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Hatsui, Toshihide
Institute of Advanced Material Study, Kyushu University

Kitashima, Toshio
Institute of Advanced Material Study, Kyushu University

Takeshita, Hitoshi
Institute of Advanced Material Study, Kyushu University

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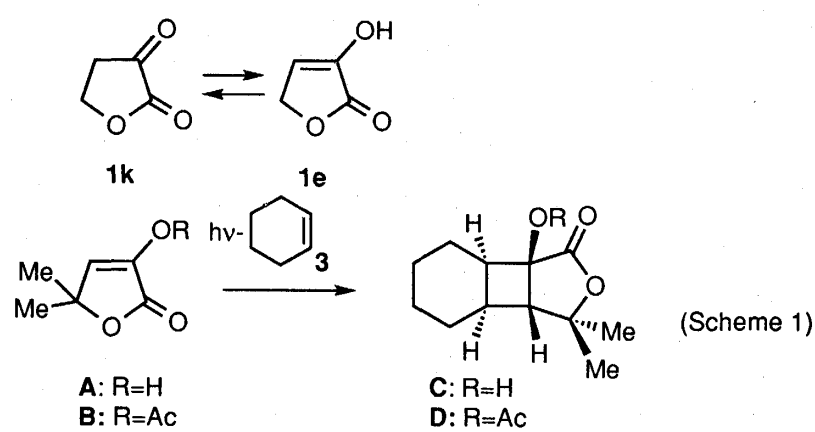
# Synthetic Photochemistry. LXVI.[1,2] The Photoaddition of 2-Oxo-$\gamma$-valerolactone to Cyclohexene

Toshihide HATSUI, Toshio KITASHIMA, and Hitoshi TAKESHITA*

Photocycloaddition of 4-methyl-2-oxo-$\gamma$-valerolactone to cyclohexene gave three [2+2] cycloadducts. The stereostructures of photoproducts were identified by detailed NMR spectral analyses including NOE experiments. The photocycloadducts were convertible to [2-(1-propenyl)cyclohexyl]glyoxylic acids.

The photoaddition reaction of enolized $\beta$-dicarbonyl compounds with alkenes has wide applications in organic syntheses.[3,4] As a modified $\beta$-dicarbonyl functions, several cyclic enol derivatives of acetoacetic acid were also reported.[5,6]

2-Oxo-$\gamma$-butyrolactone (**1**: $\alpha$-tetronic acid) is known to exist in the enol form (**1e**, a cyclic $\alpha$, $\beta$-unsaturated carbonyl system), rather than the keto form (**1k**),[7] and, therefore, its [2+2] cycloadducts should have a hydroxyl group on the cyclobutane ring, which may assist the subsequent transformations of the strained cyclobutane moiety. Herein described are results of the photoreactions, following a reaction in a same line with dimethyl derivatives, 4-methyl-2-oxo-$\gamma$-valerolactone (**A**) and its enol acetate (**B**),[8] of methyl derivatives of **1**, 2-oxo-$\gamma$-valerolactone (**2**),[9] with cyclohexene (**3**).




(Scheme 1)

**Scheme 1**

The UV-light irradiation of 2-oxo-$\gamma$-valerolactone (**2**) with cyclohexene (**3**) afforded three products (**4**, **5**, and **6**), in 35, 15, and 8% yields, respectively, which could be separated via a silica-gel column chromatography. All the products, **4**-**6**, were identified as 1:1-adducts from mass spectral measurement of the molecular weight ($M^+=196$).

In order to elucidate the structures, the $^{13}C$ NMR spectra of **4**-**6** were, first of all, compared with that of **C** and **D**, obtained from **A** and **B**,[8] as shown in Table 1; those of **4** and

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**Table 1** The $^{13}$CNMR chemical shift comparisons of **4**-**6** with **C**.

| Adducts | Assignments | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | a) | | | | | | | b) | c) | d) | e) |
| **C** | 21.6 | 21.7 | 21.7 | 23.0 | 28.1 | 36.8 | 52.9 | 24.9, 25.4 | 76.9 | 85.9 | 180.0 |
| **4** | 21.5 | 21.5 | 21.7 | 24.6 | 28.8 | 37.4 | 50.1 | 21.4 | 75.1 | 80.8 | 180.6 |
| **5** | 25.6 | 25.9 | 26.0 | 26.9 | 41.7 | 49.3 | 51.6 | 22.4 | 76.5 | 82.2 | 177.6 |
| **6** | 21.6 | 21.6 | 21.9 | 23.3 | 25.0 | 37.1 | 48.1 | 14.8 | 75.9 | 77.6 | 180.1 |

a) Signals of alicyclic carbons; b) Methyl carbon signals; c) Signals bearing the hydroxyl group; d) Signals bearing the lactonic oxygen; e) Carbonyl carbons.

**6** were more or less similar to that of **C**, suggesting the same carbon framework, but that of **5** was considerably different.

Therefore, **4** and **6** are an epimeric pair of photocycloadducts related to **C**, but, **5** might be a *trans*-fused [2+2] cycloadduct. Their IR spectra all showed lactonic carbonyl stretching absorptions, $\nu_{C=O}$, ca. 1750-1760 cm$^{-1}$ which are parallel to that at 1745 cm$^{-1}$ observed with **C**,[8] and are, therefore, reasonable as α-hydroxyl γ-lactone derivatives.

Differentiation of the geometries of the 5/4/6-ring junctures of **4**-**6** was difficult particularly due to the small differences in the chemical shifts of the methine proton signals and the complex spin-coupling systems of the derivative. However, summations of the coupling constants ($\Sigma J$), obtainble from the width, of the methine proton signals provided a reliable information. Thus, as compiled in Table 2, the 270 MHz $^1$H NMR spectra of **4**-**6** allowed to assign the methine proton signals; the $\Sigma J$ of **4**, **6** and **C** were similar in the magnitude, but $\Sigma J$ of **C** fell in a different category, suggesting **4** and **6** were *cis* as same to **C**, but **5** should be *trans*-6/4-juncture. Other signals of **4**-**6** showed good accordance with the structures depicted.

In addition to these general features, the $^1$H NMR spectrum of **4** showed a methyl doublet

**Table 2** $^1$H NMR Spectral data of **4**-**6** and **C**.

| Comds. | **4** | **6** | **C** | **5** |
|---|---|---|---|---|
| δ(Me) | 1.39 | 1.32 | 1.34, 1.45 | 1.44 |
| δ(H-3) | 4.45 | 4.82 | | 4.75 |
| δ(H-3a) | 2.65 | 2.88 | 2.66 | 2.53 |
| δ(H-3b) | 1.90(ω=25)[a] | 2.07(ω=24) | 2.00(ω=24) | 2.37(ω=33) |
| δ(H-7a) | 2.47(ω=26) | 2.44(ω=24) | 2.41(ω=27) | 2.04(ω=27) |
| δ(OH) | 3.15 | 2.9 | 3.39 | 3.6 |
| δ($CH_2$) | 1.15(1H) | 1.15(1H) | 1.14(1H) | 1.2-1.45(3H) |
| | 1.35(1H) | 1.35(1H) | 1.30(1H) | 1.55-1.7(3H) |
| | 1.45-1.8(6H) | 1.5-1.8(6H) | 1.5-1.85(6H) | 1.7-1.9(2H)S |
| $J_{3-3a}$ | 0.0 | 4.5 | | 6.2 |
| $J_{3a-3b}$ | 7.7 | 8.8 | 8.0 | 6.2 |
| $J_{3b-7a}$ | 8.2 | 8 | 8 | 12 |
| $\Sigma J_{3b-4}$ | 9 | 7.5 | 8 | 15 |
| $\Sigma J_{7a-7}$ | 16 | 16 | 19 | 15 |

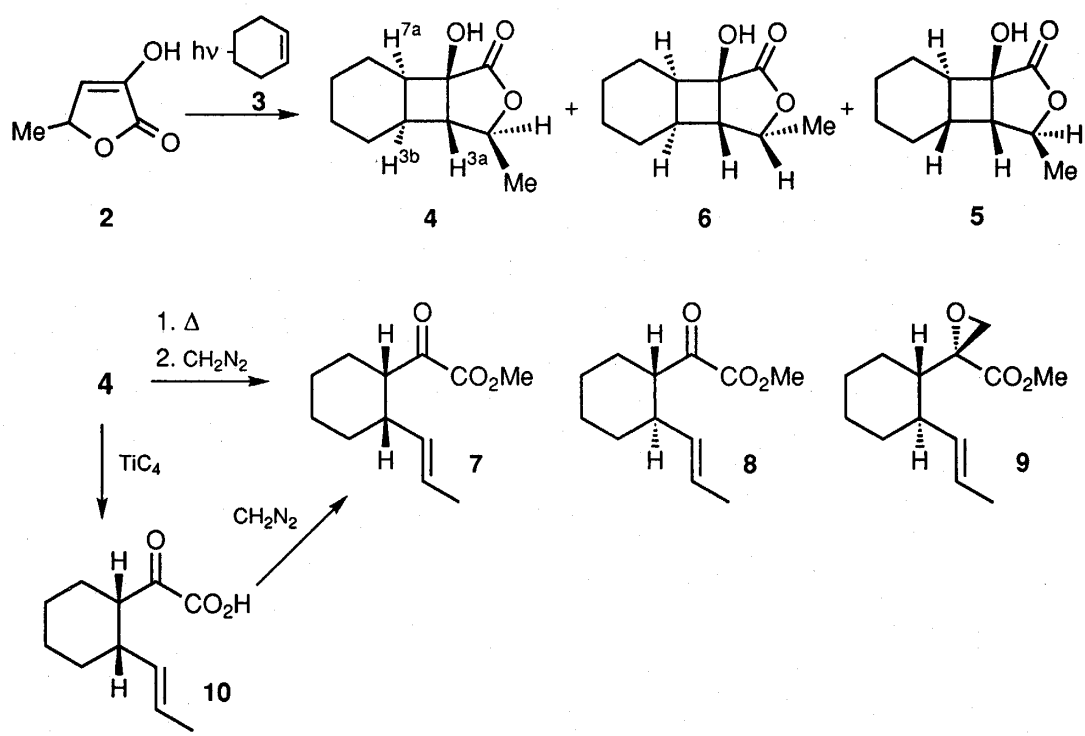
a) The symbol, ω, expresses broadness of the signal in Hz unit.

at $\delta=1.39$ and four methine proton signals, ascribable to H-3 ($\delta=4.45$), H-3a ($\delta=2.65$), H-3b ($\delta=1.91$), and H-7a ($\delta=2.47$), respectively. The coupling constant between H-3 and H-3a was zero, eliminating a *cis*-relationship for the protons. The stereochemistry was unambiguously assigned by the NOE experiments. Thus, an irradiation with the frequency of H-3 signal showed a positive NOE with H-3b but not much with H-3a signals, and an irradiation of H-3b signal caused an enhancement of H-7a signal which clearly indicates the *cis*-relationship for the ring juncture. Thus, **4** is the *cis-transoid-cis*-adduct of **2** and **3**, [3$\alpha$,3a$\alpha$,3b$\beta$,7a$\beta$,7b$\alpha$]-7b-hydroxy-3a,3b,4,5,6,7,7a,7b-octahydro-3-methylbenzo[3,4]cyclobuta[1,2-*c*]furan-1(3*H*)-one.

The **6** revealed similar features; thus in the $^1$H NMR spectrum, pronounced NOE's were observed between the secondary methyl signal at 1.32 and H-3b at 2.07, and the coupling constant, $J=4.5$ Hz, between H-3 and H-3a confirmed it to be epimeric at C-3 methyl with **4**. These led us to assign the structure of **6** to be [3$\alpha$,3a$\alpha$,3b$\beta$,7a$\alpha$,7b$\beta$]-7b-hydroxy-3a,3b,4,5,6,7,7a,7b-octahydro-3-methylbenzo[3,4]cyclobuta[1,2-*c*]furan-1(3*H*)-one.

The $^1$H NMR spectrum of the remaining product, **5**, showed, in addition to the $\Sigma J$, a dissimilarity in a criterion of chemical shifts with **C**, **4** or **6**, suggesting it to have a *trans*-fused 4/6-juncture. Again, the NOE in the $^1$H NMR spectrum was confirmative; when the signal of H-3 (at 4.75) was irradiated, clear NOE was observed with H-7a (at 2.04), and irradiation of H-3a signal (at 2.53) showed the NOE with the doublet methyl (at 1.44) but not with H-3. In addition, the coupling constant between H-7a and H-3b was estimated to be 12 Hz, respectively, indicating a *trans*-relationship for the ring juncture. These observations are only consistent with the structure depicted, *i.e.*, [3$\alpha$,3a$\alpha$,3b$\alpha$,7a$\beta$,7b$\alpha$]-7b-hydroxy-3a,3b,4,5,6,7,7a,7b-octahydro-3-methylbenzo[3,4]cyclobuta[1,2-*c*]furan-1(3*H*)-one.

Highly-strained four-membered rings of photocycloadducts **4**-**6** with a highly-reactive $\alpha$-hydroxy-$\gamma$-lactone moiety prompted us to examine thermolysis reactions, since the 1,3-dioxygenated function of the adducts might possibly cause a *retro*-Prins type fragmentation reaction to form olefin and oxalyl functions.




**Scheme 2**

After the adduct **4** was heated at 170°C for 14 h, the methylation of the mixture with diazomethane afforded isomeric esters **7** and **8** together with epoxy ester (**9**), which formed with an excess of diazomethane. From the spectroscopic analysis, **7** and **8** were identified as methyl *cis*- and *trans*-[2-(*E*-1-propenyl)cyclohexyl]glyoxylates. Their geometries were identified from the coupling patterns of methine protons; i.e., **7** had axial H-1 proton and equatorial H-2 proton. When **7** was heated for a longer time, yield of the more stable *trans*-isomer **8** was increased.

Since a Lewis acid is expected to coordinate with both hydroxyl and carbonyl oxygens, it seems to be worth examining the Lewis-acid catalyzed ring-opening reaction with **4**. Thus, when **4** was treated with titanium(IV) chloride, the sole product isolated in 39% yield was a *cis*-[2-*E*-1-propenyl)cyclohexyl]glyoxylic acid (**10**), which gave the methyl ester **7** by treatment with diazomethane. The $^1$H NMR spectrum of **10** showed signals ascribable to the methine protons at the ring-junctures at 2.97 and 3.46, whose coupling patterns closely resemble those of keto ester **7**. In addition, the olefin proton signals at $\delta=5.38$ and 5.53 showed mutual coupling constant, $J=15$ Hz, indicating the *trans*-geometry. No isomerized *trans*-disubstituted isomer was detected. Therefore, the formation of both isomers in pyrolytic conditions could be explained in terms of the thermal isomerization.

It should be mentioned that, in principle, the present ring-opening products could be obtained by sodium borohydride reduction and solvolysis of the *proto*-photocycloadducts of methyl 2,4-dioxopentanoate to olefins. However, such *proto*-products are not always available. Therefore, γ-valerolactone provides a direct entry to functionalized 1,2-disubstituted alicyclic systems. Another possibility, *retro*-benzilic acid rearrangement, was not the case as described, and the *retro*-benzilic acid rearrangement is unique for the *proro*-photocycloadducts of methyl 2,4-dioxoalkanoates to certain olefins.

## Experimental

Elemental analyses were done by Mrs. M. Miyazawa, of this Institute, Kyushu University. The $^1$H- and $^{13}$C NMR spectra were measured with a GSX-270H Spectrometer, Jeol, in $CDCl_3$. The infrared spectra were measured with an A102 Spectrophotometer, Jasco, and mass spectra were with a JMS-OISG-2 Spectrometer, Jeol.

**Photoreaction of 1 with 3.** The mixture of **1**[7] (578 mg), **3** (4.24 g) in an EtOAc solution (2 cm$^3$) was internally irradiated for 10 h by means of a 400-W high-pressure Hg lamp through an aqueous $NiSO_4$ solution (27.6 g/100 cm$^3$) filter. After evaporation of the volatile materials in vacuo, the residue thus obtained was chromatographed on silica gel to obtain **4** [colorless needles, mp 110-111°C, 259 mg, 35%. $^1$H NMR $\delta=1.15$ (1H, m), 1.33 (1H, m), 1.39 (3H, d, $J=6.5$ Hz), 1.45-1.8 (6H, m), 1.90 (1H, tm, $J=8$ Hz), 2.47 (1H, dm, $J=8$ Hz), 2.65 (1H, d, $J=8$ Hz), 3.15 (1H, s, OH), and 4.45 (1H, q, $J=6.5$ Hz). IR $\nu$: 3360, 2920, 1750, 1340, 1180, 1110, 950, and 650 cm$^{-1}$. MS *m/z* 196(M$^+$, 4), 178(17), 152(24),151(26), 123(12), 115 (100), and 82(17). Found: C, 67.63; H 7.94%. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H. 8.21%], **5** [colorless needles, mp 102-103°C, 104 mg, 15%. $^1$H NMR $\delta=1.25$-1.45 (3H, m), 1.45 (3H, d, $J=6$ Hz), 1.55-1.7 (3H, m), 1.7-1.9 (2H, m), 2.04 (1H, m), 2.37 (1H, m), 2.53 (1H, dd, $J=6.5$, 6 Hz), 3.6 (1H, s, OH), and 4.75 (1H, quint, $J=6$ Hz). IR $\nu$: 3400, 2940, 1750, 1450, 1380, 1210, and 1020 cm$^{-1}$. MS *m/z* 196(M$^+$, 1), 178(10), 151(41), 133(20), 123(63), 115(100), 81 (43), 69(35), and 67(51). Found: C, 67.32; H 8.11%. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.21%], and **6** [a colorless oil, 53 mg, 8%. $^1$H NMR $\delta=1.15$ (1H, m), 1.2-1.8 (7H, m), 1.32 (3H, d, $J=6.5$ Hz), 2.07 (1H, m), 2.44 (1H, dm, $J=8$ Hz), 2.88 (1H, dd, $J=8$, 4.5 Hz), 2.9 (1H, s, OH), and 4.82 (1H, qd, $J=6.5$, 4.5 Hz). MS *m/z* 196(M$^+$, 4), 178(25), 151(52), 133(14), 123(45), 115 (100), 82(55), 69(39), and 67(47). IR $\nu$: 3400, 2940, 1760, 1450, 1385, 1340, 1230, 1180, 1120,

1025, 990, 910, and 750 $cm^{-1}$. Found: $m/z$, 196.1103 ($M^+$). Calcd for $C_{11}H_{16}O_3$: M, 196.1099].

**Thermolysis of 4.** a) A toluene solution (2 $cm^3$) of **4** (162 mg) was heated in a sealed tube at 170°C for up to 20 h. After cooling, the mixture was treated with an ethereal $CH_2N_2$, and chromatographed on a silica-gel column. Early stage of the product mixture contained only **7** [a pale yellow oil, 30 mg, 28%. $^1H$ NMR $\delta$=1.20-1.90 (8H, m), 1.60 (3H, dd, $J$=7, 1 Hz), 2.83 (1H, m), 3.31 (1H, dt, $J$=9.5, 4. Hz), 3.84 (3H, s), 5.40 (1H, dq, $J$=16, 6 Hz), and 5.54 (1H, ddq, $J$=16, 8, 1 Hz). $^{13}C$ NMR $\delta$=18.0, 21.9, 23.0, 24.1, 31.1, 39.5, 49.1, 52.7, 126.9, 130. 0, 162.2, and 196.6] and the epimerized product, **8** [a colorless oil, 15 mg, 14%. $^1H$ NMR $\delta$= 1.20-1.90 (8H, m), 1.56 (3H, dd, $J$=6, 1 Hz), 2.21 (1H, m), 3.10 (1H, td, $J$=12, 3 Hz), 3.83 (3H, s), 5.24 (1H, ddq, $J$=16, 9, 1 Hz), and 5.39 (1H, dqm, $J$=16, 6 Hz). $^{13}C$ NMR $\delta$=17.8, 25.1, 25.3, 28.2, 32.8, 43.4, 50.8, 52.8, 125.9, 133.6, 162.0, and 197.7. IR $\nu$: 2930, 1730, 1450, 1270, 1230, 1060, and 970 $cm^{-1}$. MS $m/z$ 210($M^+$, 6), 192(39), 151(77), 133(11), 123(100), 81(44), and 67 (24)], and **9** [a colorless oil, 14 mg, 12%. $^1H$ NMR $\delta$=118 (4H, m), 1.59 (3H, dd, $J$=6, 1 Hz), 1.70 (4H, m), 2.25 (1H, qd, $J$=9, 3 Hz), 2.86 (2H, s), 3.71 (3H, s), 5.22 (1H, ddq, $J$=16, 9, 1 Hz), and 5.53 (1H, dq, $J$=16, 6 Hz). $^{13}C$ NMR $\delta$=17.9, 25.5, 25.7, 27.4, 33.5, 43.8, 43.9, 52.2, 52. 3, 59.4, 125.6, 134.6, and 171.3. IR $\nu$: 2930, 1740, 1440, 1280, 1230, 1160, 1100, 970, and 750 $cm^{-1}$].

**Thermolysis of 5.** a) A toluene solution (2 $cm^3$) of **5** (25 mg) was heated in a sealed tube at 170°C for up to 24 h. After cooling, the mixture was treated with an ethereal $CH_2N_2$, and chromatographed on a silica-gel column to give **9** [a colorless oil, 9 mg, 34%].

**$TiCl_4$-Treatment of 4.** An anhydrous $CH_2Cl_2$ solution (5 $cm^3$) of **4** (52 mg) was treated with $TiCl_4$ (583 mg) at room temperature for 14 h. The mixture was then neutralized with aq. $NaHCO_3$, acidified back with dil HCl, and extracted with $CHCl_3$. Organic solvent was evaporated in vacuo, and the residue thus obtained was chromatographed on a silica-gel column to give **10** [a pale yellow oil, 23 mg, 39%. $^1H$ NMR $\delta$=1.25-1.83 (8H, m), 1.59 (3H, dd $J$=6, 1 Hz), 3.48 (1H, dq, $J$=8, 4 Hz), 3.47 (1H, dt, $J$=9, 4 Hz), 5.40 (1H, dq, 15, 6 Hz), 5.49 (1H, ddq, $J$=15, 8, 1 Hz), and 6.12 (1H, br s)], which was characterized as the methyl ester, **7**.

## References.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