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BIPHOTONIC GENERATION OF CARBENES AND CARBOCATIONS BY LASER FLASH PHOTOLYSIS

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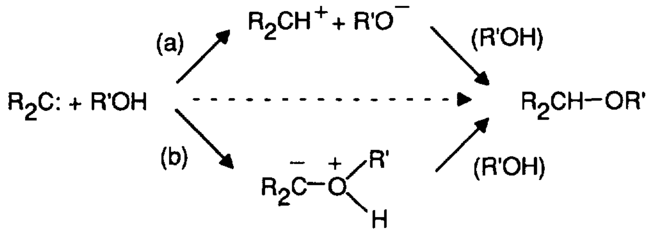
Abstract: In protic solvents, *trans*-2,3-diphenylaziridinylimines of diaryl ketones are (flash-)photolyzed in two consecutive steps, via diaryldiazomethanes and diarylcarbenes, to give eventually diarylmethyl cations. The same intermediates arise from diazo ketones by way of Wolff rearrangement and ketene photolysis. The method has been used to demonstrate the protonation of fluorenylidene by hexafluoroisopropanol.

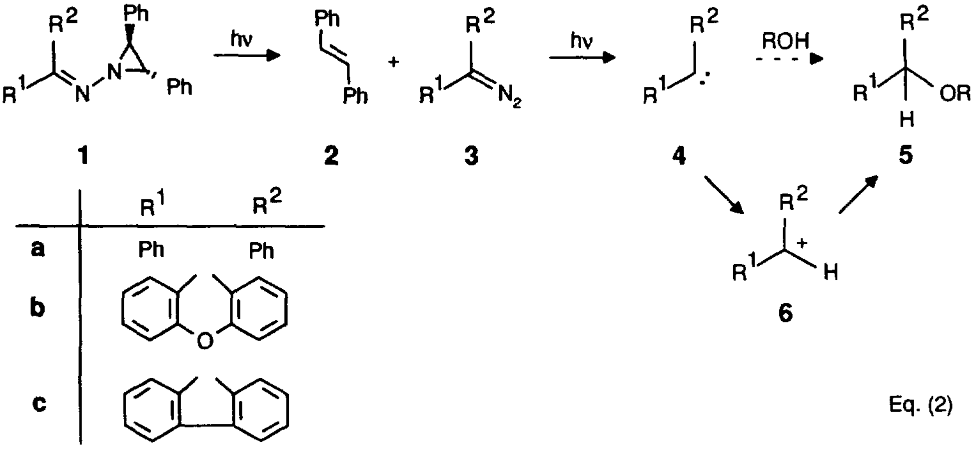
A variety of carbenes react with alcohols by way of proton transfer, generating carbocations that are eventually captured by nucleophiles, Eq (1a).[1] In many cases, product and/or isotope distributions served to distinguish the carbocation route from the alternative ylide mechanism, Eq. (1b). The protonation of diarylcarbenes, however, has been demonstrated by time-resolved spectroscopy of the resulting diarylmethyl cations.[2-4]



Eq. (1)

The application of laser flash photolysis (LFP) to O-H insertion rections of carbenes is occasionally hampered by the instability of diazo compounds in protic media.[5] In order to overcome these difficulties, we searched for more persistent substrates which would generate diazo compounds in situ. After considerable experimentation, we resorted to *trans*-2,3-diphenylaziridinylimines **1** which were widely applied in thermal reactions (Eschenmoser fragmentation)[6] but have rarely been photolyzed.[7] In view of the rich experience with diphenylcarbene, the benzophenone derivative **1a** was chosen for exploration.

Continuous irradiation (medium pressure mercury arc, pyrex vessel) of **1a**[8] in methanol afforded 44% of stilbene (**2**; *E/Z* mixture) and 42% of methoxydiphenylmethane (**4a**). The red color (λ_{max} ~ 520 nm) of diphenyldiazomethane (**3a**) became apparent when a solution of **1a** in acetonitrile was photolyzed for 3-5 min. These observations support the mechanism outlined in Eq. (2).



Eq. (2)

The lifetime of diphenylcarbenium ions (**6a**) in trifluoroethanol (TFE) is sufficient for spectroscopic detection in nanosecond LFP experiments.[2,9] Rapid decomposition of diphenyldiazomethane (**3a**) ($\tau \sim 10^2$ s) precluded the generation of diphenylcarbene (**4a**) from **3a** in neat TFE. In contrast, the aziridinylimine **1a** persists in TFE for hours. LFP of **1a** in TFE (Fig. 1) gives rise to a transient whose absorption (λ_{max} = 440 nm), reaction rate ($k_{TFE} = 6.4 \cdot 10^6$ s^{-1}), and rapid quenching by methanol ($k_{MeOH} = 4.2 \cdot 10^7$ M^{-1}s^{-1}) are in excellent agreement with previous data for **6a**.[2,9] The long-lived absorption band at ~300 nm, unaffected by methanol, is due to *E*-stilbene (**2**). The optical density (OD) at 300 nm increases linearly with the laser dose up to ~30 mJ and then levels off, owing to depletion of **1a** (Fig. 2a). An analogous plot of the OD at 440 nm is strongly curved-up at low laser doses and approaches apparent linearity above 30 mJ (Fig. 2b). These findings indicate that **6a** arises from a photoproduct of **1a** in a second light-induced step, thus confirming Eq. (2).

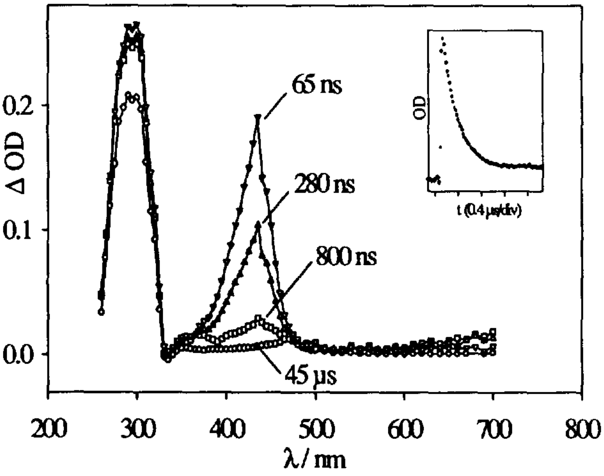


Fig. 1. Time-dependent absorption spectra obtained after laser excitation (248 nm, 20 ns, 130 mJ/pulse) of **1a** (0.066 mM) in oxygen-saturated TFE. Inset: Decay of **6a**, recorded at 440 nm.

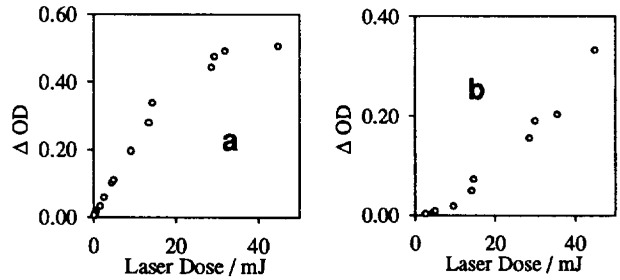
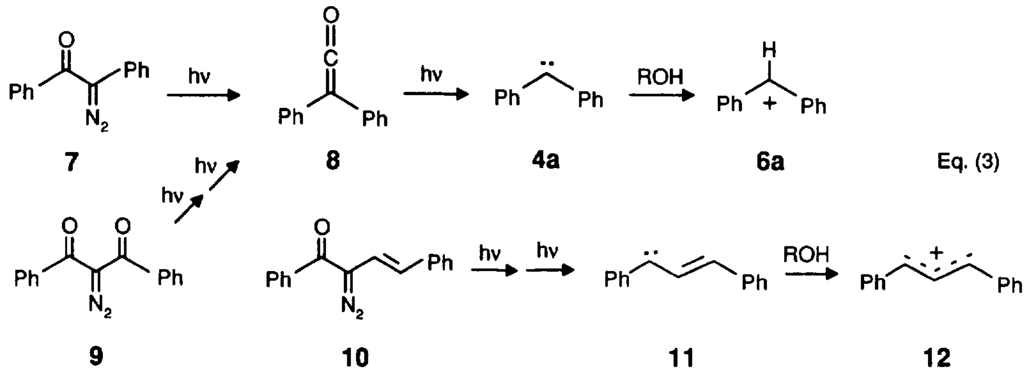


Fig. 2. Yields of **2** (a) and of **6a** (b) as a function of the laser dose (mJ/pulse), recorded 70 ns after LFP of **1a** (0.085 mM), as in Fig. 1.

The stability of the xanthylium ion (**6b**, pK_{R^+} = -0.84)[10] suggests that xanthylidene (**4b**) should be readily protonated. However, experimental verification has been lacking since 9-diazoxanthene (**3b**) is rapidly decomposed even by water. LFP of **1b** in acetonitrile-water (1:4) generates **6b** as a transient whose absorption (λ_{max} = 375 nm) and reaction rate ($k = 2.6 \cdot 10^4$ s^{-1}) conform with data from the literature.[11] More importantly, our methodology is also applicable to fluorenylidene (**4c**). Employing ns techniques, the 9-fluorenyl cation (**6c**) can be monitored in hexafluoro-2-propanol (HFIP).[12] Previous attempts at protonating **4c** failed,[2] owing to the instability of 9-diazofluorene (**3c**) in HFIP ($\tau \sim 0.5$ s).[13,14] LFP of **1c** in 99.7% HFIP gave rise to the absorption of **6c** (λ_{max} = 515 nm) which decayed acording to first order kinetics ($k = 2.4 \cdot 10^5$ s^{-1}; reported:[12] $2.4 \cdot 10^5$ s^{-1}). We conclude that fluorenylidene is in fact protonated by HFIP.[15]

A sequence of two or more photochemical steps is also triggered by LFP of diazoketones. Light-induced Wolff rearrangement leads to ketenes which are photolyzed with extrusion of CO, Eq. (3). Thus LFP of azibenzil (**7**, 0.1 mM) in TFE gives rise to the transient absorption spectrum of **6a**, with the properties described above. A weak signal of **6a** was observed even on LFP of 2-diazo-1,3-diphenylpropane-1,3-dione (**9**) although two consecutive Wolff rearrangements must occur in order to obtain diphenylketene (**8**) from **9**. In an important application, LFP of **10** in TFE-acetonitrile (8:2) was found to generate 1,3-diphenylallyl cations (**12**, λ_{max} = 490 nm,[16] $k = 2.8 \cdot 10^4$ s^{-1}).[17] Neither diazo nor aziridinylimine precursors of the carbene **11** are available.



Eq. (3)

These examples demonstrate that biphotonic processes are very useful in extending the scope of carbene protonation.

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(8) (a) The aziridinylimines **1a-c** were prepared by reaction of ketimines with *N*-amino-*trans*-1,2-diphenylaziridine[8b] in benzene: **1a** , 20°C, 2 h, 78%, m.p. 128 °C (dec.), ^{1}H NMR ($CDCl_3$): δ 3.5 (br.s, 2 H), 7.1-7.4 (m, 20 H); **1b**, 35 °C, 8 h, 73%, m.p. 105 °C (dec.),^{1}H NMR ($CDCl_3$): δ 3.70 (d, $J = 4.7$ Hz, 1H), 3.98 (d, $J = 4.7$ Hz, 1H), 7.0-7.5 (m, 16 H), 7.9-8.1 (m, 1 H), 9.0-9.2 (m, 1 H); **1c**, 1.5 h, 30 °C, 81%, m.p. 38 °C (dec.),^{1}H NMR ($CDCl_3$): δ 4.0 (br.s, 2 H), 7.0-7.7 (m, 17 H), 8.30 (dd, $J = 8/2$ Hz, 1 H). (b) Müller, R. K.; Joos, R.; Felix, D.; Schreiber, J.; Wintner, C.; Eschenmoser, A. *Org. Synth.* **1988**, Coll. Vol. 6, 56.

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(13) The half life of **3c** was obtained by extrapolating conventional rate measurements in HFIP-acetonitrile mixtures (56-83% HFIP) to neat HFIP.

(14) The reaction of **3c** with HFIP gives **5c** as well as bifluorenylidene. The vis absorption of bifluorenylidene is similar to that of **3c**. Therefore, the stability of **3c** in HFIP was not correctly assessed in our earlier work.[2]

(15) The cation **6c** can be generated by LFP of **5c** in HFIP. However, excitation of **5c** in the present experiments is unlikely, owing to an excess of the strongly absorbing **1c**. Addition of an equimolar amount of **5c** prior to LFP of **1c** did not significantly enhance the yield (OD) of **6c**. Thus, the sequence **4c** → **5c** → **6c** is excluded as an alternative route to **6c**.

(16) $\lambda_{max} = 485$ nm was reported for 1,3-diphenylpropenylium tetrafluoroborate: Hafner, K; Pelster, H.; *Angew. Chem.* **1961**, *73*, 342.

(17) For comparison,**12** has been generated by LFP of 1,3-diphenylallene in TFE ($\lambda_{max} = 490$ nm, $k = 2.1 \cdot 10^{4}\ s^{-1}$): Strehlke, I. K., unpublished results; see also Ref. (1d).

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