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Short Communication

Laser flash photolysis of 3-noradamantyl(phenyl)diazomethane: generation, detection and kinetics of 2-phenyladamantene

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ABSTRACT: Laser flash photolysis of 3-noradamantyl(phenyl)diazomethane in degassed benzene at room temperature generates 2-phenyladamantene, which decays with second-order kinetics ($2k/\varepsilon l = 1.5 \times 10^2\ \mathrm{s}^{-1}$) to give a dimer and is shown to react with oxygen and tri(*n*-butyl)tin hydride much faster than with methanol, thus revealing profound radical character of the twisted double bond. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: bridgehead alkenes; alkene strain; dimerization; polar vs radical characters

Bridgehead alkenes, often referred to as Bredt's rule violators, have had a long and glorious history[1] since the work of Bredt *et al.*[2] in the early part of this century and to date many bridgehead alkenes of varying stability have been studied. Naturally, most studies have been devoted to clarifying the relationship between chemical behaviors and twisting distortion of π bonds. Since bridgehead double bonds are readily accommodated in larger ring systems, bridgehead alkenes are classified into three categories: isolable, observable and unstable. Adamantene, solidly categorized as an unstable species, based on a heat of formation [32.36 kcal mol^{-1} (1 kcal = 4.184 kJ)] and olefinic strain (39.5 kcal mol^{-1})[3] and also the twist angle of the π portion of the double bond (64°),[4] has been a subject of considerable interest, especially owing to its contradictory history.[5,6] The complete picture of the nature of adamantene has begun to be unfolded recently by painstaking chemical analysis. More direct information obtained using time-resolved spectroscopic techniques available for the study of transient species chemistry is, however, still scant in this field. We therefore studied the chemistry of 3-noradamantyl(phenyl)diazomethane (**1**), a potential precursor of phenyladamantene (**2**), by using laser flash photolysis (LFP) techniques.

Laser flash photolysis[7] of 3-noradamantyl(phenyl)diazomethane (**1**) (prepared by oxidation of 3-noradamantyl phenyl ketone) in a degassed benzene solution at room temperature with a 308 nm pulse from a XeCl excimer laser (10 ns, 70–90 mJ) produced a transient species showing a fairly strong broad absorption at 434 nm, which appeared coincident with the pulse. A shoulder appeared at 323 nm in the transient optical density spectrum 20 µs after the laser flash. At 100 µs after the laser flash, the absorption maximum had shifted to 323 nm. Figure 1 shows the transient spectrum obtained 100 µs after the excitation where decay of the initial species (**A**) was not complete; the inset in Fig. 1 shows the decay of the 434 nm species and the formation of the 323 nm species (**B**), indicating that the decay is kinetically correlated with the growth of the new species. The decay of **A** was found to be second order ($2\ k/\varepsilon l = 1.5 \times 10^2\ \mathrm{s}^{-1}$) and the lifetime is estimated in the form of the half-life, $t_{1/2}$, to be roughly 5.6 ms. On the other hand, the secondary formed species (**B**) is too long-lived to be monitored by our system.

What are these species? It is well documented that the photolysis of diazomethanes generates carbenes as initial intermediates which then decay to form final products[8] and that some arylcarbenes are often observed in solution at room temperature by LFP.[9] However, judging from the absorption and lifetime features, it is highly unlikely that the initially formed transient species (**A**) can be assigned to phenyl(noradamantyl)carbene (**3**). For instance, the optical absorption spectra of triplet diarylcarbenes have been assigned and typically they consist of an intense UV band around 300–340 nm along with a very weak visible transition around. 400–500 nm.[10] The lifetime of triplet

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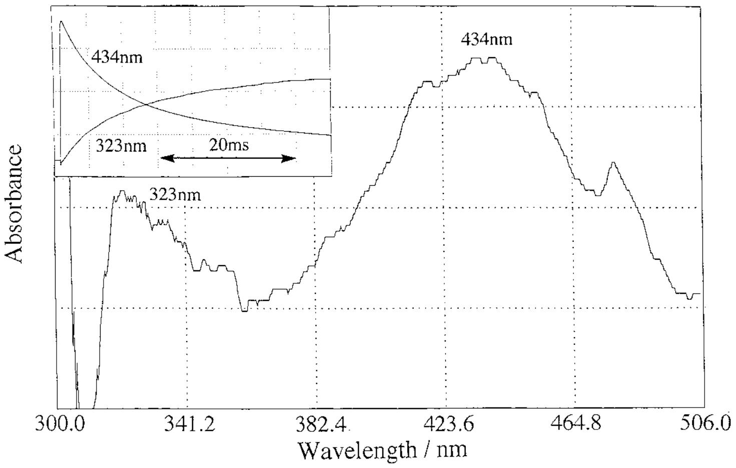


Figure 1. Absorption spectrum of the transient products formed during the irradiation of 3-noradamantyl(phenyl)diazomethane (**1**) in degassed benzene recorded 100 μs after excitation. Inset shows oscillogram traces monitored at 323 and 434 nm

diphenylcarbene in degassed benzene is 4 μs (H. Tomioka and K. Hirai, unpublished work). The absorption bands and lifetime for monoarylcarbenes should be shifted to shorter wavelength and shorter time regions compared with the diarylcarbenes.

In order to gain more insight into the nature of the transient species, the following trapping experiments were carried out. First, LFP of **1** in degassed benzene in the presence of pyridine gave essentially the same transient absorption in terms of intensity and kinetics, no new absorption bands being generated. It is well known that carbenes are readily trapped by pyridine to form ylides, which usually show intense absorption in the visible region.[11] Second, LFP of **1** in the presence of methanol also generated the transient band, although the optical yield of **A** was slightly decreased. However, the decay rate was found to increase as the methanol concentration increased. The apparent decay rate constant, k_{obs}, of the transient band is expressed as

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

where k_0 represents the rate of decay of **A** in the absence of methanol and k_{MeOH} is the quenching rate constant of **A** by methanol. A plot of the observed pseudo-first-order rate of the decay versus methanol concentration in the range 0.5–2.0 M was linear and the slope of this plot yields the rate constant for the reaction of **A** with MeOH, $k_{\mathrm{MeOH}} = 8.7 \times 10$ l mol^{-1} s^{-1}, and the intercept yields $k_0 = 7 \times 10$ s^{-1} ($r = 0.999$). Methanol is one of the most efficient trapping reagents for carbenes usually in the singlet state.[8] The bimolecular quenching rate constant for triplet diphenylcarbene, for instance, is 3×10^7 l mol^{-1} s^{-1}.[9] Even sterically hindered monophenylcarbenes, e.g. triptycyl(phenyl)carbene, is trapped by methanol at a rate of 3.2×10^5 l mol^{-1} s^{-1}.[12] Thus, k_{MeOH} observed with **A** is at least three orders of

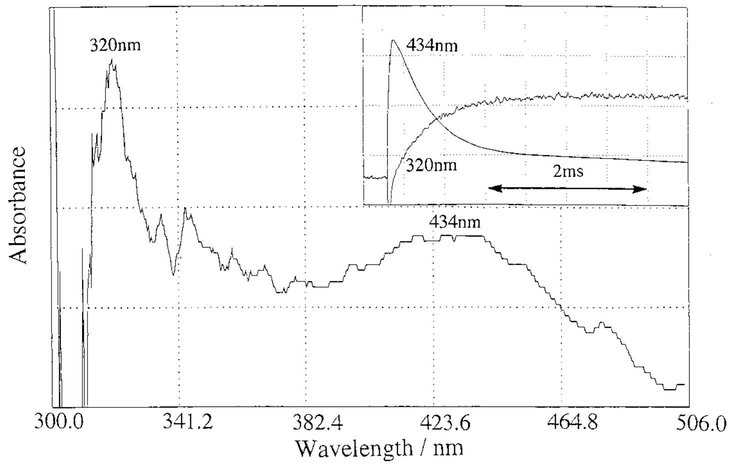
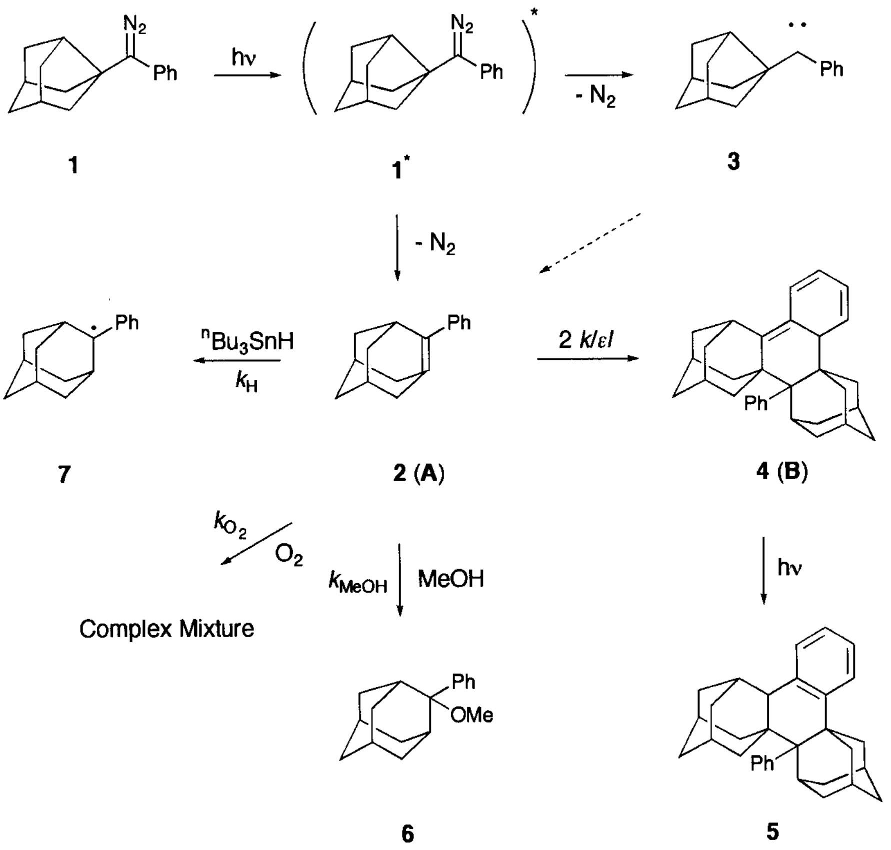


Figure 2. Absorption spectrum of the transient products formed during the irradiation of **1** in degassed benzene containing Bu$_3$SnH (3.72×10^{-2} M) recorded 20 μs after excitation. Inset shows oscillogram traces monitored at 320 and 434 nm



Scheme 1

magnitude smaller than that expected for carbene. Finally, LFP in the presence of oxygen also resulted in a decrease in the optical yield of **A** and an increase in the decay rate. Again a plot of k_{obs} against the O_2 concentration is linear, and the slope gives a bimolecular rate constant of 7.0×10^6 l mol^{-1} s^{-1} for the reaction of **A** with oxygen (k_{O_2}). It is well documented that most triplet arylcarbenes are trapped by oxygen to generate the corresponding ketone oxides very efficiently, mostly with a nearly diffusion-controlled rate constant.[9] For instance, even triptycyl(phenyl)carbene is trapped by oxygen with a bimolecular rate constant of 1.6×10^9 l mol^{-1} s^{-1}.[12] Moreover, the carbonyl oxides usually exhibit a broad band around 390–450 nm[13] and are long-lived enough to be easily observed to grow as the carbene signals decay.[9] No new transient absorption appeared in LFP of **1** in the presence of O_2 as transient bands due to **A** decayed.

All of these observations point to the same conclusion that transient absorption at 434 nm is obviously not ascribable to carbene **3**. A plausible structure is then 2-phenyladamantene (**2**), since 1-noradamantyldiazomethane is known to undergo ring expansion upon decomposition.[5,14] This assignment is supported by a product analysis study. Thus, the main product isolated from the spent solution in benzene was assigned to a dimer of the adamantene based on the following data: HRMS, calculated for $C_{32}H_{36}$ 420.2817, found 420.2829; ^{1}H NMR ($CDCl_3$, 400 MHz), δ 7.49 (br d, 1H, J = 8.0 Hz), 7.36 (br d, 1H, J = 7.6 Hz), 7.31–7.13 (m, 4H), 7.09–6.98 (m, 2H), 6.92–6.81 (m, 1H), 2.94 (br s, 1H), 2.85 (br d, 1H, J = 12 Hz), 2.68–2.39 (m, 5H), 2.32 (br d, 1H, J = 12 Hz), 2.10–1.45 (m, 16H), 1.38 (br t, 2H, J = 12 Hz), 1.31–1.21 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.4 MHz), δ 146.9 (C), 144.8 (C), 139.3 (C), 132.3 (CH), 131.6 (CH), 126.0 (CH), 125.6 (CH), 125.4 (CH), 125.24 (CH), 125.21 (CH), 125.1 (CH), 125.0 (CH), 54.4 (C), 48.0 (CH_2), 46.1 (CH), 41.4 (CH_2), 40.8 (C), 40.6 (CH_2), 39.8 (CH_2), 39.0 (C), 38.1 (CH_2), 37.22 (CH_2), 37.21 (CH_2), 36.9 (CH_2), 34.8 (CH_2), 31.5 (CH), 31.3 (CH_2), 29.8 (CH), 29.5 (CH), 29.2 (CH), 28.5 (CH), 28.4 (CH). The structure which explains these ^{1}H NMR data best is proposed to be **5**, which is produced by dimerization in $4 + 2$ fashion including the aromatic ring to form the initial dimer (**4**), followed by H migration. These product analysis data suggest that the phenyladamantene mainly decays by undergoing dimerization in the absence of trapping reagent, which is in accordance with the kinetic behavior of the initial transient species **A** observed in LFP of **1**. On the other hand, the UV absorption spectrum of the dimer (**5**) did not coincide with that observed for the product from **2**. However, we were able to isolate the initial dimer (**4**) by generating the desired adamantene (**2**) by treating 1,2-diiodo-2-phenyladamantane with *tert*-butyllithium at −78 °C. Dimer **4**: colorless crystals; m.p. 242.0–243.5 °C; HRMS, calculated for $C_{32}H_{36}$ 420.2817, found 420.2829;

^{1}H NMR (CDCl$_3$, 400 MHz), δ 7.36 (d, 1H, J = 8.3 Hz), 7.28–7.04 (m, 4H), 6.57 (d, 1H, J = 9.5 Hz), 6.11–5.97 (m, 2H), 5.88 (m, 1H), 4.04 (br s, 1H), 3.28 (br s, 1H), 2.85 (br d, 1H, J = 13 Hz), 2.75–2.58 (m, 3H), 2.31 (br d, 1H, J = 14 Hz), 2.16 (br d, 1H, J = 12 Hz), 2.05 (br s, 2H), 1.89–1.41 (m, 14H), 1.34 (br d, 1H, J = 12 Hz), 1.17 (dt, 1H, J = 13, 2.7 Hz), 0.27 (dt, 1H, J = 13, 3.4 Hz); ^{13}C NMR (CDCl$_3$, 67.8 MHz), δ 147.7 (C), 146.9 (C), 132.1 (CH), 130.6 (CH), 130.4 (CH), 127.7 (CH), 126.1 (CH), 124.7 (CH), 123.8 (CH), 122.3 (CH), 122.1 (CH), 121.5 (C), 53.5 (C), 50.3 (CH$_2$), 46.7 (CH), 45.4 (C), 43.4 (CH$_2$), 39.92 (CH$_2$), 39.87 (CH$_2$), 39.1 (CH$_2$), 38.1 (CH$_2$), 37.6 (CH$_2$), 37.5 (C), 37.2 (CH$_2$), 36.2 (CH$_2$), 35.5 (CH$_2$), 32.2 (CH), 31.9 (CH), 30.0 (CH), 29.33 (CH), 29.27 (CH), 28.0 (CH). This dimer is not only shown to undergo H migration to give the final dimer **5** upon irradiation but also exhibits an absorption maximum at 323 nm. Hence **A** is most probably phenyladamantene (**2**) which decays with second-order kinetics to form a Diels–Alder dimer (**4** = **B**), showing an absorption maximum at 323 nm. Analysis of the photoproducts in methanol, on the other hand, showed the presence of 2-phenyl-2-methoxyadamantane (**6**) as the main product, obviously formed as a result of protonation of **2** followed by nucleophilic attack of the solvent. Phenyl(noradamantyl)methyl methyl ether (**6′**), expected to be formed from carbene (**3**), was also detected, albeit in a minor amount.

The present observations revealed several interesting features of the reactivities of adamantene. It is generally accepted that the stability of bridgehead alkenes is greatly affected by substituents. For instance, in the case of homoadamant-3-ene, while the parent compound can be observed only at very low temperature,[15] the 4-phenyl derivative has been shown to have a half-life of over 12 h in solution at room temperature, presumably owing to a conjugative effect.[16] Adamantene is also stabilized by phenyl substitution to the extent that it is observable in solution at room temperature, but its half-life is still seven orders of magnitude smaller than that of the corresponding homoadamantene. This is the first quantitative experimental evidence confirming the difference in the measure of ‘olefinic stability’ between adamantene (39.5 kcal mol^{-1})[3] and homoadamantene (20.2 kcal mol^{-1}).[15]

The quenching rate constants of **2** with O$_2$ and MeOH are also noteworthy. The data suggest that phenyladamantene is five orders of magnitude more reactive towards O$_2$ than MeOH. This is unexpected in terms of both trends and magnitude since bridgehead alkenes are known to undergo polar addition of alcohols smoothly whereas their reactions with O$_2$ are rare.[16,17] More interestingly, the transient absorption band was found to be quenched even by hydrogen donors. Thus, LFP of **1** in the presence of tri(*n*-butyl)tin hydride again resulted in a dramatic decrease in the lifetime of **2** and a concurrent appearance of a new absorption band at 320 nm. The rate of increase in the band at 320 nm is almost the same as that of the decay of the peak due to **2**, showing that **2** is quenched by the hydride (Fig. 2). Since the excellent hydrogen donor properties of the tin hydride have been well recognized[18] and since most benzyl radicals show characteristic UV absorption peaks around 310–320 nm,[19] the spectral changes are interpreted as indicating that phenyladamantene abstracts hydrogen from Bu$_3$SnH to generate benzyl-type radicals (**7**). The absolute rate constants for the abstraction reaction was estimated to be 6.3×10^4 l mol^{-1} s^{-1}.

Twisted π bonds are usually believed to have a polarized character which reduces the strain energy. Therefore, frequently employed trapping reagents are polar, e.g. alcohols. However, when radical reaction channels are available, radical-type reactions are sometimes observed. For instance, in the reactions with simple alkenes and dienes, radical mechanisms are proposed mostly based on product analysis data.[5,17,20] However, these radical reactions are usually observed at much higher temperature in these cases. The present results are therefore noteworthy in that the radical nature of the twisted π bonds is verified at a much lower temperature by direct observation of the intermediates in a quantitative manner, and revealed that the twisted π bond in **2** shows profound radical over ionic character.

Finally, it is important to comment on the mechanism of the formation of **2** in the photochemical reaction of **1**. LFP data in the presence of typical trapping reagents for carbenes, e.g. pyridine, methanol, oxygen and Bu$_3$SnH, clearly suggested that carbene does not intervene at least as the main intermediate leading to **2**. What is a ‘real’ intermediate, then? It is now well documented[21,22] that excited states of diazomethanes often mimic the reactions of carbenes. Intramolecular chemistry such as 1,2-migrations is particularly bedeviled by such reactions, in which diazomethanes play the roles traditionally assigned to carbenes. The present LFP data are also compatible with a similar assumption that **2** is produced directly from the excited state of **1**.

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