Diversity in the Base-induced Photoreactions of Thiolane-2,4-dione and Derivatives. Reductive Ring Cleavage and Novel Rearrangements of the Carbon Skeleton[1]

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The irradiation of thiolane-2,4-dione (thiotetronic acid) and its derivatives, **1a**—**1d**, in methanol in the presence of bases induced the reductive ring cleavage to give β,β'-diketo esters. The base-induced reductive ring cleavage was also observed in aprotic solvents, such as acetonitrile or acetone, although the products were obtained as β,β'-diketo amides in these cases. On the other hand, the irradiation of **1a**—**1d** in water in the presence of bases induced a rearrangement of the carbon skeleton to give succinic thioanhydrides, γ-keto amides or succinamides, along with the reduction products. When pyridine was used as a base in the photolysis in water, two 3-acetyl derivatives, **1a** and **1b**, gave γ-keto thiols and the corresponding disulfides, resulted from another type of rearrangement of the carbon skeleton. Conceivable reaction mechanisms were discussed.

It has previously been reported that the photoreactions of sulfur-containing carbonyl compounds depend on the relative positions of the sulfur and carbonyl groups.[2] Previous investigations have shown that the UV spectra of cyclic keto sulfides are substantially different from those of alkyl or aryl ketones or acyclic keto sulfides, and this difference has been attributed to the transannular interaction of a lone pair of electrons on sulfur with the carbonyl group, the coupling being strongly dependent on the orientation of the two groups.[3] Several types of photoreactions—rearrangement of the ring system,[4] ring contraction,[5] fragmentation,[6] and some others[7]—have been known for cyclic β- or γ-keto sulfides, and these reactions have been interpreted as involving different degrees of interaction between sulfur and carbonyl groups.

It is well known that photoreactions in the presence of an amine proceed through a charge-transfer complex to form reduction products. Previously, we reported on the reductive cleavage of the isoxazole ring by irradiation in the presence of triethylamine.[8] We have now undertaken the photoreactions of thiolane-2,4-dione (thiotetronic acid) and its derivatives, **1a**—**1d**, in the presence of bases, expecting an unusual photoreaction caused by the intramolecular charge-transfer interaction of the two chromophores and also the intermolecular interaction of **1a**—**1d** with the bases.

Results and Discussion

When methanol solutions of 3-acetylthiolane-2,4-dione (**1a**) and its derivatives, **1b**—**1d**, containing an equal amount of such bases as piperidine, triethylamine, or sodium hydroxide (10% aqueous solution) were irradiated with Pyrex-filtered light for 8—12 h, methyl 2-acetylacetoacetate (**2a**) and its derivatives, **2b**—**2d**, were obtained. When pyridine was used as a base in the reaction of **1a**, deacetylation occurred and methyl acetoacetate (**2c**) was identified as a product along with **2a**. The corresponding ethyl ester was obtained in a 29% yield upon the irradiation of **1a** in ethanol in the presence of piperidine. The base-induced reductive ring cleavage was also observed in aprotic solvents, such as acetonitrile or acetone, although the products were obtained as amides, **3**, in these cases. The details are shown in Table 1. It should be noted that diethylamine and triethylamine gave an identical product, *N,N*-diethyl-2-acetylacetamide (**3aD**), upon the irradiation of **1a** in acetonitrile. The deethylation could proceed as is shown in **4**, a similar type of deethylation having been speculated about in the photolysis of 3,5-dimethylisoxazole in the presence of triethylamine.[8] The presence of the bases is essential for these reactions to proceed; the starting materials are recovered under the irradiation in the absence of bases, except in the case of **1c**, in which **2c** was obtained in a 22% yield as well as the main product, 4-methoxy-2-oxo-2,5-dihydrothiophene (**5c**), under irradiation in methanol.

The compounds **1a**—**1d** have enolizable protons and are acidic. Actually, **1a** formed a stable crystalline salt with piperidine, and the salt, when irradiated in methanol or in acetonitrile, afforded **2a** (24% in methanol) or piperidyl 2-acetylacetoacetamide (**3aP**, 10% in acetonitrile). It might be considered that the present reaction proceeds from the anion forms of **1a**—**1d**, but it was confirmed that the presence of an enolizable proton is not necessary because the 3,3-dimethylthiolane-2,4-dione (**6**) also afforded the corresponding reductive ring-cleavage products, as a mixture of methyl 2,2-dimethylacetoacetate (**7R**, 27%) and piperidyl 2,2-dimethylacetoacetamide (**7P**, 25%), when irradiated in methanol in the presence of piperidine.

In contrast to the reductive ring cleavage in the organic solvents described above, the reaction in an aqueous solution proceeded in a different way. The irradiation of **1a** in water containing three equivalents of piperidine gave 2-acetylsuccinic thioanhydride (**8a**) and piperidyl levulinamide (**9aP**) along with the reduction product, **3aP**. Similarly, the methyl derivative **1b** gave the corresponding products, **8b** and **9bP**. The piperidine-induced photolysis of **1c** and **1d**, on the other hand, gave two derivatives of succinamide, **10cP** and **10dP**, as well as the corresponding succinic thioanhydrides, **8c** and **8d**. It is evident from the results shown in Table 1 that the products **9** and **10** are secondary products from **8**, since the yields of **9** and **10**

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Table 1. Products and yields (%) in the photolyses of thiolane-2,4-dione derivatives (**1a**—**1d**) for 12 h

Compound	Bases	Products(%) in MeOH	in MeCN	in H_2O			
1a	Piperidine	**2a**(88)	**3aP**(41)	**8a**(12)[a]	**9aP**(7)[a]		
			3aP(45)[b]	**3aP**(31)	**8a**(7)	**9aP**(35)	
	Morpholine		**3aM**(76)	**3aM**(12)	**8a**(10)	**9aM**(32)	
	Diethylamine		**3aD**(32)	**3aD**(46)	**8a**(t)	**9aD**(17)	
	Triethylamine	**2a**(63)	**3aD**(46)	**3aD**(27)	**8a**(t)	**9aD**(30)	
	Pyridine	**2a**(28) **2c**(31)	N.R.	**12a**(3)	**13a**(36)		
	10% NaOH	**2a**(24)	N.R.	**12a**(t)	**13a**(7)		
	Aniline	**14A**(94)	**14A**(81)	**14A**(13)			
	Butylamine		**14B**(85)	**3aB**(24)	**9aB**(14)	**14B**(4)	**15B**(24)
	Cyclohexylamine		**14C**(62)	**3aC**(23)	**9aC**(10)	**14C**(4)	**15C**(35)
1b	Piperidine	**2b**(31) **3bP**(15)	**3bP**(40)	**8b**(46)[a]	**9bP**(t)[a]		
				9bP(70)			
	Morpholine			**9bM**(18)			
	Diethylamine		**3bD**(15)				
	Pyridine			**13b**(25)			
1c	Piperidine	**3cP**(81)	**3cP**(68)	**10cP**(3)[a]	**8c**(63)[a]		
				10cP(18)	**8c**(48)		
	Pyridine			**10cO**(51)			
1d	Piperidine	**3dP**(47) **5d**(19)	**3dP**(76)	**10dP**(11)[a]	**8d**(71)[a]		
				10dP(20)	**8d**(65)		
	Pyridine			**10dO**(55)			

a) Yields for 4 h. b) Yields in an acetone solution.

increased at the expense of those of **8** upon the 12 h irradiation as compared with the 4 h irradiation. Actually, **9aP** and **9bP** were obtained from **8a** and **8b** in 86% and 72% yields respectively, upon irradiation in water in the presence of piperidine for 8 h. Similarly, **10cP** and **10dP** were obtained from **8c** and **8d** in 31% and 36% yields respectively under the same conditions.

The solubility of **1a** in water is low, and three equivalents of the base were necessary to prepare homogeneous aqueous solutions. When the amount of piperidine was increased tenfold, the reductive ring-cleavage product, **3aP** (33%), was obtained in preference to the rearrangement product, **9aP** (22%).

When pyridine was used as a base in the photolysis in water (1 : 1 by volume), **1a** and **1b** gave γ-ketobutanethiol (**12**) and the corresponding disulfide, **13**, instead of **8** and **9**. The same reaction was also observed in the irradiation of **1a** in a 10% aqueous sodium hydroxide solution, but the reaction was slow in this case. No abnormality of pyridine was, however, observed in the reactions of **1c** and **1d**, and the corresponding succinic acid derivatives, **10cO** and **10dO**, were obtained.

The reactions in aqueous solutions are notable in that the products have a carbon skeleton which was not present in the starting materials. In our preliminary report,[1] we proposed two mechanistic paths for the carbon skeleton rearrangement. One mechanism involved the radical fission (a or b; see Scheme 1) of the ring, followed by the elimination of CSO or CO to give observed products, **9** and **12**, *via* cyclopropanone, **17**, or thietanone, **18**, intermediates, respectively. This mechanism is analogous to that reported by Kooi and Wynberg in the ring contraction of non-enolizable α-diketo sulfides.[9] More recently, Yates and Toong[6] reported the formation of disulfides by the photoreaction of tetrahydrothiophene-3-one through a radical cleavage of the ring. The other mechanism involved thiophene-type transposition reactions, assuming **1** to be thiophenediol, **19**, as is shown in Scheme 2. It was

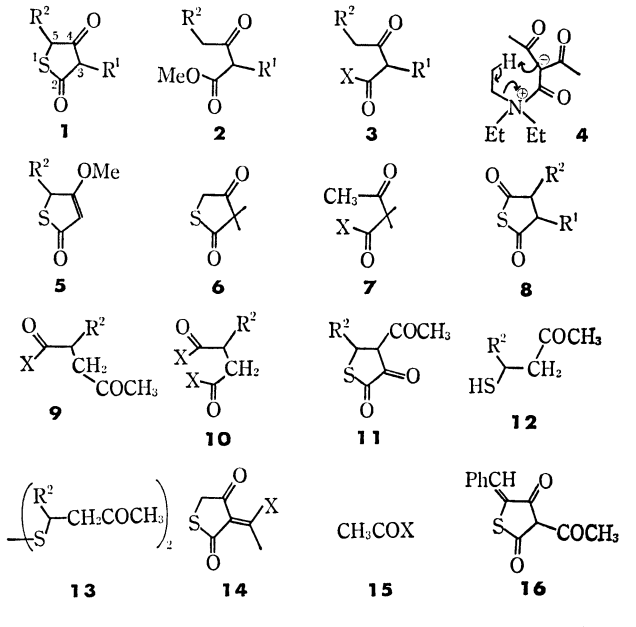
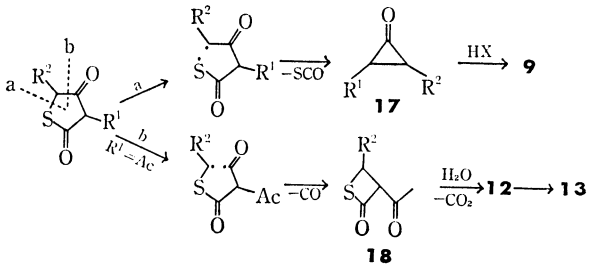
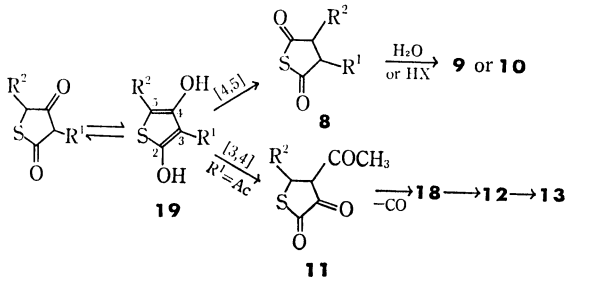


Fig. 1.



Scheme 1.



Scheme 2.

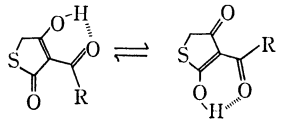
considered that the piperidine-induced reactions leading to **9** proceeded through the intermediacy of **8**, which, in turn, might have been formed through 4,5-transposition of **1**, while the pyridine-induced reactions leading to **12** and **13** could be explained in terms of involving 4-acetylthiolane-2,3-dione, **11**, as intermediates, resulting through the 3,4-transposition of **1**. This mechanism now seems preferable to the radical mechanism because (i) **8a** and **8b** were actually identified as intermediates in the reactions of **1a** and **1b**, and (ii) the formation of **10c** and **10d** from **1c** and **1d** respectively could not be explained by the radical mechanism.

When primary amines, such as aniline, cyclohexylamine, and butylamine, were used as the base in the reaction of **1a** in methanol or acetonitrile, the condensation products, **14**, became the major products and no reduction products or rearrangement products were identified at all. In an aqueous solution, however, appreciable amounts of the reduction products (**3aC**, **3aB**) and the rearrangement products (**9aB**, **9aC**) were identified, as well as the condensation products (**14B**, **14C**) and a fission product, **15C**. Since the condensation product, **14A**, was intact under the present reaction conditions, the reduction and rearrangement are considered to have proceeded prior to the condensation.

In contrast to the base-induced reductive ring cleavage in organic solvents, where the presence of enolizable proton was unnecessary, it was concluded that the base-induced reactions in an aqueous solution required the presence of the enolizable proton, because the dimethyl derivative, **6**, underwent fragmentation to afford *N*-formylpiperidine, without giving any reduction product or rearrangement product. Most of the starting material, **6**, was recovered in pyridine–water.

It is presumable that the reductive ring cleavage proceeds *via* a charge-transfer complex in organic solvents, while the carbon-skeleton rearrangements proceed through the excitation of the anion form of the substrate, which is predominant only in an aqueous solution.

The irradiation of 3-benzoyl and 3-ethoxycarbonyl derivatives (**1e** and **1f**) in the presence of piperidine or pyridine resulted in the recovery of the starting materials (62—81%) in water, methanol, or acetonitrile. Previously we demonstrated that unsymmetrical cyclic β,β'-diketo esters such as **1** may generally exist in "external" tautomers (A⇌B) in solution, as is shown in Scheme 3.[10] The presence of the "external"



Scheme 3.

tautomers in 3-acylthiolane-2,4-dione (**1a**—**1b**) was evident in view of the presence of two singlets of the ring methylene protons in their PMR spectra:[11] A: B=24: 76 for **1a** and A: B=28: 72 for **1b**. On the contrary, it was confirmed that **1e** and **1f** exist exclusively in Form A, as revealed by the single methylene signal in their PMR spectra. It is assumed that the lack of the reactivity of **1e** and **1f** might be attributable to a fixation of the tautomeric system to the Form A through the interaction of 3-benzoyl or 3-ethoxycarbonyl groups. In addition, 3-acetyl-5-benzylidenethiolane-2,4-dione (**16**) and **14A**, which have an exo-double bond on the ring, were also recovered unreacted under the same irradiation conditions. Presumably, the difficulty in attaining the thiophene chromophore might deprive these compounds of the photoreactivity.

Experimental

The mass spectra were obtained with a Hitachi RMS-4 spectrometer; the IR spectra, with a Hitachi 215 spectrometer; the PMR spectra, with a JEOL MH-60 (60 MHz) or PS-100 (100 MHz) spectrometer (with Me_4Si as the internal standard), and the CMR spectra, with a JEOL FX-10 spectrometer operated at 25.1 MHz.

The starting materials, **1a**,[12] **1b**—**1d**,[13] **1e**,[12] **1f**,[13] and **16**,[14] were prepared according to the procedures described in the literature cited.

General Procedure for the Photolysis. Unless otherwise noted, a solution (3—5 mmol, 0.033 M) of the starting material containing a base (one equivalent in the cases of the reactions in organic solvents, three equivalents in the cases of the reactions in aqueous solutions) was irradiated in Pyrex test tube by means of a high-pressure mercury lamp [Ushio UM 452 (450 W)] for 4—12 h. After the irradiation, the solution was poured into water, acidified with 6 M hydrochloric acid, and then extracted with chloroform (Procedure A). In some cases, the irradiated solution was concentrated *in vacuo*, and the crude residue, after having been dissolved in chloroform, was washed with dilute aqueous hydrochloric acid (Procedure B). The chloroform solution after Procedure A or B was dried over sodium sulfate and evaporated *in vacuo*. The residue was treated as indicated below.

Photolysis of 1a. In Alcohols: The crude material obtained by Procedure A was placed in a silica-gel column and then eluted with chloroform. Upon removing the solvent *in vacuo*

from the eluate, **2a** (in methanol) or the corresponding ethyl ester (in ethanol) was isolated; the **2a** was further purified by vacuum distillation. **2a**; Bp, 47—48 °C (3 mmHg). MS, *m/e* 158 (M), 126, 98 (base peak), and 85. IR (CCl_4), 1700 and 1550 cm^{-1}. PMR (CCl_4), δ 2.32 (s, 6H), 3.74 (s, 3H), and 18.5 (bs, 1H). CMR ($CDCl_3$), δ 26.0, 51.5, 108.3, 167.5, and 196.8. Found: C, 51.20; H, 6.48%. Calcd for $C_7H_{10}O_4$: C, 52.14; H, 6.37%. The IR and PMR spectra of the ethyl ester were identical with those of an authentic sample.[15]

In Acetone or Acetonitrile in the Presence of Piperidine, Morpholine, Diethylamine, or Triethylamine: The viscous residue obtained by Procedure B was purified on a preparative TLC (silica gel, 10% methanol in chloroform). **3aP**, **3aM**, and **3aD** were isolated depending on the bases used. **3aP**: 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). **3aM**: IR (CCl_4), 1635 cm^{-1}. PMR (CCl_4), δ 1.98 (s, 6H), 3.3—3.6 (b, 4H), and 16.8 (bs, 1H). CMR ($CDCl_3$), δ 23.2, 44.2, 47.3, 66.6, 66.7, 110.5, 166.5, and 189.1. **3aD**: 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, 107.3, 109.5, and 188.8. The amide-type structure of **3aP** was also confirmed by hydrolyzing it with a 10% aqueous potassium hydroxide solution to acetylacetone and piperidine.

In Acetonitrile in the Presence of Aniline, Cyclohexylamine, or Butylamine: After the irradiation, the solvent was removed *in vacuo*. In an aniline-induced reaction, **14A** was obtained when the crude solid was washed with carbon tetrachloride. In a cyclohexylamine-induced reaction, **14C** and **15C** were isolated by preparative TLC (silica gel, 2% methanol in chloroform). In a butylamine-induced reaction, the crude oil obtained was placed in a silica-gel column and then eluted with chloroform. Upon removing the solvent *in vacuo* from the eluate, a colorless oil of **14B** was isolated in a pure state. The spectra of **14A** and **15C** were identical with those of authentic samples.[14] **14B**: IR (CCl_4), 1680, 1600, and 1135 cm^{-1}. PMR (CCl_4), δ 0.95 (t, J=7 Hz, 3H), 1.2—1.6 (m, 4H), 2.38 (s, 3H), 3.2—3.5 (m, 4H), 3.42 and 3.36 (s, s, 2H), and 11.05 and 11.95 (bs, bs, 1H). **14C**: IR (CCl_4), 1685, 1600, and 1360 cm^{-1}. PMR (CCl_4), δ 1.2—2.0 (m, 10H), 2.46 (s, 3H), 3.42 and 3.50 (s, s, 2H), 3.4—3.6 (m, 1H), and 11.2 and 12.2 (bs, bs, 1H). The PMR analysis indicated that Compounds **14A**, **14B**, and **14C** existed as mixtures of external tautomers, as shown in Scheme 3; the A form/B form ratio was calculated to be 0.35 for **14A**, 0.43 for **14B**, and 0.33 for **14C**.

In Water in the Presence of Piperidine, Morpholine, Diethylamine, or Triethylamine: After the irradiation, the solution was shaken with chloroform (Extract A). The aqueous solution was acidified with 6 M hydrochloric acid and further shaken with chloroform (Extract B). Extract B, after the evaporation of the solvent, was purified by preparative TLC (silica gel, 10% methanol in chloroform). **3aP**, **3aM**, and **3aD** were thus obtained along with **8a** and the unreacted starting material. Extract A, after purification by preparartive TLC (10% methanol in chloroform), gave **9aP**, **9aM**, and **9aD**. **8a**: Mp 35—37 °C. MS, *m/e* 158 (M), 98 (base peak), 75, 70, 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). The IR and PMR spectra of **9aP** and **9aD** were identical with those of authentic samples.[16] **9aM**: 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).

In Water in the Presence of Aniline, Cyclohexylamine, or Butylamine: After irradiation, the solution was shaken with chloroform (Extract A). The aqueous solution was acidified with 6 M hydrochloric acid and further shaken with chloroform (Extract B). When Extract A was purified by preparative TLC (silica gel, 10% methanol in chloroform), **3aB** and **3aC** were isolated. From Extract B, **15B**, **15C**, **9aB**, and **9aC** were obtained, along with the condensation products, **14B** and **14C**. **3aB**: IR (CCl_4), 1630 and 1590 cm^{-1}. PMR (CCl_4), δ 0.97 (t, J=7 Hz, 3H), 1.2—1.6 (m, 4H), 2.09 (s, 6H), 3.29 (q, J=7 Hz, 4H), 7.52 (bs, 1H), and 10.58 (bs, 1H). **3aC**: IR (CCl_4), 1630 and 1590 cm^{-1}. PMR ($CDCl_3$), δ 1.2—2.0 (m, 10H), 2.04 (s, 6H), 3.3—3.4 (m, 1H), and 7.4 (bs, 1H). **9aB**: IR (CCl_4), 1670 and 1630 cm^{-1}. PMR (CCl_4), δ 0.97 (t, J=7 Hz, 3H), 1.2—1.6 (m, 4H), 2.30 (s, 3H), 2.0—2.15 (m, 4H), 2.95—3.05 (m, 2H), and 7.4 (bs, 1H). **9aC**: IR (CCl_4), 1670 and 1630 cm^{-1}. PMR ($CDCl_3$), δ 1.2—2.0 (m, 10H), 2.11 (s, 3H), 2.0—2.2 (m, 4H), 3.3—3.4 (m, 1H), and 6.8 (bs, 1H).

In Pyridine–Water: A solution of **1a** in pyridine–water (1 : 1 by volume) was irradiated for 12 h. When the viscous residue obtained by Procedure B was chromatographed on preparative TLC (silica gel, 5% methanol in chloroform), **12a** and **13a** were isolated; **13a** was further purified by vacuum distillation at 50—55 °C (3 mmHg). The IR and PMR spectra of **12a** and **13a** were identical with those of authentic samples.[17]

Preparation and Photolysis of 3-Acetylthiotetronic Acid Piperidinium Salt. When 0.17 g (2 mmol) of piperidine was added to a stirred solution of 0.16 g (1 mmol) of **1a** in 30 ml of dry benzene at room temperature, a white solid crystallized out in 1—2 h. The solid was filtered and recrystallized from benzene to give 3-acetylthiotetronic acid piperidinium salt; yield 175 mg (72%); Mp 98—100 °C, IR (KBr), 3400, 1680, and 1590 cm^{-1}. PMR ($CDCl_3$), δ 1.7 (b, 6H), 2.28 (s, 3H), 3.3 (b, 4H), 3.42 (s, 2H), and 7.6 (b, 2H).

A solution of the salt in methanol or in acetonitrile was irradiated for 12 h. After the irradiation, the solvent was removed *in vacuo*. The formation and yield of **2a** (42% in methanol) or **3aP** (10% in acetonitrile) were determined by means of their PMR spectra (tetrachloroethane was used as the internal standard).

Photolysis of 1b. In Methanol or Acetonitrile: When the viscous residue obtained by Procedure B was purified by preparative TLC (silica gel, chloroform), **2b** and **3bP** were isolated. **3bP** was isolated as a single product when the irradiation was carried out in acetonitrile. **2b**: IR (CCl_4), 1715 and 1550 cm^{-1}. PMR (CCl_4), δ 1.12 (t, J=7.5 Hz, 3H), 2.02 (s, 3H), 3.35 (q, J=7.5 Hz, 2H), 3.65 (s, 3H); no enolic proton could be observed. **3bP**: IR (CCl_4), 1635 cm^{-1}. PMR ($CDCl_3$), δ 1.15 (t, J=8 Hz, 3H), 1.4—1.6 (b, 6H), 2.20 (s, 3H), 2.44 (q, J=8 Hz, 2H), 3.2—3.8 (b, 4H), and 16.5 (bs, 1H).

In Water: The crude product obtained by Procedure A was purified by preparative TLC (silica gel, chloroform). **9bP** and **9bM** were obtained, along with **8b**. **8b**: IR (CCl_4), 1730, 1705, 1640, 1595, and 1220 cm^{-1}. The PMR analysis indicated that the compound existed as a mixture of 24% of the keto form and 76% of the enol form in carbon tetrachloride. PMR (CCl_4), for the keto form, δ 1.32 (d, J=7 Hz, 3H), 2.40 (s, 3H), 3.94 (q, J=7 Hz, 1H), for the enol form, δ 1.44 (d, J=7 Hz, 3H), 2.02 (s, 3H), 3.64 (q, J=7 Hz, 1H) and 12.6 (bs, 1H). **9bP**: IR ($CHCl_3$), 1717, 1640, and 1470 cm^{-1}. PMR ($CDCl_3$), δ 0.97 (d, J=7 Hz, 3H), 1.35—1.80 (m, 6H), 2.00 (s, 3H), 2.06—3.06 (m, 3H), and 3.15—3.18 (m, 4H). **9bM**: IR ($CHCl_3$), 1720, 1645, and 1550 cm^{-1}. PMR ($CDCl_3$), δ 1.03 (d, J=7 Hz, 3H), 2.06 (s, 3H), 2.15—3.21 (m, 3H), and 3.49—3.79 (m, 8H).

In Pyridine–Water: When a solution of **1b** in pyridine–water (1 : 1 by volume) was irradiated for 12 h, a solid was obtained

upon the removal of the solvent *in vacuo*. The crude residue was purified by preparative TLC (silica gel, chloroform) to give **13b**, along with an unreacted material. **13b**: IR ($CHCl_3$), 1720, 1635, and 1155 cm^{-1}. PMR ($CDCl_3$), δ 1.24 (d, J=7 Hz, 6H), 2.10 (s, 6H), and 2.30—3.55 (m, 6H).

Photolysis of ***1c*** *or* ***1d***. *In Methanol*: The crude solid obtained by Procedure B were purified by preparartive TLC (silica gel, 5% methanol in chloroform). **3cP** or **3dP** was isolated. A by-product, **5d**, was also isolated in the case of the reaction of **1d**. The IR and PMR spectra of **3cP** and **3dP** were identical with those of authentic samples. When the reaction was carried out in acetonitrile, the same products (**3cP** and **3dP**) were obtained.

In Water in the Presence of Piperidine: The oil obtained from **1c** by Procedure A gave white crystals of **8c** and a pale yellow oil of **10cP** upon vacuum distillation. The IR and PMR spectra of **8c** corresponded to those previously reported.[18] **10cP**: IR (CCl_4), 1640, 1440, and 950 cm^{-1}. PMR ($CDCl_3$), δ 1.6 (b, 12H), 2.48 (s, 4H), and 3.5 (m, 8H).

The crude material obtained from **1d** by Procedure A was placed in a silica-gel column and then eluted with chloroform. Upon removing the solvent *in vacuo* from the first eluate, an oil, **8d**, was isolated. Similarly, crystals of **10dP** were obtained from the second eluate. **8d**: IR (CCl_4), 1700 cm^{-1}. PMR (CCl_4), δ 1.42 (d, J=7 Hz, 3H), 2.56 (ABq, 1H), 3.18 (ABq, 1H), and 3.12 (m, 1H). **10dP**: IR (CCl_4), 1640 and 1440 cm^{-1}. PMR (CCl_4), δ 0.95 (d, J=7 Hz, 3H), 1.6—1.8 (b, 12H), 2.1—2.5 (m, 3H), and 3.4—3.6 (b, 8H).

In Pyridine-Water: A solution of **1c** and **1d** in pyridine–water (1: 1 by volume) was irradiated for 12 h. After the irradiation, the solution was evaporated *in vacuo*. The residue was dissolved in dry methanol containing a few drops of concd hydrochloric acid, and then refluxed for 4 h. The reaction mixture was poured into water and extracted with chloroform to afford **10cR** and **10dR**. The IR and PMR spectra of **10cR** and **10dR** corresponded to those previously reported.[19]

Preparation of ***6***. A mixture of 1.02 g (10 mmol) of **1c**, 3.0 g (20 mmol) of methyl iodide, 1.40 g of anhydrous potassium carbonate, and 50 ml of dry acetone was heated under reflux for 20 h and then allowed to cool. The insoluble material was removed by filtration and washed with acetone. The combined filtrate and acetone washings were evaporated *in vacuo*. The residue was chromatographed on a silica-gel column. The subsequent elution of the column with chloroform afforded 0.48 g of pale yellow crude oil, which was further purified by vacuum distillation to give **6** in the pure state; 0.6 g (42%), Bp 78—80 °C (3 mmHg). PMR ($CDCl_3$), δ 1.21 (s, 6H) and 3.94 (s, 2H).

Photolysis of ***6***. *In Methanol*: The reaction mixture obtained by Procedure A was chromatographed on a preparative TLC plate. Subsequent elution with 10% methanol–chloroform afforded **7R** (27%) and **7P** (25%). **7R**: IR (CCl_4), 1725 and 1630 cm^{-1}. PMR (CCl_4), δ 1.48 (s, 6H), 2.30 (s. 3H), and 3.66 (s, 3H). **7P**: IR (CCl_4), 1630 and 1610 cm^{-1}. PMR (CCl_4), δ 1.38 (s, 6H), 2.07 (s, 3H), and 3.4—3.6 (b, 4H).

In Water in the Presence of Piperidine: The brown oil obtained by Procedure A was chromatographed on a preparative TLC (silica gel, 5% methanol in chloroform). The removal of the solvent from the upper band afforded a pale yellow oil, whose IR and PMR spectra indicated it to be *N*-formylpiperidine.

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