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## Photoaddition Reaction of Methyl 2,4-Dioxopentanoate with 1,3-Butadiene

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The photoaddition reaction of methyl 2,4-dioxopentanoate with 1,3-butadiene gave isomeric dioxoesters, i.e., methyl 3- and 4-vinyl-2,4-dioxohexanoates and methyl 2-oxo-3-(2-oxopropyl)-*Z*-4-hexenoate, which is the first skeletally rearranged photoaddition products.

The photocycloaddition of methyl 2,4-dioxopentanoate (**1**) is characterized by its high reactivity and high regio-selectivity toward conjugated dienes,<sup>1)</sup> which quench the excited state of most of enones.<sup>2)</sup> To further explore this reaction, we examined the reaction with the simplest diene, 1,3-butadiene. Here we show the first observation of a radical rearrangement and a novel feature on the regioselectivity in this photoreaction.

The irradiation of **1** and butadiene in ethyl acetate at -30 °C gave a mixture of photoadducts in fairly good yield. Chromatographic separation gave a mixture of 1:1-adducts, **2**-**5** (57%) and 2:2-adduct **6** (22%).<sup>3)</sup> Attempts to purify 1:1-adducts via prepacked silica-gel column (Merck Lobar Column®) chromatography were unsuccessful due to a deposition of insoluble material in the column, but **4** (29%) and a small amount of **5** (0.3%) were obtained together with the oxidized products, **7** and **8**.

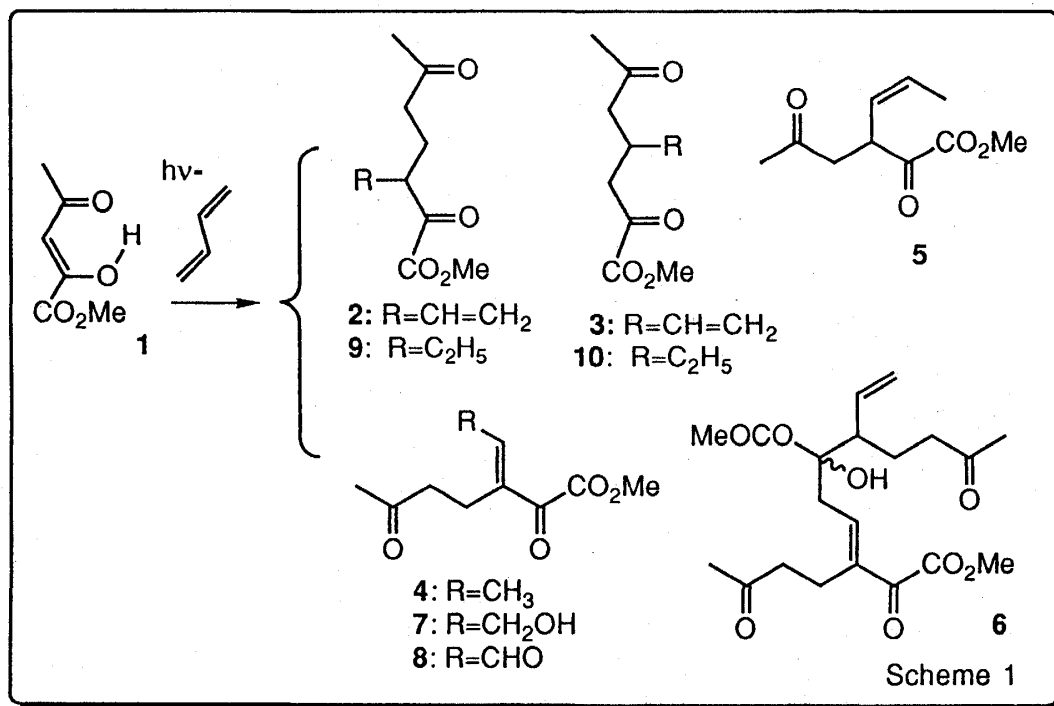
When the reaction mixture was catalytically hydrogenated, the products **9** and **10** were isolated via silica-gel chromatography in 61 and 8% yield. Therefore, the complication in the isolation of the primary photoproducts should be caused by silica gel. The structures of **9** and **10** were determined from their <sup>1</sup>H NMR spectra. Decoupling experiments revealed that the deshielded methine proton of **9** at  $\delta = 3.14$  (1 H, m) couples with the methylene protons at  $\delta = 1.50$  (1 H, m), 1.75 (1 H, m), and 1.78-1.92 (2 H, m), and the two protons at  $\delta = 1.50$  and 1.75 also couple with the methyl protons. The ethyl group, therefore, is attached on the 3-position of 2,6-dioxoheptanoate.

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On the other hand, the methine proton of **10** at  $\delta = 2.40$  showed a coupling not only with the methylene protons of the ethyl group at  $\delta = 1.34-1.44$  but also with two other methylene groups at  $\delta = 2.74$  (1 H, dd,  $J=17, 7$  Hz) and  $2.92$  (1 H, dd,  $J=17, 5$  Hz) and  $2.4-2.53$  (2 H, m); thus, the ethyl group must be at 4-position. Hence, the structures of the primary photo-products, **2** and **3**, are methyl 3-vinyl- and 4-vinyl-2,6-dioxohexanoates.

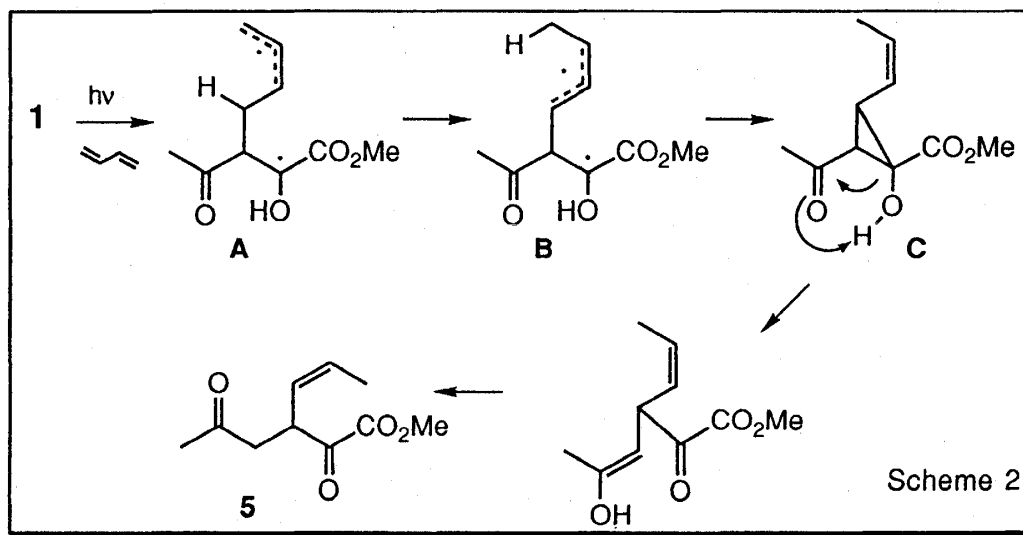


The  $^1\text{H}$  NMR of **4** showed a vinyl methyl group at  $\delta = 2.01$  as a doublet ( $J=7.3$  Hz) and an olefinic proton at  $\delta = 6.79$  (q,  $J=7.3$  Hz). The *E* configuration of the double bond was established on the basis of NOE evidence between the vinyl methyl group and methylene protons. Thus **4** must be a silica-gel-catalyzed isomerization product of **3**.

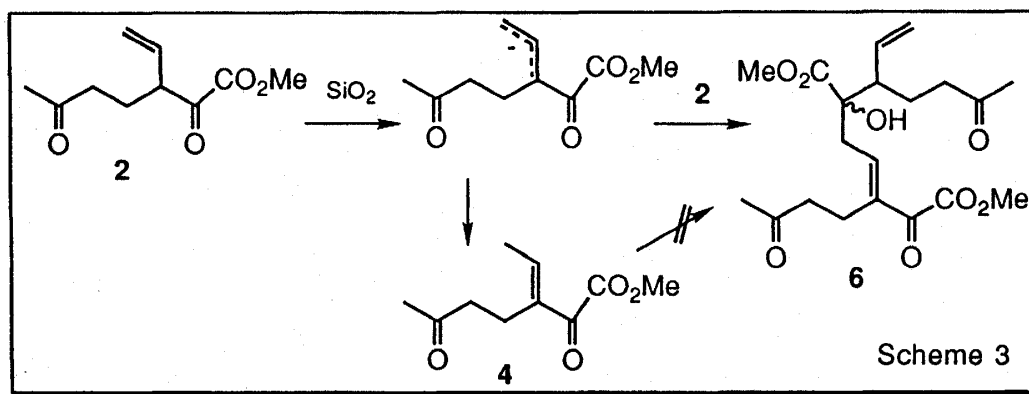
The  $^1\text{H}$  NMR of the minor product **5** showed two olefinic protons at  $\delta = 5.06$  and  $5.74$ , which together with a vinyl methyl group at  $\delta = 1.78$  suggested a *Z*-1-propenyl group. A methine proton at  $\delta = 4.66$ , showing couplings with these olefinic protons with  $J=10.3$  and  $0.7$  Hz, was adjoined to a methylene group observed at  $\delta = 2.66$  and  $3.17$ . Thus, the structure of methyl 2-oxo-3-(2-oxopropyl)-*Z*-4-hexenoate was derived.

The formation of **5** has no precedence in the photochemistry of **1**, and could not be interpreted by a simple cycloaddition-*retro*-aldol reaction. It must involve an intermediate, cyclopropanecarboxylate **C** (Scheme 2), which is formed by the abstraction of an active hydrogen by the allyl radical in **A** to form **B** followed by recombination to **C**. Recently, we have observed that the stability of the intermediate diradicals is important for the regioselectivity of the cycloadducts.<sup>4)</sup> The present result, the isolation of **5**, can be regarded as a chemical evidence for the biradical mechanism having a sufficient life

time to cause a skeletal rearrangement prior to completing the cyclization.



The structure of **6** was determined from the  $^{13}\text{C}$  NMR revealing five carbonyl carbons, and from the  $^1\text{H}$  NMR showing the existence of a vinyl group and one olefinic proton at  $\delta = 6.63$  (dd,  $J=8, 7$  Hz) coupling with the methylene protons at  $\delta = 2.70$  and  $2.73$ . As the isolated **4** was stable to chromatographic conditions, it is evident that the precursor of **6** was **2**, but not **4**, via its enolate, which is also the intermediate of the isomerization of **2** to **4**.



The photoreaction of **1** with 1,3-butadiene proved to have a relatively low regio-selectivity as compared to the other olefins,<sup>5)</sup> e.g.,  $> 100/1$  for isoprene. These observations suggest the regio-selectivity of **1** is affected not only by the electronic effect but also by the steric effect of the substituents. In the reaction with 2,5-dimethyl-2,4-hexadiene,<sup>6)</sup> however, no reverse type adducts like **3** have been obtained. Further investigations should be pursued hereafter.

## References

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- 2) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, Inc., New York (1973), pp27-35.
- 3) The new compounds were fully characterized including following  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data (in  $\text{CDCl}_3$  with a GSX 270 H spectrometer, JEOL.):
  - 4 :  $^1\text{H}$  NMR  $\delta$  = 2.01 (3H, d,  $J$  = 7 Hz), 2.14 (3H, s), 2.56-2.59 (4H, m), 3.88 (3H, s), and 6.79 (t,  $J$  = 7 Hz).  $^{13}\text{C}$  NMR  $\delta$  = 14.9, 18.4, 29.4, 41.1, 52.1, 137.6, 148.5, 164.9, 188.4, and 207.2.
  - 5 :  $^1\text{H}$  NMR  $\delta$  = 1.78 (3H, dd,  $J$  = 7, 2 Hz), 2.16 (3H, s), 2.66 (dd,  $J$  = 18, 4.5 Hz), 3.17 (dd,  $J$  = 18, 10 Hz), 3.88 (3H, s), 4.66 (dddd,  $J$  = 10.5, 10, 4.5, 0.7 Hz), 5.06 (tq,  $J$  = 10.5, 2 Hz), and 5.74 (dq,  $J$  = 10.5, 7, 0.7 Hz).  $^{13}\text{C}$  NMR  $\delta$  = 13.4, 29.5, 41.5, 45.8, 53.0, 123.7, 131.1, 161.3, 192.7, and 206.3.
  - 6 :  $^1\text{H}$  NMR  $\delta$  = 1.46-1.56 (2H, m), 2.12 (3H, s), 2.13 (3H, s), 2.34 (m), 2.33-2.46 (2H, m), 2.53-2.58 (4H, m), 2.70 (dd,  $J$  = 15, 8 Hz), 2.73 (dd,  $J$  = 15, 7 Hz), 3.82 (3H, s), 3.87 (3H, s), 5.15 (dd, 17, 2 Hz), 5.29 (dd,  $J$  = 10, 2 Hz), 5.59 (dt,  $J$  = 17, 10 Hz), 6.60 (1H, dd,  $J$  = 8, 7 Hz);  $^{13}\text{C}$  NMR  $\delta$  = 19.4, 22.6, 29.9, 30.1, 37.6, 40.7, 41.6, 51.4, 52.6, 53.3, 78.6, 120.3, 135.7, 138.9, 146.8, 164.7, 175.5, 188.5, 207.5, and 208.1.
  - 7 :  $^1\text{H}$  NMR  $\delta$  = 2.13 (3H, s), 2.18 (s, OH), 2.60-2.68 (4H, m), 3.89 (3H, s), 4.55 (2H, d,  $J$  = 6 Hz), and 6.75 (t,  $J$  = 6 Hz).  $^{13}\text{C}$  NMR  $\delta$  = 19.3, 30.1, 41.3, 52.7, 59.8, 136.2, 151.0, 164.7, 189.0, and 208.8.
  - 8 :  $^1\text{H}$  NMR  $\delta$  = 2.14 (3H, s), 2.73 (2H, t,  $J$  = 7 Hz), 3.02 (2H, t,  $J$  = 7 Hz), 3.93 (3H, s), 6.61 (d,  $J$  = 6 Hz), and 10.4 (t,  $J$  = 6 Hz).
  - 9 :  $^1\text{H}$  NMR  $\delta$  = 0.90 (3H, t,  $J$  = 7 Hz), 1.50 (m), 1.75 (m), 1.78-1.92 (2H, m), 2.13 (3H, s), 2.35-2.50 (2H, m), 3.14 (m), and 3.88 (3H, s).  $^{13}\text{C}$  NMR  $\delta$  = 11.3, 23.4, 23.7, 29.9, 40.6, 48.2, 52.9, 162.2, 197.2, and 207.9.
  - 10 :  $^1\text{H}$  NMR  $\delta$  = 0.90 (3H, t,  $J$  = 7 Hz), 1.34-1.44 (2H, m), 2.13 (3H, s), 2.39-2.53 (3H, m), 2.74 (dd,  $J$  = 17, 7 Hz), 2.92 (dd,  $J$  = 17, 5 Hz), and 3.88 (3H, s).  $^{13}\text{C}$  NMR  $\delta$  = 11.1, 27.2, 30.3, 31.2, 43.2, 47.2, 53.0, 161.4, 193.6, and 208.1.
- 4) Results in our laboratory will be published elsewhere.
- 5) Until now, no olefins, except cyclopentadiene and indene,<sup>7)</sup> have given the adducts of type 3.
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