Novel Photochemical Reaction of Alcohols in the Presence of an Olefin and 2-Aminobenzenethiol

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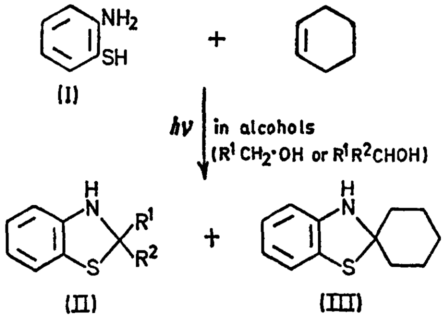
Summary Photolysis of simple primary alcohols in the presence of 2-aminobenzenethiol and cyclohexene afforded 2-alkyl-2-methylbenzothiazolines in which the methyl group may arise from a carbon atom of cyclohexene.

Recently we elucidated some of the solution photochemistry of simple aliphatic acids. Photolysis of the carboxylic acids in the presence of 2-aminobenzenethiol (I) gave several 2,2-dialkylbenzothiazolines (II) in which the alkyl groups appear to have originated from apparent fragmentation of the alkyl residue of the acid.[1]

This observation implies that (I) may also be efficient both for inducing photolysis of alcohols, and capture of the products formed by the subsequent fragmentation. We have now found that photolysis of simple primary alcohols in the presence of both (I) and cyclohexene affords the benzothiazolines (II; R^1 = alkyl, R^2 = Me) together with (III). The origin of the methyl group in (II) is of particular interest. This methyl group can arise only from a carbon atom of the cyclohexene molecule, indicating occurrence of a novel type of photochemical reaction.

The general procedure is as follows. A mixture of (I) (0·1M) and cyclohexene (1·0M) in an aliphatic alcohol was irradiated under nitrogen with a 100 W high-pressure mercury lamp through a Pyrex filter for 15 h. The reaction mixture was concentrated and the residue was chromatographed on silica gel to separate solid and liquid phases. The liquid phase was analysed by g.l.c.–m.s. The products (II) were identified by comparison of their g.l.c. retention times, and n.m.r. and mass spectra with those of authentic samples.[2] In all experiments, (III) was isolated in 2—6% yields. Minor products of undetermined structure were also detected.



Scheme

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

Table

Photochemical reaction of alcohols in the presence of 2-aminobenzenethiol and cyclohexene

Alcohol	2,2-Dialkylbenzothiazoline (II) R^1	R^2	Yield (%)
Ethanol	Me	Me	16
Propan-1-ol	Et	Me	8
Butan-1-ol	Pr	Me	7
2-Methylpropan-1-ol ..	Pr^i	Me	5
Propan-2-ol	Me	Me	42
Butan-2-ol	Et	Me	36
Pentan-3-ol	Et	Et	55

In the cases of secondary alcohols, the $R^1R^2C_2$ parts of (III) correspond to the carbon skeleton of the parent alcohols, as shown clearly for pentan-3-ol. This is explained in terms of oxidation of the secondary alcohols[3] to the corresponding ketones and subsequent thiazoline formation by photochemical condensation of (I) with the ketones. It was demonstrated independently that the formation of (II) from (I) and ketones was accelerated by irradiation.

In the cases of primary alcohols, however, the $R^1R^2C_2$ parts of (II) have an extra carbon atom (methyl) in addition to the carbon atoms from the alcohols used.

In the absence of, or at a low concentration of, cyclohexene in the reaction mixture no (II) was formed. Addition of 1-methylcyclohexene (1·0M) to a mixture of (I) (0·1M) and cyclohexene (1·0M) in ethanol resulted photochemically in the formation of (II; R^1 = Et, R^2 = Me) as well as (II; $R^1 = R^2$ = Me).

These results show that cyclohexene takes part in the photolysis of primary alcohols and supplies a carbon atom (methyl) to the product (II).

In the absence of alcohols, irradiation of a mixture of (I) and cyclohexene gave (III) and 2-aminophenyl cyclohexyl sulphide. Aminophenyl cyclohexyl sulphide was converted into (III) with acetone as solvent. Accordingly, the concurrent formation of (III) in all experiments listed in Table is explained as the photochemical cyclization of 2-aminophenyl cyclohexyl sulphide which is formed by photochemical addition of (I) to cyclohexene.

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