Elusive Arylalkylcarbenes in Solution and in Crystals: Facile 1,2-R (R = H, Ph) Migrations of 1,2,2-Triphenylethylidene

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ABSTRACT: Highly reactive arylalkylcarbenes generated in solution by photolysis of their aryldiazoalkane precursors tend to undergo competing inter- and intramolecular reactions to yield a complex mixture of products. Having previously shown the use of crystals to effectively control the reactivity of arylalkylcarbenes to afford high yields of a single product, it was of interest to investigate whether the crystalline environment could also enable spectroscopic detection of these intermediates *en route* to photoproduct. Using 1,2,2-triphenyldiazoethane (**3**) as a model substrate to probe the effect of alternative reaction trajectories that yield triphenylethylene (**5**) by competing 1,2-H shift or 1,2-Ph migration, we report selectivities consistent with reaction from a spin-equilibrated carbene **4** in solution, while reactions in crystals primarily afford alkene **5** via a lattice-controlled 1,2-H shift. Attempts to detect 1,2,2-triphenylethylidene **4** in crystals by nanosecond laser flash photolysis or by triplet-triplet fluorescence at 77 K were unsuccessful, indicating that arylalkylcarbenes possessing α-H substituents undergo facile 1,2-H shifts both in solution and in the solid state. However, related *tert*-butylphenylmethylene with no α-H substituents could be observed by triplet-triplet fluorescence at 77 K in glassy matrices.

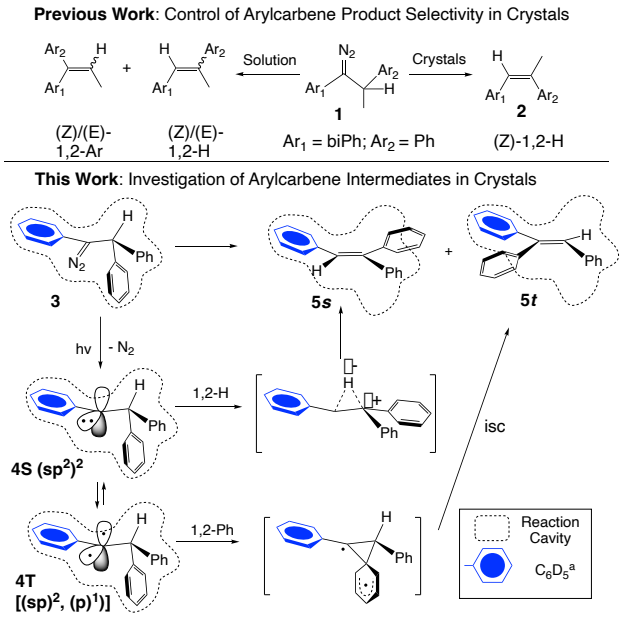
INTRODUCTION

Arylalkylcarbenes remain among the most elusive reactive intermediates in organic chemistry.[1] In contrast to their diarylcarbene relatives, which are sufficiently stable and long-lived to be observed by time-resolved pump-probe spectroscopy and cryogenic methods,[2] mechanistic analyses of arylalkylcarbenes have revealed ultrafast intramolecular 1,2-H shifts and 1,2-Ph migrations to olefin photoproducts in competition with intermolecular trapping reactions.[3] Although femtosecond and picosecond time-resolved methods have enabled direct observation of arylalkylidenes in a few instances, these measurements still suffer from weak signals and complications associated with rearrangements from excited states that bypass relaxed carbenes.[4,5]

We previously demonstrated that the crystalline solid-state can serve as a platform to control the reactivity of arylalkylcarbene intermediates. While irradiations of dilute solutions of 1,2-diaryldiazopropanes were shown to give a mixture of *E*- and *Z*-alkene isomers via competing 1,2-H shifts and 1,2-Ph migrations, photoreactions carried out in powdered crystals gave only the *Z*-olefin via 1,2-H shift (Scheme 1, top).[6] Of note, 1-(4′-biphenylyl)-2-phenyldiazopropane (**1**) underwent a stereoselective 1,2-H shift to yield (*Z*)-1-(4′-biphenylyl)-2-phenylpropene (**2**) with > 95% yield in an efficient and highly selective solid-to-solid reaction (Scheme 1, top).[7a] A mechanistic investigation of the photoreaction of diazo **1** revealed that the single conformer of the aryldiazoalkane in crystals is primed to generate a carbene intermediate that retains a nearly identical conformation.[7b]

It is known that arylalkylcarbenes tend to exist in rapid equilibrium between a closed-shell singlet with the two

Scheme 1. Crystalline Solid-State Photochemistry of Aryldiazoalkanes[a]



[a]For subsequent figures, deuterated phenyl groups will be depicted with a solid blue circle.

electrons occupying the carbene sp^2 orbital [**4S** $(sp^2)^2$], and an open-shell triplet with one electron in each of the carbene sp^2 and pure p orbitals [**4T** $(sp^2)^1(p)^1$] (Scheme 1, bottom). While singlet arylalkylcarbenes are known to undergo preferential 1,2-H shifts and triplet carbenes to accommodate efficient 1,2-Ph migrations, both rearrangements require geometries where

the migrating group is aligned parallel to the carbene *p* orbital; thus, 1,2-H shifts resemble hydride migrations and 1,2-Ph migrations proceed through a Cram phenonium-type spirocyclooctadienyl biradical that intersystem crosses (isc) along its pathway to photoproduct(s) (Scheme 1, bottom).[8] In solution, multiple 1,2-R migrations can occur with relative ease due to facile conformational equilibration and readily accessible transition states. By contrast, reactions in crystals that occur under topochemical control are generally predisposed for one of the α-groups to migrate. Therefore, we previously suggested that the stereochemistry of the olefin photoproduct can be predicted *a priori* based on stereoelectronic considerations of the carbene deduced from the molecular structure of the corresponding aryldiazoalkane precursor obtained from single crystal X-ray diffraction (SC-XRD), or relatively simple molecular mechanics calculations.[9] In the case of **1**, a reasonable structural overlap between the starting aryldiazoalkane and ensuing alkene product **2** enabled the reaction to proceed to completion via a solid-solution with retainment of crystallinity in the form of a metastable phase of the reactant.[7b] As a result, photolysis of **1** leads to a 1,2-H shift to form **2** as the single product by a least motion pathway enforced by the rigidity of medium.

Considering the product-determining role of the crystalline environment on arylalkylcarbene reactivity, we became interested in exploring their direct spectroscopic detection in this medium. We reasoned that detection in crystals might be possible if 1,2-R migration rates are significantly reduced under the constraints imposed by the van der Waals boundaries constituting a reaction cavity formed by the surrounding close neighbors (dotted line in Scheme 1, bottom). In particular, steric restrictions to conformational changes and molecular motion required for 1,2-R migrations may result in potential energy barriers that extended the arylalkylcarbene lifetime enough to carry out spectroscopic characterization by nanosecond laser-flash photolysis or cryogenic steady-state fluorescence measurements. Moreover, crystalline constraints on structural geometries could alter the rates of carbene singlet-triplet interconversion and their equilibrium population, potentially facilitating their observation.

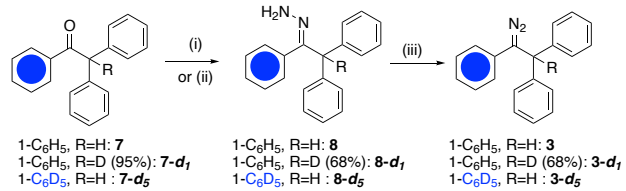
Herein we report the solution and crystalline state photochemistry of 1,2,2-triphenyldiazoethane (**3**). Irradiation of phenyl-deuterated isotopologue **3-*d*$_5$** in solution yields a mixture of triphenylethylene regioisotopologs **5*s*** and **5*t*** via 1,2-H shift and 1,2-Ph migration, respectively, with temperature-dependent selectivities consistent with a spin state-equilibrated 1,2,2-triphenylethylidene (**4**) intermediate. By contrast, photolysis of crystalline samples of **3-*d*$_5$** primarily affords **5*s*** via a lattice-controlled 1,2-H shift. Room temperature nanosecond laser-flash photolysis measurements in solution suggest that transformation of **3** to **5** can occur within the ca. 10 ns width of our excitation pulse. Analogous experiments with nanocrystalline suspensions hint that conversion of **3** to photoproduct(s) also occurs on similar timescales in the solid state. Attempts to detect **4** by steady-state triplet-triplet (T-T) fluorescence in methylcyclohexane glasses or in crystals at 77 K also yielded final product **5** as the only detectable species. By contrast, T-T fluorescence of *tert*-butylphenylmethylene unable to undergo 1,2-H shifts could be readily observed, highlighting the efficiency of this rearrangement both in solution and the crystalline solid state.

RESULTS AND DISCUSSION

Synthesis and Characterization of 3. Aryldiazoalkane **3** was prepared from 1,2,2-triphenylethanone (**7**) by mercuric oxidation of the corresponding hydrazone (**8**) in overall 32% yield (Scheme 2). Isotopologue **3-*d*$_1$**, of interest for the solid-state studies discussed below, was synthesized with 68% deuterium incorporation starting from **7-*d*$_1$**. Alternatively, isotopologue **3-*d*$_5$** containing a perdeuterated 1-phenyl group used to distinguish **5*s*** from a 1,2-H shift from its regioisotopomer **5*t***, formed by a 1,2-Ph migration, was prepared starting from **7-*d*$_5$**.

Compounds **7**, **8**, and **3** were fully characterized by a suite of spectroscopic methods. As the chemistry along the reaction sequence occurs at the original carbonyl center, successful functional group interconversion of ketone **7** to hydrazone **8** to diazo **3** is most easily tracked by their diagnostic infrared vibrations and $^{13}C\{^1H\}$ NMR resonances; **7**, **8**, and **3** display ν(CO) = 1684 cm^{-1} and δ(C=O) = 198.3 ppm, ν(NH) = 3354 cm^{-1} and δ(C=NNH$_2$) = 152.3 ppm, and ν(C=N$_2$) = 2037 cm^{-1} and δ(C=N$_2$) = 61.3 ppm, respectively.

Scheme 2. Synthesis of **3**, **3-*d*$_1$**, and **3-*d*$_5$**



(i) N2H4, AcOH, EtOH, reflux; (ii) N2H4, AcOH-d4, EtOD, reflux; (iii) HgO, MgSO4, KOEt, Et2O, room temperature

Acetonitrile solutions of **3** display a strong absorption maximum at λ_{max} = 289 nm (ε_{289} = 2.0 x 10^4 M^{-1} cm^{-1}) along with a much weaker visible band at λ_{max} = 511 nm (ε_{511} = 40 M^{-1} cm^{-1}) that gives rise to the red color characteristic of aryldiazoalkanes. These absorption maxima and molar absorptivities are in good agreement with those assigned to π→π* and n→π* transitions in related 1,2-diaryldiazoalkanes.[6] Analogous absorption bands in ketone **7** occur at λ_{max} = 249 nm (ε_{249} = 1.3 x 10^4 M^{-1} cm^{-1}) and λ_{max} = 328 nm (ε_{328} = 178 M^{-1} cm^{-1}), respectively.[10]

Single-crystals of **3** suitable for SC-XRD analysis were grown by slow evaporation of a concentrated diethyl ether (Et$_2$O) solution at –15 °C. Gratifyingly, red crystals obtained in this fashion have a high melting point of 112–115 °C. Diazo compound **3** crystallizes in the space-group P$\bar{1}$ with one molecule per asymmetric unit displaying torsion angles of C3–C2–C1–N1 = –7°, C4–C2–C1–N1 = –120°, and H1–C2–C1–N1 = –124° (Figure 1a). The latter two angles describe the direction of the C4-α-phenyl and α-H1 substituents relative to the plane of the diazo group. They are both relatively close to the ideal torsion angle of 90° required for migration into the carbene *p*-orbital (Scheme 1, bottom) and similar to those observed in the molecular structure of diazo **1** (Scheme 1). The topochemical postulate suggests that migrations involving large phenyl groups should be unfavored in crystals, and the expected reaction trajectories for both phenyl groups in **3** suggest they would have to undergo relatively large amplitude motions. Such displacements are greatest for the C4-α-phenyl group (Figure 1), which must rotate about the C2–C4 bond to

present a co-facial orientation, as well as around the C1–C2 bond to attain a torsion angle closer to 90°. By analogy to crystalline **1**, whose photoreaction favors a 1,2-H shift (*vide supra*), we anticipate **3** to yield **5** by a 1,2-H shift rather than a 1,2-Ph rearrangement.

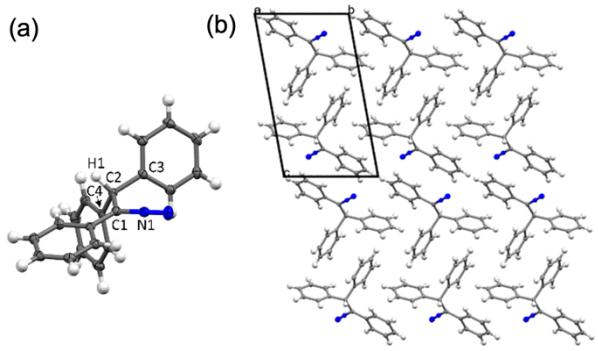


Figure 1. (a) Molecular and (b) packing structure of **3** with thermal ellipsoids set at 50% probability.

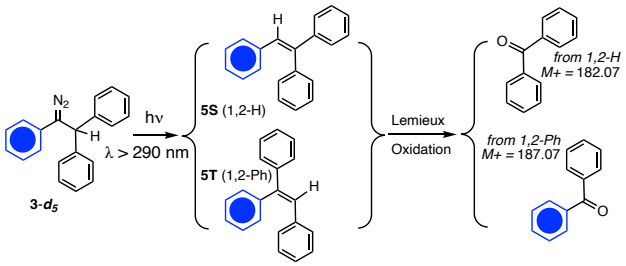
The packing structure of **3** viewed along its crystallographic *a* axis is illustrated in Figure 1b. Whereas stacked columns of molecules of **3** along the *a* direction do not feature any significant interactions, columns of diazo molecules running along the *c* axis are held together by pairwise centrosymmetric edge-to-face and face-to-face interactions between phenyl groups of adjacent molecules. Edge-to-face interactions are also discernible along the *b* direction.

Solution and Solid-State Product Selectivity Studies with λ > 380 nm. Reliable mechanistic conclusions from product analysis studies of aryldiazoalkanes must consider the involvement of wavelength-dependent rearrangements in the excited state (RIES), which yield carbene-like products but bypass relaxed carbene intermediates.[11] Longer wavelengths and triplet sensitization are known to minimize RIES.[12] With this in mind, we first selectively irradiated the visible band of diazo **3** with λ > 380 nm.

An important design feature of **3** is that both 1,2-H shift and 1,2-Ph migration processes produce photoproduct **5**, allowing us to investigate the importance of steric interactions along different reaction trajectories in the crystalline solid state. To determine the identity of the migrating group and the origin of **5**, we therefore carried out photochemical experiments with isotopologue **3-*d*$_5$**. Quantification of labeled regioisotopologues **5*s*** and **5*t*** was carried out by gas chromatography-mass spectrometry (GC-MS) single ion monitor analysis of benzophenone and benzophonone-d_5 fragments obtained following Lemieux oxidation of the alkene product mixture with $NaIO_4$ and $KMnO_4$ (Table 1).

As shown in entry 2 of Table 1, irradiation of **3-*d*$_5$** in dilute methylcyclohexane (MeCy) solution at 298 K produced 55% **5*s*** via a 1,2-H shift (from **4S**) and 45% **5*t*** via 1,2-Ph migration (from **4T**). Thermolysis at 353 K favored **5*s*** (entry 1), whilst photoreaction at 195 K yielded a notable increase in the yield of **5*t*** (entry 3). However, reactions conducted at 77 K in a rigid glass produced **5*s*** (97%) almost exclusively (entry 4). Results in fluid solution are consistent with selectivities expected for a spin-equilibrated free arylalkylcarbene, with an increasing population of the triplet ground state at lower temperatures leading to preferential 1,2-Ph migration until the solvent freezes, preventing the displacement of the bulkier group. Similar findings have been reported for related 1,2-diphenyl-1-diazopropane.[6,13]

Table 1. 1,2-H Shift vs 1,2-Ph Migration Selectivities[a]



Entry	Media	T (K)	1,2-H (%)	1,2-Ph (%)
1	MeCy	353/Δ[b]	65	35
2	MeCy	298[c]	55	45
3	MeCy	195[c]	43	57
4	MeCy	77[c]	97	3
5	Crystals	298[c]	91	9
6	Crystals	77[c]	90	10

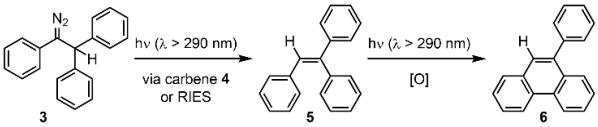
[a]Yields determined by GC-MS analysis. See Supporting Information for details. [b]Thermolysis reaction. [c]Photochemical reaction with λ > 380 nm.

In contrast to photoreactions in solution, the ratio of 1,2-H shift versus 1,2-Ph migration in polycrystalline samples of **3-*d*$_5$** displayed no appreciable temperature dependence, with a ca. 9:1 selectivity both at room temperature and 77 K (Table 1, entries 5 and 6). That experiments at cryogenic temperature result in the formation of **5*s*** via 1,2-H shift when population of the triplet carbene **4T** should be preferred[14] suggests the dominant role of rigidity for the selection of the less encumbered reaction pathway.[15] An alternative explanation would be that **4S** rather than **4T** is the ground state when the carbene is constrained within the crystal lattice of the diazo precursor. It is plausible that structural constraints alter the relative energies and equilibrium concentrations of **4S** and **4T** as compared to solution. Nonetheless, the formation of **5*s*** by a singlet-state 1,2-H shift suggests spin-equilibration at 77 K within crystals, whereupon a facile 1,2-H shift occurs, potentially with quantum mechanical tunnelling contributions (*vide infra*) from conformationally primed **4S**.

To explore the nature of the solid-to-solid transformation we crushed a polycrystalline sample of **3** between two microscope slides and exposed it to λ > 400 nm (at ambient temperature or 0 °C) until reaching full conversion. End-point analysis by powder X-ray diffraction (PXRD) exhibited patterns in excellent agreement with those simulated and experimentally measured for the stable crystal phase of photoproduct **5** (Figure S181). With melting points well-above 0 °C (**3**: 112–115 °C; **5**: 69–71 °C),[16] these results suggest that the solid-to-solid reaction proceeds via a reconstructive phase transition.[17] This is in contrast to the solid-state photoreaction previously reported for **1**, where a metastable phase of the crystal lattice of the starting diazo is retained throughout the entire reaction, indicating that a solid-solution is more stable in the case of **1** than **3**.[7b]

Solution and Solid-State Product Selectivity Studies with λ > 290 nm. Considering that laser-flash photolysis measurements of **3** were to be carried out with 266 nm pulsed-excitation (*vide infra*), we conducted steady-state irradiation of samples with λ > 290 nm supplied by a Hanovia 450 W medium-pressure mercury vapor lamp equipped with a Pyrex filter. Irradiation of a dilute C_6D_6 solution of **3** deaerated by bubbling argon through the sample prior to photolysis led to the formation of **5** and 9-phenylphenanthrene **6** as the two main photoproducts (Scheme 3).

Scheme 3. Photochemistry of 3 with λ > 290 nm



The identity of **6** was confirmed by comparison of its spectroscopic data with those reported in the literature, and by independent irradiation of a C_6D_6 solution of **5**, which also produced **6**. This observation suggests that excitation of diazo **3** initially forms alkene **5**, which undergoes an efficient secondary photoreaction to form 9-phenyldihydrophenanthrene; the latter is in turn oxidized to **6** (Scheme 3). Photochemical cyclodehydrogenation of stilbenes, including of **5** to **6**, are well documented in the literature.[18] Consistent with our interpretation, analogous photoreactions performed in J-Young NMR tubes with thoroughly freeze-pump-thaw degassed C_6D_6 samples of **3** and **5** showed only **5** at the conclusion of irradiation, confirming that both λ < 360 nm and O_2 (which serves as the oxidant) are necessary for the formation of **6**.[19] Hexanes and MeCN solutions of **3** displayed nearly full conversion to **6**.

Irradiation of polycrystalline samples of **3** or **5** crushed between microscope slides also resulted in complete conversion to **6**. In contrast to the solid-to-solid transformation observed when employing λ > 380 nm, under these conditions the reaction appeared to proceed via a melt phase that likely facilitated reaction with O_2. Performing the photoreactions in sealed vessels under an argon atmosphere resulted in only traces of **6** and little-to-no melting.

Nanosecond Laser-Flash Photolysis (ns-LFP) Studies in Solution. While free triplet arylalkylcarbenes[5,20] generated by photoexcitation of appropriate precursors and lacking facile intramolecular decay pathways are sufficiently long-lived for spectroscopic detection by ns-LFP, related arylalkylcarbenes bearing hydrogens at the alkyl carbon undergo ultrafast 1,2-H shifts that render them unobservable on such a timescale.[4] In our case, the use of pyridine-ylides[3] to explore the kinetics of transients derived from carbene **4** is limited by the fact that precursor **3** does not absorb at 355 nm, and pyridine saturates the absorbance at 266 nm at the high concentrations (ca. 0.1–1 M) required to trap short-lived arylalkylidenes (Figure S146). Instead, we explored the transients derived from diazo **3** by ns-LFP following 266 nm pulsed-excitation.

LFP of a ca. 10 μM solution of **3** in argon saturated MeCN solution produced a strong signal with negative ΔOD in the region 340–440 nm at the first available timepoint (Figure S184). Considering that **3** does not absorb strongly in this region (Figure S133), the signal could not be assigned to bleaching. Suspecting instead that it may arise from photoproduct emission, we confirmed that the signal can be removed by use of a fluorescence-background correction during measurements (Figure S184). Notably, the position of the band and measured fluorescence lifetime of τ_{flu} = 38 ns are in excellent agreement with that reported in the literature for **6** (Figure 2).[21] Moreover, identical results were obtained from LFP of solutions of **5** and **6** (Figure 2; Figures S182–S183).

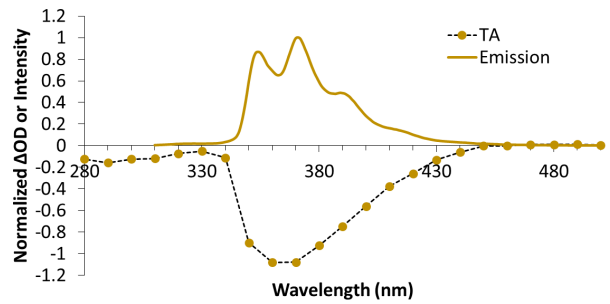


Figure 2. Normalized steady-state fluorescence and ns-LFP spectra of **6** in MeCN solution. The LFP spectrum was recorded 50 ns after 266 nm pulsed excitation; data is represented by solid circles and the dotted line is provided as a guide for the eye only.

While polar, coordinating solvents like MeCN are known to stabilize singlet arylcarbenes and accelerate rates of 1,2-H shifts, non-polar, non-coordinating solvents tend to favor longer-lived triplet carbenes.[22] However, LFP of **3** in hexanes produced transient absorption spectra similar to those in MeCN (Figure S185), with **4** remaining undetected. Platz and co-workers previously failed to observe any transients assignable to arylalkylidene intermediates upon ns-LFP of a number of related 1-phenyldiazoalkanes in deoxygenated pentane solution.[23] While the direct observation of triplet phenylalkylcarbenes by ns-LFP is possible,[5,20] the presence of a single phenyl chromophore often leads to weak, overlapping transient signals that make them difficult to detect. Comparison of hexanes and MeCN data also yielded no evidence for the formation of an acetonitrile-ylide of **4**.

While conversion of **3** to **5** to **6**, and subsequent excitation within the ca. 10 ns laser pulse, may be possible, it is more likely that traces of photoproduct **6** (fluorescence quantum yield of ϕ_{flu} = 0.39)[21] remains as an impurity within sampled solution volumes.[24] Nonetheless, we propose that conversion of **3** to photoproduct **5** via initially formed carbene **4S** occurs within the ca. 10 ns resolution of our instrument.[25] As validation for this scenario, we previously estimated the rate of 1,2-H shift ($k_{1,2\text{-H}}$) for 1,2-diphenylethylidene in non-polar Freon-113 solution to have a lower bound of 5 x 10^9 s^{-1}.[12b] Substitution of an α-H atom for a phenyl group in the case of **4** is expected to accelerate $k_{1,2\text{-H}}$ by several orders of magnitude.[26] Moreover, a recent ultrafast transient absorption investigation of related (2-adamantyl)diazophenylmethane, which also bears an α-H, did not observe the intermediate arylalkylcarbenes, suggesting the 1,2-H shift from the singlet carbene occurred with $k_{1,2\text{-H}} > 10^{12}$ s^{-1}; the corresponding triplet carbene was also not observed.[5]

ns-LFP Studies in Aqueous Nanocrystalline Suspensions. We have shown that nanocrystals with sizes smaller than the wavelength of light (ca. 200 nm) suspended in water

mitigate optical challenges arising from their high optical density, dichroism, birefringence, and light scattering, such that one can use conventional LFP methods.[27] Aqueous nanocrystalline suspensions (NCSs) of **3**, **5**, and **6** were prepared by the re-precipitation method[28] whereby an aliquot of stock solution of the desired compound in MeCN was injected into a rapidly vortexing solution of sub-micellar cetyltrimethylammonium bromide (CTAB) in water. Crystal forms of the NCSs crafted in this manner were confirmed by PXRD analysis to be the same as those in the bulk crystals (Figures S177–S179), and their sizes determined by dynamic light scattering (Figures S174–S176). UV-visible absorbance of NCSs measured as a function of time displayed the broadening and increase in baseline characteristic of particle aggregation (Figures S139–S141), such that a flow system was used to continually analyze freshly prepared batches and prevent photoproduct accumulation during LFP measurements.

Neither NCSs of **3** or **5** produced any useable signals in the region 250–500 nm. While NCSs exposed to laser irradiation were shown to be photoreactive (Figures S143–S145), the lack of signals may be the result of transient lifetimes that are shorter than the laser pulse, signals too weak to be detected, or a combination thereof. While triphenylethylene **5** is known to exhibit aggregation-induced emission (AIE; ϕ_{flu} = 0.26) in the solid state,[29] and NCSs of **5** display a steady-state fluorescence spectrum identical to that of a bulk crystalline sample (Figure S147), the fluorescence lifetimes of related tri- and tetraarylethylenes in solid or aggregate phases (τ_{flu} < 10 ns)[30] fall outside the time resolution of our instrument. On the other hand, NCSs of phenanthrene **6** afforded transient spectra similar to those obtained in solution (Figure S186) that are by analogy assigned to solid-state fluorescence. However, as solid-state photocyclization to **6** requires two consecutive bimolecular reactions[24] under conditions of comparatively low O_2 concentration and diffusion,[31] we do not expect significant formation of **6** in NCSs of **3** or **5** on the nanosecond timescale. LFP measurements performed on NCSs of **3**, **5**, or **6** of higher concentration, using different laser powers, or prepared from a stock NCS yielded identical results. Thus, carbene **4** remained undetected even in the solid state, suggesting that the kinetics for 1,2-hydrogen atom shifts in crystals remain largely unaffected, such that $k_{1,2\text{-H}} > 10^9$ s^{-1}.[15] As in the product selectivity and solution ns-LFP studies discussed above, at this time we cannot definitely rule out RIES contributions to photoproduct formation.

Steady-State Emission Studies at 77 K. To explore the prospect of observing carbene **4** by its T-T fluorescence,[32,33,34] a ca. 10^{-4} M MeCy glass sample of **3** at 77 K was subjected to fluorescence analysis. Using the fluorimeter instrument as both the irradiation and excitation source, steady-state measurements revealed only fluorescence from photoproduct **5** (Figure 3, top). To test the possibility that carbene **4** may be kinetically trapped, but not emissive, we monitored the growth of the emission of **5** (Figure 3, bottom) in search for a sigmoidal delay that might indicate fast carbene formation and accumulation, followed by slow carbene rearrangement. The lack of a delay in the growth of triphenylethylene **5** suggested that its formation is not preceded by a dark carbene Intermediate, in line with our previous findings on **1**.[7b]

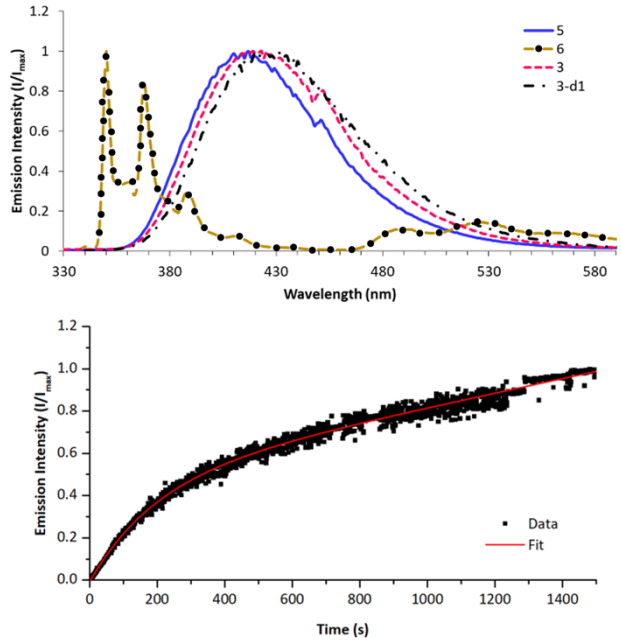


Figure 3. (Top) Normalized 77 K emission spectra from ca. 10^{-4} M **3** and **3-*d*$_1$** in MeCy glass following 290 nm excitation. For reference, spectra of **5** and **6** are also included. (Bottom) Profile of the growth of the fluorescence from **5** formed in the sample of **3** from the top panel upon sustained fluorimeter irradiation (λ_{exc} = 290 nm; λ_{park} = 420 nm).

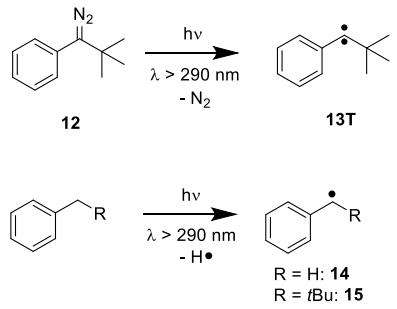
Having established that photoreaction at 77 K in MeCy glass occurs primarily by a 1,2-H shift (Table 1, entry 4), we considered the possibility that rearrangement from **4** takes place by quantum mechanical tunneling, which could potentially be slowed down significantly by isotopic substitution of the α-H for an α-D in compound **3-*d*$_1$**. However, just as in the case of **3**, only fluorescence attributable to **5**/**5-*d*$_1$** was detected (Figure 3, top). Analogous experiments carried out with crystalline samples resulted in similar observations, indicating that carbene **4** reacts comparably fast in amorphous glasses and in crystalline solids. Finally, mixed crystals of ketone **7** with 5% of **3** (or **3-*d*$_1$**) also did not sensitize the formation and T-T fluorescence of carbene **4**.[34]

Control experiments conducted with mixed crystals of diphenyldiazomethane **10** in benzophenone **9** (Figure S162–S164) showed the ketone phosphorescence to be completely quenched with the only observable emission being the characteristic T-T fluorescence of diphenylcarbene **11**, formed by triplet-triplet energy transfer from ketone **9** to diazo **10** as previously reported.[35] Based on all the above observations we conclude that carbene **4** is not observed in any of these media because it is too short-lived and does not accumulate.

To confirm that the 1,2-H shift limits the lifetime of **4** we endeavored to investigate *tert*-butylphenyldiazomethane **12** with no α-hydrogens (Scheme 4).[36] In addition to forming in near-quantitative yield upon photolysis of **12**, we anticipated that in glassy matrices at 77 K *tert*-butylphenylmethylene **13** would be reticent towards both 1,2-methyl migration and intramolecular 1,3-(C–H) insertion, which would yield alkene and cyclopropane products, respectively. Indeed, excitation of a ca. 10^{-4} M MeCy glass of **12** at 77 K produced the emission spectrum shown in Figure 4 that is distinct from that of

pivalophenone or potential photoproduct(s). Notably, the emission (and corresponding excitation) spectrum is blue-shifted with respect to that of diphenylcarbene **11** (Figure S171), as would be expected upon replacement of a phenyl substituent by an alkyl group. As a result, we tentatively assign the spectrum in Figure 4 to the T-T fluorescence from carbene **13T**.[37] Consistent with this assignment, the fluorescence signal disappears upon warming of the sample to room temperature.

Scheme 4. Generation of samples of **13** and **15**



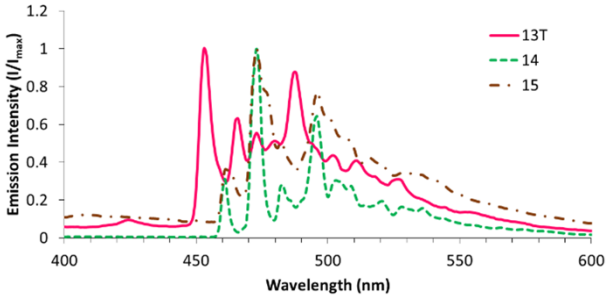


Figure 4. Normalized 77 K emission assigned to *tert*-butylphenylmethylene **13T**, benzyl radical **14**, and *tert*-butylphenylmethyl radical **15**.

Knowing that the highly structured emission attributed to **13T** is reminiscent of the fluorescence spectra of benzyl-type radicals, we sought to rule out the possibility of such emission arising from carbene-derived (*tert*-butyl)(phenyl)methyl radical **15**. Radical **15** was generated by photolysis of a ca. 10^{-3} M 77 K MeCy glass of (*tert*-butyl)(phenyl)methane for 30 min with a 450 W medium-pressure Hg lamp (Scheme 4). The emission and excitation spectra obtained for **15** are in excellent agreement with those previously reported and experimentally measured for similarly prepared parent benzyl radical **14** (Figures 4 and S165–167).[38] Importantly, the spectra for these benzyl radicals are shifted to lower energies with respect to those of **13T** (Figure 4 and S170). Scaiano and co-workers previously reported that the fluorescence spectra of diphenylcarbenes are blue-shifted relative to their diarylmethyl radical congeners,[32b] and we suggest that arylalkylcarbenes also follow this trend.[39] Thus, the emission observed following excitation of **12** is most consistent with T-T fluorescence from carbene **13T**.

To the best of our knowledge, this represents the first report of T-T fluorescence from an arylalkylcarbene. Fluorescence spectroscopy can thus serve as a powerful orthogonal technique by which to characterize these seldomly observed reactive intermediates when transient absorption spectroscopic results are inconclusive). Based on the above, we also suggest that **4T** remains elusive to fluorescence detection owing to its facile intramolecular reactivity rather than inherent lack of T-T fluorescence.

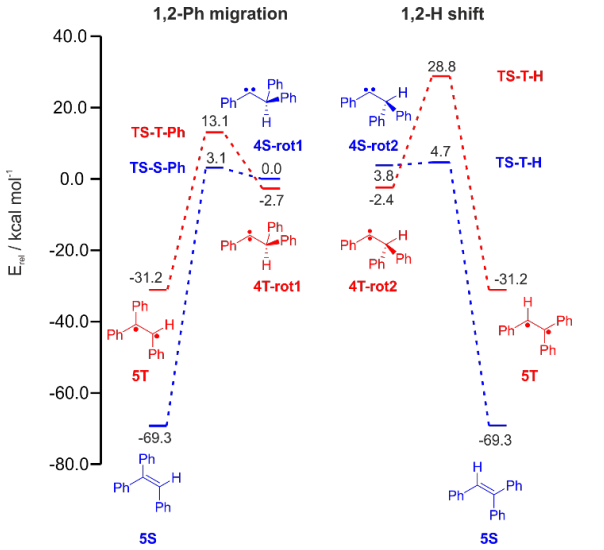


Figure 5. Energetics for the competing reaction pathways for 1,2,2-triphenylethylidene **4** in both its singlet and triplet state. All values are zero-point energy corrected and all calculations were performed at the B3LYP-D3/def2TZVP level of theory.

Potential energy surface for 1,2-H shift and 1,2-Ph migration in carbene 4. The potential energy surfaces for the 1,2-Ph migration and the 1,2-H shift proceeding from 1,2,2-triphenylethylidene **4** in both its singlet and triplet state were explored quantum chemically (Figure 5). These calculations predict a triplet ground state with a singlet-triplet gap $\Delta E_{S\text{-}T}$ of 2.7 or 6.2 kcal mol^{-1} for its two reactive rotamers denoted, respectively, as rot1 (in blue) and rot2 (in red), with rot1 being closer to the conformation expected in the crystal based on the X-ray structure of the reactant. A conformationally equilibrated singlet carbene **4S** in solution should undergo facile 1,2-H shift and slightly slower 1,2-Ph migration via activation barriers of E_A = 0.9 and 3.1 kcal mol^{-1}, respectively. Meanwhile, a conformationally equilibrated and energetically preferred triplet carbene **4T** encounters significantly higher barriers of E_A = 31.2 kcal mol^{-1} for the 1,2-H shift and E_A = 15.8 kcal mol^{-1} for the 1,2-Ph migration. Encouragingly, these predictions agree well with the Skeel-Woodworth rules and the Bethell mechanism[7b] as well as the experimental results for the temperature-dependence of the migration selectivities in solution outlined in Table 1. The observation of product formation exclusively via 1,2-H shift in crystalline state is consistent with the absence of conformational equilibration and the low barrier expected for a rot1-like structure, and the lack of phenyl migration at low temperatures implies that that reaction is not sterically allowed, and/or that spin equilibration remains fast in the solid state for hydrogen shift to occur from the available singlet carbene population. The detailed influence of a rigid crystalline cavity and the potential of contributions from quantum mechanical tunnelling should be addressed in the future.

CONCLUSIONS

In summary, product selectivity following excitation of diazoalkane **3** is highly dependent on the reaction medium.

While intermediate 1,2,2-triphenylethylidene **4** undergoes both 1,2-H shift and 1,2-Ph migration in solution, rigid media such as MeCy glasses or crystalline solids favor the displacement of the much smaller hydrogen atom. Efforts to detect carbene **4** within aqueous nanocrystalline suspensions of **3** using ns-laser-flash photolysis suggest that the 1,2-H shift to yield **5** occurs within the pulse linewidth, with $k_{1,2\text{-H}} > 10^9\ s^{-1}$. Attempts to detect carbene **4** via its T-T steady-state fluorescence from crystals at 77 K also revealed triphenylethylene **5** as the only detectable species. Thus, the 1,2-H shift remains facile in the solid state, even at cryogenic temperature, suggesting that this rearrangement benefits from a favorable conformation of **4** within crystals, and potentially from quantum mechanical tunnelling. The role of an ultrafast reaction in the solid state was supported by observations of T-T fluorescence from *tert*-butylphenylmethylene **13T** derived from *tert*-butylphenyldiazomethane **12** with no migrating groups in the carbene α-position.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at http://pubs.acs.org.

Experimental and computational details; characterization data; spectroscopic data (NMR, IR, UV–visible absorbance, steady-state emission, dynamic light scattering, laser-flash photolysis transient absorption); PXRD and SC-XRD refinement details; Cartesian coordinates (PDF).

Accession Codes

CCDC 2351167 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Platz, M. S. A Perspective on Physical Organic Chemistry. *J. Org. Chem.* **2014**, *79*, 2341–2353.

(2) Hirai, K.; Itoh, T.; Tomioka, H. Persistent Triplet Carbenes. *Chem. Rev.* **2009**, *109*, 3275–3332.

(3) Based on the latter, carbene-ylides formed by reaction with Lewis-basic reagents, such as pyridine, have been extensively exploited to gain indirect kinetic information of the kinetics of the corresponding arylalkylidenes. See: (a) Platz, M. S.; White III, W. R.; Modarelli, D. A.; Celebi, S. A. Time Resolved Spectroscopy of Carbene-Pyridine Ylides: Distinguishing Carbenes from Diazirine Excited States. *Res. in Chem. Interm.* **1994**, 20, 175–193. (b) Jackson, J. E.; Platz, M. S. Laser Flash Photolysis Studies of Ylide Forming Reactions of Carbenes. U. Brinker, ed., *Adv. Carbene Chem.* **1994**, *1*, 89–160.

(4) (a) Wang, J.; Burdzinski, G.; Gustafson, T. L.; Platz, M. S. Ultrafast Study of *p*-Biphenylyldiazoethane. The Chemistry of the Diazo Excited State and the Relaxed Carbene. *J. Am. Chem. Soc.* **2007**, *129*, 2597–2606. (b) Zhang, Y.; Burdzinski, G.; Kubicki, J.; Platz, M. S. Direct Observation of Carbene and Diazo Formation from Aryldiazirines by Ultrafast Infrared Spectroscopy. *J. Am. Chem. Soc.* **2008**, *130*, 16134–16135. (c) Zhang, Y.; Burdzinski, G.; Kubicki, J.; Vyas, S.; Hadad, C. M.; Sliwa, M.; Poizat, O.; Buntinx, G.; Platz, M. S. Study of the S1 Excited State of para-Methoxy-3-phenyl-3-methyl Diazirine by Ultrafast Time Resolved UV-Vis and IR Spectroscopies and Theory. *J. Am. Chem. Soc.* **2009**, *131*, 13784–13790. (d) Burdzinski, G.; Platz, M. S. "Ultrafast Kinetics of Carbene Reactions." In *Contemporary Carbene Chemistry*; Moss, R. A.; Doyle, M. P., Eds.; John Wiley & Sons, Inc.: Hoboken, NJ, 2014; pp 166– 192.

(5) Brusar, V.; Forjan, M.; Ljubić, I.; Alešković, M.; Becker, K.; Vdović, S. Ultrafast Photoelimination of Nitrogen from Upper Excited States of Diazoalkanes and the Fate of Carbenes Formed in the Reaction. *J. Org. Chem.* **2023**, *88*, 4286–4300.

(6) Garcia-Garibay, M. A.; Shin, S.; Sanrame, C. N. Engineering Reactions in Crystalline Solids: Prediction of Intramolecular Carbene Rearrangements. *Tetrahedron* **2000**, *56*, 6729–6737.

(7) (a) Shin, S. H.; Keating, A. E.; Garcia-Garibay, M. A. Transforming a Nonselective Carbene Rearrangement into a Highly Selective Process by Using Crystalline Media. *J. Am. Chem. Soc.* **1996**, *118*, 7626–7627. (b) Shin, S. H.; Cizmeciyan, D.; Keating, A. E.; Khan, S. I.; Garcia-Garibay, M. A. Control of Carbene Reactivity by Crystals. A Highly Selectivity 1,2-H Shift in the Solid-to-Solid Reaction of 1-(4'-Biphenyl)-2-phenyl-diazopropane to (Z)-1-(4'-Biphenyl)-2-phenyl-propene. *J. Am. Chem. Soc.* **1997**, *119*, 1859–1868.

(8) Tomioka, H.; Hayashi, N.; Izawa, Y.; Senthilnathan, V.P.; Platz, M. Solid-State Chemistry, Kinetics, and Spectroscopy of 1,2-Diphenylpropylidene. *J. Am. Chem. Soc*. **1983**, *105*, 5053-5057.

(9) Garcia-Garibay, M. A. Engineering Carbene Rearrangements in Crystals: From Molecular Information to Solid-State Reactivity. *Acc. Chem. Res.* **2003**, *36*, 491–498.

(10) Heine, H. G.; Hartmann, W.; Kory, D. R.; Magyer, J. C.; Hoyle, C. E.; McVey, J. K.; Lewis, F. D. Photochemical α Cleavage and Free-Radical Reactions of Some Deoxybenzoins. *J. Org. Chem.* **1974**, *39*, 691–698.

(11) Tokihiro, J.; Fitzpatrick, C.; Platz, M. S. Wavelength-Dependent Photochemistry of 1-Phenyl-1-Diazopropane *J. Phys. Org. Chem.* **2022**, *35*, e4298.

(12) (a) Motschiedler, K. R.; Toscano, J. P.; Garcia-Garibay, M. A. Arylalkylcarbenes from Triplet Arylalkyldiazoalkanes. *Tetrahedron Lett.* **1997**, *38*, 949–952. (b) Motschiedler, K.; Gudmundsdottir, A.; Toscano, J. P.; Platz, M.; Garcia-Garibay, M. A. Excited Precursor Reactivity, Fast 1,2-H Shifts and Diffusion-Controlled Methanol Insertion in 1,2-Diphenylalkylidenes. *J. Org. Chem.* **1999**, *64*, 5139–5147.

(13) (a) Tomioka, H.; Ueda, H.; Kondo, S.; Izawa, Y. Temperature and Matrix Effects on Migratory Aptitude and Stereochemistry in 1,2-Migration to a Divalent Carbon. *J. Am. Chem. Soc.* **1980**, *102*,

7817–7818. (b) Tomioka, H.; Hayashi, N.; Izawa, Y.; Senthilnathan, V. P.; Platz, M. S. Solid-state Chemistry, Kinetics, and Spectroscopy of 1,2-Diphenylpropylidene *J. Am. Chem. Soc.* **1983**, *105*, 5053–5057.

(14) Evidence for this hypothesis comes from observation of an EPR signal attributable to 1-(4′-biphenylyl)-2-phenyldiazopropylidene following irradiation of single crystals of **1** at 77 K. See ref. 7b.

(15) Keating, A. E.; Shin, S. H.; Houk, K. N.; Garcia-Garibay, M. A. Combining Quantum Mechanical Reaction Pathways with Force Field Lattice Interactions to Model a Solid State Phototransformation. *J. Am. Chem. Soc.* **1997**, *119*, 1474–1475.

(16) No visible melting was observed either.

(17) (a) de Loera, D.; Garcia-Garibay, M. A. Efficient Aziridine Synthesis in Metastable Crystalline Phases by Photoinduced Denitrogenation of Crystalline Triazolines. *Org. Lett.* **2012**, *14*, 3874–3877. (b) de Loera, D.; Stopin, A.; Garcia-Garibay, M. A. Photoinduced and Thermal Denitrogenation of Bulky Triazoline Crystals: Insights into Solid-to-Solid Transformations. *J. Am. Chem. Soc.* **2013**, *135*, 6626–6632.

(18) (a) Mallory, F. B.; Mallory, C. W. *Photocyclization of Stilbenes and Related Molecules*. Organic Reactions; John Wiley & Sons, Ltd, **2005**; pp 1–456. (b) Jørgensen, K. B. Photochemical Oxidative Cyclisation of Stilbenes and Stilbenoids—The Mallory-Reaction. *Molecules* **2010**, *15*, 4334–4358. (c) Sargent, M. V.; Timmons, C. J. Studies in Photochemistry. Part I. The Stilbenes. *J. Chem. Soc.* **1964**, 5544–5552.

(19) Kojima, M.; Nakajoh, M.; Matsubara, C.; Hashimoto, S. Photooxygenation of Aromatic Alkenes in Zeolite Nanocavities. *J. Chem. Soc., Perkin Trans. 2* **2002**, *11*, 1894–1901.

(20) (a) Tomioka, H.; Nakajima, J.; Mizuno, H.; Sone, T.; Hirai, K. Triptycyl(aryl)carbenes. A Remarkably Effective Kinetic Stabilizer of Triplet Carbenes. *J. Am. Chem. Soc.* **1995**, *117*, 11355–11356. (b) Tomioka, H.; Nakajima, J.; Mizuno, H.; Iiba, E.; Hirai, K. Spectroscopic Studies on Effects of Triptycyl Group on Structures and Reactivities of Triplet Arylcarbenes. *Can. J. Chem.* **1999**, *77*, 1066–1076. (c) Wang, J.; Kubicki, J.; Gustafson, T. L.; Platz, M. S. he Dynamics of Carbene Solvation: An Ultrafast Study of *p*-Biphenyltrifluoromethylcarbene. *J. Am. Chem. Soc.* **2008**, *130*, 2304–2313.

(21) Onkelinx, A.; De Schryver, F. C.; Viaene, L.; Van der Auweraer, M.; Iwai, K.; Yamamoto, M.; Ichikawa, M.; Masuhara, H.; Maus, M.; Rettig, W. Radiative Depopulation of the Excited Intramolecular Charge-Transfer State of 9-(4-(*N*,*N*-Dimethylamino)phenyl)phenanthrene. *J. Am. Chem. Soc.* **1996**, *118*, 2892–2902.

(22) (a) Sugiyama, M. H.; Celebi, S.; Platz, M. S. A Significant Barrier to 1,2 Hydrogen Migration in Singlet 1-Phenylethylidene. A Laser Flash Photolysis Study. *J. Am. Chem. Soc.* **1992**, *114*, 966–973. (b) Wang, J.; Kubicki, J.; Hilinski, E. F.; Mecklenburg, S. L.; Gustafson, T. L.; Platz, M. S. Ultrafast Study of 9-Diazofluorene: Direct Observation of the First Two Singlet States of Fluorenylidene. *J. Am. Chem. Soc.* **2007**, *129*, 13683–13690. (c) Wang, J.; Kubicki, J.; Peng, H.; Platz, M. S. Influence of Solvent on Carbene Intersystem Crossing Rates. *J. Am. Chem. Soc.* **2008**, *130*, 6604–6609.

(23) Celebi, S.; Leyva, S.; Modarelli, D. A.; Platz, M. S. 1,2 Hydrogen Migration and Alkene Formation in the Photoexcited States of Alkylphenyldiazomethanes. *J. Am. Chem. Soc.* **1993**, *115*, 8613–8620.

(24) While photocyclization of **5** to 9-phenyldihydrophenanthrene is expected to occur on an ultrafast timescale (by analogy to parent stilbene; ref.: Rodier, J. M.; Myers, A. B. *cis*-Stilbene Photochemistry: Solvent Dependence of the Initial Dynamics and Quantum Yields. *J. Am. Chem. Soc.* **1993**, *115*, 10791–10795.), oxidation of the latter to **6** requires two consecutive bimolecular reactions. Given the low concentration of oxygen expected in the deaerated sample solution, as well as the slow nature of the biomolecular oxidation reactions relative to the nanosecond timescale (refs.: (a) Muszkat, K. A.; Fischer, E. Structure, Spectra, Photochemistry, and Thermal Reactions of the 4a,4b-Dihydrophenanthrenes. *J. Chem. Soc. B* **1967**, 662–678; (b) Bromberg, A.; Muszkat, K. A. Oxidation of 4a,4b-Dihydrophenanthrenes. I. Kinetics of the Thermal Reaction of 9,10-Cyclopentano-4a,4b-dihydrophenanthrene with Oxygen. *J. Am. Chem. Soc.* **1969**, *91*, 2860–2866; (c) Bromberg, A.; Muszkat, K. A.; Fischer, E.; Klein, F. S. Oxidation of 4a,4b-Dihydrophenanthrene. Part V. Tunnelling Effect on the Kinetics of the Initiation Step. *J. Chem. Soc., Perkin Trans. 2* **1972**, *5*, 588–591.), it is unlikely that a significant amount of **6** forms within our instrument's laser pulse. Indeed, ns-LFP of related substrates have instead observed long-lived dihydrophenanthrene-type transients rather than the terminal oxidized phenanthrene photoproducts (for representative examples see the following refs.: (a) Repinec, S. T.; Sension, R. J.; Szarka, A. Z.; Hochstrasser, R. M. Femtosecond Laser Studies of the *cis*-Stilbene Photoisomerization Reactions: the *cis*-Stilbene to Dihydrophenanthrene Reaction. *J. Phys. Chem.* **1991**, *95*, 10380–10385; (b) Cai, Y.; Du, L.; Samedov, K.; Gu, X.; Qi, F.; Sung, H. H. Y.; Patrick, B. O.; Yan, Z.; Jiang, X.; Zhang, H.; Lam, J. W. Y.; Williams, I. D.; Phillips, D. L.; Qin, A.; Tang, B. Z. Deciphering the Working Mechanism of Aggregation-Induced Emission of Tetraphenylethylene Derivatives by Ultrafast Spectroscopy. *Chem. Sci.* **2018**, *9*, 4662–4670).

(25) Some amount of **5** is also anticipated to form on an ultrafast timescale by RIES.

(26) (a) Keating, A. E.; Garcia-Garibay, M. A.; Houk, K. N. Influence of Bystander Substituents on the Rates of 1,2-H and 1,2-Ph Shifts in Singlet and Triplet Carbenes. *J. Phys. Chem. A* **1998**, *102*, 8467–8476. (b) Substitution of an α-H atom for a phenyl group results in acceleration of *k*1,2-H by several orders of magnitude in 1,2-diphenylethylidene versus 1-phenylethylidene (ref. 12b). Extrapolating this trend to our present carbene **4**, which can be construed as resulting from addition of one more phenyl group to 1,2-diphenylethylidene, we anticipate *k*1,2-H (**4**) >> 5 x 109 s–1 in solution.

(27) (a) Chin, K. K.; Natarajan, A.; Gard, M. N.; Campos, L. M.; Shepherd, H.; Johansson, E.; Garcia-Garibay, M. A. Organic Molecular Nanocrystals: Triplet–Triplet Absorption, Phosphorescence, and Circular Dichroism of Chiral Crystals of Benzophenone. *Chem. Commun.* **2007**, 4266–4268. (b) Park, J. H.; Hughs, M.; Chung, T. S.; Ayitou, A. J.-L.; Breslin, V. M.; Garcia-Garibay, M. A. Generation and Reactivity Studies of Diarylmethyl Radical Pairs in Crystalline Tetraarylacetones via Laser Flash Photolysis Using Nanocrystalline Suspensions. *J. Am. Chem. Soc.* **2017**, *139*, 13312–13317.

(28) Kasai, H.; Nalwa, H. S.; Oikawa, H.; Okada, S.; Matsuda, H.; Minami, N.; Kakuta, A.; Ono, K.; Mukoh, A.; Nakanishi, H. N. H. A Novel Preparation Method of Organic Microcrystals. *Jpn. J. Appl. Phys.* **1992**, *31*, L1132.

(29) (a) Viglianti, L.; Villafiorita-Monteleone, F.; Botta, C.; Mussini, P. R.; Ortoleva, E.; Cauteruccio, S.; Licandro, E.; Baldoli, C. A Comparative Study of Electrochemical, Spectroscopic and Structural Properties of Phenyl, Thienyl and Furyl Substituted Ethylenes. *ChemistrySelect* **2017**, *2*, 2763–2773. (b) Li, N.; Gu, Y.; Chen, Y.; Zhang, L.; Zeng, Q.; Geng, T.; Wu, L.; Jiang, L.; Xiao, G.; Wang, K.; Zou, B. Pressure-Induced Emission Enhancement and Piezochromism of Triphenylethylene. *J. Phys. Chem. C* **2019**, *123*, 6763–6767.

(30) (a) Zhang, G.-F.; Chen, Z.-Q.; Aldred, M. P.; Hu, Z.; Chen, T.; Huang, Z.; Meng, X.; Zhu, M.-Q. Direct Validation of the Restriction of Intramolecular Rotation Hypothesis via the Synthesis of Novel *ortho*-Methyl Substituted Tetraphenylethenes and Their Application in Cell Imaging. *Chem. Commun.* **2014**, *50*, 12058–12060. (b) Garg, K.; Ganapathi, E.; Rajakannu, P.; Ravikanth, M. Stereochemical Modulation of Emission Behaviour in *E/Z* Isomers of Diphenyldipyrroethene from Aggregation Induced Emission to Crystallization Induced Emission. *Phys. Chem. Chem. Phys.* **2015**, *17*, 19465–19473. (c) Howe, M. E.; Garcia-Garibay, M. A. Fluorescence and Rotational Dynamics of a Crystalline Molecular Rotor Featuring an Aggregation-Induced Emission Fluorophore. *J. Org. Chem.* **2019**, *84*, 9570–9576. (d) Fan, Y.; Han, M.; Huang, A.; Liao, Q.; Tu, J.; Liu, X.; Huang, B.; Li, Q.; Li, Z. Multi-photoresponsive Triphenylethylene Derivatives with Photochromism, Photodeformation

and Room Temperature Phosphorescence. *Mater. Horiz.* **2022**, *9*, 368–375.

(31) Simoncelli, S.; Kuzmanich, G.; Gard, M. N.; Garcia-Garibay, M. A. Photochemical Reaction Mechanisms and Kinetics with Molecular Nanocrystals: Surface Quenching of Triplet Benzophenone Nanocrystals. *J. Phys. Org. Chem.* **2010**, *23*, 376–381.

(32) In typical closed-shell molecules with a singlet ground state, fluorescence occurs by radiative decay from the singlet excited state back to the singlet ground state (singlet-singlet fluorescence). Since the arylakylcarbenes investigated in this work feature a triplet ground state, their spin-allowed emission is a triplet-triplet fluorescence.

(33) (a) Trozzolo, A. M.; Gibbons, W. A. The Absorption, Emission, and Excitation Spectra of Diarylmethylenes. *J. Am. Chem. Soc.* **1967**, *89*, 239–243. (b) Scaiano, J. C.; Weir, D. Effect of Ring Substituents on the Fluorescence Spectra of Substituted Diarylcarbenes. *Can. J. Chem.* **1988**, *66*, 491–494.

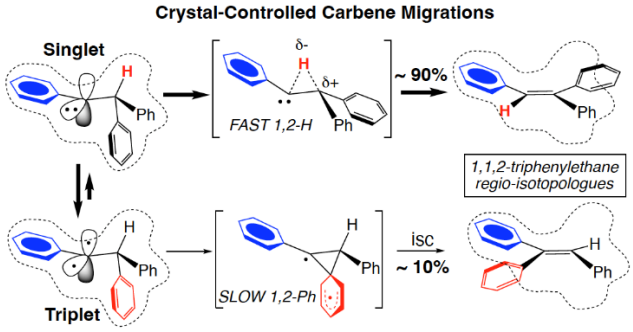
(34) Garcia-Garibay, M. A.; Dang, H. Photochemical Generation, Intramolecular Reactions, and Spectroscopic Detection of Oxonium Ylide and Carbene Intermediates in a Crystalline *ortho*-(1,3-Dioxolan-2-yl)-diaryldiazomethane. *Org. Biomol. Chem.* **2009**, *7*, 1106–1114.

(35) Graham, D. J.; Wohler, K. W. A Sensitized Luminescence Study of a Ground-State Triplet Impurity in Benzophenone Single Crystals. *Chem. Phys. Lett.* **1985**, *116*, 497–500.

(36) (a) Ishiguro, K.; Ikeda, M.; Sawaki, Y. Formation and Reactivity of σ-Radical Cation Intermediates in the C-C Coupling Reaction of Phenyldiazomethanes by One-Electron Oxidation. *J. Org. Chem.* **1992**, *57*, 3057–3066. (b) Like its ketone precursor, pivalophenone, **12** was an oil in our hands.

(37) We previously speculated on the preliminary observation of T-T fluorescence from **13T** in ref. 7b, although no conclusive data was provided at the time.

(38) (a) Morrison, V. J.; Laposa, J. D. Luminescence of Benzyl Radical and Deuterium-Substituted Benzyl Radicals at 77 K in Polycrystalline Methylcyclohexane. *Spectrochim. Acta A* **1976**, *32*, 1207–1213. (b) Hiratsuka, H.; Okamura, T.; Tanaka, I.; Tanizaki, Y. Electronic Spectra of Benzyl and Methyl-substituted Benzyl Radicals. *J. Phys. Chem.* **1980**, *84*, 285–289. (c) Hiratsuka, H.; Okamoto, T.; Kuroda, S.; Okutsu, T.; Maeoka, H.; Taguchi, M.; Yoshinaga, T. Photochemical Reaction Intermediates of Benzyl Chloride in Condensed Phase. *Res. Chem. Interm.* **2001**, *27*, 137–153.

(39) To lend credence to this hypothesis, we note that phenylcarbene also appears to follow this trend. For the T-T fluorescence spectrum of phenylcarbene, see: Haider, K. W.; Platz, M. S.; Despres, A.; Migirdicyan, E. Laser-Induced Fluorescence Spectra of Phenylcarbene, 2-Naphthylcarbene and 10,10-Dimethylanthrylidene in Glassy Media at 77 K. *Chem. Phys. Lett.* **1989**, *164*, 443–448. For the fluorescence spectrum of benzyl radical, see ref. 38.

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