Photoinduced 1,5-Acyl Shift of 3-Acylated 3-Methyloxepin-2(3*H*)-ones

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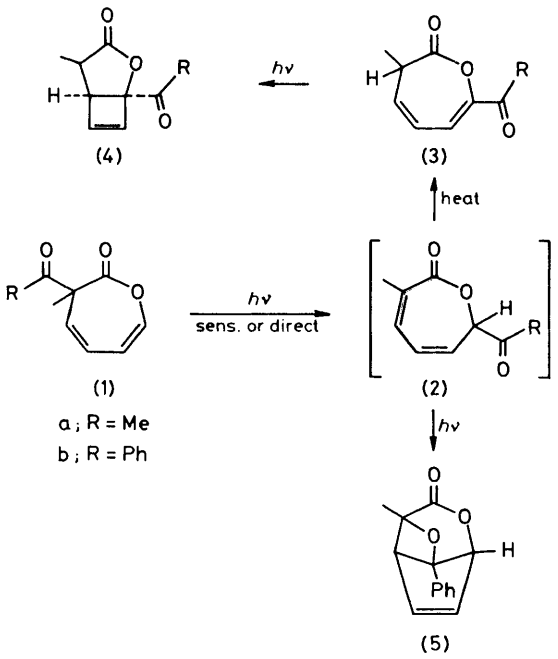
Summary The photolysis of 3-acylated 3-methyloxepin-2(3*H*)-ones leads to the products through a 1,5-acyl shift.

IN a previous paper, we reported that the photorearranging pathway of 3-phenylated oxepin-2(3*H*)-ones involves two sequential sensitized processes, a 1,5-phenyl shift leading to 7-phenyloxepin-2(7*H*)-ones and a subsequent di-π-methane rearrangement leading to 7-phenyl-2-oxabicyclo[4.1.0]hept-4-en-3-ones.[1] We also found that, upon photolysis, a 3-acyl group in the 3-methyl derivative undergoes a 1,5-shift initially.[2]

The sensitized photolysis (1 equiv. of methyl 2-naphthyl ketone, diethyl ether, room temp., 4 h, 500 W high-pressure mercury lamp through Pyrex) of the 3-acetyl derivative (**1a**)† afforded 7-acetyl-3-methyloxepin-2(3*H*)-one (**3a**) (35%), its cyclisation product (**4a**) (19%), and unchanged (**1a**) (18%), respectively.‡ 5-Acetyl-3-methyloxepin-2(5*H*)-one, the 1,3-acetyl shift product, could not be detected. Thus, the formation of (**3a**) is most readily accounted for by an initial 1,5-acetyl shift rather than by successive 1,3-acetyl shifts, (analogous to the case of the 3-phenyl derivatives) and the subsequent double bond isomerisation of the

† Compounds (**1**) were prepared by photo-oxygenation of the dimethyl acetals of 6-acetyl- and 6-benzoyl-6-methylfulvenes, followed by hydrolysis of the resulting acetals of compounds (**1**), respectively. See W. Skorianetz, K. H. Schulte-Elte, and G. Ohloff, *Helv. Chim. Acta*, 1971, **54**, 1913; N. Harada, S. Suzuki, H. Uda, and H. Ueno, *J. Am. Chem. Soc.*, 1972, **94**, 1777. The experimental details will be published elsewhere.

‡ Yields are for the isolated pure products. All new stable compounds were characterized by combustion analysis as well as by i.r., u.v., and ^{1}H and ^{13}C n.m.r. spectroscopy.



resulting thermally unstable 2(7*H*)-isomer (**2a**).§ Cyclisation of (**3a**) to (**4a**) is a common photoreaction in such a system.[1] The thermal isomerisation and, therefore, the second photoreaction leading to (**4a**), could be suppressed completely by low temperature photolysis. Thus, when the photolysis was carried out at −60 °C for 6 h and the photolysate was left at room temperature overnight to complete the thermal double bond isomerisation, a 79% yield of (**3a**) was obtained together with an 11% recovery of (**1a**).

Similarly, photolysis of the benzoyl derivative (**1b**) with or without¶ the use of methyl 2-naphthyl ketone (CH_2Cl_2, 25 °C, 12 h, the same lamp through Pyrex) gave (**4b**) as the sole isolable product in 63% and 50% yield, respectively. In this case, the precursor (**3b**) was unstable and could not be isolated but could be detected by ^{1}H n.m.r. spectroscopy, as could the initial product (**2b**). After irradiation of a deuteriochloroform solution of (**1b**) in an n.m.r. tube at 0 °C for 2 h (85% conversion), the peaks due to an olefinic methyl (δ 2·24 br. s) and a low field methine proton (δ 5·64, m, C-7-H) were observed, assignable to (**2b**). The spectrum changed gradually on standing at 35 °C and finally (after 3 h) showed the formation of (**3b**): δ 1·56 (3 H, d, *J* 6·5 Hz, CH_3–CH), 2·76 (1 H, br. quint., *J ca.* 6 Hz, CH_3–C*H*), 5·75 (1 H, dd, C-4-H), 6·37 (1 H, dd, C-5-H), and 6·96 (1 H, d, C-6-H).

It should be noted that the intramolecular Paterno–Büchi reaction took place at the second stage depending on reaction temperature and time. When the photolysis of compound (**1b**) was conducted in an acetone solution at −60 °C for 5 h, the bridged oxetan lactone (**5**) was obtained in 30% yield. The structure of (**5**) was elucidated on the basis of the following spectral properties: a single carbonyl absorption at 1765 cm^{-1} in the i.r. spectrum, and only one methine group bearing an ethereal oxygen atom at δ 5·18 (m) in the ^{1}H and δ 83·66 p.p.m. (d) in ^{13}C n.m.r. spectra, in addition to other ^{1}H n.m.r. peaks: δ 1·69 (3 H, s, CH_3–C–O–), 3·88 (1 H, split d, *J* 3·5 Hz, –C*H*–CH=), 6·32 (1 H, split dd, *J* 3·5 and 5·0 Hz, –CH–C*H*=CH–), 6·75 (1 H, dd, *J* 5·0 and 2·5 Hz, =C*H*–CH–O–), and 7·34 (5 H, s, Ph), and ^{13}C n.m.r. peaks: δ19·65 (q), 62·18 (d), 88·51 (s), 91·21 (s), 125·16 (d), 128·68 (d), 129·10 (d), 136·44 (2 peaks, s and d), 142·33 (d), and 170·86 (s) p.p.m. Thus, compound (**5**) arose from the intermediate (**2b**).

In contrast with the case of a cyclohepta-3,5-dienone system,[3] the nearly exclusive 1,5-shift of a 3-acyl as well as a 3-phenyl group is a very notable photochemical characteristic of the triplet excited state of the oxepin-2(3*H*)-one system.

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§ The oxepin-2(3*H*)-one system, except for the 3-phenyl derivative, is more stable than the 2(5*H*)- and 2(7*H*)-ones. See A. Kawamoto, H. Kosugi, and H. Uda, *Chem. Lett.*, 1972, 807.

¶ In contrast with the 3-phenylated derivatives, the 3-acyl derivative (**1**) underwent the photorearrangement on direct photolysis.

[1] N. Hoshi, H. Hagiwara, and H. Uda, *Chem. Lett.*, 1979, 1295, and references cited therein.
[2] For the precedents of photoinduced 1,5-acyl shift see A. van Wageningen, P. C. M. van Noort, and H. Cerfontain, *J. Chem. Soc., Perkin Trans.* 2, 1974, 1662; D. W. Jones and G. Kneen, *J. Chem. Soc., Chem. Commun.*, 1972, 1038.
[3] H. Ushiyama, H. Hagiwara, K. Sato, and H. Uda, *Chem. Lett.*, 1977, 925.