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

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ABSTRACT

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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 \sim 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.

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-CI**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.

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.



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.





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In fact, *thermal* generation of **1-Cl** or **1-Br** from **2-Cl** or **2-Br** (70 °C, 9 h, in 1,2-dichloroethane in a stainless steel bomb fitted with a PTFE liner) gave *stereospecific* additions to *cis*-butene: from **1-Cl** and *cis*-butene, we isolated 54% of **3** and 26% of **4**; from **1-Br** and *cis*-butene, we obtained 55% of **6** and 35% of **7**. The *trans*-dimethylcyclopropanes **5** and **8** were absent.

Nevertheless, in view of the Cl and Br 'heavy atoms' directly bonded to the carbene centers of PNPCC and PNPBC, we do not regard these stereochemical results as definitively excluding the possible presence of the triplet carbenes. We therefore turned to an examination of the reactions of PNPCC and PNPBC with cumene, searching for the abstraction–recombination products that might indicate triplet intervention.

Photolysis (350 nm, Pyrex, 5 h) or thermolysis (70 °C, 5 h) of diazirine **2-Cl** in cumene gave (via carbene **1-Cl**) the C–H 'insertion' product **9** (70%) and the ArCHCl·dimer **10** (10%),¹⁰ along with traces of the cis and trans dimers of **1-Cl**; cf., Eq. (3), Ar = *p*-nitrophenyl. As mentioned above, products were isolated by preparative TLC on silica gel, eluted with 20:1 pentane/ether, and identified by ¹H and ¹³C NMR, and mass spectroscopy; cf., the Supplementary data.

2-CI
$$\xrightarrow{hv}$$
 1-CI $\xrightarrow{PhCHMe_2}$ ArCHCICMe₂Ph
9 (70 %)
+ ArCHCICHCIAr + ArCIC=CCIAr
10 (10 %) trace (3)

Control experiments demonstrated the stability of product **9** to the photochemical or thermal conditions; it was not a source of product **10**.

A concise mechanistic rationale for the formation of products **9** and **10** appears in Scheme 1. Here, singlet and triplet PNPCC rapidly equilibrate.⁴ The singlet reacts with cumene directly to yield insertion product **9**. The triplet, however, *abstracts* a hydrogen atom from cumene, generating the *p*-nitrophenylchloromethyl (**11**)-cumyl (**12**) triplet radical pair. Some of the radical pair (after spin inversion) collapses to form **9**, but some radical **11** escapes, ultimately dimerizing to give product **10**.

We did not observe the formation of bicumyl, the dimer of cumyl radical **12**, although bicumyl readily forms from the cumyl radicals generated from azocumene¹¹ or α -cumylazocyclohexane.¹² NMR spectroscopy demonstrated the absence of both cumyl chlo-



Scheme 1. Formation of products 9 and 10; Ar = *p*-nitrophenyl.

ride and 2-phenylpropene (Cl-abstraction and disproportionation products, respectively, of cumyl radical).

As a model for the mechanism of Scheme 1, we examined the reaction of the known triplet diphenylcarbene¹³ with cumene. Thermolysis of diphenyldiazomethane¹⁴ in cumene (80 °C, 30 h) gave 30% of 'insertion' (abstraction–recombination) product **13**,¹⁵ 14% of diphenylmethyl radical dimer **14**,¹⁶ 28% of benzophenone azine,¹⁶ and 5% of tetraphenylethene (carbene dimer). Products **13** and **14** are analogs of **9** and **10** in Eq. (3), but here, just as in Eq. (3), we did *not* observe a bicumyl product.

In parallel to Eq. (3), photolysis (350 nm, 4 h) or thermolysis (70 °C, 4 h) of diazirine **2-Br**⁹ in cumene gives (via carbene **1-Br**) 'insertion' product **15** (75%) and abstraction dimer **16**^{10b,17} (12%). Unfortunately, control experiments reveal that **15** is unstable to the photolysis or thermolysis conditions in cumene solution; **16** is formed from **15**.

ArCHBrCMe2Ph	ArCHBrCHBrAr	ArCHBrCH ₂ Ph
15	16	17

However, in *toluene*, thermolysis of **2-Br** (70 °C, 5 h) affords 19% of 'insertion' product **17** together with 39% of dimer **16**, and the products *are* thermally stable. These results can be explained by the intervention of triplet **1-Br**, which abstracts a proton from toluene leading to the *p*-nitrophenylbromomethyl radical, which affords **16** upon dimerization. We did not, however, observe bibenzyl, the dimer of the benzyl radical.¹⁸ Neither *p*-nitrobenzylbromide nor benzyl bromide was detectable by TLC.

Sawaki and co-workers⁴ estimated small singlet-triplet separations for **1-Cl** and **1-Br** (~2 kcal/mol), so that small fractions of the triplet carbenes could be in equilibrium with the singlets at ambient temperature or above. On the other hand, computed singlettriplet separations of *p*-nitrophenylfluorocarbene (**1-F**) or phenylchlorocarbene (PhCCl) are considerably larger (both ~10 kcal/ mol⁴), so that triplet states of these carbenes should *not* intrude in their reactions with cumene. Indeed, thermolyses of diazirine **2-F**⁹ (80 °C, 45 h) or of phenylchlorodiazirine¹⁹ (80 °C, 10 h) in cumene afford *only* the respective insertion products, **18** (57%) and **19**²⁰ (90%); no H-abstraction radical dimers form.

Given the importance of the arylhalocarbene singlet-triplet gaps to our study, we recalculated these data at the R(U)B3LYP/6-311+G(d) level of theory; details appear in the Supplementary data. Our results appear in Table 1, where a negative value of ΔG_{S-T} denotes a singlet ground state.^{21–23}

There are significant differences between our results and those of Ref. 4 ("BLYP/6-311G^{*}"). Our values of ΔG_{S-T} are generally less negative; that is, the singlet and triplet are closer in energy. In the critical cases of PNPCC and PNPBC, our R(U)B3LYP/6-311+G(d) values for ΔG_{S-T} suggest a substantial presence of the triplet carbene in equilibrium with the singlet at ambient temperature. The computed ΔG_{S-T} values are consistent with the mechanism of Scheme 1 for the reaction of triplet PNPCC with cumene,

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

-	-	
Carbene	$\Delta G_{\text{S-T}}^{ab}$	$\Delta G_{\text{S-T}}$ (Ref. 4) ^{b,c}
PhCF	-13.71	
PhCCl	-5.18	-9.56
PhCBr	-4.29	-6.69
p-O ₂ NPhCF	-9.22	-9.56
p-O2NPhCCl	-0.89	-2.10
p-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.

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



Figure 1. LFP of diazirine **2-CI** 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) absorbances 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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