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# Addition of Arenesulphonyl Iodides to Substituted Phenylacetylenes[1]

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The products of the addition of toluene-*p*-sulphonyl iodide to substituted phenylacetylenes (and styrenes) are studied. The regiospecificity and stereoselectivity of *trans* addition to acetylenes is inferred from $^1H$ n.m.r. spectroscopy. The effect of substituents on the reactivity of substituted phenylacetylenes towards substituted benzenesulphonyl radicals generated by photolysis of sulphonyl iodides is studied. Phenylacetylenes with electron-donating substituents react faster. Relative reactivities yield good Hammet–Brown correlations showing the electrophilic character of sulphonyl radicals towards phenylacetylenes. The selectivity of the addition (measured by $\rho$) of different sulphonyl radicals towards the same set of acetylenes ranges from $-0.53$ to $-0.93$ and shows a tendency to be smaller for benzenesulphonyl iodides carrying electron-donating substituents. Results are discussed in terms of polar effects on the transition state and frontier molecular orbital theory.

Although the free-radical addition of sulphonyl halides to olefins have been the subject of several studies since the addition of *N*-chlorosulphonylphthalimide to oct-1-ene carried out by Kharasch and his co-workers,[2] similar studies with acetylenes were started much later.[3] Amiel[4] studied the copper-catalysed addition of sulphonyl chlorides to hex-1-yne, hept-1-yne, hex-3-yne, phenylacetylene, and diphenylacetylene. The reaction occurs in high yield and it affords a one-step synthesis of β-chlorovinyl sulphones. The stereochemical course of the reaction was investigated and it was shown that *trans*-addition was predominant. This redox-transfer chain reaction can be controlled by polar factors (excess of chloride ion and change of solvent polarity) to give preferentially either *trans* or *cis* addition products.[5] The copper-catalysed addition of methane-, benzene-, and toluene-*p*-sulphonyl bromide to phenylacetylene[6] yields the *Z* and *E* adducts but the thermal reaction (*via* a concerted mechanism) leads exclusively to the *E* isomer.

As in the case of olefins,[2a,7] sulphonyl iodides add readily to various acetylenes in the presence of visible light, as found by Truce and his co-workers.[8] The stereoselectivity of the reaction was established by reducing the adducts to the corresponding vinyl sulphones and by *X*-ray crystallography. Although electron-withdrawing substituents on the triple bond seem to lower the yield of addition products, no relative rates of addition have been measured.

Following our previous work on the relative reactivities of sulphonyl radicals towards olefins,[9] we report now a structure–reactivity study concerning the photochemically promoted addition of arenesulphonyl iodides to substituted phenylacetylenes.

## Results and Discussion

*Adducts of Toluene-*p*-sulphonyl Iodide with Substituted Phenylacetylenes.*—The addition of $p$-MeC$_6$H$_4$SO$_2$I to HC≡CC$_6$H$_4$X in benzene solution, under visible light, yields vinyl sulphones (**1a**—**f**) in good yield (Table 1). Yields did not change appreciably when the reaction was carried out under N$_2$ or air.

$$p\text{-MeC}_6\text{H}_4\text{SO}_2\text{I} + \text{CH}{\equiv}\text{CC}_6\text{H}_4\text{X} \xrightarrow{h\nu} p\text{-MeC}_6\text{H}_4\text{SO}_2\text{CH}{=}\text{CIC}_6\text{H}_4\text{X} \quad (1)$$

**(1)**

**a**;X = $p$-Me  **d**;X = $m$-NO$_2$
**b**;X = $p$-Cl  **e**;X = $p$-NO$_2$[8]
**c**;X = $p$-MiO  **f**;X = H[8]

The adducts (**1**) were reduced with zinc in acetic acid [equation (2)] yielding the correspondent β-arylsulphonylstyrenes (Table 2). The addition reaction (1) is regiospecific since $^1H$ n.m.r. chemical shifts and coupling constants did not indicate the presence of geminal hydrogen atoms in the reduction products.

$$p\text{-MeC}_6\text{H}_4\text{SO}_2\text{CH}{=}\text{CIC}_6\text{H}_4\text{X} \xrightarrow{\text{Zn–CH}_3\text{COOH}} p\text{-MeC}_6\text{H}_4\text{SO}_2\overset{(a)}{\text{CH}}{=}\overset{(b)}{\text{CH}}\text{C}_6\text{H}_4\text{X} \quad (2)$$

**(2)**

The *Z* configuration of (**2**) was established by comparison with the *E* isomers obtained from independent synthesis[7c] (Table 5). The *Z* isomer of (**2a**) was quantitatively converted into the *E* isomer after irradiation in the presence of bromine. No *E* isomer could be detected by n.m.r. in the crude reaction products (**2a**—**f**).

Although Truce and his co-workers[8] have shown that the reduction of sulphonyl adducts (**1**) with Zn–CH$_3$COOH is stereoselective, the stereochemistry of these adducts was confirmed by us based on the fact that chemical shifts of aromatic ($p$-MeC$_6$H$_4$) and methylic protons of adducts (**1**) changed, respectively, from δ 7.41 to 7.88 and δ 2.34 to 2.40 [(**1f**)], after isomerization.

This is quite useful to demonstrate the presence of only one isomer in the crude addition products mixture. It was also useful in confirming the stereoselectivity of the Zn–CH$_3$COOH reduction of sulphonyl iodides adducts, since, when a 1:1 mixture of *E* and *Z* isomers of (**1f**) was reduced, the reaction product (**2f**) yielded a similar 1:1 isomer ratio, showing no isomer interconversion.

Either the regiospecificity or the stereoselectivity of the addition reaction may be understood on the basis of steric effects.

The homolytic nature of the reaction was confirmed by studying the effects of light, oxygen, and hydroquinone on the reaction rate.

*The Effect of Substituents on the Rate of Addition.*—The relative reactivities of substituted phenylacetylenes (XC$_6$H$_4$C≡CH) towards substituted benzenesulphonyl radicals (YC$_6$H$_4$SO$_2^{\cdot}$), generated by photolysis of the corresponding sulphonyl iodides were measured by competition experiments based on reactions (3) and (4) (where Y = $p$-MeO, $p$-Me, H, $p$-Cl, or $m$-NO$_2$; X = $p$-MeO, $p$-Me, H, $p$-Cl, $p$-NO$_2$, or $m$-NO$_2$)

**Table 1.** Adducts of toluene-*p*-sulphonyl iodide with acetylenes ($XC_6H_4C{\equiv}CH$)

| Product | X | Yield (%) | M.p. (solvent) (°C) | $\delta_H$ (90 MHz; $CDCl_3$; standard $Me_4Si$) | *m/z* (Relative intensity) | Ref. |
|---|---|---|---|---|---|---|
| **(1a)** | *p*-Me | 90 | 109—110<br>(MeOH) | 7.40 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 7.18 (1 H, s, CH:C), 7.20—7.06 (6 H, m, $C_6H_4SO_2$ + $C_6H_4CI$), and 2.37 (6 H, Ar*Me*) | 398 ($M^+$, 18%), 271 (52), 207 (65), 155 (28), 91 (100), and 65 (22) | New |
| **(1b)** | *p*-Cl | 89 | 143—145<br>($C_6H_6$) | 7.50 (2 H, d, *J* 9 Hz, $C_6H_4SO_2$), 7.34 (1 H, s, CH:C), 7.27—7.19 (6 H, d, d, d, *J* 9 Hz, $C_6H_4SO_2$ + $C_6H_4CI$), and 2.41 (3 H, s, Me) | 418 ($M^+$, 17%), 291 (32), 227 (32), 155 (55), 91 (100), and 65 (22) | New |
| **(1c)** | *p*-MeO | 89 | 119—120<br>(EtOH) | 7.47 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 7.30—7.17 [5 H, d, d, *J* 8 Hz, $C_6H_4$-$SO_2$ + $C_6H_4CI$, (7.21) s, C:CH], 6.75 (2 H, d, *J* 8 Hz, $C_6H_4CI$), 3.82 (3 H, s, OMe), and 2.39 (3 H, s, Ar*Me*) | 414 ($M^+$, 10%), 287 (97), 223 (97), 155 (80), 91 (98), and 65 (53) | New |
| **(1d)** | *m*-$NO_2$ | 89 | 157—158<br>($C_6H_6$) | 8.14 (1 H, m, $C_6H_4CI$), 7.89 (1 H, m, $C_6H_4CI$), 7.62—7.45 (4 H, m, $C_6H_4CI$ + $C_6H_4SO_2$), 7.42 (1 H, s, C:CH), 7.22 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), and 2.39 (3 H, s, Me) | 429 ($M^+$, 33%), 302 (34), 238 (10), 155 (100), 91 (95), and 65 (14) | New |
| **(1e)** | *p*-$NO_2$ | 80 | 199<br>(decomp.)<br>($C_6H_6$) | 8.15 (2 H, d, *J* 9 Hz, $C_6H_4CI$), 7.54 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 7.38 (2 H, d, *J* 9 Hz, $C_6H_4CI$), 7.36 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 7.32 (1 H, s, C:CH), and 2.42 (3 H, s, Me) | 429 ($M^+$, 2%), 302 (20), 237 (5), 155 (85), 91 (100), and 65 (25) | 8<br>(m.p. 203—204 °C) |
| **(1f)** | H | 85 | 85—86<br>(EtOH) | 7.41 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 7.30 (1 H, s, C:CH), 7.20 (5 H, s, Ph), 7.11 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), and 2.34 (3 H, s, Me) | | 8<br>(m.p. 83—84 °C) |

**Table 2.** Reduction products ($XC_6H_4CH{=}CHSO_2C_6H_4Me$) of adducts of toluene-*p*-sulphonyl iodide and acetylenes

| Product | X | Yield (%) | M.p. (solvent) (°C) | $\delta_H$ (90 MHz; $CDCl_3$; standard $Me_4Si$) | *m/z* (Relative intensity) | Ref. |
|---|---|---|---|---|---|---|
| **(2a)** | *p*-Me | 56 | 105—106<br>(EtOH) | 7.67 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 7.47 (2 H, d, *J* 8 Hz, $C_6H_4C$:), 7.34—7.15 (4 H, d, d, *J* 8 Hz, $C_6H_4C$: and $C_6H_4SO_2$), 6.93 (1 H, d, *J* 12 Hz, $SO_2CH$:), 6.36 (1 H, d, *J* 12 Hz, ArC*H*:), and 2.33 (6 H, s, Me) | 272 ($M^+$, 38%), 133 (28), 116 (100), 115 (34), 91 (17), and 65 (13) | New |
| **(2b)** | *p*-Cl | 74 | 149—150<br>(EtOH) | 7.67 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 7.49 (2 H, d, *J* 8 Hz, $C_6H_4C$:), 7.28 (2 H, d, *J* 8 Hz, $C_6H_4C$:), 7.23 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 6.83 (1 H, d, *J* 12 Hz, $SO_2CH$:), 6.46 (1 H, d, *J* 12 Hz, ArC*H*:), and 2.39 (3 H, s, Me) | 292 ($M^+$, 47%), 153 (31), 139 (100), 135 (65), 91 (22), and 65 (15) | New |
| **(2c)** | *p*-MeO | 76 | 92—96*<br>(EtOH) | 7.72 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 7.60 (2 H, d, *J* 8 Hz, $C_6H_4C$:), 7.20 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 6.74 (1 H, d, *J* 12 Hz, $SO_2CH$:), 6.73 (2 H, d, *J* 8 Hz, $C_6H_4C$:), 6.26 (1 H, d, *J* 12 Hz, ArC*H*:), 3.79 (3 H, s, OMe), and 2.36 (3 H, s, Me) | 288 ($M^+$, 24%), 223 (36), 132 (100), 91 (65), and 65 (27) | New |
| **(2f)** | H | 75 | 75—76<br>(EtOH) | | | 8<br>(m.p. 75—76 °C) |

* Modification at 67—69 °C.

by using equation (5) where $[M]_o$,$[M']_o$, and $[M]$,$[M']$ are the initial and final concentrations of both acetylenes in competition.

$$YC_6H_4SO_2^{\cdot} + \begin{cases} C_6H_5C{\equiv}CH \xrightarrow{k_H} \text{Radical adduct} & (3) \\ XC_6H_4C{\equiv}CH \xrightarrow{k_X} \text{Radical adduct} & (4) \end{cases}$$

$$k_X/k_H = (\log[M] - \log[M]_o)/(\log[M'] - \log[M']_o) \quad (5)$$

The unchanged actylenes were analysed by g.l.c. Equation (5) holds also for reversible addition if both propagating steps are much faster than the reverse of the addition steps.[10]

This technique was applied to the homolytic addition of toluene-*p*-sulphonyl iodide to substituted styrenes by Corrêa and Waters[9a] that have shown the electrophilic character of toluene-*p*-sulphonyl radicals and the participation of polar effects in the addition reaction.

**Table 3.** Relative reactivities of addition of $YC_6H_4SO_2I$ to $XC_6H_4C{\equiv}CH$ in $CCl_4$ at 25 °C

| | Y | | | | |
|---|---|---|---|---|---|
| X | *p*-MeO | *p*-Me | H | *p*-Cl | *m*-$NO_2$ |
| *p*-MeO | 2.44[a] | 2.83 | 2.64 | 2.29 | 3.43 |
| | (0.32) | (0.22) | (0.31) | (0.29) | (0.48) |
| *p*-Me | | 1.80 | | | |
| | | (0.20) | | | |
| H | (1) | (1) | (1) | (1) | (1) |
| *p*-Cl | 0.85 | 0.80 | 0.75 | 0.62 | 0.48 |
| | (0.07) | (0.06) | (0.08) | (0.08) | (0.12) |
| *p*-$NO_2$ | | 0.33 | | | |
| | | (0.09) | | | |
| *m*-$NO_2$ | 0.41 | 0.28 | 0.38 | 0.27 | 0.17 |
| | (0.05) | (0.09) | (0.07) | (0.04) | (0.04) |
| $\rho^+$ | −0.53 | −0.66 | −0.58 | −0.64 | 0.93 |
| *r* | 0.999 | 0.987 | 0.998 | 0.984 | 0.985 |

[a] Mean value (6—14 independent estimations) and standard deviation.

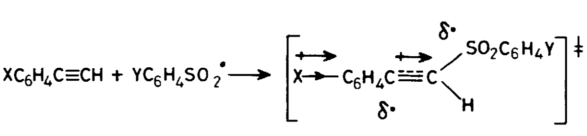
**Table 4.** Competition reaction of *p*-$ClC_6H_4C{\equiv}CH$ (CA) and $C_6H_5C{\equiv}CH$ (A) with *p*-$MeC_6H_4SO_2I$ (140 mg, 0.49 mmol) in $CCl_4$ (5 ml) at 25 °C for 5 min

| | A | | CA | | |
|---|---|---|---|---|---|
| Expt. | mg | mmol | mg | mmol | $k_{CA}/k_A$ |
| 1 | 54.84 | 0.54 | 74.75 | 0.55 | 0.83 |
| 2 | 110.61 | 1.08 | 77.75 | 0.57 | 0.74 |
| 3 | 51.25 | 0.50 | 127.10 | 0.93 | 0.89 |
| 4 | 96.23 | 0.94 | 129.25 | 0.95 | 0.85 |
| 5 | 53.30 | 0.52 | 68.49 | 0.50 | 0.72 |
| 6 | 55.21 | 0.54 | 68.90 | 0.50 | 0.79 |
| 7 | 54.57 | 0.54 | 174.26 | 1.29 | 0.77 |
| 8 | 114.07 | 1.12 | 66.86 | 0.49 | 0.78 |

Mean value of $k_{CA}/k_A$ 0.80. Standard deviation 0.06 (8%).

The study of the homolytic addition of several substituted benzenesulphonyl iodides to substituted styrenes[9b] has shown that benzenesulphonyl radicals with electron-withdrawing substituents are more selective towards substituted styrenes. The validity of equation (5), when applied to chain addition reactions with fast propagating steps, was demonstrated recently by the results of Ito and Matsuda[11] that determined by the flash photolysis technique absolute rate constants for the addition reactions of the benzenethiyl radical and its *p*-chloro derivatives to substituted styrenes and α-methylstyrenes and found Hammett ρ values of similar magnitude to those obtained in competition experiments using equation (5).

Table 3 summarizes the results of competition experiments of several arenesulphonyl iodides and substituted phenylacetylenes. A typical set of results of $k_X/k_H$ is given in Table 4. Consistent results were also obtained when the amount of sulphonyl iodide was changed from 0.209 to 0.054 mmol (Table 6), according with previous results.[9,12] Table 3 shows that, as with substituted styrenes,[9] phenylacetylenes with electron-donating substituents react faster. A plot of $\log(k_X/k_H)$ *versus* $\sigma^+$ has led to good correlations showing the importance of polar effects (although the ρ values were small). The correlation with $\sigma^+$ is better than with σ. The close reactivity of *p*- and *m*-nitrophenylacetylene towards *p*-$MeC_6H_4SO_2^{\bullet}$ radical (Table 3) is a good indication of the very small radical character developed on the α-carbon atom in the transition state, in spite of the linear (*sp*-hybridized) configuration of the vinyl radical[13] and the possibility of direct conjugation with the aromatic ring.



$$XC_6H_4C{\equiv}CH + YC_6H_4SO_2^{\bullet} \longrightarrow \left[ \overset{\longleftrightarrow}{X \rightarrow} C_6H_4\underset{\delta\bullet}{C}\overset{\longleftrightarrow}{\equiv} C\overset{\delta\bullet}{\ }{<}^{SO_2C_6H_4Y}_{H} \right]^{\ddagger} \qquad (6)$$

(4) (5)

This is usual in exothermic reactions such as the free radical additions to double and triple bonds.[14] Results may be rationalized on the basis of an early polarized transition state (**5**) stabilized by electron-donating substituents in the benzene ring. The selectivity of addition (measured by ρ) of different sulphonyl radicals (**4**) towards the same set of acetylenes ranges from −0.53 to −0.93 and a tendency of radicals (**4**) with electron-withdrawing substituents Y to be more selective is apparent. Since sulphonyl radicals react as electrophilic species, electron-withdrawing substituents Y may increase the reactivity of such radicals, that is, once more the Reactivity Selectivity Principle (RSP) does not hold in radical reactions.[15]

The relative reactivities and the selectivities of the addition of arenesulphonyl iodides to substituted phenylacetylenes can also be explained by frontier molecular orbital (FMO) theory. If the favoured FMO interaction is SOMO–HOMO, the energy gap ($E_i$) between frontier orbitals (FO) increases when electron-withdrawing power ($\sigma_X$) of substituents X (in $XC_6H_4C{\equiv}CH$) increases; the perturbation energy ($\Delta E_i$) decreases, the activation energy increases, and the reaction is slower.[16]

The effect of radical structure can also be rationalized on the same grounds.[16] The increase of electron-withdrawing capacity of substituent Y decreases the SOMO energy[16] and the energy gap between FO, leading to a greater perturbation energy ($\Delta E_2 > \Delta E_1$); the radical reactivity is then increased. When the average energy gap between FO ($E_i$) is small, the relative effect of substituents X on the energy gap ($\Delta e$) is more important than when this average gap is greater ($\Delta e/E_1 > \Delta e/E_2$); that is, the selectivity (ρ) increases when Y is an electron-withdrawing substituent.

## Experimental

*Materials.*—Arenesulphonyl iodides were prepared from $YC_6H_4SO_2Na$ (Y = *p*-Me,[17] H,[17], *p*-Cl,[17], *p*-MeO,[18] and *m*-$NO_2$[18]) and iodine as described by Whitmore and Thurman.[19] Arenesulphonyl bromides were also prepared from the corresponding sodium sulphinate salts and bromine either in $H_2O$–ethanol (Y = *p*-Me[20]) or in benzene suspension[21] (Y = *p*-MeO, H, *p*-Cl, *m*-$NO_2$). *p*-Methoxybenzenesulphonyl iodide was extracted from the aqueous solution with $CCl_4$ and used in solution after drying ($MgSO_4$). Toluene-*p*-sulphonyl chloride (B.D.H.) was recrystallized from light petroleum (b.p. 60—80 °C). Phenylacetylene and substituted phenylacetylenes, $XC_6H_4C{\equiv}CH$, were prepared from the corresponding benzaldehydes (X = H, *p*-MeO, *p*-Cl, *m*-$NO_2$) *via* cinnamic acids[22] and corresponding bromine adducts (X = H,[23] *p*-Cl,[23] *m*-$NO_2$,[24] *p*-MeO[25]) followed by transformation in β-bromostyrenes (X = H,[26], Cl,[26], *m*-$NO_2$,[27] *p*-MeO[25]) and phenylacetylenes (X = H,[28] *p*-Cl,[29], *m*-$NO_2$,[25] *p*-MeO[25]). In the synthesis of *p*-methoxyphenylacetylene, after the reaction mixture has been poured into ice–water, the organic material (low m.p. solid) was collected by extraction with ether. *p*-Methylphenylacetylene was prepared from methylacetophenone[28] that was obtained by acylation of toluene[29] with acetic anhydride. *p*-Nitrophenylacetylene was prepared by nitration of ethyl cinnamate[30] followed by addition of bromine to the double bond, elimination of HBr[26] to give the corresponding β-bromostyrene, and transformation into the final acetylenic compound.[31] *p*-Chlorostyrene was prepared by decarboxylation of *p*-chlorocinnamic acid in quinoline in the

**Table 5.** Adducts (**3**) ($p$-$MeC_6H_4SO_2CH_2$–$CHIC_6H_4X$) and vinyl sulphones (**2**) obtained from toluene-*p*-sulphonyl iodide and styrenes ($XC_6H_4CH{=}CH_2$)

| Product | X | Yield (%) | M.p. (solvent) (°C) | $\delta_H$ (90 MHz; $CDCl_3$; standard $Me_4Si$) | *m/z* (Relative intensity) | Ref. |
|---|---|---|---|---|---|---|
| (**3a**) | *p*-Me | 82 | 99—100 (MeOH) | 7.43 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 7.14—7.06 (4 H, $A_2B_2$, *J* 8 Hz, $C_6H_4CI$), 6.88 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 5.56 (1 H, q, *J* 11, and 5 Hz, Part X in ABX, CHI), 4.30 (1 H, m, *J* 11 and 15 Hz, $CH_2SO_2$) + 4.02 (1 H, m, *J* 5 and 15 Hz, $CH_2SO_2$; Part AB in ABX), 2.36 (3 H, s, $SO_2$Ar*Me*), and 2.23 (3 H, s, CIAr*Me*) | 273 ($M^+$ − 1, 97%), 209 (92), 155 (100), 91 (98), and 65 (81) | New |
| (**3b**) | *p*-Cl | 93 | 108—109 ($C_6H_6$) | 7.41 (2 H, d, *J* 9 Hz, $C_6H_4SO_2$), 7.16—7.12 (4 H, $A_2B_2$, *J* 9 Hz, $C_6H_4CI$), 7.06 (2 H, d, *J* 9 Hz, $C_6H_4SO_2$), 5.51 (1 H, d, d, *J* 12 and *J* 3 Hz, CHI), 4.25 (1 H, d, d, *J* 12 and 15 Hz, $CH_2SO_2$), 4.02 (1 H, d, d, *J* 3 and 15 Hz, $CH_2SO_2$), and 2.41 (3 H, s, Me) | 293 ($M^+$ − I, 11%), 229 (10), 155 (92), 91 (100), and 65 (45) | New |
| (**3d**) | *m*-$NO_2$ | 93 | 128—130 ($C_6H_6$) | 8.00 (1 H, d, *J* 9 Hz, ArCI, 4-H), 7.95 (1 H, s, ArCI, 2-H), 7.62 (1 H, d, *J* 9 Hz, ArCI, 6-H), 7.45—7.39 (3 H, m, *J* 9 Hz, ArCI + $C_6H_4SO_2$), 7.13 (2 H, d, *J* 3 Hz, $C_6H_4SO_2$), 5.58 (1 H, d, *J* 12 and 3 Hz, CIH), 4.32 (1 H, d, d, *J* 12 and 15 Hz, $CH_2SO_2$), 4.06 (1 H, d, d, *J* 3 and 15 Hz, $CH_2SO_2$), and 2.34 (3 H, s, Me) | 304 ($M^+$ − I, 10%), 239 (2), 155 (100), 91 (87), and 65 (23) | New |
| (*E*)-(**2a**) | *p*-Me | 78 | 150—151 (EtOH) | 7.81 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 7.61 (1 H, d, *J* 16 Hz, $SO_2CH$:), 7.35 (2 H, d, *J* 8 Hz, $C_6H_4C$:), 7.30 (d, *J* 8 Hz, $C_6H_4C$:), 7.16 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 6.78 (1 H, d, *J* 16 Hz, ArC*H*:), 2.41 (3 H, s, $SO_2$Ar*Me*), and 2.35 (3 H, s, *Me*ArC:) | 272 ($M^+$, 48%), 139 (22), 133 (46), 116 (100), 91 (37), and 65 (31) | New |
| (*E*)-(**2b**) | *p*-Cl | 64 | 149—150 ($CCl_4$) | 7.81 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 7.60 (1 H, d, *J* 16 Hz, $SO_2CH$:), 7.40—7.26 (6 H, d, d, d, $C_6H_4SO_2$ + $SO_2CH$:), 6.82 (1 H, d, *J* 16 Hz, ArC*H*:), and 2.43 (3 H, s, Me) | 292 ($M^+$, 93%), 153 (73), 139 (100), 136 (98), 91 (71), and 65 (58) | New |
| (*E*)-(**2d**) | *m*-$NO_2$ | 68 | 138—139 ($C_6H_6$) | 8.28 (1 H, m, *ArCH*:, 2-H), 8.18 (1 H, m, *ArCH*:, 4-H), 7.87—7.28 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 7.78—7.59 (1 H, d, *J* 16 Hz, $SO_2CH$:), 7.93—7.48 (2 H, m, *Ar*CH:, 5- and 6-H), 7.34 (2 H, d, *J* 8 Hz, $C_6H_4SO_2$), 7.02 (1 H, d, *J* 16 Hz, ArC*H*:), and 2.44 (3 H, s, Me) | 303 ($M^+$, 78%), 238 (67), 139 (100), 91 (98), and 65 (85) | New |

**Table 6.** The effect of the concentration of $p$-$MeC_6H_4SO_2I$ on the relative reactivity of its addition to $p$-$MeOC_6H_4C\equiv CH$ (MtA) and $C_6H_5C\equiv CH$ (A) in $CCl_4$ (5 ml) at 25 °C

| Expt. | $p$-$MeC_6H_4SO_2I$ mg | mmol | Relative reactivity $k_{MtA}/k_A$ |
|---|---|---|---|
| 1 | 58.85 | 0.209 | 2.84 |
| 2 | 30.02 | 0.106 | 2.74 |
| 3 | 15.31 | 0.054 | 2.83 |

presence of copper.[32] *m*-Nitrostyrene was obtained by a similar route.

Styrene (B.D.H.) and *p*-methylstyrene (Koch-Light) were distilled before use. Carbon tetrachloride (B.D.H.; AnalaR), diethyl ether (B.D.H.; AnalaR), and benzene (B.D.H.; AnalaR) were dried and distilled.

*Addition of Toluene-*p*-sulphonyl Iodide to Substituted Phenacetylenes.—General procedure.* An equimolecular solution of substituted phenylacetylene (0.5—2.5 g) and toluene-*p*-sulphonyl iodide in benzene (or diethyl ether) was allowed to react under visible light (Philips lamp; HP/T-250W) for 15—20 min by which time all the reactants has been consumed.

The mixture was cooled and solid products separated in several cases (**1b**—**e**). When no solid separated, the mixture was diluted and successively washed with aqueous sodium metabisulphite (10%) and water, dried ($CaCl_2$), and evaporated *in vacuo* to give the addition product, which was recrystallized and analysed by i.r., n.m.r., and m.s. Results are summarized in Table 1.

*The Reduction of Adducts* (**1**).—Compound (**1**) were reduced to the corresponding vinyl sulphones by Zn–acetic acid, following the general procedure described by Truce *et al.*[8] for 2-iodo-2-phenylethenyl *p*-tolyl sulphone. Results are summarized in Table 2.

*Addition of Toluene-*p*-sulphonyl Iodide to Substituted Styrenes.—General procedure.* A solution of substituted styrene and toluene-$p$-sulphonyl iodide in benzene (20 ml) was irradiated for 10—15 min (visible light; Philips lamp; HP/T-250W), by which time all the reactants had been consumed. Reaction mixtures were worked up as in the case of phenylacetylenes. Results, $^1$H n.m.r., and m.s. data are summarized in Table 5 [products (**3a**, **b**, and **d**)].

*Conversion of Addition Products* (**3a**, **b**, *and* **d**) *into Vinyl Sulphones.—General procedure.* Sulphones (**3a**, **b**, and **d**) (2—2.5 g) were dissolved in warm benzene or ethyl acetate (15—20 ml), treated with triethylamine (2.5—3 ml), and refluxed for 30 min in the dark. The solution was then diluted with benzene and cooled. The precipitated triethylammonium iodide was removed and the filtrate washed successively with aqueous HCl (5%) and water, and dried ($\text{CaCl}_2$). The solvent was evaporated under reduced pressure and the residue (1.0—1.2 g) was recrystallized. Results are summarized in Table 5.

*Effect of Light, Air, and Quinol on the Addition of* $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{I}$ *to* $\text{C}_6\text{H}_5\text{C}{\equiv}\text{CH}$.—Reactions were performed in $\text{CCl}_4$ at room temperature (18 °C) in the presence of $p$-dichlorobenzene as an internal standard for g.l.c. analysis of unchanged phenylacetylene. The addition is faster in the presence of light and when air is excluded from the reaction system. Quinol shows a retarding effect during the induction period followed by an apparent acceleration.

*Competition Experiments.*—Weighted quantities (0.2—1.5 mmol) of two phenylacetylene derivatives (one of which was phenylacetylene) were placed in Pyrex glass tubes (12 ml) surrounded by aluminium foil, 5.00 ml of 1% solution of internal standard in $\text{CCl}_4$ was added, followed by $\text{ArSO}_2\text{I}$ (*ca.* 0.1M; final). The tubes were homogenized, stoppered, and placed in a thermostat at 25 °C for 10 min. The aluminium foil was removed and the yellow solution irradiated under visible light (Philips lamp; HP-T-200W) for 5—120 min. The reaction tubes were cooled and the solution analysed by g.l.c. (Varian Aerograph-3700 and Tracor-565 chromatographs, equipped with hydrogen flame ionization detectors and coupled to Hewlett-Packard 3390A and Perkin-Elmer M-2 calculating integrators. The nitrogen rate flow was 30 ml min$^{-1}$; the column (1.5 m × $\frac{1}{8}$ in) was 3% SE 30 on Chromosorb W, 100—120 mesh, acid washed; temperature (linearly programmed) and internal standards were as follows: (a) $p$-MeO–H (46 °C for 6 min, 45—90°, 35° min$^{-1}$, 90 °C for 4 min; bromobenzene); (b) $p$-Me-H (45 °C for 8 min, 45—110°, 40° min$^{-1}$, 110 °C for 2 min; $p$-bromochlorobenzene); (c) $p$-Cl-H (45 °C for 6 min, 45—75°, 15° min$^{-1}$, 75 °C for 2 min; bromobenzene); (d) $p$-$\text{NO}_2$–H (45 °C for 4 min, 45—200°, 20° min$^{-1}$, 200 °C for 2 min; $p$-dichlorobenzene); (e) $m$-$\text{NO}_2$–H (45 °C for 4 min, 45—180°, 20° min$^{-1}$, 180 °C for 1 min; $p$-dichlorobenzene). Relative reactivities were calculated by using equation (5).

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