

A LASER-SPECIFIC C-C BOND FORMATION OF BICHROMOPHORIC COMPOUNDS

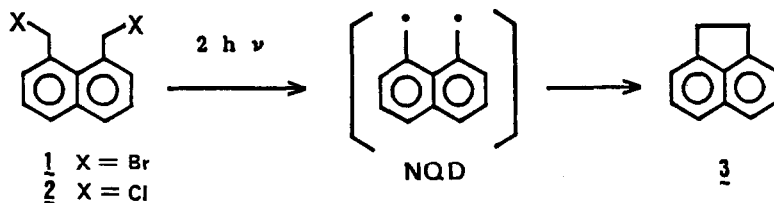
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The formation of acenaphthene from less photoreactive 1,8-bis(bromomethyl)naphthalene and 1,8-bis(chloromethyl)naphthalene by high-fluence KrF excimer laser irradiation was observed; the result contrasts with failed attempts using a low-pressure mercury lamp.

Photochemical double-activation of a bichromophoric system is of current interest. It is usually accomplished with biphotonic excitations of highly photoreactive compounds; utilization of lasers seemed to be most appropriate for this purpose.^{1,2,3} In spite of extensive use of lasers in many fields, however, applications in preparative organic reactions are still uncommon.⁴ In this letter we report a laser-induced preparative C-C bond formation of organic dihalides.

Although halides are less photoreactive than benzyl ketones¹ or diazo compounds³, they are more easily accessible; this factor is an advantage in preparative chemistry. Effective photochemical C-C bond formation, however, had not been reported for organic dihalides, probably because of the fast recombination of carbon and halogen radicals.⁵ It was anticipated that if an efficient double-activation could be achieved, two carbon-radical coupling might predominate over the recombination of carbon and halogen radicals. A laser-specific reaction of such a system has been found; the irradiations of high-intensity KrF excimer laser (248 nm) to 1,8-bis(bromomethyl)naphthalene^{6a} **1** and 1,8-bis(chloromethyl)naphthalene^{6b} **2** gave acenaphthene **3** as the expected product, probably via biphotonic generation of diradical intermediate and successive radical coupling.⁷



The reactions were conducted with irradiation of KrF excimer laser⁸ to the degassed 10⁻⁵ M cyclohexane solutions of **1** and **2**. The flux of photons used in the laser irradiations varied from 6.2 x 10¹⁴ to 3.1 x 10¹⁸

photons·cm⁻²·pulse⁻¹. Control experiments with a conventional lamp were conducted with >250 nm light⁸ (3.4×10^{14} photons·cm⁻²·s⁻¹) to the 10⁻⁵ M cyclohexane solutions of 1 and 2.

The yields of 3, and the decreases of 1 and 2 are shown in Figure 1 as a function of the number of irradiated photons. As seen in the figure, the maximum yields of 3 varied markedly depending on the fluence of the light; the yields of 3 were <1% in the cases of irradiations with the fluxes below 4.7×10^{15} photons·cm⁻²·pulse⁻¹. Other products were suspected to be oligomers and polymers.⁹

The formation of 3 can be explained by a one-photon process, a multi-centered reaction.¹⁰ However, 3 was not obtained by the irradiation with

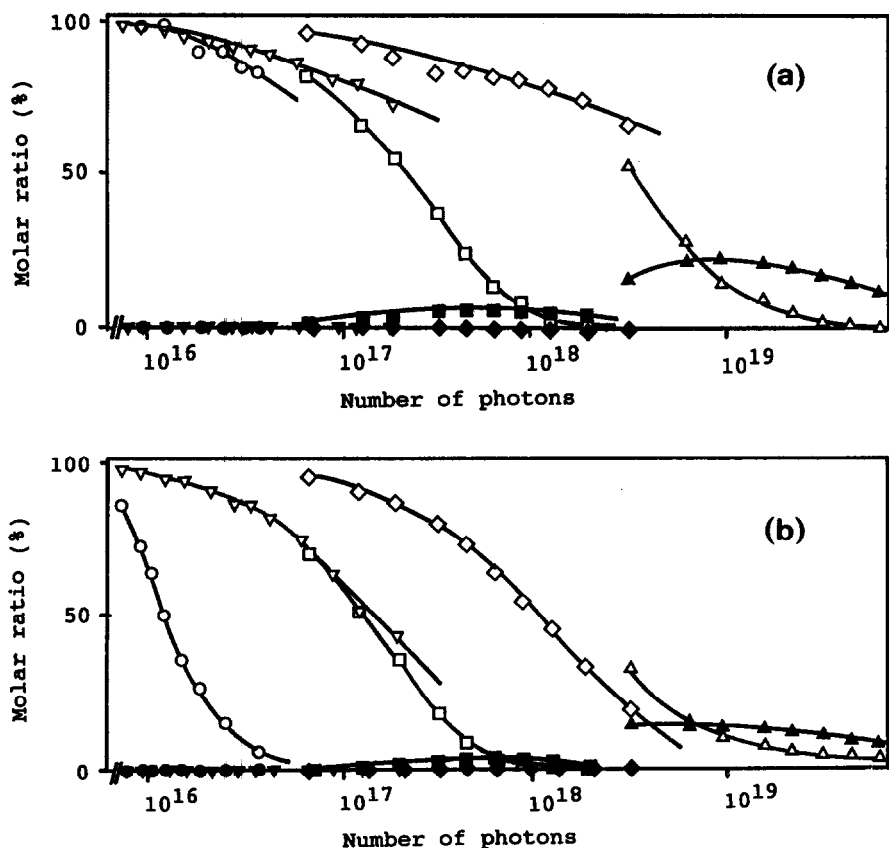


Fig. 1 Molar ratio of (a) 1,8-bis(bromomethyl)naphthalene 1 and acenaphthene 3, and (b) 1,8-bis(chloromethyl)naphthalene 2 and 3, as a function of the number of irradiated photons. Concentration of the cyclohexane solutions: 10⁻⁵ M. 1 and 2: white symbols; 3: black symbols. KrF laser fluences (photons·cm⁻²·pulse⁻¹): Δ : 3.1×10^{18} ; \square : 6.2×10^{16} ; \circ : 6.2×10^{14} ; \diamond : 6.2×10^{16} (10⁻³ M); ∇ : Conventional light at >250 nm (3.4×10^{14} photons·cm⁻²·s⁻¹).

a low-pressure mercury lamp, which reaction undoubtedly proceeds by a one-photon process, although a considerable amount of 1 and 2 was consumed during the irradiation. The result indicates that the intense laser-specific formation of 3 is not ascribed to such multi-centered reaction but to a biphotonic reaction.¹¹

The yields of 3 showed a gradual decrease under further irradiations after reaching a maximum. The decrease is ascribed to the secondary reactions of 3 - photochemical reactions with and without participation of halogen atoms which are generated during the reactions. The control experiments showed the decrease of 3 in the absence and presence of equimolar bromine molecules; the results are shown in Table 1. Considerable decrease of 3 was observed in both cases and, as expected, faster decrease was seen in the presence of bromine molecules.

The figure also shows the difference in the reactivities between 1 and 2. Although faster decrease of 2 to 1 was observed, the yield of 3 was greater in the cases of 1 compared with 2; the comparison was made between the results at the first laser pulse in order to avoid the effect of secondary reactions.

The faster decrease of 2 may be rationalized by higher reactivity of chlorine radicals towards solvent molecules. Intimate radical pairs are initially formed by photochemical homolytic C-X bond cleavage,¹² but fast recombination often takes place within such radical pairs.⁵ Besides recombination, the halogen radicals react with solvent molecules; more efficient reactions take place with chlorine radicals, thus giving faster decrease of 2. The products from solvent molecules were actually observed in our experiments.¹³

The reason for the higher yield of 3 in the reactions of 1 to 2 is still not clearly understood; however, one interpretation is the difference

Table 1. Decomposition of acenaphthene 3 by the laser irradiations^a in the presence and absence of bromine.

No. of laser pulse	Conversions (%)	
	No additives	Br ₂ additive (1 eq.)
1	4.7	15.1
2	11.3	29.7
3	14.7	39.1
5	20.0	45.8
7	23.9	61.3
10	32.1	63.5
14	36.3	65.1
20	46.6	--

^a KrF excimer laser: 3.1×10^{18} photon·cm⁻²·pulse⁻¹; pulse width: ca. 34 ns; cyclohexane solution: 10^{-5} M.

in the intermediate state, presumably in the vibrationally excited state. Excess internal energy which facilitates the reaction from an intermediate, probably a diradical, to 3 is expected to be larger in the case of the intermediate generated from 1 because the bond dissociation energy of C-Br is smaller than that of C-Cl.¹⁴ The reaction from 1 is facilitated accordingly, giving the higher yield of 3.

References and Notes

- 1 J.A.Butcher, Jr., H.R.Hinz, N.Tsou, and S.Shah, *Tetrahedron Lett.*, **25**, 5483 (1984).
- 2 A.Yabe, A.Ouchi, and H.Moriyama, *J. Chem. Soc., Chem. Commun.*, 1987, 1744.
- 3 K.Hannemann and J.Wirz, *Angew. Chem. Int. Ed. Engl.*, **27**, 853 (1988).
- 4 Review: K.Kleinermanns and J.Wolfrum, *Angew. Chem. Int. Ed. Engl.*, **26**, 38 (1987).
- 5 J.G.Calvert and J.N.Pitts, Jr.: *Photochemistry*, John Wiley & Sons, New York 1966, Section 5-8.
- 6 a) Preparation of 1: L.A.Carpino, *J. Am. Chem. Soc.*, **85**, 2144 (1963); b) Preparation of 2: V.Boekelheide and G.K.Vick, *J. Am. Chem. Soc.*, **78**, 653 (1956).
- 7 *Eg.*: M.Gisin and J.Wirz, *Helv. Chim. Acta*, **59**, 2273 (1976); M.S.Platz, *J. Am. Chem. Soc.*, **102**, 1192 (1980).
- 8 The laser used was Lambda Physik Model EMG-201MSC (pulse width: ca.34 ns) and >250 nm light was obtained by a 10 W low-pressure mercury lamp fitted with a UV-25 (Toshiba) filter; the flux of the conventional lamp was calculated as 254 nm light. Product analyses were performed with HPLC, and 3 was identified by the comparison of retention time and electronic spectra with those of the authentic sample.
- 9 The photochemical products of 1-chloromethylnaphthalene by the irradiation of 266 nm pulsed laser were found to be dimers: G.H.Slocum and G.B.Schuster, *J. Org. Chem.*, **49**, 2177 (1984).
- 10 K.W.Egger and A.T.Cocks in S.Patai (Ed.): *The chemistry of the carbon-halogen bond, Part 2*, John Wiley & Sons, London 1973, Ch. 10, pp. 716.
- 11 The lifetime of naphthylmethyl radical was reported to be several microseconds⁹ and it is generated within 15 ps after irradiation of a 266 nm laser pulse to 1-chloromethylnaphthalene.¹⁵ In our experiments, therefore, the second photon absorption to the monoradicals generated, before the reactions of the monoradicals, seems to be highly possible within the laser pulse width.
- 12 a) P.G.Sammes in S.Patai (Ed.): *ibid.*, Ch. 11, pp. 761; b) G.Lodder in S.Patai and Z.Rappoport (Ed.): *The chemistry of halides, pseudo-halides and azides, Part 2*, John Wiley & Sons, Chichester 1983, Ch. 29, pp. 1615.
- 13 The control experiments - intense KrF laser irradiations to cyclohexane in the presence of 10^{-5} M bromine molecules - showed the formation of the same products as in the laser reactions; benzene, cyclohexadiene, and small amount of some other unidentified products were observed.
- 14 The bond dissociation energies reported for the benzylic C-Br and C-Cl bonds are 54 and 68 kcal·mole, respectively: Ref. 10, pp.687.
- 15 D.F.Kelley, S.V.Milton, D.Huppert, and P.M.Rentzepis, *J. Phys. Chem.*, **87**, 1842 (1983).