

A Novel Photochemical Reaction of Alcohols in the Presence of an Olefin and 2-Aminothiophenol¹⁾

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Photolysis of simple primary alcohols in the presence of 2-aminothiophenol (I) and cyclohexene afforded 2-methyl-2-alkylbenzothiazolines (II: $R_1=CH_3$, $R_2=alkyl$) having the methyl group arising from a carbon of cyclohexene.

Similar irradiation of secondary alcohols resulted in the formation of 2,2-dialkylbenzothiazolines (II) in which the R_1R_2C parts correspond to the carbon skeleton of the parent alcohols.

The concurrent formation of 2-cyclohexylthioaniline (III) and 2,2-pentamethylenebenzothiazoline (IV) in these reactions was also observed.

Mechanisms for the formation of these photochemical products have been discussed.

Normally, alcohols have been observed to react with photoexcited molecules in only two ways: (1) *via* α -hydrogen abstraction and (2) *via* O-H bond cleavage.³⁾ Recently, photoalkylation of azaheterocycles with alcohols⁴⁾ has proved to be a general reaction in the field of the photochemistry of alcohols. Stermitz, *et al.*^{4b)} and Ochiai, *et al.*^{4c)} have suggested that the photoalkylation is initiated by α -hydrogen abstraction of alcohols with photoexcited azaheterocycles.

Our recent communication⁵⁾ described a finding which has shed some light on the solution photochemistry of simple aliphatic acids. Photolysis of the carboxylic acids in the presence of 2-aminothiophenol (I) resulted in the formation of several 2,2-dialkylbenzothiazolines (II) in which the alkyl groups appear to have originated from apparent fragmentation of the alkyl residue of the acid.

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 alcohols in the presence of both I and cyclohexene affords 2,2-dialkylbenzothiazolines (II). It is of particular interest that employment of primary alcohols led to the formation of 2-methyl-2-alkylbenzothiazolines (II: $R_1=CH_3$, $R_2=alkyl$). The methyl group in II appears to arise from a carbon of the cyclohexene molecule.

- 1) For a preliminary account of this work, see Y. Maki, M. Suzuki, Y. Masada and K. Hashimoto, *Chem. Commun.*, 1972, 209.
- 2) Location: *Sakanoshita, Mitahora, Gifu.*
- 3) a) For a review on the photochemistry of alcohols, see A. Schönberg, "Preparative Organic Photochemistry," 2nd ed., Springer-Verlag New York Inc., 1968, pp. 525-526; b) Recently, it has been reported that the aryl radical produced by irradiation of an arylchloride abstracts efficiently α -hydrogen of an alcohol, see E.A. Caress and I.E. Rosenberg, *J. Org. Chem.*, 36, 769 (1971).
- 4) a) P. Cerutti and H. Schmid, *Helv. Chim. Acta.*, 45, 1992 (1962); b) F.R. Stermitz, R.P. Seiber and D.E. Nicodem, *J. Org. Chem.*, 33, 1136 (1968); c) M. Ochiai, E. Mizuta, Y. Asahi and K. Morita, *Tetrahedron*, 24, 5861 (1968); d) H. Linschitz and J.S. Connolly, *J. Am. Chem. Soc.*, 90, 2979 (1968); e) D. Elad, I. Rosenthal and H. Steinmaus, *Chem. Commun.*, 1969, 305; f) E.C. Taylor, Y. Maki and B.E. Evans, *J. Am. Chem. Soc.*, 91, 5181 (1969); g) E.F. Tarvecedo and V.I. Stenberg, *Chem. Commun.*, 1970, 609; h) F.R. Stermitz, C.C. Wei and C.M. O'Donnell, *J. Am. Chem. Soc.*, 92, 2745 (1970); i) R. Gault and A.I. Meyers, *Chem. Commun.*, 1971, 778.
- 5) Y. Maki and M. Suzuki, *Chem. Commun.*, 1971, 117.

We believe that the present results provide new findings on the photochemistry of alcohols and the photochemical fragmentation. In this paper, we wish to describe the experimental results and present a conceivable mechanism for the novel photochemical reaction.

Irradiation of a mixture of I and cyclohexene in an aliphatic alcohol with a high-pressure mercury lamp through a Pyrex filter resulted in the formation of II, 2-cyclohexylthioaniline (III) and 2,2-pentamethylenebenzothiazoline (IV). Some products of undetermined structure were also detected.

The reactions studied and the products (II) obtained are described in Table I.

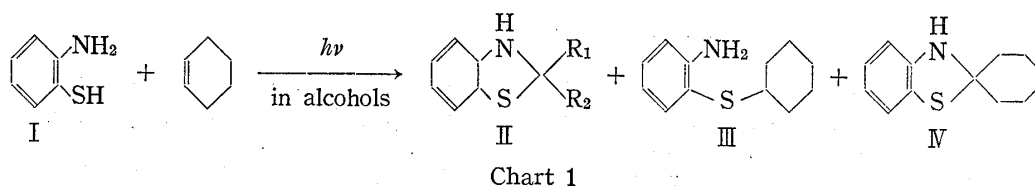
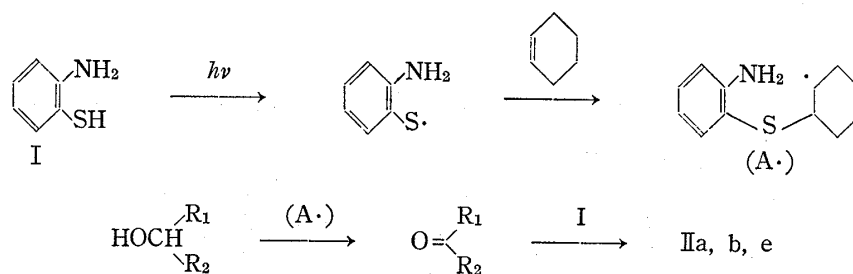


TABLE I. Photochemical Reaction of Alcohols in the Presence of 2-Aminothiophenol (I) and Cyclohexene

Alcohols	2,2-Dialkylbenzothiazolines	Yield (%)
CH ₃ CH ₂ OH	(IIa) R ₁ =CH ₃ R ₂ =CH ₃	16
CH ₃ CH ₂ CH ₂ OH	(IIb) R ₁ =CH ₃ R ₂ =C ₂ H ₅	8
(CH ₃) ₂ CHCH ₂ OH	(IIc) R ₁ =CH ₃ R ₂ =(CH ₃) ₂ CH	10
(CH ₃) ₂ CHCH ₂ CH ₂ OH	(II d) R ₁ =CH ₃ R ₂ =(CH ₃) ₂ CHCH ₂	5
(CH ₃) ₂ CHOH	(IIa) R ₁ =CH ₃ R ₂ =CH ₃	42
(CH ₃)(C ₂ H ₅)CHOH	(IIb) R ₁ =CH ₃ R ₂ =C ₂ H ₅	36
(C ₂ H ₅) ₂ CHOH	(IIe) R ₁ =C ₂ H ₅ R ₂ =C ₂ H ₅	55

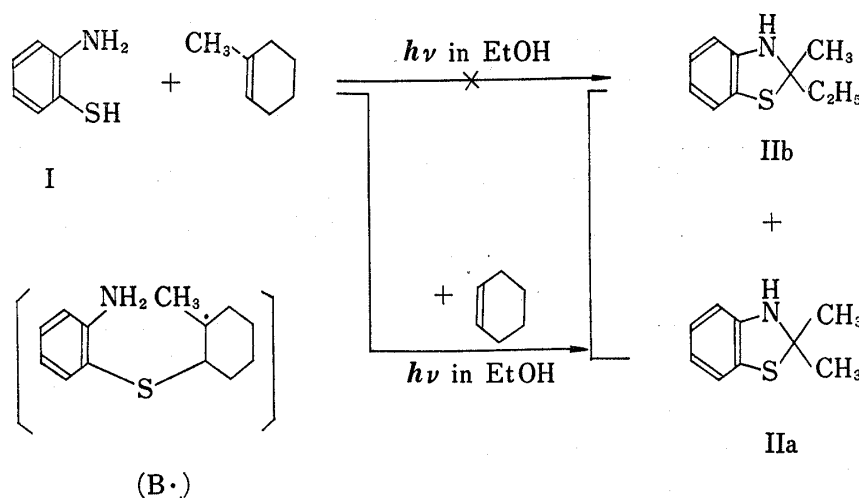
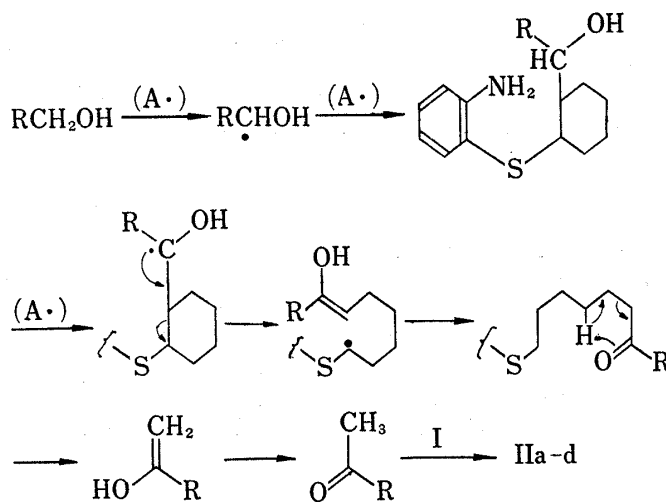
In the cases of secondary alcohols, the R₁R₂C parts of II correspond to the carbon skeleton of the parent alcohols, as shown clearly in the case of (C₂H₅)₂CHOH. These facts suggest the reaction path as follows: 1) light-induced formation of a thiyl radical, 2) addition of the thiyl radical to cyclohexene to produce an alkyl radical (A·),⁶⁾ 3) oxidation of the secondary alcohols to the corresponding ketones⁷⁾ *via* hydrogen abstraction by the radical (A·) and 4) subsequent thiazoline formation by photochemical condensation of I with the ketones⁸⁾ (*cf.* Chart 2). It was demonstrated independently that the formation of II from I and ketones was accelerated by irradiation.



- 6) Electron spin resonance (ESR) spectra of radicals of the type RSCHXCY have been observed, see T. Kawamura, M. Ushio, T. Fujimoto, and T. Yonezawa, *J. Am. Chem. Soc.*, **93**, 908 (1971).
 7) *cf.* N. Nicolae and F.L. Minn, *J. Am. Chem. Soc.*, **90**, 1544 (1968).
 8) Generally, a thiyl radical adds to a double bond rather than abstracts a hydrogen. In fact, upon irradiation of I in alcohols without cyclohexene, no formation of II was observed.

In the cases of primary alcohols, however, the R_1R_2C parts of II have an extra carbon (methyl) in addition to the carbons of alcohols employed. For the explanation of this interesting observation, we tentatively suggest the reaction path as shown in Chart 3.

When 1-methylcyclohexene was employed as an olefin, II was not obtained. However, addition of cyclohexene to a mixture of I and 1-methylcyclohexene in EtOH led photochemically to the formation of 2-methyl-2-ethylbenzothiazoline (IIb) as well as 2,2-dimethylbenzothiazoline (IIa) (see Chart 4). This observation may be explained by assuming that the secondary carbon radical (A·) is superior to the tertiary one (B·), which is produced by addition of a thiyl radical to 1-methylcyclohexene,⁹⁾ on the ability of hydrogen abstraction from EtOH.¹⁰⁾ An ethyl group in IIb may arise from 1-methylcyclohexene. These results point to the fact that cyclohexene takes part in the photolysis of alcohols and can supply a carbon (methyl) to the product (II).



Irradiation of a mixture of I and cyclohexene in C_2H_5OD resulted in the formation of IIa, in which a hydrogen of methyl groups is partly deuterated (about 20%, determined by mass spectrometry). This observation suggests that the photochemical reaction may involve an enolizable intermediate as shown in Chart 3.

In the absence of alcohols, irradiation of a mixture of I and cyclohexene gave rise to III and IV. Photochemical conversion of III into IV was achieved when acetone was employed as a solvent. Accordingly, the concurrent formation of IV in all experiments listed in Table I is explained as the photochemical cyclization of III resulting from an intermediate

9) The orientation of photochemical addition of thiols to 1-methylcyclohexene has been shown to proceed contrary to Markownikoff's rule, see J.I. Cunneen, *J. Chem. Soc.*, 1947, 36.

10) It was generally accepted that a tertiary alkyl radical is less reactive than a secondary one in hydrogen abstraction.

(A·) by the abstraction of a hydrogen.

Recently photo α -hydroxyalkylation of an azomethine bond in azaheterocycles with alcohols has been studied by several research groups.⁴⁾ Photo α -hydroxyalkylation of the conjugated C=C bond in α,β -unsaturated acids¹¹⁾ or in an α,β -unsaturated ketone¹²⁾ with alcohols has been also reported. Our present observation provides a first example of α -hydroxyalkylation of the isolated C=C double bond, induced by a thiyl radical. The photochemical fragmentation as shown in Chart 3 also merits attention. Experiments designed to further elucidate the mechanism of this fascinating photochemistry are now in progress.

Experimental

General Irradiation Procedure—Irradiations were conducted in an immersion reactor (Rikosha Model UVL-300P) using a 100W high-pressure mercury lamp with a Pyrex filter. Prior to irradiation, the solution was flushed with nitrogen and nitrogen was bubbled through the solution constantly during irradiation. This prevented the rapid oxidation of 2-aminothiophenol (I) to its disulfide which occurred when nitrogen was omitted. The solution was stirred magnetically during the entire irradiation. Reagent grade aliphatic alcohols were redistilled prior to use.

Analysis of Liquid Products—The liquid products were analyzed by a gas chromatograph interfaced with a mass spectrometer. The gas chromatography (GC) was carried out on a Hitachi Model K-53 instrument employing a 2 m \times 0.3 cm galss column packed with 2% OV-17 chromosorb W at 120° or 130°. The mass spectra were determined at 70 eV on a Hitachi Model RMU-6E instrument, which can be connected with the gas chromatograph.

Photochemical Reaction of Alcohols in the Presence of I and Cyclohexene—A mixture of I (0.1M) and cyclohexene (1.0 M) in an aliphatic alcohol was irradiated for 15 hr. The reaction mixture was concentrated under reduced pressure and the residue was submitted to silica gel chromatography (solvent-CHCl₃) to separate solid and liquid phases. The solid phase was recrystallized from *n*-hexane to give 2,2-pentamethylenbenzothiazoline (IV) as colorless prisms, mp 113–115° (reported¹³⁾ mp 114–115°), in 2–6% yields. IR (nujol) cm⁻¹: 3300 (NH). NMR (CDCl₃) ppm: 1.0–2.5 (10H, m, pentamethylene protons), 3.87 (1H, s, NH, D-exchangeable), 6.5–7.2 (4H, m, aromatic protons). *Anal.* Calcd. for C₁₁H₁₅NS: C, 70.36; H, 7.37; N, 6.82. Found: C, 70.16; H, 7.54; N, 6.95.

The liquid phase was analyzed by GC-mass spectroscopy to be 2-cyclohexylthioaniline (III) and 2,2-dialkylbenzothiazolines (II). III was identified by comparing its GC retention time (655 sec/column temperature: 150°) and mass spectrum (M⁺: *m/e* 207) with those of an authentic sample.¹⁴⁾

TABLE II. NMR Spectral Data and GC Retention Times of 2,2-Dialkylbenzothiazolines (II)

	NMR ^{a)}	GC ^{b)} retention time (sec)	Column temp. (°C)
IIa	1.71 (6H, s)	238	133
		281	124
IIb	1.02 (3H, t), 1.66 (3H, s), 1.91 (2H, q)	403	133
		481	124
IIc	1.00 (3H, d), 1.05 (3H, d), 1.61 (3H, s), 2.12 (1H, h)	581	133
IId	1.01 (6H, d), 1.68 (3H, s), 1.5–2.2 (1H, m), 1.88 (2H, d)	730	133
IIe	1.02 (6H, t), 1.89 (4H, q)	762	124

a) NMR spectra were obtained using a Hitachi Model R-20B instrument and samples were dissolved in CDCl₃ containing tetramethylsilane as internal standard. Signal multiplicities were represented by s(singlet), d(doublet), t(triplet), q(quartet), h(heptet) and m(multiplet). Chemical shifts were reported in ppm values. In all spectra, signals at 3.9 (1H, s, NH, D-exchangeable) and 6.45–7.15 (4H, m, aromatic protons) were observed.

b) The GC was carried out on a Shimadzu Model GC-4A gas chromatograph. The GC analytical measurements were made with a 1.5 m \times 0.3 cm stainless steel column packed with 3% OV-17 chromosorb W and gas-flow rate was 30 ml/min.

11) See ref. 3a) pp. 231–233.

12) I.A. Williams and P. Bladon, *Tetrahedron Letters*, **1964**, 257.

13) R.C. Elderfield and E.C. McClenachan, *J. Am. Chem. Soc.*, **82**, 1982 (1960).

14) D.G. Foster and E.E. Reid, *J. Am. Chem. Soc.*, **46**, 1936 (1924).

Benzothiazolines (II) were identified by comparison of their GC retention times, nuclear magnetic resonance (NMR) spectra and mass spectra with those of authentic samples. GC retention times and NMR data of II are described in Table II. The authentic samples (II) were prepared by the method of Elderfield and McCleanachan¹³ except 2,2-diethylbenzothiazoline (IIe) (bp₁₅ 157—158°), which was prepared by the reaction of I with diethylketone.

Photolysis of I in Acetone—1.3 g of I in 100 ml of freshly distilled acetone was irradiated for 5 hr. After irradiation, acetone was evaporated under reduced pressure and the residue was purified by silica gel chromatography (solvent-CHCl₃) and recrystallized from *n*-hexane to give 1.5 g of 2,2-dimethylbenzothiazoline (IIa) as colorless prisms, mp 45—46° (reported¹³) mp 46—48°. *Anal.* Calcd. for C₉H₁₁NS: C, 65.41; H, 6.71; N, 8.48. Found: C, 65.79; H, 6.88; N, 8.51.

Photolysis of EtOH in the Presence of I, Cyclohexene and 1-Methylcyclohexene—A mixture of I (0.2 M), cyclohexene (1.0 M) and 1-methylcyclohexene (1.0 M) in EtOH was irradiated for 25 hr. The irradiated solution was concentrated under reduced pressure and the oily residue was analyzed by GC-mass spectroscopy to be confirmed the formation of IIa and 2-methyl-2-ethylbenzothiazoline (IIb). The gas chromatogram and the mass spectral data of IIa and IIb are given in Fig. 1 and Table III respectively.

Photolysis of I in Cyclohexene—A mixture of 5.0 g of I (0.04 mole) and 32.8 g of cyclohexene (0.4 mole) was irradiated for 20 hr. After irradiation, the reaction mixture was concentrated under reduced pressure and the residue was chromatographed on silica gel using CHCl₃ as eluant to give 0.8 g of crystalline (IV), which was identified in every respect with a specimen obtained above, and a second oily fraction. This was submitted to GC-mass spectroscopy to established its structure as III.

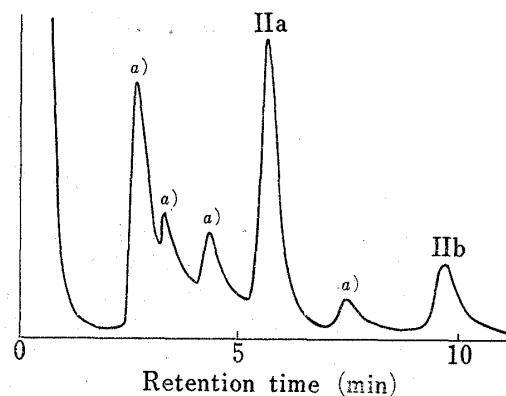


Fig. 1. Gas Chromatogram of the Irradiated Mixture of 2-Aminothiophenol (I), Cyclohexene and 1-Methylcyclohexene in EtOH

2% OV-17 chromosorb W, glass column: length; 2 m, *i.d.*; 3 mm, column temperature: 130°, detection: FID, carrier gas: N₂, instrument: Hitachi Model K-58

a) undetermined peaks

IIa: 2,2-dimethylbenzothiazoline

IIb: 2-methyl-2-ethylbenzothiazoline

TABLE III. Mass Spectral Data of 2,2-Dimethylbenzothiazoline (IIa) and 2-Methyl-2-ethylbenzothiazoline (IIb)

IIa		IIb	
<i>m/e</i>	% of base	<i>m/e</i>	% of base
165	30	179	22
150	100	164	18
109	28	150	100
		109	26

Photolysis of III in Acetone—1.0 g of III was irradiated in 100 ml of freshly distilled acetone for 20 hr. After irradiation, the solvent was evaporated and the resulting residue was purified by silica gel chromatography (solvent-CHCl₃) and recrystallized from *n*-hexane to give 0.5 g of IV, identified by mixed mp determination and IR comparison with a specimen obtained above.

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