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PHOTOCHEMICAL CONVERSION OF 8-THIABICYCLO[3,2,1]OCT-3-EN-2-ONES INTO BRIDGED 3-THIETANONE DERIVATIVES[1)]

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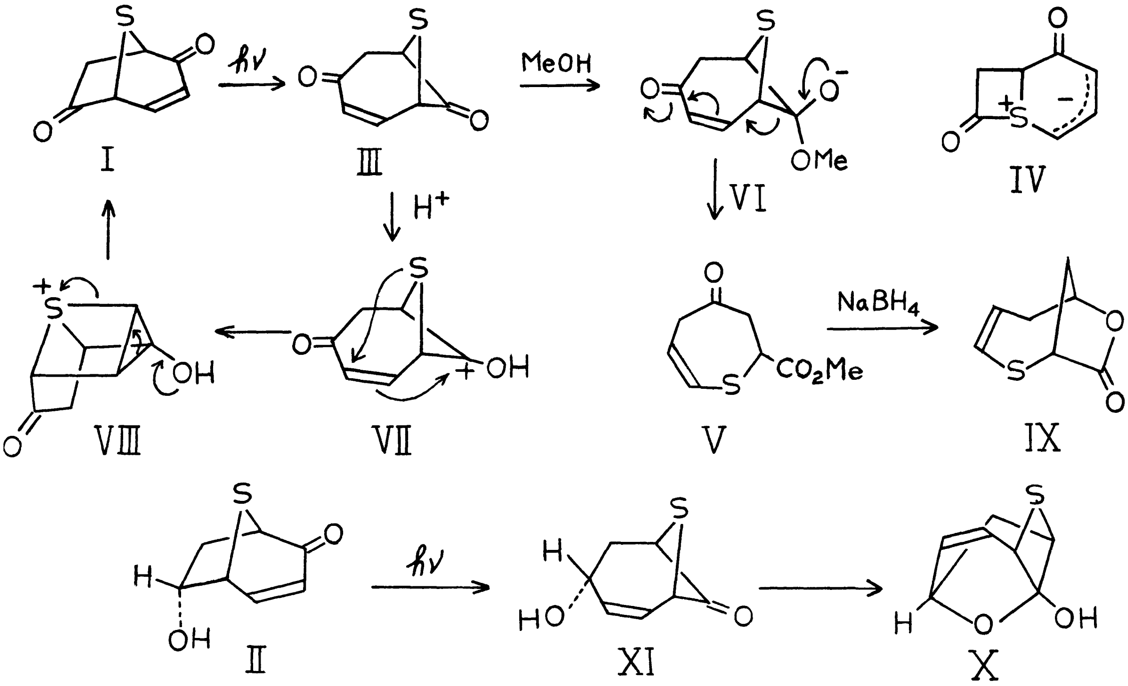
A peculiar 3-thiethanone (III) was produced by the irradiation of cyclic β-ketosulfide (I). Upon treating with acid, III regenerate I, while with methanol, III afforded 4-thiacyclohept-5-enone (V). The photoreaction of II was also studied. The mechanisms of these reactions are discussed here.

In the uv spectra of cyclic β-ketosulfides, there appear, in general, transannular interactions between the divalent sulfur and the carbonyl group.[2,3)] It has been pointed out that such interactions affect the photoreactions of β-ketosulfides, which include the C-T excitation reaction[2,4)] C_α-S bond fission,[2,5,6,7)] and 1,3-carbon shift,[8)] in addition to α-cleavage of the carbonyl group.[5,6)] It is also noted that a cyclic δ-thia-α,β-unsaturated ketone exhibits a different type of reaction, e.g., photo-1,3-sulfur shift.[9)] However, there are no unified explanations concerning the relation between the type of reactions and the structure of materials, because of a limited number of available papers. From the view-point of mechanistic interest and synthetic utility, we studied the photochemical behavior of the titled compounds, which contain both β-ketosulfide and δ-thia-α,β-unsaturated ketone moieties.

Compounds used for this purpose are 8-thiabicyclo[3,2,1]oct-3-en-2,6-dione (I) and 6α-hydroxy-8-thiabicyclo[3,2,1]oct-3-en-2-one (II),[10)] which were both new and synthesized by oxidation of the corresponding diol[11)] with Sarett reagent or manganese oxide in acetonitrile. Their spectral data are as follows: uv max (CH_3OH), 220 nm (ε, 3080), 239 (2250), 254 (2100), 294 (570), 309 (420, sh) and 322 (300, sh) for I and 238 nm (ε, 2970), 298 (3190) and 359 (760) for II; ir max (neat), 1740 and 1680 cm^{-1} for I and 1670 cm^{-1} for II. Irradiation was carried out in benzene using a Rayonet 3500 A lamp to excite absorption bands in the long wavelength region. Thus, I afforded a dione (III), m.p. 94.0-95.5°, (55% yield) accompanied by recovery of I (20 %). Elemental analysis and the mass spectrum (M^+, 154) indicate that III is an isomer of I. The structure of III was confirmed to be 8-thiabicyclo[4,1,1]oct-4-ene-3,7-dione, which was formed by 1,3-shift of the sulfur bridge, from the following spectral data and chemical evidence : ir max ($CHCl_3$), 1780 (carbonyl of 3-thietanone)9,12) and 1660 cm^{-1} (α,β-unsaturated ketone); nmr (100 MHz, $CDCl_3$), δ 3.35 (m, 2H, methylene protons), 4.90 (m, 2H, bridge-head protons), 6.20 (splitted d, 1H, olefinic proton, J=11.2 and 0.8 Hz) and 7.16 (q, 1H, olefinic proton, J=11.2 and 7.8 Hz). The assignment of these protons was provided by the decoupling technique. In addition, existence of W-shape coupling (J=3.5 Hz) between two bridge-head protons should eliminate an expected zwitterionic structure (IV) which would be derived from I by the C-T excitation mechanism suggested by Padwa and Battisti.2,4)



The photoproduct (III) is labile to alcohol and the thietanone ring underwent two types of bond cleavage.9) Treatment of III with methanol at room temperature afforded a methanol adduct (V)(80% yield) accompanied by I (20 %)13) but III regenerated I in quantitative yield in the presence of silicic acid or a trace of p-toluenesulfonic acid. The structure of V was assigned as 3-methoxycarbonyl-4-thiacyclohept-5-enone on the basis of the following spectral properties : ir max (neat), 1735, 1715 cm^{-1} (ester and saturated ketone), and no carbonyl absorption for thietanone and α,β-unsaturated ketone: uv max (CH$_3$OH), 216 nm (ε, 3890), 257 (1710, sh)(thiovinyl); mass, 186 (M$^+$), 154 (M-S), 114 (M-C$_3$H$_4$-S); nmr (100 MHz, CDCl$_3$) suggest the presence of -CH$_2$-CH< (δ 3.01, 3.28 and 4.16, J=5.0, 9.0 and 15.0 Hz) and -CH$_2$-CH=CH- (δ 3.25, 3.50, 6.02, 6.20, J=14.5, 10.0, 7.5, 5.0 and 1.0 Hz). As shown in VI, the formation of V resulted from the initial attack of methanol at the thietanone carbonyl group followed by C$_1$-C$_7$ bond cleavage; whereas the regeneration of I would be ascribed to a 1,3-sulfur shift.$^{13)}$ Although an analogous sulfur shift was observed during irradiation of isothiochroman-4-one and its isomer,$^{9)}$ the conversion of III into I is peculiar and seems to proceed via a protonated cation (VII) and a sulfonium ion (VIII).

Reduction of V with sodium borohydride afforded a lactone (IX), m.p. 79°, (95 %). The following spectral data elucidate the structure of IX as 2-thia-7-oxabicyclo[4,2.1]non-3-en-8-one: ir max (KBr), 1760 cm^{-1} (γ-lacton); mass, 156 (M$^+$); nmr (100 MHz, CDCl$_3$), δ 2.27 and 3.19 (t x d and m, 2H, bridged methylene protons, J=13.0 Hz etc.), 2.29 and 2.40 (m, 2H, allylic protons, J=19.0 Hz etc.), 3.59 and 5.02 (m, 2H, bridge-head protons, J=9.0, 1.5, 0.5 and 4.0, 8.0 Hz), 5.72 and 5.94 (m and q x d, 2H, olefinic protons, J=12.5 Hz, suggesting that the double bond is located in a seven-memberd ring). If the photoproduct from I were the zwitterionic structure IV, compounds V and IX could not be derived by reaction with methanol and reduction, thus providing additional support for the structure of III.

To examine the preferential occurrence of a 1,3-sulfur shift in the photoreaction of the 8-thiabicyclo[3,2,1]oct-3-en-2-one system, the photoreaction of II was studied. After irradiation for 1 hr under the same conditions as the diketone (I), II afforded product X (30% yield), m.p. 119°, whose structure could be assigned as a hemiketal on the basis of the following data: uv max (CH$_3$OH), 231 nm (ε, 2050, sh), 289 (440); mass, 156 (M$^+$); ir max (KBr), 3350 (OH), 1044 cm^{-1} (ether), and no carbonyl absorption; nmr (100 MHz, CDCl$_3$), δ 6.24 and 6.45 (d and d, 2H, olefinic protons, J=9.3, 4.0 and 4.3), 4.84, 4.03, 3.72, 2.40 and 2.20 (5H, other C-protons). W-shape coupling (J=3.0 Hz) exists between two bridge-head protons as in the case of III. Decoupling experiments also proved the structure of the hemiketal (X). The precursor of X should be 4α-hydroxy-8-thiabicyclo[3,2,1]oct-2-en-7-one (XI), which was formed from II by the expected 1,3-sulfur shift. In such a highly strained ketol (XI), the hydroxyl group located at the α-side can easily attack the four-membered keto group, affording X. Thus, these results have shown that in the 8-thiabicyclo[3,2,1]oct-3-en-2-one system the 1,3-shift of the sulfur bridge is the predominant photoreaction compared with α-cleavage, C_α-S fission and C-T excitation reaction. In connection with our observation, it should be noted that such photo-behavior of I is different from the photoreaction of 9-thia[3,3,1]nona-3,7-diene-2,6-dione, which exhibited a 1,3-carbon shift, although both have the same chromophore, i.e., δ-thia-α,β-unsaturated carbonyl group.8)

References

1) Organic Photochemistry. XXXIV. Part XXXIII. T. Tezuka, O. Seshimoto, and T. Mukai, J. C. S. Chem. Comm., (1974).

2) A. Padwa and A. Battisti, J. Amer. Chem. Soc., 94, 521 (1972) and cited papers therein.

3) E.A. Fehnel and M. Carmack, ibid., 71, 84 (1949).

4) (a) A. Padwa, A. Battisti and E. Shefter, ibid., 91, 4000 (1969). (b) A. Padwa and A. Battisti, ibid., 93, 1304 (1971).

5) R.R. Maheshwari and G.A. Berchtold, Chem. Comm., 13 (1969).

6) (a) C. Ganter and J.-F. Moser, Helv. Chim. Acta, 51, 300 (1968). (b) Idem, ibid., 52, 725 (1969).

7) J.R. Collier and J. Hill, Chem. Comm., 702 (1968).

8) J.M. Mellor and C.F. Webb, J. Chem. Soc., Perkin I, 211, (1972).

9) (a) W.C. Lumma and G.A. Berchtold, J. Amer. Chem. Soc., 89, 2761 (1967). (b) Idem, J. Org. Chem., 34, 1566 (1969).

10) Elemental analyses were satisfactory for all new compounds.

11) F. Lautenschlager, J. Org. Chem., 33, 2627 (1968). Treatment of 2,6-diacetoxy-8-thiabicyclo[3,2,1]oct-3-ene, which was obtained by refluxing the 2,6-dichloro compound in acetic acid with potassium carbonate, gave the diol in 80 % yield.

12) G. Claesson and A. Thalen, Acta Chim. Scand., 17, 2763 (1963).

13) Treatment of III with ethanol without acids afforded I in good yields, in which case no ethanol adduct was formed.

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