

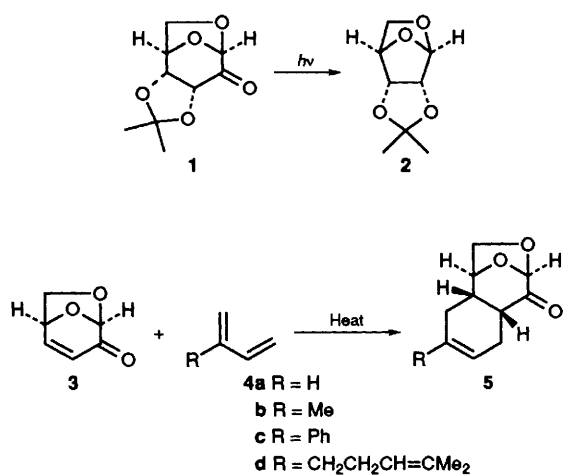
An Unusual Photochemical Extrusion of Carbon Dioxide from Laevoglucosenone Derivatives *via* Carbene Intermediates

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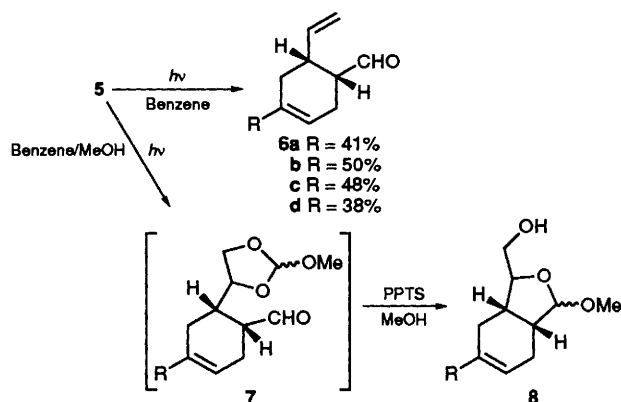
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Irradiation of laevoglucosenone derivatives **5** in benzene affords unexpected products **6**, which are formed *via* extrusion of carbon dioxide from intermediate dioxycarbenes.

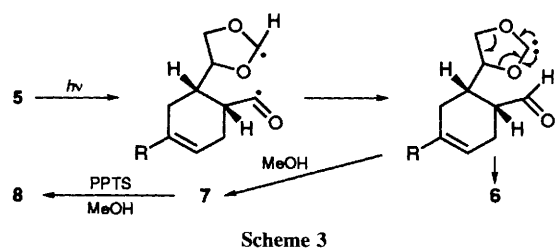
The photochemical decarbonylation reaction has been applied to the ring contraction of a variety of cyclic ketones; the irradiation of **1** gives a ring-contracted compound **2**.¹ Continuing our research² on photochemical reactions of laevoglucosenone derivatives, we describe here that the irradiation of Diels–Alder adducts of laevoglucosenone **3** does not produce the corresponding ring contracted compounds but gives 6-vinyl-3-cyclohexene-1-carbaldehydes **6**. Furthermore, we also describe that the products **6** are afforded *via* extrusion of carbon dioxide from intermediate dioxycarbenes.



Scheme 1



Scheme 2



Scheme 3

The substrates **5a**³ and **5b–d** were readily prepared in high yield by Diels–Alder reaction of **3** with dienes **4** in an autoclave at 140–160 °C for 20 h (Scheme 1). Each reaction gave only one regio- and stereo-isomer, which was determined by decoupling experiments of ¹H NMR. The results were almost comparable with those of reported.³ The adduct **5a** (2.0 mmol) in benzene (40 ml) was irradiated with unfiltered 450 W high-pressure mercury arc under a nitrogen atmosphere at room temp. for 35 h. Separation of the reaction mixture by silica gel column chromatography gave (–)-*cis*-6-vinyl-3-cyclohexene-1-carbaldehyde **6a**[†] in 41% yield without detectable amount of ring-contracted compound such as **2**. During the reaction, evolution of carbon dioxide was observed; when the generated gas was bubbled into a barium hydroxide solution, a white precipitate of BaCO₃ was detected. **6a** has already been synthesized by Boland⁴ as a synthetic intermediate of (+)-aucantene from dimethyl *cis*-4-cyclohexene-1,2-dicarboxylate *via* five steps. The spectral data of **6a** were in agreement with those reported. Similar results were also obtained for **5b–d**. When irradiation of **5a** and **5b** were carried out in a 1 : 4 mixed solvent of methanol and benzene, unstable compounds were produced instead of **6a** and **6b**. Treatment of the unstable products with PPTS in methanol gave **8a** and **8b**[‡] in 19.5 and 16.9% yields, respectively. These results indicate that **8a** and **8b** are derived from orthoesters **7a** and **7b** (Scheme 2).

A possible pathway for the formation of **6** and **7** is summarized in Scheme 3. Thus, irradiation of **5** generates acyl and acetal radicals through α -cleavage. The acyl radical abstracts the hydrogen atom of the acetal group to give a carbene, which results in **6** *via* extrusion of carbon dioxide. Although there has been no report of the formation of the carbene by way of the intramolecular H-abstraction of the acyl radical, the formation of **8a** and **8b** through intermediary **7** suggests the existence of the carbene intermediate. Furthermore, Lemal *et al.*⁵ describe that an ethylenedioxycarbene generated from 1,2,3,4-tetrachloro-7,7-ethylenedioxy-5-phenylbicyclo[2.2.1]hepta-2,5-diene by pyrolysis releases ethylene and carbon dioxide also supports the carbene intermediate. The difference in the reactions between **1** and **5** seems to be attributed to the change in the substituent at the α -position of the carbonyl group. Thus, the alkoxy group of **1** stabilizes the radical generated through the elimination of carbon monoxide, whereas, there is no such group in **5**. The conformational difference in the diradicals generated from **1** and **5** through α -cleavage could be an alternative explanation.

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Footnotes

[†] Specific rotation of **6a**: [α]_D = –62.5 (c 0.024, CH₂Cl₂); ref. 1(c): [α]₅₇₈ = –80.8 (c 1.788, CH₂Cl₂).

[‡] Spectroscopic data for **8b**: ¹H NMR (CDCl₃) δ 1.65 (s, 1H), 1.75–1.86 (m, 2H), 2.13–2.24 (m, 4H), 2.60 (br q, *J* 7.3 Hz, 1H), 3.39 (s, 3H), 3.54 (dd, *J* 3.90, 11.72 Hz, 1H), 3.79 (dd, *J* 2.93, 11.72 Hz, 1H), 3.87 (ddd, *J* 2.93, 3.90, 4.40 Hz, 1H), 4.63 (s, 1H), 5.41 (d, *J* 3.41

Hz, 1H); MS m/z (relative intensity) 198 (M^+ , 23), 167 ($M^+ - OMe$, 100), 121 (42), 107 (72), 105 (35); IR (neat) 3438, 2929, 1096, 1039, 945 cm^{-1} .

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