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Highly Efficient C-C Bond Formation in the Two-Photon Chemistry of 1,8-Bis(substituted-methyl)naphthalenes by Direct Excitation of Photoactive Leaving Groups

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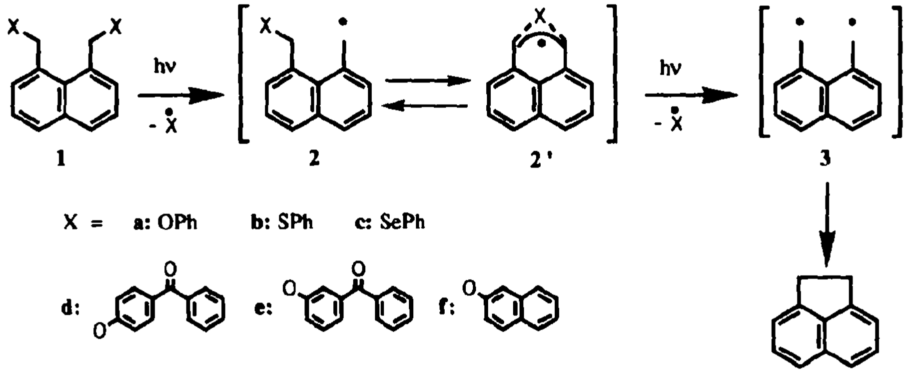
Abstract: *High efficiency in the two-photon intramolecular C-C bond formation to the two-photon product acenaphthene (4), obtained in a maximum yield of 72%, was achieved by direct activation of two separate leaving groups of 1,8-bis(phenoxymethyl)- (1a), 1,8-bis(phenylthiomethyl)- (1b), and 1,8-bis(phenylselenomethyl)-naphthalenes (1c) during KrF excimer laser (248 nm) and of 1,8-bis(4-benzoylphenoxymethyl)- (1d), 1,8-bis-(3-benzoylphenoxymethyl)- (1e), and 1,8-bis(2-naphthoxymethyl)naphthalenes (1f) during XeF excimer laser (351 nm) photolyses.*

We have recently reported laser-induced photolyses of 1,8-bis(substituted-methyl)naphthalenes (1), which generated acenaphthene (4) through a two-photon process. Excimer laser[1] [X=Br, Cl] and Ar ion laser jet[2] [X=Br, Cl, OPh, SPh, SePh] techniques were used to generate 4 from multichromophoric substrates by cyclization of the intermediary 1,8-dimethylenenaphthalene diradical (3) (Scheme 1). Presumably, the first photon is absorbed by the naphthalene and the second by the naphthylmethyl radical π chromophore. While with such "one-color/one-laser" experiments two-photon chemistry can be performed adequately, they suffer from the disadvantage that (i) energy migration from the excited chromophore (naphthalene moiety or 1-naphthylmethyl radical) to the photolabile leaving group may not take place efficiently, and (ii) the absorption of the second photon may not occur efficiently at the wavelength which is best suited for the absorption of the first photon. To overcome these disadvantages, in this letter we report an effective two-photon C-C bond formation process by employing two separate photolabile leaving groups which themselves become directly electronically excited, both for the *first* and the *second* photon in the two-photon process.



Scheme 1

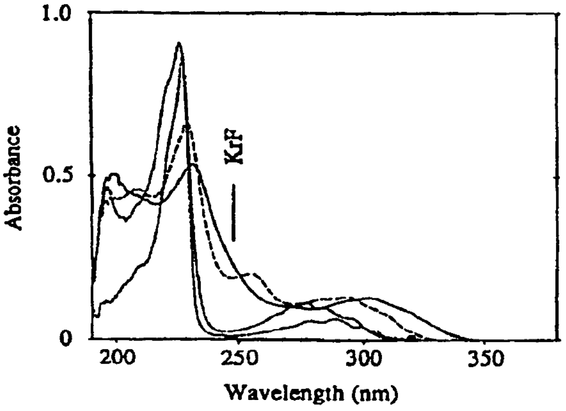


Fig. 1 Absorption spectra of **1a** (—·—·—), **1b** (– – –), **1c** (——), and 3 (-----) in cyclohexane. Concentrations and optical path: 10^{-5} M, 10 mm. The wavelength of the KrF excimer laser (248 nm) is indicated by the vertical bar.

As the first class of substrates, the 1,8-bis(phenoxymethyl)- (**1a**), 1,8-bis(phenylthiomethyl)- (**1b**), and 1,8-bis(phenylselenomethyl)-naphthalenes (**1c**) were used. The reactions were conducted by irradiation of the degassed cyclohexane solutions of **1a-c** (10^{-5} M) with a KrF (248 nm) excimer laser at high (**HF**: 3.1 x 10^{22} photons·m^{-2}·pulse^{-1}) and low fluence (**LF**: 6.2 x 10^{20} photons·m^{-2}·pulse^{-1}).[3] The UV spectra of **1a-c** and **4** (Figure 1) show that the first photon absorption of **1a** at 248 nm is likely to correspond to $S_1(\pi,\pi^*)$ excitation of the naphthalene[1] and also to the secondary absorption band of phenyl groups.[4a] Those of **1b** and **1c** seem to have three possibilities, *i.e.* excitation to the $S_2(\pi,\pi^*)$ state of naphthalene ,[1] π,π^* excitation at the primary absorption band of phenyl groups,[4a] and n,π^* excitation of the group 16 atoms.[4b] The absorption spectrum of **1b** shows clear n,π^* absorption of the sulfur chromophore at 245 - 265 nm, π,π^* excitation of the phenyl groups centered at ca. 270 nm, which seems to overlap partly with the absorption to the $S_1(\pi,\pi^*)$ of naphthalene, and the excitation to the $S_2(\pi,\pi^*)$ state of naphthalene. The spectrum of **1c** is similar to that of **1b**, although the absorption bands are broadened and lack fine structure.

Figures 2a-c show the consumption of **1a-c** and the yield of **4** as a function of the number of laser shots. The consumption of **1a-c**, the highest yield of **4**, the highest efficiency — defined as 100 x (yield of **4**)/(conversion of **1**) — all decreased in the order **1b** > **1c** >> **1a** (for **HF**) and **1c** > **1b** >> **1a** (for **LF**). The fast consumption of **1b** and **1c** compared to that of **1a** is best explained by the higher absorption of the former compounds at 248 nm. The high yield of **4** in the KrF laser photolysis may be rationalized not only by the direct activation of the leaving groups through absorption by the phenyl groups or group 16 functionalities, but also participation of the higher $S_2(\pi,\pi^*)$ state of the naphthalene ring because energy transfer from this state to the

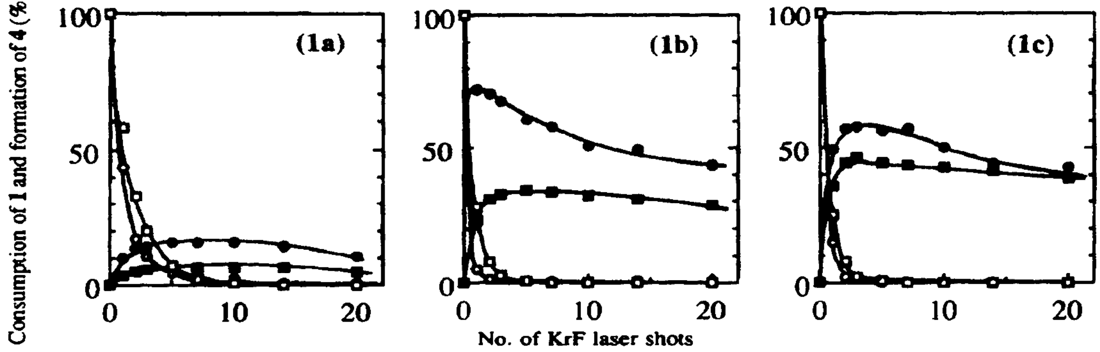


Fig. 2 The consumption of **1a-c** and the formation of **4** as a function of the number of KrF excimer (248 nm) laser shots at concentrations of 10^{-5} M; **1a-c**: open symbols, **4**: solid symbols. Fluence of the KrF excimer laser: 3.1 x 10^{22} photon·m^{-2}·pulse^{-1} (●, ○) and 6.2 x 10^{20} photon·m^{-2}·pulse^{-1} (■, □).

leaving groups was reported to be efficient.[5] Decreasing yield of **4** by the reduction of the fluence implies the occurrence of side reactions,[6] most likely from monoradicals **2** (or **2'**). It is noteworthy that the yield of **4** was higher for **1b** than **1c** in the HF photolysis, whereas it was *vice versa* for LF photolysis. The large decrease in the yield of **4** for **1b** compared to that of **1c** can be explained by the persistence of the intermediary monoradicals, *i.e.* **2'c** (or **2c**) > **2'b** (or **2b**);[7] thus, the more persistent radicals have a higher chance for absorbing the second photon at the lower fluence and give higher a yield of **4**.

As second class of substrates the 1,8-bis(4-benzoylphenoxymethyl)- (**1d**), 1,8-bis(3-benzoylphenoxy)-methyl (**1e**), and 1,8-bis(2-naphthoxymethyl)naphthalenes (**1f**) were employed. These leaving groups were chosen so as to conduct the photolyses at comparatively long wavelengths, *i.e.* XeF excimer laser (351 nm), an essential requisite for selective organic photoreactions to avoid undesirable side reactions. The absorption spectra of **1d-f** and **4** are displayed in Figure 3. In comparison to the phenoxy (**1a**) leaving group, the wavelengths of the XeF laser emissions match the absorptions of the chromophores of the leaving groups in substrates **1d-f**.[8]

The excimer laser photolyses were performed at a fluence of 3.1 x 10^{22} photons·m^{-2}·$pulse^{-1}$ in degassed acetonitrile solutions (10^{-5} M).[3] The consumption of the substrates **1d-f** and formation of product **4** as a function of the number of laser shots are shown in Figure 4. Significant consumption of substrate **1f** was not observed in the XeF excimer photolysis; presumably, this substrate possesses too low absorption at 351 nm. The consumption of **1d,e** and the formation of **4** followed the order **1d** > **1e** >> **1f**; consequently, the weaker C-O bond in the substrates **1d-f** is more effectively photocleaved when the substrate possesses adequate absorption at the laser wavelength.[9] The efficiency was calculated to be **1d** (53%) > **1e** (43%) >> **1f** (9.1%) [at the first shot]. The low efficiency of **1f** implies the existence of undesirable side reactions of the intermediary monoradical **2**[6] with aryloxy radicals, *i.e.* the more reactive the aryloxy radical, the more **2** and **4** are consumed along undesirable channels.

The electron density at the oxygen atom in the SOMO provides a measure of the reactivity of aryloxy radicals in that the higher the electron density at the radical site, the more localized the unpaired electron and the more reactive the radical.[11] The electron densities were calculated to be 0.010 for 4-benzoylphenoxy (**5d**), 0.024 for 3-benzoylphenoxy (**5e**), and 0.130 for 2-naphthoxy (**5f**) radicals[10] and their reactivity expected in the order **5f** > **5e** > **5d**. The secondary reactions should increase in that sequence and the efficiency in the formation of the

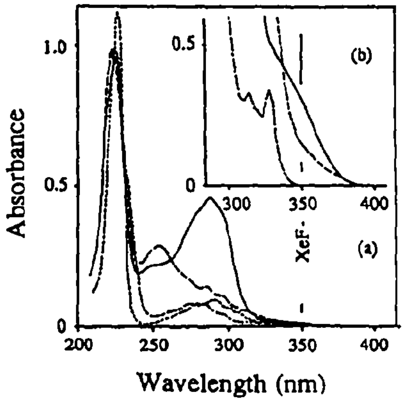


Fig. 3 Absorption spectra of **1d** (——), **1e** (– –), **1f** (—-), and **4** (-----) in CH_3CN. Concentrations: [**1d**], [**1e**], and [**4**] at 10^{-5} M (a) and 10^{-3} M (b); [**1f**] at 5 x 10^{-6} M (a) and 10^{-4} M (b). Optical path: 10 mm. The wavelengths of the XeF excimer laser (351 nm) line is marked by the vertical bar.

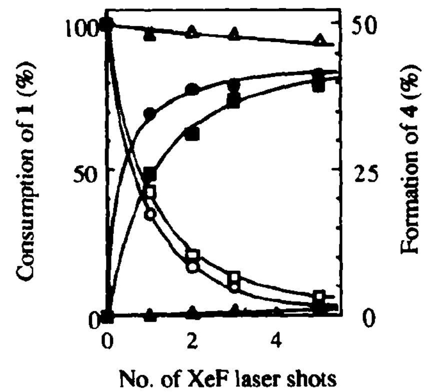


Fig. 4 The consumption of **1a-c** and the formation of **4** as a function of the number of laser shots at a laser fluence of 3.1 X 10^{22} photons·m^{-2}·$pulse^{-1}$ and a concentrations of 10^{-5} M; **1a-c** open symbols and **4** solid symbols, **1a** (● , ○), **1b** (■ , □), and **1c** (▲ , △).

two-photon product **4** accordingly decrease, which matches well the experimental trend **1d** > **1e** > **1f**.

In conclusion, effective two-photon C-C bond formation was accomplished by direct excitation of two separate, photolabile leaving groups. A maximum yield of 72% for the two-photon product **4** was achieved from substrate **1b**. The photolyses proceeded also effectively (up to 42%) at long-wavelength (351 nm) laser irradiations, which is suitable for synthetic purposes.

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3. The laser used was Lambda Physik EMG 201 MSC; fwhm (typical) 34 ns (KrF) and 30 ns (XeF), repetition rate ca. 1 Hz. The products were identified by comparison of HPLC retention times with authentic samples and quantified by HPLC analysis.
4. (a) Benzene has three absorptions in UV-Vis region: first primary band (ca. 200 nm), second primary band (ca. 180 nm), and secondary band (230 – 260 nm). Red shift of the absorption bands were observed by substitution with sulfur and selenium atoms: Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy;* John Wiley and Sons, Inc.: New York 1962; Chap. 12: (b) *ibid.* Chap. 17, Sect. 17.2.
5. *cf.* Kelley, D. F.; Milton, S. V.; Huppert, D.; Rentzepis, P. M. *J. Phys. Chem.* **1983**, 87, 1842-1843; Hilinski, E. F.; Huppert, D.; Kelley, D. F.; Milton, S. V.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, 106, 1951-1957.
6. Intermolecular reactions are also plausible, which lead to dimers, oligomers, and polymers.[1,2]
7. The dissociation energies of the C-X bond, which provide a measure of the relative stability of the radicals, was calculated[10] to be **2a**: 367, **2'a**: 473, **2b**: 373, **2'b**: 322, **2c**: 370, and **2'c**: 270 kJ/mol.
8. The second photon absorption can occur either at the leaving group or at naphthylmethyl radical moiety; the absorption edge of naphthylmethyl radical is ca. 380 nm, cf. Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, 107, 6368-6372, Tokumura, K.; Udagawa, M.; Itoh, M. *J. Phys. Chem.* **1985**, 89, 5147-5149, and Getoff, N.; Solar, S.; Haenel, M. W. *Radiat. Phys. Chem.* **1985**, 26, 317-323.
9. Dissociation energies for the Me-O bond cleavage of 4-methoxybenzophenone (**6a**), 3-methoxybenzophenone (**6b**), and 2-methoxynaphthalene (**6c**),which provide a measure for the C-O bond dissociation energies of **1d-f**, was calculated[10] to follow the order **6b** > **6a** > **6c**, in qualitative agreement with the experimental results.
10. Calculated by the PM3 method (RHF, CI) in MOPAC Version 6.01; cf. Stewart, J. J. P. *MOPAC Version 6.0, QCPE Bull.* **1989**, 9, 10 and revised as Version 6.01 for UNIX machines by Hirano, T. *JCPE Newsletter* **1989**, 1, 10.
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