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Reaction of tetramethylpiperidine *N*-oxides with persistent triplet diphenylcarbenes

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Persistent triplet diphenylcarbenes with considerable stability have been shown to be trapped by tetramethylpiperidine *N*-oxides (TEMPOs) to give the corresponding benzophenones as major products along with tetramethylpiperidine, which indicates that the reaction pattern is essentially identical with that observed for parent triplet diphenylcarbene. The absolute rate constants for the quenching reaction were measured by a laser flash photolysis technique and compared with those for quenching by other typical triplet carbene quenchers. The results showed that the reactivity of TEMPOs toward triplet carbenes was lower than that of oxygen but higher than that of 1,4-cyclohexadiene. The advantages of TEMPOs as a triplet carbene quencher as opposed to the other quenchers are discussed, and TEMPOs are shown to be very convenient reagents to estimate the reactivity of triplet carbenes.

Tetramethylpiperidine *N*-oxides (TEMPOs) are excellent trapping reagents for carbon-centered radicals and have been used to study reactions involving radicals.[1] For instance, TEMPOs react with a radical to produce the corresponding *N*-alkoxylpiperidines, which are generally used as convincing evidence to demonstrate the intervention of the alkyl radicals.[2–6] The rate at which simple alkyl and benzyl radicals react with TEMPO has been shown, however, to be about an order of magnitude lower than a diffusion controlled rate, unlike those of the corresponding alkyl radical plus radical reactions.[2–5]

TEMPOs are also supposed to be efficient trapping reagents for triplet carbenes, but only one report has been published on this reaction. Thus, Scaiano and coworkers found that triplet diphenylcarbene (^{3}**2a**) reacts with TEMPO by abstracting oxygen atoms, leading to the corresponding ketones **3a** rather than a simple coupling.[7] This reaction has a few parallels in free-radical chemistry, such as the reaction of *tert*-butoxyl carbon monoxide to yield carbon dioxide[8] or with phosphorus(III) substrates to yield P(V) products,[9] where the valency of the central atom can increase by two units. This reaction is spin-allowed and over 100 kcal mol^{-1} exothermic. However, the rate is well below the diffusion limit.

In order to know more about the nature of this reaction and also to elucidate the role of TEMPOs in the chemistry of triplet carbenes,[10] kinetic studies of the trapping reaction of persistent triplet diphenylcarbenes with TEMPOs were carried out.

The persistent triplet carbenes[11] that we used in this study were the following three diphenylcarbenes (DPCs), which have two kinds of substituents at their *ortho* positions as kinetic protectors. They are bis(2,4,6-trichlorophenyl)carbene (^{3}**2b**),[12] bis(2,4,6-tribromophenyl)carbene (^{3}**2c**),[13] and bis(2,6-dibromo-4-*tert*-butylphenyl)carbene (^{3}**2d**).[13] Each of the three DPCs exhibited unique behavior. For instance, they decayed mainly by undergoing dimerization to form tetraarylethylenes under the conditions in which most unprotected DPCs reacted with the precursor diazo compounds to give the corresponding azines. This indicates that the carbene is stable and its concentration builds up to the point at which dimerization occurs. Kinetic studies clearly indicated that those carbenes have anomalous stability compared to unprotected DPCs. The transient absorption bands due to these carbenes decayed in second-order kinetics, indicating that they underwent dimerization. Thus, the rough lifetimes for ^{3}**2b**, ^{3}**2c**, and ^{3}**2d** are estimated in the form of half-life and are 18, 1000, and 16000 ms, respectively, in degassed benzene at room temperature. Since the lifetime of a "parent" DPC(^{3}**2a**) is only a few µs under identical conditions, it is apparent that they are stabilized by many orders of magnitude.

Although the DPCs ^{3}**2b**, ^{3}**2c**, and ^{3}**2d** are extremely stable and show unique behavior in the absence of proper trapping reagents, they still react with typical triplet quenchers in a normal manner. Thus, they are trapped either by molecular oxygen to form the corresponding diaryl ketones by way of carbonyl oxides[14,15] or by a good hydrogen donor, such as 1,4-cyclohexadiene, to produce the corresponding diarylmethanes by way of diarylmethyl radicals.[16] The quenching rate constants are, however, markedly reduced as opposed to that of parent DPC and are roughly correlated with the half-life of the carbenes (see Table 1).

It is, thus, very interesting to know how persistent DPCs behave toward TEMPOs.

Results and discussion

All the triplet DPCs were efficiently and cleanly generated by photolysis of the corresponding diazo precursors. All irradiations were carried out in a carefully degassed solution by repeated freeze–degas–thaw cycles at pressures near 10^{-5} Torr in order to avoid possible perturbation by oxygen.

Laser flash photolysis (LFP) of **1b** (1×10^{-4} M) in a degassed benzene solution at room temperature with a 10 ns, 70–90 mJ, 308 nm pulse from a XeCl excimer laser produced a transient species showing a strong absorption at 357 nm and a weak absorption extending from 410 to 520 nm, which appeared coincident with the pulse and disappeared within *ca.* 100 ms. On the basis of the low-temperature spectrum, we assigned the transient product to bis(2,4,6-trichlorophenyl)carbene ^{3}**2b**. The decay of ^{3}**2b** in the absence of trapping reagents is found to be second-order, with a rate constant of $2k_d/\varepsilon l = 8.9 \times 10^{-4}$ s^{-1}, where k_d is the dimerization rate constant, ε the extinction coefficient, and l the optical path. The rough lifetime of ^{3}**2b** is estimated in the form of the half-life, $t_{1/2}$, to be 18 ms. The dimerization reaction rate constant, k_d, can be determined from the extinction coefficient (ε) of ^{3}**2b** and the optical path length (l) to be $1.2 \pm 0.1 \times 10^7$ M^{-1} s^{-1}.

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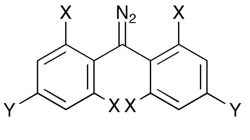
Table 1 Bimolecular rate constants for the reaction of diarylcarbenes and their half lives[a]

Carbenes	$t_{1/2}$/ms	$k_{\mathrm{TEMPO(H)}}$/M^{-1} s^{-1}	$k_{\mathrm{O_2}}$/M^{-1} s^{-1}	k_{CHD}/M^{-1} s^{-1}
2a	0.002[b]	2.7×10^8 [c]	5.0×10^9 [d]	1.0×10^7 [e]
2b	18[f]	2.1×10^6	7.4×10^7 [f]	3.5×10^3 [f]
2c	1000[g]	9.8×10^3	1.1×10^7 [g]	7.4×10^2 [g]
2d	16000[g]	1.7×10^3 1.8×10^3 [h] 2.0×10^3 [i] 1.6×10^3 [j]	2.1×10^7 [g]	5.3×10^2 [g]

[a] All measurements were done in benzene at 20 °C unless otherwise noted. [b] In cyclohexane. Ref. 17. [c] In MeCN. Ref. 8. [d] In MeCN. Ref. 15. [e] Ref. 16*c*. [f] Ref. 12*b*. [g] Ref. 13*c*. [h] Reaction with TEMPO(OH). [i] Reaction with TEMPO(OMe). [j] Reaction with TEMPO(O).



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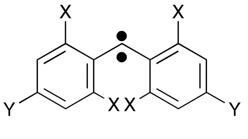

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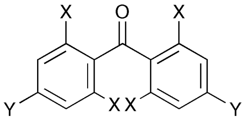

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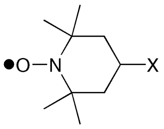
a : X = Y = H, **b** : X = Y = Cl, **c** : X = Y = Br, **d** : X = Br, Y = ^{t}Bu



TEMPO(X) [X = H, OH, OMe, O]

When LFP was carried out in the presence of TEMPO(H), the half-life of ^{3}**2b** decreased dramatically. The spent solution was found to contain hexachlorobenzophenone (**3b**) as the main product along with tetramethylpiperidine, indicating that ^{3}**2b** is trapped by TEMPO(H). The decay followed clean first-order kinetics. The pseudo-first-order rate constant for carbene decay k_{obs} is expressed as given in eqn. (1)

$$k_{\mathrm{obs}} = k_0 + k_{\mathrm{TEMPO}}[\mathrm{TEMPO}] \qquad (1)$$

where k_0 represents the rate of decay of ^{3}**2b** in the absence of TEMPO(H) and k_{TEMPO} is the quenching rate constant of ^{3}**2b** by TEMPO. The plot of the observed pseudo-first-order rate constant against [TEMPO] is linear (Fig. 2). From the slope of this plot, k_{TEMPO} was determined to be 2.1×10^6 M^{-1} s^{-1}, which is approximately 2 orders of magnitude smaller than that observed with the "parent" DPC ^{3}**2a** ($k_{\mathrm{TEMPO}} = 2.7 \times 10^8$ M^{-1} s^{-1}).[7]

Similar LFP using bis(2,4,6-tribromophenyl)diazomethane (**1c**) and bis(2,6-dibromo-4-*tert*-butylphenyl)diazomethane (**1d**) generated a transient absorption band assignable to triplet carbenes ^{3}**2c** and ^{3}**2d**, respectively, both of which decayed with second-order kinetics ($2k_d/\varepsilon l$ = 8.9 and 0.36 s^{-1}) with half-lives of 1000 ms and 16 s, respectively. Again, the decay rate was markedly accelerated in the presence of TEMPO(H) (Fig. 1b and 1c), and the corresponding benzophenones were detected as the main product in the spent solution, indicating that the carbene is trapped by TEMPO(H). From a plot of the observed pseudo-first-order rate constant against [TEMPO] (Fig. 2), k_{TEMPO} values were determined to be 9.8×10^3 for ^{3}**2c** and 1.7×10^3 M^{-1}s^{-1} for ^{3}**2d**, which are approximately two and three orders of magnitude smaller than that observed with ^{3}**2b**, respectively.

Those observations clearly indicate that all the persistent triplet DPCs are trapped by TEMPO(H) in a reaction pattern identical with that observed for the parent DPC. Thus, the main product formed in all the spent solution is only the corresponding ketones (along with piperidine), no other product from the carbene being detected. The only difference observed

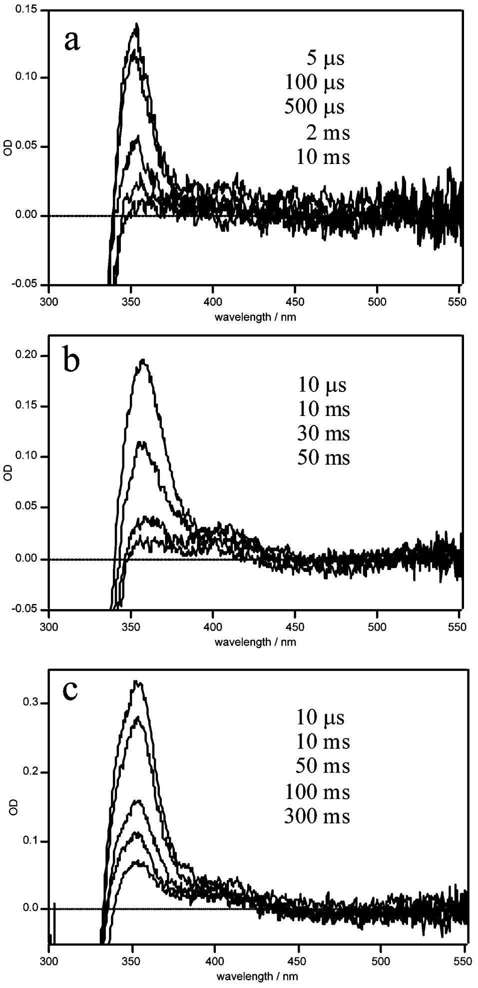


Fig. 1 Absorption spectra of the transient products formed by pulsing diazomethanes [(a) **1b**, (b) **1c**, and (c) **1d**] in degassed benzene with a 308 nm excimer laser in the presence of TEMPO.

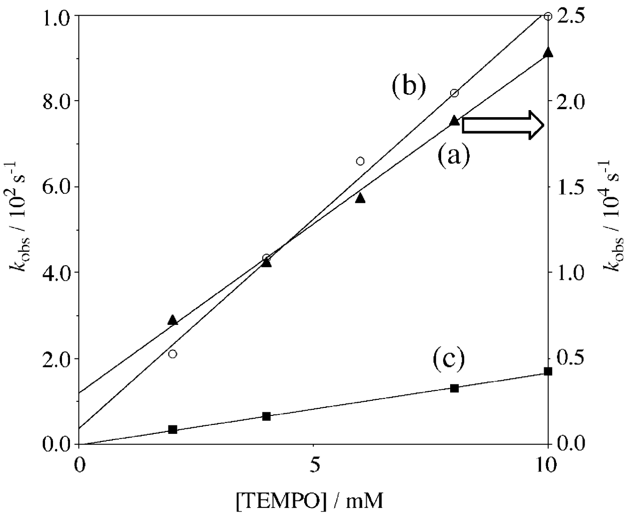


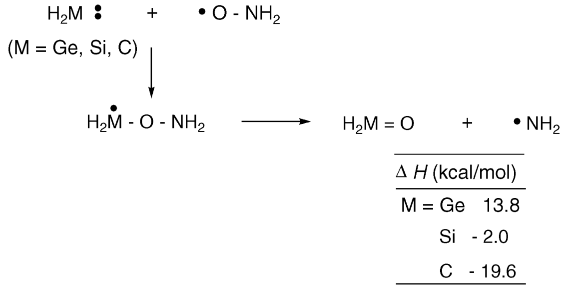
Fig. 2 Plot of k_{obs} measured at 20 °C for quenching triplet DPCs [(a) **2b**, (b) **2c**, and (c) **2d**] in degassed benzene as a function of TEMPO concentration. The scales on the right are for **2b** while those on the left are for **2c** and **2d**.

between simple DPC and persistent ones in the reaction with TEMPO(H) is the quenching rate constants. As summarized in Table 1, the rate constants markedly decrease as more bulky groups are introduced at the *ortho* positions of DPCs and are roughly correlated with the half-life of triplet DPCs.

It is thus very interesting to compare the quenching rate constants, k_{TEMPO}, with those for other triplet carbene quenchers, such as oxygen (k_{O_2}) and 1,4-cyclohexadiene (CHD) (k_{CHD}), and also to assess their usability as a reagent to estimate the reactivity of a triplet carbene. Inspection of the data in Table 1 indicates that the reactivities of TEMPO(H) toward triplet carbenes are lower than that of oxygen and higher than that of CHD. The reactivity differences between the three quenchers become larger as triplet carbenes become more persistent. Thus, a parent DPC is quenched by oxygen with nearly a diffusion-controlled rate, while the quenching rate constants by TEMPO and CHD are one and two orders of magnitude smaller than k_{O_2}, respectively. For brominated DPC ^{3}**2d**, the quenching rate constant with oxygen is two orders of magnitude lower than that for the parent DPC, but the decrease in the quenching rate constants for TEMPO(H) and CHD is much larger; k_{TEMPO} and k_{CHD} are, thus, three and four orders of magnitude smaller than k_{O_2}, respectively.

Thus, the present investigation reveals that TEMPO can be used as a convenient trapping reagent for triplet carbene, showing reactivity somewhere between oxygen and 1,4-cyclohexadiene. It has several advantages over the other quenchers. Oxygen is an excellent quencher for triplet carbenes, but its handling is not easy, especially in kinetic measurements, since the concentration must be adjusted by bubbling N_2/O_2 mixtures of the known composition. CHD is also frequently employed as a trapping reagent for triplet carbenes, but its moderate reactivity substantially limits its use. Very persistent triplet carbenes do not react with CHD.[18] In addition, the trapping products are not always simple. For instance, the reaction with O_2 resulted in the formation of the corresponding ketones as an almost exclusive product in many cases, but esters and other products, derived from the initially formed carbonyl oxides, sometimes accompanied them. The reaction with CHD is usually accompanied by cage-escaped products, such as radical dimers. The reaction of TEMPOs with amino or hydroxyl groups at the 4-position with triplet DPC is also shown to react in essentially the same manner leaving those potentially reactive functional groups intact.[7] We also found that the reactivity of TEMPOs toward those persistent triplet DPCs is not affected by substituents at this position. For instance, the quenching rate constants of ^{3}**2d** by TEMPOs having hydroxy, methoxy, and carbonyl groups at the 4 position were essentially identical with that by simple TEMPO(H) (Table 1).

Finally, it will be very interesting to learn how triplet carbenes eventually abstract oxygen from TEMPOs, leading to the corresponding ketone. No transient bands ascribable to a discrete reaction intermediate in the reaction of DPCs with TEMPO were observed by our LFP measurement. The recent report[19] by Kira and coworkers on the reaction of TEMPO with stable divalent compounds of 14 elements from a heavier group is especially intriguing in this respect. They found that, while germylene and stannylene reacted with 2 equivalents of TEMPO to afford the corresponding 1:2 adducts by a stepwise addition *via* intermediate radicals, silylene gave a 1,3-dioxadisiletane derivative, which was most probably formed by dimerization of the initially generated silanone. The results appear to indicate that an intermediate silyl radical formed by an initial attack of TEMPO with silylene undergoes a unimolecular N–O bond cleavage rather than an expected coupling with TEMPO, while the addition of a second TEMPO to the initially formed germanium and tin radicals is very efficient. Theoretical calculations for a model reaction of N–O bond cleavage in $H_2M–O–NH_2$ (M = Ge, Si, and C) (Scheme 1) indicated that the reaction for M = Si is slightly exothermic (-2.0 kcal mol^{-1}), while that for M = Ge is endothermic ($+13.8$ kcal mol^{-1}). Presumably, the exothermicity is increased for the reaction with M = C. Indeed, our calculations at the B3LYP/6-311+G(d) level showed that this reaction is exothermic by 19.6 kcal mol^{-1}.[20]



Scheme 1

The stability of triplet carbenes can be estimated either by measuring the lifetime in an inert solvent, usually benzene, or estimating the temperature at which the carbene signal decayed upon thawing the matrix containing triplet carbenes. However, these data cannot be regarded as a quantitative scale for reactivity since the decay pathways are not always the same. Therefore, the quenching rate constant by typical triplet carbene quenchers can only be used as a more reliable scale to estimate the reactivity of the triplet carbenes. Thus, TEMPOs can be used as a very convenient reagent to estimate the reactivity of triplet carbenes.

Experimental

General methods

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-AC300FT/NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. IR spectra were measured on a JASCO-Herschel FT/IR-600H spectrometer, and UV-vis spectra were recorded on a JASCO CT-560 spectrophotometer. The mass spectra were recorded on a JEOL JMS-600H mass spectrometer. Thin-layer chromatography was carried out on a Merck Kieselgel 60 PF_{254}.

Unless otherwise noted, all the reagents employed in this study are commercial products and were used after standard purification. Benzene was purified by distillation from sodium/benzophenone.

Materials

The preparation of all the diazo compounds and ketones was reported elsewhere.[12,13] TEMPO (Tokyo Kasei, >98.0%), 4-hydroxy-TEMPO (Hakuto Chemicals, >99.0%), 4-methoxy-TEMPO (Tokyo Kasei, >98.0%) and 4-oxo-TEMPO (Tokyo Kasei, >95.0%) were purchased from commercial sources and used without further purification.

Irradiation for product analysis

In a typical run, a solution of the diazo compound (**1**, *ca.* 10 mg) and TEMPO (10 equiv.) in solvent was placed in a Pyrex tube and irradiated with a high-pressure, 300 W mercury lamp until all the diazo compound was destroyed. The irradiation mixture was then concentrated on a rotary evaporator below 20 °C. Individual components were isolated by preparative TLC and identified by NMR and MS.

Flash photolysis

All flash measurements were made on a Unisoku TSP-601 flash spectrometer. A Lamda Physik LEXTRA XeCl excimer laser (308 nm pulses of up to 200 mJ per pulse and 17 ns duration) was used as an excitation lamp. The beam shape and size were controlled by a focal length cylindrical lens.

A Hamamatsu 150 W xenon short-arc lamp (L 2195) was used as the probe source, and the monitoring beam, guided with an optical fiber scope, was arranged perpendicular to the excitation source. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701-512Q MOS linear image sensor (512 photodiodes used). Timing of the excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu Model DS-8631 digital synchro scope, which was interfaced to an NEC 9801 RX2 computer. This allowed for rapid processing and storage of the data and provided printed graphic capabilities. Each trace was also displayed on an NEC CRT N5913U monitor.

A sample was placed in a long-necked Pyrex tube with a side arm connected to a quartz fluorescence cuvette and degassed using a minimum of four freeze–degas–thaw cycles at a pressure near 10^{-5} Torr immediately prior to being flashed. The sample system was flame-sealed under reduced pressure, and the solution was transferred to the quartz cuvette, which was placed in the sample chamber of the flash spectrometer. A cell holder block of the sample chamber was equipped with a thermostat and allowed to come to thermal equilibrium. The concentration of the sample was adjusted so that it absorbed a significant portion of the excitation light.

Computational procedures

DFT calculations were carried out using the GAUSSIAN 94,[21] programs. Optimized geometries were obtained at the B3LYP/6-31G(d)[22,23] levels of theory. Vibrational frequencies obtained at the B3LYP level of theory were scaled by 0.961 and zero-point energies (ZPE) by 0.981.[23] Transition states were located using Gaussian program (Rational Function Optimization-pseudo-Newton-Raphsonthe method).[24] The nature of each stationary point was confirmed with harmonic frequency calculations, *i.e.*, minima have exactly one imaginary frequency related to the expected movement.

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