Photocycloaddition of Thiocarbonyl Compounds to Multiple Bonds. X. Photocycloaddition of *O*-Alkyl Thiobenzoates to Olefins

Atsuyoshi Ohno, Tamotsu Koizumi, and Yutaka Akasaki
Sagami Chemical Research Center, Nishiohnuma, Sagamihara-shi, Kanagawa 229

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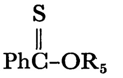
Photochemical reactions of *O*-ethyl and *O*-methyl thiobenzoates with various olefins have been studied. Some olefins afford ketones, others yield thietanes, and in some cases both products are obtained. Thiobenzoate *O*-esters in the n,π^* triplet state are the reacting species. The mechanism of the reaction has been elucidated: photocycloaddition of a thioester to an olefin results in the formation of a thietane. Photosensitized decomposition of the thietane yields an α,β-unsaturated ether, which is converted to a ketone by general acid-catalyzed hydrolysis.

Photochemistry of carbonyl compounds has been received intensive attention for many decades. In contrast, the photochemical behavior of thiocarbonyl compounds has generated little interest. Although several groups have recently published in this area, almost all the studies dealt with aromatic and alicyclic thioketones.[1–7)]

This study was initiated to determine the substituent effects on either the reactivity of photo-excited thiocarbonyl compounds or the transient intermediates in photocycloaddition to olefins, and to synthesize multifunctional compounds that may have synthetic utility.

Results and Discussion

Products. The reaction of *O*-alkyl thiobenzoates (**1**) with some olefins afforded ketone, **3** or **4** or both (Eq. 1), whereas with other olefins thietane derivative, **5** or **6** or both, or **7** or **8** or both, were obtained (Eq. 2). In some cases ketones and thietanes were obtained.



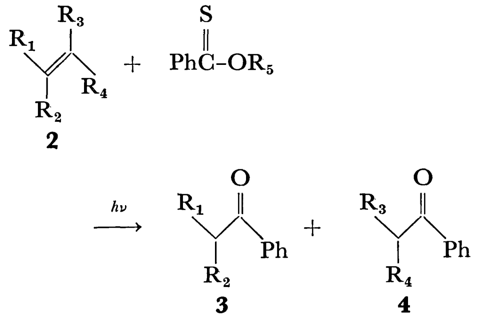
$$\overset{S}{\overset{\|}{PhC}}\text{-}OR_5$$

1a: R=Et
1b: R=Me

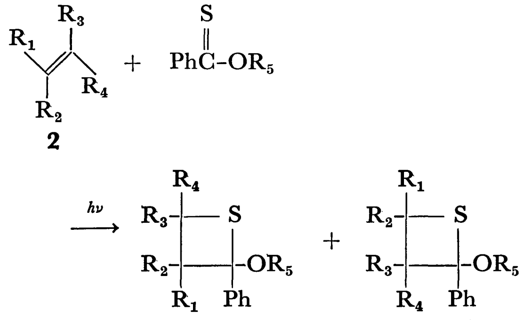
Table 1. Designation of compounds, **2**—**8**[a)]

Designation	R_1	R_2	R_3	R_4
a	$PhCH_2$	H	H	H
b	$PhCH_2$	H	H	CH_3
c	$PhCH_2$	H	CH_3	CH_3
d	$CH_3\diagdown$ CH $Ph\diagup$	H	H	H
e	n-C_3H_7	H	H	H
f	C_2H_5	H	H	CH_3
g	n-C_3H_7	CH_3	H	H
h	C_2H_5	H	CH_3	CH_3
i	$CH_3\diagdown$ CH $C_2H_5\diagup$	H	H	H
j	Ph	H	H	CH_3
k	Ph	H	H	C_2H_5
l	Ph	H	H	$CH_3\diagdown$ CH $CH_3\diagup$
m	Ph	CH_3	H	H

a) Stereoisomerism is not represented.



(R$_5$=Et, Me) (1)

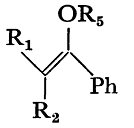


(2)

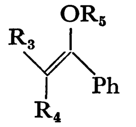
5 (R_5=Et) **6** (R_5=Et)
7 (R_5=Me) **8** (R_5=Me)

The unified designation used for compounds **2**—**8** is shown in Table 1 and the reactions are summarized in Tables 2 and 3.

Generally, the reaction mixture was subjected to column chromatography on silica gel and the yield of the isolated products were calculated from their weights. When the reaction mixture was analyzed by vpc before it was subjected to the column chromatography, the yields of ketones were surprisingly lower than those determined after column chromatography, as shown by parenthesized numbers in Tables 2 and 3. However, the vpc analysis indicated that the deficit of ketones was compensated by the presence of corresponding amounts of α,β-unsaturated ethers, **9** or **10** or both, or **11** or **12** or both.



9 (R_5=Et)
11 (R_5=Me)



10 (R_5=Et)
12 (R_5=Me)

(R_i's are those defined in Table 1)

TABLE 2. THE PHOTOREACTION OF **1a** WITH OLEFINS[a)]

Run	Olefin, g	**1a**, mg	Irrad. time, day	Product and yield, %[b)]			
1	**2a**, 2.78	500	11	**3a** 100 (9)			
2	**2b**, 2.66	561	13	**3b** 85			
3	**2c**, 2.38	469	12	**3c** 25			**6c** 65
4	**2d**, 3.09	603	23	**3d** 40			
5	**2e**, 2.51	497	9	**3e** 62 (19)	**4e** — (4)		
6	**2f**, 2.25	442	11	**3f** 28) (11)	**4f** 28 (11)		
7	**2g**, 3.19	617	12	**3g** 84 (5)	**4g** — (trace)	**5g** 8	**6g** 4
8	**2h**, 3.16	535	3			**5h** 33	**6h** 53
9	**2i**, 2.53	676	34	**3i** 29			
10	**2j**, 2.85	574	5			**5j** 62	**6j** 19
11	**2k**, 2.52	479	6		**4k** — (trace)	**5k** 53	**6k** 19
12	**2l**, 1.01	202	16		**4l** 64	**5l** 48	**6l** 16
13	**2m**, 2.52	557	22	**3m** 72		**5m** 26	

a) The reaction mixture contains 2 ml of benzene in addition to **1** and **2**. b) Isolated yields. Numbers in parentheses are yields determined by vpc. See text for details.

TABLE 3. THE PHOTOREACTION OF **1b**, WITH OLEFINS[a)]

Run	Olefin, g	**1b**, mg	Irrad. time, day	Product and yield, %			
14	**2a**, 2.59	508	12	**3a** 100			
15	**2b**, 3.09	593	17	**3b** 52	**4b** — (20)		
16	**2c**, 3.14	769	12	**3c** 20			**8c** 48
17	**2e**, 2.26	407	10	**3e** 25 (7)	**4e** — (trace)		
18	**2f**, 2.97	557	9	**3f** 14 (8)	**4f** 18 (5)		
19	**2g**, 2.55	510	16	**3g** 40 (8)	**4g** — (trace)	**7g** 12	**8g** 5
20	**2h**, 2.99	549	6			**7h** 26	**8h** 37
21	**2j**, 2.44	524	8	**3j** 18	**4j** —	**7j** 52	
22	**2k**, 3.17	620	4	**3k** 7	**4k** — (trace)	**7k** 64	

a) See footnotes in Table 2.

Some of these ethers were isolated by subjecting the reaction mixture to column chromatography on neutral alumina. This surprising observation was explained when an authentic sample of the ether was quantitatively converted into the corresponding ketone by the treatment with silica gel—apparently an effective catalyst for this transformation.

Reacting Species. *O*-alkyl thiobenzoates have absorption maxima at around 290 nm ($\varepsilon\approx12000$) and 420 nm ($\varepsilon\approx120$) that are attributable to π,π^* and n,π^* transitions, respectively.[8)] Excitation at either transition was found to bring about the reaction.

As shown in Fig. 1, when a mixture of *cis*- or *trans*-2-pentene and **1a** in *n*-dodecane was photo-irradiated, *cis-trans* isomerization of the olefin took place and the thermodynamically equilibrated composition of 75% *trans*- and 25% *cis*-2-pentene[9–11)] was asymptotically attained.

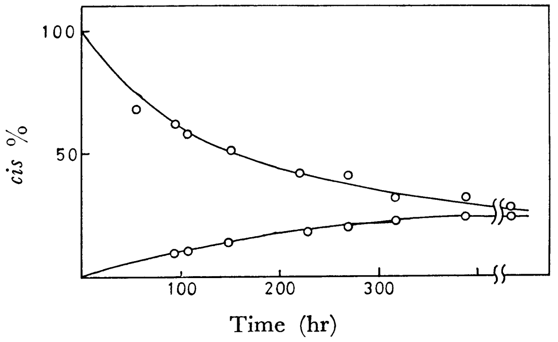


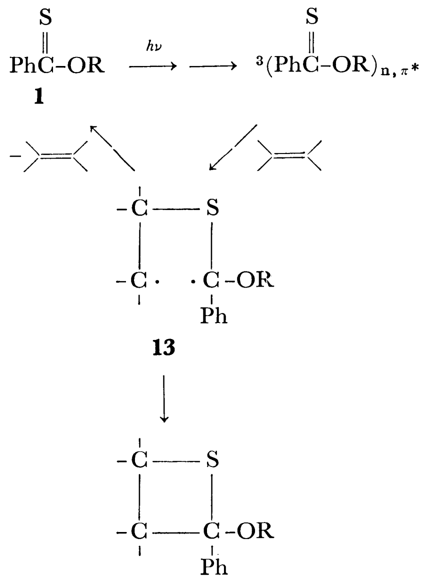
Fig. 1. Photo-initiated isomerizations of *cis*- and *trans*-2-pentene in the presence of *O*-ethyl thiobenzoate.

It is known that thiobenzophenone in the n,π^* triplet state behaves like a thiyl radical, *i. e.*, it attacks an olefin reversibly.[3a)] The reactivities of benzophenone in the n,π^* triplet state and an alkoxy radical have also been compared.[12)] The *cis-trans* isomerization of 2-pentene reported here suggests that photo-activated **1** is also in the n,π^* triplet state.

Further evidence of the multiplicity of the excited state responsible for the reaction was obtained from the photosensitized reaction of **1a** (E_T=57—58 kcal/mol)[13)] with allylbenzene in the presence of Michler's ketone (λ_{max}=370 nm, ε=31000, E_T=62 kcal/mol).[14)] Under the condition that more than 99% of the irradiated light was absorbed by Michler's ketone, the reaction was found to proceed similarly to that effected by direct photo-irradiation. However, quantitative observations were precluded by the fact that the quantum yield of the reaction is too low to be measured accurately (as is recognized from the reaction time). The observed effect of the photosensitizer together with the physico-chemical data on thiobenzoate *O*-esters[13)] provide additional support for the electronic configuration and state of the reacting **1**.

Since the lowest triplet energies of simple alkenes (74—82 kcal/mol)[15)] and substituted styrenes (60—70 kcal/mol)[16)] are higher than that[13)] of **1**, it is not necessary to take into account the energy transfer from **1** to olefins.

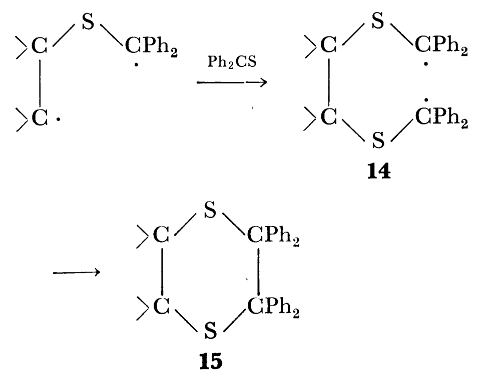
Mechanism of the Reaction. As discussed above,


(3)

there is strong indication to propose that the reaction initiated by the attack of **1** in the *n,π* triplet state* on an olefin yielding a composite biradical **13** (Eq. (3)), which may regenerate ground-state **1** and the olefin, or cyclize into a thietane.[17]

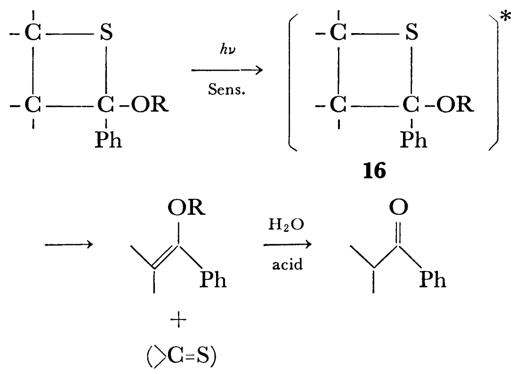
The product distribution reveals that the attack of photo-excited **1** on an olefin takes place so as to form the more stable radical. However, when the olefin has a bulky substituent, attack on the less-hindered side is favored (Runs 3, 8, 12, 16, and 20). This observation is consistent with the general trend found in the chemistry of thiyl radicals.[18] In this connection, it is noteworthy that photo-excited **1** reacts with equal facility with tri-, di- or mono-substituted olefins, whereas the addition of thiyl radicals to tri-substituted olefins (compared to di- and mono-substituted olefins) proceeds slower and with increasing amounts of side products.[18]

In the reaction of thiobenzophenone with alkenes the **13**-type biradical, formed as an intermediate, reacted with another molecule of thiobenzophenone giving **14**, then **15**.[3a] This reaction occurred with thiobenzophenone because it is a powerful scavenger of free radicals.[19] In contrast, since **1** has no tendency to react with free radicals,[20] the reactions described here do not afford 1,4-dithiane derivatives.


(4)

Again, in the reaction of thiobenzophenone a 1,3-dithiane is the proposed precursor of a thietane.[4b] Although we do not have proof that a 1,3-dithiane derivative is intermediary in the formation of a thietane, it should be noted that 2,4-diphenyl-2,4-diethoxy-1,3 dithiadecalin was obtained in 27% yield by the reaction of **1a** with cyclohexene.[21]

Unsubstituted and alkyl-substituted thietanes are known to be photolyzed into olefins.[22–24] However, there is no evidence for the photochemical transformation of alkoxythietanes into corresponding α,β-unsaturated ethers. Therefore, we studied the photolysis of an alkoxythietane (**7g**) as a controlled experiment. When a benzene solution of **7g** was irradiated with light from a high-pressure mercury lamp (315 and 366 nm), the majority of the products was tarry polymer. The vpc analysis showed that the yield of the ketone, **3g**, was only 7% and the ether, **11g**, was absent. On the other hand, in the presence of a large excess (about 9 equivalents) of **1b**, yields of **3g** and **11g** were improved to 59 and 16.5%, respectively. The present result reveals that α,β-unsaturated ethers are afforded by photosensitized decomposition of alkoxythietanes (Eq. (5)), although detailed mechanism is not known.


(5)

The fact that irradiation with wavelengths longer than 390 nm is effective in producing the ether (*e. g.*, **2a**+**1a**→**9a**) also supports the idea that the decomposition of the thietane is a photosensitized process. Based on the results reported by Barton and co-workers,[13] **16** is supposed to be in the triplet state. Photochemical reactions of alkoxy- and hydroxyoxetanes leading to the formation of an α,β-unsaturated ether and a ketone, respectively, have also been proposed.[25,26]

As described above, it is confirmed that the α,β-unsaturated ether is easily hydrolyzed into corresponding ketone in the presence of an acid like silica gel or hydrogen chloride.[27]

Experimental

Materials. As previously reported,[28] *O*-alkyl thiobenzoates (**1**) were prepared from the corresponding orthoesters[29] or imido ethers.[30,31] Olefins **2c** and **2l** were prepared according to Klages.[32] A mixture of **2b** and **2d**, obtained by the reaction of phenylmagnesium bromide and 1-chloro-2-butene,[33] was fractionally distilled by a Podbielniak Model 3475 apparatus yielding **2b** and **2d** of 70 and 90% purities, respectively. Other olefins were commercially available. An α,β-unsaturated ether, **11g** (a mixture of *cis-* and *trans-*isomers), was synthesized by refluxing a mixture of α-methylvalerophenone (1.7 g), trimethyl orthoformate (2.4 g), and *p*-toluenesulfonic acid (5 mg) in absolute methanol (8 ml) for 4 hr, followed by fractional distillation under a reduced

Table 4. NMR spectral data for thietanes, **5**—**8**[a)]

Compd	Ring-H	Alkoxy-H	Phenyl-H	Other H
6c	3.90 (d-d, *J*=6, 9)	1.21 (t, *J*=7) 2.88 (d-q, *J*=9, 7) 3.47 (d-q, *J*=9, 7)	6.80—7.40 (m)	0.85 (s, 3H) 1.16 (s, 3H) 2.65 (d-d, 1H, *J*=9, 13) 2.86 (d-d, 1H, *J*=6, 13)
8c	3.89 (d-d, *J*=6, 9)	2.98 (s)	7.02—7.36 (m)	0.86 (s, 3H) 1.14 (s, 3H) 2.66 (d-d, 1H, *J*=9, 14) 2.87 (d-d, 1H, *J*=6, 14)
5g	2.31 (d, *J*=8) 3.18 (d, *J*=8)	1.20 (t, *J*=7) 2.88 (d-q, *J*=9, 7) 3.48 (d-q, *J*=9, 7)	7.00—7.60 (m)	0.86 (s, 3H) 1.10—2.00 (m, 4H)
6g	2.52 (d, *J*=9) 2.96 (d, *J*=9)	1.18 (t, *J*=7) 2.80 (d-q, *J*=9, 7) 3.30 (d-q, *J*=9, 7)	7.00—7.60 (m)	0.94 (s, 3H) 1.10—2.00 (m, 4H)
7g	3.14 (d, *J*=9) 3.28 (d, *J*=9)	3.04 (s)	7.10—7.45 (m)	0.86 (s, 3H) 0.93 (t, 3H, *J*=8) 1.10—1.80 (m, 4H)
8g	2.50 (d, *J*=9) 2.95 (d, *J*=9)	3.04 (s)	7.10—7.45 (m)	0.95 (t, 3H, *J*=8) 1.21 (s, 3H) 1.40—2.10 (m, 4H)
5h	2.60 (t, *J*=8)	1.15 (t, *J*=7) 2.86 (d-q,, *J*=9.7) 3.48 (d-q, *J*=9, 7)	7.04—7.50 (m)	0.82 (s, 3H) 0.93 (t, H, *J*=7) 1.19 (s, 3H) 1.60—2.04 (m, 2H)
6h	3.50 (t, *J*=9)	1.16 (t, *J*=7) 2.83 (d-q, *J*=9, 7) 3.40 (d-q, *J*=9, 7)	7.00—7.50 (m)	0.72 (s, 3H) 0.89 (t, 3H, *J*=7) 1.19 (s, 3H) 1.50 (d-q, 2H, *J*=9, 7)
7h	2.62 (t, *J*=8)	2.97 (s)	7.05—7.40 (m)	0.81 (s, H) 0.92 (t, 3H, *J*=7) 1.15 (s, 3H) 1.90 (d-q, 2H, *J*=8, 7)
8h	3.59 (d-d, *J*=6, 10)	3.02 (s)	7.08—7.66 (m)	0.74 (s, 3H) 0.88 (t, 3H, *J*=7) 1.18 (s, 3H) 1.35—1.70 (m, 2H)
5j	3.78 (d, *J*=9) 4.28 (d-q, *J*=6, 9)	1.15 (t, *J*=7) 2.98 (d-q, *J*=9, 7) 3.60 (d-q, *J*=9, 7)	7.21 (s) 7.24 (s)	1.40 (d, 3H, *J*=6)
6j	3.57 (d-q, *J*=6, 8) 4.25 (d, *J*=8)	1.20 (t, *J*=8) 2.95 (d-q, *J*=10, 8) 3.32 (d-q, *J*=10, 8)	6.66—7.20 (m) 7.20—7.70 (m)	1.55 (d, 3H, *J*=6)
7j	3.83 (d, *J*=9) 4.28 (d-q, *J*=9, 6)	3.09 (s)	7.20 (s) 7.25 (s)	1.39 (d, 3H, *J*=6)
5k	3.85 (d, *J*=6) 4.00 (d-t, *J*=9, 6)	1.08 (t, *J*=6) 3.02 (d-q, *J*=8, 6) 4.04 (d-q, *J*=8.6)	7.20 (s) 7.22 (s)	0.88 (t, 3H, *J*=6) 1.60—2.00 (m, 2H)
6k	3.39 (d-t, *J*=8, 6) 4.25 (d, *J*=8)	1.16 (t, *J*=7) 2.65—3.02 (m)	6.68—7.50 (m)	0.91 (t, H, *J*=6) 1.50—2.05 (m, 2H)
7k	3.82 (d, *J*=10) 4.11 (d-d-d, *J*=10, 8, 6)	3.05 (s)	7.14 (s) 7.20 (s)	0.87 (t, 3H, *J*=7) 1.74 (m, 1H)
5l	3.78—4.17 (m)	1.10 (t, *J*=7) 2.93 (d-q, *J*=9, 7) 3.56 (d-q, *J*=9, 7)	7.16 (s) 7.20 (s)	0.65 (d, 3H, *J*=7) 0.96 (d, 3H, *J*=7) 1.65—1.98 (m, 1H)
6l	3.20 (t, *J*=8) 4.30 (d, *J*=8)	1.15 (t, *J*=7) 2.92 (d-q, *J*=9, 7) 3.28 (d-q, *J*=9, 7)	6.70—8.00 (m)	0.77 (d, 3H, *J*=7) 0.97 (d, 3H, *J*=7) 1.85—2.16 (m, 1H)
5m	2.58 (d, *J*=8) 4.12 (d-d, *J*=1, 8)	1.03 (t, *J*=7) 2.98 (d-q, *J*=9, 7) 3.46 (d-q, *J*=9, 7)	7.10—7.43 (m)	1.37 (d, 3H, *J*=1)

a) Chemical shifts are expressed by δ from TMS in CCl_4 and coupling constants, *J*, have the unit of Hz.

pressure: bp 85 °C/2 Torr; NMR (δ from TMS, CCl_4) 0.60—1.75 (m), 1.57 (s), 1.71 (s), 1.75—2.35 (m), 3.19 (s), and 7.20 (s); IR 3070—3000, 2900—2800, 1440, 1135, 1070, 770, and 700 cm^{-1}.

Found: C, 81.90; H, 9.31%. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54%.

Purities of materials were confirmed by NMR, IR, and vpc.

General Procedure. Reaction solutions were prepared in a dry box under an atmosphere of CO_2 by placing 0.5 g of **1**, 2.5 g of **2** and 2 ml of benzene in a Pyrex vessel.[34] Photoreactions were carried out by external irradiation method with a 400 W high-pressure mercury lamp (Toshiba H-400P) at a temperature of running water. Some reactions were carried out with a Toshiba UV-39 filter (transparent for >390 nm), and it was found that application of the filter did not alter the product distribution.

Photo-irradiation was continued until **1** disappeared completely. At the end of the reaction, products were analyzed directly by vpc (Hitachi K-53, TCD or FID, 20% XF-1150, 1 m, 140 °C for thietanes and **1**; 20% XF-1150, 1 m, 120 °C for alkyl aryl ketones and corresponding ethers; 5% XF-1150, 1 m, 140 °C for aralkyl aryl ketones and corresponding ethers) or, after evaporation of benzene and excess olefin, by column chromatography on silica gel with appropriate compositions of *n*-hexane–benzene mixtures.

cis-trans *Isomerization of 2-Pentene (**2f**).* A mixture of *trans*-2-pentene (578.4 mg, 8.26 mmol) and **1a** (1.0104 g, 6.09 mmol) in *n*-dodecane was irradiated. At an appropriate interval, aliquots were taken out from the mixture with a syringe and compositions of isomers were analyzed by vpc (40% $AgNO_3$/PEG, 1 m, room temperature). Similar experiments were also done with the *cis*-isomer. Results are shown in Fig. 1.

Photosensitized Reaction of O*-Ethyl Thiobenzoate (**1a**) with Allylbenzene (**2a**).* A mixture of **1a** (100.6 mg, 0.606 mmol), **2a** (495.2 mg, 4.20 mmol), and Michler's ketone (164.0 mg, 0.612 mmol) in acetonitrile (15 ml) was irradiated. A filter solution of aqueous 2,3-dihydro-5,7-dimethyl-1,4-diazepine perchlorate[35] (400 mg/l) was circulated through the outer shell of the reaction vessel. Under the condition, more than 99% of the irradiated light (366, 405/408, and 436 nm)[36] was absorbed by Michler's ketone. After 9 days, when no **1a** remained, the reaction mixture was worked-up and subjected to column chromatography on silica gel and the ketone, **3a**, was isolated in quantitative yield.

*Photolysis of 2-Methoxy-2-phenyl-3-methyl-3-propylthietane (**7g**).* A solution composed of **7g** (40 mg, 0.169 mmol) and **1a** (226.7 mg, 1.49 mmol) in 4 ml of benzene was irradiated for 13 days until **7g** had disappeared completely. The

Table 5. IR spectral data for thietanes, **5**—**8**

Compd	Absorption, cm^{-1}
6c	3050, 3020, 2960, 2900, 2850, 1600, 1490, 1445, 1380, 1360, 1250, 1225, 1110, 1070, 1030, 915, 880, 860, 830, 800, 755, 745, 730, 700, 675, 610, 505
8c	8050, 2020, 2975, 2930, 2860, 2820, 1600, 1495, 1470, 1450, 1390, 1370, 1320, 1255, 1235, 1185, 1155, 1130, 1090, 1080, 1030, 1020, 965, 950, 915, 870, 830, 805, 760, 710, 700, 680, 670, 620, 560, 510
5g and **6g**	3050, 3010, 2960, 2920, 2850, 1600, 1480, 1445, 1390, 1375, 1310, 1270, 1250, 1210, 1170, 1160, 1150, 1115, 1090, 1070, 1030, 970, 920, 910, 885, 855, 825, 805, 750, 700, 675, 635, 625, 500
7g and **8g**	3040, 3005, 2940, 2920, 2860, 2810, 1600, 1490, 1470, 1445, 1380, 1315, 1280, 1255, 1230, 1190, 1175, 1145, 1090, 1080, 1035, 1005, 980, 960, 920, 905, 860, 810, 780, 755, 675, 635, 550, 500
5h and **6h**	3050, 3010, 2950, 2900, 2865, 1600, 1490, 1460, 1445, 1380, 1360, 1310, 1300, 1270, 1235, 1175, 1140, 1120, 1085, 1075, 1030, 970, 940, 920, 885, 850, 820, 755, 705, 685, 665, 600, 520
7h and **8h**	3050, 3020, 2950, 2810, 1600, 1490, 1460, 1450, 1385, 1365, 1315, 1300, 1270, 1240, 1190, 1180, 1140, 1115, 1085, 1035, 1005, 950, 940, 915, 870, 855, 820, 755, 700, 675, 665, 600, 550
5j and **6j**	3050, 3010, 2960, 2900, 2875, 1600, 1495, 1450, 1390, 1375, 1280, 1270, 1220, 1205, 1170, 1160, 1130, 1100, 1080, 1065, 1055, 1035, 980, 945, 920, 900, 870, 825, 780, 760, 705, 665, 615, 505
7j	3050, 3025, 2950, 2925, 2820, 1600, 1495, 1450, 1380, 1285, 1270, 1220, 1170, 1110, 1080, 1070, 1040, 1030, 1015, 955, 870, 820, 785, 755, 705, 660, 610, 510,
5k and **6k**	3030, 3000, 2950, 2910, 2850, 1600, 1490, 1450, 1445, 1390, 1335, 1310, 1275, 1240, 1200, 1175, 1155, 1120, 1090, 1075, 1030, 975, 930, 915, 900, 865, 830, 780, 765, 755, 700, 660, 610, 570, 515
7k	3050, 3020, 2950, 2925, 2870, 2820, 1600, 1495, 1450, 1380, 1310, 1280, 1245, 1205, 1190, 1180, 1160, 1110, 1080, 1040, 1030, 960, 945, 910, 870, 830, 790, 775, 755, 705, 660, 610, 560, 505
5l and **6l**	3040, 3010, 2950, 2910, 2850, 1600, 1490, 1445, 1385, 1370, 1310, 1275, 1245, 1215, 1175, 1175, 1160, 1120, 1095, 1075, 1050, 1030, 980, 920, 890, 825, 815, 780, 760, 700, 660, 610, 570, 525
5m	3020, 3000, 2950, 2910, 2850, 1600, 1490, 1445, 1390, 1370, 1310, 1270, 1230, 1200, 1175, 1155, 1125, 1085, 1070, 1030, 965, 920, 900, 880, 855, 800, 760, 740, 715, 700, 670, 630, 590, 555

TABLE 6. MASS SPECTRAL DATA FOR THIETANES, **5**—**8**[a)]

Compd	Intensity, %								
	$M^{+\cdot}$	(**1**)$^{+\cdot}$	(**1**+H)$^{+\cdot}$	(**2**)$^{+\cdot}$	(**9** or **11**)$^{+\cdot}$	(**10** or **12**)$^{+\cdot}$	$PhC\equiv S^+$	$PhCHS^{+\cdot}$	$PhC\equiv O^+$
6c[b)]	0.3	21	51	26	0	7	12	18	66
8c	0.2	33	100	41	0	16	21	10	12
7g[c)]	1.0	100	25	0	7	0	30	19	15
6h	0.4	64	80	7	0	18	34	58	100
8h	1.9	66	100	13	0	16	35	20	14
5j	1.1	13	21	100	9	0	12	14	46
6j	1.2	12	18	100	0	8	27	17	74
7j	0.1	28	5	100	7	0	35	7	78
5k[d)]	0.2	17	68	100	54	0	14	15	98
6k	0.2	12	46	100	0	6	24	17	79
7k	0.2	14	19	100	9	0	16	5	19
5l	0.2	55	7	100	5	0	14	13	55
6l[e)]	0.1	5	15	29	0	4	42	7	100
5m	1.8	93	14	44	19	0	29	48	100

a) Important peaks are selected. b) **2c**−H=100%. c) **11g**−C_2H_5=42%. d) **2k**−$CH_3\cdot$=53%.
e) $M^{+\cdot}$−EtOH=77%.

TABLE 7. ELEMENTAL ANALYSES OF THIETANES

Compd	Mclecular formula	Calcd (%)			Found (%)		
		C	H	S	C	H	S
6c	$C_{20}H_{24}OS$	76.88	7.74	10.26	76.89	7.70	10.07
8c[a)]	$C_{19}H_{22}OS$	76.47	7.43	10.74	76.73	7.67	10.71
5h	$C_{15}H_{22}OS$	71.95	8.86	12.81	72.20	8.96	12.80
7h	$C_{14}H_{20}OS$	71.14	8.53	13.56	71.20	8.58	13.72
7k	$C_{18}H_{20}OS$	76.01	7.09	11.27	75.54	6.89	11.29

a) Molecular Weight: Calcd for $C_{19}H_{22}OS$; 298. Found; 300.7.

vpc analysis of the reaction mixture showed that **3g** and **11g** were afforded in 59 and 16.5% yields, respectively. However, in the absence of **1a**, the reaction afforded large amount of tarry polymer and the yield of **3g** was only 7% after 21 days. Although aliquots were analyzed by vpc every day, no indication was obtained for the formation of **11g** from this reaction solution.

*Hydrolysis of 1-Methoxy-1-phenyl-2-methyl-1-pentene (**11g**).* A CCl_4 solution (5 ml) of **11g** (190 mg, 1 mmol) containing catalytic amount of silica gel was stirred at room temperature and aliquots were analyzed by vpc. After 2 weeks almost all **11g** was converted into **3g**. When a drop of hydrochloric acid was added to the solution in place of silica gel, the ether transformed into the ketone within a day. Furthermore, a solution of **11g** in benzene was passed through a column of silica gel and the ketone, **3g**, was obtained in quantitative yield. However, a column of neutral alumina did not catalyze this transformation.

Characterization of Products. Ketones and ethers were identified by comparing their NMR, IR spectra, and vpc with those of authentic samples. All thietanes described here are new compounds. Their NMR, IR, and mass spectral data are summarized in Tables 4, 5, and 6, respectively. Since the thietanes are unstable oily materials,[37)] most efforts to purify them were not successful and only limited numbers of compounds gave satisfactory results on elemental analyses (Table 7).

Structures of thietanes were determined by NMR: a ring proton bound to a carbon adjacent to the sulfur appears more down-field than that of the other isomer.[3a)] Mass spectra provided another support for the structures. Photochemical conversion of **7g** into **3g** and **11g** also confirmed the structure of this thietane.

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37) They decompose gradually into tarry polymers even in a refrigerator. Thietanes **6g**, **8g**, **5h**, and **7h** are contaminated by the other isomers, respectively.