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Photolysis of Dispiro-substituted 3-Thioxo-1-cyclobutanones

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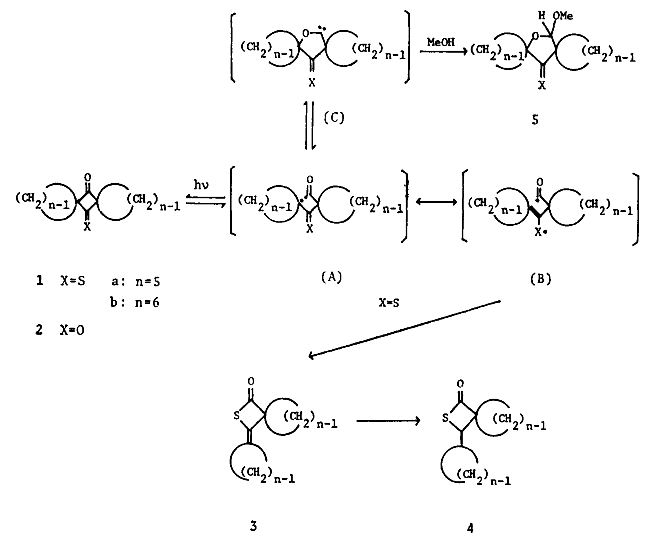
Synopsis. Photolysis of dispiro-substituted 3-thioxo-1-cyclobutanones in dichloromethane or even in methanol gave rise to the photoisomerization to afford thiolactones preferentially.

As part of our studies on the photolysis of 1,3-cyclobutanediones, we previously reported[1] that three primary competing photochemical processes,[2] consisted in α-fission, β-fission (cycloelimination), and ring expansion (the formation of α-oxacarbene), were markedly affected by the ring size of spiro alicyclic groups substituted at the 2- and 4-positions of the diones. In this connection, our interest is focused on the effect of the ring size of 2,4-dispiro alicyclic substituents on the photochemical behavior of 3-thioxo-1-cyclobutanones, being similar in structure to 1,3-cyclobutanediones. However, little is known concerning the photochemistry of 3-thioxo-1-cyclobutanones except for only one report on the photooxygenation of 2,2,4,4-tetramethyl-3-thioxo-1-cyclobutanone to give the corresponding 1,3-cyclobutanedione.[3]

Accordingly, we wish to report in the first place on the alternative photochemical behavior of dispiro-substituted 3-thioxo-1-cyclobutanones, compared with that of the corresponding 1,3-cyclobutanediones. In addition, the effect of the ring size of 2,4-dispiro alicyclic substituents on the product-formation is mentioned.

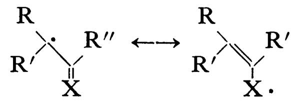
When 12-thioxodispiro[4.1.4.1]dodecan-6-one (**1a**) was irradiated in dichloromethane in a degassed sealed Pyrex tube at −70 °C for 50 h,[4] photoisomerization took place to afford the unsaturated thiolactone (**3a**) almost quantitatively. Moreover, photolysis of **1a** under the similar conditions in methanol,[5] a good trapping agent of an α-oxacarbene intermediate, led to the formation of **3a** (26%) along with the ring-expanded acetal (**5a**, X=S, 38%) *via* an α-oxacarbene intermediate (**C**, X=S).[6] Since the most preferential photoprocess of cyclobutanones or cyclobutanediones in methanol is widely known to be the ring expansion *via* an α-oxacarbene intermediate,[2] it is very significant that the photoisomerization takes place appreciably even in methanol. In the similar irradiation of the dichloromethane solution of 14-thioxodispiro[5.1.5.1]-tetradecan-7-one (**1b**), the photoisomerization also proceeded predominantly. In this case, however, the formation of the unsaturated thiolactone (**3b**, 6%) was minor and, interestingly, the saturated thiolactone (**4b**, 46%) was obtained as the major product. Furthermore, photolysis of **1b** in methanol afforded **4b** (40%), accompanied by the ring-expanded acetal (**5b**, X=S, 23%). On the other hand, no formation of **3b** was observed.

The photolysis of **1a** and **1b** may be considered to proceed in the following scheme.



Scheme 1.

Unlike the case of the corresponding dispiro-1,3-cyclobutanediones (**2a** and **2b**), the preferential occurrence of photoisomerization in **1a** and **1b**, regardless of the ring size of spiro substituents and solvents, may be explained on the basis of the great differences in contribution between two canonical formula of the radical of allylic structures, (**6A′**) and (**6B′**), which are each part of 1,4-biradical intermediates, that is, the 1-acyl 4-cycloalkyl biradical (**A**, X=S) and the 1-acyl 4-thiyl biradical (**B**, X=S), derived from the initial α-fission of **1a** and **1b**.



6 X=S (A′) (B′)
7 X=O

Of two canonical formula, (**6A′**) and (**6B′**), the contribution of (**6B′**) to the radical of allylic structure, in which the unpaired electron is localized on sulfur atom, is greater than that of (**6A′**), because radical stabilization energies[7,8] are strongly influenced by the electronegativity of the atom bearing the unpaired electron and the stabilization energies of a series of structurally related oxygen, carbon, and sulfur centered radicals increase in this order. Consequently, it appears that (**B**, X=S) would form thiolactone (**3**) by ring closure. In the case of **7**, on the contrary, the contribution of (**A′**) is greater than that of (**B′**).[9,10] Therefore, in the case of 1,3-cyclobutanediones (**2**), no isomerized product was obtained. In conclusion, the difference in the electronegativities of sulfur and oxygen plays a key role in determining the reaction pathways after the photochemical α-fission.

In addition, it was found that the ring size of spiro alicyclic groups substituted at 2- and 4-positions affected the process of product-formation in a striking manner. In order to clarify the photochemical conversion of **3b** into **4b**, **3b** was irradiated in dichloromethane or deuterodichloromethane under the similar conditions. As expected, the photochemical hydrogen abstraction of **3b** proceeded smoothly to give **4b**, and, moreover, the NMR spectrum of reaction product in dichloromethane showed the doublet peak (δ 2.92, 1H) assigned to the signal of the methine proton attached to the position α to the sulfur atom in **4b**, whereas, in the case of deuterodichloromethane, such peak was absent. Concerning the high reactivity of **3b** toward hydrogen abstraction, it is not clear at present, but we tentatively infer that the rotation around the double bond of **3b** in the excited state may be fairly restricted owing to the nonbonded interaction of hydrogens between the adjacent two cyclohexyl substituents, just like the photochemically excited triplet olefin.[11] Further study on the above photochemical hydrogen abstraction is now undertaken.

Experimental

Materials. 12-Thioxodispiro[4.1.4.1]dodecan-6-one (**1a**) and 14-thioxodispiro[5.1.5.1]tetradecan-7-one (**1b**) were prepared by the modification of the method of Krapcho.[12] **1a**, mp 35—36 °C; IR (KBr) 1780 cm^{-1}; NMR (CCl_4) δ 1.9 (m, 16H); Mass (*m/e*) 208 (M$^+$); UV (MeOH) λ_{max} 241 (ε, 7160), 326 (90), 513 (8), 527 nm (8); Found: C, 69.21; H, 7.71; S, 15.53%. Calcd for $C_{12}H_{16}OS$: C, 69.18; H, 7.74; S, 15.39%. **1b**, mp 113—114 °C (lit,[12] 113—115 °C); IR (KBr) 1765 cm^{-1}; UV (MeOH) λ_{max} 237 (ε, 8940), 326 (104), 514 nm (8).

General Irradiation Procedure. A solution of **1a** or **1b** (0.2 mol dm^{-3}) was irradiated in a degassed sealed Pyrex tube at −70 °C for 40—50 h. After the solvent was evaporated, the residue was chromatographed on silica gel and was subjected to purification by preparative GLC. The yields were determined by GLC analysis (10% FFAP).

Irradiation of 1a. *In CH_2Cl_2*: Preparative GLC afforded the isomeric product (**3a**) almost quantitatively. **3a**, IR (neat) 1770, 1675 cm^{-1}; NMR (CCl_4) δ 1.6—2.8 (m, 16H); Mass (*m/e*) 208 (M$^+$), 180; Found: C, 69.23; H, 7.69; S, 15.51%. Calcd for $C_{12}H_{16}OS$: C, 69.18; H, 7.74; S, 15.39%.

In MeOH: Analysis of the photolysate by GLC revealed the isomeric product (**3a**, 26%), the ring-expanded acetal (**5a**, 38%), and the unidentified product (16%). **5a**, IR (neat) 1180, 1085, 1015 cm^{-1}; NMR (CCl_4) δ 1.4—2.2 (b, 16H), 3.3 (s, 3H), 4.7 (s, 1H); Mass (*m/e*) 240 (M$^+$), 207, 180; Found: C, 65.16; H, 8.39; S, 13.34%. Calcd for $C_{13}H_{20}O_2S$: C, 64.96; H, 8.39; S, 13.42%.

Irradiation of 1b. *In CH_2Cl_2*: Analysis of the photolysate by GLC revealed the following products: the unsaturated thiolactone (**3b**, 6%), the saturated thiolactone (**4b**, 46%). **3b**, IR (neat) 1760, 1675 cm^{-1}; NMR (CCl_4) δ 1.4—1.8 (m, 20H); Mass (*m/e*) 236 (M$^+$), 208; UV (CH_2Cl_2) 268 nm (ε, 69); Found: C, 71.28; H, 8.39; S, 13.61%. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; S, 13.56%. **3b** was also confirmed by the comparison of the sample which was synthesized by the treatment of **1b** with sodium methoxide. **4b**, IR (neat) 1755 cm^{-1}; NMR (CCl_4) δ 1.1—1.8 (m, 21H), 2.9 (d, 1H); Mass (*m/e*) 238 (M$^+$), 210; Found: C, 70.44; H, 9.46; S, 13.23%. Calcd for $C_{14}H_{22}OS$: C, 70.54; H, 9.30; S, 13.45%. Irradiation of **3b** in CH_2Cl_2 at −70 °C for 2 h gave **4b**, on the other hand, reflux of **3b** in CH_2Cl_2 failed to form **4b**.

In MeOH: Saturated thiolactone (**4b**) and the ring-expanded acetal (**5b**) were obtained in 40% and 23% yields, respectively, along with trace of methyl cyclohexanecarboxylate. **5b**, IR (neat) 1230, 1130, 1100 cm^{-1}; NMR (CCl_4) δ 1.2—2.2 (m, 20H), 3.4 (s, 3H), 5.1 (s, 1H); Mass (*m/e*) 268 (M$^+$), 237, 208; Found: C, 67.29; H, 8.87; S, 11.58%. Calcd for $C_{15}H_{24}O_2S$: C, 67.12; H, 9.01; S, 11.95%.

Quantum Yield Measurement. The quantum yields for disappearance of **1a** and **1b** were measured according to the method of Jones[13] by employing a merry-go-round apparatus and valerophenone as the actinometer.[14]

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4) Irradiation of **1a** or **1b** in the presence of oxygen gave rise to the corresponding 1,3-cyclobutanedione (**2a**) or (**2b**) and its further reaction products.

5) Quantum yield for disappearance of **1a** or **1b** in MeOH is 0.043 or 0.015, which is somewhat lower than that for 1,3-cyclobutanediones (**2a**, 0.10; **2b**, 0.07).

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