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Communications to the Editor

New Type of Photochemical Carbon Skeletal Rearrangement: Transformation of α,*β*-Unsaturated Carbonyl to 1,4-Dicarbonyl Compounds

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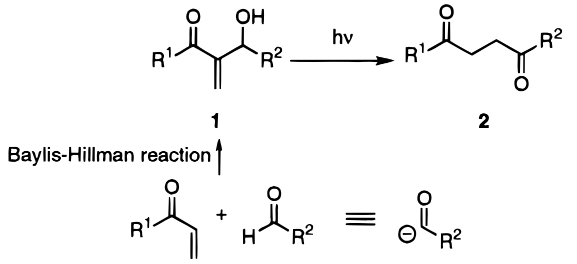
Reactions of carbonyl compounds in photoexcited states have attracted much attention, and hence, the precedented examples are well classified.[1] However, we herein report a new type of photochemical carbon skeletal rearrangement of α-hydroxymethylated α,*β*-unsaturated carbonyl compounds (**1**). Molecules of type **1** selectively rearrange to 1,4-dicarbonyl compounds **2**, which are highly desirable intermediates for the synthesis of cyclopentenones and five-membered heterocycles[2] (Scheme 1). The substrates **1** were easily prepared by the Baylis−Hillman reaction of α,*β*-unsaturated carbonyl compounds with aldehydes.[3,4] Therefore, the overall transformation can be regarded as 1,4-addition of acyl anions derived from the aldehydes to the starting α,*β*-unsaturated carbonyl compounds.[5] This new and synthetically interesting pathway to 1,4-dicarbonyl compounds is the subject of this paper.

Scheme 1



Scheme 2

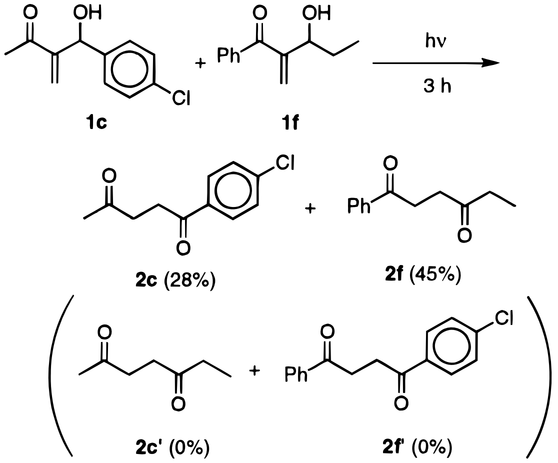


Table 1. Rearrangement of α,*β*-Unsaturated Carbonyl Compounds **1**[a]

substrate **1**	R^1	R^2	**2** (% yield)
a	Me	Ph	53
b		*p*-MeO-Ph	41
c		*p*-Cl-Ph	66
d	Ph	Ph	54
e		Me	62[b]
f		Et	50[c]

[a] Irradiated for 6 h in 0.01 M benzene solution with high-pressure mercury lamp. [b] Irradiated for 4 h. [c] Irradiated for 2 h.

The enones **1** was irradiated with a high-pressure mercury lamp, and the 1,4-dicarbonyl compounds **2** were isolated simply by silica gel chromatography through carbon skeletal rearrangement with almost complete consumption of **1** (<8% recovery).[6] The present carbon skeletal rearrangement can be applied to a variety of alkyl- and aryl-substituted ones (**1**) (Table 1). The quantum yields with **1a** or **1e** at 313 nm using valerophenone as an actinometer[7] were calculated to be ca. 0.1. This rearrangement can be quenched by a triplet quencher, NaI.[8] The substrates without hydroxy group at the allylic position such as 2-methyl-1-phenyl-2-penten-1-one did not give any rearrangement product **2** under the same reaction conditions. This suggests the requirement for the hydroxy group to weaken the allylic C−H bond.

To clarify the intra- or intermolecular courses, the crossover experiment was examined between **1c** and **1f** (Scheme 2). However, bimolecular products (**2c**′ or **2f**′) were not observed at all, thus indicating that this reaction proceeds in an intramolecular fashion.

To gain a deeper insight into the mechanism, we next examined the methyl- and silyl-protected substrates **3c** and **5a**, respectively (Scheme 3). After irradiation of **3c** for 6 h, the rearrangement product **4c**[9] and the resultant 1,4-dicarbonyl compound **2c** were isolated by silica gel chromatography in 68% combined yield.

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[1] (a) Special issue on photochemical strategy in organic synthesis: Ramamurthy, V., Turro, N. J., Eds. *Chem. Rev.* **1993**, *93* (1). (b) Mattay, J.; Griesbeck, A. G. *Photochemical Key Steps in Organic Synthesis*; VCH: New York, 1994. (c) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233. (d) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; Blackwell Scientific: Oxford, 1991. (e) Wagner, P. J.; Park, B.-S. *Org. Photochem.* **1991**, *11*, 227. (f) Porco, J. A., Jr.; Schreiber, S. L. *Comprehensive Organic Synthesis*; Pergamon: London, 1991; Vol. 5, p 151. (g) Demuth, M.; Mikhail, G. *Synthesis* **1989**, 145. (h) Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453. (i) *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3. (j) Koizumi, M.; Kato, S.; Mataga, N.; Matsuura, T.; Usui, Y. *Photosensitized Reactions*; Kagakudojin: Kyoto, 1978.

[2] (a) Texier-Boullet, F.; Klein, B.; Hamelin, J. *Synthesis* **1986**, 409. (b) Trost, B. M. *Chem. Soc. Rev.* **1982**, *11*, 141.

[3] (a) Basavaiah, D.; Rao, P. D.; Hyma, R. S. *Tetrahedron* **1996**, *52*, 8001. (b) Drewes, S. E.; Roos, G. H. P. *Tetrahedron* **1988**, *44*, 4653.

[4] Procedure for the Baylis−Hillman reaction as follows: To a solution of α,*β*-unsaturated carbonyl compound (methyl vinyl ketone or phenyl vinyl ketone) and aldehyde (1−2 equiv) in THF was added DABCO (15 mol %) and stirred for 7−10 days at room temperature. The reaction mixture was poured into saturated NH_4Cl solution. Standard workup followed by silica−gel chromatography afforded the product (**1**) in 15−86% yield.

[5] For reviews on the synthesis of 1,4-dicarbonyl compounds, see: (a) Stetter, H.; Kuhlmann, H. *Org. React.* **1991**, *40*, 407. (b) Miyakoshi, T. *Org. Prep. Proc. Int.* **1989**, *21*, 659. (c) Reissig, H.-U. *Top. Curr. Chem.* **1986**, *144*, 73. (d) Via 1,4-addition reaction of radicals: Vassen, R.; Runsink, J.; Scharf, H.-D. *Chem. Ber.* **1986**, *119*, 3492 and references therein.

[6] When **1d**, **1e** and **1f** were used, 1,3-dicarbonyl compounds were obtained in about 10−26% yields by olefin isomerization. No other byproduct was observed in the crude ^1H NMR spectra.

[7] Lewis, F. D.; Hilliard, T. A. *J. Am. Chem. Soc.* **1972**, *94*, 3852.

[8] Fukuzumi, S.; Kuroda, S.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305.

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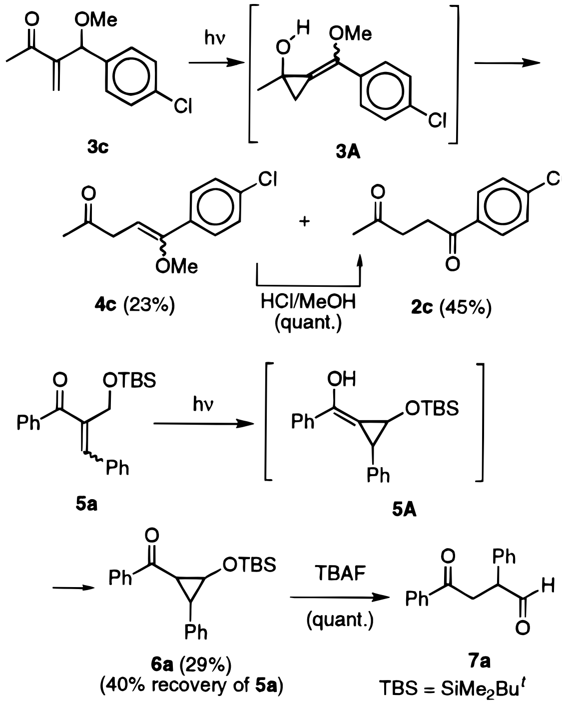
Scheme 3

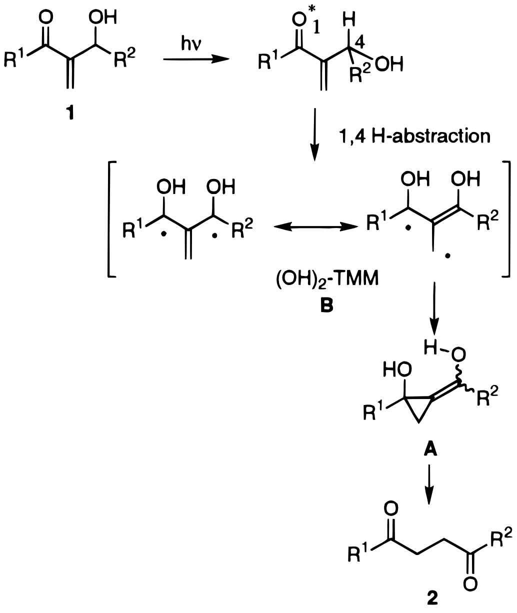


When **5a** was irradiated for 5 h, siloxycyclopropane **6a**[10] was obtained. Indeed, **6a** gave the 1,4-dicarbonyl compound **7a**[11] in quantitative yield after treatment with tetrabutylammonium fluoride (TBAF).

On the basis of these results, the hydroxymethylenecyclopropanol (**A**) is shown as the common intermediate as follows (Scheme 4): (1) rarely precedented 1,4-hydrogen abstraction[12] takes place by the assistance of allylic hydroxy group in the photoexcited state of carbonyl compounds;[13] (2) cyclopropanol (**A**) is formed through coupling of the dihydroxytrimethylenemethane[14] (**B**) thus generated; (3) The rearranged products **2** are eventually obtained by double tautomerization of enol and cyclopropanol portions in **A**.

In summary, we have reported the new type of photochemical carbon skeletal rearrangement of α,β-unsaturated carbonyl compounds to 1,4-dicarbonyl compounds. This transformation can be regarded as the consequence of high level of control over photochemical pathways by the introduction of an allylic alcohol *"functionality"* in the carbonyl substrates.

Scheme 4



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Supporting Information Available: Experimental procedure of photoirradiation, ^{1}H and ^{13}C NMR data of products and the quantum yield, and kinetic isotope effect determination (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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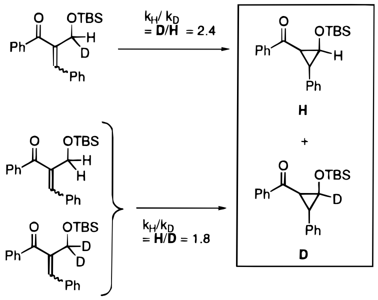
[9] ^{1}H NMR (CDCl$_3$): δ 2.12 (s, 3H), 3.16 (d, $J = 7.7$ Hz, 2H), 3.70 (s, 3H), 4.90 (t, $J = 7.7$ Hz, 1H), 7.27 (dm, $J = 8.9$ Hz, 2H), 7.35 (dm, $J = 8.9$ Hz, 2H). IR (neat): 2906, 1717, 1491, 1375, 1359, 1160, 1125, 1093, 1015, 839 cm^{-1}.

[10] ^{1}H NMR (CDCl$_3$) δ 0.17 (s, 6H), 0.93 (s, 9H), 3.10 (dd, $J = 4.8$, 10.6 Hz, 1H), 3.26 (dd, $J = 3.3$, 10.6 Hz, 1H), 4.63 (dd, $J = 3.3$, 4.8 Hz, 1H), 7.10−7.30 (m, 5H), 7.42 (tm, $J = 7.8$ Hz, 2H), 7.52 (tm, $J = 6.9$ Hz, 1H), 7.91 (dm, $J = 7.2$ Hz, 2H). ^{13}C NMR (CDCl$_3$): δ −4.8, 18.1, 25.9, 36.3 ($J_{\mathrm{C-H}} = 162.6$ Hz), 39.5 ($J_{\mathrm{C-H}} = 158.9$ Hz), 59.4 ($J_{\mathrm{C-H}} = 182.0$ Hz), 126.9, 128.0, 128.2, 128.6, 129.1, 132.7, 134.6, 138.5, 195.0.

[11] Araki, S.; Butsugan, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 727.

[12] The rarity of 1,4-hydrogen abstraction is generally believed to reflect a geometric problem. (a) Cyclic system in a favorable geometry for 1,4-hydrogen abstraction: Scheffer, J. R.; Dzakpasu, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 2164. (b) For a similar reaction of 3-methylene-4-phenoxy-2-butanone leading to methyl phenoxycyclopropoxyl ketone (17% yield), see: Cormier. R. A.; Schreiber, W. L.; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 4873.

[13] Indeed, the significant levels of intra- and intermolecular kinetic isotope effects ($k_{\mathrm{H}}/k_{\mathrm{D}} = 2.4$ and 1.8, respectively) were observed.



[14] For reviews on trimethylenemethane, see: (a) Little, R. D. *Chem. Rev.* **1986**, *86*, 875. (b) *Diradical*; Borden, W. T., Ed.; Wiley: New York, 1982. (c) Berson, J. A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, p 334. (d) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. (e) Doering, W. E.; Roth, H. D. *Tetrahedron* **1970**, *26*, 2825.