

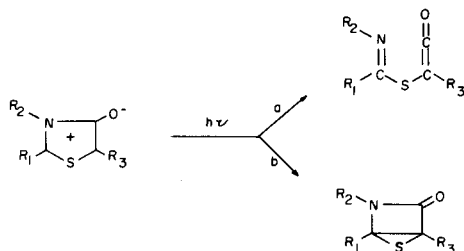
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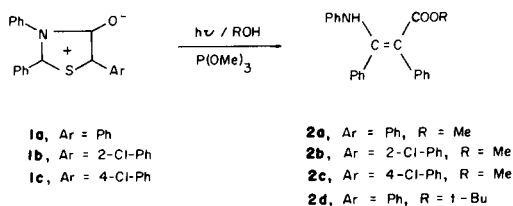
The photolysis of anhydro-4-hydroxy-2,3,5-triphenylthiazolium hydroxide and of two substituted derivatives in methanol or *t*-butyl alcohol in the presence of trimethylphosphite, leads exclusively and stereospecifically to α -aryl- β -anilinoacrylate esters. A mechanism which involves ring contraction to a bicyclic β -lactam is suggested.

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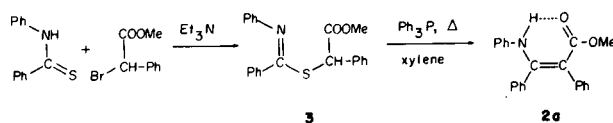
It is well documented (1) that heterocyclic mesoionic compounds undergo, upon photolysis, either ring opening to heterocumulenes (path a) or ring contraction to bicyclic systems (path b). In the case of anhydro-4-hydroxythiazolium hydroxides path b is particularly attractive as it constitutes a new route to β -lactams. This has been demonstrated (2) in the photolysis of a variety of 2-alkylthio derivatives ($R_1 = SR$).



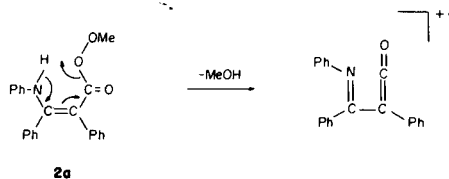
The photolysis of the 2,3,5-triphenyl derivative ($R_1 = R_2 = R_3 = Ph$, **1a**) which is the subject of this paper, has also been reported (3). It led to an extensive decomposition and yielded (in ethanol) benzanilide (44%), thiobenzanilide (9%) and a number of unidentified products. Obviously these results cannot lead to any conclusions concerning the reaction course. We expected that an induced immediate desulfurization of the primary photoproducts would offer considerable improvement and provide stable products. Accordingly the irradiation of **1a** was carried out in methanol in the presence of trimethylphosphite (3 equivalents) and indeed a single product was obtained in 95% yield. It was identified as methyl α -phenyl- β -anilinoacrylate (**2a**). In the same manner the irradiation of the mesoionic compounds **1b** and **1c** (4) afforded the esters **2b** and **2c** respectively, and **1a** in *t*-butyl alcohol gave **2d**.



The structure of **2a** was established by an independent synthesis. The reaction of methyl α -bromophenylacetate with thiobenzanilide gave compound **3** in 85% yield. Sulfur elimination (5) from **3** (triphenylphosphine in boiling xylene) gave (93%) a product identical in all respects with the photoproduct **2a**. The synthesis also confirms the stereochemistry of **2a**, as the Eschenmoser sulfur elimination always gives the stereoisomer which is stabilized by intramolecular hydrogen bonding (5), thus the carbomethoxy and anilino groups in **2a** are in a *cis*-relationship.



The spectral properties of compounds **2** are in accord with the proposed structure and are characteristic for *cis*-2-aminoacrylates. The ir ester carbonyl absorption appears at the unusually low frequency of 1640 cm^{-1} . The ^{13}C -nmr shows the two olefinic protons at 102 (α -carbon) and 159 (β -carbon) ppm. The mass spectra exhibits elimination of methanol, probably through the cyclic mechanism shown (Tables 1 and 2).



The formation of a new carbon-carbon bond between C-2 and C-5 of the substrate indicates a ring contraction reaction and the intermediacy of the bicyclic lactam **4**. In order to rule out the possibility that **2** was formed by ring opening followed by sulfur elimination (path a above), compound **3** was irradiated under the same conditions as **1a** and was recovered quantitatively unchanged.

The transformation of **4** to **2** probably proceeds through the unsaturated lactam **5** formed in the desulfurization of **4**. The alternative possible route, which involves the lac-

Table I

Alkyl β -Anilino- α -phenylcinnamates (2)

No.	Mp °C	IR (C=O) cm ⁻¹	UV nm (log ϵ)	Formula	Found (Calcd.) %			
					C	H	N	Cl
2a	145-146	1640	240 (4.07), 336 (4.25)	C ₂₂ H ₁₉ NO ₂	80.24 (80.22)	5.89 (5.81)	4.44 (4.25)	
2b	99-101	1640	240 (4.04), 337 (4.20)	C ₂₂ H ₁₈ ClNO ₂	72.65 (72.62)	4.90 (4.95)	3.75 (3.85)	9.41 (9.76)
2c	115	1640	245 (4.03), 337 (4.20)	C ₂₂ H ₁₈ ClNO ₂	72.62	4.91	3.79	9.60
2d	146	1645	247 (4.05), 337 (4.24)	C ₂₅ H ₂₅ NO ₂	80.67 (80.82)	6.78 (6.76)	3.77 (3.79)	

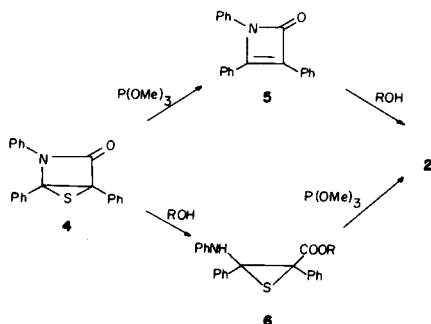
Table II

Mass Spectra of Compounds 2 (Relative Intensity, %) (a)

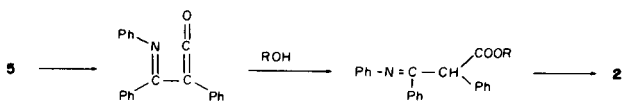
No.	M ⁺	M ⁺ -OR	M ⁺ -ROH	M ⁺ -COOR	Others
2a	329 (99)	298 (15)	297 (20)	270 (30)	
2b	363 (67)	332 (13)	331 (10)	304 (20)	
2c	363 (44)	332 (24)	331 (19)	304 (22)	
2d	371 (14)	298 (34)	297 (40)	—	315 (M ⁺ , C ₆ H ₅ , 4)

(a) The parent peak (100%) was m/e 180, [PhCH=N-Ph]⁺.

tam ring opening by the solvent followed by desulfurization of the intermediate **6** is highly unlikely, particularly with the weakly nucleophilic *t*-butyl alcohol.



For the same reason it is most probable that the opening of the lactam **5** by alcohols is not direct, but proceeds through electrocyclic ring opening ($\pi 2a + \pi 2s$). Reaction of the highly reactive iminoketene with the alcohol and double bond migration then afforded **2**. In a previously reported (6) case which involves an unsaturated β -lactam, this opening mode was evident by the formation of the two stereoisomeric olefins. In the present case only one isomer was formed and this may be due to the relative stability of the isomers, which is also revealed in the synthesis of **2** from **3** which also involves a double bond migration and is stereospecific.



EXPERIMENTAL

Melting points were taken on a Tomas-Hoover capillary apparatus. Spectra were obtained with the following instruments: ir (Nujol mulls) on a Perkin-Elmer 157 spectrometer, uv (ethanol solutions) on a Varian Techtron 635 spectrometer. ¹³C-nmr on a Bruker WH-300 and proton nmr on a Varian EM-360 spectrometer. Mass spectra were taken on a Varian MAT-311 spectrometer.

Photolysis of Compound 1.

All irradiations were carried out using an Hanovia 450 W immersion lamp under nitrogen atmosphere. The solutions were of 1 mmole of the substrate **1** and 0.372 g (3 mmoles) of trimethylphosphite in 450 ml of the alcohol. Reactions were monitored by the disappearance of the absorption band at ca. 450 nm. For best results irradiations were stopped after 60-80% conversion (3-4 hours). The solutions were then evaporated and the residue chromatographed on silica gel. The first fractions (benzene-hexane 1:1) contained the phosphite and its sulfide. Further elution with benzene afforded the products **2** in 95% yield and these were crystallized from ethanol. Further elution with ethyl acetate gave unreacted **1**.

Physical properties of compounds **2** obtained are given in Tables I and II.

Methyl α (Thiobenzylidenaniline)phenylacetate (**3**).

A solution containing thiobenzanilide (2.13 g, 10 mmoles), methyl α -bromophenylacetate (2.29 g, 10 mmoles) and triethylamine (1 g) in benzene (40 ml) was stirred at room temperature for 24 hours. It was then filtered and evaporated and the residue chromatographed on silica gel. Elution with benzene gave compound **3** (3.06 g, 85%) which was crystallized from ethanol, mp 101°; ir: 1735 cm⁻¹ (C=O); nmr 3.70 (s, 3H), 5.43 (s, 1H) and 6.90-7.70 (m, 15H); ms: m/e (relative intensity) 361 (4, M⁺), 330 (4, M⁺-OMe), 302 (2, M⁺-COOMe), 212 (12), 180 (100) and 122 (35).

Anal. Calcd. for C₂₂H₁₉NO₂S: C, 73.12; H, 5.30; N, 3.88; S, 8.85. Found: C, 72.88; H, 5.18; N, 3.81; S, 9.12.

Desulfurization of Compound 3.

A solution of **3** (2.89 g, 8 mmoles) and triphenylphosphine (5.64 g, 20 mmoles) in dry xylene (50 ml) was refluxed for 24 hours. Evaporation and chromatography of the residue (silica gel) afforded 2.15 g (93%) of **2a**, mp 145-146°.

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