Photosolvolysis of 2-Alkoxy-2-phenyl-1,3-dithiolane

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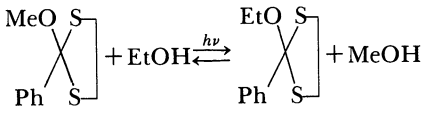
Synopsis. 2-Methoxy- and 2-ethoxy-2-phenyl-1,3-dithiolane are hydrolyzed to the thioester in neutral aqueous solution by irradiation with a low-pressure Hg lamp. Irradiation of a solution of the alkoxy dithiolanes in alcohol induces easily the alcohol exchange.

Photosolvolysis of benzylic compounds and alkyl halides has been studied and a mechanism involving excited-state heterolysis or homolysis followed by electron transfer is proposed.[1-3] Similar photosolvolysis was observed with ortho thioester derivatives in aqueous and alcoholic solutions and the results are reported in the present paper.

Results and Discussion

Although 2-alkoxy-1,3-dithiolane undergoes hydrolysis in acidic aqueous solution, it is quite stable in neutral aqueous and alcoholic solutions.[4] However, alcohol exchange of 2-methoxy-2-phenyl-1,3-dithiolane (**1a**) takes place readily in ethanol when the solution is irradiated with a low-pressure mercury lamp through a Vycor filter (Eq. 1).

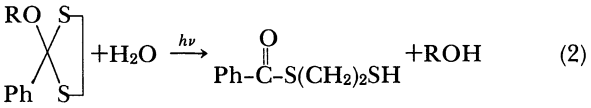


(1)

1a **1b**

The course of reaction was followed by analysis of aliquots of the reaction mixture with HPLC. The methoxy derivative **1a** is smoothly converted to the ethoxy derivative **1b** in ethanol as shown in Fig. 1. The conversion reaches about 90% in 20 min. The reaction was not affected by bubbling with oxygen. The conversion curve in the presence of sodium ethoxide is closely similar to that in its absence. The reverse alcohol exchange was observed with **1b** on irradiation in methanol, showing a similar conversion curve.

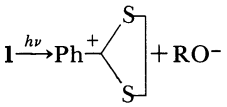
Photochemical hydrolysis of **1** is effected by irradiation of the solution in neutral or alkaline aqueous acetonitrile. The reaction is complete in 10 min to give thioester **2** essentially in a quantitative yield (Fig. 2).



(2)

1 **2**

The ^{1}H NMR spectra of the reaction products substantiated the results obtained from HPLC analysis that photosolvolysis takes place essentially quantitatively. Only some small peaks due to by-product(s) were detectable in the NMR spectra. The reaction must proceed through a 1,3-dithiolanylium ion **3** as an intermediate. This intermediate can be seen spectroscopically as a transient (λ_{max} 345 nm) by flash photolysis with a xenone lamp.[5] Reaction of **3** with a nucleophilic solvent leads to alcohol exchange or hydrolysis.



(3)

3

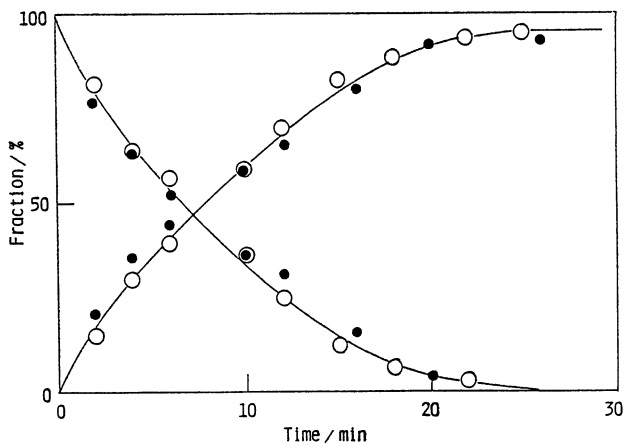


Fig. 1. Photochemical conversion of **1a** to **1b** in ethanol. Closed circles show reaction in the presence of sodium ethoxide at 5×10^{-3} mol dm^{-3}. Decreasing and increasing curves show fractions of **1a** and **1b**, respectively.

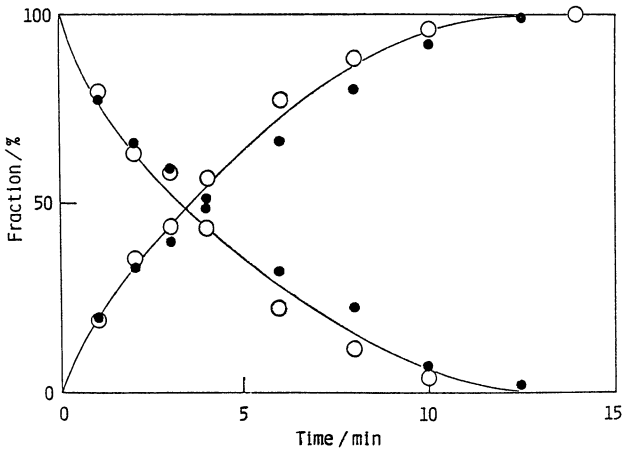


Fig. 2. Photochemical conversion of **1a** in 4:1 (v/v) CH_3CN-H_2O. Closed circles show reaction in the presence of sodium hydroxide at 1.0×10^{-3} mol dm^{-3} Decreasing and increasing curves show fractions of **1a** and **2**, respectively.

Although the chromophore of **1** may be the phenyl and/or the C-S bondings (n-σ^* absorption around 250 nm), the electronic excited state will eventually fall into a vibrational excited state to lead to bond cleavage to afford the most stable species in the medium. In the present case, the heterolysis leading to the carbocation **3** stabilized by the two adjacent sulfur atoms[6] is the most facile pathway in the polar medium. The weaker bond of C-S could also be broken either homolytically or heterolytically; however, the effective intramolecular recombination of an incipient intermediate might readily occur to give back the starting dithiolane **1**. So, the observed reaction is predominantly photosolvolysis in polar solvolytic media.

Experimental

Methanol and ethanol were treated with activated magnesium and distilled. Acetonitrile was distilled from phosphorus pentaoxide.

2-Methoxy-2-phenyl-1,3-dithiolane (1a). 2-Phenyl-1,3-dithiolan-2-ylium perchlorate prepared from benzoyl chloride (25 mmol) and 1,2-ethanedithiol (25 mmol)[7] was dissolved in methanol (30 cm^3) while it was still wet with ether[7] and triethylamine was added under stirring until red color of the solution disappeared. After filtration of the precipitates, the solution was concentrated to about 5 cm^3 under vacuum. The residues were dissolved in ether, washed with 5% aqueous sodium carbonate and saturated sodium chloride, and dried over $MgSO_4$. After removal of the ether, the products were distilled in a glass-tube oven at 0.02 mmHg (1 mmHg=133.322 Pa) and the fraction obtained at about 120 °C was collected. The overall yield was 38%. ^{1}H NMR ($CDCl_3$) δ=3.43 (s, 3H), 3.47 (dd, 4H), 7.2—7.8 (m, 5H).

2-Ethoxy-2-phenyl-1,3-dithiolane (**1b**) was obtained in the same way in 36% yield. ^{1}H NMR δ=1.26 (t, 3H), 3.48 (dd, 4H), 3.56 (q, 2H), 7.2—7.8 (m, 5H).

***S*-(2-Mercaptoethyl) Thiobenzoate (2).** A chloroform solution (30 cm^3) of benzoyl chloride (50 mmol) was added dropwise to the solution of 1,2-ethanedithiol (80 mmol) and pyridine (50 mmol) in chloroform (30 cm^3) under magnetic stirring on an ice bath. After washing with water and drying with $MgSO_4$, distillation gave a middle fraction boiling at 95—96 °C (0.3 mmHg) in 30% yield.

Photochemical Reaction. Photosolvolysis was carried out in a standard photoreaction vessel equipped with an immersion well made of fused quartz. A 30-W low-pressure mercury lamp and a Vycor filter sleeve were placed inside the well. A solution (80 cm^3) of the substrate (ca. 1 mmol) was placed in the vessel and bubbled with argon. The vessel was kept in a constant temperature bath at 25 °C during the irradiation. After an appropriate time of irradiation the reaction mixture was concentrated under reduced pressure. The products were extracted with dichloromethane, washed with water, and dried over $MgSO_4$. After the solvent was removed in vacuo, the residues were analyzed by ^{1}H NMR spectroscopy.

In following the progress of reaction, the aliquots were taken with a syringe at appropriate time intervals and an exact amount of the aliquot (usually 5 μl with a microsyringe) was applied directly to the HPLC analysis. An HPLC analyzer JASCO BIP-1 equipped with a Finepak SIL $C_{18}S$ column and a UV detector UVIDEC 100-V was used with 1 : 1 (v/v) CH_3CN-H_2O as an eluent. The retention times were compared with the authentic samples. Relative molar intensities of the peak areas, obtained from an integrator SIC-12, were determined at 270 nm using the authentic samples.

References

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