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Photorearrangement of 4,4,5,5-Tetramethoxycyclohepta-2,6-dienones to 6,6,7,7-Tetramethoxybicyclo[3.2.0]hept-3-en-2-ones

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The photorearrangement of 2,6-cycloheptadienones to bicyclo[3.2.0]hept-3-en-2-ones was observed. The bicycloketones further photoisomerized to bicyclo[2.2.1]heptenones via a [1,3] sigmatropy.

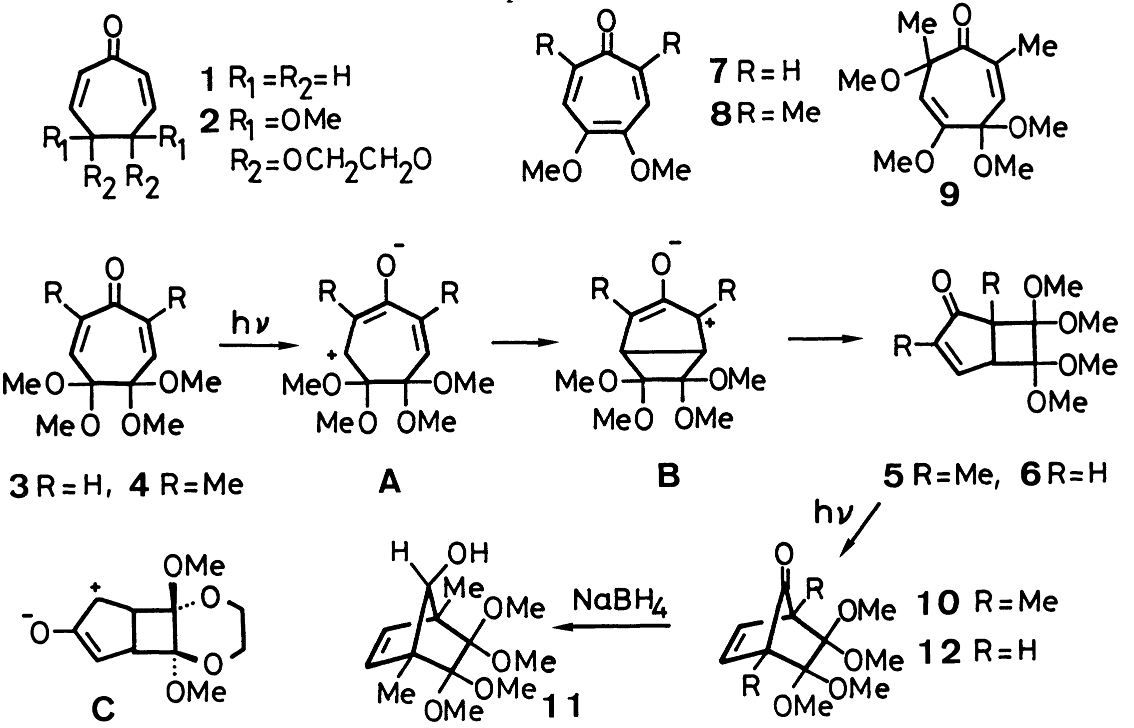
Unlike the photorearrangement of 2,5-cyclohexadienones to bicyclo[3.1.0]hexenones (lumiketones) via zwitterion intermediates,$^{1)}$ only few studies of homologous 2,6-cycloheptadienones are known, i.e., irradiations of unsubstituted 2,6-cycloheptadienone (**1**) gave dimers in cyclohexane, methanol adducts in MeOH, bicyclo[3.2.0]heptan-3-ones in AcOH,$^{2)}$ and 5-ethylidenecyclopentenone via hydroxyheptatrienyl cation in FSO_3H.$^{3)}$ Other than these, photoreaction of p-tropoquinone bisacetal (**2**) with electron-rich olefins is known to give mainly oxetanes, but without olefins, **2** is unreactive.$^{4)}$

To compare with **2**, we have investigated the photoreaction of cross-conjugated 4,4,5,5-tetramethoxycyclohepta-2,6-dienone (**3**) and its 2,7-dimethyl derivative (**4**), and found a formation of synthetically useful bicyclo[3.2.0]hept-3-en-2-ones (**5** and **6**), " homologous lumiketones", for the first time.

Thus, the anodic oxidation$^{5)}$ of 4,5-dimethoxytropone (**7**)$^{6)}$ in MeOH gave an acetal (**3** [δ(H)=3.3(6H, br s), 3.5(6H, br s), 6.10(2H, d, J=12.5 Hz), and 6.42 (2H, d, J=12.5 Hz)], 36%).$^{7,8)}$ 4,5-Dimethoxy-2,7-dimethyltropone (**8**)$^{9)}$ also gave acetals (**4** [δ(H)=1.93(6H, d, J=1.4 Hz), 3.27(6H, br s), 3.45(6H, br s), and 6.14(2H, q, J=1.4 Hz)],$^{8)}$ 77%, and **9**, 4,4,5,7-tetramethoxy-2,7-dimethylcyclohepta-2,5-dienone [δ(H)=1.37(3H, s), 1.92(3H, d, J=1.4 Hz), 3.15(3H, s), 3.26(3H, s), 3.28(3H, s), 3.63(3H, s), 4.46(1H, s), and 6.06(1H, q, J=1.4 Hz)], 8%).

Irradiation of **4** in benzene gave two products (**5**, 50%, and 10, 4%); the ^1H NMR of **5** showed two Me signals at 1.27(s) and 1.84(dd, J=1.6, 1.5 Hz), four MeO singlets, and a methine and an olefinic protons at 2.81(dq, J=2.9, 1.6 Hz) and 7.16 (dq, J=2.9, 1.5 Hz); the signals at 1.84, 2.81, and 7.16 constituted an A_3BX-system. Since the ^{13}C NMR [δ(C)=10.9, 14.7, 49.9, 51.0, 51.2, 51.8(2C), 53.7, 104.6, 104.7, 145.3, 152.0, and 209.2] disclosed a C=O and a C=C functions together with four sp^3-carbons and intact MeO and Me groups, **5** is 1,3-dimethyl-6,6,7,7-tetramethoxybicyclo[3.2.0]hept-3-en-2-one, a homologous lumiketone.

The minor product, **10**, obtained by further irradiation of **5**, revealed a symmetry element in the NMR [δ(H)=1.32(6H, s), 3.40(6H, s), 3.47(6H, s), and 6.25(2H, s). δ(C)=9.8(2C), 52.0(2C), 52.5(2C), 60.3(2C), 106.9(2C), 136.0(2C), and 204.5] and a strained IR carbonyl absorption band at 1780 cm^{-1}. Therefore, **10** is 2,2,3,3-tetramethoxy-1,4-dimethylbicyclo[2.2.1]hept-5-en-7-one. Reduction of **10** with $NaBH_4$ gave a dihydro derivative (**11**); its methine proton signal at 3.05, which is considerably higher than expected, spin-coupled to an OH proton signal at 3.68 with J= 12.8 Hz, indicating a tight intramolecular hydrogen bond with an MeO group. These led us to formulate the structure as depicted.



Similarly, irradiation of **3** in $CHCl_3$ solution gave two products (**6**, 42% and **12**, 1%), whose structures were elucidated by NMR comparisons with **5** and **10**.

The mechanism of this photorearrangement, 2,6-cycloheptadienones to lumiketones could be interpreted on the basis of the zwitterion intermediates (**A** and **B**) as in the case of cyclohexadienones to bicyclo[3.1.0]hexenones. The unreactivity of **2** under the conditions might be due to a large ring strain for the trans-fused zwitterion (**C**). Further conversion of lumiketones to bicycloheptenones via an intramolecular [1,3] sigmatropy is reasonable; in such a photoequilibration, conversion of α,β-unsaturated ketones to β,γ-unsaturated ketones may be favorable.[10)]

References

1) D. I. Schuster, Acc. Chem. Res., 11, 65(1978).
2) H. Nozaki, M. Kurita, and R. Noyori, Tetrahedron Lett., 1968, 3635.
3) R. Noyori, Y. Ohnishi, and M. Kato, J. Am. Chem. Soc., 94, 5105(1972).
4) A. Mori, S. Kasai, Y. Isayama, and H. Takeshita, Kyushu Daigaku Sogo Rikogaku Kenkyuka Hokoku, 10, (1988) in press.
5) A. Mori, T. Kubota, S. Kasai, and H. Takeshita, Chem. Lett., 1987, 1931.
6) For synthesis of **7**, see K. Tajiri, Thesis of M. Eng.(1978), Kyushu University.
7) The NMR were measured in chloroform-d by a JEOL GSX 270 H Spectrometer.
8) The methoxy signals showed a considerable broadening due to a ring inversion.
9) A. Mori, Y. Isayama, T. Kusaba, and H. Takeshita, Kyushu Daigaku Sogo Rikogaku Kenkyuka Hokoku, 6, 185(1985).
10) U. Klinsmann, J. Gauthier, K. Schaffner, M. Pasternak, and B. Fuchs, Helv. Chim. Acta, 55, 2643(1972); J. J. Hurst and G. H. Whitham, J. Chem. Soc., 1960, 2864.

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