The Thermal and The Copper-Catalyzed Addition of Sulfonyl Bromides to Phenylacetylene[1]

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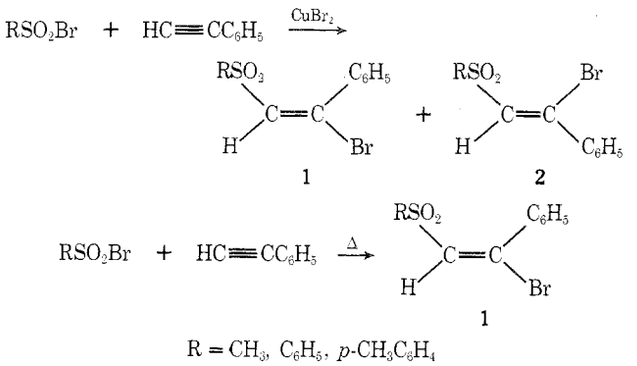
The copper-catalyzed addition of methane-, benzene-, and *p*-toluenesulfonyl bromide to phenylacetylene yields mixtures of trans (1) and cis addition products (2). In contrast, the thermal reaction leads exclusively to 1. In the catalyzed reaction, excess of bromide ions promotes the formation of 1. Both 1 and 2 undergo facile elimination of HBr to give the α-acetylenic sulfone (3). Two distinct mechanisms for the addition reaction are suggested, namely, a trans addition process operating *via* a free-radical chain, and, concurrently, a cis addition process, *via* a concerted reaction mechanism, directed by the copper catalyst.

We previously described the stereoselective, copper-catalyzed 1:1 addition of aliphatic and aromatic sulfonyl chlorides to acetylenes by a free-radical, redox-transfer chain mechanism, yielding mixtures of *trans*- and *cis*-β-chlorovinyl sulfones.[2] In the copper-catalyzed addition of sulfonyl chlorides to phenylacetylene, the course of addition could be controlled by polar factors to give preferentially either trans or cis addition products;[3] no adduct was formed in the absence of copper chloride, in spite of prolonged heating.[2] We now discovered that, in contrast to sulfonyl chlorides, the corresponding bromides undergo addition across the triple bond in the dark, and in the absence of any catalyst, thus demonstrating homolysis of the S–Br bond under mild thermal conditions.

A comparison between the thermal and the copper-catalyzed addition of sulfonyl bromides to phenylacetylene has enabled us to elucidate the specific role of the catalyst in directing the stereochemistry of the addition; such a comparative study could not be performed with sulfonyl chlorides.

This paper presents examples of thermal as well as copper-catalyzed 1:1 additions of methane-, benzene-, and *p*-toluenesulfonyl bromide to phenylacetylene, yielding in the catalyzed process mixtures of trans (1) and cis addition products (2); and in the thermal process exclusively trans addition product (1). Sulfonyl bromides have been used in



synthesis to a much lesser extent than sulfonyl chlorides, even though they are more reactive; they can be made by simple one-step procedures.[4] It is worthwhile mentioning here that sulfonyl iodides are much more reactive, as shown for instance by Truce and Wolf, who described the light-catalyzed trans addition of sulfonyl iodides to acetylenes, leading to β-iodovinyl sulfones.[5] Thus far, alkanesulfonyl iodides have not been isolated owing to their instability, and had therefore to be prepared *in situ*.[5,6] Sulfonyl bromides have the advantage over sulfonyl iodides of being stable compounds, and at the same time being more reactive than the corresponding sulfonyl chlorides.

Only a few β-bromovinyl sulfones have been reported in the literature; their syntheses consist of several steps, in which, for instance, in the final step a bromovinyl sulfide is oxidized to the corresponding sulfone[7] or hydrogen bromide is added to an α-ethynyl sulfone.[8]

A one-step synthesis of β-bromostyryl sulfones by the direct addition of sulfonyl bromides to acetylenes has been reported briefly in two instances.[9,10]

Zakharkin and Zhigareva described recently a thermal addition of benzenesulfonyl bromide to phenylacetylene, leading to a cis addition product.[9] We prove that under such conditions the trans addition product (1) is being formed exclusively (see below).

Results and Discussion

The Copper-Catalyzed Addition. The copper-catalyzed addition of methane-, benzene-, and *p*-toluenesulfonyl bromide to phenylacetylene was performed as described for the addition of sulfonyl chlorides to acetylenes.[2] Like the chlorides, sulfonyl bromides gave mixtures of cis and trans addition products, reacting somewhat faster than the corresponding chlorides. The reaction may be conducted with equimolar amounts of the reactants[11] in an inert solvent such as acetonitrile, at reflux temperatures or preferably in a sealed tube, where rates of reaction could be conveniently followed by dilatometry. The reaction in a sealed tube proved to be cleaner and faster, particularly when degassing removed atmospheric oxygen which resulted in decreased induction periods. Cupric bromide was used in a catalytic amount; lithium bromide, as a source of excess bromide ions, promoted preferential formation of trans addition products, as chloride ions did in the addition of sulfonyl chlorides to phenylacetylene[3] (see Table I, No. 1, 4, and 7). In the absence of additional bromide ions, the reaction was slower, and a higher proportion of cis addition products was formed (see Table I, No. 2, 5, and 8).

The Thermal Addition. Alkyl- and arylsulfonyl bromides were found to add smoothly to phenylacetylene, in the absence of any catalyst or light, affording high yields of a single 1:1 addition product which turned out to be identical with the trans addition product (1) obtained in the copper-catalyzed reaction. No trace of the corresponding cis addition isomer (2) could be detected after careful column as well as thin-layer chromatographic, separations (see Table I, No. 3, 6, and 9).[12]

Configurational Assignments Based on Spectral Data. Structural proof and configurational assignments were based on similar criteria as applied to the characterization of the *trans*- and *cis*-β-chlorostyryl sulfones.[2,3] As mentioned previously,[2] only the cis addition products (2) can accommodate a coplanar conformation. This is impossible for the trans addition products (1), due to steric hin-

Table I
Reactions of Sulfonyl Bromides (10 mmol) with Phenylacetylene (11 mmol) in Acetonitrile (2G) at 100°

No.	RSO_2Br R=	$CuBr_2$, mmol	LiBr, mmol	Time, hr	Conversion, %	Adduct Distribution, % 1	2
1	CH_3	0.2	0.3	6	90	88	12
2	CH_3	0.2		6	86	55	45
3	CH_3			9	90	100	
4	C_6H_5	0.2	0.3	4	90	85	15
5	C_6H_5	0.2		6	92	44	56
6	C_6H_5			6	88	100	
7	p-$CH_3C_6H_4$	0.2	0.3	6	93	83	17
8	p-$CH_3C_6H_4$	0.2		6	88	52	48
9	p-$CH_3C_6H_4$			9	85	100	

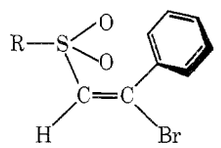
Table II
Ultraviolet Spectra

R	1 Phenyl bands λ_{max}	1 Phenyl bands ϵ	1 Styryl bands λ_{max}	1 Styryl bands ϵ	2 Phenyl bands λ_{max}	2 Phenyl bands ϵ	2 Styryl bands λ_{max}	2 Styryl bands ϵ
CH_3	212	8,000	254	8,000	213	8,000	264	16,000
C_6H_5	211	20,000	258	10,000	213	18,000	276	20,000
p-$CH_3C_6H_4$	209	20,000	238	14,000	219	18,000	273	20,000

Table III
Nuclear Magnetic Resonance Data[a]

R	1 Vinyl protons(s)	1 Methyl protons (s)	1 Phenyl protons (m)	2 Vinyl protons (s)	2 Methyl protons (s)	2 Phenyl protons (m)
CH_3	7.09	2.71 (3 H)	7.37–7.65 (5 H)	7.22	3.21 (3 H)	7.37–7.70 (5 H)
C_6H_5	7.17		7.25–7.65 (10 H)	7.33		7.36–7.70 (8 H) 8.09 (d, 2 H, J = 7.5)[b]
p-$CH_3C_6H_4$	7.15	2.37 (3 H)	7.51 (d, 2 H, J = 8.5)[c] 7.19 (d, 2 H, J = 8.5)[c] 7.40 (m, 5 H)	7.30	2.45 (3 H)	7.97 (d, 2 H, J = 8.5)[c] 7.34 (d, 2 H, J = 8.5)[c] 7.46–7.60 (5 H)

[a] Measured in $CDCl_3$ on a Varian A-60 with TMS as internal standard; chemical shifts reported in δ (ppm) and apparent spin couplings (J) in Hz units; s = singlet, d = doublet, m = multiplet. [b] Phenyl protons ortho to the carbon atom attached to the electronegative sulfone group. [c] Pair of doublets of a typical AA'BB' pattern for a para-disubstituted phenyl ring.



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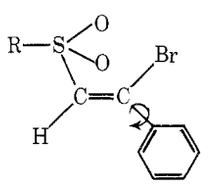
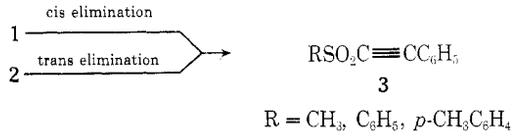


2

drance. The styryl band for the cis addition products (2) absorbs at longer wavelengths, and with much stronger intensity than for the trans isomers (1) (see Table II). The infrared spectra were very much like those of the chloro analogs. In the C=C stretching frequencies region, a strong adsorption peak at 6.19 μ was found to be characteristic for the trans addition products (1), and a strong absorption peak at 6.36 μ was typical for the planar and more conjugated cis addition isomers (2); it was also possible to characterize the structural isomers on the basis of sharp and strong-CH= out-of-plane bending vibrations at 11.3 μ of the trans addition products (1) and at 11.05 μ of the cis addition products (2).

The nmr spectra of the addition compounds were quite similar to those of the chloro analogs.[2,3] The vinylic protons of the bromo adducts were generally more deshielded than those of the corresponding chloro adducts; also, these protons, as well as the methyl proton in 2 (R = CH_3, R = p-$CH_3C_6H_4$) were more deshielded in the coplanar configurations (see Table III).[2,3]

Elimination of HBr. Elimination experiments with both stereoisomeric adducts, involving an excess of triethylamine at room temperature, revealed that not only the cis addition products (2) are capable of undergoing a facile β-trans elimination to give an α-acetylenic sulfone (3) but, surprisingly, also the trans addition products (1), in which H and Br are in a cis relationship,[13] the only difference being, that cis elimination is slower than the trans process.

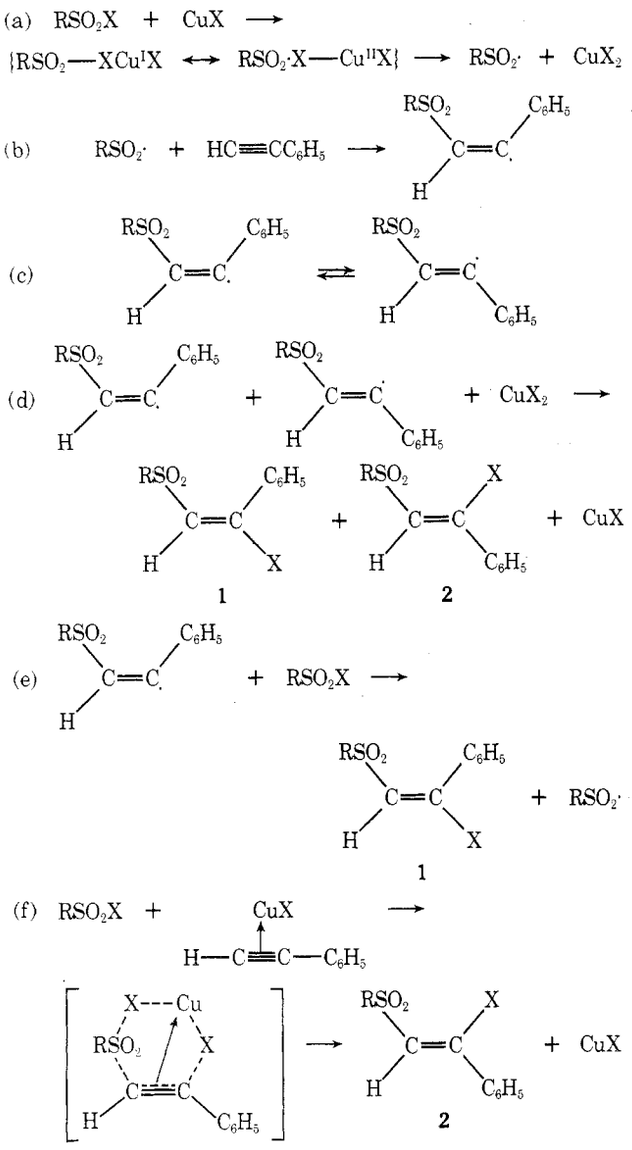


It was possible to follow the elimination of HBr from the two isomeric 2-methanesulfonyl-1-bromostyrenes (1 and 2, R = CH_3) by nmr, by the increase of $CH_3SO_2C{\equiv}C-$ singlet at δ 3.31 at the expense of the singlets of the methyl protons of 1 (R = CH_3) at δ 2.71 and of 2 (R = CH_3) at δ 3.21. A benzene solution of 2 (R = CH_3) which was stirred[14] for 20 hr with a large excess of Et_3N at room temperature gave a mixture of 80% of 3 (R = CH_3) and 20% of the unchanged bromo adduct. Under these conditions 1 (R = CH_3) eliminated only 35% HBr.

Dehydrobrominations of 2-benzenesulfonyl-1-bromostyrenes (1 and 2, R = C_6H_5) where somewhat faster, as compared to rates of elimination of HBr from the 2-methanesulfonyl adducts, due to the stronger inductive effect of the 2-benzenesulfonyl group.

As mentioned earlier, Zakharkin and Zhigareva claimed that the thermal addition of benzenesulfonyl bromide to phenylacetylene gave a cis addition product;[9] their structural evidence was based on the fact that the adduct underwent facile elimination of HBr, and hence their conclusion that H and Br had to be in a trans relationship. They apparently did not consider the possibility that a cis elimina-

Scheme I



tion could take place as well. Although the β-trans elimination is the most common elimination process, cis eliminations are also encountered, particularly when the β-hydrogen atom is activated by an electron attracting such as alkyl- or arylsulfonyl group, which favors a two-step E1cb carbanion mechanism.[15]

The reason for the greater ease of cis elimination of HBr from **2**, compared the HCl from its analog, is evidently due to the enhanced leaving ability of the bromide ion from such system.[16] Generally, rates of hydrogen bromide elimination are greater than of hydrogen chloride.[15d,17] The eliminations of hydrogen bromide from the easily accessible adducts of sulfonyl bromide and acetylenes offers a convenient synthesis for α-acetylenic sulfones.

Mechanism for the Addition Reaction. The mechanistic possibilities are summarized in Scheme I. The striking difference between the copper-catalyzed reaction in which mixtures of cis and trans isomers are obtained, and the thermal process which leads exclusively to trans addition products, demonstrates the specific role of the copper catalyst enabling a cis addition process to take place. The possibility of a free-radical reaction including an equilibration step, in which a cis intermediate radical is partially inverted into its trans isomer (step c), leading after halogen transfer (step d), to a mixture of both stereoisomers, was raised previously.[3]

The fact that only the kinetically formed[3] trans addition products are obtained under thermolytic conditions argues strongly against the possibility of an equilibration process (step c) in these reactions. Evidently, the resonance-stabilized cis vinyl radical does not isomerize, and reacts with another sulfonyl halide molecule to give, *via* an halogen chain transfer (step e), the trans addition product. In the presence of cupric halides, which are known as highly reactive halogen donors,[18] the much faster ligand transfer step d supersedes step e;[19] consequently, inversion of the initially formed vinyl radical becomes very improbable, suggesting that the energy barrier for such process (step c) may be fairly high.[20] We suggest, therefore, that the two stereoisomers do not have a common intermediate, and, in general, the formation of the trans addition product, either in the thermal or the copper-catalyzed reaction, is a result of a normal radical chain be it that, in the product forming step, halogen is transferred from the sulfonyl halide or from the copper(II) halide. On the other hand, the cis addition product, which is formed concurrently in the copper-catalyzed reaction, arises presumably from a concerted reaction as depicted in (f). In the stereoselective copper-catalyzed addition of sulfonyl halides to phenylacetylene, the course of the addition could be controlled by polar factors to give preferentially either trans or cis addition products; excess of halide ions, or highly polar solvents, promoted formation of trans addition products, while absence of a supplementary halide salt, or applying a low polarity solvent,[21] resulted a higher ratio of cis addition products.

Excess halide ions give halocuprates with copper(II) ions, which are more soluble in acetonitrile and make for a homogeneous reaction. In the absence of such additives, or in solvents of low polarity, the copper salt is only partly dissolved and we propose that the reaction takes place also on the surface of the undissolved copper catalyst leading to cis addition products; added halide ions may intervene and hinder that process.

In the copper-catalyzed addition of sulfonyl bromides to phenylacetylene, carried out in the absence of excess bromide ions (see Table I, No. 2, 5, and 8), the preference for cis addition products was not as high as in the case of the chloro analogs,[3] apparently due to the competitive thermolytic trans addition.

Experimental Section[22]

Materials. Phenylacetylene obtained from Fluka (puriss) was distilled before use; methanesulfonyl bromide was prepared from methanesulfonyl chloride;[23] benzenesulfonyl bromide and *p*-toluenesulfonyl bromide were prepared from the corresponding arylsulfinic acid sodium salts,[24] or from the corresponding arylsulfonylhydrazides;[4d] anhydrous cupric bromide (Baker Chemical Co., reagent grade) and lithium bromide (B.D.H., reagent grade) were dried at 110° to constant weight; acetonitrile from Fluka (puriss) was dried over P_2O_5; Kieselgel 70–325 mesh was obtained from Merck.

(*E,Z*)-2-Benzenesulfonyl-1-bromostyrenes (1 and 2, R = C_6H_5). A mixture of 2.21 g (10 mmol) of benzenesulfonyl bromide, 1.12 g (11 mmol) of phenylacetylene, 45 mg (2 mmol) of anhydrous cupric bromide, and 52 mg (6 mmol) of anhydrous lithium bromide in 2 g of acetonitrile was introduced into a Carius tube, cooled in liquid air, degassed (three times) at 0.1 mm, sealed, and heated for 4 hr at 100°. After contraction was stopped the tube was cooled in liquid air and then opened. The semisolid reaction mixture was dissolved in methylene chloride, transferred to a separatory funnel, and washed with water and an aqueous solution of disodium ethylenediaminetetraacetate until free from copper, and the organic layer was dried (Na_2SO_4). The solvent was evaporated and the crude reaction mixture (3.2 g) was dissolved in a minimum amount of methylene chloride (3–5 ml) and chromatographed over 70 g of Kieselgel. Elution with ether–*n*-hexane (1:6) gave 2.45 g

(76%) of 1 (R = C_6H_5): mp 82° (methanol); ir 6.19, 6.28, 6.72, 6.92, 7.17, 7.58, 7.78, 8.80, 9.24, 9.75, 10.0, 10.85, 11.4, and 12.4 μ.

Anal. Calcd for $C_{14}H_{11}BrO_2S$: C, 52.02; H, 3.43; Br, 24.72; S, 9.92. Found: C, 52.18; H, 3.55; Br, 24.50; S, 9.87.

Further elution with ether–*n*-hexane (1:4) of the same chromatogram afforded 0.45 g (14%) of **2** (R = C_6H_5): mp 88° (methanol); ir 6.28, 6.37, 6.72, 6.92, 7.17, 7.58, 7.78, 8.08, 8.50, 8.72, 9.22, 10.0, 10.05, 10.35, 10.85, 11.1, 11.3, and 12.3 μ.

Anal. Calcd for $C_{14}H_{11}BrO_2S$: C, 52.02; H, 3.43; Br, 24.72; S, 9.92. Found: C, 52.18; H, 3.55; Br, 24.50; S, 9.87.

(*E,Z*)-2-Methanesulfonyl-1-bromostyrenes (1 and 2, R = CH_3). The addition reaction and the work-up procedure were carried out as described for benzenesulfonyl bromide using 1.59 g (10 mmol) of methanesulfonyl bromide. Elution with ether–*n*-hexane (1:4) gave 2.07 g (79%) of **1** (R = CH_3): mp 60.5° (ethanol); ir 6.19, 6..29, 6.72, 6.92, 7.16, 7.58, 7.75, 8.82, 9.4, 10.5, 11.3, 11.5, and 12.4 μ.

Anal. Calcd for $C_9H_9BrO_2S$: C, 41.39; H, 3.47; Br, 30.60; S, 12.28. Found: C, 41.35; H, 3.54; Br, 30.80; S, 12.13.

Further elution with ether–*n*-hexane (1:3) of the same chromatogram afforded 0.28 g (11%) of **2** (R = CH_3): mp 76° (ethanol); ir 6.29, 6.36, 6.72, 6.92, 7.16, 7.58, 8.82, 9.4, 10.5, 11.15, and 12.3 μ.

Anal. Calcd for $C_9H_9BrO_2S$: C, 41.39; H, 3.47; Br, 30.60; S, 12.28. Found, C 41.20; H, 3.50; Br, 30.89; S, 12.09.

(*E,Z*)-2-*p*-Toluenesulfonyl-1-bromostyrenes (1 and 2, R = *p*-$CH_3C_6H_4$). The addition reaction and the work-up procedure were carried out as described for benzenesulfonyl bromide using 2.35 g (10 mmol) of *p*-toluenesulfonyl bromide. Elution with ether–*n*-hexane (1:6) gave 2.6 g (77%) of 1 (R = *p*-$CH_3C_6H_4$): mp 103–104° (methanol); ir 6.19, 6.28, 6.72, 6.92, 7.17, 7.55, 7.65, 7.75, 8.70, 9.25, 9.65, 9.85, 10.0, 10.85, 11.2, 11.3, and 12.4 μ.

Anal. Calcd for $C_{15}H_{13}BrO_2S$: C, 53.42; H, 3.89; Br, 23.70; S, 9.51. Found: C, 53.20; H, 3.79; Br, 23.94; S, 9.56.

Further elution with ether–*n*-hexane (1:3) of the same chromatogram afforded 0.54 g (16%) of **2** (R = *p*-$CH_3C_6H_4$): mp 108–109° (methanol); ir 6.26, 6.30, 6.37, 6.72, 6.92, 7.16, 7.55, 7.65, 7.71, 8.68, 9.20, 9.62, 9.8, 10.0 10.85, 11.15, 11.3, and 12.4 μ.

Anal. Calcd for $C_{15}H_{13}BrO_2S$: C, 53.42; H, 3.89; Br, 23.70, S, 9.51. Found: C, 53.60; H, 3.84; Br, 23.99; S, 9.62.

Eliminations of HBr from 1 and 2 (R = CH_3, C_6H_5, *p*-$CH_3C_6H_4$). Eliminations were carried out by stirring[14] a solution of the adduct (2 mmol) in benzene (2 ml) and triethylamine (2 ml) at room temperature; dehydrobromination was noted by precipitation of the amine hydrobromide and reaction was followed by nmr [disappearance of vinylic proton, or shift of the methyl singlet (1 and 2 → **3**, R = CH_3, *p*-$CH_3C_6H_4$)]. The acetylenic sulfones were obtained after removal of the hydrobromide by filtration, evaporation of the volatiles, and crystallization from methanol. Yields were almost quantitative. Reaction times (hr) required for complete elimination of HBr from 1 and 2 under these conditions were

	CH_3	C_6H_5	*p*-$CH_3C_6H_4$
1	72	16	36
2	30	12	24

1-Phenyl-2-metanesulfonylethyne (3, R = CH_3). This compound was prepared either from 1 (R = CH_3) or 2 (R = CH_3) by the above described procedure: mp 68–69° (lit.[5,25] 63–64°, 68.5–69.5°); ir 4.59 (–C≡C–), 7.65, and 8.60 μ (–SO_2–); nmr δ 3.31 (S, 3 H, CH_3), 7.35–7.65 (m, 5 H, aromatic).

Anal. Calcd for $C_9H_8O_2S$: C, 59.98; H, 4.47; S, 17.79. Found: C, 59.92; H, 4.53; S, 17.85.

1-Phenyl-2-benzenesulfonylethyne (3, R = C_6H_5). This compound was prepared either from 1 (R = C_6H_5) or 2 (R = C_6H_5) by the above described procedure: mp 74.5° (lit.[26] 73–74°) was identical with that of an authentic sample.[2]

1-Phenyl-2-*p*-toluenesulfonylethyne (3, R = *p*-$CH_3C_6H_4$). This compound was prepared either from 1 (R = *p*-$CH_3C_6H_4$) or 2 (R = *p*-$CH_3C_6H_4$) by the above described procedure: mp 82–83° (lit.[5,27] 83–84°, 80–81°); ir 4.59 (–C≡C–), 7.65, and 8.60 μ (–SO_2–); nmr δ 2.43 (s, 3 H, CH_3), 7.20–7.70 (m, 7 H, aromatic), 7.98 (d, 2 H, aromatic, J = 8.5 Hz).

Anal. Calcd for $C_{15}H_{12}O_2S$: C, 44.09; H, 8.81; S, 23.54. Found: C, 44.16; H, 8.78; S, 23.60.

Registry No.—1 (R = C_6H_5), 52920-43-1; 1 (R = CH_3), 52920-44-2; 1 (R = *p*-$CH_3C_6H_4$), 52920-45-3; 2 (R = C_6H_5), 52920-46-4; 2 (R = CH_3), 52920-47-5; 2 (R = *p*-$CH_3C_6H_4$), 52920-48-6; 3 (R = CH_3), 24378-05-0; 3 (R = C_6H_5), 5324-64-1; 3 (R = *p*-$CH_3C_6H_4$), 28995-88-2; phenylacetylene, 536-74-3; benzenesulfonyl bromide, 2297-65-6; methanesulfonyl bromide, 41138-92-5; *p*-toluenesulfonyl bromide, 1950-69-2.

References and Notes

(1) Presented before the IVth International Symposium on Organic Sulphur Chemistry, Bangor, Wales, U.K., July 1974.
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(9) L. I. Zakharkin and G. G. Zhigareva, *Zh. Org. Khim.*, **9**, 891 (1973).
(10) Truce and Wolf have mentioned, only as part of a footnote (ref 5, footnote 16) that from the cupric bromide catalyzed addition of benzenesulfonyl bromide to phenylacetylene, two bromo(benzenesulfonyl)-styrenes can be isolated, no details were given.[11]
(11) Usually a slight excess of phenylacetylene is used because of a minute amount of the acetylene undergoes bromination. Same results were obtained when a large excess of sulfonylbromide was used; prolonged heating did not lead to the addition of a second molecule of sulfonyl bromide to the ethylenic bond of the 1:1 adduct.
(12) In acetonitrile, reactions were generally cleaner but a bit slower than without any solvent.
(13) The chloro analogs of **1** do not undergo eliminations, and are recovered unchanged even after prolonged heating with a tertiary amine.[2]
(14) Without stirring the dehydrobromination is much slower.
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