Tetrahedron Letters, Vol.22, No.44, pp 4421 - 4424, 1981
Printed in Great Britain

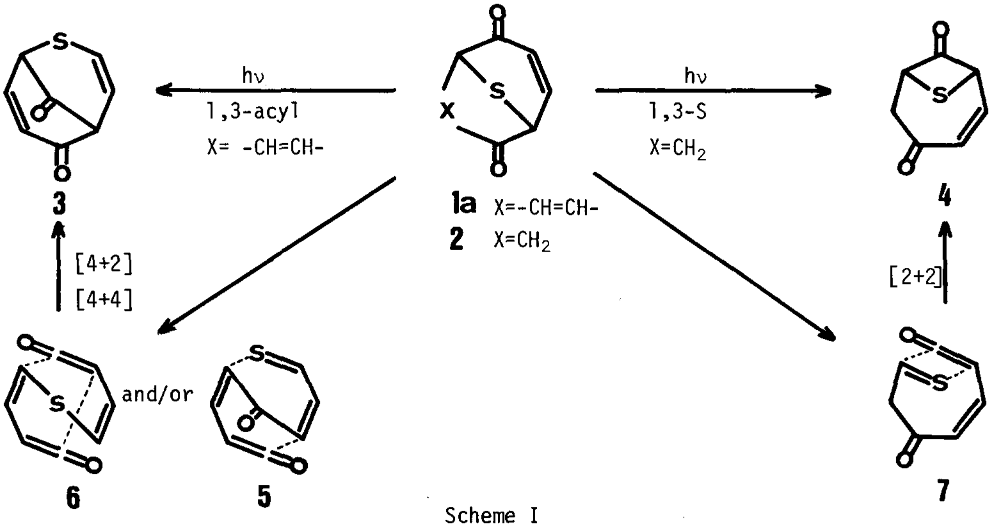
0040-4030/81/444421-04$02.00/0

PHOTOCHEMISTRY OF BICYCLIC δ-THIA-α,β-UNSATURATED KETONES A VINYLKETENE MECHANISM[1]

Tsutomu Miyashi, Nobukazu Suto, Takayuki Yamaki, and Toshio Mukai*
Photochemical Research Laboratory and Department of Chemistry
Fuculty of Science, Tohoku University, Sendai 980, Japan

Summary: Photolyses and pyrolyses of bicyclic δ-thia-α,β-unsaturated ketones (8) and (1a) were investigated. Experimental and spectroscopic evidences support a vinylketene mechanism both for photolysis and pyrolysis.

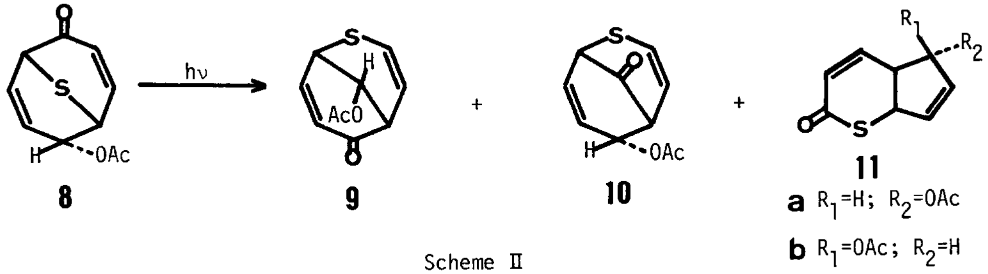
Apart from β-ketosulfides which upon irradiation undergo complex photorearrangements initiated by the C-T excitation between the divalent sulfur and the carbonyl groups,[2] the unsaturated analogue, δ-thia-α,β-unsaturated ketones were reported to behave differently depending on their structures. For instance, the photorearrangement of (1a) to (3)[3] was formally accounted for by a usual 1,3-acyl migration mechanism, whereas the 1,3-sulfur migration[4] took place to give (4) in photolysis of (2). Explanation of these formally different types of reactions, however, can be unified by a vinylketene mechanism if (1a) and (2) generate, respectively, vinylketenes (5) and/or (6) and (7), which, in turn, undergo intramolecular [4+2]- or [4+4]- and [2+2]-cycloadditions at the designated positions to give (3) and (4), respectively, as shown in Scheme I. In fact, (1a) and (2) exhibited a ketene absorption at 2125 and 2100 cm^{-1}, respectively, when irradiated at 77°K. This spectroscopic evidence likely suggests the involvement of a vinylketene mechanism which we often encounter both in photolyses and pyrolyses[6] of unsaturated ketones.



Scheme I

In order to gain further insights into a mechanism, photolysis and pyrolysis of (8)[7] and pyrolysis of (1a)[3] were investigated. Herein we report experimental evidences to support a vinylketene mechanism.

We previously report that irradiation of (8) with 350 nm in methanol afforded the formal 1,3-acyl- and 1,3-carbon migration products (9) and (10).[7] Irradiation of (8) with 350 nm in dry benzene for 3 hr, however, afforded two stereoisomeric thiolactones (11a) (15%) and (11b) (13%) together with (9) (11%) and (10) (18%). Similarly, (10), (11a) and (11b) were isolated when (9) was irradiated with 350 nm in dry benzene. The structural determinations of these products were based on their spectral properties.[8]

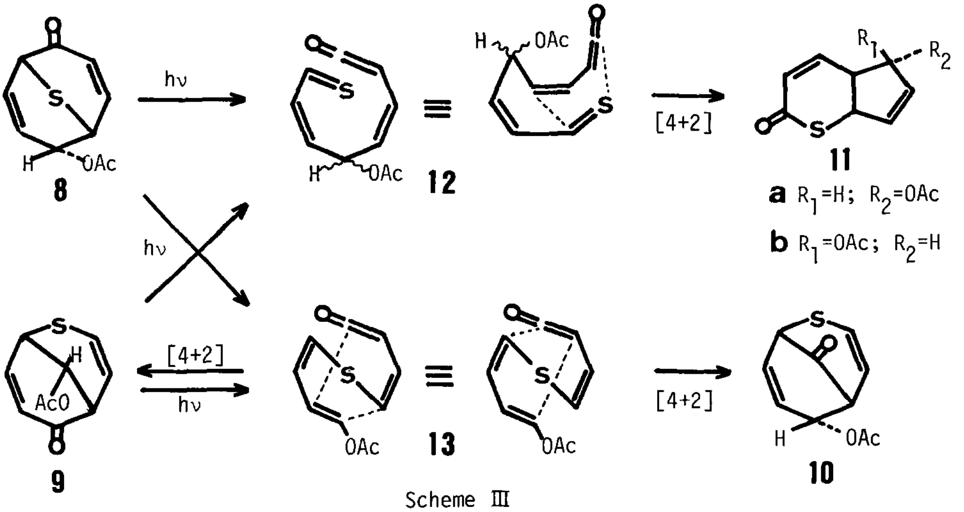


Scheme II

One of intriguing features of these reactions is that (9) and (10) are formed with retention of configuration, whereas (11) is formed in a non-stereospecific manner. In especial, the formation of (11a) and (11b) can not be explained by a simple sigmatropic mechanism[3] such as that applied to the rearrangement of (1a) to (3), but can most likely accounted for by the intramolecular [4+2]-cycloaddition between the vinylketene and the thioaldehyde functions in an intermediate analogous to (5), expected to be generated from (8), (9) and (10). The reaction sequence was, thus, monitored by liquid chromatographic analysis in order to know the interrelation among these photoproducts which would provide a clue to a mechanism.

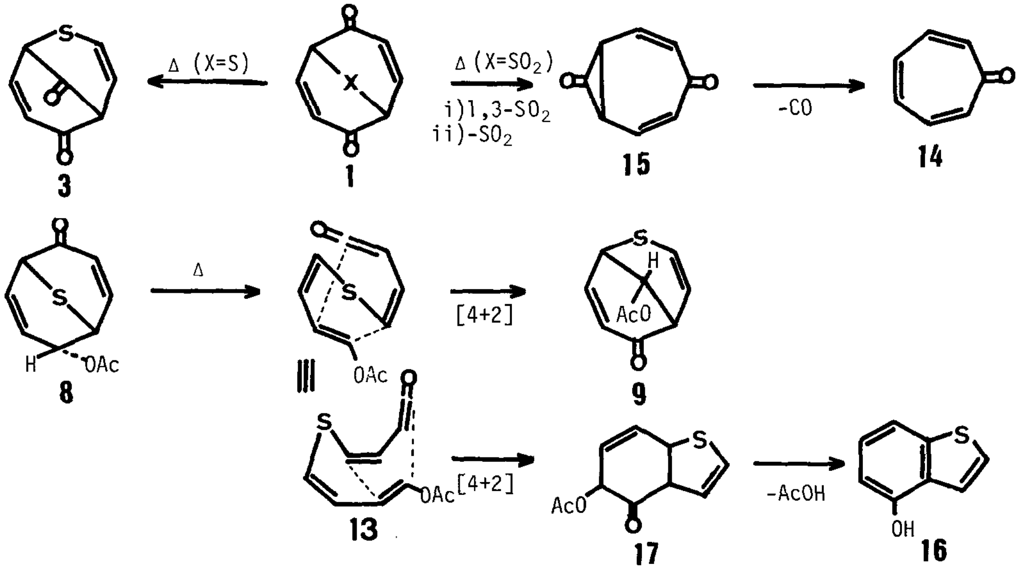
It was found that at the initial stage of irradiation the almost same amounts of (9) and a 1:1 mixture of (11a) and (11b) were formed, while the formation of (10) was slow as compared with those of (9), (11a) and (11b). Upon prolonged irradiation, the once formed (9) gradually diminished with an increase in the yields of (10), (11a) and (11b) even after (8) disappeared. Combining these evidences with spectroscopic one that upon independent irradiation of (8) and (9) at 77°K both showed a ketene absorption at 2100 cm^{-1}, a plausible mechanism to account for the stereospecific formation of (9) and (10) and the non-stereospecific one of (11a) and (11b) can be proposed as shown in Scheme III, where vinylketenes such as (12) and (13) serve as key intermediates.

δ-Thia-α,β-unsaturated ketones (8) and (9), upon irradiation, undergo two ways of cycloreversions to give the common intermediates (12) and (13). In vinylketene (12), the bond rotation is possible around the carbon bearing the acetoxy group and then the [4+2]-cycloaddition between the vinylketene and the thioaldehyde functions affords (11a) and (11b) in a non-stereospecific manner. Although (12) is also capable of giving (9) and (10) by the [4+4]-cycloaddition between the thiobutadiene and the vinylketene functions and by the [4+2]-cycloaddition between the ketene and the thiobutadiene functions, respectively, the stereochemical concern excludes this possibility. Vinylketene (13), however, can afford (9) and (10) with retention of configuration by the [4+2]-cycloaddition between the vinylketene and the vinylacetate functions and by that between the acetoxybutadiene and the ketene functions, respectively.



Scheme III

If this mechanism is correct, a similar type of rearrangement can be expected to occur in pyrolyses of (1a) and (8). Although sulfoxide (1b) (X=SO)[9] was found to be stable at 500°C and sulfone (1c) ($X=SO_2$)[10] underwent the sulfur dioxide extrusion reaction to give tropone (14) (47%) probably via (15)[11] at 500°C, the same rearrangement of (1a) (X=S) to (3) (43%) as that observed in photolysis of (1a), as was expected, occured when pyrolyzed at 510°C.



Scheme IV

On the other hand, pyrolysis of (8) at 520°C afforded (9) (19%) and 4-hydroxy-1-thiaindene (16) (mp 82°C) (28%)[13] together with a trace of (10). The formation of (16) is best explained by the other [4+2]-cycloaddition between the vinylketene and the vinylacetate functions to give (17) which is similar to that in (12) to give (11a) and (11b). The successive elimination of acetic acid followed by aromatization affords (16).

It is, however, not clear whether the C-S bond fission to give (12) occured or not in pyrolysis since (11a) and (11b) mostly decomposed at this temperature. Nevertheless results obtained in pyrolyses of (8) and (1a) supplement the operation of a vinylketene mechanism in photolysis of bicyclic δ-thia-α,β-unsaturated ketones.

References and Notes

1) Organic Photochemistry 53. No 52; see H. Saiki and T. Mukai, *Chem. Lett.*, in press. s

2) A. Padwa, A. Battisti, and E. Shefter, *J. Amer. Chem. Soc.*, **91**, 4000 (1969); A. Padwa and A. Battisti, *ibid.*, **93**, 1304 (1971); C. Ganter and J. -H. Moser, *Helv. Chim. Acta*, **51**, 300 (1968) and **52**, 725 (1969).

3) J. M. Mellor and C. F. Webb, *J. Chem. Soc., Perkin I*, 1030 (1972).

4) H. Tsuruta, M. Ogasawara, and T. Mukai, *Chem. Lett.*, 887 (1974). See also W. C. Lumma, Jr. and G. A. Berchtold, *J. Org. Chem.*, **34**, 1567 (1969).

5) For instance, R. O. Kan, *"Organic Photochemistry"*, McGraw-Hill, New York, N. Y., p94, 1966.

6) For instance, M. J. Goldstein and S. -H. Dai, *J. Amer. Chem. Soc.*, **95**, 933 (1973).

7) T. Miyashi, N. Suto, and T. Mukai, *Chem. Lett.*, 157 (1978).

8) (11a): ir (CHCl$_3$), 1740, 1660, 1635 cm^{-1}; uv, λ_{max}(CH$_3$OH), 233 (ε9000), 281 (ε2100) nm; *m/e* (rel intensity), 210 (M$^+$, 7%), 168 (50%), 150 (M$^+$-OAc, 36%), 140 (7%), 135 (10%), 122 (100%); pmr (CDCl$_3$), δ 2.12 (s, 3H), 3.22 (ddd, J=4.0, 4.0, 7.0 Hz), 4.72 (ddd, J=2.0, 2.0 7.0 Hz), 5.64 (ddd, J=2.0, 2.0, 4.0 Hz), 6.04 (dd, J=2.0, 6.0 Hz), 6.08 (d, J=11.0 Hz), 6.16 (dd, J=2.0, 6.0 Hz), 6.72 (dd, J=4.0, 11.0 Hz).
(11b): mp 62°C; ir (CHCl$_3$), 1735, 1660, 1635 cm^{-1}; uv, λ_{max}(CH$_3$OH), 222 (ε8600), 279 (ε 1800) nm; *m/e* (rel intensity), 210 (10%), 182 (7%), 168 (84%), 150 (M$^+$-OAc, 100%), 140 (20%), 135 (25%), 122 (66%); pmr (CDCl$_3$), δ 2.04 (s, 3H), 3.34 (ddd, J=4.0, 6.0, 7.0 Hz), 4.64 (dd, J=2.0, 7.0 Hz), 6.16 (m, 3H), 6.64 (dd, J=4.0, 11.0 Hz).

9) (1b) was prepared by oxidation of (1a) with peracetic acid. mp 180°C; ir (KBr), 1670, 1065 cm^{-1}; *m/e* (rel intensity), 182 (M$^+$, 3%), 134 (55%), 106 (21%), 95 (72%), 78 (100%); pmr (CDCl$_3$), δ 4.54 (d, J=8.0 Hz), 4.64 (d, J=7.5 Hz), 6.18 (d, J=10.5 Hz), 6.26 (d, J= 10.5 Hz), 6.74 (dd, J=7.5, 10.5 Hz), 6.86 (dd, J=8.0, 10.5 Hz).

10) (1c) was prepared by oxidation of 2,6-dihydroxy-9-thiabicyclo[3.3.1]nona-3,7-diene with peracetic acid followed by oxidation with manganese dioxide. mp 227°C; ir (KBr), 1690, 1325, 1120, 1105 cm^{-1}; *m/e* (rel intensity), 198 (M$^+$, 15%), 134 (12%), 106 (22%), 95 (100%), 78 (96%); pmr (DMSO-d$_6$), δ 5.54 (d, J=8.0 Hz), 6.32 (d, J=11.0 Hz), 7.32 (dd, J=11.0, 8.0 Hz).

11) R. Hoffmann, *Pure and Appl. Chem.*, **28**, 187 (1971). An alternative mechanism involves bicyclo[3.3.0]octa-3,7-diene-2,6-dione[12] as an intermediate. The 1,3-acyl migration followed by decarbonylation can also afford tropone (14).

12) D. G. Farnum and A. A. Hagedorn, III, *Tetrahedron Lett.*, 3987 (1975).

13) (16) showed possitive thiophene and phenol color tests. The structure was determined by comparisons of melting point, ir and pmr spectra with those of the authentic compound prepared by the procedure[14] reported.

14) A. Biedermann, *Ber.*, **19**, 1615 (1886).

(Received in Japan 24 August 1981)