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DIVERSITY IN THE BASE-INDUCED PHOTOREACTIONS OF 3-ACETYL-2,4-DIOXOTHIOLANE (3-ACETYLTHIOTETRONIC ACID)

Kimitoshi SAITO and Tadashi SATO*
Department of Applied Chemistry, Waseda University,
Nishiookubo 4, Shinjuku-ku, Tokyo 160

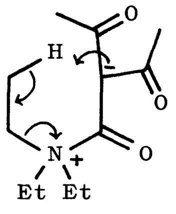
Base-induced photolysis of 3-acetyl-2,4-dioxothiolane (3-acetylthiotetronic acid) undergoes (a) reductive ring cleavage or (b) two types of fragmentation with carbon-skeleton rearrangement, depending upon the irradiation conditions. Conceivable reaction schemes were presented.

The photoreduction of organic compounds by amines is a well-documented reaction. Previously, we reported on the reductive ring cleavage of 3,5-dimethylisoxazole by the irradiation in the presence of triethylamine.$^{1)}$ We found now that 3-acetyldioxothiolane (1), which is photostable under the neutral conditions, undergoes three types of ring cleavage depending upon the reaction conditions when irradiated in the presence of bases.

(a) Reductive ring cleavage.

Solutions of 1 (0.79 g, 5 mmol) in methanol (150 ml), containing an equivalent amount of bases such as piperidine, triethylamine, or sodium hydroxide (2 ml 10% aqueous solution), were irradiated in Pyrex tubes with a high-pressure mercury lamp (Ushio UM-452, 450 W) for 8 - 12 h at the temperature of running water, and products were separated on a silica-gel column and/or a preparative TLC (silica gel) followed by vacuum distillation. β,β'-Diketo ester 2a was obtained together with a by-product 3a (only in case of pyridine-induced reaction) and unreacted starting material (1) in yields summarized in the table. The corresponding ethyl ester 2b was also obtained in 29% yield upon the irradiation of 1 in ethanol in the presence of piperidine. Structure elucidations of the products were accomplished on the basis of the spectroscopic data.$^{2)}$

When the photolyses in the presence of piperidine, morpholine, diethylamine, or triethylamine were carried out in acetonitrile, the corresponding amides 4a - 4c$^{3)}$ were obtained. The amide-type structure of 4a was confirmed by hydrolyzing it to acetylacetone and piperidine. It should be noted that diethylamine and triethylamine gave the identical product 4c. The deethylation could proceed as shown in A, the similar type deethylation having been speculated in the photolysis of 3,5-dimethylisoxazole with triethylamine.$^{1)}$ The amide 4a was also obtained in acetone. In benzene or in carbon tetrachloride, however, the addition of piperidine induced the precipitation of 1 as an insoluble salt, and the yield of 4a was low. The salt was soluble in methanol or in acetonitrile, and the irradiation of the salt in these solvents afforded 2a (42%, in methanol) or 4a (10%, in acetonitrile). Evidently, the present reactions are initiated by the excitation of the anion form of 1.

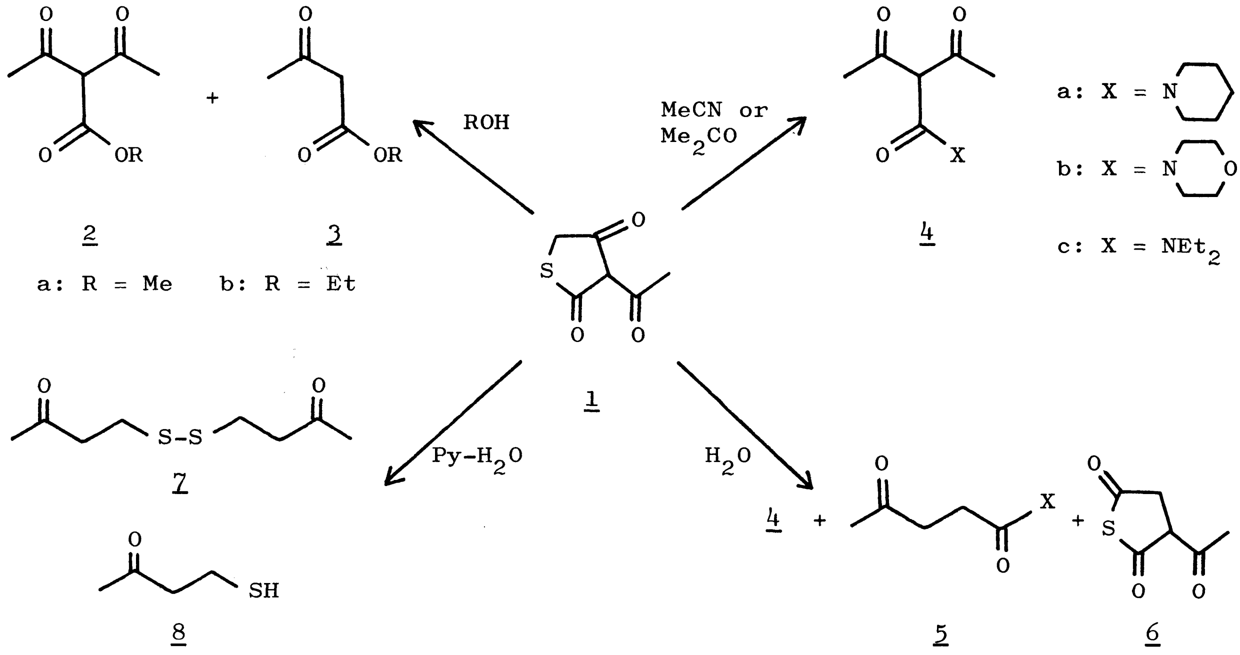


A

Table. Products and yields (%) in the photolyses of 1 in the presence of bases.

bases	in MeOH		in MeCN		in H_2O					
	2a	1	4	1	4	5	6	7	8	1
piperidine	88	tr[a]	41(4a) (45(4a)	14 27)[b]	31(4a)	35(5a)	7	0	0	12
morpholine			67(4b)	6	12(4b)	32(5b)	10	0	0	27
diethylamine			32(4c)	54	46(4c)	17(5c)	tr	0	0	18
triethylamine	63	9	46(4c)	32	27(4c)	30(5c)	tr	0	0	31
pyridine	(28	16)[c]	0	82	(0	0	0	18	3	42)[d]
10% $NaOH_{aq}$	24	58	0	87	0	0	0	7	tr	74

a) Trace. b) Yields in acetone solution. c) By-product 3a (31%) was also isolated. d) Yields in pyridine-water (1 : 1 by volume).

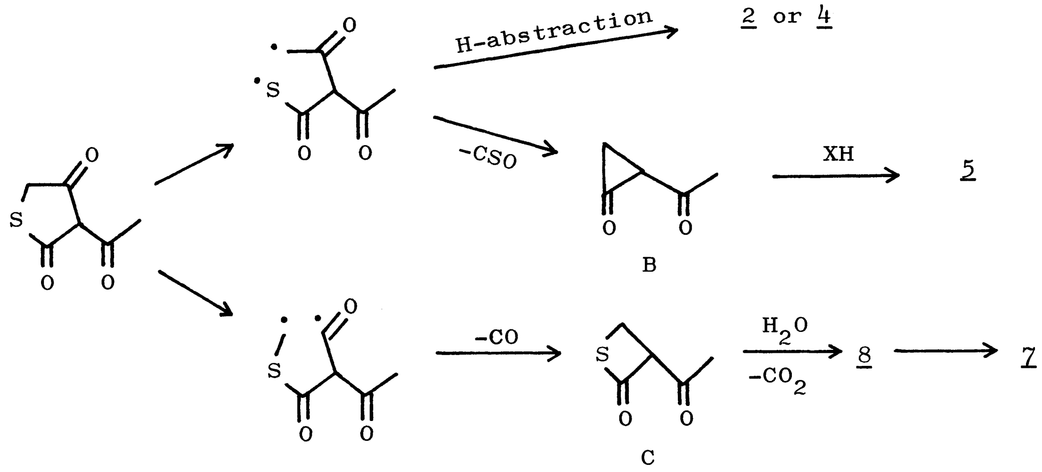


(b) Fragmentations with carbon-skeleton rearrangements.

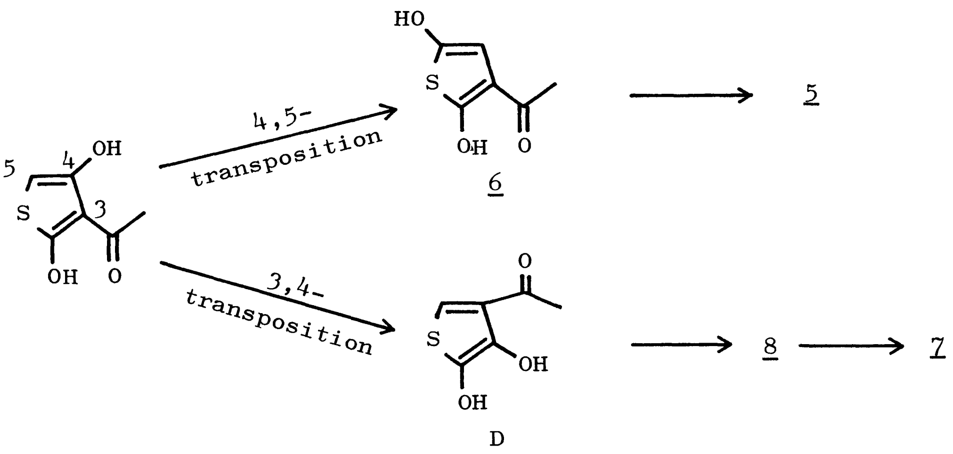
In contrast with the reductive ring cleavage described thus far, two types of fragmentation with carbon-skeleton rearrangement were observed in the photolyses in aqueous solutions. Irradiation of 1 (0.52 g, 3.3 mmol) in water (100 ml) containing amines (10 mmol) gave 4-oxopentanamides 5a - 5c along with 4a - 4c and small amounts of 6.4) Some amounts of the starting material were also recovered. The products 5a and 5c were identical with the authentic samples, and the structure 5b was deduced from the spectroscopic data.5)

When the irradiation of 1 was carried out in pyridine-water (1 : 1 by volume), however, a different type of the skeleton rearrangement occurred and sulfur-containing compounds 7 and 8 were obtained. The same compounds were also obtained by the irradiation of 1 in 10% aqueous sodium hydroxide solution, but the reaction was slow in this case. Products 7 and 8 were identified by comparing them with the authentic samples.

Scheme I



Scheme II



The formations of 2 and 4 can be schemed as involving C-S bond fission followed by the hydrogen abstraction and the attacks by nucleophiles. Two formal reaction schemes can be presented for the carbon-skeleton rearrangements.6) In Scheme I, cyclopropanone B or thietanone C were speculated as intermediates in order to account for the formations of 5, 7, and 8.

Alternatively, the reaction can be schemed as involving thiophene-type transposition reactions, which are well known in literature (Scheme II). Although the functional groups on the thiophene nucleus are known to inhibit the transposition reactions,7) the Scheme II is favorable in that a minor amounts of 6 can be isolated in the reactions in aqueous solutions (see Table). Although the spectroscopic data alone can not eliminate the alternative structure D for this product, we still favor for the structure 6 because it transformed cleanly into 5a under the same irradiation conditions as those of 1. A photochemical fragmentation to thietanone involving species corresponding to 6 has been discussed.8) Further details of these reactions are now in progress.

References and footnotes

1) T. Sato and K. Saito, J. C. S. Chem. Comm., 1974, 781; T. Sato, K. Yamamoto, K. Fukui, K. Saito, K. Hayakawa, and S. Yoshiie, J. C. S. Perkin I, 1976, 783.
2) 2a: MS, m/e 158 (M), 126, 98 (base peak), and 85. IR (CCl_4), 1710 and 1550 cm^{-1}. PMR (CCl_4), δ 2.32 (s, 6H) and 3.74 (s, 3H). CMR ($CDCl_3$), δ 26.0, 51.5, 108.3, 167.5, and 196.8. 2b: IR (CCl_4), 1710 and 1560 cm^{-1}. PMR (CCl_4), δ 1.35 (t, J = 7 Hz, 3H), 2.38 (s, 6H), 4.30 (q, J = 7 Hz, 2H), and 18.6 (s, 1H).
3) 4a: IR (CCl_4), 1630 cm^{-1}. PMR (CCl_4), δ 1.4 - 1.6 (b, 6H), 1.95 (s, 6H), 3.2 - 3.8 (b, 4H), and 16.8 (bs, 1H). 4b: IR (CCl_4), 1635 cm^{-1}. PMR (CCl_4), δ 1.98 (s, 6H), 3.3 - 3.6 (b, 4H), 3.52 (s, 4H), and 16.8 (bs, 1H). CMR ($CDCl_3$), δ 23.3, 42.2, 47.3, 66.6, 66.7, 110.5, 166.5, and 189.1. 4c: IR (CCl_4), 1630 cm^{-1}. PMR (CCl_4), δ 0.98 (t, J = 8 Hz, 3H), 1.06 (t, J = 8 Hz, 3H), 1.98 (s, 6H), 3.19 (q, J = 8 Hz, 2H), 3.24 (q, J = 8 Hz, 2H), and 16.6 (bs, 1H). CMR ($CDCl_3$), δ 14.1, 14.2, 23.1, 40.2, 41.8, 109.5, 170.3, and 188.8.
4) 6: mp 35 - 37°C. MS, m/e 158 (M), 98 (base peak), 70, 55, and 43. IR (CCl_4), 1740, 1715, 1625, and 1600 cm^{-1}. PMR (CCl_4), δ 1.95 (s, 3H), 3.52 (s, 2H), and 12.3 (bs, 1H).
5) 5b: MS, m/e 185 (M), 99, 98, 86 (base peak), 84, and 69. IR (CCl_4), 1720 and 1630 cm^{-1}. PMR (CCl_4), δ 2.0 - 2.3 (m, 4H), 2.12 (s, 3H), 3.3 - 3.6 (m, 4H), and 3.62 (s, 4H).
6) The structures are shown in neutral form for convenience.
7) H. Wynberg, Acc. Chem. Res., 4, 65 (1971).
8) J. Kooi, H. Wynberg, and R. M. Kellogg, Tetrahedron, 29, 2135 (1973).

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