

assay is sensitive down to submicromolar concentrations of EPSP. Figure 2 is an Eadie-Hofstee plot of the data obtained by performing the coupled assay over a range of EPSP concentrations from 0.5 to 16  $\mu\text{M}$ . The  $K_m$  of unlabeled EPSP was determined to be  $2.2 \pm 0.2 \mu\text{M}$ , in close agreement with the published value of  $2.7 \mu\text{M}$ .<sup>16</sup> The line for the (6*R*)-[6-<sup>2</sup>H]EPSP has a different gradient and intercepts on both axes, showing a change in both  $V_{\text{max}}$  and  $K_m$ . The ratio  $(V_{\text{max}}/K_m)_{\text{H}}/(V_{\text{max}}/K_m)_{\text{D}}$  is  $1.6 \pm 0.1$ , with  $(K_m)_{\text{D}} = 1.4 \pm 0.1 \mu\text{M}$ . From this data the ratio  $(V_{\text{max}})_{\text{H}}/(V_{\text{max}})_{\text{D}}$  is  $2.5 \pm 0.2$ , which agrees, within experimental error, with the value obtained directly from the UV assay.

The experimental data clearly show a primary kinetic isotope effect for carbon-hydrogen bond cleavage at C-6. Values of  $k_{\text{H}}/k_{\text{D}}$  of 2-3 are typical for enzymic reactions involving carbon-hydrogen cleavage where this step is partially rate limiting.<sup>20</sup> The reduced isotopic discrimination in the ratio  $(V_{\text{max}}/K_m)_{\text{H}}/(V_{\text{max}}/K_m)_{\text{D}}$  of 1.6 indicates a high commitment to catalysis.<sup>21</sup>

This result is important as it opens up the way for a detailed kinetic analysis of the chorismate synthase reaction which can address the question of concertedness of bond breaking at C-6 and C-3. It has been reported that pre-steady-state experiments did not detect a burst of phosphate release, showing that loss of phosphate is not a fast step prior to the rate-determining step.<sup>4</sup> The absence of a burst of phosphate release and the isotope effect at C-6 together can best be accommodated by a concerted mechanism, and this mechanism must now receive serious consideration.

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## Photoinduced Through-Bond Electron Transfer: Remote Activation of Unique Aroyl Azide Reactivity

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Photoinduced electron transfer reactions play an important role in chemical and biochemical processes.<sup>1</sup> Experimental investigations have shown that this reaction may occur between species separated by distances far greater than the sum of their van der Waals radii.<sup>2</sup> Theoretical analyses are consistent with these findings.<sup>3</sup> Of particular relevance to the present investigation

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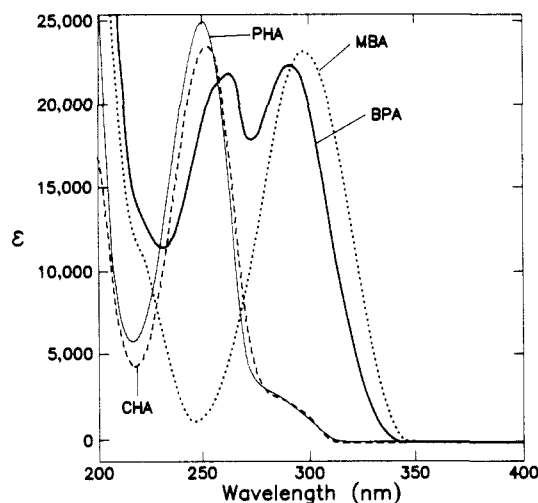
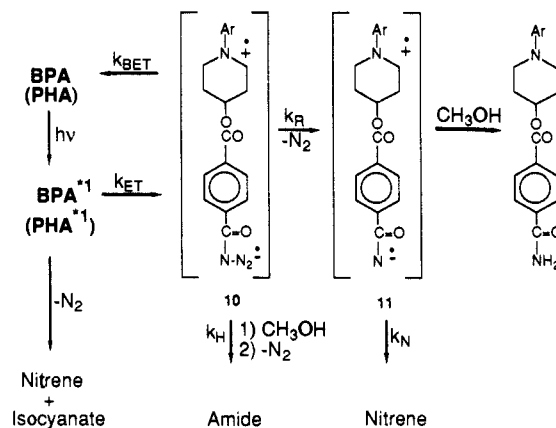


Figure 1. The absorption spectra of *N,N*-dimethyl-4-biphenylamine (MBA) and cyclohexyl-substituted (CHA), *N*-phenylpiperidiny-substituted (PHA), and *N*-biphenylpiperidiny-substituted (BPA) benzoyl azides in  $\text{CH}_3\text{CN}$  solutions at room temperature.

### Scheme I



are the efficient intramolecular photoinduced electron transfer reactions reported for acceptor-substituted *N*-arylpiperidines.<sup>4</sup> In previous work in this field, through-bond electron transfer has been detected spectroscopically. The systems examined were selected for study particularly because electron transfer does not initiate an irreversible chemical change. Herein we report the first example<sup>5</sup> of unique photochemical reactivity associated with through-bond electron transfer in aroyl azide substituted *N*-arylpiperidines (see Chart I).<sup>6</sup> In methyl alcohol solution, light absorbed by the biphenylamine chromophore of BPA initiates reaction of an aroyl azide radical anion formed by through-bond electron transfer.

The absorption spectra of *N,N*-dimethyl-4-biphenylamine (MBA) and cyclohexyl-substituted (CHA), *N*-phenylpiperidiny-substituted (PHA), and *N*-biphenylpiperidiny-substituted (BPA) benzoyl azides in  $\text{CH}_3\text{CN}$  solutions are shown

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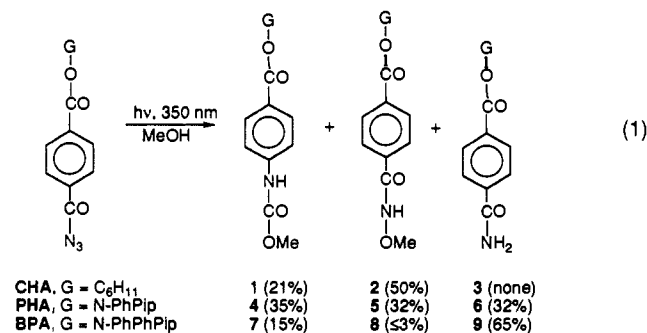
(5) We earlier attempted a similar reaction with partial success. Shields, C. J.; Falvey, D. E.; Schuster, G. B.; Buchardt, O.; Nielsen, P. E. *J. Org. Chem.* 1988, 53, 3501.

(6) All new compounds gave acceptable elemental analyses and exhibited expected spectral properties.

in Figure 1. The spectrum of BPA is essentially the sum of the spectra of CHA and MBA, its chromophoric parts. There may be some ground-state interaction between the biphenylamine-like electron donor group of BPA and the aroyl azide electron acceptor, but it is not revealed by a detectable charge-transfer absorption band.<sup>7</sup> It is significant that the absorption of MBA extends to longer wavelength than does that of CHA. This reveals its singlet energy (84 kcal/mol) to be lower than that of CHA (ca. 92 kcal/mol). Also, experimentally, it is possible to irradiate BPA with light absorbed primarily by its arylamine chromophore.

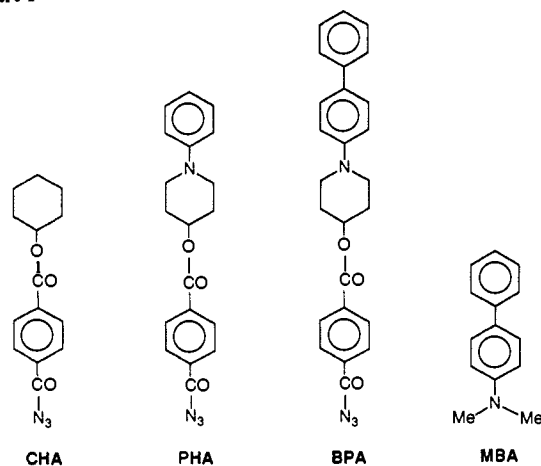
The relatively strong fluorescence of MBA in CH<sub>3</sub>CN solution decays with a lifetime of 3.1 ns. The fluorescence efficiency of BPA is at least 100 times less than that of MBA (excited at 290 nm). Clearly, a rapid ( $k \geq 3 \times 10^{10} \text{ s}^{-1}$ ) nonradiative decay route is available to the excited biphenylamine chromophore of BPA that is absent in MBA itself. The oxidation potential of MBA ( $E_{\text{ox}}$ , CH<sub>3</sub>CN, vs Ag) is 0.75 V. Reduction of CHA gives an irreversible cyclic voltammetric wave with a peak at -1.4 V. Calculation from the Weller equation<sup>8</sup> ( $r = 6 \text{ \AA}$ , see below) reveals that electron transfer from the excited biphenylamine portion of BPA to the aroyl azide group is exothermic by more than 1.4 eV. On this basis, and by reference to the spectroscopic results of Verhoeven and co-workers,<sup>4</sup> the rapid nonradiative reaction of excited BPA is assigned to electron transfer ( $k_{\text{ET}}$ ) from the biphenylamine to the azide group as shown in Scheme I. This conclusion is supported by the results of flash photolysis measurements. Irradiation of BPA (308 nm, 20 ns, 10 mJ, CH<sub>3</sub>CN) reveals instantaneous formation of a transient absorption band at 625 nm essentially identical with that of independently generated MBA radical cation.

As shown in eq 1, photolysis of a dilute solution of CHA (Rayonet, 350 nm, CH<sub>3</sub>OH, -10 °C) gives carbamate **1** (21%), characteristic of isocyanate generation by the photo-Curtius rearrangement, and hydroxamate **2** (50%), indicative of nitrene formation.<sup>9</sup> Significantly, amide **3** is not detected as a product



of this reaction. In contrast, photolysis of BPA under the same conditions gives amide **9** as the predominant product (65%) with lesser amounts of carbamate **7** (15%) and hydroxamate **8** ( $\leq 3\%$ ).<sup>10</sup> Irradiation of PHA gives an intermediate result: carbamate **4**, hydroxamate **5**, and amide **6** are formed in 35, 32, and 32% yields, respectively. These results may be understood by reference to Figure 1. Light absorbed by the aroyl azide chromophore of CHA, PHA, and BPA leads to the carbamates and hydroxamates; light absorbed by the arylamine chromophore gives the amides. This conclusion is supported by a sensitization experiment. Irradiation of a mixture of MBA (10<sup>-3</sup> M) and CHA (10<sup>-4</sup> M) gives amide **3** in high yield. Formation of amide **9** by a route requiring an intermediate triplet azide is unlikely. Irradiation of BPA in the

Chart I



presence of 1,3-cyclohexadiene (1.3 M) has no significant effect on the formation of **9**.

The three-dimensional structure of BPA was investigated by molecular mechanics<sup>11</sup> and by NMR spectral methods. The findings are consistent with X-ray crystallographic analysis of related *N*-arylpiperidines.<sup>4b</sup> The calculations predict that the piperidine ring of BPA adopts a chair-like conformation with the aroyl azide group in an equatorial position. The piperidine nitrogen group is nonplanar with the *N*-aryl substituent ca. 15° from the plane defined by the nitrogen atom and its two adjacent carbon atoms. In this lowest energy conformation, the minimum distance from donor (defined as the ring nitrogen atom) to acceptor group (the ester carbonyl group) is ca. 6 Å. There are other low-energy conformations of BPA, but none of these bring the donor and acceptor closer together. Clearly, at room temperature the *N*-aryl and aroyl azide groups are not within van der Waals contact distance.

The mechanism outlined in Scheme I accommodates the experimental findings. Irradiation generates an electronically excited state localized on the arylamine chromophore for BPA and approximately equally distributed between the arylamine and the aroyl azide chromophores for PHA. The photochemistry of the aroyl azide-localized excited state is the same as for CHA: nitrene and isocyanate formation. The arylamine-localized excited state undergoes rapid electron transfer to form charge-transferred state **10**, which may lose N<sub>2</sub> before ( $k_{\text{R}}$ ) or after protonation ( $k_{\text{H}}$ ) or undergo back electron transfer ( $k_{\text{BET}}$ ). Evidently, the rate of N<sub>2</sub> loss is competitive with back electron transfer, which is normally very fast.<sup>12</sup> In Scheme I, nitrene radical anion **11** may be protonated to give, ultimately, amides **6** and **9** or undergo back electron transfer ( $k_{\text{N}}$ ) to form the nitrene. If the latter reaction occurs, it plays only a minor role ( $\leq 3\%$ ) in the photochemistry of BPA.

This work reveals a new reaction path for specially substituted aroyl azides. Light absorbed by a remote chromophore can activate the azide by intramolecular long-distance electron transfer to form the azide radical anion. Loss of N<sub>2</sub> from the charge-transferred state is rapid and leads to selection of a unique path for azide reaction. This path may find application in the development of photolabeling agents and of novel compounds capable of cleaving DNA.<sup>13</sup>

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## Synthesis of Simple $\text{CrL}_4$ (alkyne) Complexes by Displacement of a Labile Cyclooctadiene Ligand

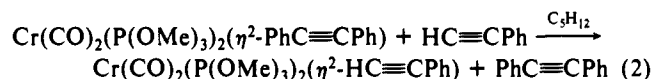
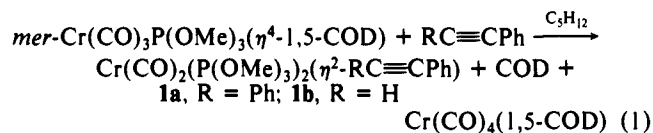
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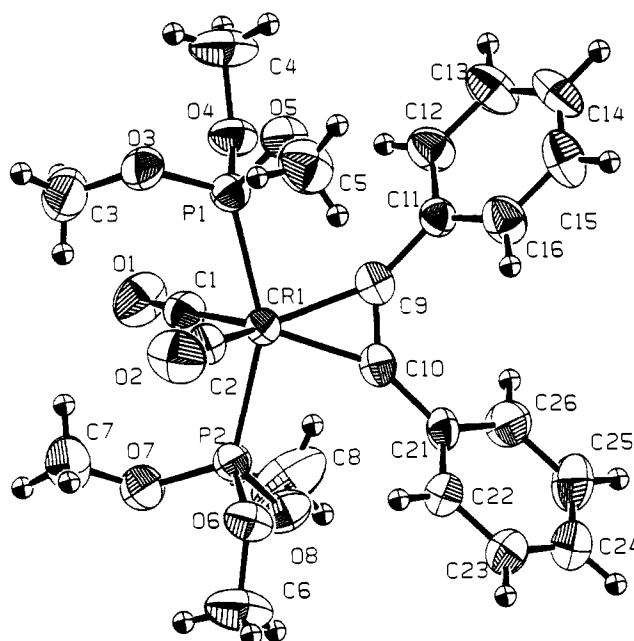
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We have shown that, in contrast to the simple tetracarbonyl system  $\text{M}(\text{CO})_4(\text{diene})^{1,2}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ), 1,5-cyclooctadiene (1,5-COD) is displaced from  $\text{M}(\text{CO})_3(\text{P}(\text{OMe})_3)(\eta^4\text{-1,5-COD})$  by conjugated dienes.<sup>3</sup> As reported here, alkynes, which are similar to 1,3-dienes in their frontier orbital characteristics,<sup>4</sup> also displace the COD in  $\text{Cr}(\text{CO})_3(\text{P}(\text{OMe})_3)(\eta^4\text{-1,5-COD})$  to afford unprecedented  $\text{CrL}_4(\text{PhC}\equiv\text{CR})$  complexes.

Diphenylacetylene and phenylacetylene react in a few hours with *mer*- $\text{Cr}(\text{CO})_3(\text{P}(\text{OMe})_3)(\eta^4\text{-1,5-COD})$  to give products of COD substitution and phosphite and carbonyl ligand redistribution (eq 1).<sup>7,8</sup> The  $\text{PhC}\equiv\text{CPh}$  complex **1a**<sup>9</sup> forms in good yield as black crystals *directly from the reaction mixture* in pentane while the  $\text{PhC}\equiv\text{CH}$  complex **1b** is crystallized separately in lower yield. A superior route to **1b** is alkyne exchange with **1a** (eq 2).<sup>10</sup>

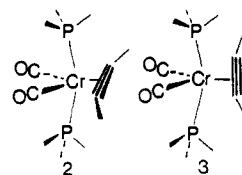


Integration of the <sup>1</sup>H NMR spectra supports a 2:1 phosphite:alkyne stoichiometry, and a pair of bands in the IR spectra for  $\nu(\text{CO})$  indicates a *cis*-dicarbonyl structure. The signals for the alkyne carbons for **1a** appear at  $\delta$  180.2 and for **1b** at  $\delta$  174.3 ( $\equiv\text{CPh}$ ) and  $\delta$  163.7 ( $\equiv\text{CH}$ ). These are downfield from the region generally cited for the carbons of a four-electron alkyne,<sup>11</sup> but of course the metal in this case is quite electron rich. Resonances for the alkyne and carbonyl carbons for both complexes and for the alkyne hydrogen in **1b** appear as *triplets* due to coupling to two phosphorus ligands. This is consistent with either structure **2**, with magnetically equivalent phosphorus atoms, or **3**, in which the phosphorus atoms would be rendered equivalent only by rotation of the alkyne. Variable-temperature NMR experiments with **1b** establish that the ground-state structure is



**Figure 1.** ORTEP diagram of  $\text{Cr}(\text{CO})_2(\text{P}(\text{OMe})_3)_2(\eta^2\text{-PhC}\equiv\text{CPh})$ . Important bond lengths (Å) and angles (deg): Cr1–P1, 2.252 (2); Cr1–P2, 2.264 (2); Cr1–C1, 1.857 (7); Cr1–C2, 1.827 (7); Cr1–C9, 1.959 (6); Cr1–C10, 1.958 (5); C1–O1, 1.144 (6); C2–O2, 1.166 (7); C9–C10, 1.311 (7); P1–Cr1–P2, 153.94 (7); C1–Cr1–C2, 107.0 (3); C10–C9–C11, 135.0 (5); C9–C10–C21, 136.0 (5).

**3**; the triplet with  $J_{\text{PH}} = 20$  Hz for the acetylenic proton “loses” the central resonance and becomes a doublet with  $J_{\text{PH}} = 40$  Hz upon cooling.<sup>12</sup> A barrier to formal rotation of the alkyne of 13.3 (3) kcal mol<sup>-1</sup> is calculated from the decoalescence of the <sup>13</sup>C NMR resonance for the phosphite methyl carbons at ca. –5 °C ( $\Delta = 51$  Hz).<sup>13</sup>



An X-ray diffraction study<sup>14</sup> of **1a** confirms that in the solid state the alkyne ligand lies almost perpendicular<sup>15</sup> with respect to the P–Cr–P plane in a distorted trigonal-bipyramidal geometry (P–Cr–P, 153.94 (7)°; OC–Cr–CO, 107.0 (3)°) (Figure 1). Distances and angles involving the alkyne are consistent with those in other chromium–diphenylacetylene complexes.<sup>16</sup>

The alkyne ligands in these complexes are labile to displacement by a variety of donor ligands, including carbon monoxide and trimethyl phosphite, to apparently give other  $\text{CrL}_6$  complexes. Decomposition occurs, with liberation of free alkyne, in the presence of thf and ethyl diazoacetate. There is no reaction with conjugated or nonconjugated dienes.

Molecular orbital calculations at the extended Hückel level performed on a  $\text{Cr}(\text{CO})_4(\eta^2\text{-HC}\equiv\text{CH})$  model show that the conformation with the alkyne perpendicular to the P–Cr–P plane is preferred by 15 kcal mol<sup>-1</sup>. This orientation maximizes the

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(4) The isolobal character of alkynes and other four-electron donors has been discussed before.<sup>5</sup> This is especially true for 1,3-dienes, which also possess an excellent  $\pi$ -acceptor orbital.<sup>6</sup>

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(9) Complex **1a** is prepared in 58% yield (29% based on Cr). <sup>13</sup>C NMR:  $\delta$  180.2 (t,  $J_{\text{PC}} = 15$  Hz,  $\text{C}_{\text{alkyne}}$ ). IR:  $\nu(\text{CO}) = 1932, 1850$  cm<sup>-1</sup>. Complete details are provided in the supplementary material.

(10) Complex **1b** is prepared from **1a** in 57% yield. <sup>13</sup>C NMR: 175.5 (t,  $J_{\text{PC}} = 9$  Hz,  $\equiv\text{CPh}$ ), 163.7 (t,  $J_{\text{PC}} = 18$  Hz,  $\equiv\text{CH}$ ). IR:  $\nu(\text{CO}) = 1934, 1840$  cm<sup>-1</sup>.

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