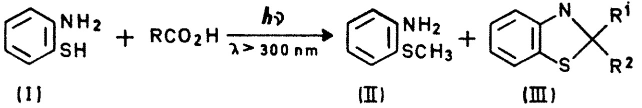
Photochemical Reaction of Aliphatic Carboxylic Acids in the Presence of 2-Aminothiophenol

By Y. MAKI* and M. SUZUKI

(*Gifu College of Pharmacy, Mitahora, Gifu, Japan*)

Summary Photolysis of aliphatic carboxylic acids in the presence of 2-aminothiophenol resulted in the formation of 2-methylthioaniline and several 2,2-dialkylbenzothiazolines having alkyl groups arising from apparent fragmentation of the alkyl residue of the acid.

VERY little is known about the photochemistry of aliphatic carboxylic acids.[1,2] We therefore report the preliminary results of our studies, which may shed some light on the solution photochemistry of simple aliphatic acids. Irradiation of a benzene solution containing the aliphatic acid and 2-aminothiophenol (I) gave 2-methylthioaniline (II) regardless of the acid used, together with a mixture of several 2,2-dialkylbenzothiazolines (III). These latter compounds differed only with respect to the alkyl group at position 2. These alkyl groups included the alkyl residue of the acid employed and also lower alkyl homologues.



(I) (II) (III)

As a typical example, a benzene solution of propionic acid (1·0 M) and (I) (0·1 M) was irradiated with a 100 W high-pressure mercury lamp through a Pyrex filter under nitrogen for 6 h. The reaction mixture was concentrated and the residue was chromatographed on silica gel using chloroform as eluant, to obtain crystalline (III; R^1, R^2 = Me) in 21% yield and a second oily fraction. This was submitted to gas chromatography† to separate (II), (III; R^1 = Me, R^2 = Et), and (III; R^1, R^2 = Et) in 6, 8, and 3% yields, respectively.‡

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† A 1 m × 0·3 cm stainless-steel column packed with 2% OV-17 Chromosorb W was employed.

‡ In the case of acetic acid (III; R^1, R^2 = Me) was isolated in 24% yield. Yields of all oily products except (III; R^1, R^2 = Me) are 2—10%.

The products thus separated were identified by comparison of their gas chromatographic retention times, n.m.r. spectra, and mass spectra with those of authentic samples.[3]

Photochemical reaction of carboxylic acids with 2-aminothiophenol

Carboxylic acid	2,2-Dialkylbenzothiazolines (III)				
Acetic acid	$R^1 =$ Me				
	$R^2 =$ Me				
Propionic acid	$R^1 =$ Me	Me	Et		
	$R^2 =$ Me	Et	Et		
Isobutyric acid	$R^1 =$ Me	Me	Me	Et	
	$R^2 =$ Me	Et	Pr^i	Et	
Isovaleric acid	$R^1 =$ Me	Me	Me	Me	Et
	$R^2 =$ Me	Et	Pr^i	Bu^i	Et

The reactions studied and the products obtained are described in the Table.

This type of photochemical reaction is unprecedented and unexpected. The formation of (II) and (III) substituted with *different* alkyl groups from that of the parent acid is of particular interest. Although the mechanism of this reaction is not clear, the results suggest fragmentation of the aliphatic carboxylic acids to various alkyl radicals as a partial pathway. This might be induced by photo-activated (I).

Recently, Nozaki and his co-workers reported[2] the photochemical alkylation of N-containing heterocyclic compounds by aliphatic carboxylic acids. However, in contrast with our observation, this reaction does not involve further fragmentation of the alkyl residue of the carboxylic acid.

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