THE JOURNAL OF Organic Chemistry®

VOLUME 36, NUMBER 13 | JULY 2, 1971

© Copyright 1971 by the American Chemical Society

Adducts of Sulfonyl Iodides with Acetylenes[1]

WILLIAM E. TRUCE* AND GORDON C. WOLF

Purdue University, West Lafayette, Indiana 47907

Received November 10, 1970

Sulfonyl iodides, including three previously unknown alkane derivatives, add readily and stereoselectively to acetylenes to form 1:1 adducts in good to excellent yields. That the addition occurs in a trans manner was established by reducing the adducts to the *cis*-vinyl sulfones with zinc and acetic acid and by three-dimensional X-ray crystallography. The adducts represent convenient precursors to sulfonylacetylenes and, on treatment with cuprous phenylacetylide, yield the novel ene–yne sulfones. The acetylenic sulfones undergo a smooth thermally induced extrusion of sulfur dioxide in several cases.

Free-radical additions of sulfonyl halides to olefins have been studied extensively. Thus, Kharasch, *et al.*, initially found that *N*-chlorosulfonylphthalimide and 1-octene combined, in the presence of traces of peroxide, to give a 1:1 adduct.[2] Cristol and coworkers[3] studied the reactions between benzenesulfonyl halides (chloride, bromide, and iodide) and norbornadiene, and Skell, *et al.*,[4,5] carried out extensive synthetic investigations and rate studies with the same three sulfonyl halides. For addition to olefins, the chain mechanism as shown in Scheme I is generally accepted.

SCHEME I

$$\mathrm{C_6H_5SO_2X} \longrightarrow \mathrm{C_6H_5SO_2\cdot} + \mathrm{X\cdot} \qquad (1)$$

$$\mathrm{C_6H_5SO_2X} + \mathrm{In\cdot} \longrightarrow \mathrm{C_6H_5SO_2\cdot} + \mathrm{InX} \qquad (2)$$

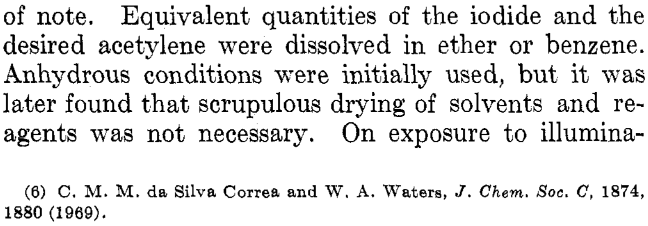
$$\mathrm{C_6H_5SO_2\cdot} + \mathrm{RCH{=}CH_2} \longrightarrow \mathrm{R\underset{\cdot}{C}HCH_2SO_2C_6H_5} \qquad (3)$$

$$\mathrm{R\underset{\cdot}{C}HCH_2SO_2C_6H_5} + \mathrm{C_6H_5SO_2X} \longrightarrow \mathrm{R\underset{\underset{X}{|}}{C}HCH_2SO_2C_6H_5} + \mathrm{C_6H_5SO_2\cdot} \qquad (4)$$

Steps 1 and 2 are the initiating steps (where In· represents an added initiator such as peroxide) and steps 3 and 4 are the propagating steps. Although all three sulfonyl halides undergo the above sequence, there is a marked difference in the rate at which each proceeds. Thus, benzenesulfonyl chloride combines with norbornadiene very slowly (giving a 7.3% combined yield of 1:1 adducts after 56 hr near a 150-W clear electric bulb), while the sulfonyl bromide adds smoothly (90% after 27 hr near illumination) and the iodide and the diene combine in a violent, exothermic manner.[3]

Although sulfonyl halide additions to olefins have received considerable attention[2-9] and constitute a valuable synthetic approach to various sulfones, like additions to other unsaturated systems seem to have been neglected. Amiel[10] stated that aromatic sulfonyl chlorides add to acetylenes to give 1:1 adducts, but no experimental details have been forthcoming. Also, a preliminary report of our investigations, concerning the additions of sulfonyl iodides to allenes,[11,12] has appeared.

p-Toluenesulfonyl iodide has been found to add readily and stereoselectively to numerous acetylenes. The ease with which the reactions were carried out is worthy of note. Equivalent quantities of the iodide and the desired acetylene were dissolved in ether or benzene. Anhydrous conditions were initially used, but it was later found that scrupulous drying of solvents and reagents was not necessary. On exposure to illumina-



$$p\text{-}\mathrm{CH_3C_6H_4SO_2I} + \mathrm{RC{\equiv}CR'} \longrightarrow \mathrm{(R)(I)C{=}C(}p\text{-}\mathrm{SO_2C_6H_4CH_3)(R')}$$

3

---

[1] Abstracted from the Ph.D. Thesis of G. C. W., Purdue University, 1970.

[2] (a) M. S. Kharasch and A. F. Zavist, *J. Amer. Chem. Soc.*, **73**, 964 (1951); (b) M. S. Kharasch and R. A. Mosher, *J. Org. Chem.*, **17**, 453 (1952).

[3] (a) S. J. Cristol and J. A. Reeder, *ibid.*, **26**, 2182 (1962); (b) S. J. Cristol and D. I. Davies, *ibid.*, **29**, 1282 (1964).

[4] (a) P. S. Skell and J. H. McNamara, *J. Amer. Chem. Soc.*, **79**, 85 (1957); (b) P. Skell, R. C. Woodworth, and J. H. McNamara, *ibid.*, **79**, 1253 (1957).

[5] J. H. McNamara, Ph.D. Thesis, The Pennsylvania State University, 1956.

[6] C. M. M. da Silva Correa and W. A. Waters, *J. Chem. Soc. C*, 1874, 1880 (1969).

[7] C. T. Goralski, Ph.D. Thesis, Purdue University, 1969.

[8] M. Assher, *Chem. Ind. (London)*, 32 (1964).

[9] M. Asscher and D. Vofsi, *J. Chem. Soc.*, 4962 (1964).

[10] Y. Amiel, Abstracts of Papers, Second Organic Sulfur Symposium, Groningen, The Netherlands, 1966.

[11] W. E. Truce and G. C. Wolf, *Chem. Commun.*, 150 (1969).

[12] Whereas allene yields p-$\mathrm{CH_2{=}CICH_2SO_2C_6H_4CH_3}$, phenylallene yields $\mathrm{C_6H_5CH{=}C(}p\text{-}\mathrm{SO_2C_6H_4CH_3)CH_2I}$.

TABLE I

ADDUCTS OF *p*-TOLUENESULFONYL IODIDE WITH ACETYLENES

Product	Acetylene	Yield, %	Mp, °C	C, % Calcd	C, % Found	H, % Calcd	H, % Found	I, % Calcd	I, % Found	S, % Calcd	S, % Found
3a	$C_6H_5C\equiv CH$	87	83–84	46.89	46.72	3.41	3.55	33.03	32.83	8.34	8.50
3b	$c\text{-}C_6H_{11}C\equiv CH$	74	108.5–109.5	46.16	46.28	4.91	5.16	32.52	32.62	8.22	7.99
3c	$C_6H_5C(O)C\equiv CH$	83	155–156	46.62	46.56	3.18	3.25	30.78	30.90	7.78	8.00
3d	$C_2H_5O_2CC\equiv CH$	32	98–99	37.91	38.12	3.45	3.65	33.38	33.55	8.43	8.72
3e	$NCC\equiv CH$	16	123–124	36.05	35.92	2.42	2.22	38.09	37.90	9.62	9.82
3f	$p\text{-}NO_2C_6H_4C\equiv CH$	68	203–204	41.97	42.25	2.82	2.93	29.56	29.27	7.47	7.76
3g	$n\text{-}C_4H_9C\equiv CH$	82	50.0–50.5	42.87	42.87	4.70	4.59	34.84	34.58	8.80	8.80
3h	$p\text{-}CH_3C_6H_4SC\equiv CH$	80	135–136	44.66	44.37	3.51	3.55	29.49	29.69	14.90	14.89
3i	$(CH_3)_2CHC\equiv CH$	69	71–72	41.15	41.23	4.32	4.37	36.24	35.99	9.16	9.23
3j	$n\text{-}C_6H_{13}C\equiv CH$	74	55–56	45.93	45.74	5.40	5.51	32.35	32.35	8.17	8.17
3k	$(CH_3)_3CC\equiv CH$	86	70–105[a]	42.87	42.90	4.70	4.89	34.84	34.90	8.80	8.90
3l	$C_6H_5C\equiv CC_6H_5$	35	192–193	54.79	54.53	3.72	3.91	27.57	27.57	6.97	6.75
3m	$C_6H_5C\equiv CCl$	79	146–147	43.03	43.03	2.89	3.00	30.31	30.01	7.66	7.49
3n	$C_2H_5C\equiv CC_2H_5$	84	66–67	42.87	42.63	4.70	4.84	34.84	34.84	8.80	9.03

[a] This is the only instance where both isomers were observed; the analysis was obtained on the mixture.

TABLE II

ADDITION OF ALKANESULFONYL IODIDES TO ACETYLENES

Product	Acetylene	Iodide	Yield, %	Mp, °C [bp (mm), °C]	C, % Calcd	C, % Found	H, % Calcd	H, % Found	I, % Calcd	I, % Found	S, % Calcd	S, % Found
4a	$C_6H_5C\equiv CH$	CH_3SO_2I	73	84–85, 94–95[a]	35.08	34.87	2.94	3.20				
4b	$C_2H_5C\equiv CC_2H_5$	CH_3SO_2I	24	54–55	29.18	29.46	4.55	4.57				
5a	$C_6H_5C\equiv CH$	$C_2H_5SO_2I$	80	77–78	37.28	37.45	3.44	3.34				
5b	$n\text{-}C_4H_9C\equiv CH$	$C_2H_5SO_2I$	44	[120–124 (0.01)]	31.80	31.97	5.00	5.15				
6	$C_6H_5CC\equiv CH$	$i\text{-}C_3H_7SO_2I$	53	130–131	39.30	39.59	3.89	3.84	37.75	37.50	9.54	9.50
7	$C_6H_5CC\equiv CH$	$tert\text{-}C_4H_9SO_2I$	15	213–214	41.15	41.43	4.32	4.26	36.24	36.00	9.16	9.00

[a] Two interconvertible crystalline forms were obtained.

tion,[13] the yellow solution usually began to lighten after 5–20 min (in some cases, the solution darkened instead, and, when this occurred, the yield of adduct was generally less). Solvent removal gave the product as a solid residue and, after one recrystallization from ethanol–water, the essentially pure *trans*-β-iodovinyl sulfone was obtained (Table I). Although electron-withdrawing substituents on the triple bond seem to lower the yield of adduct in some cases (*i.e.*, **3d** and **3e**), in other instances there is little apparent effect (**3c**, **3f**, **3m**). Furthermore, internal acetylenes (**3m**, **3n**) react in a comparable fashion to terminal ones. (Note, however, the lowered yield of adduct when tolane was the substrate.) All products in Table I were obtained as crystalline solids; however, their stability varied. Whereas most were seemingly unchanged after 1 year in the dark, **3h** decomposed quite rapidly. When exposed to the atmosphere and incident light for as little as 24 hr, the adduct began to decompose noticeably; after 1 week, it was quite dark and iodine vapors were apparent above the solid.

With the encouraging results obtained above, the scope of the reaction was extended to include other sulfonyl iodides. The only alkanesulfonyl iodide described in the literature to date is the methyl derivative.[14] Methanesulfonyl iodide was prepared as intense green needles which defied our attempts at purification. It could not be dried under vacuum without decomposition nor did we find a suitable solvent system to effect recrystallization. Hence, it was initially used as the impure, wet solid. However, though a 1:1 adduct was obtained with phenylacetylene when this solid was used, 1,2-diiodostyrene was also formed in large quantities. For this reason, as well as for convenience, methanesulfonyl iodide was prepared and used *in situ* by mixing an aqueous solution of sodium methanesulfinate with a benzene solution of iodine. In the same manner, ethane-, 2-propane-, and *tert*-butanesulfonyl iodides were prepared. The yields were generally lower than with *p*-toluenesulfonyl iodide, but perhaps more noteworthy is the fact that the adducts could be prepared at all. Thus, at the end of the reaction period, the biting odor of sulfur dioxide was evident above each solution; presumably the intermediate alkanesulfonyl radical was extruding sulfur dioxide.

$$RSO_2I \longrightarrow I\cdot + RSO_2\cdot \longrightarrow R\cdot + SO_2$$

Indeed, van Aller, *et al.*,[15] have reported that *tert*-butanesulfonyl chloride is unstable and decomposes to *tert*-butyl chloride, isobutylene, sulfur dioxide, and hydrogen chloride with a half-life of 34 hr at 35°. The iodide would be expected to be less stable.

As noted in Table I, only in the *p*-toluenesulfonyl iodide–*tert*-butylacetylene reaction were two isomeric products found. The adducts listed in Table II were also obtained as a single pure isomer in each case. To eliminate the possibility that a second isomer was being lost during purification procedures, several of the crude reaction mixtures were analyzed by nmr spectroscopy before work-up. For example, in the preparation of **3i**, after the normal reaction period, the volatile materials were removed at reduced pressure and a bath temperature not exceeding 45°. An nmr spectrum of

---

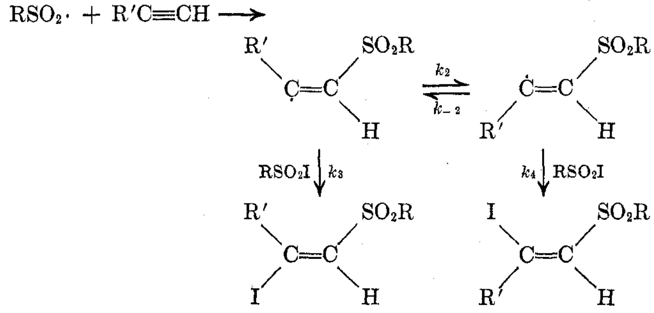
[13] For the reactions discussed here, a 250-W General Electric heat lamp was employed; however, the additions could also be effected by the influence of a 200-W Hanovia medium-pressure lamp (using a Pyrex filter). Indeed, the reactions proceeded in the dark but were markedly catalyzed by light. Thus, after 132 min in the dark, the reaction between 1-hexyne and *p*-toluenesulfonyl iodide had proceeded to 29% completion; after an additional 15 min near the heat lamp, the reaction was 70% complete (by nmr).

[14] L. Field, T. F. Parsons, and R. R. Crenshaw, *J. Org. Chem.*, **29**, 918 (1964).

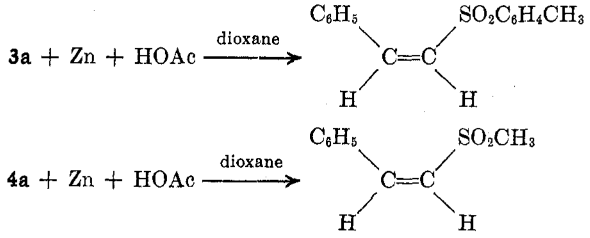
[15] R. T. van Aller, R. B. Scott, Jr., and E. L. Brockelbank, *ibid.*, **31**, 2357 (1966).

the residue showed only one vinyl proton peak and only one set of isopropyl protons. Analogous results were obtained for several other reactions. Furthermore, the reaction between *p*-toluenesulfonyl iodide and 1-hexyne was followed from 0 to 75% completion by periodically withdrawing samples, removing the solvent, and analyzing the residue by nmr. Again, throughout the course of the reaction, only one vinyl proton and one vinyl methylene group could be detected. This remarkable stereoselectivity parallels that reported by Cristol, *et al.*[3] It would appear that chain transfer by the sulfonyl iodide (k_3) is much faster than isomerization of the intermediate vinyl radical (k_2) (Scheme II).[16]

SCHEME II

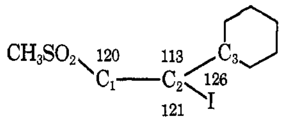


That the sulfonyl iodides were, indeed, adding in a trans fashion was established by two methods. Thus, **3a**, **3b**, and **4a** were reduced with zinc and acetic acid



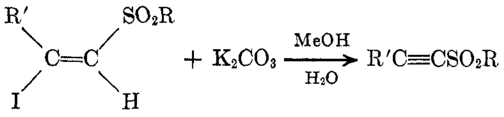
to give only the *cis*-vinyl sulfone. No trans product could be detected by nmr in the crude reaction mixture.

A more unambiguous structural proof was sought, and to this end an X-ray crystallographic analysis was performed on one of the adducts.[17] Crystals of the adduct from methanesulfonyl iodide and phenylacetylene were found to belong to the C2/C monoclinic space group and yielded 2400 good intensities. The cell dimensions were a = 12.393 Å, b = 10.463 Å, c = 17.220 Å, and β = 101.91°. The results of this study confirm our chemical evidence. A more detailed account will be reported later, but these preliminary results (with an R value = 0.17) unequivocally show that the iodine and sulfur atoms are located trans to



each other. The pertinent bond angles are shown in structure a. The atoms S, C_1, C_2, C_3, and I very nearly lie in the same plane. There is a possible twist of less than 10° about the carbon-carbon double bond. Interestingly, the plane of the benzene ring is close to perpendicular to that described by S, C_1, C_2, C_3, and I.

As β-bromo vinyl ketones can be dehydrohalogenated to the acetylenic ketones *via* treatment with potassium carbonate in methanol-water,[18] so can these adducts (Table III). Attempts to dehydroiodinate **3c**, **3f**, and



3h met with only limited success. The crude products in each case showed a band at *ca.* 4.5 μ in the ir spectrum, but the pure acetylenic sulfone could not be isolated. In all three cases, spectral evidence indicated the presence of varying amounts of the products resulting from methoxide and hydroxide displacement on the vinyl iodide.

Compounds **12–15** smoothly extrude sulfur dioxide to yield the disubstituted acetylenes on heating, *i.e.*,

$$C_6H_5C{\equiv}CSO_2R \xrightarrow{180\text{–}250°} C_6H_5C{\equiv}CR + SO_2$$

16a, R = CH_3; 40%
b, R = C_2H_5; 68%
c, R = *i*-C_3H_7; 66%
d, R = *tert*-C_4H_9; 73%

Though thermal rearrangements of organic sulfur compounds have been reported (*i.e.*, α disulfones,[19] α-sulfinyl sulfones,[20] and allylic sulfones[21]), as far as we are aware, this is the first report of acetylenic sulfones behaving likewise. The present rearrangement is limited in scope, however. For the reaction to proceed significantly, R in **16** must be an alkyl group; and also, the substituent on the acetylenic carbon must be aryl. When R = C_6H_5, the pyrolysis gave large quantities of sulfur dioxide but none of the hoped-for tolane. Further, no 3-octyne was obtained when 1-ethanesulfonyl-1-hexyne was heated to 300°, although sulfur dioxide was again evolved. Finally, only starting material (no sulfur dioxide) was recovered when 1-*p*-toluenesulfonyl-1-octyne was heated to 280°.

Copper acetylides have recently been shown to be

---

(16) Vinyl radicals have recently received much attention regarding their structure and configuration. Several reports have appeared dealing with the additions of various radicals to terminal acetylenes. Such addends include chloroform, thiolacetic acid, tetrafluorohydrazine, organic disulfides, and thiols. In every case but one (tetrafluorohydrazine), the predominate product was that resulting from trans addition of the attacking reagent. The current work is unique in that only one isomer was detected in all the additions studied (save that employing *tert*-butylacetylene). This suggests that sulfonyl iodides are much better chain transfer agents than any of the above-mentioned addends. Moreover, we have found that in the cupric bromide catalyzed addition of benzenesulfonyl bromide to phenylacetylene there can be isolated two isomeric α-bromo-β-(benzenesulfonyl)-styrenes. This result serves to enforce the work of Skell and McNamara who found that, in the additions to norbornadiene, benzenesulfonyl bromide and chloride both led to much greater amounts of internally rearranged products than did benzenesulfonyl iodide. For leading references in this area of vinyl radicals and radical additions to terminal acetylenes, see J. A. Kampmeier and G. Chen, *J. Amer. Chem. Soc.*, **87**, 2608 (1965); R. M. Fantazier and J. A. Kampmeier, *ibid.*, **88**, 5219 (1966); R. M. Kopchik and J. A. Kampmeier, *ibid.*, **90**, 6733 (1968); G. N. Sausen and A. L. Logothetis, *J. Org. Chem.*, **32**, 2261 (1967); E. I. Heiba and R. M. Dessau, *ibid.*, **32**, 3837 (1967); L. A. Singer and J. Chen, *Tetrahedron Lett.*, 4849 (1969).

(17) The authors express their sincere gratitude to Dr. R. Parthasarathy of the Center of Crystallographic Research, Roswell Park Division of Health Research, Inc., Buffalo, N. Y., for carrying out the difficult and time-consuming analysis.

(18) P. Eaton and C. Stubbs, *J. Amer. Chem. Soc.*, **89**, 5722 (1967).

(19) J. L. Kice and N. A. Favstritsky, *J. Org. Chem.*, **35**, 114 (1970).

(20) J. L. Kice and N. E. Pawlowski, *J. Amer. Chem. Soc.*, **86**, 4898 (1964).

(21) E. M. LaCombe and B. Stewart, *ibid.*, **83**, 3457 (1961).

TABLE III

ACETYLENIC SULFONES

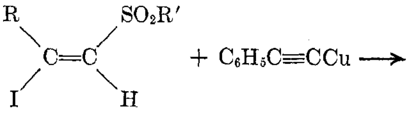
Compd	Formula	Yield, %	Mp, °C [bp (mm), °C]	C, % Calcd	C, % Found	H, % Calcd	H, % Found	S, % Calcd	S, % Found
8	$p\text{-}C_6H_5C{\equiv}CSO_2C_6H_4CH_3$	86	83–84						
9	$p\text{-}(CH_3)_3CC{\equiv}CSO_2C_6H_4CH_3$	100	99.5–100.5	66.08	66.07	6.83	6.70	13.55	13.58
10	$p\text{-}(CH_3)_2CHC{\equiv}CSO_2C_6H_4CH_3$	61	44–45	64.83	65.18	6.35	6.45	14.42	14.34
11	$n\text{-}C_4H_9C{\equiv}CSO_2C_2H_5$	31	[124–126 (1.3)]	55.14	54.88	8.09	8.08	18.40	18.28
12	$C_6H_5C{\equiv}CSO_2CH_3$	88	63–64	59.98	60.09	4.47	4.57	17.79	17.81
13	$C_6H_5C{\equiv}CSO_2C_2H_5$	*a*	*a*	61.83	61.31	5.19	4.96	16.51	16.08
14	$C_6H_5C{\equiv}CSO_2CH(CH_3)_2$	52	*a*	63.43	63.56	5.81	5.94		
15	$C_6H_5C{\equiv}CSO_2C(CH_3)_3$	72	66–67	64.83	64.78	6.35	6.38	14.42	14.30

[a] The product was purified by elution chromatography; these two acetylenes were viscous oils and could not be purified by vpc or distilled because of decomposition.

valuable intermediates in organic synthesis.[22–24] To date, most of this work has dealt with the displacement of aryl iodides by the acetylides. Only one instance of attack on vinyl halides has been reported. Burdon, *et al.*,[25] have briefly described the reaction between various copper acetylides and simple iodoethylenes.

$$CHI{=}CHCl + C_6H_5C{\equiv}CCu \xrightarrow{\text{pyridine}} \underset{90\%}{C_6H_5C{\equiv}CCH{=}CHCl}$$

We have found that copper phenylacetylide reacts with our 1:1 adducts to yield the novel ene–yne sulfones.



$C_6H_5C{\equiv}CC(R){=}CHSO_2R'$

17a, $R = c\text{-}C_6H_{11}$; $R' = p\text{-}CH_3C_6H_4$; 80%

b, $R = C_6H_5$; $R' = C_2H_5$; 56%

c, $R = C_6H_5$; $R' = p\text{-}CH_3C_6H_4$; 15%

Whether the stereochemistry about the double bond was retained during the reaction has not yet been determined.

Experimental Section[26]

Materials.—Phenylacetylene, cyclohexylacetylene, ethylpropiolate, and diphenylacetylene were purchased from Aldrich Chemical Co. and were used without further purification. 1-Hexyne, 3-hexyne, 3-methyl-1-butyne, 3,3-dimethyl-1-butyne, and 1-octyne were obtained from Farchan Research Laboratories. Phenyl ethynyl ketone was prepared by the method of Bowden, *et al.*;[27] *p*-nitrophenylacetylene was also prepared according to the literature[28] as were *p*-toluenethioacetylene[29] and phenyl chloroacetylene.[30] The sulfonyl iodides were prepared from the sodium sulfinates and molecular iodine. The alkanesulfinates were prepared from the corresponding sulfonyl chlorides by their reduction with sodium sulfite and sodium bicarbonate. Methane- and ethanesulfonyl chloride were purchased from Aldrich and Eastman, respectively. 2-Propanesulfonyl chloride had to be prepared from Eastman's sodium 2-propanesulfonate. Sodium *tert*-butanesulfinate was prepared from *tert*-butylmagnesium chloride and sulfur dioxide.[15] Sodium *p*-toluenesulfinate was purchased from Aldrich.

General Procedure for the Preparation and Additions of the Sulfonyl Iodides.—*p*-Toluenesulfonyl iodide[31] was prepared by adding an equivalent quantity of a concentrated ethanolic solution of iodine to a very dilute solution of sodium *p*-toluenesulfinate in water. The sulfonyl iodide precipitated out immediately as a flocculent, yellow solid. Recrystallization from carbon tetrachloride gave the product as bright yellow needles which began to decompose in a few hours, mp 90–95° dec (lit.[31] mp 90–91° dec). Consequently, it was prepared fresh each time that it was used. However, it was found that the solid was relatively stable if kept at −10 to 0° in carbon tetrachloride. For the acetylene additions, the sulfonyl iodide was used as the yellow solid which had been dried under vacuum for 1 hr.

The alkanesulfonyl iodides were prepared *in situ* from an aqueous solution of an excess of the sodium sulfinate and a benzene solution of iodine. On vigorous mixing of these two solutions, the intense purple color of the iodine faded and was replaced by the yellow-orange color of the sulfonyl iodide. The benzene layer was separated and dried briefly over anhydrous magnesium sulfate and filtered to give a clear, orange solution of the sulfonyl iodide. For the addition reaction, the desired acetylene was dissolved in a small amount of benzene and added to the iodide solution. Under the influence of a light,[13] the solutions (ether was the solvent used for the *p*-toluenesulfonyl iodide additions) were allowed to stir for 1–20 hr. Removal of the solvent under reduced pressure left the adduct. When feasible, the residue was recrystallized from ethanol–water. With the alkanesulfonyl iodides, the yields are based on the amount of iodine used. The following experiments illustrate the general procedure.

1-Iodo-1-cyclohexyl-2-*p*-toluenesulfonylstyrene (3a).—The sulfonyl iodide (13.02 g, 0.0462 mol) and cyclohexylacetylene (5.00 g, 0.0462 mol) were combined in *ca.* 200 ml of Mallinckrodt anhydrous ether. The resulting homogeneous yellow solution was stirred under illumination for 18 hr. The ether was removed at reduced pressure leaving a pale orange oil which solidified on standing. This solid was dissolved in hot 95% ethanol and water was added until the solution became faintly cloudy. After overnight refrigeration the 1:1 adduct was collected by filtration to give, after vacuum drying, 13.35 g (74%) of **3a** as white platelets, mp 108.5–109.5°.

1-Iodo-1-*tert*-butyl-2-*p*-toluenesulfonylethene (3k).—3,3-Dimethyl-1-butyne (2.46 g, 0.03 mol) and the iodide (8.46 g, 0.03 mol) afforded 9.44 g (86%) of **3k** (Table I). Analysis of this mixture by nmr showed it to consist of a 55:45 mixture of trans–cis adducts (trans refers to the adduct resulting from trans addition). The isomers were separated by adsorption chromatography using a silica gel column with benzene as the eluent. The trans adduct had mp 77–78°; the cis adduct melted at 136–137°. This same reaction was carried out two more times and in all three cases the trans: cis ratio was essentially the same.

α-Iodo-*cis*-β-methanesulfonylstyrene (4a).—The sulfonyl iodide, prepared according to the published procedure,[24] was obtained as intense, deep green needles. The needles were filtered from an aqueous solution and were wet; they could not be dried under vacuum as they readily decomposed. Hence, it was impossible to determine an accurate weight of the starting material

---

[22] C. E. Castro and R. S. Stephens, *J. Org. Chem.*, **28**, 2163, 3313 (1963).

[23] C. E. Castro, E. J. Gaughan, and D. C. Owsley, *ibid.*, **31**, 4071 (1966).

[24] R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1097, 1108, 1117 (1964).

[25] J. Burdon, P. L. Coe, C. R. Marsh, and J. C. Tatlow, *Chem. Commun.*, 1259 (1967).

[26] All melting points are uncorrected; microanalysis were performed by Dr. C. S. Yeh and staff of Purdue University.

[27] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[28] S. Cristol, A. Begoon, W. Norris, and P. Ramey, *J. Amer. Chem. Soc.*, **76**, 4558 (1954).

[29] W. E. Truce, H. E. Hill, and M. M. Boudakian, *ibid.*, **78**, 2760 (1956).

[30] R. Truchet, *Ann. Chim. (Paris)*, **16**, 309 (1931).

[31] F. C. Whitmore and N. Thurman, *J. Amer. Chem. Soc.*, **45**, 1068 (1923).

and, likewise, the "true" yield of addition product obtained was certainly higher than indicated.

The reaction between methanesulfonyl iodide (8.24 g, 0.04 mol) and phenylacetylene (4.60 g, 0.045 mol) was carried out in 200 ml of ether. (The sulfonyl iodide, when dissolved in ether, was so wet that several droplets of water formed in the bottom of the flask.) After 2 hr of stirring, the solution was washed with aqueous sodium thiosulfate and dried, and the solvent was removed under vacuum. The residue was dissolved in ethanol–water and cooled. By fractional crystallization two products were isolated. The less soluble (3.40 g) proved to be 1,2-diiodostyrene. The expected product was obtained by further cooling. There was collected 3.04 g (24%), mp 82–84°.

The same reaction was carried out a second time without isolating the wet methanesulfonyl iodide. Thus, sodium methanesulfinate (71.46 g, 0.70 mol) was dissolved in 200 ml of water and mixed with 1000 ml of a benzene solution containing 126.90 g (0.50 mol) of iodine. Separation and drying gave a solution which was more of a dark orange-brown color than the *p*-toluenesulfonyl iodide solution, but it was much lighter than the solid, green methanesulfonyl iodide. Phenylacetylene (61.28 g, 0.60 mol) in 500 ml of benzene was added and the mixture was stirred near a light for 2 hr, at which time the color was a light orange. Solvent removal left a residue which was dissolved in 900 ml of 95% ethanol. Decolorization with activated charcoal and filtration gave a clear yellow solution. On cooling, 99.57 g of a product in the form of white platelets was collected, mp 94–95°. Water was added to the mother liquor and, on further cooling, there was isolated 20.10 g of white needles, mp 73–85°. This second crop was recrystallized from ethanol–water to give 3.60 g of broad white needles which were identified as 1,2-diiodostyrene. Also obtained was 13.36 g of white needles, mp 84–85°. This product was identified as the sulfonyl iodide–acetylene adduct. The difference in melting points and crystalline forms of this product and that obtained initially was resolved on finding that the needles (mp 84–85°) could be dissolved in, and recrystallized from, ethanol–water to give the white platelets (mp 94–95°) and, conversely, the platelets could be recrystallized in the form of the lower melting needles. Hence, the methanesulfonyl iodide–phenylacetylene adduct could exist in either of two different crystalline forms. Total yield = 99.57 g + 13.36 g = 112.93 g (73%).

1-Iodo-2-ethyl-*cis*-1-ethyl-2-*p*-toluenesulfonylethene (4b).—Methanesulfonyl iodide (13.40 g, 0.065 mol, as a wet green solid[14]) and 3-hexyne (16.43 g, 0.20 mol) were combined in ether. After 2 hr the solvent was removed under reduced pressure to leave an oily residue. On attempted distillation, a red liquid was collected at bp 65–70° (0.05-mm pressure) to leave a dark pot residue. On standing, this residue solidified and was recrystallized from ethanol–water to give 4.50 g (24%) of **4b** (Table II).

General Procedure for Preparation of Acetylenic Sulfones.—The acetylene–sulfonyl iodide adducts were dissolved in sufficient methanol to effect solution. An equivalent quantity of potassium carbonate was dissolved in a minimum amount of water and added to the alcoholic solution. The mixture was heated slightly (40–70°) for 0.5–3 hr with stirring. The methanol–water solution was placed under reduced pressure and *ca.* $^2/_3$ of the solvent was removed. To the residue was added 200 ml of water. This mixture was extracted with ether or chloroform. Evaporation of the solvent left the crude product.

1-Phenyl-2-*p*-toluenesulfonylethyne (8).—**3a** (15.37 g, 0.04 mol) and potassium carbonate (5.53 g, 0.04 mol) afforded 8.83 g (86%) of **8** (Table III), mp 83–84° (lit.[32] mp 80–81°).

1-*tert*-Butyl-2-*p*-toluenesulfonylethyne (9).—**3k** (a mixture of both isomers, 3.64 g, 0.01 mol) and potassium carbonate (1.38 g, 0.01 mol) afforded 2.36 g (100%) of **9** (Table III).

1-Isopropyl-2-*p*-toluenesulfonylethyne (10).—**3i** (7.20 g, 0.02 mol) and potassium carbonate (2.76 g, 0.02 mol) afforded 2.70 g (61%) of **10** (Table III).

1-*n*-Butyl-2-ethanesulfonylethyne (11).—**5b** (4.53 g, 0.015 mol) and potassium carbonate (2.07 g, 0.015 mol) gave a pale yellow liquid which was subjected to vacuum distillation. There was obtained 0.81 g (31%) of **11** (Table III).

1-Phenyl-2-methanesulfonylethyne (12).—**4a** (30.81 g, 0.10 mol) and potassium carbonate (13.82 g, 0.10 mol) afforded 15.80 g (88%) of **12** (Table III).

1-Phenyl-2-ethanesulfonylethyne (13).—**5a** (29.00 g, 0.09 mol) and potassium carbonate (12.43 g, 0.09 mol) gave the product as a viscous yellow liquid. Drying under vacuum gave 19.09 g (theoretical yield was 17.39 g) of a product which was shown by nmr spectroscopy to be nearly pure acetylenic sulfone. Part of this oil was chromatographed on a silica gel column using a 1:3 mixture of chloroform–hexane as the eluent. Suitable fractions were collected and combined to give a sample for microanalysis.

1-Phenyl-2-isopropanesulfonylethyne (14).—**6** (6.72 g, 0.02 mol) and potassium carbonate (2.76 g, 0.02 mol) gave the product as a yellow oil. Chromatography on a silica gel column with hexane–chloroform (300 ml of a 4:1 mixture and then 300 ml of a 1:4 mixture) gave 2.16 g (52%) of **14** as a nearly colorless oil.

1-Phenyl-2-*tert*-butanesulfonylethyne (15).—**7** (3.40 g, 0.00971 mol) and potassium carbonate (1.34 g, 0.00971 mol) afforded 1.55 g (72%) of **15** (Table III).

***cis*-β-*p*-Toluenesulfonylstyrene.**—A solution of **3a** (19.21 g, 0.05 mol) and zinc (3.92 g, 0.06 g-atom) in acetic acid (4.80 g, 0.08 mol) and 5 ml of water was refluxed for 1.75 hr and allowed to cool. Water (500 ml) was added, and the resulting mixture was extracted with two 100-ml portions of chloroform. Evaporation of the solvent left a crude yellow oil, an nmr spectrum of which showed only the cis-substituted styrene to be present. This oil was dissolved in ethanol–water and, on cooling overnight, there was obtained 10.73 g (83%) of *cis*-β-*p*-toluenesulfonylstyrene, mp 75–76° (lit.[33] 76–77°).

***cis*-1-Cyclohexyl-2-*p*-toluenesulfonylethene.**—**3b** (7.81 g, 0.02 mol) and zinc (1.96 g, 0.03 g-atom) were combined in acetic acid (2.40 g, 0.04 mol) and 2 ml of water. After 1.5 hr of gentle reflux, the solution was treated as above. Again, nmr analysis of the crude oil showed only the reduced cis olefin. There was obtained 3.77 g (71%) of *cis*-1-cyclohexyl-2-*p*-toluenesulfonylethene, mp 50–51°.

Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.63. Found: C, 68.39; H, 7.51.

***cis*-β-Methanesulfonylstyrene.**—When **4a** (3.08 g, 0.01 mol) and zinc (0.65 g, 0.01 g-atom) were combined as above with water (0.60 ml) and acetic acid (0.60 g, 0.01 mol), there was obtained 1.31 g of a clear, pale yellow oil. An nmr spectrum of this liquid was nearly identical with that of the known[34] *cis*-β-methanesulfonylstyrene. No trans product could be detected.

Pyrolysis of Acetylenic Sulfones.—The pyrolyses were carried out by two different methods. For compounds **12–14**, the sulfone was slowly dropped into a flask half filled with glass beads and immersed in an oil bath preheated to 250–270°. A vacuum distillation assembly was employed to distil the product as it was formed. For the pyrolysis of **15**, the acetylenic sulfone was gradually heated neat in a vacuum distillation apparatus.

1-Methyl-2-phenylethyne (16a).—**12** (10.81 g, 0.06 mol) gave 2.76 g (40%) of **16a**, bp 79–81° (15 mm) [lit.[35] bp 74–75° (14 mm)].

1-Ethyl-2-phenylethyne (16b).—**13** (11.66 g, 0.06 mol) afforded 5.28 g (68%) of **16b**, bp 96–100° (45 mm) [lit.[30] bp 87–90° (18 mm)].

1-Isopropyl-2-phenylethyne (16c).—**14** (10.35 g, 0.0502 mol), on pyrolyzing at 270°, gave 6.48 g of distillate which proved to be a mixture of starting material and product. Redistillation afforded 4.76 g (66%) of pure **16c**, bp 99–101° (20 mm) [lit.[36] bp 88–89° (10 mm)].

1-*tert*-Butyl-2-phenylethyne (16d).—**15** (0.90 g, 0.00405 mol), when heated with several glass beads, began to decompose at a bath temperature of *ca.* 150° (the product began to distil), and, by the time a temperature of 200° was reached, the extrusion was complete. There was collected 0.64 g (73%) of **16d**, bp 93–96° (20 mm) [lit.[36] bp 84° (10 mm)].

General Procedure for Coupling of Cuprous Phenylacetylide with Iodovinyl Sulfones.—The sulfone and acetylide[22] were combined in 100 ml of dry pyridine and the solution was refluxed 15 hr. The cooled mixture was poured into 300 ml of water and extracted three times with 150-ml portions of ether. The combined ether extracts were then washed twice each with water, dilute hydrochloric acid, water, dilute sodium bicarbonate solution, and finally water again. The organic layer was dried

---

[32] S. I. Miller, C. E. Orzech, C. A. Welch, G. R. Ziegler, and J. I. Dickstein, *J. Amer. Chem. Soc.*, **84**, 2020 (1962).

[33] W. E. Truce and J. A. Simms, *ibid.*, **78**, 2756 (1956).

[34] D. J. Vrencur, Ph.D. Thesis, Purdue University, 1970.

[35] J. U. Nef, *Justus Liebigs Ann. Chem.*, **310**, 333 (1916).

[36] B. S. Kupin and A. A. Petrov, *Zh. Obshch. Khim.*, **31**, 2958 (1961)

over magnesium sulfate and decolorized with activated charcoal. Solvent removal gave the crude product.

2,4-Diphenyl-1-*p*-toluenesulfonylbut-1-en-3-yne (17c).—From **3a** (7.68 g, 0.02 mol) and cuprous phenylacetylide (3.29 g, 0.02 mol) there was obtained 1.05 g (15%) of **17c**, mp 117–118°.

Anal. Calcd for $C_{23}H_{18}O_2S$: C, 77.07; H, 5.06; S, 8.94. Found: C, 77.33; H, 5.00; S, 8.96.

2,4-Diphenyl-1-ethanesulfonylbut-1-en-3-yne (17b).—**5a** (6.44 g, 0.02 mol) and the acetylide (3.29 g, 0.02 mol) afforded 3.47 g (59%) of **17b**, mp 76–77°.

Anal. Calcd for $C_{18}H_{16}O_2S$: C, 72.99; H, 5.44; S, 10.82. Found: C, 73.08; H, 5.60; S, 10.58.

4-Phenyl-2-cyclohexyl-1-*p*-toluenesulfonylbut-1-en-3-yne (17a).—When **3c** (7.81 g, 0.02 mol) and the acetylide (3.29 g, 0.02 mol) were combined as before, a viscous yellow oil was obtained (5.84 g, 80%) which could not be induced to solidify. The ir and nmr spectra of this oil were identical with those obtained on the pure product (see the following). A portion of this oil was then chromatographed on a silica gel column using chloroform–hexane (1:1) as the eluent. Again, the same viscous, yellow oil was encountered and, after vacuum drying, it was analyzed as such.

Anal. Calcd for $C_{23}H_{24}O_2S$: C, 75.78; H, 6.64; S, 8.80. Found: C, 75.79; H, 6.83; S, 8.92.

Registry No.—**3a**, 22183-12-6; **3b**, 22214-91-1; **3c**, 22297-38-7; **3d**, 29038-88-8; **3e**, 28995-73-5; **3f**, 28995-74-6; **3g**, 28995-75-7; **3h**, 28995-76-8; **3i**, 28995-77-9; **3j**, 28995-78-0; *trans*-**3k**, 28995-79-1; *cis*-**3k**, 22214-90-0; **3l**, 22214-94-4; **3m**, 22214-93-3; **3n**, 22214-92-2; **4a**, 28995-82-6; **4b**, 28995-83-7; **5a**, 28995-84-8; **5b**, 28995-85-9; **6**, 28995-86-0; **7**, 28995-87-1; **8**, 28995-88-2; **9**, 28995-90-6; **10**, 28995-91-7; **11**, 28995-92-8; **12**, 24378-05-0; **15**, 28995-94-0; **17b**, 28995-95-1; **17c**, 28995-96-2; *cis*-1-cyclohexyl-2-*p*-toluenesulfonylethene, 28995-97-3.

Acknowledgment.—The authors express their gratitude to the National Cancer Institute for financial support of this work in the form of Public Health Service Research Grant No. CA-04536-11.

Reaction of Carbethoxycarbene with Aliphatic Sulfides and Allyl Compounds

WATARU ANDO,* TOMIO YAGIHARA, SUJI KONDO, KEIJI NAKAYAMA,
HIDEO YAMATO, SETUKO NAKAIDO, AND TOSHIHIKO MIGITA

Department of Chemistry, Gunma University, Kiryu, Gunma, Japan

Received September 10, 1970

Reactions of carbethoxycarbene produced by photolysis of ethyl diazoacetate with dialkyl and alkyl allyl sulfides were investigated. Reactions in dialkyl sulfides bearing β-hydrogen atoms resulted in the formation of ethyl alkylmercaptoacetates. On the other hand, the reactions in alkyl allyl sulfides gave mixtures of 1-alkyl 1-alkylmercaptoacetates (C—S insertion) and cyclopropane derivatives (C═C addition). These product formations are explained by the mechanism involving ylide formation from the carbene and sulfides. Copper-catalyzed thermal decomposition of ethyl diazoacetate in these sulfides resulted in more selective reactions and gave high yields of the acetates, the formation of cyclopropane derivatives being drastically reduced. Allyl ethers and chlorides react less selectively with carbethoxycarbene to produce mixtures of insertion and addition products.

Although the reactions of carbenes with molecules containing heteroatoms have been extensively studied, little has been recorded of the photochemical and thermal reactions with aliphatic sulfides and allyl compounds containing sulfur, oxygen, and halides.[1] Some of the reactions of the allyl compounds have been reported with dichlorocarbene derived from the acid–base-catalyzed reaction of the halo ester[2] and with methylene produced by the decomposition of diazomethane with metal salts.[3] Kirmse has reported that the copper salt catalyzed thermal decomposition of diazomethane in allyl sulfides yields methylene insertion products into the carbon–sulfur bond as major products, together with some cyclopropane derivatives. In the allyl ethers and amines, however, the cyclopropane derivatives have been obtained as the major products. Furthermore, the addition products have been formed from allyl chlorides without substantial formation of insertion products. This is contrasted with the reaction in allyl bromide in which the insertion product has been obtained in about 80% yield. The formation of insertion products may be ascribed to ylide formation by the attack of the carbene on the lone-pair electrons of a heteroatom, followed by allylic rearrangement which is a thermally symmetry-allowed process. Similar results in the copper-catalyzed thermal decomposition of ethyl diazoacetate in allyl halides have been obtained. Thus, the addition of the carbene to the double bond in allyl chlorides competes effectively with insertion into the carbon–chlorine bond, whereas no cyclopropanes have been obtained from allyl bromides and iodides.[4,5] However, these reaction species have been known as carbenoids and should be significantly different in nature from the free carbenes formed by photolysis of the diazo compounds.[6–8]

Recently we reported that the photochemical reaction of dimethyl diazomalonate in aliphatic sulfides forms stable sulfonium ylides[9] and in allyl compounds forms the carbene insertion products into the carbon–sulfur, oxygen, and halogen bond.[10,11] We have sug-

---

[1] (a) J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964; (b) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; (c) J. I. G. Cadogan and M. J. Perkins, "The Chemistry of Alkenes," Wiley-Interscience, New York, N. Y., 1964; (d) G. L. Closs in "Topics in Stereochemistry," Vol. 3, Wiley-Interscience, New York, N. Y., 1968.

[2] W. E. Parham and S. H. Groen, *J. Org. Chem.*, **29**, 2214 (1964); **30**, 728 (1965); **31**, 1694 (1966). W. E. Parham and J. R. Potoski, *ibid.*, **32**, 275, 278 (1967).

[3] W. Kirmse and M. Kapps, *Chem. Ber.*, **101**, 994, 1004 (1968); W. Kirmse and H. Arold, *ibid.*, **101**, 1008 (1968).

[4] I. A. Dykonov and N. B. Vinogradova, *Zh. Obshch. Khim.*, **22**, 1349 (1952); **23**, 66 (1953). I. A. Dyakonov and T. V. Domeareva, *ibid.*, **25**, 934, 1486 (1955).

[5] D. D. Philips, *J. Amer. Chem. Soc.*, **76**, 5385 (1956).

[6] G. L. Closs and R. A. Moss, *ibid.*, **86**, 4074 (1964).

[7] D. O. Cowab, M. M. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964).

[8] S. H. Goh, L. E. Closs, and G. L. Closs, *ibid.*, **34**, 25 (1969).

[9] (a) W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 2786 (1969); (b) W. Ando, T. Yagihara, S. Tozune, S. Nakaido, and T. Migita, *Tetrahedron Lett.*, 1979 (1969).

[10] W. Ando, K. Nakayama, K. Ichibori, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 5164 (1969).

[11] W. Ando, S. Kondo, and T. Migita, *ibid.*, **91**, 6516 (1969).