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THE LASER VS. THE LAMP: PHOTOCHEMISTRY OF LONG-CHAINED *BIS*-DIBENZYLKETONES

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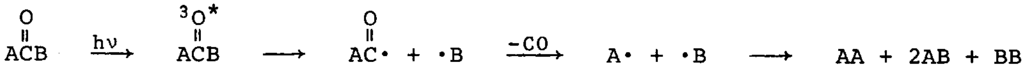
Abstract: A comparison of products formed during photolysis of 1,12-bis-[4-(2-oxo-3-phenylpropyl)phenyl]dodecane (1) reveals a difference in laser and lamp photolysis in that the use of a laser increases the yield of macrocyclic paracyclophane rings (2) by a factor of three.

Dibenzylketone (DBK) photochemistry has been carefully studied and well characterized.[1] Norrish Type I cleavage from the triplet state of an unsymmetrical dibenzylketone followed by decarbonylation and radical coupling, as shown in Scheme I, leads to a statistical distribution of diarylethanes in fluid solution. In marked contrast, photolysis in detergent solution suppresses the formation of cross-products.[2] This non-statistical behavior is attributed to the influence of the micelle, which effectively prevents the benzyl radicals from diffusing apart. The validity of this explanation is substantiated by experiments in which ^{13}C enrichment is achieved by coupling of the incipient radical pair after ^{13}C mediated intersystem crossing to the singlet radical pair.[3] By analogy, connecting two dibenzylketones by a hydrocarbon chain should result in the formation of macrocyclic paracyclophanes under conditions leading to cleavage of the ketones at both ends of the molecule during the radical lifetime and coupling. The radicals cannot diffuse apart because of the alkyl chain. The difference between lamp and laser photolysis is schematically depicted in Scheme II and specifically illustrated in Scheme III for the compound used in this study. Two photons are required if macrocyclic paracyclophane rings $\left\{(\overline{BRB})_n\right\}$ are to form, thus a comparison of Hg-lamp and excimer laser photolysis was undertaken.[4] Preliminary results indicate that at least three times as many paracyclophane rings form during laser photolysis, because it leads to the simultaneous absorption of 2 photons while lamp photolysis is a sequential 2-photon process. This approach should produce knots in the presence of a template.[5]

Scheme I



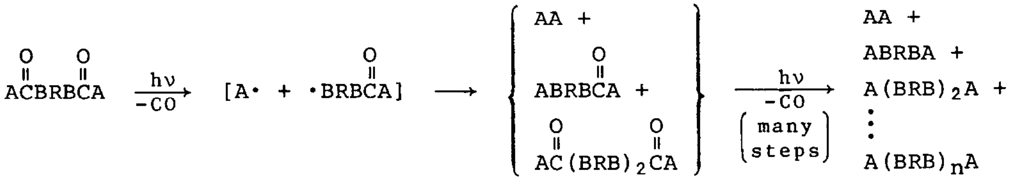
$$\overset{O}{\overset{\|}{ACB}} \xrightarrow{h\nu} \overset{^{3}O^{*}}{\overset{\|}{ACB}} \longrightarrow \overset{O}{\overset{\|}{AC\cdot}} + \cdot B \xrightarrow{-CO} A\cdot + \cdot B \longrightarrow AA + 2AB + BB$$

Commencing from *bis*-[4-chloromethylphenyl]dodecane (4)[6] and benzyl-1,3-dithiane anion in THF at -15° the *bis*-1,3-dithiane corresponding to 1 can be obtained in 60% yield by published procedures.[7] The pure compound is an odoriferous brown oil which is instantly hydrolyzed to the *bis*-DBK (1)[8] using excess NBS in wet acetone at 0°.[9] Chromatography on Florisil® (FLORIDIN Co.) followed by crystallization from 30% benzene in cyclohexane affords the white diketone (m.p. = 94°) in 50% yield. Traces of phenylacetaldehyde which are always present following the hydrolysis are removed by heating the crude product *in vaquo* at

100°. Interestingly, Hg^{2+} and Ag^{+} hydrolysis procedures[10] led to the formation of an amorphous substance which appears to be a very stable metal enolate complex.[11]

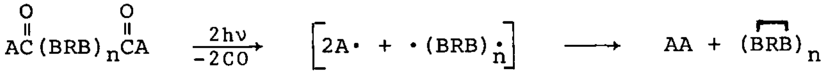
Scheme II

Lamp photolysis leads to linear oligomers:



$$\mathrm{A\overset{\overset{O}{\|}}{C}BRB\overset{\overset{O}{\|}}{C}A} \xrightarrow[-\mathrm{CO}]{h\nu} [\mathrm{A}\cdot + \cdot\mathrm{BRB\overset{\overset{O}{\|}}{C}A}] \longrightarrow \left\{\begin{matrix} \mathrm{AA} + \\ \mathrm{ABRB\overset{\overset{O}{\|}}{C}A} + \\ \mathrm{A\overset{\overset{O}{\|}}{C}(BRB)_2\overset{\overset{O}{\|}}{C}A} \end{matrix}\right\} \xrightarrow[\substack{-\mathrm{CO} \\ \left(\substack{\text{many}\\ \text{steps}}\right)}]{h\nu} \begin{matrix} \mathrm{AA} + \\ \mathrm{ABRBA} + \\ \mathrm{A(BRB)_2A} + \\ \vdots \\ \mathrm{A(BRB)_nA} \end{matrix}$$

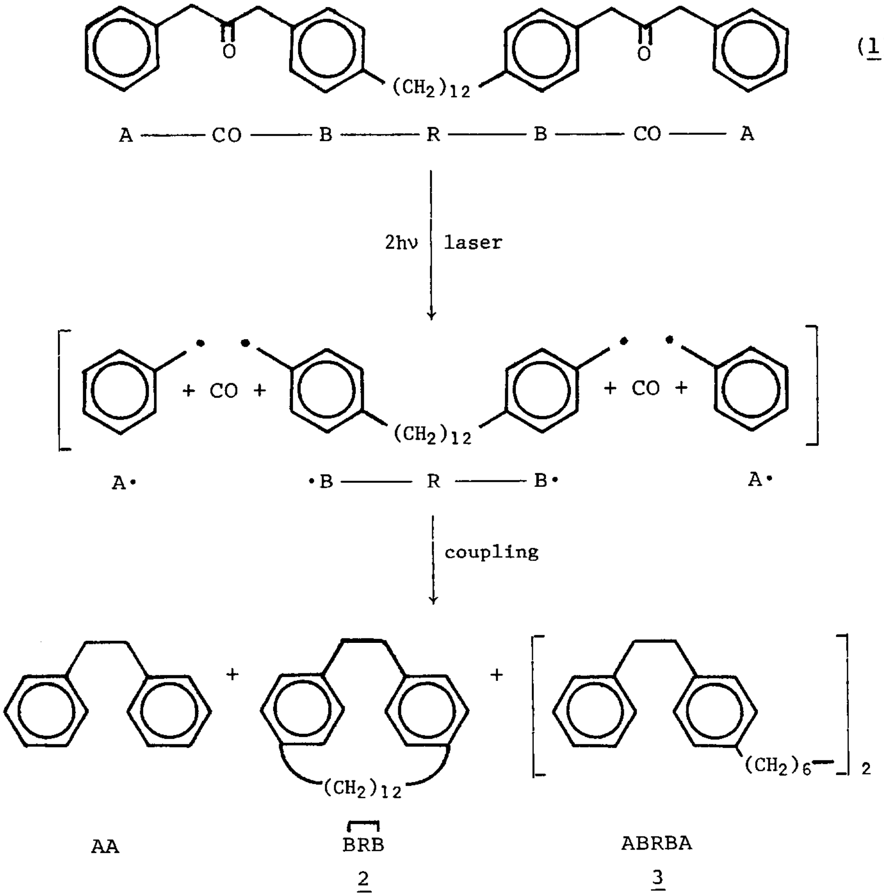
In addition to the processes shown above, laser photolysis includes:



$$\mathrm{A\overset{\overset{O}{\|}}{C}(BRB)_n\overset{\overset{O}{\|}}{C}A} \xrightarrow[-2\mathrm{CO}]{2h\nu} \left[2\mathrm{A}\cdot + \cdot(\mathrm{BRB})\dot{}_n\right] \longrightarrow \mathrm{AA} + (\overline{\mathrm{BRB}})_n$$

where A, B, and R are defined as shown in Scheme III, and n = 1, 2, 3, . . .

Scheme III



+ higher oligomers

Laser and lamp photolyses were carried out in nmr sample tubes. *Bis*-DBK (40 mg) was irradiated in N_2-purged C_6D_6 (0.5 ml) and monitored by ^{1}H nmr. Experimentally, lamp photolysis posed no problem and after 0.5 hr of irradiation through pyrex with a medium pressure Hg lamp, no detectable nmr signal for the ketone remained. Laser photolysis[12] was significantly more difficult. The pyrex sample tube was mounted on a movable stand and irradiated at ~20 pulses/sec @ 100 mj/pulse using the XeCl 308 nm line. The (3 × 20 mm) laser beam was focused into the sample using a quartz lens. The nmr tube was moved frequently to prevent damage to the tube from the intense light. After ~1000 pulses from the laser, nmr indicated that >90% of the ketone was consumed.

The nmr spectrum of the photolyzed solutions exhibited three singlets in the bibenzyl region corresponding to the three types of linkages possible: Ph-$(CH_2)_2$-Ph, Ph$(CH_2)_2$Ar, and Ar$(CH_2)_2$Ar. The integral indicated a 1:2:1 ratio for these signals consistent with a statistical distribution of AA, AB, and BB linkages. HPLC analysis was more revealing. The solvent and low molecular weight products (bibenzyl) were removed *in vaquo* and the residue separated by size exclusion chromatography.[13] The constituents present were identified by comparison to authentic samples.[14] The results are presented in Table 1 and clearly illustrate the differences between laser and lamp photolysis: (1) Laser photolysis leads to the formation of macrocyclic rings in ~9% yield, and while this is a low yield it is significantly greater than the yield in lamp photolysis; and (2) more high molecular weight material forms during laser photolysis. These observations are consistent with the differences noted in Scheme II and demonstrate the potential of laser photolysis for forming products which are unobtainable by lamp photolysis.

Table 1. Product yields from laser and lamp photolysis of 1.

Band #	Time (min)	Laser (%)	Lamp (%)	Ratio (laser/lamp)	Assignment
1	30.6	29.1	19.3	1.51	High MW Products
2	31.7	12.3	12.2	1.01	A$(BRB)_2$A
3	33.2	19.1	21.8	0.88	$(\overline{\mathrm{BRB}})_2$
4	35.8	30.6	39.7	0.77	ABRBA (3)
5	39.3	8.96	2.95	3.04	$\overline{\mathrm{BRB}}$ (2)
6	>40	--	3.00	--	Low MW Products

Analytical separation and characterization of the high molecular weight fraction is presently in progress. Likewise, the preparation of knotted paracyclophanes by this approach is being vigorously investigated.

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8. ^{1}H nmr ($CDCl_3$) δ: 7.25(10H,m), 7.08(8H,s), 3.69(4H,s), 3.67(4H,s), 2.58(4H,t), 1.58 (4H,bm), 1.26(16H,s). ^{13}C-nmr ($CDCl_3$) δ: 205.91, 141.81, 131.14, 129.54, 129.41, 128.82, 128.78, 127.06, 49.02, 48.86, 35.64, 31.53, 29.64, 29.41. IR (CCl_4): 3080-2980(b,w), 2930(w), 1720(m), 1550(m), 1420(w), 1355(w), 1220 cm^{-1}(m). Calculated for $C_{42}H_{50}O_2$ C: 85.88%, H: 8.50, O: 5.45. Found C: 85.88%, H: 8.78, O: 5.56.
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12. Lumonics TE861-S Excimer Laser, XeCl mixture: 100 mj/12 ns pulse @ 308 nm.
13. Waters Ultrastyragel 500 Å/CH_2Cl_2 @ 0.3 ml/min, UV-detection (254 nm). Integrals were measured using a Hewlett-Packard 3390 A recording integrator.
14. All reference compounds for the HPLC analysis were made from 4 by standard techniques. The paracyclophanes were obtained by the procedure of Otsubo and Misumi[15] using Givens' procedure for SO_2 extrusion.[16] The details will be published separately.
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