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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(phenoxymethyl)- (1a), 1,8-bis(phenylthiomethyl)- (1b) and 1,8-bis(phenylselenomethyl)-naphthalene (1c) strongly depends on the hetroatom 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.¹ 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.[†] 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(phenoxymethyl)-(1a), 1,8-bis(phenylthiomethyl)- (1b) and 1,8-bis(phenylselenomethyl)-naphthalene (1c), (Scheme 1) which liberate the less aggressive PhO', PhS' and PhSe' 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.¹ 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 µm and the flow rate 2.0 ml min⁻¹, which was maintained by means of a Bischoff HPLC 2200 pump. The photolyses of **Ia-c** were conducted in acetonitrile (10⁻⁴ mol dm⁻³) 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‡ (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 $S_1(\pi,\pi^*)$ to the $T_1(\pi,\pi^*)$ of the naphthalene chromophore through the heavy-atom effect,^{2.3}§ 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 suggest that the bridged monoradicals 2' participate. For example, the heats of formation were calculated to be 64 and 90 kcal mol⁻¹ (1 cal = 4.184 J) for 2a and 2a', 104 and 92 kcal mol⁻¹ for 2b and 2b' and 81 and 58 kcal mol⁻¹ 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 phenylthiosubstituted radical 2b'), but substantial destabilization is predicted for the bridged phenoxy-substituted species 2a'. Under the premise that efficient intermolecular energy transfer in the π,π^* -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 coplaner conformation of the C-XPh



§ The first bond cleavage proceeds from the triplet state.^{3,4}

¶ Calculated by using PM3 method in the MOPAC version 6.01.

[†] 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.

[‡] Direct photolysis of **1a–c** through the $S_2(\pi,\pi^*)$ 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.



Number of laser-jet cycles

Fig. 1 The consumption of la-c (\bigcirc, \square) and the formation of 4 $(\textcircled{\bullet}, \textcircled{\bullet})$ as a function of the number of laser-jet cycles; $\bigcirc, \textcircled{\bullet}$ represent direct photolysis (type i mode) and \square, \blacksquare 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^a

	Laser-jet cycles	Consumption of 1c			Formation of 4		
		Without BP(%)	With BP (%)	Efficiency factor ^b	Without BP(%)	With BP (%)	Efficiency factor ^b
	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

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

bond with the naphthalene π -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 π,π^* -excited phenoxysubstituted 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-sub-stituted 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 π,π^* -excited monoradical 2c is the overriding factor, so that the cleavage order 2c' > c'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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