



Triplet halocarbene chemistry: *p*-nitrophenylchlorocarbene and *p*-nitrophenylbromocarbene

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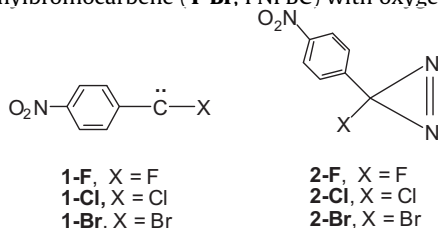
Triplets

ABSTRACT

Reactions of *p*-nitrophenylchlorocarbene with cumene and of *p*-nitrophenylbromocarbene with toluene afford C–H abstraction–recombination products that suggest the involvement of triplet arylhalocarbenes.

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Dihalocarbenes and monohalocarbenes appear to have singlet ground states,¹ and their chemistry is in general agreement with this conclusion.² The parent arylhalocarbenes, PhCX (X=F, Cl, and Br), also behave as singlets, manifesting stereospecific addition to *cis*- and *trans*-butene, electrophilic selectivity toward alkenes, and a lack of hydrogen abstraction or other radical reactions.³ However, triplet chemistry has been suggested to account for the relatively rapid reactions of *p*-nitrophenylchlorocarbene (**1-Cl**, PNPCC) and *p*-nitrophenylbromocarbene (**1-Br**, PNPBC) with oxygen.⁴

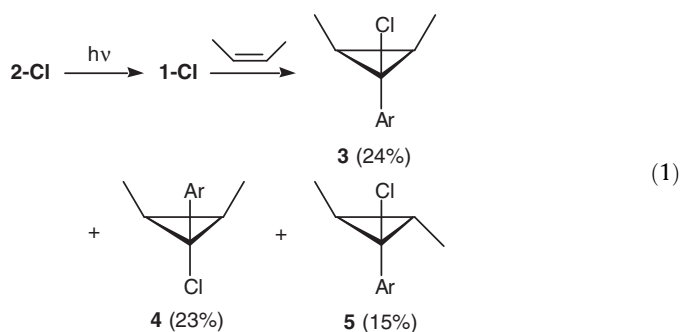


These reactions were suggested to involve thermally driven equilibration between ground singlet states and nearby triplet states of **1-Cl** or **1-Br**, followed by rapid reactions of the triplet carbenes with (triplet) oxygen.⁴ Singlet–triplet separations of ~2 kcal/mol were estimated experimentally for these carbenes.⁴ We wondered whether other triplet chemistry could be observed for PNPCC and PNPBC. We report the results of our investigations herein.

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Triplet carbene chemistry in solution is frequently signaled by non-stereospecific additions to *cis*- or *trans*-butene,^{5,6} so that we subjected PNPCC and PNPBC to this test. Photolysis of diazirine **2-Cl**⁷ with *cis*-butene in a Rayonet reactor⁸ for 9 h in CH₂Cl₂ gave cyclopropanes **3–5** in the indicated isolated yields; cf., Eq. (1), where Ar = *p*-nitrophenyl. The cyclopropanes were separated and isolated by preparative TLC on silica gel (eluted with 20:1 v/v, pentane/ether). Structures were established by ¹H and ¹³C NMR, and mass spectroscopy; see the [Supplementary data](#) for details.



An analogous photoreaction of diazirine **2-Br**⁹ (i.e., carbene **1-Br**) with *cis*-butene gave the results outlined in Eq. (2). Product spectra appear in the [Supplementary data](#). Control experiments, however, demonstrated that the cyclopropanes were configurationally *unstable* to 350 nm irradiation; in particular, **6** was readily converted to **8**. The apparent non-stereospecific additions of **1-Cl** and **1-Br** to *cis*-butene therefore cannot be regarded as mechanistically significant.

Table 1
 ΔG_{S-T} computed for some arylhalocarbenes

Carbene	$\Delta G_{S-T}^{a,b}$	ΔG_{S-T} (Ref. 4) ^{b,c}
PhCF	–13.71	
PhCl	–5.18	–9.56
PhCBr	–4.29	–6.69
<i>p</i> -O ₂ NPhCF	–9.22	–9.56
<i>p</i> -O ₂ NPhCl	–0.89	–2.10
<i>p</i> -O ₂ NPhCBr	–0.011 ^d	–1.29
	0.49 ^e	

^a In kcal/mol. Calculated at the R(U)B3LYP/6-311+G(d) level of theory; see the Supplementary data for details.

^b A negative sign denotes a singlet ground state.

^c Calculated at the R(U)B3LYP/6-311G(d) level. Converted to kcal/mol ($\times 0.239$) from kJ/mol in Ref. 4.

^d All electrons.

^e Effective core potential: R(U)B3LYP/6-311+G(d)/LAN2DZ(pd); cf., Supplementary data for details.

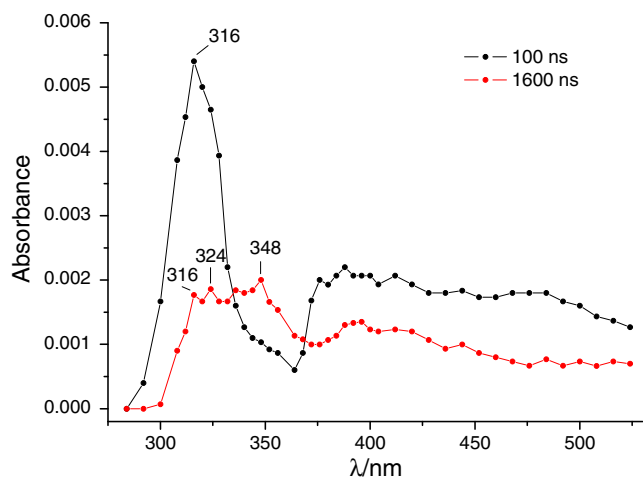


Figure 1. LFP of diazirine **2-Cl** at 351 nm in 1:1 cumene/pentane solution. UV transient absorptions are shown at 100 ns (black) and 1600 ns (red) after the laser flash; see text for discussion.

and for a similar abstraction–recombination mechanism for the reaction of triplet PNPBC with toluene.

Finally, we examined the laser flash photolysis (LFP) of diazirine **2-Cl** in a 1:1 cumene/pentane solution; results are illustrated in Figure 1. At 100 ns after the 351 nm laser flash, the UV spectrum is dominated by the $\pi \rightarrow p$ absorbance of singlet PNPCC at 316 nm.⁷ After 1600 ns, the carbene has substantially decayed, and other (weak) absorptions can be seen at, for example, 324 and 348 nm. We suggest that the 324 nm absorbance represents the cumyl radical (**12** in Scheme 1), which is reported at 322 nm in cyclohexane or isooctane.²⁴ The signal at 348 nm is tentatively assigned to the *p*-nitrophenylchloromethyl radical (**11** in Scheme 1). This species absorbs at 360 nm in 3 M aqueous isopropyl alcohol,²⁵ but is calculated to absorb at 345 nm in vacuo.²⁶

In conclusion, reaction of PNPCC (**1-Cl**) with cumene and of PNPBC (**1-Br**) with toluene afford C–H abstraction–recombination products consistent with the incursion of triplet halocarbenes. This scenario is supported by computational studies and LFP experiments, and dovetails with Sawaki's findings for the reactions of PNPCC and PNPBC with oxygen.⁴

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.09.018.

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