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PHOTOCHEMISTRY OF 1,3-CYCLOPENTANEDIONES. OXETANE FORMATION INVOLVING BOTH ENERGY TRANSFER AND ELECTRON TRANSFER PROCESSES

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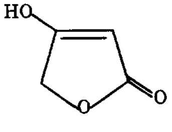
Abstract - Photolysis of 2,2-dimethyl-1,3-cyclopentanedione in acetone resulted in oxetane formation in a two photon process involving energy transfer from triplet excited acetone and electron transfer from singlet excited acetone.

In an attempt to synthesize naturally occurring derivatives of tetronic acid (1)[1] we have investigated the photochemistry of model compound 2.[2] Photolysis[3] of 2 in a variety of solvents (acetonitrile, hexane, ethanol, diethyl ether) gave the lactone 3. The reaction is very clean giving 3 as the only isolated product in >90 % yield. Identification of 3 was based on spectral data.[4] These results are in agreement with previously reported results on other cyclic β-diketones.[5]



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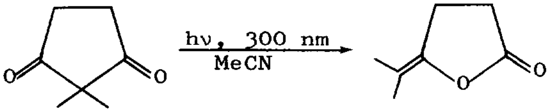
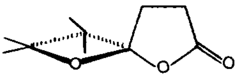


2 3

The formation of 3 was quenched in acetonitrile by the typical triplet quencher, isoprene, giving $k_q\tau = 0.92\ M^{-1}$, where k_q is the bimolecular quenching rate constant, and τ is the lifetime of the reacting excited state of 2.[6] This result suggests a triplet pathway. However, when acetone was used as sensitizer, only 5-10 % of 3 was isolated. The main product (>75 %) was the oxetane 4, identified from its spectral data.[7] The oxetane must have the ketal structure 4 rather than 5, since the proton and C-13 NMR spectra show four non-equivalent methyl groups.[7] The structure of 4 indicates that 3 *is* an intermediate on the pathway 2 → 4. Indeed, whereas 3 was photostable in acetonitrile, diethyl ether, hexane, and ethanol, photolysis in acetone led to rapid formation of 4. Irradiation of 3 in acetone-d_6 led analogously to 6.[8] Thus, by triplet energy transfer acetone is able to sensitize the formation of 3 which, however, in a separate process gives 4.



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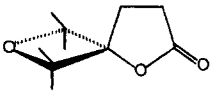

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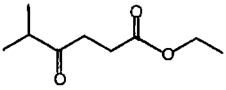

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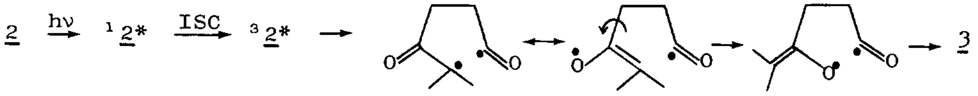
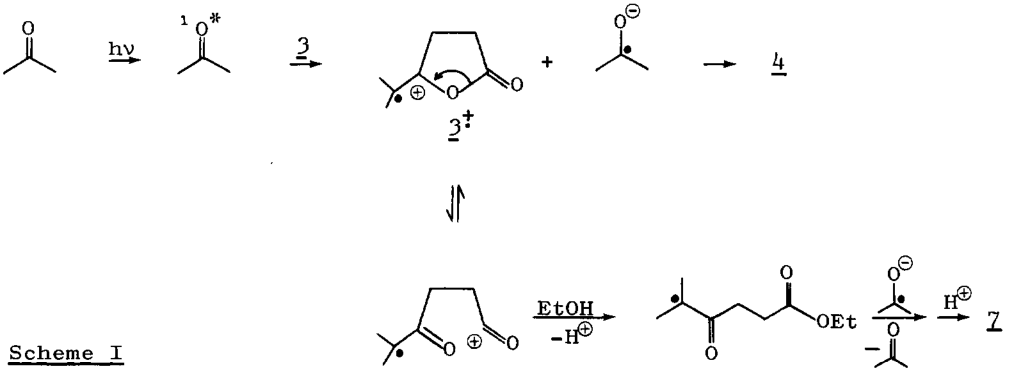
These results are in agreement with a mechanism involving α-cleavage of the triplet excited state of 2, followed by bond rotation, spin-flip, and re-closure of the biradical. If the photolysis of 2 or 3 was carried out in acetone containing small amounts (5-10 % v/v) of ethanol, the formation of 4 was totally suppressed and the only isolated product was the ketoester 7.[9] This has led us to believe that 4 and 7 arise from a common intermediate $3^{+\cdot}$ formed by electron transfer from 3 to the singlet excited state of acetone (Scheme I). If no external nucleophiles are present, $3^{+\cdot}$ and the generated radical anion of acetone collapse to 4. In the presence of ethanol the valence isomer of $3^{+\cdot}$ is trapped to give 7 as shown in Scheme I.



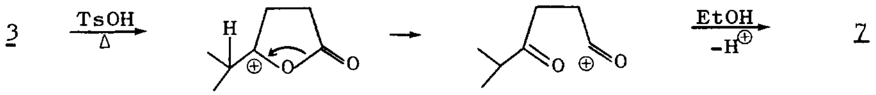


Scheme I

The formation of 7 from 2 is postulated to involve 1) sensitization by triplet acetone via energy transfer to give 3, 2) sensitization by singlet excited acetone via electron transfer to give 4 or 7 depending on the presence or not of ethanol. The validity of Scheme I demands quenching of acetone fluorescence by 3. Indeed, using Stern-Volmer kinetics and procedures already described[10] we obtained a quenching efficiency in N_2-saturated acetonitrile of $k_q\tau_A = 29.5\ \underline{M}^{-1}$, where k_q is defined as above and τ_A is the singlet excited state lifetime of acetone. Using $\tau_A = 1.7$ nsec,[11] $k_q = 1.7 \times 10^{10}\ \underline{M}^{-1}s^{-1}$ which equals a diffusion controlled rate.

An electron transfer mechanism from electron-rich alkenes to singlet excited ketones leading to oxetanes has been postulated already by Schore and Turro.[11] Likewise, the addition of alcoholic solvents to radical cations generated by photochemical electron transfer is precedented.[12,13] In the present system both pathways are followed, depending on the availability of external nucleophiles.

To further justify the mechanism proposed in Scheme I, we attempted to generate a cation analogous to 3$^{+\cdot}$ by heating 3 in benzene containing 5-10 % ethanol (v/v) and catalytic amounts of *p*-toluenesulfonic acid (TsOH). Indeed, 7 was isolated in high yield. If ethanol was excluded from the reaction mixture, only starting material (3) was isolated.



Since starting materials such as 2 are easily available and the described photochemical reactions proceed with high yields and specificity (often no purification of the photoproducts is needed) the procedure described here should prove synthetically useful. We are currently investigating further possibilities.

Acknowledgment. This work was supported by the Danish Natural Science Research Council, grant No. 511-15406.

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2. For synthesis of 2, see W.C.AGOSTA and A.B.SMITH, III, J.Org.Chem. 35 (1970) 3856.
3. All photolyses were carried out on 10^{-2} M solutions at 300 nm in a Rayonet Model RPR-208 Photochemical Reactor. Nitrogen was bubbled through the solutions for 5 min prior to irradiation.
4. Spectral data on 3: ^{1}H NMR δ_{TMS} (CDCl$_3$): 1.59 (s, 3H), 1.70 (s, 3H), 2.70 (br. s, 4H). IR ν_{neat}: 2960, 2920, 1800 (s), 1720, 1450, 1305, 1290, 1190, 1125 (s), 950, 880 cm^{-1}. MS m/e: 126 (M$^{\oplus}$, 100 %), 111 (M$^{\oplus}$-Me), 98, 97, 84, 83, 71, 70, 69, 56, 55, 43, 42, 41, 39.
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6. See f.ex. D.O.COWAN and R.L.DRISKO, Elements of Organic Photochemistry, Plenum Press, New York, N.Y., 1976, p.139.

7. Spectral data on 4: ^{1}H NMR δ_{TMS} (CDCl$_3$): 1.13 (s, 3H), 1.23 (s, 3H), 1.30 (s, 3H), 1.44 (s, 3H), 2.0-2.8 (complex m, 4H); ^{13}C NMR δ_{TMS} (CDCl$_3$): 175.4, 116.1, 86.2, 45.7, 29.8, 27.6, 25.4, 24.3, 20.3, 18.1. MS m/e: 126 (M$^{\oplus}$-Me$_2$CO), 111, 84, 69, 46, 33, 31, 30. IR ν_{neat}: 3560, 2950, 2260, 1770 (s), 1450, 1365, 1260, 1215, 1150, 1020, 900, 830, 725 cm^{-1}. UV λ (ether) : ca. 250 nm (sh, ϵ = 130).

8. Spectral data on 6: ^{1}H NMR δ_{TMS} (CDCl$_3$): 1.13 (s, 3H), 1.23 (s, 3H), 2.0-2.8 (complex m, 4H); compared to the spectral data of 4[7] the two low-field methyl groups at δ 1.30 and 1.44 are missing in 6.

9. Spectral data on 7: ^{1}H NMR δ_{TMS} (CDCl$_3$): 1.12 (d, 6H, J = 7 Hz), 1.27 (t, 3H, J = 7 Hz). 2.3-2.8 (complex m, 5H), 4.08 (q, 2H, J = 7 Hz); ^{13}C NMR δ_{TMS} (CDCl$_3$): 212.5, 172,7, 60.4, 40.7, 34.7, 28.0, 18.1, 14.1. IR ν_{neat}: 3450, 2940, 1730, (s), 1710 (s), 1465, 1370, 1190, 1090, 1035, 1010, 755 cm^{-1}. MS m/e: 172 (M$^{\oplus}$), 129, 127 (M$^{\oplus}$-OEt), 101, 73, 71, 55, 45, 43, 41.

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