

Photochemistry of Acyl–Alkyl Biradicals

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Acyl–alkyl biradicals are produced upon (n,π^*) excitation of cyclic ketones, followed by α -cleavage.^{1,2} Their transient absorption spectra are practically coincident with those of the corresponding alkyl radicals. Thus, for the series of 2-phenylcycloalkanones, the spectra of the resulting biradicals compare very well with those typical of benzyl radicals.^{3,4} In the case of 2,2-dialkylcycloalkanones, the biradicals possess a tertiary radical center, which leads to a weak absorption maximum at 320 nm,^{4,5} similar to that of the *tert*-butyl radical ($\lambda_{\max} = 307$ nm, $\epsilon_{\max} = 200$ M⁻¹ cm⁻¹). These substitution patterns have facilitated detection of the intermediates since acyl radicals do not absorb at 300–320 nm.

Despite the considerable efforts devoted to the study of alkyl–acyl biradicals, due to their wide occurrence and general interest, it seems surprising that the photobehavior of these short-lived species has not been studied yet. Such species are generated almost “instantaneously” when irradiating the corresponding cycloalkanone at room temperature;^{2,4,6} however, two-laser two-color flash photolysis experiments could be difficult to carry out due to the relatively short lifetimes (10–100 ns) of these intermediates.² In view of the existing interest for establishing the photochemistry of short-lived intermediates via two-photon processes,⁷ we decided to photolyze biradicals **2** ($n = 4$ –6), since they possess a benzyl radical terminus strongly absorbing at 258 nm ($\epsilon_{\max} = 31,400$ M⁻¹ cm⁻¹) which could allow their excitation using a 266 nm laser, the same that could be suitable for their generation from the precursor cycloalkanones.⁴

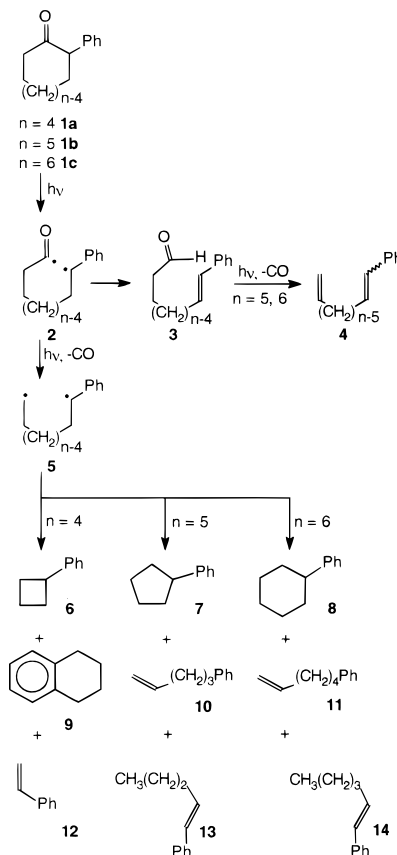
In this Communication we report a comparative study of the chemistry and photochemistry of acyl–alkyl biradicals **2** in cyclohexane. Thus, the products obtained in the low-intensity irradiation (medium-pressure mercury, quartz, or Pyrex filter, 30 min) of deaerated 10 mM cyclohexane solution of ketones **1a–c** were compared with those observed upon laser excitation [Nd:YAG, 266 nm, 2200 pulses] of 1

Table 1. Product Distribution Obtained upon Laser Irradiation of Ketones **1a–c**

ketone	product distribution (%)		
	primary enals	secondary Norrish II products	two-photon products ^a
1a	3a (47)		6 (12), 9 (27), 12 (12) ^b
1b	3b (29)	4b (27)	7 (34), 10 (4), 13 (4)
1c	3c (46)	4c (18)	8 (20), 11 (8), 14 (8)

^a The structural assignment of photoproducts was confirmed by unambiguous synthesis, using well-established methods,^{9–15} or by comparison with available authentic samples. Part of styrene could have been evaporated when rotoevaporating the photolyzate before analysis.

Scheme 1



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mM cyclohexane solution of the ketones. Our results revealed that acyl–alkyl biradicals are photolyzed within the laser pulse (10 ns) giving rise to new products arising from dialkyl biradicals.

It has been previously reported^{2,6,8} that lamp irradiation ($\lambda = 313$ nm) of ketones **1a–c** leads to unsaturated aldehydes **3a–c** probably formed from the primary acyl–alkyl biradicals **2a–c** through an H abstraction process. In the present work we have confirmed these observations; however, we have observed that under our reaction conditions (either Pyrex or quartz filter) **1b,c** led to the expected enals and also to dienes **4b,c**, the Norrish type II secondary products of **3b,c**. GC/MS analysis showed that not even traces of other products were formed.

By contrast, analysis of the photolyzate obtained after laser irradiation of ketone **1a** indicated that significant

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amounts of phenylcyclobutane (**6**), tetraline (**9**), and styrene (**12**) were also generated. In the case of ketone **1b** ($n = 5$), phenylcyclopentane (**7**) and minor amounts of 5-phenyl-1-pentene (**10**) and 1-phenyl-1-pentene (**13**) were found in the irradiated sample (Table 1). Finally, laser irradiation of ketone **1c** ($n = 6$) led to cyclohexylbenzene (**8**) and minor amounts of 6-phenyl-1-hexene (**11**) and 1-phenyl-1-hexene (**14**) as the new products (Table 1).

In all laser experiments the amounts of products arising from irradiation of (thermally) unreactive photoproducts were minimized by keeping the conversion of starting ketone low (less than 25%).

A satisfactory rationalization of the above results can be found in Scheme 1. Laser excitation of ketones **1** agrees with the photodecarbonylation of acyl-alkyl biradical **2** during the 266 nm laser pulse, leading to dialkyl biradical **5**. Its cyclization or disproportionation generates the photoproducts **6–14**,^{9–15} which are the fingerprints for two-photon processes. A final point of interest is whether the absorbing chromophore in biradicals **2** at the photolysis laser wave-

length is the acyl or the benzyl radical site. Taking into account the much different extinction coefficients, it seems highly probable that the biradical **5** is generated via light absorption by the benzyl radical, followed by an intramolecular energy transfer process.

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