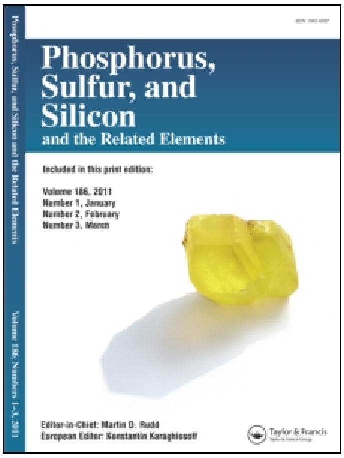


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# PHOTOCHEMICAL AND THERMAL E-Z-ISOMERIZATION OF γ-KETO VINYL SULFIDE, SULFOXIDE, SULFONE

Naomichi Furukawa[a]; Mitsuo Fukumura[a]; Takehiko Nishio[a]; Shigeru Oae[a]
[a] Department of Chemistry, University of Tsukuba, Niihari-gun, Ibaraki, Japan

**To cite this Article** Furukawa, Naomichi , Fukumura, Mitsuo , Nishio, Takehiko and Oae, Shigeru(1978) 'PHOTOCHEMICAL AND THERMAL E-Z-ISOMERIZATION OF γ-KETO VINYL SULFIDE, SULFOXIDE, SULFONE', Phosphorus, Sulfur, and Silicon and the Related Elements, 5: 2, 191 — 196

**To link to this Article: DOI:** 10.1080/03086647808069885

**URL:** http://dx.doi.org/10.1080/03086647808069885

*Phosphorus and Sulfur*
1978, Vol. 5, pp. 191–196

# PHOTOCHEMICAL AND THERMAL E-Z-ISOMERIZATION OF γ-KETO VINYL SULFIDE, SULFOXIDE, SULFONE

NAOMICHI FURUKAWA, MITSUO FUKUMURA, TAKEHIKO NISHIO and SHIGERU OAE

*Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 300-31, Japan*

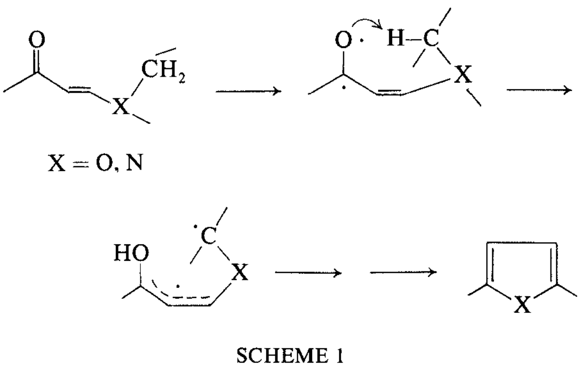
(*Received May 15, 1978*)

γ-Keto vinyl sulfides(Ia–d and IIe,f), sulfoxides (IIIa–d) and sulfones(Va–c) were prepared and their behavior under UV-irradiation or thermal treatments were examined by nmr. Upon uv irradiation, a few γ-keto vinyl sulfides(Ia–d), having E forms were found to be isomerized to the corresponding Z-forms, while those of Z-form were transformed to the E-form when they were treated at elevated temperatures.

## INTRODUCTION

Photochemical reactions of a few γ-keto vinyl sulfides, sulfoxides and sulfones have been reported. However, the examples cited in the literature are limited to the cyclic compounds[1–3] and photochemical reactions of acyclic analogues have received very little attention.

Recently, we found that photolysis of a few γ-keto vinyl amines or ethers having at least one methyl or methylene group attached to nitrogen or oxygen atom afforded the corresponding pyrrole or furan derivatives.[4,5] These reactions are shown in the following Scheme 1.



SCHEME 1

In order to extend this reaction to the sulfur analogues, expecting to see photochemical thiophene ring formation, we photolyzed a few γ-keto vinyl sulfides, sulfoxides and sulfones. However, contrary to our expectation these compounds did not give the corresponding thiophene derivative; instead the photochemical Z–E isomerization was observed. Therefore, in order to explore the scope of this photochemical isomerization of keto vinyl sulfur compound, several derivatives of γ-keto vinyl sulfides, sulfoxides and sulfones were prepared and subjected to both photochemical and thermal isomerization.

This paper describes the results obtained in the photochemical and thermal E–Z isomerizations of these γ-keto vinyl sulfides, sulfoxides and sulfones.

## RESULTS AND DISCUSSION

### *Preparation of γ-Keto Vinyl Sulfides, Sulfoxides and Sulfones*

γ-Keto vinyl sulfides were prepared according to the following two methods: first the acid-catalyzed condensation of benzoylacetone and mercaptans (Method A);[6] and second the nucleophilic addition of thiolate anion to benzoylacetylene (Method B),[7] as shown below.

$$\text{Method A.}\quad PhCOCH_2COCH_3 + RSH \xrightarrow{TsOH} PhCOCH{=}C(CH_3)SR$$

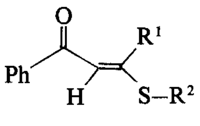
R = Et, Pr

Method B. $$\mathrm{PhCOC{\equiv}CH + RSH \xrightarrow{MeONa} PhCOCH{=}CHSR}$$

$\mathrm{R = Et, Pr, Ph, PhCH_2}$

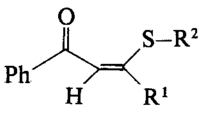
Under the reaction conditions of both A and B, the γ-keto vinyl sulfides(Ia–d, IIe,f) formed are a single stereoisomer, namely the E- or the Z-isomer. The structure of Ia or Ib obtained by method A was assigned as the E-form by comparison of the uv, ir and nmr spectra with those of the Z-isomer. However, the stereochemistry of the formation of the γ-keto vinyl sulfides by method B is not simple and appears to depend on the structure of the thiol employed in the reaction. Generally, addition of nucleophiles to acetylene is considered to proceed preferentially with trans geometry. Thus, the addition of thiophenol or benzyl mercaptan gave normally (Z)-γ-keto vinyl sulfide i.e., IIe or IIf, whereas either ethyl or propyl mercaptan gave only (E)-γ-keto vinyl sulfide. The structures of these olefinic products may be assigned by the usual spectroscopic analysis and by their behavior toward uv-irradiation; namely, the olefin IIe or IIf does not isomerize to Ie or If, whereas Ic or Id isomerizes by uv-irradiation to IIc or IId, which is readily converted back to Ic or Id at room temperature in the nmr tube. Therefore, although IIc or IId was formed initially, the Z-isomer IIc or IId appears to be thermally unstable and underwent facile isomerization to the E-isomer during the isolation.

γ-Keto vinyl sulfoxides were prepared by oxi-



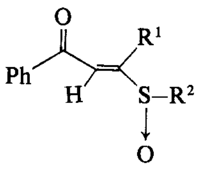
E-form (I)

| | $R^1$ | $R^2$ |
|---|---|---|
| a | Me | Et |
| b | Me | $Pr^n$ |
| c | H | Et |
| d | H | $Pr^n$ |



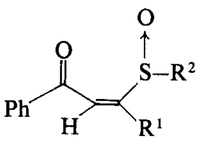
Z-form (II)

| | $R^1$ | $R^2$ |
|---|---|---|
| a | Me | Et |
| b | Me | $Pr^n$ |
| c | H | Et |
| d | H | $Pr^n$ |
| e | H | Ph |
| f | H | $CH_2Ph$ |



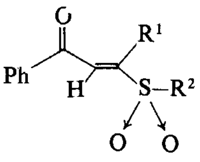
E-form (III)

| | $R^1$ | $R^2$ |
|---|---|---|
| a | H | Et |
| b | H | $Pr^n$ |
| c | H | Ph |



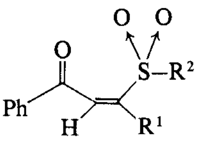
Z-form (IV)

| | $R^1$ | $R^2$ |
|---|---|---|
| a | H | Et |
| b | H | $Pr^n$ |
| c | H | Ph |
| d | H | $CH_2Ph$ |



E-form (V)

| | $R^1$ | $R^2$ |
|---|---|---|
| a | H | Et |
| b | H | Ph |
| c | H | $CH_2Ph$ |



Z-form (VI)

| | $R^1$ | $R^2$ |
|---|---|---|
| a | H | Et |
| b | H | Ph |
| c | H | $CH_2Ph$ |

$$\mathrm{I\,(a\text{–}d)} \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} \mathrm{II\,(a\text{–}d)}$$

$$\mathrm{III\,(a\text{–}c)} \underset{\Delta \text{ or } H^+}{\overset{h\nu}{\rightleftarrows}} \mathrm{IV\,(a\text{–}c)}$$

$$\mathrm{V\,(a)} \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} \mathrm{VI\,(a)}$$

SCHEME 2

dation of the respective sulfides with such oxidizing agents as $NaIO_4$, *m*-chloroperbenzoic acid, and sulfones were obtained by treatment with $H_2O_2$. The detailed structural assignments of the respective E or Z forms are described in the following section.

The products thus obtained either by synthetic methods or by photochemical transformation are shown in Scheme 2 and their properties are summarized in Table I. The nmr data of the compounds are summarized in Tables II, III and IV.

TABLE I

Physical properties of (E)- or (Z)-$\gamma$-ketovinylsulfides, sulfoxides, sulfones

| | $R^1$ | $R^2$ | Yield (%) | bp (°C/torr) or mp (°C) | $\nu$ max ($cm^{-1}$) | EtOH $\lambda$ max (nm) | Elementary analysis (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| Ia | Me | Et | 42.7 | 125/1 | 1645 | 251 ($\varepsilon = 0.86 \times 10^4$)<br>320 ($\varepsilon = 2.3 \times 10^4$) | $C_{12}H_{14}OS$:<br>Calcd.<br>Found | C<br>69.9<br>69.9 | H<br>6.84<br>6.87 |
| IIa | Me | Et | 76.7 ($C_6H_6$, 100 h)[a]<br>62.5 (EtOH, 100 h) | 77.5–78.5 | 1620 | 215 ($\varepsilon = 0.93 \times 10^4$)<br>254 ($\varepsilon = 0.70 \times 10^4$)<br>332 ($\varepsilon = 1.50 \times 10^4$) | — | | |
| Ib | Me | $Pr^n$ | 52.5 | 130/1 | 1645<br>(1650)[b] | 252 ($\varepsilon = 0.99 \times 10^4$)<br>320 ($\varepsilon = 2.4 \times 10^4$) | $C_{13}H_{16}OS$:<br>Calcd.<br>Found | C<br>70.87<br>70.87 | H<br>7.33<br>7.27 |
| IIb | Me | $Pr^n$ | 70.0 ($C_6H_6$, 100 h)[a] | 63.0–64.0 | 1620<br>(1630[b]<br>1645) | 214 ($\varepsilon = 1.1 \times 10^4$)<br>253 ($\varepsilon = 0.83 \times 10^4$)<br>333 ($\varepsilon = 1.9 \times 10^4$) | — | | |
| Ic | H | Et | 70.4 | 146–7/3<br>(lit.[7] 125–6/0.5) | 1640 | — | — | | |
| Id | H | $Pr^n$ | 47.0 | 170–1/2 | 1638 | — | $C_{12}H_{14}OS$:<br>Calcd.<br>Found | C<br>69.86<br>69.59 | H<br>6.84<br>6.68 |
| IIe | H | Ph | 52.0 | 79.0–80.0<br>(lit.[8] 80–81) | 1630 | — | — | | |
| IIf | H | $CH_2Ph$ | 44.6 | 61.5–62.5 | 1620 | — | $C_{16}H_{14}OS$:<br>Calcd.<br>Found | C<br>75.56<br>75.53 | H<br>5.55<br>5.55 |
| IIIa | H | Et | 95.5 | 65.5–66.5 | 1660<br>1060 | — | $C_{11}H_{12}O_2S$:<br>Calcd.<br>Found | C<br>63.44<br>63.46 | H<br>5.81<br>5.77 |
| IIIb | H | $Pr^n$ | 95.2 | 79.5–80.5 | 1655<br>1065 | 210 ($\varepsilon = 0.9 \times 10^4$)<br>228 (sh)<br>271 ($\varepsilon = 1.01 \times 10^4$) | $C_{12}H_{14}O_2S$:<br>Calcd.<br>Found | C<br>64.84<br>64.79 | H<br>6.35<br>6.31 |
| IVb | H | $Pr^n$ | 50.3 ($C_6H_6$, 3 h)[a]<br>58.2 ($C_6H_6$, 20 h)<br>9.0 (MeOH, 5 h) | liquid | 1650<br>1065 | 210 ($\varepsilon = 0.95 \times 10^4$)<br>228 ($\varepsilon = 0.79 \times 10^4$)<br>269 ($\varepsilon = 0.85 \times 10^4$) | — | | |
| IVc | H | Ph | 70.0 | 93.0–94.0 | 1659<br>1042 | — | $C_{15}H_{12}O_2S$:<br>Calcd.<br>Found | C<br>70.29<br>70.29 | H<br>4.72<br>4.72 |
| IVd | H | $CH_2Ph$ | 64.1 | 85.0–86.0 | 1640<br>1050 | — | $C_{16}H_{14}O_2S$:<br>Calcd.<br>Found | C<br>71.09<br>71.04 | H<br>5.22<br>5.18 |
| Va | H | Et | 55.8 | 115–116 | 1670, 1340<br>1310, 1140 | 205 ($\varepsilon = 1.21 \times 10^4$)<br>221 ($\varepsilon = 1.04 \times 10^4$)<br>267 ($\varepsilon = 0.92 \times 10^4$) | $C_{11}H_{12}O_3S$:<br>Calcd.<br>Found | C<br>58.91<br>59.08 | H<br>5.39<br>5.55 |
| VIa | H | Et | 70.1 ($C_6H_6$, 20 h)[a] | 96.0–97.0 | 1665, 1345<br>1305, 1120 | 205 ($\varepsilon = 1.23 \times 10^4$)<br>254 ($\varepsilon = 0.95 \times 10^4$) | — | | |
| VIb | H | Ph | 59.0 | 145–146<br>(lit.[8] 146–147) | 1675, 1340<br>1310 | — | — | | |
| VIc | H | $CH_2Ph$ | 62.0 | 138.0–138.5 | 1670<br>1340<br>1310 | — | $C_{16}H_{14}O_3S$:<br>Calcd.<br>Found | C<br>67.11<br>67.17 | H<br>4.93<br>4.93 |

[a] Irradiation solvent and time in the parentheses.

[b] Measured in $CCl_4$ solution.

TABLE II

Nmr Data of $\gamma$-ketovinylsulfides (I and II)

| | $R^1$ | $R^2$ | Solvent | E-form (I) | Z-form (II) |
|---|---|---|---|---|---|
| a | Me | Et | $CDCl_3$ | 1.37 (t, 3 H), 2.50 (s, 3 H), 2.91 (q, 2 H), 6.63 (s, 1 H), 7.30–7.65 (m, 3 H), 7.75–8.10 (m, 2 H) | 1.31 (t, 3 H), 2.36 (s, 3 H), 2.89 (q, 2 H), 6.92 (s, 1 H), 7.30–7.60 (m, 3 H), 7.80–8.01 (m, 2 H) |
| b | Me | $Pr^n$ | $CDCl_3$ | 1.05 (t, 3 H), 1.50–2.00 (m, 2 H), 2.46 (s, 3 H), 2.93 (t, 2 H), 6.50 (s, 1 H), 7.25–7.55 (m, 3 H), 7.65–8.00 (m, 2 H) | 1.09 (t, 3 H), 1.40–2.05 (m, 2 H),2.40 (s, 3 H), 2.87 (t, 2 H), 6.95 (s, 1 H), 7.20–7.65 (m, 3 H), 7.80–8.10 (m, 2 H) |
| c | H | Et | $CDCl_3$ | 1.40 (t, 3 H), 2.92 (q, 2 H), 6.87 (d, 1 H, 15 Hz), 7.92 (d, 1 H, 15 Hz), 7.30–7.60 (m, 3 H), 7.80–8.10 (m, 2 H) | 1.38 (t, 3 H), 2.93 (q, 2 H), 7.03 (d, 1 H, 8.5 Hz), 6.80–7.45 (m, 4 H), 7.75–8.10 (m, 2 H) |
| d | H | $Pr^n$ | $CDCl_3$ | 1.00 (t, 3 H), 1.30–2.03 (m, 2 H), 2.80 (t, 2 H), 6.90 (d, 1 H, 15 Hz), 7.17–7.53 (m, 3 H), 7.77–8.03 (m, 2 H) | 1.00 (t, 3 H), 1.30–2.03 (m, 2 H), 2.07 (t, 2 H), 7.17 (d, 1 H, 10 Hz), 7.19–7.53 (m, 3 H), 7.77–8.03 (m, 2 H) |
| e | H | Ph | $CDCl_3$ | — | 7.10 (d, 1 H, 9.0 Hz), 7.25–7.60 (m, 9 H), 7.87–8.07 (m, 2 H) |
| f | H | $CH_2Ph$ | $CDCl_3$ | — | 3.93 (s, 2 H), 6.97 (d, 1 H, 10 Hz), 7.23–7.63 (m, 9 H), 7.77–7.93 (m, 2 H) |

TMS was used as the internal standard in $CDCl_3$.

TABLE III

Nmr data of $\gamma$-ketovinylsulfoxides (III and IV)

| | $R^1$ | $R^2$ | Solvent | E-form (III) | Z-form (IV) |
|---|---|---|---|---|---|
| a | H | Et | $CDCl_3$ | 1.37 (t, 3 H), 2.47–3.26 (m, 2 H), 7.37–7.77 (m, 5 H), 7.93–8.10 (m, 3 H) | — |
| b | H | $Pr^n$ | $CDCl_3$ | 1.10 (t, 3 H), 1.86–2.39 (m, 2 H), 2.87 (t, 2 H), 7.33–7.77 (m, 5 H), 7.93–8.13 (m, 2 H) | 1.10 (t, 3 H), 1.50–2.17 (m, 2 H), 2.92 (t, 2 H), 7.33–7.77 (m, 5 H), 7.93–8.13 (m, 2 H) |
| c | H | Ph | $CDCl_3$ | 7.03–7.60 (m, 10 H), 7.87–8.03 (m, 2 H) | 6.95 (d, 1 H, 10 Hz), 7.30–7.77 (m, 7 H), 7.97–8.10 (m, 4 H) |
| d | H | $CH_2Ph$ | $CDCl_3$ | — | 4.30 (s, 2 H), 6.87 (d, 1 H, 10 Hz), 7.30–7.70 (m, 9 H), 7.93–8.10 (m, 2 H) |

TABLE IV

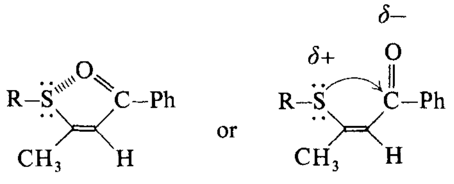
Nmr data of $\gamma$-ketovinylsulfones (V and VI)

| | $R^1$ | $R^2$ | Solvent | E-form (V) | Z-form (VI) |
|---|---|---|---|---|---|
| a | H | Et | $CDCl_3$ | 1.37 (t, 3 H), 3.13 (q, 2 H),7.18–7.77 (m, 5 H), 7.87–8.07 (m, 2 H) | 1.37 (t, 3 H), 3.12 (q, 2 H), 6.50 (d, 1 H, 11 Hz), 7.20 (d, 1 H, 11 Hz), 7.37–7.60 (m, 3 H) |
| b | H | Ph | $CDCl_3$ | 7.33–7.53 (m, 8 H), 7.87–8.17 (m, 4 H) | 6.83 (d, 1 H, 10 Hz), 7.33–7.70 (m, 7 H), 7.87–8.17 (m, 4 H) |
| c | H | $CH_2Ph$ | $CDCl_3$ | 7.13–7.60 (m, 8 H), 7.70–7.97 (m, 4 H) | 4.43 (s, 2 H), 6.47 (d, 1 H, 12 Hz), 7.13 (d, 1 H, 12 Hz), 7.40–7.60 (m, 8 H), 7.77–7.97 (m, 2 H) |

### *Isomerization of $\gamma$-Keto vinyl Sulfides, Sulfoxides and Sulfones*

As a typical run, when (E)-3-ethylthio-1-phenyl-2-buten-1-one (Ia) was irradiated in benzene or methanol with a high pressure mercury lamp through a Pyrex filter in an argon atmosphere for 100 h, the ratio of (E):(Z)-isomer (Ia):(IIa) was 23.3:76.7 (in $C_6H_6$) and 37.5:62.5 (in EtOH) % yields, respectively. The uv spectrum of Ia has an absorption maximum at 320 nm ($\varepsilon = 2.3 \times 10^4$), whereas that of IIa appears at 332 nm ($\varepsilon = 1.5 \times$

$10^4$). The ir absorption band due to the carbonyl stretching frequency of Ia appears at 1645 $cm^{-1}$, and that of IIa is found at 1620 $cm^{-1}$, respectively. These uv and ir data seem to indicate clearly that there is a definite interaction between the carbonyl group and divalent sulfur atom in the Z-isomer resulting in the ir stretching of the carbonyl band and a shorter wave length shift of its uv spectrum as shown below.[8]



(A) (IIa or IIb) (B)

SCHEME 3

The nmr spectra of Ia showed a singlet at δ6.63 ppm(1H) in $CDCl_3$, attributed to the olefinic proton, whereas that of the IIa appeared at δ6.92 ppm(1H). These nmr observations were in good agreement with the generally accepted phenomena of the E–Z relationship which is observed in β-substituted α,β-unsaturated ketones.[9–11] These spectroscopic analyses suggest that Ia and IIa have E(Ia)- and Z(IIa)-forms, respectively. An analogous photochemical treatment of Ib afforded IIb without any decomposition of Ib. However, when either Z-form (IIa) or Z-form (IIb) was heated in benzene at 60°C for 5 h, the Z-E-isomerization took place affording the E-isomer (Ia) or (Ib) quantitatively. Similarly, upon irradiation, the (E)-γ-keto vinyl sulfide (Ic) or (Id) isomerized to the Z-isomer (IIc) or (IId), which was converted back to the corresponding (E)-isomer upon keeping it in benzene or methanol even at room temperature. Therefore, isolation of the pure IIc or IId was unsuccessful and hence the E–Z isomerization was followed by the change of their nmr spectra. However, the (Z)-γ-keto vinyl sulfide (IIe or IIf), which was prepared by the known method (Method B), was not converted to the corresponding isomer (Ie or If) upon UV-irradiation.

The (E)-γ-keto vinyl sulfoxide (IIIc), which was obtained by treatment of (IVc) with acid, isomerized to the (Z)-isomer (IVc) upon irradiation. Furthermore, upon irradiation of (E)-γ-keto vinyl sulfoxide (IIIa) or (IIIb), a mixture of (E) and (Z) isomers (IIIa and IVa) or (IIIb and IVb) was obtained in a ratio of 2:5 or 1:2, respectively. Although these (Z)-compounds (IVa or IVb) were not isolated, their formation was confirmed by their nmr patterns (see Table III), since the (Z)-isomer (IVa) or (IVb), which was photochemically produced was not stable enough to be isolated but converted back to the (Z)-isomer on standing at room temperature. Uv irradiation of the (E)-γ-keto vinyl sulfone (Va) in benzene at room temperature for 20 h also gave the (Z)-isomer (VIa) in 70.1% yield. Thus the photolyses of the γ-keto vinyl sulfides, sulfoxides and sulfone are quite different from those of the similar keto vinyl amines and ethers; i.e., no ring formation is observed but isomerization takes place. The different behavior of the sulfur compounds may be due to the longer sulfur–carbon bond as compared to those of the nitrogen–carbon or oxygen–carbon bonds, suggesting that the stereoelectronic requirements for the hydrogen-abstraction step is not favored for the formation of a thiophene ring.[12]

## EXPERIMENTAL

### *Preparation of γ-keto Vinyl Sulfides*

*Method A* A mixture of benzoylacetone (5g), ethylmercaptan (3g) and *p*-toluenesulfonic acid (0.5g) in benzene (50 ml) was refluxed for 5 h and then water was removed by a Dean Stark separator during the reaction. The benzene solution was washed with water, dried over $MgSO_4$, and distilled in vacuo and the residual oil was distilled to give (E)-3-ethylthio-1-phenyl-2-buten-1-one(Ia) (2.37 g, 43.2%), bp 125°C/1 mm Hg. (E)-3-Propylthio-1-phenyl-2-butene-1-one (1b) was prepared similarly, bp 130°C/1 mm Hg.

*Method B* To a mixture of benzoylacetylene (10 g) and a catalytic amount of sodium methoxide in ether (30 ml), a solution of ethyl mercaptan (5 g) in ether (20 ml) was added dropwise with vigorous stirring and cooling in an ice bath. After addition of the mercaptan, the mixture was stirred for 1 h at room temperature. The solvent was distilled in vacuo. The residual crude product was distilled in vacuo to give pure (E)-3-ethylthio-1-phenyl-2-propen-1-one(Ic) (10.4 g, 70.4%), b.p. 146–7°C/3 mm Hg.[7] Other γ-keto vinyl sulfides(Id, IIe, f) were prepared similarly. The sulfide (Id) was an oil and was purified by distillation, bp 170–1°C/2 mm Hg, but IIe and IIf were crystalline and were recrystallized from ethyl acetate-hexane, mp (IIe), 79–80°C (lit.[8] 80–1°C), IIf, 61.5–2.5°C.

### *Preparation of γ-keto vinyl sulfoxides*

*(E)-3-Ethylsulfinyl-1-phenyl-2-propen-1-one(IIIa)* To a solution of Ic(3g) in isopropyl alcohol (30 ml), 91.3% aqueous methanol solution of $NaIO_4$(54 ml)[13] was added dropwise with stirring at room temperature. Then the mixture was stirred for 24 h at room temperature.[14] The reaction mixture was then extracted with chloroform. The extract was dried over $MgSO_4$ and the solvent was removed in vacuo. The solid residue was recrystallized from ethyl acetate-hexane affording pure sulfoxide(IIIa) (3.1 g, 95.5%), mp 65.5–6.5°C.

(E)-3-Propylsulfinyl-1-phenyl-2-propen-1-one(IIIb) was prepared similarly, mp 79.5–80.5°C.

*(Z)-3-Phenylsulfinyl-1-phenyl-2-propen-1-one(IV)* To a solution of IIe (2.5 g) in chloroform (50 ml), a solution of *m*-chloroperbenzoic acid (3.2 g) in chloroform (50 ml) was added slowly. The solution was stirred at room temperatre for 24 h. The reaction mixture was then filtered to remove *m*-chlorobenzoic acid. The filtrate was washed twice with 100 ml of 5% aqueous $Na_2CO_3$, dried over $MgSO_4$ and the solvent was removed in vacuo to afford the sulfoxide (IVc). The crude sulfoxide was purified by column chromatography on silica gel and eluted with chloroform to afford pure IVc (1.73 g, 70.0%), mp 93–4°C.

*(Z)-3-Benzylsulfinyl-1-phenyl-2-propen-1-one(IV)* To a solution of IIf (2.7 g) in acetonitrile (30 ml), a solution of $NaIO_4$ (6.3 g) in acetonitrile (60 ml) was added slowly.[15] Then the solution was stirred at room temperature for 24 h. The precipitates were filtered and the filtrate was extracted twice with 50 ml portions of chloroform. The chloroform extract was dried over $MgSO_4$. The crude sulfoxide (IV), obtained after the solvent was removed in vacuo was chromatographed (silica gel-chloroform) to afford pure IVd (1.36 g, 64.3%), mp 85–6°C.

### *Preparation of γ-keto Vinyl Sulfone*

*(E)-3-Ethylsulfonyl-1-phenyl-2-propen-1-one(Vc)* To a solution of Ic (2g) in acetic acid (30 ml), a solution containing excess 35% $H_2O_2$[16] was added dropwise with stirring at 40–50°C and then kept for 24 h. Then the reaction mixture was extracted with chloroform. The extract was washed with 5% aqueous $NaHCO_3$ and dried over $MgSO_4$. The crude product obtained upon removal of the solvent in vacuo was purified by recrystallization from ethyl acetate-hexane to afford Va (1.3 g, 55.8%), mp 115–6°C.

*(Z)-3-Phenylsulfonyl-1-phenyl-2-propen-1-one(VIa)* To a solution of IIe (1.0 g) in chloroform (30 ml), pulverized *m*-chloroperbenzoic acid (2.5 g) was added portionwise with stirring at room temperature. The solution was kept stirring for 3 days at room temperature. Then the precipitates were filtered. The filtrate was washed twice with 5% aqueous $NaHCO_3$ and dried over $MgSO_4$. After solvent was removed in vacuo, the crude sulfone was recrystallized from ethyl acetate-hexane to afford pure VIb (0.67 g, 59%), mp 145–6°C (lit.[9] 146–7°C).

(Z)-3-Benzylsulfonyl-1-phenyl-2-propen-1-one(VIc) was prepared similarly, mp 93–4°C.

*A typical run of the uv-irradiation of the sulfide* A solution of (E)-form (Ia) (300 mg) in benzene (30 ml) or methanol (30 ml) was irradiated with a high pressure mercury lamp with a Pyrex filter under an argon atmosphere at room temperature for 100 h. After removal of the solvent, the residual oil was chromatographed through a silica gel column with benzene-ethyl acetate (19:1). The crystalline compound obtained was recrystallized from hexane to give (Z)-form (IIa) (230 mg, 76.7% in the case of benzene solution), m.p. 77.5–8.5°C. Other compounds (Ib, IIIb, Va) were irradiated similarly but the products of IVb or VIa were purified by column chromatography (silica gel-chloroform) and recrystallized from ethyl acetate-hexane. The physical properties of the photoproducts are shown in Table I.

*Photolysis of γ-keto Vinyl Sulfide (Id)* A solution of Id (50 mg) in deuterobenzene (0.8 ml, internal standard; cyclohexane) was irradiated in a Pyrex nmr tube under the conditions described above. The nmr spectrum was checked from time to time, i.e., 0.5, 1, 3, 5, 10 and 20 h, respectively, at room temperature. The ratio of E–Z photoisomerization was measured by integration of nmr shifts at several time intervals. The sulfoxides (IIIa,b) and sulfone (Va) were measured similarly.

## REFERENCES AND FOOTNOTES

1. P. Y. Johnson and G. A. Berchtold, *J. Am. Chem. Soc.* **89**, 2761 (1967), P. Y. Johnson and M. Berman, *J. Chem. Soc. (Chem. Commun.)* **1974**, 779.
2. P. Yates and M. J. Jorgenson, *J. Am. Chem. Soc.* **85**, 2956 (1963), P. Yates and J. W. Still, *J. Am. Chem. Soc.* **85**, 1206 (1963), N. Sugiyama, Y. Sato, H. Kataoka, C. Kashima and K. Yamada, *Bull. Chem. Soc. Japan*, **42**, 3005 (1969), N. Ishibe and M. Odani, *J. Org. Chem.* **36**, 4132 (1971), N. Ishibe, M. Odani and M. Sunami, *Tetrahedron*, **29**, 2005 (1973).
3. I. W. J. Still and M. S. Chauhan, *Tetrahedron Lett.* **1973**, 1311.
4. The photolysis of the compound (Ic) was reported and no photoproduct was detected by TLC inspection (H. Aoyama, T. Nishio, Y. Hirabayashi, T. Hasegawa, H. Noda and N. Sugiyama, *J. Chem. Soc.* (Perkin I), **1975**, 298).
5. T. Nishio and Y. Omote, *Chem. Lett.* **1976**, 103.
6. Although the mechanism is not well known, the γ-keto vinyl sulfides obtained by the method A should be composed of the E-isomer predominantly, since the most stable conformation of the intermediates resulting from condensation of the ketone and thiols should be the conformer (A) which is shown to give the E-olefin (E. Campaigne and J. R. Leal, *J. Am. Chem. Soc.* **76**, 1954)).
7. K. Bowden, E. A. Brande and R. H. Jones, *J. Chem. Soc.* **1946**, 945.
8. W. E. Truce, *Organic Sulfur Compound*, Vol. I. ed. by N. Kharasch (Pergamon Press, London, 1961) p. 112.
9. Montanari *et al.*, prepared IIe and suggested that the Z-form is markedly stabilized by such an interaction of the sulfenyl sulfur with the carbonyl carbon as shown by (B) in Scheme 3.
   (D. Landini and F. Montanari, *J. Chem. Soc.*, (*Chem. Commun.*) **1976**, 188).
10. J. Daborowski and M. Tencer, *Tetrahedron*, **32**, 584 (1976).
11. M. T. Omar and M. N. Basyouni, *Bull. Chem. Soc. Japan*, **49**, 2325 (1976).
12. Turro and Weiss have stated that in the transition state of the photochemical hydrogen transfer reaction of alkyl ketones, the hydrogen to be abstracted needs to approach the half vacant non-bonding orbital of the carbonyl oxygen atom (N. J. Turro and D. W. Weiss, *J. Am. Chem. Soc.* **90**, 2185 (1968)). However, these γ-keto vinyl sulfides, sulfoxides and sulfones cannot achieve the required transition state.
13. A. E. Hill, *J. Am. Chem. Soc.* **50**, 2678 (1928).
14. L. Field and Y. H. Khim. *J. Org. Chem.* **37**, 2710 (1972).
15. G. A. Russell and L. A. Ochrymowycz, *ibid.* **35**, 2106 (1970).
16. N. K. Kochetkov and N. N. Vinogradova, *Zhur. Obshchei. Khim.* **27**, 2745 (1975); *Chem. Abstr.* **52**, 7192f (1958).