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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,[1] which quench the excited state of most of enones.[2] 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 ℃ 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%).[3] 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 ^{1}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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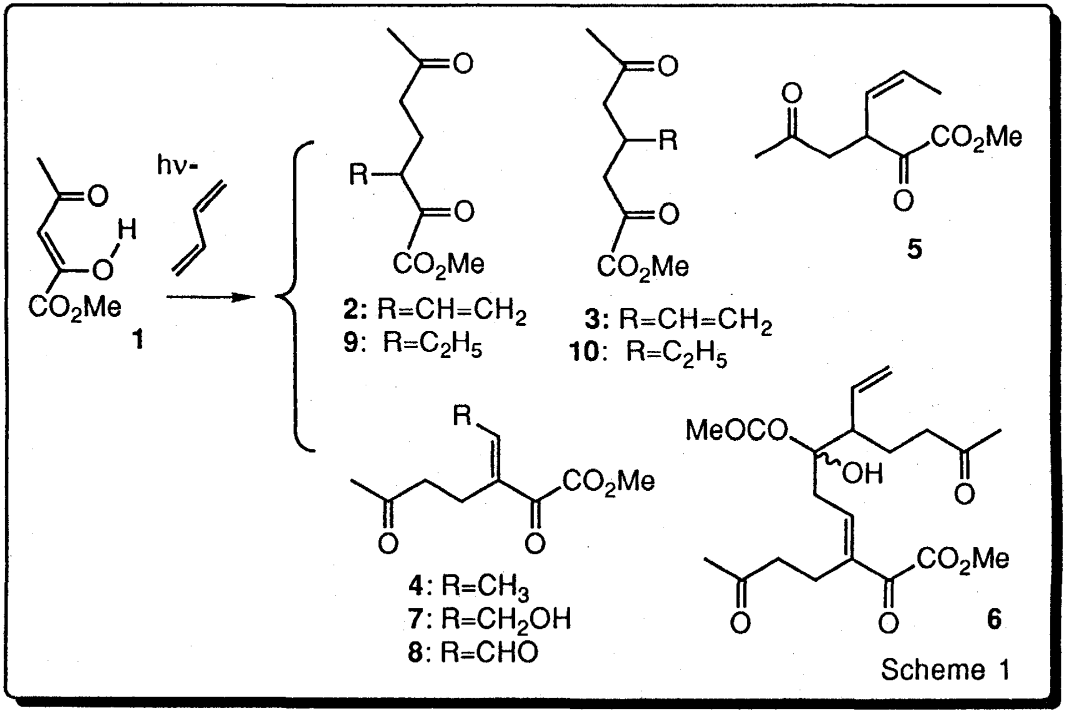
On the other hand, the methine proton of **10** at δ =2.40 showed a coupling not only with the methylene protons of the ethyl group at δ =1.34-1.44 but also with two other methylene groups at δ =2.74 (1 H, dd, J=17, 7 Hz) and 2.92 (1 H, dd, J=17, 5 Hz) and 2.4-2.53 (2 H, m); thus, the ethyl group must be at 4-position. Hence, the structures of the primary photoproducts, **2** and **3**, are methyl 3-vinyl- and 4-vinyl-2,6-dioxohexanoates.

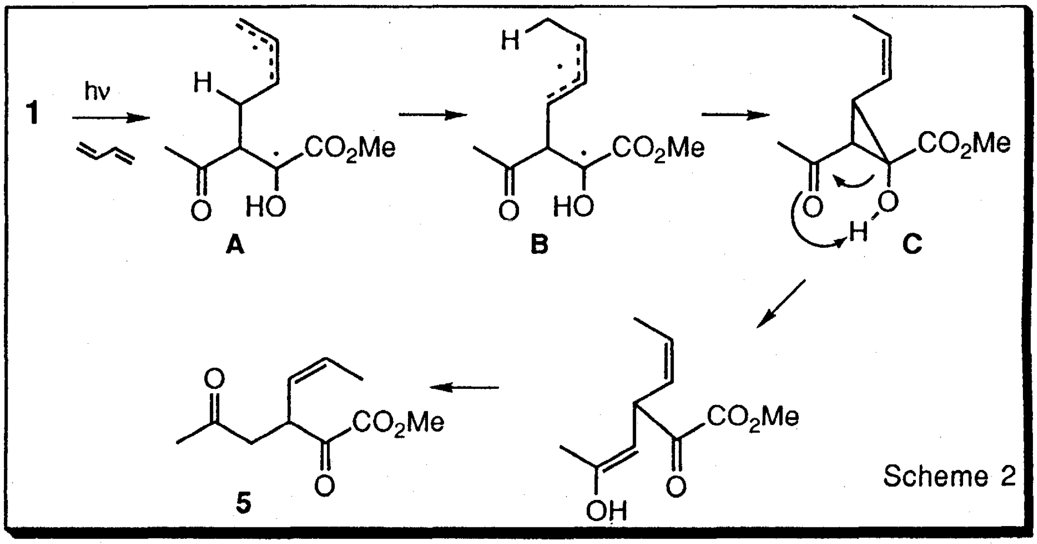


Scheme 1

The ^{1}H NMR of **4** showed a vinyl methyl group at δ =2.01 as a doublet (J=7.3 Hz) and an olefinic proton at δ =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**.

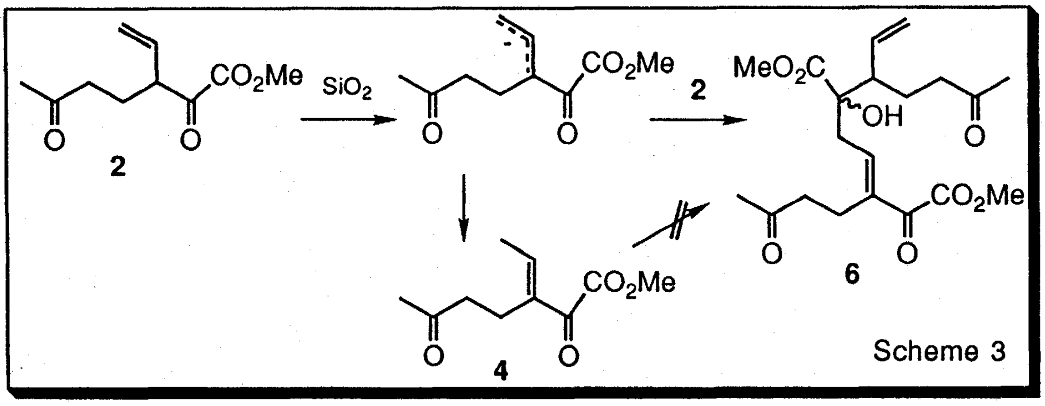
The ^{1}H NMR of the minor product **5** showed two olefinic protons at δ =5.06 and 5.74, which together with a vinyl methyl group at δ =1.78 suggested a *Z*-1-propenyl group. A methine proton at δ =4.66, showing couplings with these olefinic protons with J=10.3 and 0.7 Hz, was adjoined to a methylene group observed at δ =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.4) 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.



Scheme 2

The structure of **6** was determined from the ^{13}C NMR revealing five carbonyl carbons, and from the ^{1}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**.



Scheme 3

The photoreaction of **1** with 1,3-butadiene proved to have a relatively low regio-selectivity as compared to the other olefins,[5] 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,[6] however, no reverse type adducts like **3** have been obtained. Further investigations should be pursued hereafter.

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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}H and ^{13}C NMR spectral data (in $CDCl_3$ with a GSX 270 H spectrometer, JEOL.):

4 : ^{1}H NMR δ=2.01 (3 H, d, J=7 Hz), 2.14 (3 H, s), 2.56-2.59 (4 H, m), 3.88 (3 H, s), and 6.79 (t, J=7 Hz). ^{13}C NMR δ=14.9, 18.4, 29.4, 41.1, 52.1, 137.6, 148.5, 164.9, 188.4, and 207.2.

5 : ^{1}H NMR δ=1.78 (3 H, dd, J=7, 2 Hz), 2.16 (3 H, s), 2.66 (dd, J=18, 4.5 Hz), 3.17 (dd, J=18, 10 Hz), 3.88 (3 H, s), 4.66 (dddd, J=10.5, 10, 4.5, 0.7 Hz), 5.06 (tq, J=10.5, 2 Hz), and 5.74 (dqd, J=10.5, 7, 0.7 Hz). ^{13}C NMR δ=13.4, 29.5, 41.5, 45.8, 53.0, 123.7, 131.1, 161.3, 192.7, and 206.3.

6 : ^{1}H NMR δ=1.46-1.56 (2 H, m), 2.12 (3 H, s), 2.13 (3 H, s), 2.34 (m), 2.33-2.46 (2 H, m), 2.53-2.58 (4 H, m), 2.70 (dd, J=15, 8 Hz), 2.73 (dd, J=15, 7 Hz), 3.82 (3 H, s), 3.87 (3 H, s), 5.15 (dd, 17, 2 Hz), 5.29 (dd, J=10, 2 Hz), 5.59 (dt, J=17, 10 Hz), 6.60 (1 H, dd, J=8, 7 Hz); ^{13}C NMR δ=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}H NMR δ=2.13 (3 H, s), 2.18 (s, OH), 2.60-2.68 (4 H, m), 3.89 (3 H, s), 4.55 (2 H, d, J=6 Hz), and 6.75 (t, J=6 Hz). ^{13}C NMR δ=19.3, 30.1, 41.3, 52.7, 59.8, 136.2, 151.0, 164.7, 189.0, and 208.8.

8 : ^{1}H NMR δ=2.14 (3 H, s), 2.73 (2 H, t, J=7 Hz), 3.02 (2 H, t, J=7 Hz), 3.93 (3 H, s), 6.61 (d, J=6 Hz), and 10.4 (t, J=6 Hz).

9 : ^{1}H NMR δ=0.90 (3 H, t, J=7 Hz), 1.50 (m), 1.75 (m), 1.78-1.92 (2 H, m), 2.13 (3 H, s), 2.35-2.50 (2 H, m), 3.14 (m), and 3.88 (3 H, s). ^{13}C NMR δ=11.3, 23.4, 23.7, 29.9, 40.6, 48.2, 52.9, 162.2, 197.2, and 207.9.

10 : ^{1}H NMR δ=0.90 (3 H, t, J=7 Hz), 1.34-1.44 (2 H, m), 2.13 (3 H, s), 2.39-2.53 (3 H, m), 2.74 (dd, J=17, 7 Hz), 2.92 (dd, J=17, 5 Hz), and 3.88 (3 H, s). ^{13}C NMR δ=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,$^{7)}$ have given the adducts of type **3**.

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