Received: 31 August 2009,

Revised: 16 October 2009,

Published online in Wiley InterScience: 25 January 2010

(www.interscience.wiley.com) DOI 10.1002/poc.1651

Triplet diphenylcarbene protected by iodine and bromine groups

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Diphenyldiazomethane having two iodine and two bromine groups at the ortho positions, (2,6-dibromo-4-tertbutylphenyl)(2,6-diiodo-4-tert-butylphenyl)diazomethane (1a-N₂), has been synthesized. Triplet diphenylcarbene ³1a is generated from the precursor and is characterized by UV-Vis spectroscopy at low temperature and laser flash photolysis (LFP) techniques at room temperature. Irradiation of 1a-N₂ in a 2-methyltetrahydrofuran (2-MTHF) matrix at 77 K gives the UV-Vis spectrum of ³1a, but ESR signals that can be assigned to a triplet species are not detected. The LFP of 1a-N₂ in a degassed benzene solution produces the transient absorption ascribable to ³1a at 351 nm, which decays in a second-order process with a rate constant of 0.17 s^{-1} . The first half-life of ³1a is estimated to be 24 s. Triplet carbene ³1a is trapped by oxygen to generate benzophenone oxide 1a-O, with maximum absorbance at 415 nm, with a rate constant of $7.3 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$, and also by 1,4-cyclohexadiene (CHD) to produce the diphenylmethyl radical (1a-H₂, $\lambda_{max} = 380 \text{ nm}$) with a rate constant of $39 \text{ M}^{-1} \text{s}^{-1}$. The carbene is also trapped by methanol with a rate constant of $0.30 \text{ M}^{-2} \text{s}^{-1}$. Steady-state irradiation of $1a-N_2$ in degassed benzene affords only a small amount of the phenanthrene 2a as an assignable product. Copyright © 2010 John Wiley & Sons, Ltd. Supporting information may be found in the online version of this paper.

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Keywords: diazo compound; kinetics; steric protection; triplet carbene

INTRODUCTION

Triplet carbenes are highly reactive organic radicals that are notoriously difficult to stabilize.^[1–7] To isolate the triplet carbene with its electronic integrity (one center diradical) intact, steric protection is the ideal conceptual method. Attempts to stabilize triplet diphenylcarbenes by introducing various substituents at the ortho positions have been reported.^[8–11] The strategy, however, encounters a limitation when alkyl groups are employed as protecting groups. Triplet carbenes abstract a hydrogen even from very poor sources of electrons such as CH bonds. Thus, *tert*-butyl groups, which have been successfully used to protect many reactive centers, are almost powerless to stabilize triplet carbene center.^[12]

The halogen group was found to be a very effective protector.^[13–16] While the van der Waals radius of bromine atom is similar to that of methyl (Br, 185 pm; Me, 175 pm),^[17] the C—Br bond length (181 pm) is longer than the C—C (Me) (177 pm),^[17] suggesting that the o-bromine groups overhang the reactive site more effectively than o-methyl groups. Moreover, halides are usually reactive toward singlet carbenes to form halonium ylides, but they are not reactive with the triplet state.^[18-20] In addition, the value of ξ_1 which gives a measure of the strength of the spin-orbit interaction is large (2460 cm⁻¹) for bromine,^[21] suggesting that the intersystem crossing from the nascent singlet carbene to the triplet should be accelerated by introducing a bromine atom. Based on these viewpoints, we prepared bis(2,6-dibromo-4-tert-butylphenyl)diazomethane (**1b**-N₂) and demonstrated that triplet bis(2,6-dibromo-4-tert-butylphenyl) carbene (³1b) generated therefrom was shown to have a half-life of 16 s in solution at room temperature (Scheme 1),^[15] ca. eight orders of magnitude greater than 'parent' diphenylcarbene. Product analysis studies indicate that the main decay pathway is dimerization at the carbenic center followed by photocyclization.^[13–16] This indicates that the carbene center is not completely shielded and hence the carbene still has a space in which the carbenes are coupled with each other. To realize stable triplet carbene, we need to explore kinetic protectors that are bulkier than bromine.

lodine atom has been regarded as a better kinetic protector of triplet carbene than bromine atom because the van der Waals radius (200 pm) is bigger than bromine group (185 pm).^[17] In addition, according to the theoretical calculations,^[22,23] the C—I bond length (212 pm) of iodobenzene is longer than the C—Br (189 pm) of bromobenzene. More persistent triplet diphenylcar-

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Scheme 1. Generation of diarylcarbenes **1**

benes than the tetrabromodiphenylcarbenes may be realized, if one can generate a diphenylcarbene having four iodine groups at all of the ortho positions. However, we cannot prepare the desired diazomethane at present. We were able to prepare diphenyldiazomethane having two iodine groups in addition to two bromine groups at all of the ortho positions, that is, (2,6-dibromo-4-*tert*-butylphenyl)(2,6-diiodo-4-*tert*-butylphenyl)diazomethane (**1a**-N₂). Herein, we wish to report that triplet diphenylcarbene ³**1a** generated from the precursor **1a**-N₂ is more persistent than the tetrabromo analog ³**1b** (Scheme 1).

RESULTS AND DISCUSSION

Preparation of precursor diazomethane

(2,6-Dibromo-4-*tert*-butylphenyl)(2,6-diiodo-4-*tert*-butylphenyl)diazomethane (**1a**-N₂) was prepared according to the reaction procedure outlined in Schemes 2 and 3. Thus, 2,6-diiodo-4-*tert*-butyltoluene (**3**)^[24] was converted to the acetate **4** by oxidizing with KMnO₄ in a mixture of acetic anhydride, acetic acid, and sulfuric acid, which was then hydrolyzed and oxidized to 2,6-diiodo-4-*tert*-butylbenzaldehyde (**6**) with PCC (Scheme 2). 1-*tert*-Butyl-3,5-dibromo-4-iodobenzene (**7**)^[25] was lithiated by simply treating with butyl lithium (BuLi), which was then reacted with aldehyde **6** to give the diphenylmethanol **8**. The alcohol was then converted to the corresponding diazomethane (**1a**-N₂) by way of a carbamate^[26] (Scheme 3). The diazomethane was



Scheme 2. Preparation of 4-tert-butyl-2,6-diiodobenzaldehyde (6)



Scheme 3. Preparation of (2,6-dibromo-4-tert-butylphenyl)(2,6-diiodo-4-tert-butylphenyl)diazomethane (1a-N₂)

purified by repeated chromatography on a gel permeation column. Diazomethane 1a-N₂ was rather stable for diazomethane and could be stored in a refrigerator for several months without any appreciable decomposition.

Spectroscopic studies

ESR studies in rigid matrix at low temperature

Irradiation ($\lambda > 300$ nm) of **1b**-N₂ in 2-methyltetrahydrofuran (2-MTHF) at 77 K gave rise to ESR signals with a typical fine structure of randomly oriented triplet carbene.^[15,27,28] However, similar irradiation of **1a**-N₂ in 2-MTHF at 77 K gave no triplet signals of carbene **1a** (Fig. 1(a)). Not only **1b** but also most sterically hindered diphenylcarebenes generally gave rise to the stable triplet signals under the same conditions.^[12–16,29–33] It has been observed that the ESR signals sometimes become sharper and the signal intensities increase when the measurements are made after the sample is warmed and recooled. This is partly because as the temperature is raised, the matrix softens and allows the carbene to assume a single preferred orientation rather than several slightly distorted orientations dictated by the trapping of the precursor in the frozen matrix.^[34–39] We examined whether or not triplet signals appeared by warming the matrix.



Figure 1. (a) ESR spectra obtained by irradiation of diazo compound 1a-N₂ in 2-methyltetrahydrofuran at 77 K. (b)–(f) The same sample measured at 77 K after thawing to 160 K (b), 170 K (c), 180 K (d), 190 K (e), and 300 K (f)

The ESR measurements were carried out after warming the matrix involving the photoproducts and recooling again to 77 K. This procedure can compensate weakening of signals due to the Curie law.^[40-42] The photolyzed sample was gradually warmed up to 150 K, but no ESR signals appeared. However, when the sample was warmed to 160 K, a new doublet signal appeared around 327 mT (Fig. 1(b)). The signal intensity increased gradually as the sample was warmed up to 190 K (Fig. 1(c)–(e)) and the signal could be observed even at 300 K (Fig. 1(f)). The ESR signals of carbene **1b** were stable at 77 K and disappeared irreversibly when the matrix was warmed to 170 K.^[43]

It has been reported that the sharp peak due to the radical species around 330 mT is found when some triplet signals in 2-MTHF at 77 K decrease by thawing the matrix.^[29,30,44] This means that the triplet diarylcarbenes decayed by abstracting a hydrogen from 2-MTHF to form the corresponding diarylmethyl radicals. In the case of the irradiation of **1a**-N₂, the radical signal may be due to (2,6-dibromo-4-tert-butylphenyl)(2,6-diiodo-4-tert-butylphenyl)methyl radical generated by a hydrogen abstraction of triplet carbene ³1a because the radical signal appears upon warming the matrix. The observation indicates that the signals due to carbene ³1a are invisible, but that the carbene exists in the matrix. We assumed the temperature (T_d) at which signals due to triplet carbene disappeared as a measure of the thermal stability of triplet carbenes.^[11] If the temperature at which ³1a abstracts a hydrogen from the solvent is assumed to the T_{d_1} that of ³**1a** is higher than that (130 K) for bis(2,4,6tribromophenyl)carbene^[15] and is similar to that (170K) for bis(2,6-dibromo-4-phenylphenyl)carbene.^[16] The UV-Vis spectrum due to ³1a also disappeared at the same temperature (vide infra).

Influence of iodine atom on ESR signals. Triplet carbene ³1a was observed by UV–Vis spectroscopy at low temperature and LFP at room temperature (*vide infra*) but not by ESR spectroscopy.

Sander and co-workers reported that the radical pair of 2,3,5,6-tetrafluorophenylnitren-4-yl and iodine atom was produced by the photolysis of 2,3,5,6-tetrafluoro-4-iodophenylnitrene in Ar at 4K, but that the iodine atoms formed during the photolysis could not be observed in the ESR spectra.^[45] It is explained that no detection of the iodine signals is attributed to the orbital degeneracy and strong spin-orbit coupling in the iodine atoms. Moreover, they found that triplet species having an iodine atom at the ortho position afforded almost no the ESR signals in Ar matrix at cryogenic temperature.^[46] For instance, 2,3,4,5-tetrafluoro-6-iodophenylnitrene has broad ESR signals at 4K but no signal at 15K. 2-lodophenylnitrene and 2-iodophenyl(phenyl)carbene have no signals even at 4K. We performed the ESR measurement of 1a at 5 K, but no triplet signals were observed. Since carbene 1a possesses two iodine groups at the ortho positions, the influence of the iodine atoms on ESR spectrum of ³1a may be larger than those of the mono iodo-substituted species.

UV-Vis studies in rigid matrix at low temperature

Photolysis ($\lambda > 300$ nm) of **1a**-N₂ in a 2-MTHF matrix at 77 K resulted in the appearance of new bands at the expense of the original absorption due to the starting diazo compound (Fig. 2A(b)). The new bands consist of two identifiable features, strong and sharp maxima at 336 and 367 nm and a weak and



Figure 2. UV–Vis spectra obtained by irradiation of diazo compound **1a**-N₂. (A) (a) Spectrum of **1a**-N₂ in 2-methyltetrahydrofuran at 77 K. (b) The same sample after irradiation ($\lambda > 300$ nm). (c) The same sample after thawing to 100 K. (B) UV–Vis spectral changes measured upon thawing the same sample from 100 to 300 K.

broad band from 440 to 520 nm. These features, rather strong absorption bands in the UV region and a weak and broad band in the visible region, are usually present in the spectra of triplet diphenylcarbenes.^[27,28] The glassy solution did not exhibit any changes for hours when kept at 77 K, but disappeared irreversibly when it was allowed to warm to room temperature and cooled to 77 K. On the basis of similarity with the spectrum and thermal behavior of ³1b,^[15] the absorption spectrum can be attributed to triplet carbene ³1a.

The thermal stability is estimated by raising the sample temperature in 10 K increments to the desired temperature, allowing it to stand for 15 min, and measuring the absorption bands. The characteristic bands due to ³1a shifted the maxima from 336 and 367 nm to 348 and 369 nm at 100 K, respectively (Fig. 2A(c)). Similar changes in the UV–Vis spectra upon thawing the matrix were also observed for other sterically congested diarylcarbenes and were generally interpreted in terms of geometrical changes of the carbenes (*vide infra*).^[27,28,39–42] The bands started to decay slowly at 150 K and decayed rather sharply at around 180 K (Fig. 2(B)). The temperature at which the bands of ³1a start to decrease is roughly consistent with the temperature at which the ESR signal due to the (2,6-dibromo-4-*tert*-butylphenyl)(2,6-diiodo-4-*tert*-butylphenyl) methyl radical appeared.

It should be noted here that absorption bands of most triplet diphenylcarbenes having no kinetic protectors at the ortho positions in 2-MTHF disappear in the temperature range of $100-105 \text{ K}^{[28,29]}$ where the viscosity of the matrix changes dramatically from 10^7 to $10^3 \text{ P}^{[39]}$ Even the absorption bands of triplet tetrabromo analog ³**1b** disappear up to 170 K in 2-MTHF.^[15] This observation demonstrates that the thermal stability of ³**1a** is slightly larger than that of ³**1b**.



Figure 3. Absorption of transient products formed during laser irradiation (308 nm) of diazo compound **1a**-N₂ in degassed benzene at room temperature recorded from immediately after irradiation to 240 s after excitation. The inset shows the time course of the absorption at 351 nm.

Laser flash photolysis (LFP) studies in solution at room temperature

The lifetime of carbene **1a** was estimated in degassed benzene at room temperature, in which we have measured the lifetime of a series of sterically congested diarylcarbenes.^[8–11] The lifetime of carbene **1a** was too long to monitor by the LFP technique, which has been routinely used for the determination of the decay rate constants of triplet diarylcarbenes. Thus, a conventional UV–Vis spectroscopic method was more conveniently employed in this case.^[29,30]

Brief irradiation of **1a**-N₂ in degassed benzene at 25 °C with a 150 mJ, 308 nm pulse from XeCl excimer laser produced transient absorption bands, showing strong maxima at 351 and 366 nm (Fig. 3). The maxima of the bands were shifted slightly from those observed in the photolysis of **1a**-N₂ in 2-MTHF at 100 K. However, the transient bands were markedly quenched by oxygen to give the corresponding ketone oxide (*vide infra*), and hence we assigned the bands to triplet ³**1a**. The absorption bands decayed very slowly, and did not disappear completely even after 2 min under these conditions. The decay was found to be a second order ($2k/\epsilon l = 0.17 \text{ s}^{-1}$) (Table 1). The approximate half-life ($t_{1/2}$) of ³**1a** was estimated to be 24 s. The data indicated that ³**1a** was more persistent than the tetrabromo analog ³**1b** ($2k/\epsilon l = 0.35 \text{ s}^{-1}$, $t_{1/2} = 16 \text{ s}$).^[15]



Figure 4. Transient absorption spectra obtained in LFP of **1a**-N₂ (a) in degassed benzene and (b) in O₂ saturated benzene with a 308 nm excimer laser recorded after 100 μ s. The inset shows an oscillogram trace in O₂ saturated benzene monitored at 415 nm.

The half-life is just a measure of lifetime and cannot be regarded as a quantitative scale for reactivity. In this respect, the rate constant of the triplet carbene with a typical triplet quencher can be employed as a more quantitative scale of the reactivity. It is well-documented that carbenes with triplet ground states are readily trapped with oxygen or a good hydrogen donor such as 1,4-cyclohexadiene (CHD).^[47] Therefore, the rate constants of the trapping reactions by O₂ and CHD are used as a more quantitative scale to estimate the reactivities of the triplet carbenes.

LFP of 1a-N₂ in O₂ saturated benzene resulted in a dramatic decrease in the lifetime of ³1a and a concurrent appearance of a new broad absorption band at 415 nm (Fig. 4(b)). The spent solution was found to contain the corresponding benzophenone. It is well-documented^[48-55] that diarylcarbenes with triplet ground states are readily trapped by oxygen to generate the corresponding diaryl ketone oxides (Scheme 4), which show a broad absorption band centered at 390-450 nm. Thus, our observations can be interpreted as indicating that the transient absorption quenched by oxygen is due to ³1a. The rate of increase in the band at 415 nm is the same as the rate of decrease of the peak due to ³1a within experimental error, showing that ³1a is quenched with oxygen to form carbonyl oxide ³1a-O₂. The rate constant (k_{O2}) for the quenching of ³**1a** by O₂ is determined to be $7.3 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$ from a plot of the observed pseudofirst-order growth rate of 3 **1a**-O₂ as a function of [O₂] (Fig. 5, Table 1). This is some three orders of magnitude smaller than that

Table 1. Kinetic data of carbenes 1					
Carbenes	$2k/\epsilon l \ (s^{-1})$	t _{1/2} (s)	$k_{\rm O_2}~({\rm M}^{-1}{\rm s}^{-1})$	$k_{CHD} (M^{-1}s^{-1})$	Kk_{MeOH}^{a} (M ⁻² s ⁻¹)
1a 1b ^b	0.17 0.35	24 16	$\begin{array}{c} 7.3\times10^6\\ 2.1\times10^7\end{array}$	$\begin{array}{c} 3.9\times10\\ 5.3\times10^2\end{array}$	0.30 0.42 ^c
^a $K = k_{TS}/k_{ST}$. ^b Reference ^[15] . ^c Reference ^[43] .					



Scheme 4. Photolysis of diazo compounds in the presence of carbene quenchers



Figure 5. A plot of the growth of the diaryl ketone oxide $1a-O_2$ monitored at 415 nm as a function of the concentration of oxygen

observed with the 'parent' triplet diphenylcarbene $(k_{O2} = 5.0 \times 10^9 \,\text{M}^{-1}\text{s}^{-1})^{[55]}$ and three times smaller than that observed with triplet tetrabromo analog ³**1b**.^[15]

When a degassed benzene solution of $1a-N_2$ containing CHD was excited, a new species was formed, showing an absorption with $\lambda_{max} = 380$ nm (Fig. 6). The decay of ${}^{3}1a$ was again found to be kinetically correlated with the growth of the new species. Thus, this new signal was attributed to the corresponding diarylmethyl radical (1a-H) formed as a result of a hydrogen abstraction of ${}^{3}1a$ from the diene, because it is now well-documented^[47,56–65] that triplet diarylcarbenes, generated in good hydrogen donor solvents, undergo a hydrogen abstraction leading to the corresponding radicals (Scheme 4). These radicals typically have transient absorptions at longer wavelengths than those of the precursor carbenes. The excellent hydrogen donor properties of CHD have been well recognized.^[66] The spent solution was found to contain the diarylmethane as the main product. Since the absorption of the radical and the tailing band



Figure 6. Transient absorption spectra obtained in LFP of 1a-N₂ in degassed benzene in the presence of 1,4-cyclohexadiene (0.265 M) with a 308 nm excimer laser recorded after 1 ms. The inset shows a plot of the decay of triplet carbene ³1a monitored at 350 nm as a function of the concentration of 1,4-cyclohexadiene

of the carbene overlapped, the growth curves of the radical were not observed exactly. However, a plot of the observed pseudo-first-order rate constants of the decay of the carbene monitored at 350 nm against [CHD] is linear (Fig. 6 inset), and the slope of this plot yields the absolute rate constant for the reaction of ³**1a** with the diene, $k_{CHD} = 39 \text{ M}^{-1}\text{s}^{-1}$, which is approximately six orders of magnitude smaller than that observed with the 'parent' triplet diphenylcarbene ($k_{CHD} = 1.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$)^[63] and one order of magnitude smaller than that observed with triplet tetrabromo analog ³**1b** (5.3 × 10² M⁻¹\text{s}^{-1}) (Table 1).^[15]

LFP of **1a**-N₂ in a degassed benzene solution containing methanol afforded absorption bands due to triplet carbene ³**1a** detected in the absence of methanol. The decay curves of ³**1a** measured are shown in Fig. 7. The decay rate (k_{obs}) of ³**1a** increased upon the addition of methanol. However, the plot of k_{obs} versus methanol concentration was not linear for the concentration range of 2.47–9.22 M.^[44,67] A plot of better linearity was observed when the k_{obs} was plotted against the dimer concentration of methanol. The quenching rate constant ($K_{k_{MeOH}}$) by methanol was estimated to be $0.30 M^{-2} s^{-1}$ from



Figure 7. The decay curves of triplet carbene ³1a in degassed benzene in the presence of methanol monitored at 350 nm



Figure 8. A plot of the decay of triplet carbene ³1a monitored at 350 nm as a function of the concentration of methanol.

the slope of this plot (Fig. 8, Table 1). This is smaller than that $(0.42\,M^{-2}s^{-1})^{[43]}$ observed with $^3 1b.$

The mechanism of the reaction of triplet carbenes with methanol to form methyl ether is of considerable interest.^[68] Insertion reaction of carbenes with alcohols to form ethers is usually considered to occur from the singlet states of these species (Scheme 4). However, LFP studies have shown that the ground state of diphenylcarbene is efficiently quenched by methanol.^[59,69]

The reaction of the triplet carbenes with the O—H bonds of alcohols is explained either by pre-equilibrium^[70] or by surface-crossing mechanisms.^[71,72] In the pre-equilibrium mechanism, triplet to singlet interconversion occurs prior to O—H insertion of the singlet carbene, whereas, in the surface-crossing mechanism, triplet states can react with alcohols, with surface crossing occurring after the carbene begins to interact with the O—H bond. In either of the mechanisms, the decrease in Kk_{MeOH} is considered to reflect a larger free-energy difference between the ground triplet states and their singlet states.^[71-73] In other words, the difference of the rate constants, Kk_{MeOH} , in Table 1 suggests that the free-energy difference between the ground triplet and singlet states for **1a** is larger than that for **1b**.

The values of $t_{1/2}$, k_{O2} , k_{CHD} , and Kk_{MeOH} are summarized in Table 1. Inspection of the data immediately indicates that carbene ³**1a** showed not only the larger stability estimated in degassed benzene compared to ³**1b** but also essentially lower reactivities toward typical carbene quenchers such as oxygen, CHD, and methanol than ³**1b**. Thus, the half-life and the quenching rate constants of ³**1a** clearly suggest that iodine groups are better kinetic protectors than bromine groups, as expected.

Product analysis studies

Most of the sterically congested triplet diphenylcarbenes decay mainly by undergoing dimerization at the carbenic center to give tetra-arylethenes as the main product, when generated in degassed benzene at room temperature in the absence of appropriate carbene quenchers. For instance, bis(2,4,6-trichlorophenyl)carbene in benzene produced tetrakis(2,4,6-trichlorophenyl)ethene in >80% yield.^[26,31] On the other hand, bis(2,6-dibromophenyl)carbenes under the same conditions



Scheme 5. Photolysis of diazo compound $1a\text{-}N_2$ in degassed benzene at 25 $^\circ\text{C}$

afforded the corresponding 9,10-diarylphenanthrene derivatives.^[15,16] We demonstrated that bis(2,6-dibromo-4-phenylphenyl) carbene dimerized to form tetrakis(2,6-dibromophenylphenyl) ethene as an initial product which underwent photocyclization to give the corresponding phenanthrene.^[16]

Photolysis (λ > 350 nm) of **1a**-N₂ (5.0 mg) in degassed benzene-*d*₆ (0.5 ml) in a sealed NMR tube at 25 °C was monitored by ¹H NMR spectroscopy. The irradiation (18 min) gave only very weak signals at 8.94, 8.77, 7.48, 6.14, 1.22, and 1.07 ppm along with weak complex peaks from 1.5 to 0.7 ppm at the expense of the signals of **1a**-N₂. ¹H NMR spectrum of a fraction obtained by a recycled GPC of the photomixture showed the phenanthrene derivative **2a** (a brown oil in 18% yield) (Scheme 5). Carbene **1a** presumably decayed through the same pathway, namely by dimerization followed by photocyclization, to provide **2a**. ¹H NMR spectra of the other GPC fractions showed no detectable peaks.

Photolysis ($\lambda > 300$ nm) of **1b**-N₂ in an oxygen-saturated benzene solution afforded the corresponding diaryl ketone **1b**-O in 66% yield (Scheme 6). Irradiation of **1a**-N₂ under the same conditions gave ketone **1a**-O in 77% yield.

Irradiation ($\lambda > 300$ nm) of **1a**-N₂ in degassed benzene containing CHD resulted in the formation of a mixture of two products, both showing methylene protons at 4.31 and 4.70 ppm, respectively. It has been well known that triplet diarylcarbenes produce the corresponding diarylmethanes when generated in good hydrogen donors such as the diene. Unfortunately, the reaction mixture could be separated by neither TLC nor GPC. From the ¹H NMR spectrum of the mixture, however, the minor product is assigned to diarylmethane **1a**-H₂ since the aromatic and tert-butyl protons are similar to those of diazo 1a-N₂ (Scheme 6). On the other hand, the major product is assigned to (2,6-dibromo-4-tert-butylphenyl)(2-iodo-4-tert-butylphenyl)methane $1a'-H_2$ in which an iodine in $1a-H_2$ is replaced by a hydrogen since a aromatic signal (7.92 ppm) of diiodotert-butylphenyl group in 1a-N2 is converted into a double doublet at 7.18 ppm and two doublets at 7.86 and 6.48 ppm (Scheme 6). The similar irradiation at long wavelength $(\lambda > 350 \text{ nm})$ gave only **1a**-H₂ in 75% yield.

In the photolysis of 1a-N₂ in degassed benzene containing methanol, two methyl ethers were formed. The irradiation with $\lambda > 300 \text{ nm}$ of 1a-N₂ afforded a mixture of the methyl ethers, 1a-HOMe (44%) and 1a'-HOMe (38%), and the longer wavelength irradiation ($\lambda > 350 \text{ nm}$) gave 1a-HOMe (48%) as a sole product. The methyl ethers are presumably produced as a result of the interaction of carbene 1a with O—H bond of methanol.

It has been shown that the irradiation ($\lambda > 300 \text{ nm}$) of **1b**-N₂ in the presence of CHD afforded only **1b**-H₂ in 59% yield and the similar irradiation ($\lambda > 300 \text{ nm}$) in the presence of methanol gave **1b**-HOMe in 48% yield (Scheme 6).^[15]



Scheme 6. Photoproducts obtained by irradiation of diazo compound (1-N₂) at 25 °C. (a) Reference ^[15]. (b) Relative yields determined by ¹H NMR

The bond dissociation energy between carbon and halogen for Ph-I (<72.1 kcal/mol) is >11.4 kcal/mol smaller than that of Ph-Br (83.5 kcal/mol).^[74] The facility of dehalogenation of iodine atom compared to bromine atom is plausible result. It is well known that in a solvent with easily abstractable hydrogen atoms photolysis of iodoarenes gives the corresponding deiodinated arenes by photodissociation of C—I bond followed by hydrogen transfer from the solvent.^[75] Therefore, the formation of diarylmethane **1a'**-H₂ and methyl ether **1a'**-HOMe may be formed by the over-irradiation of the initial photoproducts **1a**-H₂ and **1a**-HOMe. In the degassed benzene, the corresponding monoiodo-ketone was not formed because of the absence of good hydrogen sources.

CONCLUSIONS

In the present study, diphenyldiazomethane 1a-N₂ having two iodine and two bromine groups at the ortho positions has been synthesized and triplet carbene ³1a was generated by the photolysis of the diazomethane. Triplet carbene ³1a in degassed benzene at room temperature decayed in a second-order process with a rate constant of 0.17 s^{-1} , which was half of that of the tetrabromo analog ³1b. The reaction rate constants of 1a with the carbene quenchers were also smaller than those of 1b, respectively. As expected, an iodine group shielded the carbene center better than a bromine group.

One may expect that a triplet diphenylcarbene having four iodine groups at all of the ortho positions is more persistent than the present carbene. At present, the synthesis of the precursor of the carbene is difficult. We are making an effort to synthesize it now.

It is well known that some iodoarenes can be converted to the corresponding diaryliodonium salts. One can convert an iodine group into an aryliodonium group by using certain synthetic methods. Unfortunately, the conditions employed for such conversions are rather severe and cannot be applied to diazo compounds which are usually thermally unstable. Recently, the method of converting iodoarenes into the diaryliodonium salts using mild conditions was developed.^[76] If one can convert the ortho iodine group on the present diphenyldiazomethane into the corresponding diaryliodonium salt by using this method, a carbene generated therefrom will be highly shielded by the ortho aryliodonium group.

EXPERIMENTAL SECTION

General information

¹H and ¹³C NMR spectra were determined with JEOL JNM-AL300 FT/NMR spectrometer in CDCI_3 with $\mathsf{Me}_4\mathsf{Si}$ as an internal reference. IR spectra were measured with films on NaCl plate (oils and semisolids) or KBr pellets (solids). IR spectra were recorded on a JASCO FT/IR-410 spectrometer, and UV-Vis spectra were recorded on a JASCO V-560 spectrometer or a Shimadzu MaltiSpec-1500. The mass spectra were recorded on a JEOL JMS-600H mass spectrometer or an Applied Biosystems Voyager DE-Pro MALDI-TOF mass spectrometer. Thin layer chromatography for diazo compounds was performed using Merck aluminum oxide 60 PF₂₅₄ on a glass plate (Type E). Column chromatography was performed using silica gel (63-210 µm) or neutral alumina (Act. I, inactivated with 5% water) for diazo compounds. Recycle GPC was undertaken with a JASCO PU-2086 chromatograph with a UV-2070 UV-Vis detector using a Shodex GPC H-2001 (20 mm \times 50 cm).

Preparation of 4-tert-butyl-2,6-diiodobenzyl acetate (4)

To a stirred solution of the 4-*tert*-butyl-2,6-diiodotoluene (**3**)^[24] (4.85 g, 12.1 mmol) in H₂SO₄ (3.3 ml), AcOH (20 ml), and Ac₂O (40 ml) was slowly added KMnO₄ (2.49 g, 15.8 mmol) at 40 °C over a period of 3 h and the mixture was stirred for 1 day at the same

temperature. The mixture was poured into H₂O and extracted with Et₂O. The ethereal layer was washed with 10% NaOH solution and brine, dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. The residue was chromatographed through a column of silica gel using hexane-CHCl₃ (1:1) as an eluent to give 4-*tert*-butyl-2, 6-diiodobenzyl acetate (**4**) as a yellow viscous liquid (1.13 g, 65%): ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.86 (s, 2*H*), 5.40 (s, 2*H*), 2.13 (s, 3*H*), 1.28 (s, 9*H*); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 170.7, 155.7, 137.7, 136.4, 100.3, 75.7, 34.4, 30.9, 20.7; El-MS (*m/z*) 458 (M⁺, 3.6), 331 (56.8), 289 (100); HRMS calcd for C₁₃H₁₆l₂O₂ 457.9240, found *m/z* 457.9313.

Preparation of 4-tert-butyl-2,6-diiodobenzyl alcohol (5)

To a stirred solution of acetate **4** (1.39 g, 3.14 mmol) in MeOH (25 ml) was added K₂CO₃ (114 mg, 1.05 mmol) and the mixture was stirred at room temperature for 3 h. The reaction mixture was quenched by the addition of 2 M hydrochloric acid. The mixture was extracted with ether, and the organic solution was washed with brine, dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure to give 4-*tert*-butyl-2,6-diiodobenzyl alcohol (**5**) as a yellow viscous liquid (1.21 g, 93%): ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.82 (s, 2*H*), 5.00 (d, *J* = 6.9 Hz, 2*H*), 2.10 (t, *J* = 6.9 Hz, 1*H*), 1.27 (s, 9*H*); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 154.8, 140.4, 137.4, 99.6, 74.2, 34.1, 30.9; El-MS (*m/z*) 416(M⁺, 12.7), 415 (100), 400 (57.1), 245 (39.3); HRMS calcd for C₁₁H₁₄l₂O 415.9135, found *m/z* 415.9158.

Preparation of 4-tert-butyl-2,6-diiodobenzaldehyde (6)

To a stirred solution of benzyl alcohol **5** (1.03 g, 2.48 mmol) in CH₂Cl₂ (20 ml) was added PCC (1.54 g, 7.20 mmol) and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the residue was chromatographed through a column of silica gel using hexane-CH₂Cl₂ (1:1) as an eluent to give 4-*tert*-butyl-2,6-diiodobenzaldehyde (**6**) as yellow solids (1.03 g, >99%): mp 69.8–72.2 °C; ¹H NMR (300 MHz, CDCl₃, ppm) δ 9.76 (s, 1*H*), 8.00 (s, 2*H*), 1.32 (s, 9*H*); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 195.2, 158.7, 131.9, 138.9, 98.1, 34.8, 30.7; El-MS (*m/z*) 414 (M⁺, 30.6), 413 (100), 398 (61.0); HRMS calcd for C₁₁H₁₂l₂O 413.8971, found *m/z* 413.9001.

Preparation of (2,6-dibromo-4-*tert*-butylphenyl)(2,6-diiodo-4-*tert*-butylphenyl)methanol (8)

To a solution of 1-tert-butyl-3,5-dibromo-4-iodobenzene (7)^[25] (1.00 g, 2.43 mmol) in dry Et₂O (15 ml) was added BuLi (2.60 M in hexane, 0.96 ml, 2.50 mmol) at -78 °C. The solution was stirred for 5 h, and then a solution of aldehyde 6 (1.04 g, 2.50 mmol) in dry ether (5 ml) was added dropwise at -78 °C. The mixture was stirred at room temperature overnight and then was guenched by the addition of saturated aqueous ammonium chloride. The mixture was extracted with ether, washed with water, dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure. The residue was chromatographed through a column of silica gel using hexane-CHCl $_3$ (1:2) as an eluent to give (2,6-dibromo-4-*tert*-butylphenyl)(2,6-diiodo-4-*tert*-butylphenyl) methanol (8) as colorless solids (1.10 g, 67%): mp 69.8–72.2 °C; 'H NMR (300 MHz, CDCl₃, ppm) δ 7.93 (s, 2H), 7.53 (s, 2H) 6.39 (d, J = 9.4 Hz, 1H), 2.99 (d, J = 9.4 Hz, 1H), 1.29 (s, 9H), 1.28 (s, 9H); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 153.9, 153.6, 138.6, 139.4, 134.4, 131.4, 125.4, 98.3, 83.2, 34.6, 34.1, 31.0, 30.9; EI-MS (*m/z*) 708 (M+4, 5.4), 706 (M+2, 15.5), 704 (M⁺, 7.4), 458 (100), 443 (96.3), 413 (28.0); HRMS calcd for $C_{21}H_{24}Br_2I_2O$ 703.8283, found *m/z* 703.8334.

Preparation of ethyl *N*-[(2,6-dibromo-4-*tert*-butylphenyl) (2,6-diiodo-4-*tert*-butylphenyl)methyl]carbamate (10)

A solution of alcohol 8 (0.70 g, 1.0 mmol) and SOCl₂ (10 ml) was stirred at room temperature overnight, and the mixture was evaporated under reduced pressure to give (2,6-dibromo-4-tertbutylphenyl)(2,6-diiodo-4-tert-butylphenyl)chloromethane (9) as yellow viscous solids (0.73 g, >99%), which was rather unstable and hence used without further purification: 'H NMR (300 MHz, CDCl₃, ppm) & 7.97 (s, 2H), 7.56 (s, 2H), 6.80(s, 1H), 1.29 (s, 9H) 1.28(s, 9H). A mixture of silver tetrafluoroborate (290 mg, 1.49 mmol) and ethyl carbamate (1.15 g, 12.9 mmol) was heated at 60 °C. To the mixture was added a solution of chloromethane 9 (0.73 g, 1.0 mmol) in 1,4-dioxane (10 ml), and the resulting mixture was heated at 100 °C overnight. After cooling at room temperature, the mixture was filtered, and CHCl₃ (60 ml) were added to the filtrate. The organic layer was washed well with water, dried over anhydrous Na2SO4, and the solvent was removed under reduced pressure. The residue was chromatographed through a column of silica gel using hexane- CH_2Cl_2 (1:1) as an eluent to give ethyl N-[(2,6-dibromo-4-tert-butylphenyl) (2,6-diiodo-4-tert-butylphenyl)methyl]carbamate (10) as yellow solids (156 mg, 21%): mp 91.7–93.8 °C; ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.91 (s, 2H), 7.54 (s, 2H), 6.50 (d, J = 9.0 Hz, 1H), 5.26 (d, J = 9.0 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 1.32–1.26 (m, 3H), 1.28 (s, 9H), 1.26 (s, 9H); ^{13}C NMR (75.5 MHz, CDCl3, ppm) δ 154.2, 153.3, 153.1, 139.4, 137.0, 132.6, 131.3, 125.9, 99.1 66.9, 61.1, 34.3, 33.8, 30.81, 30.79, 14.8; EI-MS (*m*/*z*) 698 (M+2-Br, 23.3), 696 (M-Br, 23.1), 651 (53.4), 649 (100), 647 (49.5), 621 (25.9); HRMS calcd for C₂₄H₂₉Brl₂NO₂ (M-Br) 695.9471, found *m/z* 695.9416.

Preparation of (2,6-dibromo-4-*tert*-butylphenyl) (2,6-diiodo-4-*tert*-butylphenyl)diazomethane (1a-N₂)

To a solution of carbamate **10** (215 mg, 279 μ mol) in Ac₂O (15 ml) and AcOH (7.5 ml) was added NaNO₂ (579 mg, 8.36 µmol) in small portions at 0 °C over a period of 3 h, and the mixture was stirred at room temperature for 1 day after the addition was complete. The mixture was poured into water and extracted with ether. The ethereal layer was washed with 5% NaHCO₃ aqueous solution, water, dried over anhydrous Na₂SO₄, and the solvent was removed under reduced pressure to give ethyl N-nitroso-N [(2,6-dibromo-4-tert-butylphenyl)(2,6-diiodo-4-tert-butylphenyl) methyl]carbamate (11) as a yellow viscous oil (207 mg, 92%); ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.89 (s, 2*H*), 7.54 (s, 2*H*), 6.87 (s, 1*H*) 4.40 (q, J = 7.2 Hz, 2H), 1.32–1.26 (m, 3H), 1.29 (s, 9H), 1.27 (s, 9H). To a solution cooled at -15°C of nitroso compound **11** in anhydrous THF (24 ml) was added potassium tert-butoxide (116 mg, 1.04 mmol) at once under an atmosphere of argon. After stirring at room temperature overnight, the mixture was poured into water and extracted with ether. The ethereal layer was washed with water, dried over anhydrous Na2SO4, and evaporated. The residue was purified by recycle GPC (16 cycles, CHCl₃) to give (2,6-dibromo-4-*tert*-butylphenyl)(2,6-diiodo-4tert-butylphenyl)diazomethane (1a-N₂) as orange solids (88 mg, 48%): mp 150.8–153.5 $^{\circ}$ C (dec.); ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.92 (s, 2H), 7.57 (s, 2H), 1.30 (s, 9H), 1.28 (s, 9H); ¹³C NMR

(75.5 MHz, CDCl₃, ppm) δ 154.0, 153.4, 138.5, 133.2, 130.9 127.0, 125.6, 100.8, 76.8, 34.7, 34.3, 31.0; IR (KBr, cm⁻¹) 2061 (ν_{CN2}).

Product analysis

Photolysis ($\lambda > 350$ nm) of **1a**-N₂ (5.0 mg, 7.0 mmol) in degassed benzene- d_6 (0.5 ml) gave the phenanthrene **2a**: a brown oil (0.7 mg, 18%); ¹H NMR (300 MHz, CDCl₃, ppm) δ 8.82 (d, J = 2.0 Hz, 2H), 8.49 (d, J = 2.0 Hz, 2H), 7.31 (s, 4H), 1.49 (s, 18H), 1.29 (s, 18H); MALDI-TOF-mass calcd for C₄₂H₄₅Br₄l₂ (M+H) 1118.83, found *m/z* 1118.77.

Photolysis (λ > 300 nm) of **1a**-N₂ (5.0 mg, 7.0 mmol) in nondegassed benzene (5.0 ml) gave the ketone **1**-O: a yellow oil (3.8 mg, 77%); ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.91 (s, 2*H*), 7.58 (s, 2*H*), 1.32 (s, 9*H*), 1.30 (s, 9*H*); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 193.9, 157.0, 156.5, 141.7, 138.5, 134.4, 130.8, 124.1, 95.3, 35.1, 34.6, 30.8; IR (KBr, cm⁻¹) 1684 (ν_{CO}); El-MS (*m/z*) 706 (M+4, 51.2), 704 (M+2, 100), 702 (M⁺, 51.6), 413 (67.5), 319 (54.0), 57 (33.6); HRMS calcd for C₂₁H₂₂Br₂l₂O 701.8127, found *m/z* 701.8136.

Photolysis ($\lambda > 350$ nm) of **1a**-N₂ (5.0 mg, 7.0 mmol) in degassed benzene (0.4 ml) in the presence of CHD (0.1 ml) gave the double-hydrogen abstraction product **1a**-H₂: a colorless oil (3.4 mg, 75%); ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.83 (s, 2*H*), 7.49 (s, 2*H*), 4.70 (s, 2*H*), 1.29 (s, 9*H*), 1.27 (s, 9*H*); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 153.0, 152.8, 140.0, 138.0, 134.6, 130.3, 126.5, 100.9, 52.4, 34.7, 34.2, 31.13, 31.10; EI-MS (*m*/*z*) 692 (M+4, 42.8), 690 (M+2, 82.0), 688 (M⁺, 40.8), 677 (26.0), 675 (51.9), 673 (27.7), 57 (100); HRMS calcd for C₂₁H₂₄Br₂l₂ 687.8334, found *m*/*z* 687.8282.

Photolysis (λ > 300 nm) of **1a**-N₂ (5.0 mg, 7.0 mmol) in degassed benzene (0.4 ml) in the presence of CHD (0.1 ml) gave a mixture of **1a**-H₂ and (2,6-dibromo-4-*tert*-butylphenyl) (2-iodo-4-*tert*-butylphenyl)methane (**1a**'-H₂). **1a**'-H₂: ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.86 (d, J = 2.0 Hz, 1H), 7.57 (s, 2H), 7.18 (dd, J = 2.0, 8.3 Hz, 1H), 6.48 (d, J = 8.3 Hz, 1H), 4.31 (s, 2H), 1.32 (s, 9H), 1.27 (s, 9H).

Photolysis ($\lambda > 350$ nm) of **1a**-N₂ (5.0 mg, 7.0 mmol) in degassed benzene (0.4 ml) in the presence of methanol (0.1 ml) gave the OH insertion product **1**-HOMe along with an unreacted **1a**-N₂ (2.6 mg): pale orange solids (1.4 mg, 48%); ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.96 (s, 2*H*), 7.54 (s, 2*H*), 5.80 (s, 1*H*), 3.48 (s, 3*H*), 1.30 (s, 9*H*), 1.28 (s, 9*H*); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 154.0, 153.9, 139.4, 135.8, 132.4, 131.5, 126.1, 99.5, 91.2, 58.7, 34.7, 34.3, 31.1, 31.0; El-MS (*m/z*) 722 (M+4, 28.7), 720 (M+2, 53.2), 718 (M⁺, 26.9), 641 (81.7), 639 (81.6), 595 (50.7), 593 (100), 591 (52.4), 412 (93.0), 57 (53.4); HRMS calcd for C₂₂H₂₆ Br₂I₂O 717.8440, found *m/z* 717.8382.

Photolysis ($\lambda > 300$ nm) of **1a**-N₂ (5.0 mg, 7.0 mmol) in degassed benzene (0.4 ml) in the presence of methanol (0.1 ml) gave a mixture of **1a**-HOMe and (2,6-dibromo-4-*tert*-butylphenyl)(2-iodo-4-*tert*-butylphenyl)methyl methyl ether (**1a**'-HOMe). **1a**'-HOMe: ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.90 (d, J = 1.8 Hz, 1*H*), 7.61 (s, 2*H*), 7.29–7.22 (m, 1*H*), 6.98 (d, J = 8.3 Hz, 1*H*), 5.93 (s, 1*H*), 3.44 (s, 3*H*), 1.33 (s, 9*H*), 1.26 (s, 9*H*).

ESR measurements

The diazo compound was dissolved in 2-MTHF (1.5×10^{-2} M) and the solution was degassed in a quartz cell by three freeze-degas-thaw cycles. The sample was cooled in an optical transmission ESR cavity at 77 K and irradiated with a Wacom 500 W Xe lamp using a filter ($\lambda > 300$ nm). ESR spectra were measured on a JEOL JES TE 200 spectrometer (X-band microwave unit, 100 kHz field modulation). The signal positions were read by using a gaussmeter. The temperature was controlled by a 9650 microprocessor-based digital temperature indicator/controller, provided the measurements accuracy is within ± 0.1 K and the control ability is within ± 0.2 K. Errors in the measurements of component amplitudes did not exceed 5%, the accuracy of the resonance fields determination was within ± 0.5 mT.

Low-temperature UV-Vis spectra

Low-temperature spectra at 77 K were obtained by using an Oxford variable-temperature liquid-nitrogen cryostat (DN 1704) equipped with a quartz outer window and a sapphire inner window. The sample was dissolved in dry 2-MTHF (1.5×10^{-3} M), placed in a long-necked quartz cuvette of 1 mm path length, and degassed thoroughly by repeated freeze–degas–thaw cycles at a pressure near 10^{-5} Torr. The cuvette was flame-sealed, under reduced pressure, placed in the cryostat, and cooled to 77 K. The sample was irradiated for several minutes in the spectrometer with a Wacom 500 W Xe lamp using a filter ($\lambda > 300$ nm), and the spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instrument Intelligent Temperature Controller (ITC 4).

LFP

All flash photolysis measurements were made on a Unisoku TSP-601 flash spectrometer. The excitation source for the LFP was a Lambada Physik LEXTRA XeCl excimer laser. A Hamamatsu 150-W xenon short arc lamp (L2195) was used as the probe source, and the monitoring beam guided using an optical fiber scope was arranged in an orientation perpendicular to the excitation source. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701-512Q linear image sensor (512 photodiodes used). Timing of the laser excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu model DS-8631 digital synchroscope, which was interfaced to a NEC 9821 RA266 computer. This allowed for rapid processing and storage of the data and provided printed graphics capabilities. Each trace was also displayed on a Mitsubishi CRT RDT152A monitor.

A sample was placed in a long-necked Pyrex tube that had a sidearm connected to a quartz fluorescence cuvette and degassed using a minimum of five freeze-degas-thaw cycles at a pressure near 10^{-5} Torr immediately prior to being flashed. The sample system was sealed, and the solution was transferred to the quartz cuvette, which was placed in the sample chamber of the flash spectrometer. The concentration of the sample was adjusted so that it absorbed a significant portion of the laser light.

Acknowledgements

The authors are grateful to the Ministry of Education, Culture, Sports, Science, and Technology of Japan for support of this work through a Grant-in-Aid for Scientific Research for Specially Promoted Research (No. 21550044). They also thank Professor W. Sander of Ruhr-Universität Bochum for sharing his results prior to publication.

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