines and the Question of Triplet–Singlet Equilibration[1]

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Abstract: The optical absorption spectrum of triplet diphenylcarbene in solution is quenched by substrates such as methanol and amines to give the respective O–H and N–H insertion products. Is this a direct reaction of the triplet carbene with the substrates which runs counter to the rules of spin selection, or does it involve thermal population of the singlet state of the carbene which then reacts with the substrates? These questions are addressed through kinetic, isotopic, and product studies of the reaction between diphenylcarbene and butylamines.

The relationship between the singlet and triplet states of diphenylcarbene has been the subject of extensive investigation.[2-8] It has been found that singlet diphenylcarbene inserts into the O–H bond of methanol at a rate which is close to the diffusion-controlled limit.[6,9] Methanol also quenches the absorption spectrum of triplet diphenylcarbene,[5-7] apparently contradicting the rules of spin selection[10] which suggest that the alcohol ought to quench the singlet alone. These observations have been rationalized in terms of a mechanism in which the triplet carbene simply acts as a reservoir for the reactive singlet and takes no direct part in the reaction itself, Scheme I.[4-6]

Two groups[5,6] have combined the mechanism of Scheme I with kinetic and product studies and have obtained estimated for the triplet–singlet energy separation of ca. 4 kcal mol^{-1}. according to scheme I, the observed activation energy for the disappearance of the triplet carbene in the presence of methanol should represent the sum of the energy for the triplet to access the singlet state, plus the activation energy for the reaction of the singlet with methanol. Even if the latter were a diffusion-controlled process, the sum of these two terms should be ca. 6 kcal mol^{-1}.

Measured values for the activation energy[7] were solvent dependent and were in the range 1–3 kcal mol^{-1}, which was significantly less than that required if Scheme I were correct. This prompted us to suggest that this scheme might not apply and to propose alternative mechanisms which fitted the available data.[7] One possible mechanism involved the *direct* reaction of the triplet carbene with alcohol to give the O–H insertion product.

In addition to these proposals, we noted deficiencies in some of the experiments[6] that were based on Scheme I and which had been used to estimate the singlet–triplet energy gap. Specifically, we pointed out that the various experiments involved[6] had not been carried out in the same solvent. We suggested that Scheme I might be valid if the rate constant for singlet–triplet intersystem crossing showed a strong dependence on the medium. In a subsequent study of this problem,[9] Eisenthal and his co-workers showed that this was indeed the case, throwing open the whole question of the applicability of Scheme I.

In an attempt to bring the weight of more experimental evidence to bear on the question of triplet–singlet equilibration, we have

Scheme I
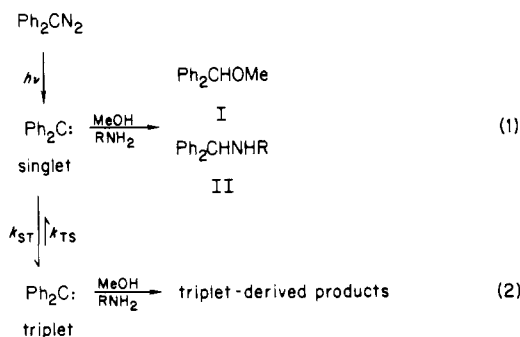
investigated the reaction of diphenylcarbene with amines.

Experimental Section

All of the experiments described in this work were carried out on samples which had been carefully purged with nitrogen.

Materials. Diphenyldiazomethane was prepared by the literature procedure[11] and was purified by sublimation. *tert*-Butyl- and *n*-butylamines were commerically available and were purified by distillation under nitrogen from calcium hydride. Deuterium labeling was achieved by repeatitive exchange of the protons bound to nitrogen by shaking with D$_2$O, followed by distillation from sodium and then potassium. Deuterium incorporation was found to be >96% by NMR.

Benzene was washed with concentrated sulfuric acid and then with water. It was then dried over magnesium sulfate and finally distilled from calcium hydride. Acetonitrile (spectrograde) was purified by distillation from calcium hydride.

The insertion product, (*N*-diphenylmethyl)butylamine, was prepared by refluxing an equimolar mixture of diphenylmethylamine and *n*-butyl bromide in absolute ethanol for 3 days.[12] The solvent and any unreacted material were distilled, and the residual solid was treated with a 10% solution of sodium hydroxide. The free amine was then extracted with ether. Removal of the ether left an oil which was distilled under reduced pressure. The product (bp 151–155 °C (3 mm); yield 50%) was analyzed by GC/MS, *m/e* 239, and by NMR in CDCl$_3$ solvent: δ 7.35 (m, 10 H), 4.84 (s, 1 H), 2.62 (m, 2 H), 1.58 (m, 5 H), 0.98 (D, 3 H).

Apparatus. Laser flash photolysis experiments were carried out on a system which has been described in detail elsewhere,[13] with the exception that light pulses at 308 nm, 80 mJ, and 4 ns width were used to photolyze the samples. Solutions were generally flowed through the sample cell so as to avoid sample depletion and the accumulation of light-absorbing products.

Product Studies. Product studies were carried out on the photodecomposition of diphenyldiazomethane in the presence of *tert*-butylamine, *n*-butylamine, and their deuterated analogues. In a typical experiment, solutions containing diphenyldiazomethane (0.06 M) and amine (0.5 M) in dry acetonitrile were purged with nitrogen and then photolyzed using a tungsten lamp until the color due to the diazo compound had disap-

(1) Issued as NRCC Pulbication No. 24557.
(2) Bethell, D.; Stevens, G.; Tickle, P. *Chem. Commun.* **1970,** 792.
(3) Bethell, D.; Newall, A. R.; Wittaker, D. *J. Chem. Soc. B* **1971,** 23.
(4) Bethell, D.; Hayes, J.; Newall, A. R. *J. Chem. Soc., Perkin Trans. 2* **1974,** 1307.
(5) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976,** *98,* 8190.
(6) Eisenthal, K. B.; Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr.; DuPuy, C.; Hefferon, G.; Hetherington, W.; Korenowski, G. M.; McAuliffe, M. J. *J. Am. Chem. Soc.* **1980,** *102,* 6563.
(7) Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984,** *106,* 198.
(8) Griller, D.; Nazran, A. S.; Scaiano, J. C. *Tetrahedron Symp.,* in press.
(9) Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984,** *106,* 1868.
(10) Woodworth, R. C.; Skell, P. S. *J. Am. Chem. Soc.* **1959,** *81,* 3383. For a review see ref 8.

(11) Smith, L. I.; Howard, K. L. "Organic Syntheses", Wiley: New York, 1955; Collect. Vol. III, p 351.
(12) Patai, S.; Weiss, S. *J. Chem. Soc.* **1959,** 1035.
(13) Scaiano, J. C. *J. Am. Chem. Soc.* **1980,** *102,* 7747.

Table I. Aromatic Products Formed by Photolysis at 25 °C of Diphenyldiazomethane (0.06 M) in the Presence of Butylamines (0.5 M) in Acetonitrile as Solvent

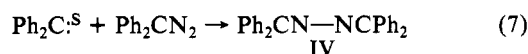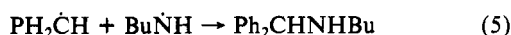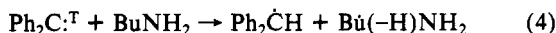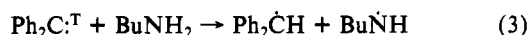|	amine			
product (%)[a]	n-BuNH$_2$	n-BuND$_2$	t-BuNH$_2$	t-BuND$_2$
II, Ph$_2$CHNHBu	73	70	38	41
III, Ph$_2$CHCHPh$_2$	7	8	14	16
IV, Ph$_2$CN—NCPh$_2$	12	15	33	36
V, Ph$_2$C=CPh$_2$	1	1	2	2
VI, Ph$_2$CO	2	3	5	3
VII, Ph$_2$CHOH	1	1	1	1

[a] The fact that the combined product yields are not equal to 100% reflects the experimental error inherent in the GC analysis.

peared. The solutions were then concentrated. Products were identified using a Hewlett-Packard 5995 GC/mass spectrometer fitted with a 10-m, 0.2-mm diameter cross-linked methylsilicon column. They were quantified by GC analysis (Varian 6000 GC, fitted with a 25-m, 0.32-mm diameter DB130W capilliary column) using an external standard and authentic samples as calibrants.

Results and Discussion

Simple product studies of the reaction of triplet diphenylcarbene with n-butyl- and *tert*-butylamines showed that the course of the reaction was substantially different from that observed when methanol (0.5 M) was used as a substrate. For the latter, ether I was obtained in high yield. In the reactions with amines, II was the major product, but there were also substantial yields of tetraphenylethane (III), and benzophenone azine (IV) (Table I).[14] Minor products included tetraphenylethylene (V), benzophenone (VI), and benzhydrol (VII).

According to the rules of spin selection for carbene reactions,[8,10] upon which Scheme I is based, the secondary amine II could be the product of a singlet insertion reaction (eq 1), or of the triplet reaction 3, followed by eq 5.[15] Tetraphenylethane (III) should

$$Ph_2C:^T + BuNH_2 \rightarrow Ph_2\dot{C}H + Bu\dot{N}H \quad (3)$$

$$Ph_2C:^T + BuNH_2 \rightarrow Ph_2\dot{C}H + B\dot{u}(-H)NH_2 \quad (4)$$

$$PH_2\dot{C}H + Bu\dot{N}H \rightarrow Ph_2CHNHBu \quad (5)$$

$$2Ph_2\dot{C}H \rightarrow \underset{III}{Ph_2CHCHPh_2} \quad (6)$$

$$Ph_2C:^S + Ph_2CN_2 \rightarrow \underset{IV}{Ph_2CN—NCPh_2} \quad (7)$$

$$2Ph_2C: \rightarrow \underset{V}{Ph_2C=CPh_2} \quad (8)$$

$$Ph_2C: + O_2 \rightarrow \underset{VI}{Ph_2CO} \quad (9)$$

$$Ph_2C: + H_2O \rightarrow \underset{VII}{Ph_2CHOH} \quad (10)$$
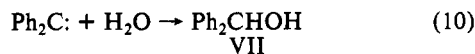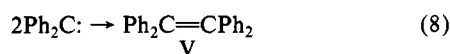
be derived from the triplet carbene (eq 3, 4, and 6).[16] Benzophenone azine (IV) should be derived from the singlet carbene (eq 7). Formation of the minor products is described in eq 8-10. Trace contamination by oxygen and water accounts for products VI and VII.

Irrespective of the precision with which Scheme I applies, the formation of significant quantities of triplet derived products in the amine reactions must indicate that singlet diphenylcarbene is substantially less reactive toward the amines in question than it is toward methanol.

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(14) Similar product distributions were obtained by thermolysis of diphenyldiazomethane in the presence of amines.[4]
(15) Reaction 3 produces triplet radical pairs which will typically escape the solvent cage before intersystem crossing. Reaction 5 will generally involve singlet pairs. CIDNP studies[4] suggest that reactions 3 and 5 do not provide substantial contribution to the yield of II.
(16) Formation of III was thought to imply[4] that diphenylmethyl-butylaminyl radical pairs do not readily disproportionate. In this context, it was noted[4] that diphenylmethane was an important product in the analogous reaction of the carbene with alcohols.[2,3,7]

Table II. Absolute Rate Constants, $k_{triplet}$, for the Reactions of Triplet Diphenylcarbene with Methanol and Butylamines in Acetonitrile at 25 °C

substrate	$k_{triplet}$,[a] (M^{-1} s^{-1})	$k_{triplet}^{CH_3OH[a]}/k_{triplet}^{BuNH_2}$	$k_1^{CH_3OH}/k_1^{BuNH_2}$
MeOH	2.4×10^{7}[b]		
n-BuNH$_2$	$(1.8 \pm 0.4) \times 10^6$	13 ± 4	5.0 ± 0.6
n-BuND$_2$	$(1.3 \pm 0.2) \times 10^6$	19 ± 6	
t-BuNH$_2$	$(1.4 \pm 0.3) \times 10^5$	171 ± 50	19 ± 2
t-BuND$_2$	$(1.1 \pm 0.3) \times 10^5$	218 ± 65	

[a] Errors stated represent two standard deviations. [b] Reference 7.

In an attempt to quantify this difference, we tried to measure the rate constant for the reactions of the amines with singlet diphenylcarbene in a Stern–Volmer experiment, in which the quantum yield for triplet formation was monitored by laser flash photolysis as a function of amine concentration. However, we encountered serious difficulties which invalidated the experiments. Specifically, at the wavelength where the yield of triplet carbene was monitored (318 nm), the diphenylmethyl radical also absorbed quite strongly. Contributions from the growth of this radical ultimately led to large uncertainties in the absorbance measurements.

To overcome these difficulties, a simple competition study was carried out using amine/methanol mixtures to scavenge singlet diphenylcarbene. Thus, diphenyldiazomethane (0.06 M) was photolyzed at 25 °C in acetonitrile solvent containing n-butyl- or *tert*-butylamine (2.5 M) and methanol (2.5 M). The molar ratios of products I/II were 5.0 ± 0.4 (n-butylamine) and 19.0 ± 1.5 (*tert*-butylamine). Under these conditions ca. 90% of the singlet carbene must have been scavenged before undergoing intersystem crossing to the triplet state (eq 1). This is because $k_1(MeOH)/k_{ST} = 5 \pm 2 M^{-1}$, where the stated error represents two standard deviations.[7]

If we account for the small percentage of singlet carbene which underwent intersystem crossing to the triplet by increasing the margins of error on the above ratios, it follows that k_1(methanol)$/k_1$(amine) = 5.0 ± 0.6 (n-butylamine) and 19 ± 2 (*tert*-butylamine).

With this information in hand, it was possible to construct a test of Scheme I. The rate of disappearance of triplet diphenylcarbene, $-\partial[T]/\partial t$ is given in eq 11. This equation was

$$\frac{-\partial[T]}{\partial t} = \frac{k_{TS}k_1[BuNH_2]}{k_1[BuNH_2] + k_{ST}}[T] + k_0[T] + k_2[BuNH_2][T] \quad (11)$$

derived by applying the steady-state approximation to the concentration of the singlet carbene and is valid because that concentration is very small when compared with [T].[5-7] The first term in this equation describeds loss of the triplet carbene via the singlet manifold to form the N–H insertion product. The term in k_0 is the pseudo-first-order rate constant for the reaction of the carbene with solvent as well as all other decay modes which do not involve amine. The term in k_2 represents hydrogen abstraction at the amine. Under conditions where $k_{ST} \gg k_1[BuNH_2]$, eq 11 reduces to:

$$\frac{-\partial[T]}{\partial t} = [T]\left\{\left[\frac{k_{TS} \cdot k_1}{k_{ST}} + k_2\right][BuNH_2] + k_0\right\} \quad (12)$$

The decay of the triplet carbene, in the presence of butylamines, was followed experimentally by laser flash photolysis and was related to k_0 and $k_{triplet}$ (eq 13). In this equation, $k_{triplet}$ represents

$$\frac{-\partial[T]}{\partial T} = [T]\{k_0 + k_{triplet}[BuNH_2]\} \quad (13)$$

the global rate constant for all of the reactions of the triplet carbene with the amine, i.e., N–H insertion via the singlet mainfold *and* direct hydrogen abstraction by the triplet.

The values obtained in this work are given in Table II. In these experiments the amine concentrations were such that the condition

$k_{ST} \gg k_1[BuNH_2]$ was fulfilled. Hence eq 12 and 13 can be combined to give:

$$k_{triplet} = (k_{TS}k_1/k_{ST}) + k_2 \qquad (14)$$

Of course, eq 12 will apply to any substrate in its reactions with triplet diphenylcarbene so long as these follow the mechanism of Scheme I. In experiments where methanol was the substrate, the singlet insertion product, Ph_2CHOMe, was formed almost quantitatively. The only detectable product which could have been formed via a hydrogen abstraction of the triplet carbene was Ph_2CH_2, but its yield was only 2–3%. If Scheme I represents a valid mechanism, these products yields imply that $k_{TS}k_1/k_{ST} \gg k_2$ (eq 14). Moreover, when methanol was used as the substrate, laser flash photolysis experiments showed that k_0 was negligible when compared with $k_{triplet}[MeOH]$.[7]

With these results in hand, we can apply eq 12–14 to derive eq 15, which links the various rate constants for the reaction of diphenylcarbene with butylamines and methanol. If this relationship holds, then Scheme I is valid for these substrates. If it fails, Scheme I does not properly describe their reactions.

$$k_{triplet}^{CH_3OH}/k_{triplet}^{BuNH_2} \leqslant k_1^{CH_3OH}/k_1^{BuNH_2} \qquad (15)$$

The data reported in Table II show that eq 15 is not satisfied and therefore that Scheme I fails by margins which are substantially greater than the experimental errors. This result obviously implies that Scheme I is not a satisfactory description of the reaction mechanism and begs the question of whether other mechanisms are possible which fit all of the experimental data.

One mechanism that fits all of the data is that the triplet carbene and amine form a complex which ultimately undergoes intersystem crossing to give the N–H insertion product. This mechanism has been discussed extensively in a study of the reaction of diphenylcarbene with methanol.[7] In essence the free triplet carbene need not cross to the singlet state before combining with the amine. So far as we are aware, none of the existing evidence runs counter to this model. Indeed, studies of isotope effects in the reaction[4] appear to support it, but these, as will be shown below, need to be reevaluated in the light of our own experimental data.

In a study of the reaction of amines and diphenylcarbene,[4] Bethell and his co-workers thermolyzed diphenyldiazomethane in the presence of individual amines in acetonitrile solvent at 80 °C. They found a tritium isotope effect on the product distribution when n-BuNHT or Bu-NHT as used as the substrate. However, they found identical product distributions on thermolysis of the diazo compound in the presence of either fully protiated or fully deuterated amines. In this work, we have confirmed the absence of an H/D isotope effect on the product distribution (Table I) and that this isotope effect on the disappearance of the triplet carbene was very small (Table II).

Bethell and his collaborators explained the observations in the following way.[4] They argued, by analogy with the reaction at alcohols,[3] that II was formed via an ylide-type mechanism in which the carbene was coordinated to the nitrogen atom of BuNHT. Hence, the H/T isotope effect on the formation of II simply reflected a preference for intramolecular H transfer within the ylide.[17]

Treatment of other isotope effects presented difficulties. There was a large H/T isotope effect on the formation of III which appeared to conflict with the absence of an isotope effect on the

product distributions when $BuNH_2$ was replaced by $BuND_2$.

As a rationalization, it was assumed that the triplet carbene reacted exclusively at the amino group (eq 3), and the absence of an H/D effect was taken as evidence that the triplet carbene, once formed, could not return to the singlet manifold (Scheme I); that is, it had no option to react with the amine, be it $BuNH_2$ or $BuND_2$. On this basis the product distribution should necessarily have been insensitive to amine deuteration. However, the explanation is incorrect.

We used GC/MS analysis to determine the extent of deuteration in III when n-$BuND_2$ and t-$BuND_2$ were used as substrates. In fact, abstraction of N-D by the triplet carbene was by no means the exclusive mode of attack. Analysis of the mass spectra showed that less than 30% of the reaction of the triplet carbene took place at the amine group of $BuND_2$. Consequently, it is perfectly reasonable to expect that the product distributions should be fairly insensitive to deuteration. Moreover, an apparently high H/T isotope effect should necessarily be detected for the formation of III when BuNHT was the substrate, simply because only a small proportion of abstraction takes place at the amino group (eq 3).

Thus, the isotope study[4] established an ylide mechanism for the formation of II but did not, as had originally been thought, completely negate the mechanism of Scheme I.

The mechanism of Scheme I has now been tested in a study of activation energies for the reaction of the carbene with methanol[7] and in the present study of the reaction with amines. In both tests it has been found wanting. It is now clear that the scheme cannot be rigorously applied in the calculation of singlet–triplet equilibrium constants and enthalpy differences.[5,6] Indeed, other mechanisms, such as that in which the triplet carbene reacts directly with the substrate to give the insertion product, are in fact quite consistent with all of the experimental data. However, one cannot deny that Scheme I has appeal as a crude representation of the experimental observations. Can it be broadly correct and yet fail quantitatively?

The answer to this question may lie in the magnitude of solvent effects on the intersystem-crossing rate constants. In going from isooctane to acetonitrile, values of k_{ST} change from 10.5×10^9 to $2.6 \times 10^9 \, s^{-1}$.[9] The molecules which have been used to scavenge the singlet carbene (alcohols and amines) are themselves very polar molecules which may well have a profound effect on both k_{ST} and k_{TS}. Indeed, in our earlier work on the methanol reaction,[7] we pointed to these possibilities.

It is therefore possible that the broad modes of singlet vs. triplet reactions expressed in Scheme I may be reasonable representations of the chemistry of the carbene. However, the precise relationship between the singlet and triplet states of the carbene may not be readily deduced by applying this mechanism if the probe molecules themselves are capable of disturbing the delicate balance of rate constants for intersystem crossing. How then is it possible to test the validity of this mechanism?

One approach to the problem would be to carry out kinetic measurements in a two-component solvent which could be adjusted to provide a constant dielectric as the concentrations of substrates were changed. This should be of particular importance in measurements of singlet to triplet intersystem rate constants. Current arguements in support of Scheme I, while appealing, are circular. We would strongly encourage an effort of this kind which might validate this otherwise attractive mechanism.

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(17) Product II cannot have been formed exclusively via reactions 3 and 4 since, when BuNHT was the substrate, the H/T isotope effects for the formation of II and III were very different. Thus reaction 1 must be an important pathway for formation of II; see also ref 15.