Photoreaction of *o*-Acylstyrenes: Formation of Benzo-Fused 8-Oxabicyclo[3.2.1]octanes

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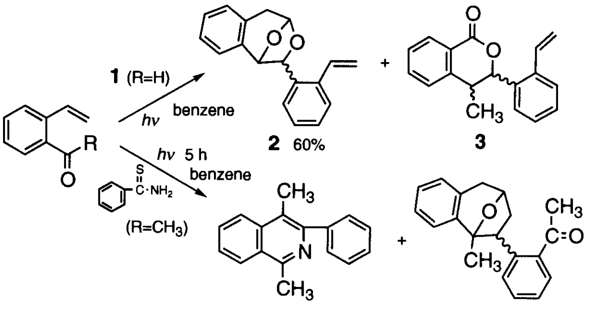
Irradiation of *o*-acylstyrenes affords a pair of stereoisomers of photodimerized benzo-fused oxygen-bridged compounds, 8-oxabicyclo[3.2.1]octane derivatives.

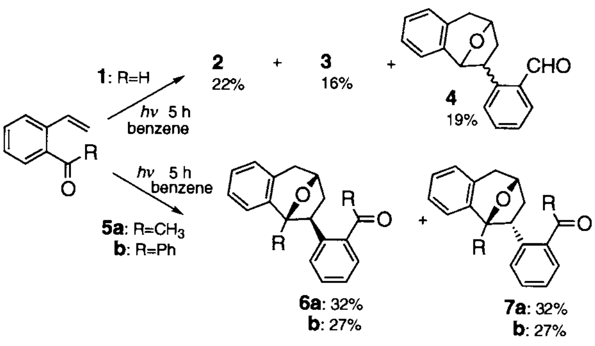
In the context of extensive investigation in the photochemistry of carbonyl compounds and styrenes, the photochemistry of *o*-acylstyrenes, which consist of a carbonyl group and a styrene moiety in conjugation system, also is a subject of continuing interest, because it is expected that some novel photoreactions ensue. Indeed, it is reported that on irradiation of *o*-formylstyrene (**1**), a novel photoreaction occurred, and consequently benzo-fused oxygen-bridged compound, 6,8-dioxabicyclooctane derivative (**2**) was obtained accompanied by a small amount of isocoumarin (**3**) (scheme 1).[1] During the course of our systematic study of the photochemistry of the arenecarbothioamide–alkene system,[2–6] we also observed the formation of oxygen-bridged compound 8-oxabicylooctane as a small amount of by-product in the photoreaction of benzenecarbothioamide with *o*-acylstyrenes (Scheme 1).



Scheme 1.

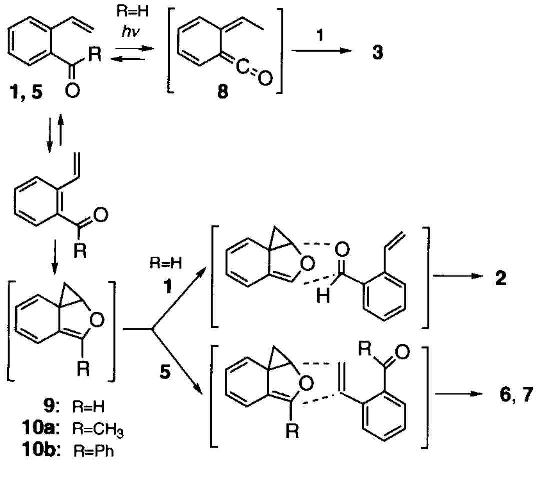
In order to investigate the pathway of formation of oxygen-bridged compounds, photoreaction of *o*-acylstyrenes was carried out in benzene using a 1 kW high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere. Irradiation of **1** for 5 h gave 6,8-dioxabicyclo[3.2.1]octane derivative **2**, isocoumarin derivative **3**, and 8-oxabicyclo-[3.2.1]octane derivative (**4**),[7] in 22, 16, and 19% yields, respectively (Scheme 2). Interestingly, this product distribution was different from that of Kessar and Mankotia, in which compound **2** is obtained in 60% yield accompanied by a small amount of **3**.[1] Similarly, photoreaction of *o*-acylstyrenes (**5a**: R = CH_3, **5b**: R = Ph) was examined. 8-Oxabicyclo[3.2.1]octanes (**6**, **7**) were effectively obtained as a pair of stereoisomers (Scheme 2). Structural assignments for **6** and **7** were made on the basis of spectral data and elemental analyses.[8]

As for a pathway in the photoreaction of *o*-formylstyrene, Kessar and Mankotia[1] proposed two pathways via a ketene methide (**8**) and an oxatricyclotriene intermediate (**9**) as shown in Scheme 3. The ketene methide intermediate **8**, which is generated through initial 1,5-hydrogen shift from formyl hydrogen to a vinyl terminus,[9] undergoes [4 + 2] addition with a carbonyl in **1** to give isocoumarin **3**.[10] The other intermediate oxatricyclotriene **9**, which arises from an initial [$\pi^2_a + \pi^4_s$] rearrangement,[1,11] reacts intermolecularly with a carbonyl group in **1** to lead dioxabicyclooctane **2**.



Scheme 2.

The generation of ketene methide **8** is possible only for *o*-formylstyrene. In fact, in the cases of **5a** and **5b**, no isocoumarin was obtained, and only oxygen-bridged compounds were obtained. When an acyl group is an acetyl and a benzoyl, oxatricyclotriene intermediate **10** was exclusively generated, and subsequently underwent addition with a vinyl moiety in a second substrate **5** to give 8-oxabicyclo[3.2.1]octanes **6**, **7,** while 6,8-dioxabicyclo[3.2.1]octane derivative was not isolated (Scheme 3). Probably, this selective addition of vinyl moiety is due to a steric factor of an acyl group, since in photoreaction of **1**, **2** and **4** were formed almost equal amounts.



Scheme 3.

In conclusion, photoreaction of *o*-acylstyrenes seems to proceed through two fold photoreactions such as rearrangement to oxatricyclotriene followed by addition of a second substrate, i.e., photodimerization. Such an unusual photodimerization is a first example and the new photodimerization reaction may be used as a tool for the synthesis of novel benzo-fused oxygen-bridged compounds. The synthetic application of the novel photodimerization is underway.

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References and Notes

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7 Compd **4**: Colorless plates; mp 117–118.5 °C; IR (Nujol) 1670 cm^{-1}, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.04 (2H, m), 2.62 (1H, m), 2.68 (1H, d, J= 16.6 Hz), 3.46 (1H, dd, J= 4.4, 16.1 Hz), 4.94 (2H, m), 6.03 (1H, d, J= 7.3 Hz), 6.54 (1H, d, J= 7.8 Hz), 6.70–7.78 (6H, m), 10.37 (1H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 34.8 (t), 37.1 (t), 48.7 (d), 74.9 (d), 80.5 (d), 125.0 (d), 125.9 (d), 126.7 (d), 127.2 (d), 128.0 (d), 129.1 (d), 131.9 (d), 133.0 (s), 133.1 (d), 134.6 (s), 136.5 (s), 140.2 (s), 192.9 (d); MS m/z: 264 (M$^+$); Anal. Calcd for $C_{19}H_{16}O_2$: C, 81.79; H, 6.10%. Found: C, 82.02; H, 6.18%.

8 The stereochemistry of **6a** and **7a** was assigned on the basis of their ^{1}H-NMR spectra by considering the anisotropic shielding effects between the two phenyl rings. Compd **6a**: Colorless plates; mp 141–143 °C; IR (Nujol) 1670 cm^{-1}, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.28 (3H, s), 2.20–2.38 (2H, m), 2.56 (3H, s), 3.46 (2H, dd, J= 4.4, 16.1 Hz), 3.98 (1H, m) 4.94 (1H, m). 7.09–7.61 (8H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 20.3 (q), 30.3 (q), 37.3 (t), 40.5 (t), 52.5 (d), 73.6 (d), 84.5 (s), 124.0 (d), 125.9 (d), 126.3 (d), 126.7 (d), 127.6 (d), 129.2 (d), 129.7 (d), 131.3 (d), 137.1 (s), 139.1 (s), 143.7 (s), 144.9 (s), 202.7 (s); MS m/z: 292 (M$^+$); Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90%. Found: C, 82.11; H, 6.98%. Compd **7a**: Colorless oil; IR (Nujol) 1670 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.54 (3H, s), 1.86 (1H, m), 2.61 (3H, s), 2.69 (1H, d, J=16.1 Hz), 2.80 (1H, m), 3.50 (1H, dd, J= 4.9, 16.1 Hz), 4.06 (1H, t, J=10.3 Hz), 4.70 (1H, m), 6.07 (1H, d, J=7.8 Hz), 6.35 (1H, d, J= 7.3 Hz), 6.88–7.49 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 20.3 (q), 30.3 (q), 37.3 (t), 40.5 (t), 52.5 (d), 73.6 (d), 84.5 (s), 124.0 (d), 125.9 (d), 126.3 (d), 126.7 (d), 127.6 (d), 129.2 (d), 129.7 (d), 131.3 (d), 137.1 (s), 139 (s), 143.7 (s), 144.9 (s), 202.7 (s); MS m/z 292(M$^+$); Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90%. Found: C, 82.01; H, 6.77%.

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