

## Laser-jet Photolysis of 1,8-Bis(substituted-methyl)naphthalenes: the Effect of Heteroatom Leaving Groups on the Two-photon C–C Bond Formation

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The formation of acenaphthene **4** by laser-jet photolysis of 1,8-bis(phenoxyethyl)- (**1a**), 1,8-bis(phenylthiomethyl)- (**1b**) and 1,8-bis(phenylselenomethyl)-naphthalene (**1c**) strongly depends on the heteroatom of the leaving group; the increasing order of naphthalene consumption was **1c**  $\approx$  **1b** > **1a**, whereas that for the formation of **4** was **1c** > **1a** > **1b**.

The laser-jet technique has provided an effective means for the study of two-photon chemistry.<sup>1</sup> In the laser-jet photolysis of 1,8-bis(halomethyl)naphthalenes we have noticed a significant dependence on the leaving group (*i.e.* Br  $\gg$  Cl) in the two-photon reaction for the formation of acenaphthene.<sup>†</sup> Unfortunately, secondary reactions of the highly reactive free halogen atoms, which are generated in the photolysis, have prevented us from exploring the mechanistic details of this interesting two-photon process. For this reason, we have conducted the laser-jet photolysis of 1,8-bis(phenoxyethyl)- (**1a**), 1,8-bis(phenylthiomethyl)- (**1b**) and 1,8-bis(phenylselenomethyl)-naphthalene (**1c**), (Scheme 1) which liberate the less aggressive PhO $\cdot$ , PhS $\cdot$  and PhSe $\cdot$  radicals. We report herein our photomechanistic investigation on this remarkable two-photon C–C bond formation process, in which the consumption of the naphthalenes **1** and the formation of acenaphthene **4** strongly depend on the radical-centred heteroatom leaving group.

The laser-jet photolysis was conducted under an argon atmosphere by using the published apparatus.<sup>1</sup> The Ar-ion laser beam [Coherent, Innova 100-20; output energy distribution: 333 nm (20%), 351 nm (40%) and 364 nm (40%)] was focused by a quartz convex lens ( $f = 80$  mm). The diameter of the capillary employed for the free-falling liquid stream was 100  $\mu$ m and the flow rate 2.0 ml min<sup>-1</sup>, which was maintained by means of a Bischoff HPLC 2200 pump. The photolyses of **1a–c** were conducted in acetonitrile (10<sup>-4</sup> mol dm<sup>-3</sup>) with and without benzophenone sensitization.

Two types of the laser-jet photolyses were used: type **i** involved direct photolysis and type **ii** benzophenone-sensitized irradiation. As shown in Fig. 1, almost no reaction took place for **1a, b** on direct photolysis<sup>‡</sup> (type **i** mode). This is due to the lack of the UV absorption of **1a, b** at the available laser emissions. However, **1c** gave a significant amount of **4** on direct photolysis (13.4%, 90% conversion, type **i** mode). This is a consequence of the red-shifted absorption of **1c** at the employed laser emissions due to the phenylselenomethyl chromophore. In the benzophenone-sensitized reactions (type **ii** mode), the consumption of the starting materials and the formation of **4** were observed for all the naphthalenes **1a–c**.

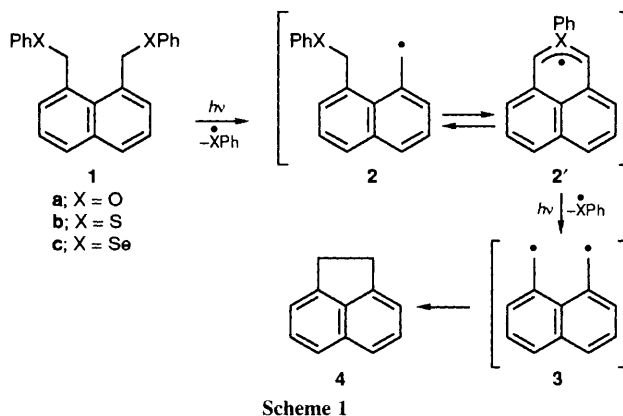
As shown in Table 1, in the case of the irradiation of **1c** in the presence of benzophenone (type **ii** mode), 40% of the first-step photolysis **1c**  $\rightarrow$  **2c** (Scheme 1) proceeded by sensitization and the rest by the direct process because a 1.7-fold increase in the consumption of **1c** was observed in the sensitized reaction. The second-step photolysis **2c**  $\rightarrow$  **3c** proceeded only by the direct photolysis, which follows from the fact that the efficiency factors of the formation of **4** are the

same within the experimental error as those for the consumption of **1c** (Table 1). This implies that benzophenone sensitization is not involved in the second step. In the case of **1a, b** the efficiency factors are not available because these substrates are inert towards direct photolysis.

The consumption of the starting materials decreased in the order **1c** (98%)  $\approx$  **1b** (98%) > **1a** (62%) (at the fifth cycle). We postulate that the more efficient consumption of **1b, c** compared with **1a**, initiated through the cleavage of the C–XPh bond (step **1**  $\rightarrow$  **2** in Scheme 1) is due to the more efficient intersystem crossing from the S<sub>1</sub>( $\pi, \pi^*$ ) to the T<sub>1</sub>( $\pi, \pi^*$ ) of the naphthalene chromophore through the heavy-atom effect,<sup>2,3§</sup> and successive intramolecular energy transfer to the cleaving C–XPh bonds.

In contrast to the consumption of the starting materials **1**, an irregular trend was observed in the formation of product **4** as a function of the heteroatom leaving group, *i.e.* **1c** (12.3%) > **1a** (9.5%) > **1b** (5.5%) (at the fifth cycle).

This unusual dependence of the yield of acenaphthene formation on the nature of the leaving group reflects the efficiency of the second step photolysis **2**  $\rightarrow$  **3** (Scheme 1). Clearly, several factors must interplay to give rise to such a complex order, in which the phenoxy-substituted derivative **1c** falls out of line. MO calculations<sup>¶</sup> suggest that the bridged monoradicals **2'** participate. For example, the heats of formation were calculated to be 64 and 90 kcal mol<sup>-1</sup> (1 cal = 4.184 J) for **2a** and **2a'**, 104 and 92 kcal mol<sup>-1</sup> for **2b** and **2b'** and 81 and 58 kcal mol<sup>-1</sup> for **2c** and **2c'**. Thus, significant stabilization of the monoradicals **2b, c** is derived from the bridged structures **2b', c'** (for the phenylseleno-substituted radical **2c'** bridging is more effective than for the phenylthio-substituted radical **2b'**), but substantial destabilization is predicted for the bridged phenoxy-substituted species **2a'**. Under the premise that efficient intermolecular energy transfer in the  $\pi, \pi^*$ -excited monoradical **2** from the naphthalene chromophore to the C–XPh bond and subsequent cleavage of the latter to generate the non-Kekulé diradical **3** (Scheme 1) require a coplanar conformation of the C–XPh

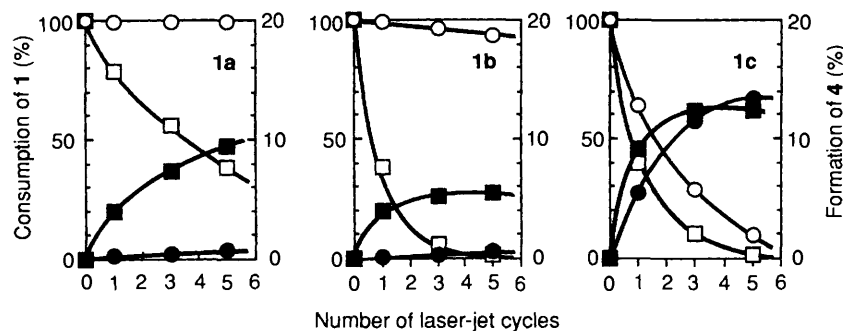


<sup>†</sup> The yield of **4** was 8.1% (61% conversion) for the bromine derivative: W. Adam and A. Ouchi, *Tetrahedron Lett.*, 1992, 33, 1875; practically no **4** was formed from the chlorine derivative: W. Adam and A. Ouchi, unpublished results.

<sup>‡</sup> Direct photolysis of **1a–c** through the S<sub>2</sub>( $\pi, \pi^*$ ) state by a KrF excimer laser (248 nm), however, gave significant yields of **4** for all compounds: A. Ouchi, H. Moriyama, H. Niino and A. Yabe, *55th Autumn Annual Meeting of the Chemical Society of Japan, Preprints II*, 4W24, 1987, p. 826.

<sup>§</sup> The first bond cleavage proceeds from the triplet state.<sup>3,4</sup>

<sup>¶</sup> Calculated by using PM3 method in the MOPAC version 6.01.



**Fig. 1** The consumption of **1a-c** (○, □) and the formation of **4** (●, ■) as a function of the number of laser-jet cycles; ○, ● represent direct photolysis (type i mode) and □, ■ in the presence of  $10^{-3}$  mol dm $^{-3}$  benzophenone (type ii mode); argon ion laser power: 3.5 W

**Table 1** Efficiency of the consumption of **1c** and formation of **4** for direct and benzophenone (BP)-sensitized laser-jet photolyses<sup>a</sup>

Laser-jet cycles	Consumption of <b>1c</b>			Formation of <b>4</b>		
	Without BP (%)	With BP (%)	Efficiency factor <sup>b</sup>	Without BP (%)	With BP (%)	Efficiency factor <sup>b</sup>
1	35.9 ± 1.9	60.3 ± 2.1	1.7	5.4 ± 0.4	9.1 ± 0.8	1.7
3	71.2 ± 3.1	89.5 ± 1.0	1.3	11.5 ± 0.2	12.4 ± 0.7	1.1
5	90.6 ± 3.2	98.3 ± 0.9	1.1	13.4 ± 0.6	12.3 ± 0.7	1.0

<sup>a</sup> Reaction conditions: MeCN as solvent, 3.5 W laser power, 2.0 ml min $^{-1}$  flow rate, 100 μm capillary,  $10^{-4}$  mol dm $^{-3}$  **1c**,  $10^{-3}$  mol dm $^{-3}$  BP. <sup>b</sup> Efficiency factor is defined as the ratio of **1c** or **4** with and without BP.

bond with the naphthalene  $\pi$ -system for maximum orbital overlap, significant contributions by the bridged structure **2'** should be disadvantageous for the photolysis step **2** (or **2'**)  $\rightarrow$  **3**. Consequently, in the case of the  $\pi, \pi^*$ -excited phenoxy-substituted monoradical **2a**, for which bridging to **2a'** is unlikely, the above favourable conformation of the C–OPh bond is unencumbered and its rupture feasible. This line of argument would imply, however, that the phenylseleno-substituted monoradical **2c'** should in view of best bridging be the least efficient in the cleavage step **2c** (or **2c'**)  $\rightarrow$  **3c**. Presumably the expectedly large selenium heavy-atom effect in the intramolecular energy transfer for the  $\pi, \pi^*$ -excited monoradical **2c** is the overriding factor, so that the cleavage order **2c'** > **2a** > **2b'** and thus the observed order in the formation of acenaphthene **1c** > **1a** > **1b** obtains. Time-resolved laser flash photolysis studies should be of interest to clarify these complex photomechanistic features of the novel two-photon C–C bond-forming process documented here in the laser-jet photolysis of the naphthalenes **1**.

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