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Photolyses of Alkyl Sulfinates and Sulfites[1)]

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Methyl, ethyl, *n*-butyl, *n*-octyl, benzyl, and allyl *p*-toluenesulfinates were photolyzed in *n*-hexane or without solvent. The products analyses indicate that the photolyses of these esters involve the fission of ArSO–OR bond, producing a sulfinyl radical and an alkoxy radical. In the case of the allyl ester, isomerization to the corresponding sulfone took place to some extent. When optically active *l*-menthyl *l*-*p*-toluenesulfinate was irradiated, its optical activity decreased fairly quickly while very little photolysis was observed. This photo-racemization was ascribed to the reversible formation of sulfinyl radical and menthyloxy radical. When di-*n*-butyl sulfite was photolyzed, the products found were explained by assuming the initial formation of *n*-butoxysulfinyl radical and *n*-butoxy radical. When *n*-butyl chlorosulfite was photolyzed, the products found indicate the initial fission of the S–Cl bond instead of the S–O bond.

Concerning the photochemistry of organo-sulfur compounds, many reports have been published.[2)] However, no papers have been published concerning the photo-reactions of sulfinic acids and their esters. Since alkyl arenesulfinates show a fairly strong absorption at about 250 nm due to $n \rightarrow d\pi$ transition,[3)] they are expected to undergo photolyses.

In connection with our investigations on sulfinyl, sulfonyl, and sulfonyloxy radicals, photolyses of some sulfinic esters have been studied, and the results will be described in this paper.

Results and Discussion

A. Photolyses of Alkyl p-*Toluenesulfinates.* Methyl, ethyl, *n*-butyl, *n*-octyl, benzyl, and allyl *p*-toluenesulfinates without or with *n*-hexane as solvent were degassed in quartz vessels, and then photolyzed at room temperature. Gaseous products formed were identified and quantitatively determined by mass-spectrometry or gas chromatography. Low-boiling products were distilled together with the solvent. The compounds in the residue and the distillate were identified and quantitatively determined.

Table 1 shows the UV absorption maxima of various sulfinates.

Table 2 shows the results of photolysis of ethyl *p*-toluenesulfinate. When a degassed solution of ethyl *p*-toluenesulfinate in *n*-hexane (0.27 mol/*l*) was irradiated for 9 hr, the gaseous products obtained were found to be CO (50.6), CH_4 (22.2), H_2 (16.9), C_2H_4 (4.6), C_2H_6 (3.5), C_3H_8 (1.3), and C_3H_6 (1.0%).

The decomposition of ethyl *p*-toluenesulfinate can be ascribed to its absorption at 250 nm, because a) no decomposition was observed in dark in 120 hr at room temperature, and b) more than 95% of the ester was recovered after irradiation with a high pressure mercury lamp in a Pyrex vessel for 147 hr.

Table 3 shows the results of photolysis of methyl *p*-toluenesulfinate in *n*-hexane.

Formation of methyl *p*-toluenesulfonate is in contrast with the results in the ethyl ester. No contamination

TABLE 1. UV ABSORPTION MAXIMA OF SEVERAL *p*-TOLUENESULFINATES (p-$CH_3C_6H_4SO_2R$) IN HEXANE

R	CH_3	C_2H_5	n-C_4H_9	n-C_8H_{17}	CH_2CHCH_2	$PhCH_2$
λ_{max} (log ε)	224 (4.27)	224 (4.02)	224 (4.02)	224 (4.02)	225 (4.25)	
	254 (3.71)	256 (3.53)	256 (3.53)	254 (3.56)	258 (3.79)	257

TABLE 2. PRODUCTS OF PHOTOLYSIS OF ETHYL *p*-TOLUENESULFINATE IN HEXANE

$[C_7H_7SO_2C_2H_5]_0$ (mol/*l*)	Time (hr)	Unreacted ester (mol%)	Products (mol/100 mol ester)				
			$C_7H_7SO_2SC_7H_7$	$(C_7H_7S)_2$	TsOH	X[d)]	CH_3CHO
0.33	70.5[a)]	6.8	21.7	14.9	1.3	9.2	8.9
0.29	100	17.6	22.2	4.8	trace	19.8	e)
0.28	125	33.6	10.3	4.6	trace	18.1	e)
0.27	(120)[b)]	(100)	0	0	0	0	0
0.38	147[c)]	95	0	0	trace	0	0

a) With a low-pressure mercury lamp. All other experiments were carried out with a high-pressure mercury lamp. b) A blank experiment with no irradiation at room temperature. c) A Pyrex vessel was used. d) A sulfone of unknown structure, in weight %. e) Not determined.

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[1)] Organic Sulfur Compounds, Part XXXIII.

[2)] A recent review: E. Lock, *Quarterly Reports on Sulfur Chemistry*, **4**, No. 4 (1969). Intra-Science Research Foundation, Santa Monica, California.

[3)] M. Kobayashi and N. Koga, This Bulletin, **39**, 1788 (1966).

TABLE 3. PRODUCTS OF PHOTOLYSIS OF METHYL *p*-TOLUENESULFINATE IN *n*-HEXANE

$[C_7H_7SO_2CH_3]_0$ (mol/l)	Time (hr)	Products (mol/100 mol ester)			
		$C_7H_7SO_2SC_7H_7$	$(C_7H_7S)_2$	TsOH	$TsOCH_3$
0.34	66	16.5	12.0	2.8	8.4
0.41	130	19.8	8.2	3.9	7.6

TABLE 4. PRODUCTS OF PHOTOLYSIS OF *n*-BUTYL *p*-TOLUENESULFINATE IN *n*-HEXANE

$[C_7H_7SO_2C_4H_9]_0$ (mol/l)	Time (hr)	Unreacted ester (mol%)	Products (mol/100 mol ester)	
			$C_7H_7SO_2SC_7H_7$	$(C_7H_7S)_2$
0.23	107	35.6	12.5	+
neat	121	28.9	10.7	+

TABLE 5. PRODUCTS OF PHOTOLYSIS OF *n*-OCTYL *p*-TOLUENESULFINATE IN *n*-HEXANE

$[C_7H_7SO_2C_8H_{17}]_0$ (mol/l)	Time (hr)	Unreacted ester (mol%)	Products (mol/100 mol ester)		
			$C_7H_7SO_2SC_7H_7$	$(C_7H_7S)_2$	TsOH
0.29	45	100	0	0	0
0.40	117	100	0	0	0
neat	123	44.5	20.8	0.5	+

TABLE 6. PRODUCTS OF PHOTOLYSIS OF ALLYL *p*-TOLUENESULFINATE IN *n*-HEXANE

$[C_7H_7SO_2C_3H_5]_0$ (mol/l)	Time (hr)	Products (mol/100 mol ester)				
		$C_7H_7SO_2SC_7H_7$	$C_7H_7SO_2C_3H_5$	a sulfone$^{b)}$	polymer$^{c)}$ sulfone	$(C_7H_7S)_2$
0.95	140	10.7	8.6	6.5	32.3	+
0.33	20	4.6	17.2	0	8.0	+
0.27	111	7.0	12.2	0	40.7	+
0.34	(192)$^{a)}$	0	0	0	0	0

a) A blank experiment with no irradiation at room temperature. No change was observed in its NMR spectrum. b) A sulfone of unknown structure, in weight %; mp 100—104.5°C: C, 66.28, 66.14%; H, 6.47, 6.52%. c) Polymeric sulfone of unknown structure, in weight %.

of the initial methyl sulfinate with *p*-toluenesulfonic acid or methyl *p*-toluenesulfonate was confirmed by the IR and NMR spectroscopy. When the solvent was removed from the reaction mixture under reduced pressure at room temperature, the NMR spectrum of the residue showed a signal ascribable to CH_3 of $TsOCH_3$ at 3.7 ppm (s), indicating that $TsOCH_3$ is present in the reaction mixture and is not produced during chromatography and other subsequent treatments.

Table 4 shows the results of photolysis of *n*-butyl *p*-toluenesulfinate in *n*-hexane. The reactivity of the butyl ester is much lower than that of the ethyl ester. The mass spectrum of the gaseous and low-boiling products shows peaks at *m/e* 92, 91, 79, 78(M), 77, 64, 56, 52, 51, 44, 39, 29, and 28, indicating the presence of some toluene.

Table 5 shows the results of photolysis of *n*-octyl *p*-toluenesulfinate in *n*-hexane.

These data show that alkyl *p*-toluenesulfinates with longer alkyl groups are less prone to undergo photolysis.

Table 6 shows the results of photolysis of allyl *p*-toluenesulfinate. When the mixture was irradiated longer, the yield of allyl *p*-tolyl sulfone decreased and that of polymeric sulfone increased. Cope, Morrison, and Field[4] reported thermal rearrangement of allyl benzenesulfinate to allyl phenyl sulfone upon heating at 100°C for 24 hr. No occurrence of such thermal rearrangement under our conditions was confirmed by a blank experiment in dark. It was also confirmed that allyl *p*-tolyl sulfone (0.02M in *n*-hexane, degassed) showed almost no change in its NMR spectrum upon irradiation for 113 hr with a high pressure mercury lamp.

When a degassed solution of benzyl *p*-toluenesulfinate (3.6 mmol) in *n*-hexane (30 m*l*) was irradiated for 192 hr with a high pressure mercury lamp, an absorption at 257 nm disappeared and a new absorption appeared at 243 nm. A weak absorption was observed at 290 nm. Analysis of the reaction mixture revealed the presence of 47 mol% of $C_7H_7SO_2SC_7H_7$, 27.4 mol% of benzaldehyde, and 2 mol% of dibenzyl. Thin layer chromatography showed the presence of some di-*p*-tolyl disulfide.

These results show that when alkyl *p*-toluenesulfinates are irradiated, the SO–O bonds are broken. The photolysis of the ethyl ester is shown as follows.

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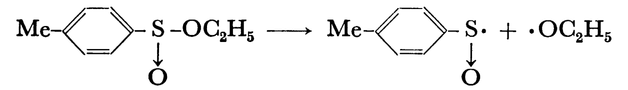
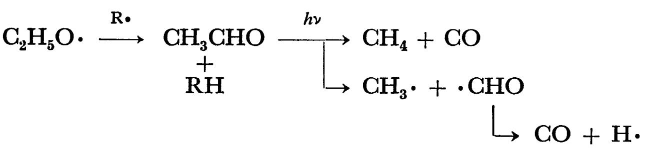
[4] A. C. Cope, D. E. Morrison, and L. Field, *J. Amer. Chem, Soc.*, **72**, 59 (1950).

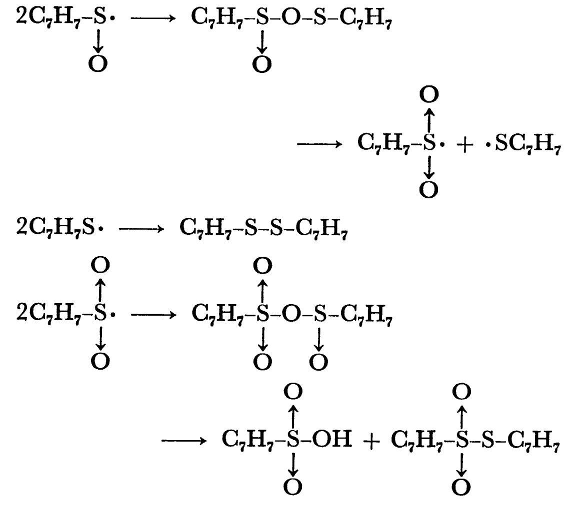


A part of the alkoxy radicals reacts with the sulfinyl radicals, yielding acetaldehyde, which undergoes further photolysis according to the scheme reported in the literature.[5]



$$C_2H_5O\cdot \xrightarrow{R\cdot} \underset{\substack{+\\ RH}}{CH_3CHO} \xrightarrow{h\nu} CH_4 + CO$$
$$\hookrightarrow CH_3\cdot + \cdot CHO$$
$$\hookrightarrow CO + H\cdot$$

The products arising from the sulfinyl radicals are $C_7H_7SO_2SC_7H_7$, $C_7H_7SSC_7H_7$, and $C_7H_7SO_3H$. Formation of these products can be explained by the following scheme.



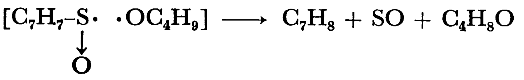
$$2C_7H_7\text{-}\underset{\substack{\downarrow\\ O}}{S}\cdot \longrightarrow C_7H_7\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}O\text{-}S\text{-}C_7H_7 \longrightarrow C_7H_7\text{-}\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}\cdot + \cdot SC_7H_7$$

$$2C_7H_7S\cdot \longrightarrow C_7H_7\text{-}S\text{-}S\text{-}C_7H_7$$

$$2C_7H_7\text{-}\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}\cdot \longrightarrow C_7H_7\text{-}\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}\text{-}\underset{\substack{\downarrow\\ O}}{O}\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}C_7H_7 \longrightarrow C_7H_7\text{-}\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}\text{-}OH + C_7H_7\text{-}\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}\text{-}S\text{-}C_7H_7$$

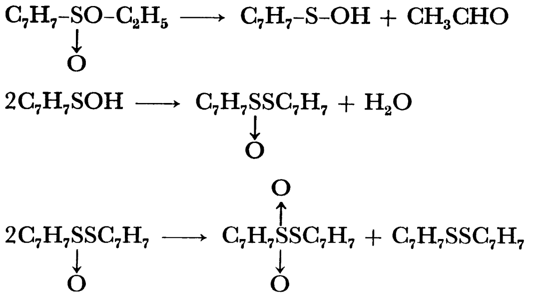
Formation of $ArSO_3H$, $ArSO_2SAr$, and ArSSAr from $Ar\dot{S}O_2$ have been reported by da Silva Correa and Waters.[6]

The mass-spectrometric analysis of the products of the photolysis of *n*-butyl *p*-toluenesulfinate showed the presence of toluene; this finding suggests the occurrence of the following process in cage.



$$[C_7H_7\text{-}\underset{\substack{\downarrow\\ O}}{S}\cdot\ \cdot OC_4H_9] \longrightarrow C_7H_8 + SO + C_4H_8O$$

The following non-radical scheme is conceivable for the photolysis of alkyl *p*-toluenesulfinates.



$$C_7H_7\text{-}\underset{\substack{\downarrow\\ O}}{S}O\text{-}C_2H_5 \longrightarrow C_7H_7\text{-}S\text{-}OH + CH_3CHO$$

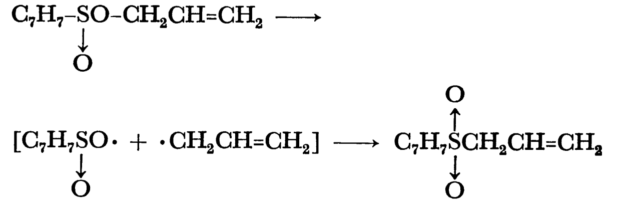
$$2C_7H_7SOH \longrightarrow C_7H_7\underset{\substack{\downarrow\\ O}}{S}SC_7H_7 + H_2O$$

$$2C_7H_7\underset{\substack{\downarrow\\ O}}{S}SC_7H_7 \longrightarrow C_7H_7\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}SC_7H_7 + C_7H_7SSC_7H_7$$

This scheme requires the formation of $ArSO_2SAr$ and ArSSAr in equal amounts. However, the yield of $ArSO_2SAr$ was much greater than that of ArSSAr in all the cases. The results of the photoracemization to be described later also favor the homolytic scheme.

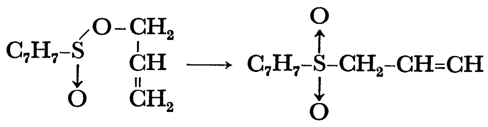
When a degassed solution of ethyl *p*-toluenesulfinate-[sulfinyl-^{18}O] (excess ^{18}O, 0.37 atom%) in *n*-hexane (0.30M) was irradiated at room temperature for 114 hr and the ^{18}O content of the *p*-tolyl *p*-toluenethiolsulfonate isolated was analyzed, it was found to contain 0.54 excess ^{18}O atom%. If only the O–C bond is cleaved, the ^{18}O content of the thiolsulfonate must be equivalent to that of the sulfinate. The result of this experiment shows that the SO–O bond is cleaved by photolysis, though not exclusively.

In the case of the allyl ester, photo-isomerization to allyl *p*-tolyl sulfone took place to some extent. It requires the SO_2–C bond cleavage, which can be rationalized in terms of the stability of allyl radical.



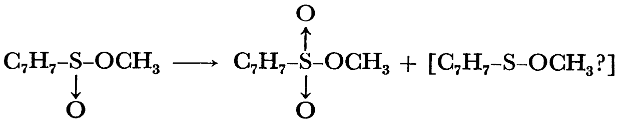
$$C_7H_7\text{-}\underset{\substack{\downarrow\\ O}}{S}O\text{-}CH_2CH{=}CH_2 \longrightarrow [C_7H_7\underset{\substack{\downarrow\\ O}}{S}O\cdot + \cdot CH_2CH{=}CH_2] \longrightarrow C_7H_7\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}CH_2CH{=}CH_2$$

However, in the case of benzyl *p*-toluenesulfinate, no benzyl *p*-tolyl sulfone was detected and much benzaldehyde (a product of the SO–O bond cleavage) was found. Therefore, it is possible that the allyl ester is the only exceptional case and the photoisomerization proceeds by a cyclic process shown below.



It has been reported that thermal isomerization of the allyl ester occurs *via* reversible dissociation to allyl cation and a sulfinate anion,[7] whereas benzyl *p*-toluenesulfinate does not isomerize thermally to the corresponding sulfone.[8]

In the case of methyl *p*-toluenesulfinate, photo-disproportionation took place to some extent, yielding methyl *p*-toluenesulfonate.



$$C_7H_7\text{-}\underset{\substack{\downarrow\\ O}}{S}\text{-}OCH_3 \longrightarrow C_7H_7\text{-}\overset{\substack{O\\ \uparrow}}{\underset{\substack{\downarrow\\ O}}{S}}\text{-}OCH_3 + [C_7H_7\text{-}S\text{-}OCH_3?]$$

Photochemical oxygen transfer has been observed in the case of dimethyl sulfoxide,[9] but in sulfinate esters this is the only example.

In an attempt to determine whether a triplet or a singlet excited state is involved in photolyses of sulfinates, degassed solutions of ethyl *p*-toluenesulfinate (1.5 mmol) in *n*-hexane (30 m*l*) with or without a

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[5] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, New York, N. Y. (1967), p. 371.

[6] C. M. M. da Silva Correa and W. A. Waters, *J. Chem. Soc., C*, **1968**, 1874.

[7] D. Darwish and R. A. McLaren, *Tetrahedron Lett.*, **1962**, 1231; D. Darwish and E. A. Preston, *ibid.*, **1964**, 113.

[8] A. H. Wragg, J. S. McFadyen, and T. S. Stevens, *J. Chem. Soc.*, **1958**, 3603.

[9] Ref. 2, p. 315.

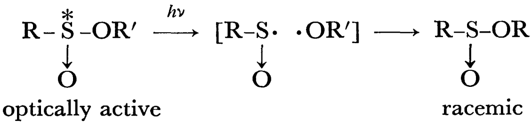
TABLE 7. CHANGE IN OPTICAL ACTIVITY OF *l*-MENTHYL *l*-*p*-TOLUENESULFINATE UPON IRRADIATION[a)]

Initial ester	Time (hr)	Recovered ester	Ph–SO–C_7H_7	% Retention of optical activity
$[\alpha]_D^{30}$ −222.0°	1	$[\alpha]_D^{30}$ −218.3°		98
$[\alpha]_D^{30}$ −210.5°	21	$[\alpha]_D^{34}$ −119.5°		57
$[\alpha]_D^{31.5}$ −263.3°	5	$[\alpha]_D^{31}$ −145.7°		55
$[\alpha]_D^{EtOH}$ −186.42°	4	—	$[\alpha]_D^{CH_2Cl_2}$ +16.87°	59
$[\alpha]_D^{EtOH}$ −186.42°	(4)[b)]	—	$[\alpha]_D^{CH_2Cl_2}$ +28.38°	(100)[b)]

a) Solvent is *n*-hexane, unless otherwise stated.
b) A blank experiment performed in dark without irradiation.

quencher (piperylene, 3.2 mmol) were irradiated by a high pressure mercury lamp in quartz vessels at room temperature for 105 hr. After the volatile components were removed under high vacuum at room temperature, the residues were dissolved in $CDCl_3$, and their NMR spectra were determined. It was found that in the presence of piperylene almost no thiolsulfonate was formed whereas in the absence of piperylene a considerable amount of thiolsulfonate was formed. However, since piperylene itself appeared to undergo some photopolymerization or addition in the presence of ethyl *p*-toluenesulfinate, no definite conclusion was obtained.

B. Photo-racemization of Sulfinate Esters. As shown in Table 1, λ_{max} and log ε of alkyl *p*-toluenesulfinates do not vary with the chain lengths of the alkyl groups, whereas the photolyses of these esters take place to much lesser extent when alkyl groups have longer chain lengths. A possible explanation for these phenomena is that internal return of the sulfinyl radicals and alkoxy radicals takes place in cage and this internal return takes place more easily when alkoxy groups are larger and less prone to diffuse away. If this is the case, irradiation of optically active sulfinate esters must result in photo-racemization.

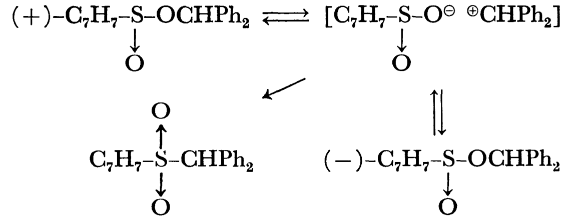


$$\underset{\downarrow\atop O}{R-\overset{*}{S}}-OR' \xrightarrow{h\nu} [\underset{\downarrow\atop O}{R-S}\cdot\ \cdot OR'] \longrightarrow \underset{\downarrow\atop O}{R-S}-OR'$$

When a degassed solution of *l*-menthyl *l*-*p*-toluenesulfinate in *n*-hexane was irradiated with a high pressure mercury lamp at room temperature and then the solvent was removed under reduced pressure at room temperature, the optical activity of the residue was much smaller than that of the initial ester, as shown in Table 7. Very little photolysis is expected to take place during such a short time of irradiation. In order to exclude the possibility of apparent decrease of optical activity of the ester by the contamination of optically inactive decomposition products, the residual ester was converted to phenyl *p*-tolyl sulfoxide by reaction with phenylmagnesium bromide in ether and the optical activity of the sulfoxide was determined.

It is remarkable that considerable racemization took place by irradiation for a short time during which no appreciable photolysis was observed.

Photo-racemization of sulfoxides has been studied fairly extensively.[10)] Racemization of optically active benzhydryl *p*-toluenesulfinate has been studied in acetic acid, and ascribed to reversible dissociation to sulfinate anion and diphenylcarbonium ion. Rates of internal return of the ion pair to the sulfinate ester are approximately equal to those of isomerization to the sulfone.



$$(+)\text{-}\underset{\downarrow\atop O}{C_7H_7\text{-}S}\text{-}OCHPh_2 \rightleftarrows [\underset{\downarrow\atop O}{C_7H_7\text{-}S}\text{-}O^{\ominus}\ {}^{\oplus}CHPh_2] \rightleftarrows (-)\text{-}\underset{\downarrow\atop O}{C_7H_7\text{-}S}\text{-}OCHPh_2$$
$$[\underset{\downarrow\atop O}{C_7H_7\text{-}S}\text{-}O^{\ominus}\ {}^{\oplus}CHPh_2] \longrightarrow C_7H_7\text{-}\overset{O\atop\uparrow}{\underset{\downarrow\atop O}{S}}\text{-}CHPh_2$$

Under our experimental conditions, extensive racemization took place while very little photolysis occurred and no sulfone was observed. Therefore, this photo-racemization should not be ascribed to the reversible dissociation to sulfinate anion and menthyl cation, but rather to the reversible formation of sulfinyl radical and menthyloxy radical.

*C. Photolyses of Di-*n*-butyl Sulfite and *n*-Butyl Chlorosulfite.* Since the photolyses of sulfinate esters were found to involve homolysis of the S–O bond, photolyses of di-*n*-butyl sulfite was investigated.

In contrast with alkyl *p*-toluenesulfinates, dialkyl sulfites show no absorption maxima in the ordinary ultraviolet region, and consequently photolysis proceeded rather slowly.

After neat liquid of di-*n*-butyl sulfite was degassed and irradiated by a high-pressure mercury lamp at room temperature for 31 hr, the gaseous portion of the products was analyzed by gas chromatography, and was found to be CO (26.5), H_2 (37.4), SO_2 (16.4), 1-butene (1.67), butane (0.086), propane (0.84), propene (0.24), ethylene (2.96), ethane (0.17), methane (0.65) (the sum of the hydrocarbons, 6.62), N_2 (14.9), and O_2 (4.32%).

Gas-chromatographic analysis of the liquid products showed that *n*-butanol (14 mol/100 mol ester) and *n*-butyraldehyde (1.7 mol%; confirmed by its 2,4-dinitrophenylhydrazone).

These results indicate that the SO–O bond of the sulfite is cleaved first. The products found can he rationalized by the scheme shown in the next page.

As another compound containing the sulfinyl group, *n*-butyl chlorosulfite was photolyzed. Since this compound has a UV absorption maximum at 230—235 nm, photolysis proceeds fairly rapidly. When neat liquid

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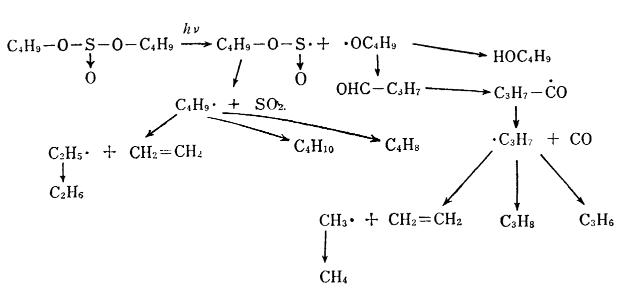
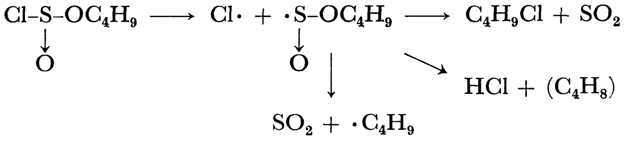
[10)] R. S. Crooke and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 2958 (1968); G. S. Hammond, H. Gotthardt, L. M. Coyne, M. Axelrod, D. R. Rayner, and K. Mislow, *ibid.*, **87**, 4959 (1965).

[11)] E. Ciuffarin, M. Isola, and A. Fava, *ibid.*, **90**, 3594 (1968).



n-butyl chlorosulfite (75 mmol) was degassed and irradiated with a high-pressure mercury lamp at room temperature for 7.5 hr, *n*-C_4H_9Cl (2.0 mmol), HCl (0.5 mmol), SO_2 (0.35 mmol), and some $(n\text{-}C_4H_9O)_2SO$ were found as the products. These results indicate that the bond initially cleaved is not the SO–O bond but the S–Cl bond.



$$\mathrm{Cl\text{-}\underset{\overset{\downarrow}{O}}{S}\text{-}OC_4H_9 \longrightarrow Cl\cdot + \cdot\underset{\overset{\downarrow}{O}}{S}\text{-}OC_4H_9 \longrightarrow C_4H_9Cl + SO_2}$$

$$\searrow \mathrm{HCl + (C_4H_8)}$$

$$\downarrow \mathrm{SO_2 + \cdot C_4H_9}$$

Experimental

Materials. Alkyl *p*-toluenesulfinates were prepared by condensation of *p*-toluenesulfinic acid and an alcohol in the presence of dicyclohexylcarbodiimide with or without solvent (dichloromethane).[12] Methyl ester, bp 78—79°C/1.5 mmHg; ethyl, 78°C/6×10^{-3} mmHg; butyl, 110—114°C/6×10^{-3} mmHg; octyl, 112°C/5×10^{-3} mmHg; allyl, 79—81°C/2×10^{-3} mmHg; benzyl, mp 48°C.

Photolyses of p-*Toluenesulfinates.* Neat ester or its solution in *n*-hexane (spectroscopic grade, 0.3—1.0 M) was placed in a quartz vessel and completely degassed. Then the vessel was irradiated with a 1 kW high-pressure or 30 W low-pressure mercury lamp. During the irradiation some solids began to appear on the wall. After the irradiation, the reaction mixture was frozen with liquid nitrogen, and the gaseous products were pumped out with a Töpler pump and analyzed by gas chromatography (molecular sieve column). In some cases these gaseous products were subjected to mass-spectrometric analysis. The remaining mixture was evaporated at room temperature under high vacuum, and the NMR spectrum of the residue was taken. Then the residue was analyzed by elution chromatography (Florisil, silica gel, or alumina column) and gas chromatography. *p*-Toluenesulfonic acid was extracted with water, and determined quantitatively as its *S*-benzylisothiuronium salt.

Photolysis of Ethyl p-*Toluenesulfinate-*[*sulfinyl-*^{18}*O*]. *p*-Toluenesulfinic acid was heated in $D_2{}^{18}O$ (^{18}O, 1.5 atom %) and converted to $C_7H_7S^{18}O_2D$, which was then allowed to react with ethanol and dicyclohexylcarbodiimide. Into 20 m*l* of *n*-hexane, 1.1 g (6.0 mmol) of the ethyl *p*-toluenesulfinate-[sulfinyl-^{18}O] thus produced was dissolved. The solution was degassed and then irradiated with a 1 kW high-pressure mercury lamp for 144 hr at room temperature. The reaction mixture was evaporated at room temperature under high vacuum, and the residue was chromatographed on a Florisil column, and the thiolsulfonate was isolated.

Photo-racemization of l-*Menthyl* l-p-*Toluenesulfinate.* *l*-Menthol and *p*-toluenesulfinic acid was allowed to react in the presence of dicyclohexylcarbodiimide in dichloromethane.[12] The diastereomeric menthyl ester mixture obtained was treated with hydrogen chloride in the presence of tetramethylammonium chloride, and the crystals of the *l-l* ester were obtained.

A solution of this *l-l* ester (1.0 g) in *n*-hexane (38 m*l*) was degassed and irradiated by a 1 kW high-pressure mercury lamp for 1—21 hr. After the optical activity of the solution irradiated was determined, the solvent was removed at room temperature under high vacuum. The residue was dissolved in ether, and converted to phenyl *p*-tolyl sulfoxide by reaction with ethereal phenylmagnesium bromide.

*Photolysis of Di-*n*-butyl Sulfite.* Di-*n*-butyl sulfite (bp 118—120°C/21 mmHg) (14.8 g; 76.2 mmol) was degassed in a quartz vessel, and irradiated with a 1 kW high-pressure mercuty lamp for 31 hr. The gaseous products collected with a Töpler pump was analyzed by gas chromatography.

Photolysis of n-*Butyl Chlorosulfite.* *n*-Butyl chlorosulfite (85—87°C/46 mmHg) (75 mmol) was degassed, and irradiated with a 1 kW high-pressure mercury lamp for 7.5 hr. The gaseous and low-boiling products were collected in a liquid-nitrogen trap by vacuum distillation, and dissolved in water. The amount of HCl was determined by titration, and that of SO_2 was determined after it was converted to sulfuric acid by H_2O_2. The amounts of *n*-butyl chloride and di-*n*-butyl sulfite were determined by gas chromatography.

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12) Y. Miyaji, H. Minato, and M. Kobayashi, This Bulletin, **44**, 862 (1971).