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LASER FLASH PHOTOLYSIS STUDY OF PHENYLCARBENE, *o*-TOLYLCARBENE AND MESITYLCARBENE

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Laser flash photolysis (LFP, XeCl, 308 nm, 20 ns) of phenyldiazomethane (PDM), *o*-tolydiazomethane (TDM) and mesitydiazomethane (MDM) produces phenylcarbene (PC), *o*-tolycarbene (TC) and mesitylcarbene (MSC), respectively. Transient spectra of PC and TC could not be detected in pentane at ambient temperature; however, these carbenes could be trapped with pyridine to form UV–Vis-active ylides. The rate of formation of these ylides was resolved in $CF_2ClCFCl_2$ (Freon-113) and yields, after analysis, values of k_{pyr} and τ, where k_{pyr} is the absolute rate constant of the reaction of the spin equilibrated carbene with pyridine and τ is the carbene lifetime in Freon-113 in the absence of pyridine. LFP of MDM produces the transient spectra of both triplet MSC and 3,5-dimethyl-1,2-benzoquinodimethane (3,5-BQM). The lifetime of ^{3}MSC in pentane is *ca* 500 ns. ^{3}MSC reacts with pyridine with an apparent rate constant of $k_{pyr} = 1{\cdot}35 \times 10^7$ M^{-1} s^{-1}. The decay of ^{3}MSC in a variety of solvents does not lead to increased absorption of 3,5-BQM in solution, nor does the presence of a carbene scavenger (methanol) lead to a reduction in yield of 3,5-dimethyl-1,2-benzoquinodimethane upon LFP of precursor. Thus, the decay of ^{3}MSC in solution does not lead to the formation of quinodimethane. This species (3,5-BQM) is formed, instead, by a hydrogen atom transfer in the excited state of the precursor. Product analysis reveals that the excited state rearrangement which forms xylylene is a minor process. Photolysis of MDM in a nitrogen matrix at 10 K leads to the UV–Vis spectra of matrix-isolated triplet mesitylcarbene and 3,5-BQM. The carbene rearranges slowly to 3,5-BQM in the cryogenic matrix, in contrast to its behavior in solution.

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INTRODUCTION

Phenylcarbene (PC, Scheme 1) is the prototypical aromatic carbene. Matrix spectroscopy[1] and *ab initio* theory[2] have convincingly demonstrated that the triplet state of PC is the ground state. Nevertheless, most of the chemistry of PC proceeds through the singlet state of the carbene.[3] This has usually been interpreted as a consequence of a small (theory[2]; 4 kcal mol^{-1}; 1 kcal = 4·184 kJ) free energy separation (ΔG_{ST}) between ^{1}PC and ^{3}PC, rapid spin equilibration and much greater reactivity of the higher energy singlet state.

Despite extensive laser flash photolysis studies of aryl and diarylcarbenes,[4] kinetic studies of PC have heretofore not been reported. In this paper, we describe such studies and their extension to *o*-tolylcarbene (TC) and mesitylcarbene (MSC) (Scheme 1). The data reveal first that PC and TC are very short-lived species and that MSC is, as expected, a much longer lived carbene intermediate. Second, the data demonstrate that intramolecular hydrogen atom transfer reactions proceed in the excited state of singlet mesityldiazomethane. This process is particularly noticeable in methanol solvent but is still a relatively minor process.

RESULTS AND DISCUSSION

Laser flash photolysis (LFP) studies of PC

LFP (308 nm) of phenyldiazomethane (PDM) in deoxygenated pentane fails to produce a UV–Vis-active transient. However, LFP of PDM under the same conditions in the presence of pyridine produces an intense transient absorption (Figure 1) attributed to ylide **1** on the basis of its similarity to other carbene pyridine ylides.[5] It was possible

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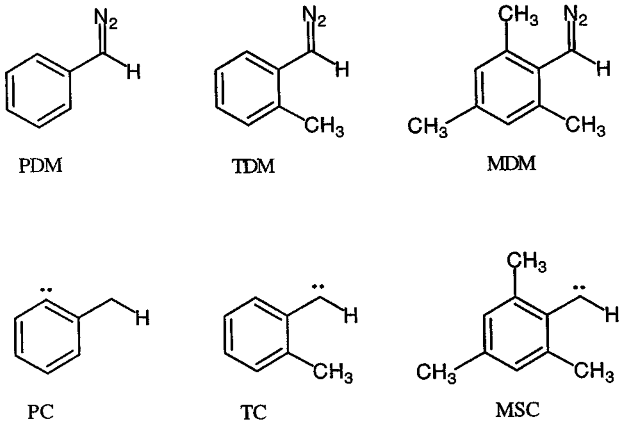


Scheme 1

to resolve the growth of ylide **1** in $CF_2ClCFCl_2$ (Freon-113). The ylide is formed in an exponential process following the laser pulse. The growth of the ylide was analyzed to yield an observed pseudo-first-order rate constant, k_{obs}, to ylide formation. The size of k_{obs} is linearly dependent on the concentration of pyridine (Figure 2). The slope of this plot was determined in three experiments and found to be $1{\cdot}9 \pm 0{\cdot}3 \times 10^7$ M^{-1} s^{-1} and is the absolute rate constant of the reaction of spin equilibrated phenylcarbene with pyridine. If one assumes that only singlet phenylcarbene can react with pyridine, then

$$k_{pyr} = {}^1k_{pyr}K$$

where ${}^1k_{pyr}$ is the absolute rate constant of PC with pyridine. A reasonable estimate[4–6] of this quantity is 1×10^9 M^{-1} s^{-1}, which predicts that K, the singlet-triplet equilibrium constant, is 0·019. Thus, one can calculate a free energy separation of the singlet and triplet (ΔG_{ST}) of 2·3 kcal mol^{-1} at 20 °C. This value is close to but smaller than that predicted by theory (4 kcal mol^{-1}) for PC in the gas phase.[2]

The intercept of the plot of Figure 2 is $4{\cdot}9 \times 10^6$ s^{-1}. The reciprocal of this value is τ or 205 ns, the lifetime of spin equilibrated PC in Freon-113.

It was also possible to resolve the growth of this ylide by nanosecond spectroscopy in pentane in the presence of dilute (0·1 M) pyridine. As before, a plot of k_{obs} versus pyridine is linear and yields after analysis $k_{pyr} = 9{\cdot}3 \times 10^6$ M^{-1} s^{-1} and $\tau = 74$ ns.

The optical yield of ylide, A_y, was also measured at 460 nm as a function of pyridine concentration. In the absence of pyridine $A_y = 0$, but this quantity grows as the concentration of pyridine increases (Figure 3) until [pyridine] ≥ 1 M. Above 1 M pyridine, in pentane, the ylide yield is saturated (A_y^∞), implying that every molecule of phenylcarbene generated in the laser pulse is captured by pyridine prior to reaction with solvent or that $k_{pyr}[pyr] \gg k_{RH}$ [RH], where ${}^1k_{pyr}$ and ${}^1k_{RH}$ are defined in Scheme 2.[6]

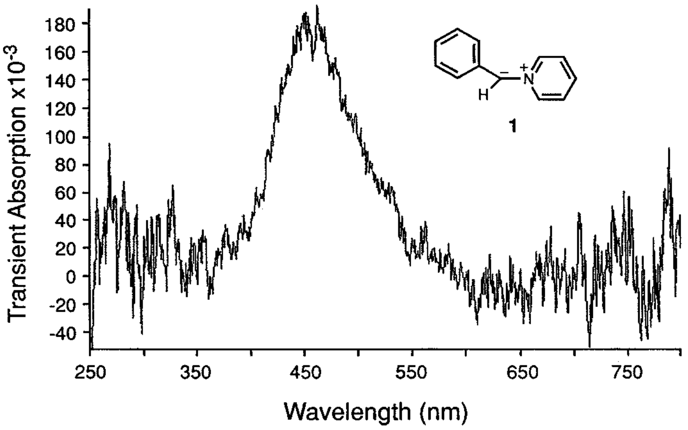


Figure 1. Transient spectrum of the phenylcarbene–pyridine ylide **1** in pentane at ambient temperature. The spectrum was recorded over a period of 400 ns immediately following the laser pulse

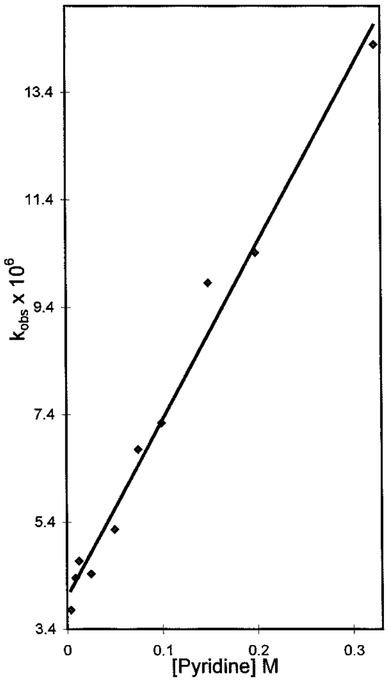


Figure 2. Plot of k_{obs} of ylide **1** versus pyridine concentration in Freon-113

The quantum yield of ylide formation is given by[6]

$$\phi_y = \frac{\phi_c k_{pyr}[\text{pyridine}]K}{({}^1k_{RH}[\text{RH}]K + {}^1k_{pyr}[\text{pyridine}])K} \tag{1}$$

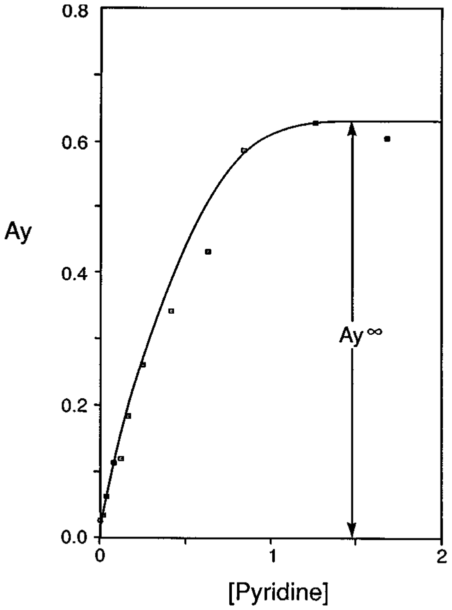
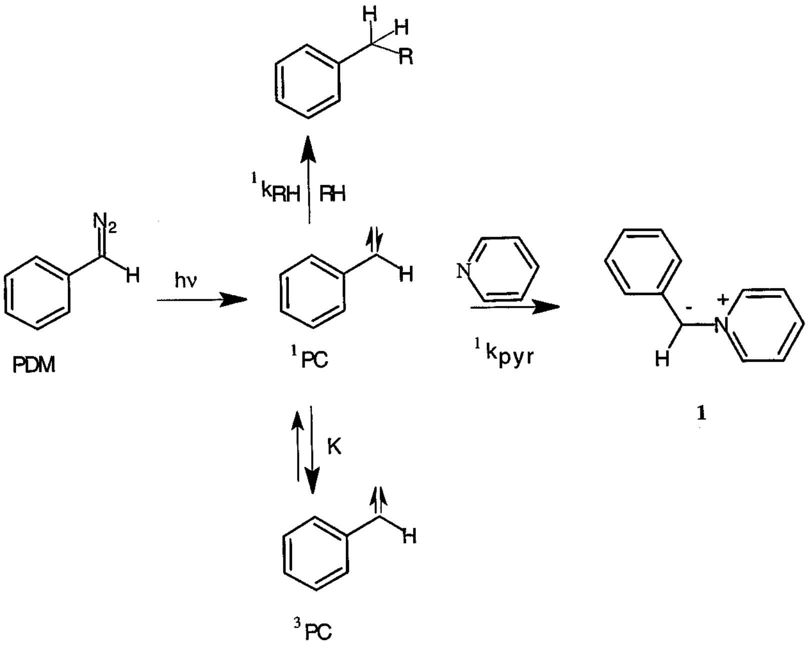


Figure 3. Plot of A_y versus [pyridine] in pentane



Scheme 2

where ϕ_c is the quantum yield of carbene formation. The optical yield of ylide is related to ϕ_{ylide} by the equation[6]

$$A_y = \phi_y A_y^{\infty} \quad (2)$$

Combining and rearranging equations (1) and (2) leads to[6]

$$\frac{1}{A_y} = \frac{{}^1k_{RH}[RH]K}{\phi_c A_y^{\infty}\,{}^1k_{pyr}[\text{pyridine}]K} + \frac{1}{\phi_c A_y^{\infty}} \quad (3)$$

Thus, a plot of $1/A_y$ versus 1/[pyridine] is predicted and found (Figure 4) to be linear. Division of the intercept by the slope gives ${}^1k_{pyr}K/{}^1k_{RH}[RH]K = 1{\cdot}61$. As ${}^1k_{pyr}K$ in pentane is $9{\cdot}3 \times 10^6$ M^{-1} s^{-1}, then τ in pentane can be estimated to be 173 ns for spin-equilibrated phenylcarbene or about twice that obtained by direct analysis, which is the more accurate procedure. This lifetime of spin-equilibrated PC is longer than that determined for fluorenylidene[7] in pentane but comparable to that of 1- and 2-naphthylcarbene.[8] As neat pentane is 8·7 M and $K = 0{\cdot}019$, then k_{RH} can be estimated to be $4{\cdot}9 \times 10^8$ M^{-1} s^{-1}.

This treatment assumes that ^{1}PC and ^{3}PC are in rapid equilibrium and can be treated as a single kinetic unit[9] and that all of the decay chemistry of PC under these conditions proceeds through the low-lying singlet state.[3] In pentane the decay processes are expected to be CH insertion reactions with the solvent.[3,9] This assumption is based on the many reported product studies involving phenylcarbene and its various simple derivatives.[3,9]

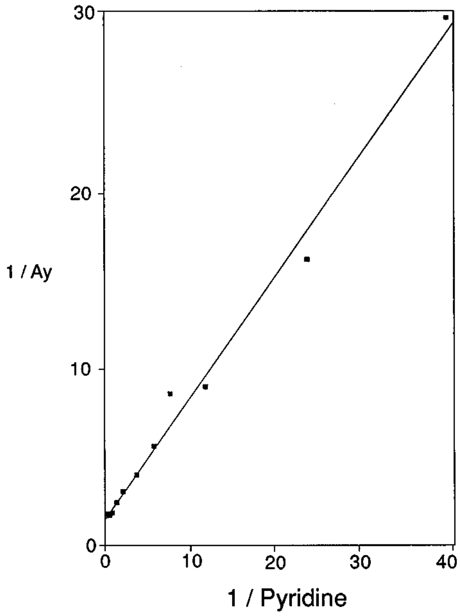


Figure 4. Double reciprocal treatment of the data of Figure 3; slope = 0·70, intercept = 1·15

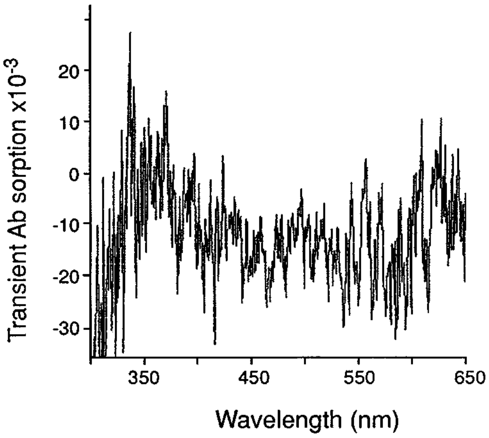


Figure 5. Transient spectrum obtained by LFP of TDM in pentane at ambient temperature. The spectrum was recorded over a window of 400 ns, immediately after the laser flash

o-Tolylcarbene

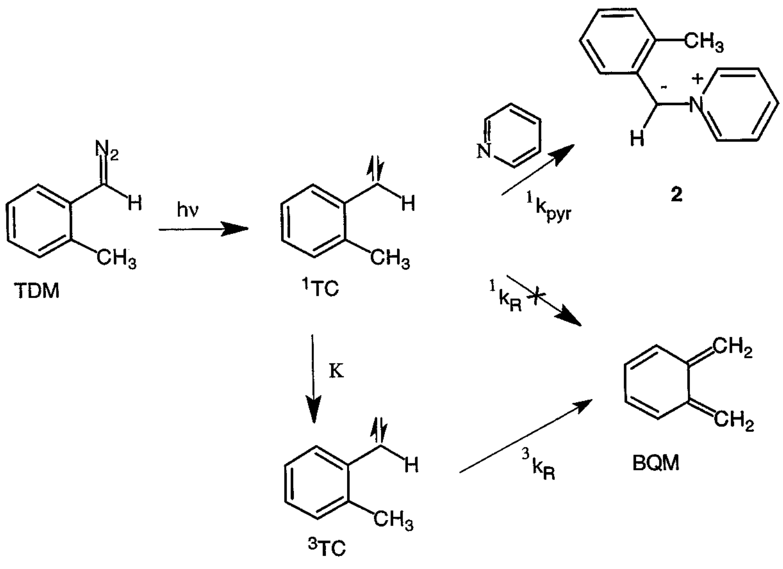
o-Tolylcarbene was studied by LFP techniques similarly to phenylcarbene. LFP of *o*-tolyldiazomethane (TDM) in pentane fails to produce a UV–Vis-active transient (Figure 5). We find that there is no evidence for the formation of 1,2-benzoquinodimethane (BQM) upon laser flash photolysis of TDM (Scheme 3).

The transient spectrum of ylide **2** is detected upon flash photolysis of TDM in pentane in the presence of pyridine. Analysis of ylide yield as a function of pyridine concentration yields, as before, the ratio $k_{pyr}/k_{RH}[RH] = 1{\cdot}75$. If k_{pyr} of *o*-tolylcarbene and phenylcarbene are similar then their lifetimes and absolute rate constants of reaction with pentane must also be comparable.

Mesitylcarbene

Isolation of mesitylcarbene in rare gas matrices

Short photolysis (six photolysis cycles, 10 s) of mesityldiazomethane (MDM) in rare gas matrices (argon or nitrogen) at 11 K with the full arc of a 200 W high pressure mercury lamp releases mesitylcarbene (MSC). These irradiation conditions result in efficient conversion of mesityldiazomethane into triplet mesitylcarbene (major UV bands at 256, 260, 301 and 315 nm). Photolysis of mesityldiazomethane is evident by the rapid disappearance of the characteristic N=N diazo band at 2060 cm^{-1}. The assignment of the spectrum to ^{3}MSC is based on the similarity of the shape and intensities of the UV–Vis absorption bands observed here (Figure 6) with those reported by McMahon and co-workers[10] with triplet *o*-tolylmethylene and of Tomioka *et al.*[11] with didurylcarbene. A small red shift of the mesitylcarbene bands relative to *o*-tolylcarbene is observed in the spectrum. The strong band at 315 nm is significant because it may be monitored by time resolved techniques at ambient temperature (see below). For



Scheme 3

aryl- and especially naphthylcarbenes it is difficult to detect carbenes directly because their absorption maxima fall underneath the absorption spectra of their precursors.[4]

Utilization of the full arc of the photolyzing light leads to the formation of a dimethyl-substituted *o*-quinodimethane (**3**, Scheme 4), which is seen clearly in the UV–Vis spectrum in the region above 330 nm ($\lambda_{max}=370$ nm). The assignment of this broad absorption, which is composed of several vibronic bands (336, 355, 367 and 385 nm), to a methylated *o*-quinodimethane is supported by comparison of this spectrum with that of *o*-xylylene described in the literature.[10]

The presence of the absorption of an *o*-quinodimethane in the initial matrix spectrum may be the result of secondary photolysis of carbene. Photolysis of mesitylcarbene with a bandpass interference filter ($\lambda_{max}=313$ nm) leads to its complete conversion to the *o*-quinodimethane. However, photolysis of mesityldiazomethane with green light (450–600 nm, $\lambda_{max}=530$ nm) is not very efficient (less than 5% of starting material was decomposed in 1 h), but it does lead exclusively to the formation of carbene with no trace of methyl-*o*-quinodimethane. The *o*-xylylene product observed by McMahon and co-workers[10] under similar irradiation conditions with *o*-tolyldiazomethane is probably a result of slow thermal rearrangements of the carbene during long periods of irradiation of the precursor.

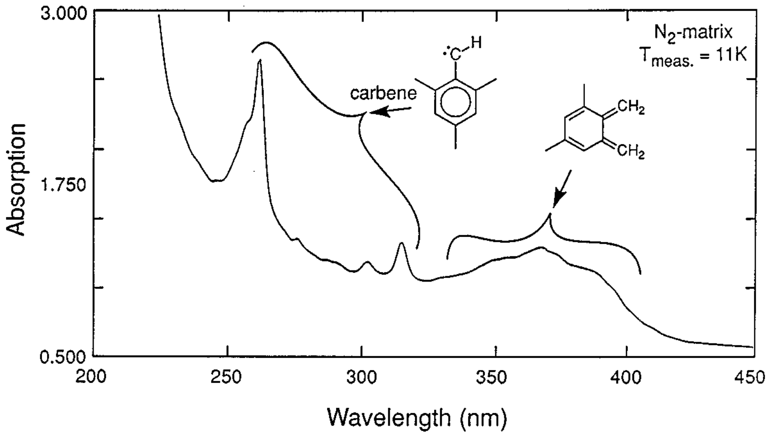
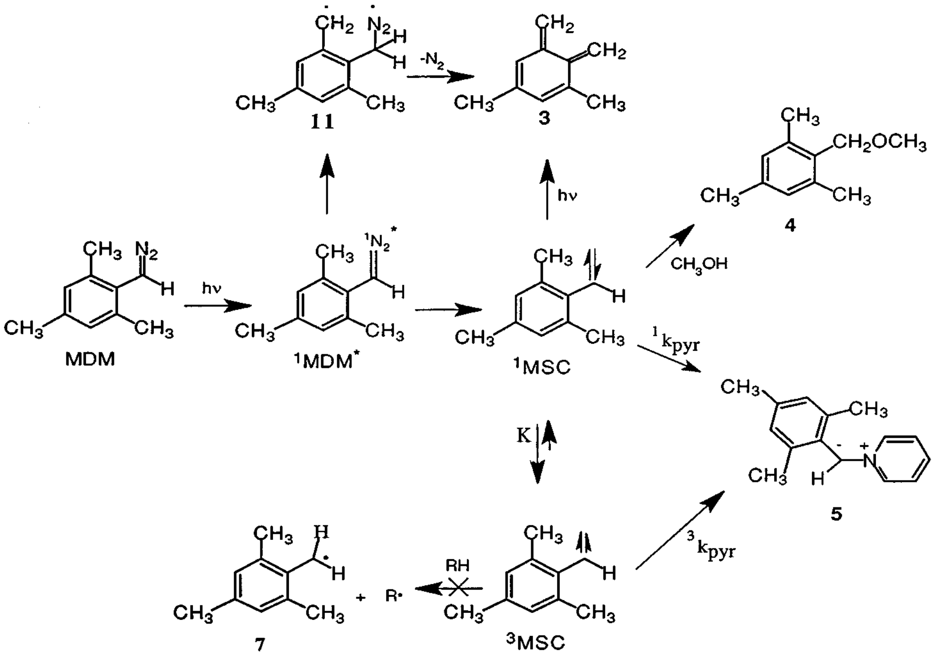


Figure 6. UV–Vis spectrum obtained after photolysis with unfiltered light of a high-pressure mercury lamp (200 W, six times 10 s) of mesityldiazomethane in a nitrogen matrix



Scheme 4

A diagnostic test for the matrix isolation of carbenes is their trapping with carbon monoxide to form a ketene. The ketene product is easily detected by IR spectroscopy and provides chemical evidence for the presence of carbenes in a matrix.[10–12] As expected, photolysis of mesityldiazomethane in a CO-doped argon matrix does generate a ketene.

In none of our experiments were we able to detect trimethylcycloheptatetraene. McMahon and co-workers[10] observed the formation of 1-methylcycloheptatetraene on photolysis of *o*-tolydiazomethane, but only as a result of secondary photolysis of *o*-tolylcarbene.

Triplet mesitylcarbene is thermally unstable even at 11 K and will isomerize to an *o*-quinodimethane. The thermal conversion can be monitored by UV–Vis spectroscopy. Figure 7 shows the decay of the carbene bands and the

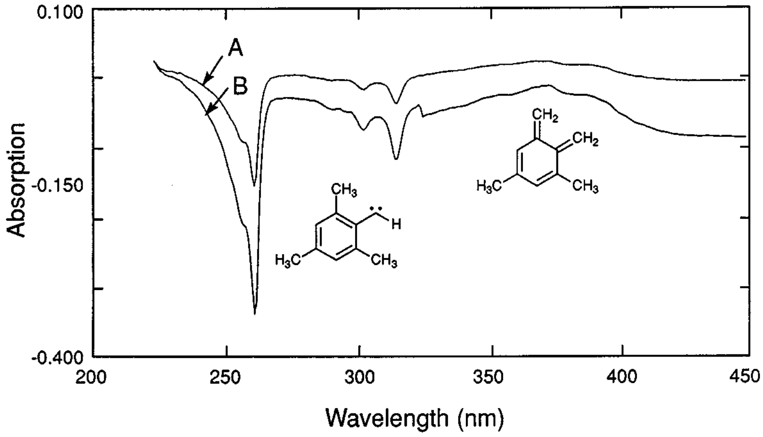


Figure 7. UV–Vis difference spectrum recorded (A) 60 min after photolysis stopped and (B) 150 min after photolysis stopped subtracted from one taken just after photolysis stopped showing the decrease in mesitylmethylene and concomitant increase in *o*-quinodimethane absorption bands

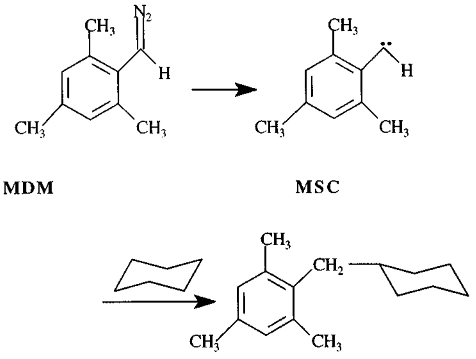
simultaneous growth of an *o*-quinodimethane absorption band. UV and IR spectroscopy demonstrate a clean conversion of carbene to *o*-quinomethane. The kinetics of this process are dispersive (dependent on time) and, if analyzed in terms of a (time)$^{1/2}$ dependence,[13] they are in agreement with data presented by McMahon and co-workers[10] ($k = 8 \times 10^{-6}$ s^{-1}, nitrogen matrix). The thermal isomerization of triplet mesitylcarbene to an *o*-quinodimethane at 11 K suggests there is a very small activation barrier for this process or more likely a quantum mechanical tunneling (QMT) mechanism of the hydrogen shift.[14]

LFP studies of MSC

LFP (308 nm) of a dilute solution of mesityldiazomethane (Scheme 4) in deaerated pentane produces a complex transient spectrum in a very narrow region (330–400 nm) (see Figure 8). However, the triplet carbene absorption band at 320 nm can be clearly discerned in this spectrum. The position of this band agrees well with that observed in rare gas matrices at cryogenic temperatures. The sharp strong absorption at 320 nm decays with a lifetime of 580 ns in pentane. This is in excellent agreement with the lifetime value deduced from pyridine ylide **5** (Scheme 5) (see below). Thus, the lifetime of spin-equilibrated MSC in pentane is at least 10 times longer than that of spin-equilibrated PC or TC under the same conditions. Steric blockade of the carbene center retards, we presume, the rate of reaction of the carbene with solvent in accord with the design principles of Zimmerman and Paskovitch[15] and of Tomioka *et al.*[11]

The broad absorption bands observed between 320 and 400 nm are attibuted to *o*-xylylene derivative **3**. The broad spectrum is in good agreement with the matrix spectrum of this intermediate and of parent 1,2-benzoquinodimethane (BQM).

The lifetimes of ^{3}MSC in Freon-113, hexafluorobenzene, cyclohexane and cyclohexane-d_{12} are 480, 470, 253 and 550 ns, respectively. The kinetic isotope effect (KIE) on the lifetime of ^{3}MSC is 1·9 in cyclohexane–cyclohexane-d_{12}. This KIE is very similar to that observed in hydrocarbon solvents with the naphthylcarbenes,[8] which do not decay in solution by intramolecular processes, and indicates that the decay of ^{3}MSC proceeds in large measure by reaction with the alkane solvent. Photolysis of MDM in cyclohexane followed by GC–MS analysis and product isolation demonstrates the clean formation of an adduct (**6**) with solvent in 53% isolated yield:



MDM **MSC**

6

Small amounts of stilbene and amine-type products were also observed as well. A product possibly resulting from dimerization of quinodimethane **3** in cyclohexane was observed by GC–MS analysis, but only in trace amounts.

The decay of ^{3}MSC in alkane solvents is not accompanied by the formation of a benzylic-type radical **7** (Scheme 4). ^{3}MSC, as per ^{3}PC,[3,9] decays primarily through singlet carbene reaction channels.

The lifetime of ^{3}MSC in hexafluorobenzene is independent of the concentration of the precursor used in our experiments. Thus, the lifetime of ^{3}MSC in hexafluorobenzene is not controlled by azine formation under the conditions employed in LFP studies.

It is surprising that the lifetime of ^{3}MSC is roughly the same in pentane, Freon-113 and hexafluorobenzene. This might lead one to conclude, despite the solvent isotope effects, that τ of ^{3}MSC is limited to some extent by reaction of the carbene with an *o*-methyl group. However, the yield of quinodimethane (A_{400}) is the same in cyclohexane and cyclohexane-d_{12} (Table 1). Thus in cyclohexane, MSC does not partition between the reaction with solvent and the formation of *o*-xylyene **3**.

Thus, if spin-equilibrated MSC reacts with an *o*-methyl group, the product must be a benzocyclobutene (**8**), which will not absorb above 300 nm, rather than an *o*-xylylene. However, GC–MS analysis provides evidence for the

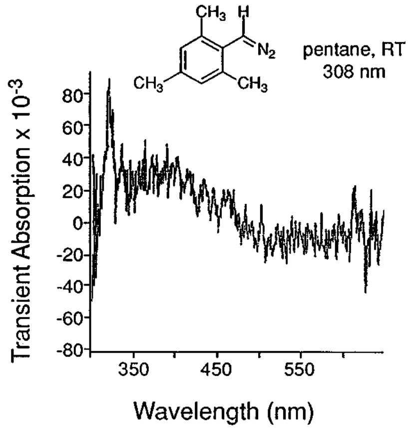


Figure 8. Transient absorption spectrum produced upon LFP of mesityldiazomethane in deaerated pentane at ambient temperature. The spectrum was recorded immediately after the 308 nm laser pulse over a window of 400 ns

formation of **8** in cyclohexane in no more than trace quantities. The lifetime data in Table 1 are consistent with GC–MS analysis, which reveals that MSC forms adducts with hexafluorobenzene and Freon-113, hence these solvents are not inert to the carbene. In fact, the lifetimes of spin-equilibrated phenylcarbene in Freon-113 and pentane are not vastly different (205 and 74 ns, respectively), which further indicates that the Freon is not an inert solvent. Hence there are neither kinetic nor GC–MS data to indicate that the lifetime of spin-equilibrated MSC is limited by its reaction with an *o*-methyl group.

The yield of quinodimethane **3** is also the same in CH_3CN and CD_3CN, demonstrating that the decay of MSC in this solvent also is not accompanied by the formation of an *o*-quinodimethane.

In acetonitrile solvent, MSC decays by formation of ylide **9** (max = 350 nm) in addition to C—H(D) insertion to give **10**, as demonstrated by the solvent isotope effect on the yield of **9**. This behavior is analogous to that of the naphthylcarbenes.[8]

The decay of carbene ^{3}MSC ($\lambda_{max} = 320$ nm) is not accompanied by any discernible increase in transient absorption of quinodimethane **3** in any solvent tested (alkanes, Freon-113, hexafluorobenzene). This is further evidence that the spin-equilibrated mixture of mesitylcarbene is not the source of the 3,5-dimethyl-*o*-xylylene **3** produced in the laser pulse. The rate constant of rearrangement must be ${}^3k_R \leqslant 2 \times 10^7\ s^{-1}$ from ^{3}MSC or ${}^1k_R K < 2 \times 10^7\ s^{-1}$ from ^{1}MSC. Later we will deduce that $K \approx 0{\cdot}0135$ and $\Delta G^{298}_{ST} \approx 2{\cdot}6$ kcal mol^{-1}, hence ${}^1k_R < 1{\cdot}5 \times 10^9\ s^{-1}$ (Scheme 5) at ambient temperature. If the Arrhenius pre-exponential factor to hydrogen shift in the carbene is $\geqslant 10^{12}\ s^{-1}$ then the activation barrier to rearrangement in the singlet state must exceed 3·9 kcal mol^{-1}. Thus, if the hydrogen shift proceeds through ^{1}MSC, then the barrier to rearrangement of ^{3}MSC is at least 5–6 kcal mol^{-1}. The facile rearrangement of ^{3}MSC at 11 K, despite these barriers, is further evidence of a QMT mechanism of hydrogen migration in the matrix.

Methanol is an excellent trap of singlet carbenes.[4] Singlet carbenes react rapidly with alcohols by formal O–H insertion reactions to form ethers (e.g. **4**, Scheme 4) at near diffusion-controlled rates. Indeed, the anticipated ether adduct is formed in 74% isolated yield along with small amounts of stilbene and mesitylaldehyde.

Upon LFP of MDM in methanol, the transient absorption of ^{3}MSC is not observed. However, the yield of *o*-xylylene **3** actually increases (Figure 9, Table 1) in methanol, relative to the less reactive hydrocarbon and Freon solvents. This is our final piece of evidence that **3** is not produced from a relaxed carbene intermediate.

We propose that **3** is produced by hydrogen migration in the singlet excited state ^{1}MDM* (Scheme 4) via intermediate **11**. Although **11** can be pictured as a biradical, it can also be thought of as a zwitterion.

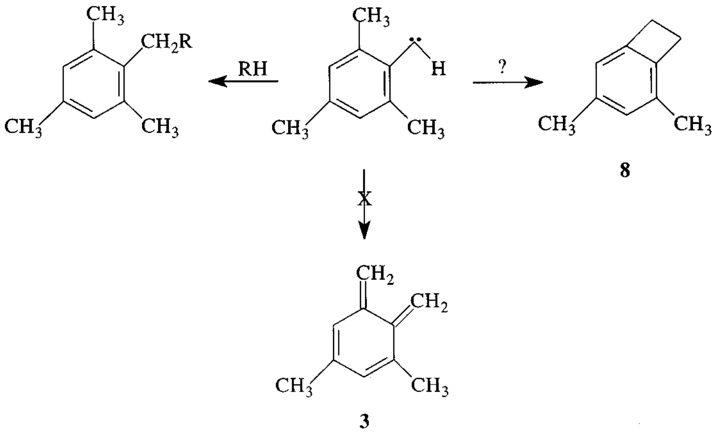
The increased yield of **3** in methanol relative to pentane indicates that the partitioning of ^{1}MDM* to **3** and ^{1}MSC must be solvent dependent. This suggests that **11** may indeed have zwitterionic character.

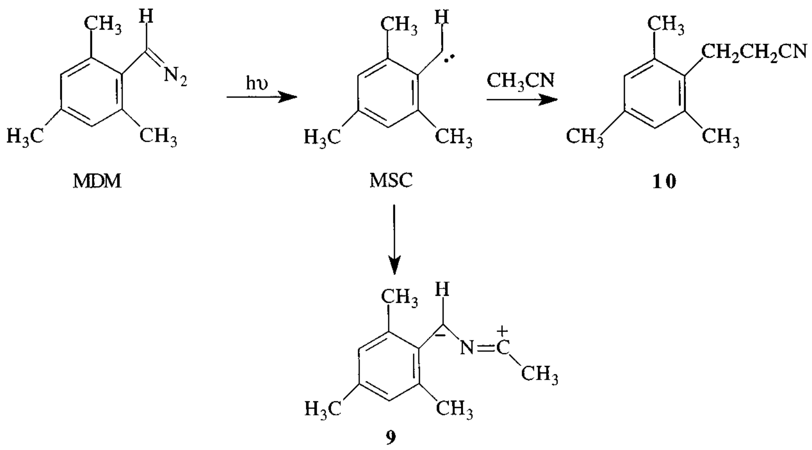
The migration of hydrogen probably does not proceed in

Table 1. The optical yield (A_{320}) and lifetime of ^{3}MSC, the optical yield of quinodimethane (**3**, A_{400}), and the optical yield of ylide **9** (A_{350}) as a function of solvent

Solvent	A_{320}[a]	A_{400}[b]	A_{350}[c]	τ_{320} (ns)[c]
Freon-113	0·3	0·06		480
Hexafluorobenzene	0·06	0·02		470
Pentane	0·21	0·03		550
Cyclohexane	0·26	0·05		253
Cyclohexane-d_{12}	0·30	0·04		550
Methanol	0	0·072		—[d]
Acetonitrile		0·045	0·12	
Acetonitrile-d_3		0·044	0·20	

[a] ±0·005.
[b] ±0·005.
[c] ±20 ns.
[d] Too short to measure.

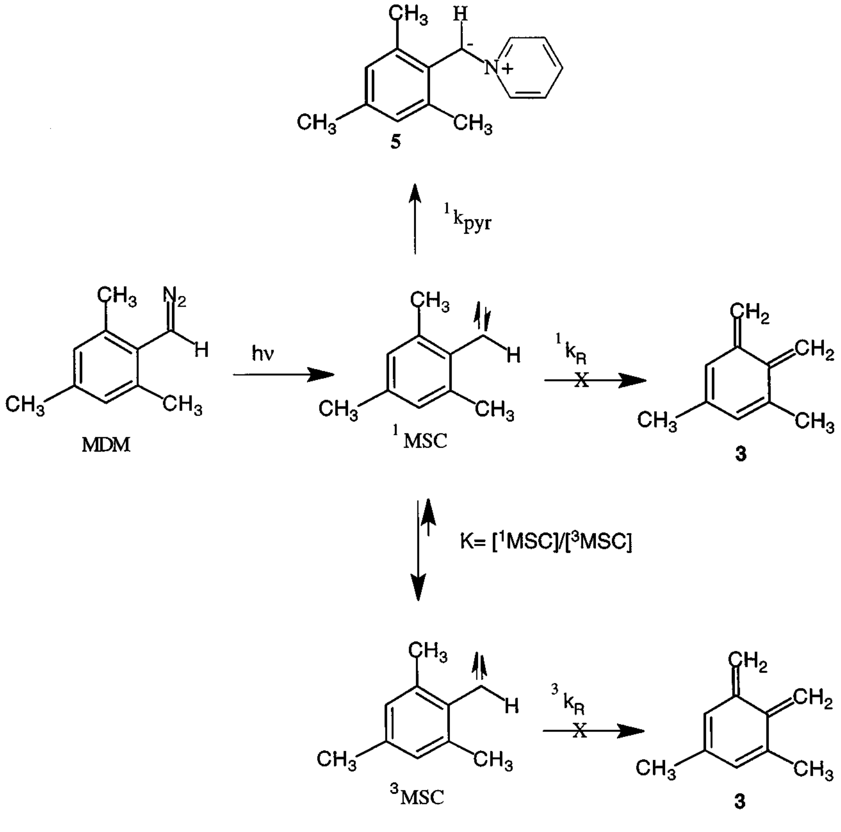




the triplet state of MDM (^{3}MDM*) because the yield of **3** is not suppressed upon LFP of MDM in the presence of 1 M isoprene.

The yield of quinodimethane, per laser pulse, from mesityldiazomethane is much more than the statistical factor of 2 relative to *o*-tolyldiazomethane. We presume that the excited state ^{1}TDM* can exist in conformations where hydrogen migration is inefficient, but that this is much less likely to be true for ^{1}MDM*.

GC–MS analyses of the products of photolysis of MDM in methanol and in methanol containing norbornene, a trap of putative *o*-xylylene **3**, indicated that products derived



Scheme 5

from **3** are present in at most very low yields. This demonstrates that even in methanol where hydrogen migration is most prevalent, the absolute yield of this process is still low.

Trapping of MSC with pyridine

LFP of mesityldiazomethane in the presence of pyridine produces an intense transient absorption at 425 nm (Figure 10), which is attributed to carbene–pyridine ylide **5** (Scheme 4). This transient spectrum is similar to that of the ylides formed from the reactions of phenylcarbene and *o*-tolylcarbene with pyridine. The absolute rate of formation of the pyridine is first order in the concentration of pyridine $k_{pyr}=1{\cdot}35\times10^{7}\ \text{M}^{-1}\ \text{s}^{-1}$ (Figure 11). This is very similar to the value observed with phenylcarbene, which indicates that pyridine is not effectively blockaded by the *o*-methyl groups.

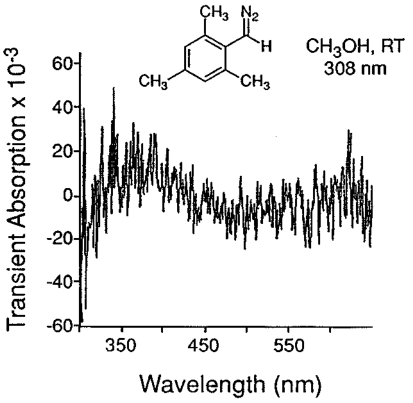


Figure 9. Transient absorption spectrum produced upon LFP of mesityldiazomethane in deaerated methanol at ambient temperature. The spectrum was recorded immediately after the laser pulse over a window of 400 ns

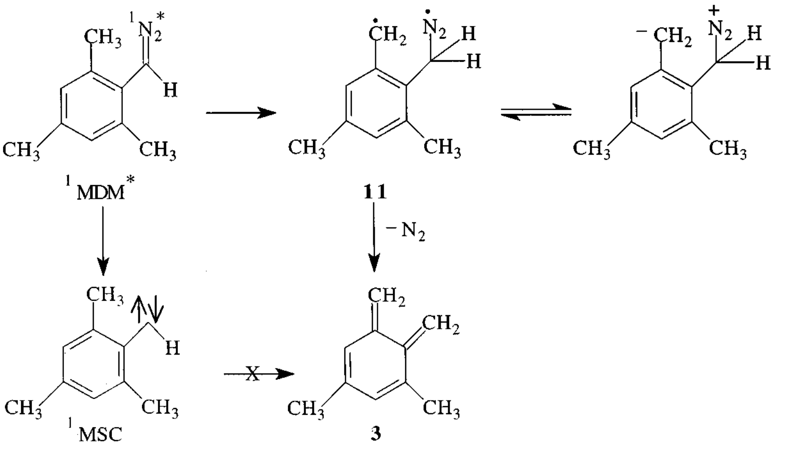
The intercept of the plot of Figure 11 is $1{\cdot}93\times10^{6}\ \text{s}^{-1}$, which predicts that the lifetime of the ylide-forming intermediate in pentane is *ca* 500 ns. This is further support for the attribution of the sharp 320 nm band to ^{3}MSC.

The reaction of ^{3}MSC with pyridine to form a singlet-state ylide is formally spin forbidden. A classical interpretation[3] maintains that it is the low-lying singlet state of the carbene which reacts with pyridine (Scheme 5). In this case, $k_{pyr}={}^{1}k_{pyr}K$, where k_{pyr} is the measured rate constant and $^{1}k_{pyr}$ is the absolute rate constant of reaction of ^{1}MSC with pyridine (Scheme 4). If $^{1}k_{pyr}=1\times10^{9}\ \text{M}^{-1}\ \text{s}^{-1}$, as is typical of singlet carbenes,[4] then $K=0{\cdot}0135$ and $\Delta G_{ST}^{298}=2{\cdot}6$ kcal mol^{-1}. These values are very similar to those derived previously for phenylcarbene and close to, but smaller than, the prediction of theory (4 kcal mol^{-1})[2] for the latter species.

Griller *et al.*[16] postulated that triplet carbenes can react via surface-crossing mechanisms, effectively bypassing the low-lying singlet state minimum. If this is indeed the mechanism of reaction of ^{3}MSC with pyridine then ΔG_{ST} must be $\geq 2{\cdot}6$ kcal mol^{-1}; the fact that the experimental value of the singlet–triplet splitting of PC is smaller than the theoretical estimate indicates that ^{3}PC (and presumably ^{3}MSC) can intersect the singlet plus pyridine surface at a point lower in energy than the singlet minimum as suggested by Griller *et al.*[16]

CONCLUSIONS

A thermal intramolecular 1,4-hydrogen shift leading to rearrangement of triplet mesitylmethylene (^{3}MSC) to singlet *o*-quinodimethane occurs at 11 K probably by a tunneling mechanism. The estimated activation barrier for this process is fairly large, $>3{\cdot}9$ kcal mol^{-1} for a singlet carbene or $>6{\cdot}5$ kcal mol^{-1} for the triplet carbene if a classical pre-equilibrium mechanism is operative. These results are in accord with previous studies by McMahon and co-workers.[10] Photolysis of mesityldiazomethane (MDM) in solution at ambient temperature produces a singlet excited



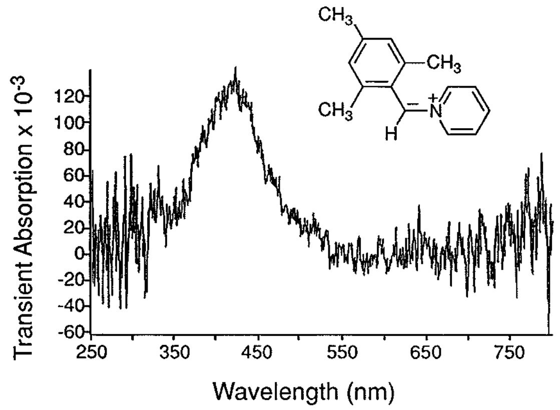


Figure 10. Transient absorption spectrum produced upon LFP of MDM in deaerated pentane containing pyridine at ambient temperature. The spectrum was recorded during a window of 400 ns immediately after the laser flash

state (^{1}MDM*), which forms a biradical or zwitterionic intermediate that partitions between nitrogen extrusion and carbene formation, and 1,4-hydrogen migration to form directly 3,5-dimethyl-1,2-benzoquinodimethane. The lifetime of ^{3}MSC in pentane solution at ambient temperature is *ca* 500 ns and is controlled by intermolecular process.

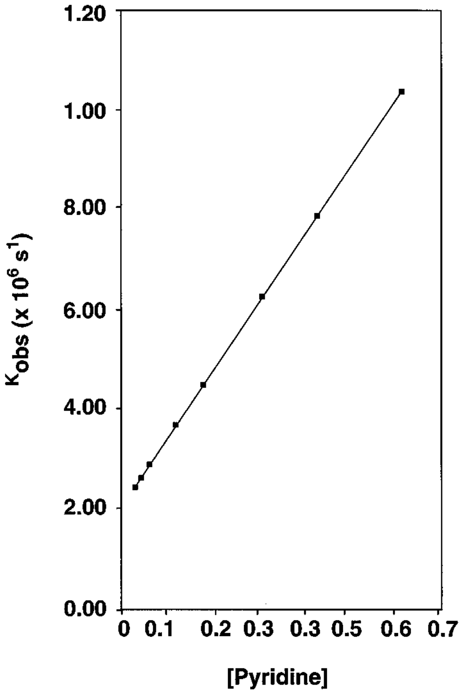


Figure 11. Observed pseudo-first-order rate constant k_{obs} of formation of pyridine ylide **5** in pentane as a function of pyridine concentration

Hydrogen migration in the excited state of the diazo compound is more significant in methanol than in hydrocarbon solvents. Phenylcarbene and *o*-tolylcarbene have much shorter lifetimes (τ=74 ns) in pentane than mesitylcarbene, as expected from the work of Zimmerman and Paskovitch[15] and of Tomioka *et al.*[11]

EXPERIMENTAL

Diazo precursors were synthesized in the standard manner[9, 10] as illustrated for phenyldiazomethane and mesityldiazomethane. Solvents and pyridine were purified and dried by standard procedures.

The matrix isolation techniques used in this study have been described elsewhere.[17] The experiments were conducted in two different matrices utilizing argon and nitrogen. Thermal processes were monitored by UV–Vis spectroscopy (Philips PU8710). The analyzing light was cut off between scans to avoid any photochemical processes.

Laser flash photolysis experiments utilized a Lambda Physik EMG 101 excimer laser emitting 20 ns pulses of 308 nm light (150 mJ per pulse) and have been described previously.[18] The absorbance of the samples were kept at 0·3–0·5 at 308 nm. An EG&G Princeton Applied Research Model 1460 optical multichannel analyzer (OMA) recorded all transient absorption spectra. When necessary, oxygen was removed by bubbling argon through the sample for 3 min.

Benzaldehyde tosylhydrazone. A 250 ml round-bottomed flask containing a magnetic stirring bar was charged with benzaldehyde (8·0 g, 0·075 mol) and 100 ml of absolute ethanol. To this solution was added 15·3 g (0·082 mol) of *p*-toluensulfonhydrazide. The flask was fitted with a condenser and the mixture was refluxed for 5 h under an atmosphere of nitrogen. The solution was cooled in an ice-bath and the white crystalline solid was filtered and washed with cold absolute ethanol. The filtrate was further concentrated and cooled in an ice-bath to give a second crop of crystals. The solid was filtered and washed with cold absolute ethanol. The combined crude product was recrystallized from hot absolute ethanol to give 18·5 g (90%) of the white crystalline tosylhydrazone. The melting point of the product was 129–131 °C. ^{1}H NMR (DMSO-d_6), δ: 2·33 (s, 3H, CH_3), 7·35–7·75 (m, 9H, aromatic-H), 7·81 (s, 1H, —CH=N—), 11·95 (s, 1H, NH).

Sodium salt of benzaldehyde tosylhydrazone. In a 100 ml Erlenmeyer flask containing a magnetic stirrer was dissolved 2·5 g (8·45 mol) of benzaldehyde tosylhydrazone in 75 ml of freshly distilled diethyl ether. The solution was cooled in ice-bath and 1·274 g (6·86 mol) of NaH (60% in mineral oil) was added with stirring. The solution was stirred at room temperature for 24 h under an atmosphere of nitrogen. The solid product which was formed, was filtered and washed with dry diethyl ether. The solid was dried completely under vacuum at room temperature. The yield of the dry colorless sodium salt was 2·7 g (80%).

Phenyldiazomethane. In a 25 ml round-bottomed flask equipped with a magnetic stirring bar and a short-path distillation condenser was placed 0·8 g (2·70 mol) of the sodium salt of benzaldehyde tosylhydrazone. A receiving flask was cooled in a dry ice–isopropyl alcohol bath. The salt was heated with stirring under vacuum (*ca* 0·5 mmHg) in an 80 °C oil-bath for 45 min. A colored gas was produced and collected as an orange solid in the receiving flask. The oil bath temperature was gradually raised to 120 °C to ensure that the salt was completely decomposed. The isolated product was quickly weighed (0·12 g, 62%) and dissolved in 100 ml of pentane. The flask containing the pentane solution was wrapped with aluminum foil to protect it from light and stored in a freezer. ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 4·88 (s, 1H, —$\mathrm{CH{=}N_2}$), 7·41–7·8 (m, 5H, aromatic-H) ppm.

Mesitaldehyde tosylhydrazone. A solution of mesitaldehyde (0·9 g, 6·1 mmol) (Aldrich) and *p*-tosylhydrazide (1·13 g, 6·1 mmol) (Aldrich) in ethanol (25 ml) was refluxed under argon for 1 h. The solution was cooled to room temperature and the crystals that formed were filtered and recrystallized from ethanol to give mesitaldehyde tosylhydrazone in 90% yield (1·7 g, 5·5 mmol), m.p. 156–158 °C, IR (KBr): 3203, 1597, 1326 and 1164 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$, 200 MHz), δ: 8·02 (s, 0·4× 1H, NC—H), 7·82 (d, 8Hz, 0·4× 2H, tosyl Ar—H), 7·75 (d, 8Hz, 0·6× 2H, tosyl Ar—H), 7·76 (s, 0·4× 1H, N—H), 7·60 (s, 0·6× 1H, NC—H), 7·50 (s, 0·6× 1H, N—H), 7·24 (d, 8 Hz, 0·6× 2H, tosyl Ar—H), 7·23 (d, 8 Hz, 0·4× 2H, tosyl Ar—H), 6·80 (s, 0·6× 2H, mesityl Ar—H) 6·75 (s, 0·4× 2H, mesityl Ar—H), 2·40 (s, 0·6× 3H, $\mathrm{CH_3}$), 2·38 (s, 0·4× 3H, $\mathrm{CH_3}$) 2·30 (s, 0·4× 3H + 0·6× 6H, $\mathrm{CH_3}$), 2·28 (s, 0·4× 3H, $\mathrm{CH_3}$), 2·05 (s, 0·6× 6H, $\mathrm{CH_3}$) ppm. MS: m/z 316 (M$^+$, 22), 161 (100), 132 (82), 91 (65).

Sodium salt of mesitaldehyde tosylhydrazone. To a solution of mesitaldehyde tosylhydrazone in THF under argon at − 10 °C was added NaH (60% in mineral oil). The resulting solution was warmed to room temperature and the white precipitate that formed was filtered and dried under vacuum to afforded sodium salt of mesitaldehyde tosylhydrazone in 80% yield (1·71 g, 5·1 mmol), m.p. 70 °C (decomp.). IR (KBr): 1250, 1221, 1140, 1094 and 1049 cm^{-1}. ^{1}H NMR (DMSO-d_3, 200 MHz), δ: 7·94 (s, 0·7× 1H, NC—H), 7·65 (d, 8Hz, 0·7× 2H, tosyl Ar—H), 7·45 (d, 8Hz, 0·3× 2H, tosyl Ar—H), 7·22 (d, 8Hz, 2H, tosyl Ar—H), 6·94 (s, 0·3× 2H, tosyl Ar—H), 6·81 (s, 0·7× 2H, NC—H), 5·42 (s, 0·3× 1H, NC—H), 2·37 (s, 3H, $\mathrm{CH_3}$), 2·30 (s, 6H, $\mathrm{CH_3}$), 2·26 (s, 0·3× 3H, $\mathrm{CH_3}$) and 2·25 (s, 0·7× 3H, $\mathrm{CH_3}$) ppm.

Mesityldiazomethane. A two-necked round-bottomed flask equipped with a magnetic stirrer was connected to a short-path distillation apparatus and an additional flask which contained the sodium salt of mesitaldehyde tosylhydrazone. A receiving flask which was placed in an isopropyl alcohol–dry-ice bath was connected to the distillation apparatus. The two-necked, round-bottomed flask was heated to 110 °C under vacuum (0·01 Torr) and the sodium salt added slowly under stirring. The red liquid that formed was collected to yield mesityl diazomethane. IR (NaCl plates, $\mathrm{CHCl_3}$); 2058 and 1610 cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$, 200 MHz), δ: 6·83 (s, 2H, Ar—H), 4·75 (s, 1H, $\mathrm{N_2}$C—H), 2·24 (s, 3H, $\mathrm{CH_3}$), 2·22 (s, 6H, $\mathrm{CH_3}$) ppm.

Preparative photolysis of MDM in cyclohexane. MDM (55 mg, 0·34 mmol) was dissolved in cyclohexane (4 ml) and argon was bubbled through the solution, after which it was sealed. This solution was irradiated in a standard Rayonet apparatus equipped with 300 nm light bulbs at 4 °C. GC Analysis of the reaction mixture indicated formation of one major compound, which was shown to be the carbene–cyclohexane insertion product, cyclohexylmesitylmethane. The solvent was removed under vacuum to yield a colorless oil, which was subjected to column chromatography on silica gel with hexane–ethyl acetate as eluent. The first fraction contained cyclohexylmesitylmethane (36 mg, 0·18 mmol, 53% yield). The second and third fractions contained *trans*-2,2′, 4,4′, 6,6′-hexamethylstilbene (14 mg, 0·053 mmol, 32% yield) and 2,4,6-trimethylbenzalazine (3 mg, 0·01 mmol, 6% yield), respectively. These three fractions accounted for *ca* 90% of the mass balance. The *trans*-2,2′,4,4′,6,6′-hexamethylstilbene was characterized by comparison of its ^{1}H NMR spectrum with that reported in the literature,[19] whereas the spectra of cyclohexylmesitylmethane and 2,4,6-trimethylbenzalazine were compared with those of the analogues compound cyclohexylbenzenemethane.[20]

Cyclohexylmesityl methane:[21] IR (neat): 2922, 2850 (C—H), 1613 (C=C) cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$, 200 MHz), δ: 6·84 (s, 2H, AR—H), 2·50 (d, 6Hz, 2H), 2·29 (s, 6H, *o*-$\mathrm{CH_3}$), 2·26 (s, 3H, *o*-$\mathrm{CH_3}$), 1·7–1·6 (m, 6H), 1·2–1·1 (m, 5H) ppm. ^{13}C NMR ($\mathrm{CDCl_3}$, 75 MHz), δ: 136·6, 134·6, 128·8, 39·1, 36·8, 33·7, 26·6, 26·5, 20·8 (C—H,*p*-$\mathrm{CH_3}$), 20·4 (C—H, *o*-$\mathrm{CH_3}$) ppm. GC—MS: m/z 216 (M$^+$), 133.

trans-2,2′, 4,4′, 6,6′-Hexamethyl stilbene:[20] ^{1}H NMR ($\mathrm{CDCl_3}$, 200 MHz), δ: 6·77 (s, 4H, Ar—H), 6·66 (s, 2H, vinyl H), 2·16 (s, 6H, *p*-$\mathrm{CH_3}$), 1·98 (s, 12H, *o*-$\mathrm{CH_3}$) ppm. GC—MS: m/z 264 (M$^+$), 250, 234.

2,4,6-Trimethylbenzalazine:[21] ^{1}H NMR ($\mathrm{CDCl_3}$, 200 MHz), δ: 8·98 (s, 2H, N = C—H), 6·92 (s, 2H, Ar—H), 2·51 (s, 6H, *o*-$\mathrm{CH_3}$), 2·30 (s, 3H, *p*-$\mathrm{CH_3}$) ppm. GC–MS: m/z 292 (M$^+$), 277, 260, 145, 131.

GC–MS analyses of reaction mixture photolyses of MDM in cyclohexane showed trace amounts of masses 132 and 266 in addition to the three products isolated from the reaction mixture. It can be speculated that the compound with an m/z of 132 is benzocyclobutane **8**, (2,4-dimethyl bicyclo[4.2.0]octa-1,3,5-triene) formed from intramolecular [2 + 2] dimerization of *o*-xylylene **3**. The compound with an m/z of 266 can be assigned to dimesitylethane, which can be formed from triplet MDM.

GC–MS analyses of photolyses mixture of MDM in cyclohexane–2-norbornene mixture showed three additional peaks, all having mass 226. Two of these peaks had identical fragmentation patterns whereas the third peak had a different fragmentation pattern. It can be suggested that one of these compounds originates from trapping of MSC and the other from Diels–Alder reaction between *o*-xylylene **3** and 2-norbornene. To confirm this idea further, product studies of MDM in methanol were undertaken.

Preparative photolysis of MDM in methanol. MDM (54 mg, mmol) was photolyzed in methanol (5 ml) under the same conditions as described above. The solvent was removed under vacuum to yield an oil. ^{1}H NMR analysis of the reaction mixture showed that four products were formed: 74% of the methanol insertion product, methyl methylmesitylene ether,[22] 10% of *trans*-2,2′,4,4′,6,6′-hexamethylstilbene,[19] 12% of mesitaldehyde and 7% of *cis*-2,2′,4,4′,6,6′-hexamethylstilbene.[19] The products were characterized by comparison of the ^{1}H NMR spectra with those reported in the literature.

Methyl methylmesitylene ether:[22] ^{1}H NMR ($CDCl_3$, 200 MHz), δ: 6·93 (s, 2H, Ar—H), 4·48 (s, 2H, Ar—CH_2—OMe), 3·41 (s, —OCH_3), 2·38 (s, 6H, *o*-CH_3), 2·28 (s, 3H, *p*-CH_3) ppm. GC–MS: m/z 292 (M^+), 277, 260, 145, 131.

cis-2,2′,4,4′,6,6′-Hexamethylstilbene:[19] ^{1}H NMR ($CDCl_3$, 200 MHz), δ: 6·93 (s, 4H, Ar—H), 6·55 (s, 2H, vinyl-H), 2·38 (s, 12H, *o*-CH_3), 2·30 (s, 6H, *p*-CH_3) ppm. GC–MS:
m/z 264 (M^+), 250, 234.

GX–MS analysis of the photolysis mixture of MDM in methanol identified (in addition to the four products analyzed from the NMR spectra) trace amounts of compounds with m/z 132 and 292. These masses can be assigned to benzocyclobutane **8** (2,4-dimethylbicyclo[4.2.0]octa-1,3,5-triene) and 2,4,6-trimethylbenzalazine, respectively.

GC–MS analysis of the photolysis mixture of MDM in cyclohexane containing 2-norbornene indicated that only one of the three mass 226 products observed in cyclohexane was obtained in methanol and it can therefore be assigned to the Diels–Alder product formed between *o*-xylylene **3** and 2-norbornene.

Conclusion. About 90% of the mass balance from photolyses in cyclohexane comes from carbene reactivity. ^{1}H NMR analysis of the photoreaction mixture from methanol identifies only those products that come from the carbene intermediate. It can therefore be concluded that less than 10% of the reaction goes through the excited state reaction.

Trapping with 2-norbornene gives one additional product in methanol and three in cyclohexane, which indicates that in methanol *o*-xylylene **3** has trapped with 2-norbornene whereas in cyclohexane both *o*-xylylene **3** and MDM were trapped with 2-norbornene.

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