

β -Cyano- and β -Carbethoxy Sulfides, Sulfoxide, and Sulfones and Their Knoevenagel Condensation

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Received August 24, 1966

Several sulfides and sulfones and one sulfoxide bearing a carboxymethyl or a cyanomethyl substituent were prepared, in some cases by improved procedures. The infrared and nuclear magnetic resonance spectra of these compounds were obtained and indicated the absence of enolization or hydrogen bonding. Various facets of the Knoevenagel condensation of these compounds with aromatic aldehydes were studied, including improved experimental conditions and ultraviolet spectra of the products. Evidence for an ionization mechanism of the condensation reaction was assembled. The base-catalyzed condensation of an *o*-hydroxy aromatic aldehyde with a cyanomethyl sulfone gave a six-membered imino lactone rather than the previously reported hydroxynitrile. Comparative data for the Knoevenagel condensation products showed that the α -arythio, α -aryl-sulfinyl, and α -arylsulfonyl derivatives produced large bathochromic shifts in the ultraviolet spectra *vs.* the parent cinnamionitriles or alkyl cinnamates, the effect of the sulfonyl group being most pronounced in a very clear demonstration of the participation of sulfur d orbitals in resonance.

In recent years there has been increasing interest in the reactions and properties of organic sulfur compounds.¹ In the present investigation, a series of β -cyano- and β -carbethoxy-substituted sulfur compounds and their Knoevenagel condensation with aromatic aldehydes were studied. New data were obtained on the preparation, infrared, nuclear magnetic resonance, and ultraviolet spectra of these compounds which add to the knowledge of the properties of organic sulfur derivatives.

The parent materials, some known and some new, and some of their physical characteristics are listed in Table I.

The sulfides (I-IV) were prepared by the condensation of the appropriate thiol with chloroacetonitrile² or ethyl chloroacetate.³

Sulfoxide V (Table I) was made simply and in good yield by the oxidation of (4-*t*-butylphenylthio)acetonitrile (II) with *N*-bromosuccinimide in water, in an extension of the method of Tagaki, *et al.*⁴ Attempts to prepare a sulfoxide from ethyl (4-*t*-butylphenylthio)acetate in similar manner failed; on prolonged standing of the reaction product, a considerable amount of crystalline material formed, mp 86.0-87.5, which proved to be bis(4-*t*-butylphenyl) disulfide by its infrared spectrum and elemental analysis. Perhaps the sulfoxide formed but was hydrolyzed *in situ* under the prevalent conditions to the (arylsulfinyl)acetic acid. Such acids are known to undergo acid hydrolysis themselves to yield an arylthiol and glyoxylic acid.⁵ The thiol may then have been oxidized to the disulfide by *N*-bromosuccinimide or sulfoxide.⁶

Sulfones VI-IX (Table I) were obtained by the reaction of the sodium arenesulfonates with chloroacetonitrile or ethyl chloroacetate.⁷

(1) Pertinent discussions are contained in the following references: (a) "Organic Sulfur Compounds," M. Kharasch, Ed., Vol. 1, Pergamon Press Inc., New York, N. Y., 1961; (b) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962; (c) C. C. Price, *Chem. Eng. News*, **42** (48), 58 (1964); (d) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.

(2) R. Dijkstra and H. J. Backer, *Rec. Trav. Chim.*, **73**, 569 (1954).

(3) Q. F. Soper, C. W. Whitehead, O. K. Behrens, J. J. Corse, and R. G. Jones, *J. Am. Chem. Soc.*, **70**, 2849 (1948).

(4) W. Tagaki, K. Kikukawa, K. Ando, and S. Oae [*Chem. Ind. (London)*, 1624 (1964)] reported that diaryl sulfides and sulfides having a benzylic methylene group were oxidized to sulfoxides by this method; sulfides having an aliphatic group adjacent to the sulfur atom failed to give sulfoxides in aqueous medium.

(5) N. Hellström and T. Lauritzen, *Ber.*, **69**, 2003 (1936).

(6) H. Heath, A. Lawson, and C. Rimington, *J. Chem. Soc.*, 2223 (1951).

According to Cram^{1d} and references therein, various electron-attracting groups have been arranged in order of their ability to confer acidity to C-H bonds ($\text{NO}_2 > \text{CO} > \text{SO}_2 > \text{COOH} > \text{COOR} > \text{CN} - \text{CONH}_2 > \text{X} > \text{H} > \text{R}$), but the effects of these groups are not additive. Although there is no general relationship between C-H acidity and proton chemical shifts in the nuclear magnetic resonance spectra, for a similar series of compounds nuclear magnetic resonance may give qualitative data on their relative acidity, with the more acidic protons appearing at lower fields.⁸ The nuclear magnetic resonance data in Table I would indicate that the (arenesulfonyl)acetonitriles are the strongest acids and the alkyl (arenethio)acetates are the least acidic. Unfortunately, attempted titrations of (phenylsulfonyl)acetonitrile (VI) and ethyl (phenylsulfonyl)acetate (VIII) in dioxane-water at several dioxane concentrations with sodium methoxide according to the method of Glover⁹ failed to give titration curves from which the pK_a values could be determined. Compounds VI and VIII appear to be too weakly acid for this method to apply.

The assignments of the infrared absorption peaks in Table I are generally unequivocal with the exception of the sulfide bands where the assignments are tentative. According to Bellamy,^{10a} the C-S vibration is variable and weak, occurring in the 14.3-16.7- μ range. The uncertainty arises from the fact that Bentley and Wolfarth^{10b} reported that alkylbenzenes exhibit a weak absorption band between 15.9 and 16.3 μ , and that *para*-substituted alkylbenzenes have a weak absorption band between 15.5 and 15.6 μ . Thus, the bands between 16.1 and 16.2 μ shown by the monosubstituted benzenes in Table I (I, III, and VIII) may not be due to a C-S vibrational mode, and the band at 15.6 and 15.4 μ in compounds II and IX (Table I) could arise from a vibrational mode of a *para*-disubstituted benzene.

The infrared data for the β -cyano- and β -carbethoxy sulfides, sulfoxide, and sulfones do demonstrate, as ob-

(7) (a) J. Tröger and W. Hille, *J. Prakt. Chem.*, **71**, 230 (1905); (b) A. Michael and A. M. Comey, *Am. Chem. J.*, **5**, 116 (1883).

(8) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw Hill Book Co., Inc., New York, N. Y., 1959, p. 24.

(9) D. J. Glover, *J. Am. Chem. Soc.*, **87**, 5275 (1965).

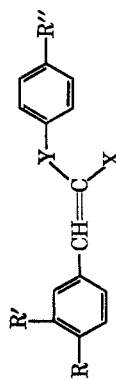
(10) (a) See footnote b, Table I; (b) F. F. Bentley and E. F. Wolfarth, *Spectrochim. Acta.*, **15**, 186 (1959).

TABLE I: PHYSICAL PROPERTIES OF ARYLTHIO-, ARYLSULFONYL-, ARYLSULFINYL-, AND ARYLSULFONYLACETONITRILES AND -ACETATES

Compd	Substituents		Mp, °C (lit.)	Bp, °C (mm) (lit.)	Calcd, %			Found, %			Nmr peak for CH ₂ , ppm ^a	Infrared peak, μ ascribed ^b to				
	R	X			C	H	S	C	H	S		SO	SO ₂	CN	>C=O	>C=O
I	H	CN	133-135 (9) [146-147 (14)] ^c	64.4	4.70	21.5	64.3	4.97	21.4	3.77	16.1			4.48		
II	<i>t</i> -C ₄ H ₉	CN	110-112 (1)	70.2	7.32	15.6	70.1	7.43	15.7	3.67	14.05 and/or 15.6			4.48		
III	H	COOC ₂ H ₅	135-136 (10) [147 (12)] ^d			16.3			16.3	3.47				5.79	7.89, 7.90	
IV	<i>t</i> -C ₄ H ₉	COOC ₂ H ₅	136-138 (3)	66.7	7.94	12.7	66.9	7.89	12.7	3.62				5.79	7.90 (br) ^e	
V	<i>t</i> -C ₄ H ₉	CN	104-105	65.1	6.78	16.5	65.0	6.90	16.6	4.12, 4.24	9.40, 9.52			4.47		
VI	H	CN	112.0-112.5 (114) ^f							4.74				7.61, 8.70	4.45	
VII	CH ₃	CN	150-151	55.4	4.59	16.4	55.5	4.57	16.3	4.67	14.3 and/or 14.7			7.59, 8.69, 17.1, and/or 19.3	4.45	
VIII	H	COOC ₂ H ₅	42-43	52.7	5.27	14.1	52.2	5.17	14.2	4.35	14.9, 16.1			7.59, 8.68, 18.0, and/or 18.9	5.81	7.79, 7.91, 8.02
IX	CH ₃	COOC ₂ H ₅	32-33	54.6	5.79	13.2	54.5	5.91	12.8	4.29	14.8, 15.4, and/or 16.3			7.53, 8.68, 18.7, and/or 19.3	5.74	7.67, 7.75, 7.80

^a Chemical shift with respect to tetramethylsilane. ^b Assignment of absorption peaks according to L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958. ^c Reference 2. ^d E. Müller and E. Freytag, *J. Prakt. Chem.*, **146**, 67 (1936). ^e J. Tröger and W. Hille, *ibid.*, [2] **71**, 230 (1905).

TABLE II: KNOEVENAGEL CONDENSATION PRODUCTS



Compd	Substituents			Calcd, %			Found, %			Mp, °C [lit.]	Bp, °C (mm)	Appearance	
	R	R'	R''	X	Y	C	H	S	C				H
X	CH ₃ O	H	H	CN	S	71.9	4.87	...	71.5	4.90	...	100-210	Colorless
XI	CH ₃ O	H	<i>t</i> -C ₄ H ₉	CN	S	74.3	6.50	...	73.9	6.72	...	206-209 (2)	Pale yellow oil
XII	OCH ₂ O	H	H	CN	S	68.3	3.92	11.4	68.1	3.95	11.5	74.5-76	Pale tan, blue fluorescence ^a
XIII	CH ₃ O	H	<i>t</i> -C ₄ H ₉	CN	SO	70.8	6.20	...	70.4	6.38	...	135-136	Colorless
XIV	H	H	H	CN	SO ₂	11.9	11.8	135-136 [135] ^f	Colorless
XV	CH ₃ O	H	H	CN	SO ₂	10.7	10.7	114.5-116 [113-114] ^e	Colorless
XVI	OCH ₂ O	H	H	CN	SO ₂	61.4	3.52	10.2	61.4	3.57	10.2	170-171.5	Pale yellow, blue fluorescence ^a
XVII	CH ₃ O	H	H	COOC ₂ H ₅	SO ₂	62.5	5.21	9.2	62.3	5.02	9.1	106-107	Colorless
XVIII	OCH ₂ O	H	H	COOC ₂ H ₅	SO ₂	60.0	4.45	8.9	59.8	4.52	8.7	110-101.5	Colorless, blue fluorescence ^a

^a Solid under ultraviolet lamp with emission maximum at ca. 360 m μ . ^b Reference 14a. ^c Reference 14c.

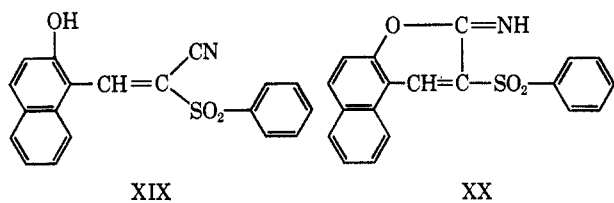
served in similar cases by others,¹¹ that there was no apparent shift of absorption peaks ascribable to enolization or hydrogen bonding in such structures. The S, SO, SO₂, >C=O, >C—O, and CN absorption bands were no different from those found in arenethio, arenesulfinyl, arenesulfonyl compounds and esters or nitriles.

The Knoevenagel condensation of β -cyano- and β -carbethoxy arene sulfides has been little studied. Baliah and Varadachari¹² reported that the base-catalyzed condensation of (arenethio)acetic acid or (arenethio)acetamide with aromatic aldehydes gave substituted cinnamic acids in 7–22% yields. We found that (arenethio)acetonitrile readily undergoes condensation with aromatic aldehydes to give (α -phenylthio)cinnamionitriles (Table II) in fairly good yields (32–46%). On the other hand, we could not isolate a condensation product of alkyl (arenethio)-acetate with aromatic aldehydes when the condensation was tried under a variety of conditions, including catalysis by acetic acid–ammonium acetate in benzene according to Cope.¹³

The Knoevenagel condensation of (4-*t*-butylphenylsulfinyl)acetonitrile (V) failed under the usual conditions. Perhaps the sulfoxide underwent base-catalyzed cleavage and/or disproportionation in the presence of piperidine (with or without acetic acid present), or potassium *t*-butoxide in ethanol, toluene, or dimethyl sulfoxide. However, the condensation of sulfoxide V in benzene solution with anisaldehyde was effected in the presence of both a basic and an acid ion-exchange resin to give 4-methoxy- α -(phenylsulfinyl)cinnamionitrile (XIII) (Table II).

The Knoevenagel condensation of the β -cyano- and β -carbethoxyaryl sulfones has been studied by several authors.¹⁴ The condensation products made during this study are listed in Table II (XIV–XVIII).

In one of the many papers in this area by Tröger, et al.,¹⁵ it was reported that the base-catalyzed condensation of 2-hydroxy-1-naphthaldehyde with sulfone VI gave nitrile XIX, mp 221. We found that the



product of this reaction (our product of mp 226–227°) actually is the imino lactone XX, based on the absence of an infrared absorption peak between 4.43 and 4.46 μ ¹⁶ for a conjugated nitrile, a band at 6.0 μ ascribable to an imino lactone,¹⁷ and the elemental analysis.

(11) *E.g.*, E. H. Holst and W. C. Fernelius, *J. Org. Chem.*, **23**, 1881 (1958), which discusses some properties of β -keto sulfones and β -disulfones.

(12) V. Baliah and R. Varadachari, *J. Indian Chem. Soc.*, **31**, 661 (1956); *Current Sci. (India)*, **23**, 19 (1954).

(13) (a) A. C. Cope, *J. Am. Chem. Soc.*, **59**, 2327 (1937); (b) A. C. Cope, C. M. Hoffmann, C. Wyckoff, and E. Hardenbergh, *ibid.*, **63**, 3452 (1942).

(14) (a) J. Tröger and A. Prochnow, *J. Prakt. Chem.*, [2] **78**, 126 (1908); (b) J. Tröger and E. Nolte, *ibid.*, **103**, 163 (1921); (c) J. Tröger and R. Dunkel, *ibid.*, **104**, 311 (1922); (d) J. Tröger and H. Bremer, *Arch. Pharm.*, **247**, 613 (1909); (e) M. Balasubramanian and V. Baliah, *J. Chem. Soc.*, **32**, 493 (1955).

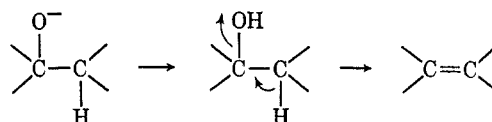
(15) J. Tröger and O. Grünthal, *J. Prakt. Chem.*, [2] **106**, 173 (1923).

(16) R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).

The imino lactone probably arises by intramolecular attack of the naphthoxide ion on the nitrile group.

Concerning the experimental conditions of the Knoevenagel condensation, it was noted that a slow, organic amine (with or without acid) catalyzed reaction could be speeded up substantially by the use of a stronger base. The rate of condensation of (phenylsulfonyl)acetonitrile with piperonal in toluene was followed by azeotropic distillation of the water formed; no water at all had collected with piperidine as the catalyst after 1.5 hr of reflux, but the reaction started immediately and was 100% complete after 0.5 hr of reflux when a catalytic amount of potassium *t*-butoxide was added.

In this connection, it has been reported repeatedly^{18a} that the Knoevenagel condensation of an aldehyde (or ketone) with an active methylene compound requires the presence of catalytic amounts of both amine and carboxylic acid, the conditions of Cope.¹³ Mechanistically, it was reported^{18b} that a formation of an imine or iminium salt of the carbonyl compound is involved; this is followed by reaction of this intermediate with the enol or enolate anion derived from the active methylene compound to give an amino compound which finally eliminates the amine catalyst. In view of the ease of condensation in the present experiment in the absence of an acid catalyst and the absence of enolization of the (arylsulfonyl)acetonitriles and alkyl (arylsulfonyl)acetates, it is more likely that the mechanism involves an ionization reaction, similar to the mechanism proposed for the reaction of malononitrile and ethyl cyanoacetate with aromatic aldehydes by Patai, *et al.*¹⁹ The carbonyl compound reacts with the carbanion of the active methylene compound and the intermediate aldol eliminates hydroxide (the acidity of the methylene compound suffices), according to the following scheme.



The condensation of benzophenone or alkyl aryl ketones with the β -cyano- or β -carbethoxy aryl sulfones could not be realized under any of the various conditions tried (including dimethyl sulfoxide solution with potassium *t*-butoxide as the catalyst), perhaps for steric reasons; Courtalds models of the corresponding aromatic aldehyde condensation products indicate that these are already very crowded substituted ethylenes. It is interesting to note that similar condensations of aryl ketones with malononitrile or ethyl cyanoacetate are known to occur with ease.²⁰

Comparative data on the ultraviolet spectra of some of the Knoevenagel condensation products prepared

(17) G. L. Schmir and B. A. Cunningham [*J. Am. Chem. Soc.*, **87**, 5692 (1965)], and H. E. Zaugg, R. W. DeNet, and R. J. Michaels, *J. Org. Chem.*, **28**, 1795 (1963)] assigned an infrared band at ca. 5.9 μ to the C=N bond in several five-membered ring imino lactones.

(18) (a) *E.g.*, H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, 1965, p 225; (b) and references therein, p 227.

(19) (a) S. Patai and Y. Israel, *J. Chem. Soc.*, 2025 (1960); (b) S. Patai and Z. Zabicki, *ibid.*, 2030 (1960).

(20) (a) R. F. Henk and H. Fincken, *Ann.*, **462**, 267 (1928); (b) H. G. Sturz and C. R. Noller, *J. Am. Chem. Soc.*, **71**, 2949 (1949); (c) N. J. Kartinos and W. W. Williams (to General Aniline and Film Corp.), U. S. Patent 2,914,551 (1959); (d) J. M. Straley, D. J. Wallace, and J. G. Fisher (to Eastman Kodak Co.), U. S. Patent 3,141,018 (1964).

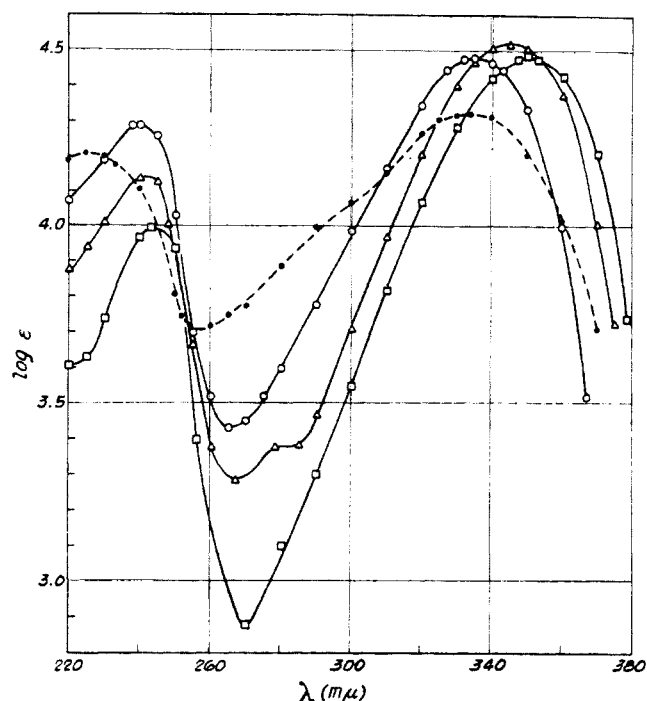
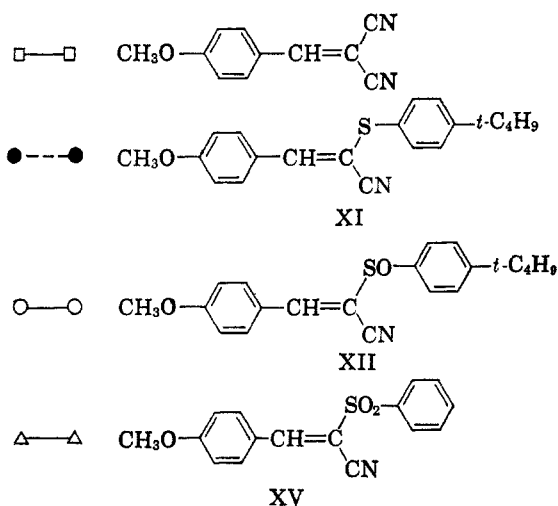


Figure 1.—Ultraviolet spectra of *p*-methoxy- α -substituted cinnamionitriles.



and of related compounds reported in the literature are shown in Table III.

The data in Table III indicate that both an α -phenyl and an α -cyano substituent produced similar pronounced bathochromic shifts (38–40 $m\mu$) of the long wavelength band of cinnamionitrile. The α -phenylsulfonyl substituent caused a similar strong shift (6–8 $m\mu$ smaller). The intensities of absorption of all three compounds were similar. For the α -substituted *p*-methoxycinnamionitriles, the α -phenylsulfonyl derivative showed a bathochromic shift of the long wavelength band of 10–12 $m\mu$ vs. the α -phenyl, α -phenylthio, and α -phenylsulfinyl derivatives. The position and intensity of the absorption peaks of the *o*-[*p*-(*t*-butyl)phenylthio] and *o*-[*p*-(*t*-butyl)phenylsulfinyl] derivatives were very similar to that of *p*-methoxy- α -phenylcinnamionitrile. This indicated that the phenylthio, phenylsulfinyl, and phenylsulfonyl groups each participate in resonance in the photo-excited state. For the *p*-methoxycinnamionitriles, the α -phenylsulfonyl substituent gave unexpectedly the largest effect; this

TABLE III
ULTRAVIOLET SPECTRA OF KNOEVENAGEL CONDENSATION
PRODUCTS AND RELATED COMPOUNDS

Compd	λ_{\max} , $m\mu$ (log ϵ)	Solvent
<i>cis</i> -Cinnamionitrile	273 (4.2) ^a	Not given
<i>trans</i> -Cinnamionitrile	272 (4.4) ^a	Not given
α -Phenylcinnamionitrile	229 (4.21)	<i>i</i> -PrOH
	311 (4.43) ^b	
α -Cyanocinnamionitrile	313 (4.12) ^c	95% EtOH
α -(Phenylsulfonyl)cinnamionitrile (XIV)	224 (4.10)	95% EtOH
	305 (4.38)	
<i>p</i> -Methoxy- α -phenylcinnamionitrile	227 (4.05)	<i>i</i> -PrOH
	333 (4.29) ^b	
<i>p</i> -Methoxy- α -(phenylthio)cinnamionitrile (X)	335 (4.38) ^d	95% EtOH
<i>p</i> -Methoxy- α -(<i>p</i> - <i>t</i> -butylphenylthio)cinnamionitrile (XI)	225 (4.21)	95% EtOH
	334 (4.34)	
<i>p</i> -Methoxy- α -(<i>p</i> - <i>t</i> -butylphenylsulfinyl)cinnamionitrile (XIII)	240 (4.30)	95% EtOH
	335 (4.49)	
<i>p</i> -Methoxy- α -(phenylsulfonyl)cinnamionitrile (XV)	240 (4.13)	95% EtOH
	278 (3.37)	
	345 (4.52)	
<i>m,p</i> -Methylenedioxy- α -(phenylsulfonyl)cinnamionitrile (XVI)	245 (4.05)	95% EtOH
	310 (3.92)	
	365 (4.38)	
Methyl <i>p</i> -methoxy- α -phenylcinnamate	230 (4.12)	<i>i</i> -PrOH
	312 (4.33) ^b	
Ethyl <i>p</i> -methoxy- α -(phenylsulfonyl)cinnamate (XVII)	232 (4.20)	95% EtOH
	318 (4.39)	
Methyl <i>m,p</i> -methylenedioxy- α -methylcinnamate	234 (4.12)	95% EtOH
	288 (4.09)	
	316 (4.15) ^e	
Ethyl <i>m,p</i> -methylenedioxy- α -(phenylsulfonyl)cinnamate (XVIII)	245 (4.01)	95% EtOH
	295 (3.92)	
	337 (4.22)	

^a W. E. Parham, W. N. Moulton, and A. Zuckerbraun, *J. Org. Chem.*, **21**, 72 (1956). ^b G. Drehfahl, G. Heublein, and G. Tetzlaff, *J. Prakt. Chem.*, [4] **23**, 318 (1964). ^c E. Campaigne, G. F. Bulbenko, W. E. Kreighbaum, and D. R. Maulding, *J. Org. Chem.*, **27**, 4428 (1962). ^d Not measured below 240 $m\mu$. ^e A. W. Schrecker and J. L. Hartwell, *J. Am. Chem. Soc.*, **76**, 4896 (1954).

is strong evidence for the participation of sulfur d orbitals in resonance which might be sterically favored in this case. Price and Oae²¹ have compared prior literature data, involving simpler compounds, to show that the interaction of SO₂ with CH=C< is only a small fraction of the effect of S on CH=C< in the ultraviolet spectra.

In the α -substituted cinnamate series, similar effects on the long wavelength ultraviolet band were noted. Ethyl *p*-methoxy- α -(phenylsulfonyl)cinnamate showed a 6- $m\mu$ shift to higher wavelength vs. methyl *p*-methoxy- α -phenylcinnamate; ethyl *m,p*-methylenedioxy- α -(phenylsulfonyl)cinnamate produced a 21- $m\mu$ bathochromic shift vs. methyl *m,p*-methylenedioxy- α -methylcinnamate, with little change in the intensities of absorption.

For additional comparison, the ultraviolet spectra of four α -substituted *p*-methoxycinnamionitriles are shown in Figure 1, and the spectra of four α -substituted *m,p*-methylenedioxy-cinnamionitriles are given in Figure 2.²² From these figures it can also be noted that an

(21) Reference 1b, p 94.

(22) We are indebted to Dr. B. B. Corson and Mr. R. Mainier of Koppers Co. for making available to us the spectra of *p*-methoxy- α -cyanocinnamionitrile and *m,p*-methylenedioxy- α -cyanocinnamionitrile [B. B. Corson and R. W. Stoughton, *J. Am. Chem. Soc.*, **50**, 2825 (1928)].

α -cyano or an α -phenylsulfonyl substituent produced similar bathochromic shifts of the long wavelength absorption band of *p*-alkoxycinnamionitriles.

Experimental Section

All melting points and boiling points are uncorrected. The nmr spectra were obtained on a Varian A-60 instrument. The infrared spectra were taken on mineral oil mulls (solid compounds) or on thin films (liquids) using a Perkin-Elmer Model 137 Infracord. The ultraviolet spectra were measured with a Cary 14 recording spectrophotometer.

The preparations of some representative compounds are described in detail below.

(4-*t*-Butylphenylthio)acetoneitrile (II).—To a solution of 32.0 g (0.2 mole) of 4-*t*-butylthiophenol (Pitt-Consol Chemical Co.) in 200 ml of absolute alcohol was added under nitrogen during *ca.* 1 hr, 4.6 g (0.2 g-atom) of sodium metal in small pieces. The thiophenoxide solution was then heated to reflux (80°) and 16.0 g (0.2 mole) of chloroacetoneitrile was stirred in during 10 min. After another 1 hr at reflux, the mixture was cooled to 25° and filtered (10.4 g of insoluble salt). The filtrate was evaporated on the steam bath and the residue (37.9 g) was distilled through a Bantamware Vigreux column to give 33.2 g (83% yield) of a heart cut, a colorless liquid, bp 110–112° (1 mm), identified as II by infrared, nmr, and S analysis (Table I).

Ethyl (4-*t*-Butylphenylthio)acetate (IV).—Similar to the preceding experiment, 64.0 g (0.4 mole) of 4-*t*-butylthiophenol in absolute ethanol was converted into the sodium salt, treated with 49.0 g (0.4 mole) of ethyl chloroacetate, and worked up as above. The crude product was distilled through a 4-in. Vigreux column to give 80.2 g (80% yield) of the desired product as a heart cut, bp 136–138° (3 mm), a colorless liquid (identification as IV given in Table I).

(*p*-*t*-Butylphenylsulfinyl)acetoneitrile (V).—A mixture of 8.2 g (0.04 mole) of (4-*t*-butylphenylthio)acetoneitrile, 50 ml of water, and 7.4 g (0.04 mole) of *N*-bromosuccinimide was stirred at room temperature. After 3 min, 20 ml of 1,4-dioxane was added. The mixture turned deep red quickly and warmed to 34° owing to an exothermic reaction. After a few minutes, the color faded to a light yellow. The suspension was stirred for another 15 min at ambient temperature and then extracted with 40-ml and 25-ml portions of benzene. The combined extracts were washed with 50 ml of water, dried over Drierite, and filtered, and the filtrate was stripped on the steam bath to give 10.3 g of a light yellow, oily residue which solidified gradually, mp 77–96°. The product was recrystallized from cyclohexane to give 6.7 g (76% yield) of the desired product (identification in Table I) as a white solid, mp 104–105°.

Oxidation of Ethyl (*p*-*t*-Butylphenylthio)acetate with *N*-Bromosuccinimide.—To a stirred mixture of 12.7 g (0.05 mole) of ethyl (4-*t*-butylphenylthio)acetate and 50 ml of water was added 12.0 g (0.06 mole) of *N*-bromosuccinimide in small portions during 5 min. The mixture gave a mild exotherm to 35° and a reddish oil formed. After stirring for 1 hr, the mixture was extracted with two 25-ml portions of benzene. The combined organic extracts were washed with water, dried over Drierite, and then filtered. The filtrate was concentrated on a steam bath to leave 12.4 g of a reddish oil. On prolonged standing in a closed vial, this oil crystallized partially. Some of this crystalline material was removed and washed thoroughly with benzene to give almost colorless crystals, mp 86–87.5°, identified as bis(4-*t*-butylphenyl) disulfide by its infrared spectrum (absorption bands at 5.28, 7.36, 11.9, and 12.0 μ) and S analysis.

Anal. Calcd for $C_{20}H_{26}S_2$: S, 19.40. Found: S, 19.42.

Ethyl (*p*-Toluenesulfonyl)acetate (IX).—A mixture of 43.0 g (0.2 mole) of sodium *p*-toluenesulfinate dihydrate (Aldrich Chemical Co.), 24.5 g (0.2 mole) of ethyl chloroacetate, and 200 ml of absolute ethanol was stirred and refluxed for 18 hr and then filtered hot. The cake (sodium chloride) was washed with 25 ml of absolute alcohol. The filtrate was concentrated on a steam bath. The residual oil was distilled through a Bantamware Vigreux column to give 31.2 g (64% yield) of the desired product (identification in Table I) as a heart cut, bp 159–166° (2 mm), a colorless liquid which crystallized on standing, mp 32–33°.

***m,p*-Methylenedioxy- α -(phenylthio)cinnamionitrile (X).**—A mixture of 7.5 g (0.05 mole) of (phenylthio)acetoneitrile, 40 ml of toluene, 7.5 g (0.05 mole) of piperonal (Eastman), and 3 drops

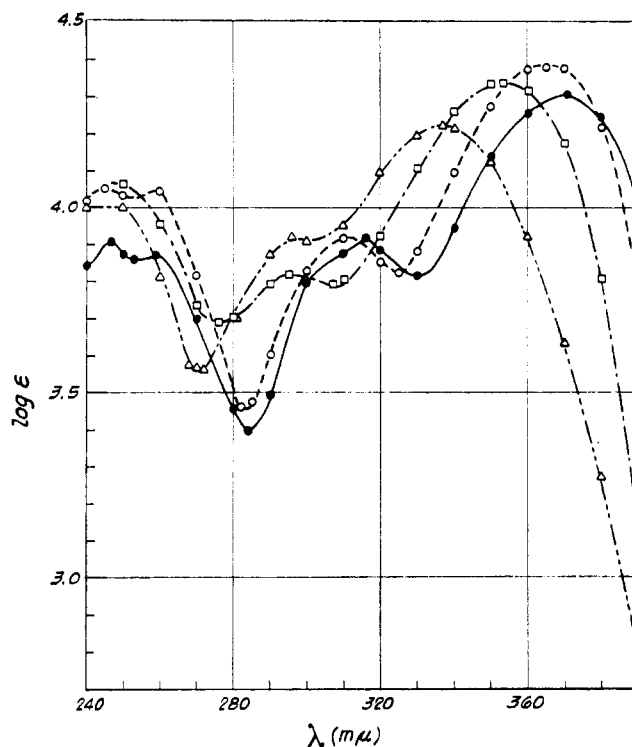
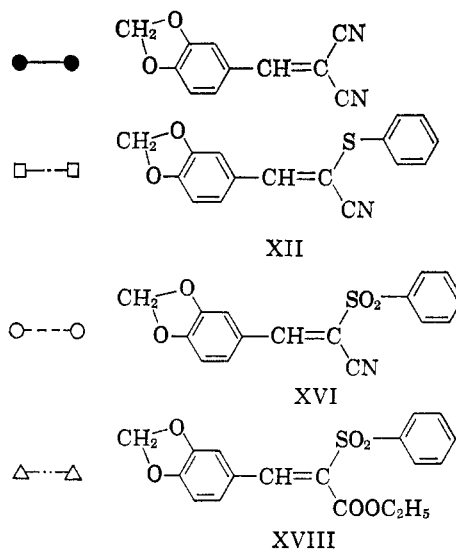


Figure 2.—Ultraviolet spectra of *m,p*-methylenedioxy- α -substituted cinnamic derivatives.



of piperidine was refluxed under a Dean-Stark apparatus. After 1.5 hr of reflux, no water had collected in the Dean-Stark trap. To the mixture was added 0.5 g of potassium *t*-butoxide (MSA Research Co.), and, after an additional 0.5 hr of stirring at reflux, 1.0 ml of an aqueous phase was collected in the Dean-Stark trap. The mixture was cooled to 25° and filtered to give 4.5 g (32% yield) of the desired product, mp 86–87°; recrystallization from 95% ethanol gave pale tan solids, mp 88–90°. Concentration of the first mother liquor gave another 2.0 g (14% yield) of crude material, mp 74–76°.

***p*-Methoxy- α -(phenylsulfinyl)cinnamionitrile (XIII).**—A mixture of 2.2 g (0.01 mole) of (*p*-*t*-butylphenylsulfinyl)acetoneitrile, 50 ml of benzene, 1.2 g (0.01 mole) of anisaldehyde, *ca.* 0.5 g of acid ion-exchange resin IR-120 (Rohm and Haas), and *ca.* 0.5 g of basic ion-exchange resin Dowex-3 (Dow) was held at 70–80° for 5 hr. The mixture was then filtered and the filtrate was evaporated to dryness to leave a yellow oil. On prolonged standing, this crystallized in part. The solids were filtered off and washed with cold *n*-heptane and 95% ethanol to leave 1.1 g of pale yellow solids, mp 92–105°; recrystallization from 95% ethanol gave colorless crystals, mp 135–136°.

The Imino Lactone XX.—A mixture of 3.5 g (0.02 mole) of 2-hydroxy-1-naphthaldehyde (Eastman), 3.6 g (0.02 mole) of (phenylsulfonyl)acetonitrile, 20 ml of absolute ethanol, and 2 drops of piperidine was boiled for 0.5 hr (insolubles present), then diluted with 40 ml of toluene, and filtered to give 5.5 g of yellow solids, mp 226–227°; the melting point was unchanged after recrystallization from xylene. The infrared spectrum did not show a nitrile peak at *ca.* 4.4 μ but had bands at 3.1, 6.0, and 7.1 μ .

Anal. Calcd for C₁₉H₁₃NO₂S (XX): N, 4.18; O, 14.3. Found: N, 4.10; O, 14.4.

Registry No.—I, 5219-61-4; II, 7605-24-5; III, 7605-25-6; IV, 7605-26-7; V, 7605-27-8; VI, 7605-28-9; VII, 5697-44-9; VIII, 7605-30-3; IX, 2850-19-3; X, 7605-32-5; XI, 7605-33-6; XII, 7605-34-7; XIII, 7605-35-8; XIV, 7605-36-9; XV, 7605-37-0; XVI, 7605-38-1;

XVII, 7605-39-2; XVIII, 7605-40-5; α -phenylcinnamionitrile, 2510-95-4; α -cyanocinnamionitrile, 2700-22-3; *p*-methoxy- α -phenylcinnamionitrile, 5432-07-5; methyl *p*-methoxy- α -phenylcinnamate, 7605-44-9; methyl *m,p*-methylenedioxy α -methylcinnamate, 7605-45-0; α -cyano-*p*-methoxycinnamionitrile, 2826-26-8; α -cyano-*m,p*-methylenedioxcinnamionitrile, 2972-82-9; bis(4-*t*-butylphenyl) disulfide, 7605-48-3; XX, 7605-49-4.

Acknowledgments.—It is a pleasure to acknowledge the interest of Dr. W. C. Fernelius in this work, the assistance of the Chemical and Instrumental Analysis Group of these laboratories (particularly Mr. R. Mainier), and the invaluable help of Mr. H. E. Sobel in the synthetic part.

Reactions of Sulfenes with Ketene Acetals and Ketene Aminals

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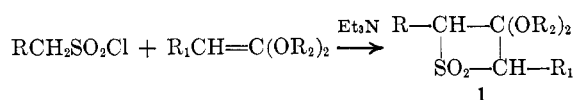
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Received August 8, 1966

Various ketene acetals cycloadd to "sulfenes" to give thietane dioxides. With benzoyl- and acetylketene diethylacetals, sulfenes undergo a Diels–Alder-like cycloaddition, yielding an unsaturated δ -sultone and a cyclic keto sulfone, respectively. Cyclic and/or acyclic products are obtained from the interaction between sulfene and a ketene aminal. The product distribution varies depending upon the nature of the substituent on the alkanesulfonyl chloride and the solvent used.

Earlier papers of this series¹ describe the reactions of alkanesulfonyl chlorides with ketene diethylacetal and with 1,1-bis(diethylamino)ethylene in the presence of triethylamine. The reactions were believed to proceed *via* sulfene intermediates, the intermediacy of which was subsequently verified through the alcoholysis of alkanesulfonyl chlorides with deuterated alcohols.²

In the course of a continuing investigation of the reactions of sulfenes with electron-rich olefins, we have found that various other ketene acetals also react readily with sulfene systems to afford the expected thietane dioxides (see I and Table I). The yields

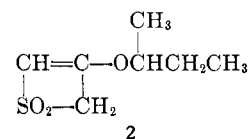


ranged from 76 to 9%, depending upon the nature of the substituents on the β carbon of the ketene acetals. The yield of 1a was improved by employing a dilution method in which an ethereal solution of phenylmethanesulfonyl chloride was added dropwise to a mixture of ketene diethylacetal and triethylamine in the same solvent (a total of 1 l. of ether was used for 0.1 mole scale). The resulting suspension was stirred overnight at room temperature. After the usual work-up, there was obtained a 76.3% yield of pure 2-phenyl-3,3-diethoxythietane 1,1-dioxide (1a). While methylketene diethylacetal ($\text{R}_1 = \text{CH}_3$) gave the sulfene cycloadduct in a fair yield (45%), bromoketene

diethylacetal ($\text{R}_1 = \text{Br}$) afforded only 9.5% yield of the corresponding adduct (1h), and phenylketene dimethylacetal ($\text{R}_1 = \text{C}_6\text{H}_5$) yielded no adduct.³ These data suggest that the most effective olefins, for trapping sulfene intermediates, are highly electron-donating, *e.g.*, ketene acetals,¹ ketene O,N-acetals,⁴ and ketene aminals,^{1c,4,5} and relatively unhindered.

The basicity of the tertiary amine and the acidity of the hydrogens α to the sulfone group are also important. Under the reaction conditions both methanesulfonyl and phenylmethanesulfonyl chlorides failed to give the sulfene adduct when pyridine was used as a base. On the other hand, bromomethanesulfonyl chloride did react in the absence of base with 1 equiv of ketene diethylacetal to give 1h in 20.3% yield, compared with 20.7–34.0% using triethylamine and 27.7% in the presence of zinc.⁶ Presumably the hydrogens on bromomethanesulfonyl chloride are sufficiently acidic⁷ to be abstracted by ketene acetal, leading to the usual sulfene reaction.

In one instance, methanesulfonyl chloride plus ketene di-*sec*-butylacetal, a thiete dioxide (2) was formed.



(3) The possibility that the formation of the four-membered ring adduct was followed by the rapid ring cleavage to give acyclic products was not entirely precluded.

(4) (a) R. H. Hasek, *et al.*, *J. Org. Chem.*, **28**, 2496 (1963); (b) R. H. Hasek, R. H. Meen, and J. C. Martin, *ibid.*, **30**, 1495 (1965).

(5) (a) G. Opitz and H. Schempp, *Z. Naturforsch.*, **19b**, 1 (1964); (b) G. Opitz and H. Schempp, *Ann. Chem.*, **684**, 103 (1965).

(6) The original objective of the usage of zinc, *i.e.*, to generate a sulfene through dehalogenation, was not achieved.

(7) (a) S. M. McElvain and D. Kundiger, *J. Am. Chem. Soc.*, **64**, 254 (1942); (b) L. Claisen and E. Hasse, *Ber.*, **33**, 1244 (1900).

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(2) (a) W. E. Truce, R. W. Campbell, and J. R. Norell, *J. Am. Chem. Soc.*, **86**, 288 (1964); **88**, 3599 (1966); (b) J. F. King and T. Durst, *ibid.*, **86**, 287 (1964); **87**, 5684 (1965).