## PHOTOCHEMICAL INCORPORATION OF PROTIC SOLVENTS BY OPEN CHAIN OLEFINS

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Abstract—Irradition of methyl styryl sulphoxide dissolved in MeOH, EtOH, or AcOH induces the photochemical polar addition of the solvents to afford the product, PhCH(OR)CH<sub>2</sub>SOMe, where R is Me, Et, or Ac. By-products are the corresponding sulphides, PhCH(OR)CH<sub>2</sub>SMe, and methyl styryl sulphide. Similar adducts of protic solvents are produced upon irradiation of certain vinylic sulphides, methyl phenethynyl sulphide, as well as appropriately substituted propenylbenzenes including *o*-anethole, *o*-anol, and *o*-propenylaniline in soln.

During xylene-sensitized irradiation, cyclohexenes and -heptenes react readily with protic solvents to afford the "polar" adducts via the highly strained ground-state of trans-cycloalkenes as the reactive species.<sup>1</sup> Little is known, however, with respect to the similar photochemical reaction of the open chain olefins,<sup>2</sup> which must involve other kinds of reactive species. The present report describes instances of novel protic solvent incorporation of certain open chain olefins occurring photochemically.<sup>†</sup>

#### Photoreaction of methyl styryl sulphoxide

When a MeOH soln of methyl styryl sulphoxide<sup>4</sup> (1) was irradiated, products isolated were found

<sup>†</sup>Part of this work was presented in the preliminary form.<sup>3</sup>

‡LAH reduction of 2a and 2b in THF gave the corresponding sulphides 3a and 3b, respectively.

§For the similar photochemical reduction of thiachroman-1-oxide, see Ref. 5.

to be methyl  $\alpha$ -[(methylsulphinyl)methyl]benzyl ether<sup>4</sup> (2a), methyl  $\alpha$ -[(methylthio)methyl]benzyl ether<sup>4</sup> (3a), and methyl styryl sulphide<sup>4</sup> (4). The photoreaction in the EtOH or AcOH soln proceeded similarly (Scheme 1 and Table 1). When the soln of 1 in each solvent was kept in the dark at room temp for 120 hr, the starting material remained totally unchanged. All the products were isolated by means of the GLC and identified on the basis of the spectral data or by the chemical correlation.<sup>‡</sup> The NMR spectra of all the sulphoxides (2a, 2b, 2c) exhibited the two singlets due to SO-Me in equal intensity, indicating the presence of two diastereomers in approximately 1:1 ratio in all cases. The formation of the  $\beta$ -alkoxy and  $\beta$ acetoxy sulphides (3a, 3b, 3c) is ascribed to the initial reductions of the vinylic sulphoxide 1 to the sulphide 4 and the subsequent photo-induced addition of the protic solvents. The photochemical reduction proceeded smoothly in the i-PrOH soln to produce acetone in the reaction mixture. In contrast, however, irradiation of the sulphoxide 2 failed to afford the reductant 3.



Solvent	Reaction time (hr)	Products, Yield <sup>a</sup> (%)			
MeOH	120	2a,4 65	3a, * 8.0	4,4 10	
EtOH	120	<b>2b</b> , 53	3b, 9·2	4,4 9.0	
AcOH	120	2c, 60	3c, 15	4. 13	
i-PrOH	70			4,* 52	

Table 1. Photoreaction of methyl styryl sulphoxide

"The yields were based on 1" initially added.

### Photoreaction of the vinylic and the acetylenic sulphides in the protic media

Photochemical cyclization of aryl vinylic sulphides affords benzothiophenes.<sup>6</sup> In order to verify the pathway of the formation of the sulphides 3 as described above, the photochemical behaviour of some vinylic sulphides in the protic media was examined.

The irradiation of methyl styryl sulphide 4 in the MeOH soln afforded methyl  $\alpha$ -[(methylthio)methyl]benzyl ether 3a together with recovered 4. The similar addition reaction proceeded smoothly with phenyl styryl sulphide' and phenyl propenyl sulphide<sup>8</sup> in EtOH as well as in AcOH to afford the respective adducts (5 and 6). The results are given in the order of the adduct, reaction time (hr), and the yield\* (%): 3a<sup>4</sup> (48, 15), 3b (48, 13), 3c (48, 57), 5a (12, 18), 5c<sup>9</sup> (12, 70), 6c (48, 43). The benzothiophene type cyclization products<sup>6</sup> were not detected in the irradiation mixture. In the dark the vinylic sulphides remained totally unchanged, even after heating under reflux for 48 hr. The photochemical polar addition was successfully applied to the reaction of the acetylenic sulphide $^{10}$  7<sup>11</sup> in the AcOH soln to provide a facile means for synthesizing the hitherto unknown, *B*-acetoxy-substituted vinylic sulphides (Scheme 2). Irradiation of methyl phenethynyl sul-

 $\pm$  the assignment of E and Z to each isomer has not been achieved.

\$The presence of acetic anhydride in the reaction mixture was detected by means of the combination of the GLC and the MS measurement.

<sup>1</sup>Several instances have been recorded with respect to the hydration of the acetylenic sulphides in the presence of the strong acids or HgO.<sup>15,16</sup>



SCHEME 2

phide<sup>11</sup> (7) dissolved in AcOH for 12 hr and the successive distillation gave  $\beta$ -acetoxystyryl methyl sulphide (8, 63%) together with recovered sulphide (7, 22%).<sup>+</sup> The NMR spectrum showed that the product 8 was a 1:1 mixture of the E and Z isomer.<sup>‡</sup> The additional proof for the structure of 8 was secured by the hydrolysis to the  $\beta$ -keto sulphide<sup>13</sup> 9 according to the House's method.<sup>14</sup> In sharp contrast to the vinylic sulphides, acetylenic 7 reacted with AcOH under reflux conditions in the dark to yield the thiolacetate15 (11, 85%) and acetic anhydride§ (78%), although the sulphide 7 was fairly stable toward AcOH at room temp. While MeOH failed to add to 7 photochemically or thermally, 7 readily reacted with MeOH in the presence of a trace of conc HCl at room temp to afford methyl phenylacetate (75%). The thermal formation<sup>1</sup> of the thiolacetate<sup>15</sup> 11 is explained by assuming the initial formation of the monoadduct 10, The following fast addition of AcOH to 10, and finally the electrocyclic elimination of acetic anhydride proceeding similarly as proposed by Arens and Doornbos<sup>17</sup> in the reaction of the ethynyl ethers with the carboxylic acids. Thus the photochemical addition of AcOH to 7 gives the  $\beta$ -keto sulphide 9, whereas the thermal addition yields the thiolacetate 11. Although the methylthio group is electrondonating in the thermal reaction, the reverse is true under the irradiation conditions. The reason for this

<sup>\*</sup>The yields were based on the olefinic substrates.

<sup>&</sup>lt;sup>†</sup>As the photochemical polar addition to tolan in the protic media has been recorded,<sup>12</sup> the photoreaction of phenylacetylene or 1-phenylhex-1-yne in the AcOH soln was attempted in order to know the possible role of the -SMe moiety in the observed polar addition to 7. The IR spectra of the crude mixture showed the absence of the desired enol ester in both cases.

The attempted detection of the monoadduct 10 was unsuccessful under the present conditions. The presence of 7 and the thiolacetate was ascertained by the NMR analyses of the residue obtained upon the removal of the volatile components and the solvent from the reaction mixture.

is probably given by the photochemical polarization of the sulphide 7 due to the  $\pi^*-3d$  interaction\* being responsible for the regiospecificity.

# Photoreaction of o-substituted propenylbenzenes in the protic media

To gain further insight of the photochemical polar addition to the open chain olefins, the behaviour of o-anethole and some analogues was examined.

When the AcOH soln of o-anethole (12x) was irradiated, the acetate 13cx was obtained almost quantitatively (Scheme 3). The formate 13dx was prepared similarly, whereas the photoaddition of MeOH required the presence of a trace of conc HCl.<sup>†</sup> No positional isomers of 13 have been isolated and this is attributed to the benzylic cation as a possible intermediate. The results are summarized in Table 2. The photoreaction was followed by determining the distribution of trans - and cis-12x and the acetate 13cx by means of the GLC analyses of the aliquots taken out periodically during the reaction (Fig 1). The fast trans to cis isomerization was observed in the early stage of the reaction. The intermediacy of cis-12x in the photoaddition was supported by the similar monitoring of the reaction of

tUnidentified dimers were formed in the absence of a drop of conc HCl.

‡Question may arise, why the intermediate 14 can not be produced from the S' state of *trans*-12x. The UV<sub>max</sub> (100% AcOH) of *trans*-12x. is observed at 297 nm (log  $\epsilon =$ 3·67), whereas *cis*-12x at 288 nm (3·58). The blue shift of *cis*-12x is naturally ascribed to the steric interaction of o-MeO with the allylic Me group. The observed reactivity of *cis*-12x is ascribed to the larger energy quanta absorbed or the higher energy level of the S' state of *cis*-12x.



 $\mathbf{R}'$ : (x) OMe, (y) OH, (z)  $\mathbf{NH}_2$  R: (a) Me, (c) Ac, (d) HCO

SCHEME 3



Fig 1. Photolysis of *trans* and *cis*-12x in AcOH. Distribution in % vs irradiation time in hr.

cis-12x itself, which is considered to be the precursor of the adduct 13cx.

The multiplicity of the reactive species was then examined. The AcOH soln of trans-12x and benzophenone (or triphenylene) was irradiated for 12 hr under the conditions that the sensitizer only absorbed the light. The GLC analyses showed that no trace of 13cx was formed and the trans to cis isomerization of 12x exclusively occurred in each case (benzophenone, t/c = 10:90; triphenylene, t/c = 12:88). Irradiation of the AcOH soln of trans-12x and benzophenone under the conditions that both substrates absorbed the light gave rise to the acetate 13cx (8.0%) in addition to a cis, trans mixture of 12x. Furthermore, the formation of the acetate 13cx was not affected by the addition of pirpervlene. These observations are explained by assuming that the photochemical polar addition of 12x occurs via the excited singlet state of cis-12x, ‡

No.	Solvent	Adduct	Reaction time (hr)	Yield (%)	Yield (%) of dimer
12x°	AcOH	13cx	20	quant	nil
	HCOOH	1 <b>3dx</b>	20	quant	nil
	MeOH⁴	13ax	20	quant	nil
12v <sup>b</sup>	AcOH	13cv	50	quant	nil
12z*	AcOH	13cz	50	quant	nil
m-12x	AcOH	m-13cx	72	. 8	92'
p-12x	AcOH	p-13cx*	72	7	93*

Table 2. Photoreaction o-substituted propenylbenzenes in protic media

"The starting material 12x contained 96% trans and 4% cis.

<sup>b</sup>Anol 12y was pure trans.

'It contained 89% trans and 11% cis.

<sup>d</sup>A drop of conc HCl was added.

'See Ref 19.

'Two dimers of unknown structure were formed.

\*The GLC and IR spectra analyses showed that the dimer was the same one as obtained by means of the irradiation of p-12x in the benzene soln. See Ref. 20.

<sup>\*</sup>The ability of the unsaturated sulphide group to participate in mesomeric interaction in the excited state involving utilization of a 3d orbital of the S atom has been mentioned on the basis of the UV spectroscopic study.<sup>16</sup>

whose olefinic  $\beta$ -carbon possibly has higher electron-density than the one in the ground state. The supposed intermediate may be formulated as 4. This in sharp contrast to the formally analogous reaction of the cycloalkenes.<sup>1</sup> Apparently, benzophenone is not an effective singlet quencher for 12x.\* o-Anisalacetone and methyl o-methoxycinnamate failed to induce the photochemical polar addition in the AcOH soln.



As shown in Table 2, the reaction of *p*-anethole (p-12x) in the AcOH soln under similar conditions as the direct irradiation of 12x afforded the expected photoadduct in much inferior yield, the photodimer<sup>20</sup> being the major product. *m*-Anethole (m-12x) behaved similarly.

Irradiation of o-anol (12y) in the AcOH soln gave the acetate 13cy quantitatively with the *trans* to *cis* isomerization. On the other hand, 12y gave only the intractable polymer upon irradiation in the MeOH soln. The adduct 13cy was methylated to give 13cx obtained from 12x. Anol photochemistry may involve the intervention of the ketonic tautomer 15 photochemically produced.<sup>†</sup>



When o-propenylaniline<sup>24</sup> (12z) was irradiated similarly, the quantitative incorporation of the solvent occured to afford 13cz.

Meanwhile, a novel type of photorearrangement has been observed. Irradiation of o-allylanisole in the AcOH soln gave the o-cyclopropylanisole,<sup>25</sup> (11%) as a sole isolable product possibly via the vinyl-di- $\pi$ -methane rearrangement<sup>27</sup> (Scheme 4).

\*Benzophenone is a singlet quencher in the photochemistry of *p*-anethole or methyl  $\beta$ -naphthyl ether.<sup>20,21</sup>

<sup>†</sup>The several attempts to trap 15, including the irradiation of 12y in the presence of the dienophile such as TCNE or dimethyl acetylenedicarboxylate, were unsuccessful. The photoinduced 1,5-hydrogen transposition of -OH in the phenol system to result in the ketonetautomerization has been recorded.<sup>22</sup> The irradiation of 2,2-dimethylchromene in the MeOH soln resulted in the addition of the solvent to the olefinic site via the intermediary o-quinoide of the similar structure as 15.<sup>23</sup>

 $\pm o$ -Cyclopropylanisole was stable to the prolonged irradiation with the light filtered through quartz for 150 hr, although several reports have appeared with respect to the photochemical polar addition to the excited phenyl-substituted cyclopropanes in the protic media.<sup>26</sup>



#### EXPERIMENTAL

All m.ps and b.ps are uncorrected. The IR spectra were obtained on a Shimazu IR-27-G spectrometer in neat liquid films unless stated otherwise. The NMR spectra were taken with a JEOL C-60-H spectrometer (60 MHz) with CDCl<sub>3</sub> as a solvent and chemical shifts are recorded in  $\delta$  values relative to TMS as an internal standard. The NMR data are given in the order of multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = unresolved multiplet), integration, and assignment. The UV spectra were taken on a Hitachi EPS-2 recording spectrophotometer. The MS spectra were obtained with a Hitachi RM-61 spectrometer at 80 eV. The column chromatography was carried out on Mallinckrodt silicic acid (100 mesh). Plates of silicagel G were used for the TLC and the spots were visualized with iodine vapour.

Photoreaction of methyl styryl sulphoxide (1). A soln of 1<sup>4</sup> [500 mg, 3.0 mmol,  $\lambda_{\text{max}}^{\text{MeOH}} = 266 \text{ nm} (\log \epsilon = 4.27)$ ] dissolved in a solvent (20 ml) was placed in a Pyrex vessel and irradiated externally by means of 200 W high-pressure mercury arc under N2 atm at room temp. The progress of the reaction was followed by the GLC analyses of the aliquots (SE 30, 0.75 m, 130°). The mixture was then concentrated in vacuo (or alternatively neutralized with Na<sub>2</sub>CO<sub>3</sub> aq, extracted with CHCl<sub>3</sub>, and the CHCl<sub>3</sub> soln concentrated) and the residue was distilled. The products were purified by the preparative GLC (SE 30, 1.0 m, 130°): 2b, b.p. 112-118°/0.4 mm, IR 1100 and 1050 cm<sup>-1</sup>, NMR δ 2.55, 2.60 (2s, 3H, CH,S(O)-), 3.28, and 3.30 ppm (2q, 2H, --CH<sub>2</sub>O---); 3b, b.p. 76-80°/0.4 mm, IR 1100 cm<sup>-</sup> NMR & 2.00 (s, 3H, CH<sub>3</sub>S---), and 3.29 ppm (q, 2H, -CH2O-); 2c, b.p. 126-130°/0.2 mm, IR 1740, 1220, and 1030 cm<sup>-1</sup>, NMR δ 2.00, 2.05 (2s, 3H, CH<sub>3</sub>C=O), 2.60, and 2.63 ppm (2s 3H, CH<sub>3</sub>S(O)-); 3c, b.p. 95-98°/0.2 mm, IR 1740 and 1220 cm ', NMR δ 2.00 (s, 3H, CH<sub>3</sub>C=O), and 2.02 ppm (s, 3H, CH<sub>3</sub>S—). The notation 2s in the NMR data means two singlets having the equal intensity.

#### Independent syntheses of solvent-incorporation products

Ethyl  $\alpha$ -[(methylsulphinyl)methyl]benzyl ether (2b).  $\alpha$ -[(Methylsulphinyl)methyl]benzyl alcohol<sup>4</sup> (300 mg, 1·6 mmol) dissolved in THF (3·0 ml) was added slowly to a suspension of NaH (41 mg, 1·7 mmol) in THF (5·0 ml). After the addition of excess Etl, the mixture was stirred for 3 hr at room temp. The mixture was then poured into water (10 ml). The aqueous mixture was extracted with CHCl<sub>3</sub>. The combined extracts were dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent and the column chromatographic treatment (silicagel, AcOEt as an eluant) of the residue gave 2b (290 mg, 85%).

Ethyl  $\alpha$ -[(methylthio)methyl]benzyl ether (3b). A THF (60 ml) soln of 2b (500 mg, 2.4 mmol) and LAH (27 mg, 0.72 mmol) was heated to reflux for 12 hr. Work-up afforded 3b (430 mg, 90%).

 $\alpha$ -[(Methylthio)methyl]benzyl acetate (3c). An ethereal (5.0 ml) soln of  $\alpha$ -[(methylthio)methyl]benzyl alcohol<sup>4</sup> (500 mg, 3.0 mmol) was treated with Ac<sub>2</sub>O (460 mg, 4.5 mmol) and a drop of BF<sub>3</sub>·Et<sub>2</sub>O at room temp for

30 min. The mixture was then poured into water (10 ml) to decompose the excess  $Ac_2O$ . Neutralization of the mixture with  $Na_2CO_3$  aq, extraction with ether, and the successive distillation gave 3c (590 mg, 93%).

 $\alpha$ -[(Methylsulphinyl)methyl]benzyl acetate (2c). The oxidation of 3c to 2c was carried out according to the method of Russell and Ochrymowycz.<sup>28</sup> An aq soln (6-0 ml) of NaIO<sub>4</sub> (560 mg, 2-6 mmol) was added to the CH<sub>3</sub>CN (6-0 ml) soln containing 3c (500 mg, 2-4 mmol) at – 10°. The mixture was stirred at room temp for 12 hr, the soln was filtered to remove NaIO<sub>3</sub>, and extracted with CHCl<sub>3</sub>. The removal of the solvent *in vacuo* and the column chromatographic treatment (silicagel, AcOEt) gave 2c (470 mg, 86%).

The IR spectra of 2b, 3b, 3c, and 2c thus obtained superimposable with those of the photoproducts, respectively.

#### Photoreaction of unsaturated sulphides

The vinylic sulphides. The soln of the vinylic sulphide (3.0 mmol, 4:  $\lambda_{max}^{ACOH} = 286$  nm (log  $\epsilon = 4.51$ ), phenyl styryl sulphide:<sup>\*</sup>  $\lambda_{max}^{ACOH} = 290$  (4.63), phenyl propenyl sulphide:<sup>9</sup>  $\lambda_{max}^{ACOH} = 266$  (3.90)) dissolved in a solvent (20 ml) was irradiated in a similar manner. After the usual work-up, all the products were isolated by means of the preparative GLC (SE 30, 1.0 m, 100°) or the column chromatography: **5a**, b.p. 110–116°/0.08 mm, IR 1100 cm ', NMR  $\delta$  2.68, 2.82 (2*q*, 2H, methylene), and 3.20 ppm (*s*, 3H, CH<sub>3</sub>O—); **6c**, b.p. 80–83°/5 mm, IR 1740 and 1225 cm '', NMR  $\delta$  1.28 (*d*, 3H, CH<sub>3</sub>CH—). 1.90 (*s*, 3H, CH<sub>3</sub>C=O), 2.90, and 3.08 ppm (2*q*, 2H, methylene).

Methyl phenethynyl sulphide (7). The photoreaction of 7 (500 mg, 3·4 mmol,  $\lambda_{max}^{n,OH} = 248$  (log  $\epsilon = 4.04$ ) and 260 nm (4·02)) dissolved in AcOH (20 ml) was performed for 12 hr as described. After the irradiation, the usual work-up and distillation gave **8**, b.p. 100–105°/0·3 mm, IR 1760, 1690, and 1200 cm<sup>-1</sup>, NMR  $\delta$  2·08 (s, 3H, CH<sub>3</sub>C=O), 2·18 (s, 3H, CH<sub>3</sub>S=), 5·90, and 6·21 ppm (2s, 1H, vinylic), MS m/e 208 (M<sup>+</sup>), 166 (B<sup>+</sup>).

Irradiation in a quartz vessel gave practically the same results, though the reaction proceeded rather sluggishly.

#### Independent synthesis of 2-acetoxypropyl phenyl sulphide (6c)

The sulphide **6c** was prepared by the oxymercuration.<sup>29</sup> Allyl phenyl sulphide<sup>8</sup> (500 mg, 3·3 mmol) was added to a THF (6·0 ml) soln of Hg(OAc)<sub>2</sub> (1·1 g, 3·3 mmol). The mixture was stirred for 15 min at room temp and treated successively with NaOH aq (3·0 M, 3·0 ml) and NaBH<sub>4</sub> aq (0·50 M, 7·0 ml). Work-up afforded 2-hydroxypropyl phenyl sulphide. The crude alcohol was subjected to acetylation by means of Ac<sub>2</sub>O (340 mg, 3·3 mmol) and a catalytic amount of BF<sub>3</sub>·Et<sub>2</sub>O in ether (3·0 ml). The distillation afforded **6c** (b.p. 80-83<sup>o</sup>/5 mm, 530 mg, 77% based on allyl phenyl sulphide<sup>\*</sup>). The IR spectrum of the acetate **6c** thus formed was superimposable with that of the photoproduct.

#### Hydrolysis of $\beta$ -acetoxystyryl methyl sulphide (8)

The enol acetate **8** was hydrolysed according to the method of House *et al.*<sup>14</sup> An ethereal (8-0 ml) soln of **8** (500 mg, 2-4 mmol) and MeLi (2-6 mmol) was stirred at 0° for 30 min. To the resulting soln, water (5-0 ml) was added. Work-up and the distillation gave  $9^{13}$  (b.p.  $102-104^{\circ}/2$  mm, 300 mg, 75%).

#### Thermal reaction of methyl phenethynyl sulphide 7

Addition of AcOH. An AcOH (5.0 ml) soln of 7 (500 mg, 3.4 mmol) was stirred under reflux for 12 hr. Work-up followed by the distillation afforded 11<sup>15</sup> (b.p. 130-132°/25 mm, 480 mg, 85%).

Addition of MeOH. A MeOH (5.0 ml) soln of 7 (500 mg, 3.4 mmol) was stirred in the presence of a drop of conc HCl at room temp for 120 hr. Work-up gave methyl phenylacetate (b.p. 120-121°/20 mm, 380 mg, 73%).

#### Preparation of trans and cis isomers of o-anethole (12x)

The KHSO<sub>4</sub>-catalysed dehydration of o-(1-hydroxypropyl)anisole<sup>30</sup> afforded almost pure *trans*-12x, which was contaminated by a small amount of *cis* isomer (4.0%). Meanwhile, the methylation<sup>31</sup> of *o*-anol obtained via the KOH-catalysed isomerization of *o*-allyl phenol yielded the mixture of *trans*-12x (85%) and the *cis* isomer (15%). The *cis* isomer was purified by means of the preparative GLC (HVSG 20%, 2m, 130°).

## Photoreaction of 0-substituted propenylbenzenes 12 in the protic media

Direct irradiation of 12x. The irradiation of 12x (440 mg, 3.0 mmol) dissolved in a solvent (20 ml) was conducted with the light filtered through Pyrex in the similar manner to that above. In the reaction of 12x with HCOOH, the mixed soln of HCOOH (10 ml) and ether (10 ml) was used to dissolve 12x.

Irradiation in a quartz vessel gave practically the same results, though the reaction proceeded rather sluggishly.

Irradiation of 12x in the presence of benzophenone (> 350 nm). The soln of 12x (100 mg, 0.68 mmol) and benzophenone (250 mg, 1.4 mmol) in AcOH (20 ml) (or triphenylene (320 mg, 1.4 mmol) in PhH (10 ml) and AcOH (10 ml)) was irradiated through a 10% soln (1.5 cm thick) of CuSO<sub>4</sub> aq<sup>32</sup> as a filter at room temp for 12 hr.

Irradiation of 12x in the presence of benzophenone (> 280 nm). The soln of 12x (100 mg, 0.68 mmol) and benzophenone (120 mg, 0.68 mmol) dissolved in AcOH (20 ml) was irradiated with the light filtered through Pyrex for 12 hr.

Irradiation of 12x in the presence of piperylene. The soln of 12x (100 mg, 0.68 mmol) and piperylene (140 mg, 2.0 mmol) dissolved in AcOH (20 ml) was irradiated as described.

p-Anethole (p-12x), m-anethole (m-12x), o-anol (12y), and o-propenylaniline (12x) were irradiated similarly. The results are given in Table 2 and the physical properties of the adducts are summarized in Table 3.

#### Independent syntheses of 13cx, m-13cx, and 13ax

The acetates 13cx and m-13cx were synthesized via the acetylation of o-(1-hydroxy-propyl)anisole<sup>w</sup> and its m-isomer<sup>30</sup> obtained by the reaction of the corresponding anisaldehydes with EtMgI. The authentic specimen of 13ax was obtained via the methylation of o-(1-hydroxy-propyl)anisole<sup>30</sup> with NaH and MeI. The IR spectra of the specimen thus obtained were superimposable with those of the photoproducts.

Methylation of the photoproduct 13cy. The methylation was attained according to the method of Neeman and Hashimoto." The soln of 13cy, (500 mg, 2.6 mmol) photochemically obtained, and excess diazomethane, and  $BF_1 \cdot Et_2O$  (140 mg, 1.0 mmol) dissolved in  $Et_2O$  (10 ml) and  $CH_2Cl_2$  (10 ml) was stirred at room temp for 12 hr. The excess diazomethane was decomposed with a few drops of AcOH. Work-up afforded the acetate (13cx,

Table 3. Physical properties of resultant adducts in propenylbenzene reactions

No	b.p. (°/mm) or m.p. [°]	IR (cm <sup>-1</sup> )	NMR (å, ppm)
13cx	110-116/6	1740, 1240	0.83 (t, 3H, CH <sub>3</sub> CH <sub>2</sub> ), 1.80 (m, 2H, CH <sub>3</sub> CH <sub>2</sub> ), 1.99 (s, 3H, CH <sub>3</sub> C=O), 3.75 (s, 3H, CH <sub>3</sub> O)
13dx	84-85/3	1720, 1170	0.90 (t, 3H, CH <sub>3</sub> CH <sub>2</sub> ), $1.80$ (m, 2H, CH <sub>3</sub> CH <sub>2</sub> ), 3.75 (s, 3H, CH <sub>3</sub> O), $7.95$ (s, 1H, HC=O)
13ax	74–75/3	1240, 1100	0.90 ( $\dot{t}$ , 3H, CH <sub>3</sub> CH <sub>2</sub> ), 1.60 ( $m$ , 2H, CH <sub>3</sub> CH <sub>2</sub> ), 3.18 ( $s$ , 3H, CH <sub>3</sub> OCH), 3.75 ( $s$ , 3H, CH <sub>3</sub> O attached to aromatic ring)
13cy	[66-67]	3350, 1710, 1240	0.85 (t, 3H, CH <sub>3</sub> CH <sub>2</sub> ), $1.83$ (m, 2H, CH <sub>3</sub> CH <sub>2</sub> ), 1.95 (s, 3H, CH <sub>3</sub> C=O), $5.40$ (s, 1H, OH)
13cz	110-113/15	1740, 1240	0.85 (t, 3H, CH <sub>3</sub> CH <sub>2</sub> ), $1.82$ (m, 2H, CH <sub>3</sub> CH <sub>2</sub> ), 2.00 (s, 3H, CH <sub>3</sub> C=O), $4.15$ (s, 2H, NH <sub>2</sub> )
<i>m</i> -13cx	110–115/4	1740, 1240	0.85 (t, 3H, CH <sub>3</sub> CH <sub>2</sub> ), $1.74$ (m, 2H, CH <sub>3</sub> CH <sub>2</sub> ), 1.95 (s, 3H, CH <sub>3</sub> C=O), $3.70$ (s, 3H, CH <sub>3</sub> O)

Table 4. Elemental analyses of new compounds

		Required, %		Found, %	
No.	Formula	С	H	Ċ	H
2Ъ	$C_{11}H_{16}O_2S$	62.3	7.6	62.5	7.4
2c	$C_{11}H_{14}O_3S$	58-4	6.2	58.6	6.3
3b	$C_{11}H_{16}OS$	67.3	<b>8</b> ∙2	67·0	8∙2
3c	$C_{11}H_{14}O_2S$	62.8	6.7	62.4	6.9
5a	C15H16OS	73.8	6.6	73-3	6.5
6с	C <sub>11</sub> H <sub>14</sub> O₂S	62.8	6.7	63.1	6.5
8	$C_{11}H_{12}O_2S$	63-5	5.8	63·2	5.7
13ax	$C_{11}H_{16}O_2$	73.3	<b>9</b> .0	73.6	8.8
13cx	$C_{12}H_{16}O_{3}$	69·2	7.7	69·5	7.7
13dx	$C_{11}H_{14}O_3$	<b>68</b> ∙0	7.3	68·4	7.6
13cy	$C_{11}H_{14}O_{3}$	<b>68</b> ∙0	7.3	67·7	7.1
13cz	C11H15NO2"	<u>68</u> ∙4	7.8	68·2	7.7
m-13cx	$C_{12}H_{16}O_3$	69·2	7.7	69.4	7.7

"Required: N, 7.3. Found: N, 7.7%.

420 mg, 76%), whose IR spectrum was identical with that of the authentic specimen.

Photoreaction of o-allylanisole. A soln of o-allylanisole (500 mg, 3.4 mmol) dissolved in AcOH (20 ml) was irradiated in a quartz vessel under N<sub>2</sub> atm for 120 hr. Neutralization of the mixture, extraction, and distillation afforded o-cyclopropylanisole<sup>25</sup> (b.p. 95–96°/8 mm, 55 mg, 11%).

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