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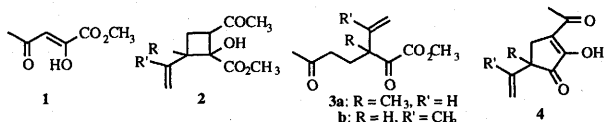
Photoaddition Reaction of Methyl 2,4-Dioxopentanoate with Chloroprene

Toshihide Hatsui, Tomokazu Hashiguchi*, and Hitoshi Takeshita†

The photoaddition reaction of methyl 2,4-dioxopentanoate with chloroprene gave two de Mayo type adducts, methyl 3-(1-chlorovinyl)-2,6-dioxoheptanoate and methyl 3-chloro-2,6-dioxo-3-vinylheptanoate. No regio isomers, 4-substituted esters, were observed. The photoadducts were converted to cyclohexenones and the selectivity of photoaddition was discussed.

Introduction

The photoaddition reaction of methyl 2,4-dioxopentanoate (**1**) occurs with high regioselectivity. One peculiar feature is the excellent reactivity with conjugated dienes,¹⁻⁵ which are known as quencher of most α,β -unsaturated ketones. The intermediate photocycloadducts (cyclobutanols, **2**) provide 2,6-dioxoheptanoate (**3**) via retro-aldol reaction (de Mayo reaction), or 3-acetylcyclopentane-1,2-dione (**4**) via retro-benzilic acid rearrangement.^{4,5} As a versatile C5-synthon for preparing cyclohexane or cyclopentane ring, **1** has been utilized in natural product syntheses, e.g., terpenoids having six-membered ring,^{1,6} or five-membered ring² were synthesized from **3**. Sesquiterpenoids having spiro[4.5]nonane skeleton were also synthesized via the latter reaction.⁵



The reaction of **1** with isoprene and other dienes occurs smoothly and regioselectively. Alkenyl groups are observed in most case at the 3-position of the product **3**, e.g., **3a** and **3b** from isoprene. But until now no reaction of **1** with heteroatom substituted alkadienes have been reported. Here the reaction with chloroprene (2-chloro-1,3-butadiene) is examined to obtain an information of the effect of heteroatom substituent on the reactivity.

Results and Discussion

The ethyl acetate solution of **1** and chloroprene was irradiated by means of 400 W-high pressure mercury lamp at 5 °C for 6 h. The removal of the solvent and chloroprene gave **5** (14%) and **6** (13%) together with gummy material. No product having vinyl group at 4-position was obtained.

The structure of **5** was elucidated from its ¹³C-NMR

spectrum showing three carbonyl carbons at δ 161.0, 190.5 and 207.5, and ¹H-NMR spectrum where protons of vinylidene group were observed at δ 5.42 and 5.50 and methine proton at δ 4.25 as dd having 8 and 6 Hz of *J* value. On the other hand, the ¹H-NMR spectrum of **6** exhibited three olefinic protons ascribable to vinyl group at δ 5.46 (d, *J* = 11 Hz), 5.55 (d, *J* = 17 Hz) and 6.06 (dd, *J* = 17, 11 Hz), and the ¹³C-NMR spectrum at δ 162.1, 189.5 and 206.7.

Because of the formation of large amount of gum, exact yield of **5** and **6** or ratio of **5/6** was not obtained. Addition of 2,4,6-tri-*t*-butylphenol or di-*t*-butyl-*p*-cresol as radical inhibitor had no effect in preventing the formation of gum. Next, the aldol reaction of the crude reaction mixture was expected to make the separation of the products easier.

The photoreaction mixture, after removing roughly most part of polymer by silica-gel column chromatography, was heated in benzene with the Dean-Stark dehydrator, and was separated to give **6** (20%), **7** (8%), **8** (5%), **9** (13%), and **10** (16%). The products **7** and **8** were considered to be derived from **6**, and **9** and **10** were from **5**. Therefore the selectivity of the reaction (**5/6**) is = 29/33.

The structure of **7** was deduced to the cyclohexanone produced by the aldol reaction of **5**. It showed protons due to a vinyl group at δ 5.40 (d, *J* = 10 Hz), 5.53 (d, *J* = 17 Hz) and 6.17 (dd, *J* = 17, 10 Hz), an isolated methylene group at δ 2.48 and 3.30, methoxycarbonyl group at δ 3.85, and no acetyl group in its ¹H-NMR spectrum. In the ¹³C-NMR spectrum two olefinic and two carbonyl carbons, one of which was esteric and the other was ketonic, were observed at δ 118.2, 136.0, 171.7 and 205.7. An sp³ carbon observed at δ 80.9 supported the structure.

Contrary to this, the ¹H-NMR spectrum of **8** exhibited three aromatic protons due to 1,2,4-trisubstituted benzene derivative. Further, the existence of ethoxy group was suggested in addition to methoxycarbonyl group and vinyl group. Thus the structure of 5-ethoxy-2-vinylbenzoate was obtained. IR and Mass spectra also supported this aromatized structure. The ethoxy group must be derived

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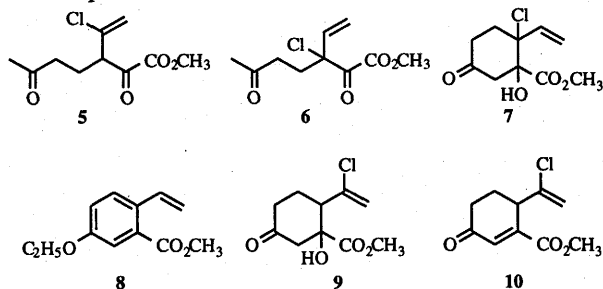
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from ethyl acetate via hemiacetal, and hydrochloric acid and/or silica catalyzed the reaction.

The $^1\text{H-NMR}$ spectrum of **9** was very similar to that of **7** except that the vinylidene group was observed instead of vinyl group. The $^{13}\text{C-NMR}$ and IR spectra were consistent with this structure.

The structure of **10** was concluded to be the dehydrated product of **9**. In stead of isolated methylene group of **9**, an olefinic proton was observed at δ 6.83.



In conclusion the photoreaction of **1** with chloroprene proceeds without difficulty and gives two de Mayo type adducts. Although the gummy material was produced during the reaction, yield of the products was fairly good, and little of **1** was lost as polymerized material; that means the cycloaddition of **1** was an independent process of the polymerization of chloroprene, and was not inhibited by the polymerization. The regio-selectivity of the reaction was excellent, but the site-selectivity between two double bonds was low. Considering the ratio of **3a/3b** in the reaction with isoprene is ca. 2, the directing effect of chlorine was too small.

As a synthetic tool, the photoreaction with such heteroatom substituted olefins must have more interest as synthetic reaction, for example, as an equivalent of acetyl group or allenic bond.

Experimental

All solvents were used after distillation of the commercial EP grade products. Chromatographic separation was performed on silica-gel column (Wako C-200), or HPLC (Waters). The NMR spectra were measured in chloroform-*d* solution with the Jeol GSX-270H FT-NMR spectrometer at 270 MHz for ^1H and 67.8 MHz for ^{13}C and recorded by δ scale using tetramethylsilane as standard. Digital resolutions were 0.4 Hz for ^1H - and 1 Hz for ^{13}C -spectra. IR spectra were measured with JASCO A102 spectrophotometer as CCl_4 solution. Mass spectra were measured with Jeol 01SG-2 spectrometer.

Photo-reaction of 1: The mixture of **1** (500 mg) and 30 % toluene solution of chloroprene was irradiated by means of 400 W-high pressure mercury lamp at 5 $^\circ\text{C}$ for 6 h. After the removal of the solvent and chloroprene under reduced pressure, residual gummy material was extracted with ether and chromatographed with benzene-ether mixture (3 : 1) to give **5** (115 mg, 14 %. $^1\text{H-NMR}$ δ 2.15 (3H, s), 2.30-2.54 (4H, m), 3.88 (3H, s), 4.25 (1H, dd, J =

8, 6 Hz), 5.42 (1H, d, J =2 Hz), and 5.50 (1H, d, J =2 Hz); $^{13}\text{C-NMR}$ δ 21.8, 39.6, 52.9, 54.1, 54.9, 118.7, 136.4, 161.0, 190.5, and 207.5; IR $\nu(\text{NaCl})$ 2960, 1720, 1625, 1435, 1360, 1260, 1240, 1165, 1095, 1045, 985, and 890 cm^{-1} . Exact Mass: m/z 232.0490 (Calcd for $\text{C}_{10}\text{H}_{13}\text{O}_4^{35}\text{Cl}$ 232.0501), 234.0484 (Calcd for $\text{C}_{10}\text{H}_{13}\text{O}_4^{37}\text{Cl}$ 234.04872)) and **6** (101 mg, 13 %. $^1\text{H-NMR}$ δ 2.17 (3H, s), 2.35-2.65 (4H, m), 3.89 (3H, s), 5.46 (1H, d, J =11 Hz), 5.55 (1H, d, J =17 Hz), and 6.06 (1H, dd, J =17, 11 Hz); $^{13}\text{C-NMR}$ δ 30.0, 32.1, 38.3, 52.9, 75.5, 119.8, 134.6, 162.1, 189.5, 206.7; IR $\nu(\text{NaCl})$ 2960, 1720, 1435, 1405, 1365, 1280, 1160, 1100, 1050, 980, 935, and 910 cm^{-1} . Exact Mass: m/z 232.0494 (Calcd for $\text{C}_{10}\text{H}_{13}\text{O}_4^{35}\text{Cl}$ 232.0501), 234.0489 (Calcd for $\text{C}_{10}\text{H}_{13}\text{O}_4^{37}\text{Cl}$ 234.0472)) as yellowish oils.

Acidic Cyclization of Crude Photoproduct: After the irradiation of **1** as above, the reaction mixture was passed through a short silica-gel column to eliminate most part of gum and chromatographed with benzene-ether as eluent. The obtained elute was collected and the volatile materials was eliminated in vacuum. The residue was transferred into a flask equipped with the Dean-Stark dehydrator, added a small amount of *p*-toluenesulfonic acid and refluxed for 15 h. After removing the solvent chromatographic separation on silica-gel using hexane/ethyl acetate as eluent gave **6** (155 mg, 20 %), **8** (38 mg, 5 %. $^1\text{H-NMR}$ δ 1.42 (3H, t, J =7 Hz), 3.57 (1H, m), 3.90 (3H, s), 4.07 (2H, q, J =7 Hz), 5.25 (1H, d, J =11 Hz), and 5.55 (1H, d, J =17 Hz), 7.02 (1H, dd, J =17, 11 Hz), 7.02 (1H, dd, J =9, 3 Hz), 7.38 (1H, d, J =3 Hz), 7.50 (1H, J =9 Hz); $^{13}\text{C-NMR}$ δ 14.7, 52.1, 63.7, 114.7, 115.2, 119.1, 128.4, 129.5, 132.0, 135.2, 158.1, and 167.8; IR $\nu(\text{NaCl})$ 3080, 290, 1720, 1600, 1560, 1475, 1435, 1390, 1285, 1250, 1215, 1135, 1110, 1065, 1045, 980, 905, 830, and 790 cm^{-1} . MS: m/z 206(100), 177(18), 175(18), 163(31), 147(41), 91(26), and 43(17). Exact Mass: m/z 206.0942 (Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$ 206.0942)), **7** (65 mg, 8 %. $^1\text{H-NMR}$ δ 2.49-2.54 (4H, m), 2.48 (d, J =15 Hz), 3.30 (d, J =15 Hz), 3.75 (1H, br s), 3.85 (3H, s), 5.40 (1H, d, J =10 Hz), 5.53 (1H, d, J =17 Hz), and 6.17 (1H, dd, J =17, 10 Hz), 7.02 (1H, dd, J =17, 11 Hz); $^{13}\text{C-NMR}$ δ 33.7, 37.1, 46.6, 53.4, 70.8, 80.9, 118.2, 136.0, 171.7, and 205.7; IR $\nu(\text{NaCl})$ 3500, 2950, 1720, 1435, 1360, 1245, 1120, 1080, 980, 935, and 820 cm^{-1} ; MS: m/z 234(3), 232(7), 214(7), 197(14), 173(14), 130(83), 102(66), 88(49), 67(42), and 43(100). Exact Mass: m/z 232.0510 (Calcd for $\text{C}_{10}\text{H}_{13}\text{O}_4^{35}\text{Cl}$ 232.0502), 234.0460 (Calcd for $\text{C}_{10}\text{H}_{13}\text{O}_4^{37}\text{Cl}$ 234.0472)), **10** (128 mg, 16 %. $^1\text{H-NMR}$ δ 2.20-2.57 (4H, m), 3.82 (1H, m), 3.85 (3H, s), 5.15 (1H, dd, J =2, 1 Hz), 5.38 (1H, d, J =2 Hz), and 6.83 (1H, s); $^{13}\text{C-NMR}$ δ 25.8, 33.4, 42.7, 52.9, 114.8, 134.3, 140.3, 146.5, 165.9, and 199.2; IR $\nu(\text{NaCl})$ 2950, 1715, 1440, and 1240 cm^{-1} . MS: m/z 216(3), 214(9), 200(18), 179(100), 158(10), and 43(13). Exact Mass: m/z 214.0400 (Calcd for $\text{C}_{10}\text{H}_{11}\text{O}_3^{35}\text{Cl}$ 214.0396), 216.0374 (Calcd for $\text{C}_{10}\text{H}_{11}\text{O}_3^{37}\text{Cl}$ 216.0367)), and **9** (105 mg, 13 %. $^1\text{H-NMR}$ δ 2.49-2.54 (4H, m), 2.50 (d, J =15 Hz), and

2.90 (d, $J=15$ Hz), 3.18 (1H, dd, $J=12, 4$ Hz), 3.84 (3H, s), 5.35 (1H, d, $J=2$ Hz), and 5.37 (1H, d, $J=2$ Hz); $^{13}\text{C-NMR}$ δ 26.2, 40.2, 50.3, 51.1, 53.3, 78.0, 115.9, 140.0, 173.4, and 205.8; IR $\nu(\text{NaCl})$ 3540, 2950, 1735, 1630, 1440, 1265, 1235, 1110, 985, 950, and 890 cm^{-1} ; MS: m/z 234(16), 232(49), 173(28), 153(53), 131(100), 130(62), 103(59), 102(82), 88(66), 53(43), and 43(97). Exact Mass: m/z 232.0515 (Calcd for $\text{C}_{10}\text{H}_{13}\text{O}_4^{35}\text{Cl}$ 232.0502), 234.0485 (Calcd for $\text{C}_{10}\text{H}_{13}\text{O}_4^{37}\text{Cl}$ 234.0472)) as yellowish oils.

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