

## Polarography of Electrophilic Alkenes and Alkynes bearing Sulphonyl, Sulphinyl, and Sulphonium Groups †

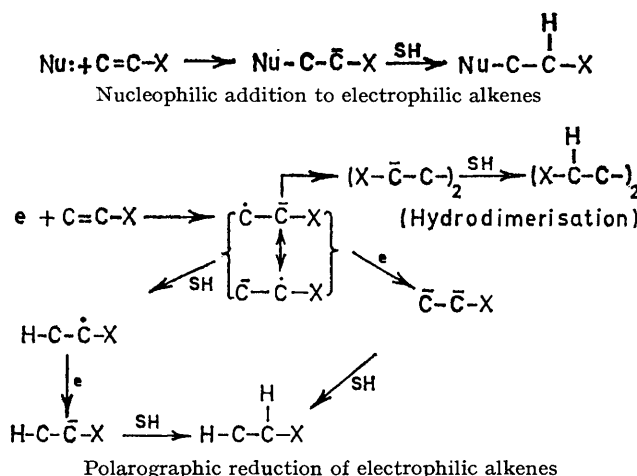
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Polarographic half-wave potentials have been obtained for a series of substrates bearing sulphonyl, sulphinyl, sulphonium, and other related substituents. The ease of polarographic reduction is discussed with relation to the structures of the substrates in terms of the stability of anionic intermediates. Comparisons are drawn with work on nucleophilic additions to these and related substrates, and the dependence of half-wave potential on the pH value of the medium employed is related to the ease of prototropy in the substrates concerned.

POLAROGRAPHIC reduction of alkenes bearing electro-negative groups has mainly been restricted to simple substrates such as acrylonitrile.<sup>1-3</sup>

Polyalkenes, and especially acetylenes, have received much less attention in this respect, in spite of the recent, considerable interest in nucleophilic additions to such substrates.<sup>4-7</sup>

The relationship between nucleophilic addition and polarographic reduction is clear in terms of the requirement for stabilisation of the anionic intermediates (or transition states for those processes, if any, which are concerted<sup>8</sup>) (Scheme 1). With this in mind we have



SCHEME 1 X = Carbanion-stabilising group, e.g. C=O, SO<sub>2</sub>, etc. SH = proton donor, often the solvent. In the case of polarographic reduction, subsequent reaction of the first-formed radical anion depends on its stability and environment, especially with respect to the availability of protons from the solvent.

measured polarographic half-wave potentials of a series of twenty-eight related compounds (Table 1). Our objectives were to investigate substituent effects on the electroactivity of unsaturated substrates bearing electro-negative groups attached directly to the unsaturated moiety, to discover the propensity of non-conjugated substrates to isomerise to conjugated and hence electro-

active isomers, and to examine the electroactivities of polyunsaturated substrates.

TABLE 1

Polarographic half-wave potential values (for 0.1M methanolic Me<sub>4</sub>NBr<sup>+</sup> at 25°)

	First wave E <sub>1</sub> /V	Second wave (when determined) E <sub>2</sub> /V
(1) ArSO <sub>2</sub> -Me	-2.24	
(2) ArSO <sub>2</sub> -CH <sub>2</sub> -Ph	-2.07	
(3) ArSO <sub>2</sub> -CH:CH <sub>2</sub>	-1.61	
(4) ArSO <sub>2</sub> -CH:CHMe	-2.13	
(5) ArSO <sub>2</sub> -CH <sub>2</sub> -CH:CH <sub>2</sub>	-2.09	
(6) ArSO-CH:CH <sub>2</sub>	-1.99	
(7) ArSO <sub>2</sub> -CH <sub>2</sub> -C:CH	-1.32	-2.08
(8) ArSO <sub>2</sub> -CH:C:CH <sub>2</sub>	-1.36	-2.09
(9) ArSO <sub>2</sub> -C:CMe	-1.46	-2.04
(10) PhCH <sub>2</sub> -SO-CH <sub>2</sub> -C:CH	-1.44	
(11) ArS-CH <sub>2</sub> -C:CH	No wave	
(12) Me <sub>2</sub> S <sup>+</sup> -CH <sub>2</sub> -C:CH Br <sup>-</sup>	-1.00 †	
(13) Ph <sub>3</sub> P <sup>+</sup> -CH <sub>2</sub> -C:CH Br <sup>-</sup>	-1.34	
(14) Et <sub>3</sub> N <sup>+</sup> -CH <sub>2</sub> -C:CH Br <sup>-</sup>	No wave	
(15) ArSO <sub>2</sub> -CH:C:CHMe	-1.35	-2.10
(16) ArSO <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -C:CH	-2.08	
(17) ArSO <sub>2</sub> -CH <sub>2</sub> -C:Me	-2.01	
(18) ArSO <sub>2</sub> -O-CH <sub>2</sub> -C:CH	-1.78	
(19) Me <sub>2</sub> S <sup>+</sup> -CH <sub>2</sub> -C(OMe):CH <sub>2</sub> Br <sup>-</sup>	-1.40 †	
(20) ArSO <sub>2</sub> -CH <sub>2</sub> -C(OBz):CH <sub>2</sub>	-2.00	
(21) ArSO <sub>2</sub> -CH <sub>2</sub> -C(OAc):CH <sub>2</sub>	-2.00	
(22) ArSO <sub>2</sub> -CH <sub>2</sub> -CH:CH-CH <sub>2</sub> -SO <sub>2</sub> Ar	-1.89	
(23) PhSO <sub>2</sub> -CH <sub>2</sub> -C:CH-CH <sub>2</sub> -SO <sub>2</sub> Ph	-0.97	
(24) PhSO <sub>2</sub> -CH:CH-CH:CH-SO <sub>2</sub> Ph	-0.96	
(25) PhCH <sub>2</sub> -SO <sub>2</sub> -CH:CH-CH:CH <sub>2</sub>	-1.50	
(26) PhCH <sub>2</sub> -SO <sub>2</sub> -CH:CH-CH:CH <sub>2</sub>	-1.50	
(27) PhSO <sub>2</sub> -CH <sub>2</sub> -C:C:C-CH <sub>2</sub> -SO <sub>2</sub> Ph	-1.41	
(28) PhSO <sub>2</sub> -CH <sub>2</sub> -CH:CH-C:CH <sub>2</sub> -SO <sub>2</sub> Ph	-0.89	

Ar = *p*-Tolyl [Substrate] = 5 × 10<sup>-4</sup>M.

\* In 0.2M-phosphate buffer, pH 6.6, there is no initial wave. Wave at -1.10 V appears on standing. † In KH<sub>2</sub>PO<sub>4</sub>-NaHPO<sub>4</sub>-NaCl-H<sub>2</sub>O, pH 7, E<sub>1</sub> = 1.15 V; in borax-NaOH-H<sub>2</sub>O, pH 10, E<sub>1</sub> = 1.005 V. ‡ This wave disappears in methanolic sodium methoxide.

The details of the polarographic conditions are in the Experimental section; an important aspect of these

† S. T. McDowell and C. J. M. Stirling, *J. Chem. Soc. (B)*, 1967, 351, and references therein.

\* A. M. Nesmeyanov, M. I. Rybinskaya, and L. V. Rybin, *Russ. Chem. Rev.*, 1967, 453.

† Part of this work was carried out at King's College, London.

<sup>1</sup> C. L. Perrin, *Progr. Phys. Org. Chem.*, 1965, 3, 165.

<sup>2</sup> L. Meites, 'Polarographic Techniques,' Interscience, New York, 1965.

<sup>3</sup> J. Simonet and D. Bretelle, *Compt. rend. (C)*, 1970, 270, 591.

<sup>4</sup> C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5856.

<sup>7</sup> B. Capon and C. W. Rees, 'Organic Reaction Mechanisms 1968,' Wiley, London, 1969.

<sup>8</sup> F. G. Bordwell, *Accounts Chem. Res.*, 1970, 3, 281.

conditions is that the majority of the half-wave potential values have been determined at pH (nominal) 9.2, conditions under which isomerisation of labile prototropic systems can occur. These conditions were selected when, in preliminary investigations, it was observed that the non-conjugative acetylenic sulphone (7) showed the same half-wave potential as the allene (8) (see Discussion section).

#### EXPERIMENTAL

**Polarographic Determinations.**—An AMEL model 462 multi-purpose instrument was employed with, unless otherwise stated, methanolic solutions of substrate ( $5 \times 10^{-4}M$  at 25 °C) and tetramethylammonium bromide (0.1M) as electrolyte, solutions being at pH (nominal) 9.2 (glass electrode). Standard settings were mercury column height 40 cm, sensitivity setting 2 $\mu$ A, and drop time 3 s. All potentials quoted are relative to the saturated calomel electrode and all solutions contained 0.0044% w/v gelatine and were prepurged with nitrogen. Voltage sweep was from 0 to -2.3 V. For prop-2-ynyl *p*-tolyl sulphone (7) it was confirmed that the wave height was proportional to (height of mercury column)<sup>1/2</sup>, confirming the observation of diffusion-limited current.<sup>9</sup> In two cases,  $E_{1/2}$  was determined at pH values other than 9.2. Changes in  $E_{1/2}$  were relatively small; details are in Table 1. Waves were not tested for reversibility.

**Preparation of Substrates.**—Methyl *p*-tolyl sulphone (1),<sup>10</sup> benzyl *p*-tolyl sulphone (2),<sup>11</sup> *p*-tolyl vinyl sulphone (3),<sup>12</sup> *trans*-propenyl *p*-tolyl sulphone (4),<sup>13</sup> allyl *p*-tolyl sulphone (5),<sup>14</sup> *p*-tolyl vinyl sulphoxide (6),<sup>15</sup> prop-2-ynyl *p*-tolyl sulphone (7),<sup>16</sup> allenyl *p*-tolyl sulphone (8),<sup>16</sup> prop-1-ynyl *p*-tolyl sulphone (9),<sup>16</sup> benzyl prop-2-ynyl sulphoxide (10),<sup>17</sup> prop-2-ynyl *p*-tolyl sulphide (11),<sup>16</sup> dimethyl(prop-2-ynyl)sulphonium bromide (12),<sup>18</sup> triphenyl(prop-2-ynyl)phosphonium bromide (13),<sup>18</sup> triethyl(prop-2-ynyl)ammonium bromide (14),<sup>18</sup> buta-1,2-dienyl *p*-tolyl sulphone (15),<sup>19</sup> prop-2-ynyl toluene-*p*-sulphonate (18),<sup>20</sup> 1-(tolyl-*p*-sulphonylmethyl)vinyl benzoate (20),<sup>21</sup> 1-(tolyl-*p*-sulphonylmethyl)vinyl acetate (21),<sup>21</sup> and benzyl *cis*-buta-1,3-dienyl sulphone (26)<sup>22</sup> were obtained by reported methods.

**But-3-ynyl *p*-Tolyl Sulphone (16).**—But-3-ynyl toluene-*p*-sulphonate<sup>23</sup> (3 g, 0.0124 mol) was treated with a solution of toluene-*p*-thiol (1.625 g, 0.01135M) in methanolic sodium methoxide [prepared by the addition of sodium (0.302 g) to methanol (13.6 ml)]. After 1 h the mixture was poured into water, extracted with dichloromethane, and washed with aqueous sodium hydroxide. Evaporation gave the corresponding *sulphide* (2.335 g, 99%), b.p. 104° at 1.5 mmHg (Found: C, 75.0; H, 6.5. C<sub>11</sub>H<sub>10</sub>S requires C, 75.0; H, 6.8%). The sulphide (500 mg) in acetic acid (3 ml) was

<sup>9</sup> P. Zuman, 'Organic Polarographic Analysis,' Pergamon, London, 1964, p. 25.

<sup>10</sup> H. J. Backer and G. J. De Jong, *Rec. trav. chim.*, 1948, **67**, 884.

<sup>11</sup> F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.*, 1955, **77**, 572.

<sup>12</sup> L. I. Smith and H. R. Davis, *J. Org. Chem.*, 1950, **15**, 824.

<sup>13</sup> J. Weinstock, R. G. Pearson, and F. G. Bordwell, *J. Amer. Chem. Soc.*, 1956, **78**, 3468.

<sup>14</sup> R. Otto, *Annalen*, 1894, **283**, 181.

<sup>15</sup> D. J. Abbott and C. J. M. Stirling, *Chem. Comm.*, 1971, 472.

<sup>16</sup> D. J. Abbott, Ph.D. Thesis, University of London, 1969.

<sup>17</sup> H. C. McMullen and C. J. M. Stirling, *J. Chem. Soc. (B)*, 1966, 1217.

<sup>18</sup> G. D. Appleyard and C. J. M. Stirling, *J. Chem. Soc. (C)*, 1969, 1904.

treated with aqueous 30% hydrogen peroxide (2 ml) and the mixture was kept at 100 °C for 1 h. The mixture was poured into water, and extraction with dichloromethane gave the *sulphone* (460 mg), m.p. 53° (from hexane) (Found: C, 63.1; H, 5.2. C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>S requires C, 63.3; H, 5.8%).

**1,4-Bis(phenylsulphonyl)but-2-yne (23).**—Thiophenol (18 g) in ethanolic sodium ethoxide [prepared from sodium (3.81 g) and ethanol (150 ml)] was added dropwise over 30 min to but-2-yne-1,4-diyl bis(toluene-*p*-sulphonate)<sup>23</sup> (31.6 g) in dichloromethane (60 ml) and ethanol (100 ml) at 40°. When the addition was complete, the mixture was boiled for 10 min, poured into water (300 ml), and extracted with dichloromethane. Evaporation of the extracts gave the *bis-sulphide* (21.5 g), m.p. 44–45° (from methanol) (Found: C, 70.8; H, 5.35. C<sub>16</sub>H<sub>14</sub>S<sub>2</sub> requires C, 71.1; H, 5.1%). Oxidation of the *bis-sulphide* with aqueous 30% hydrogen peroxide in acetic acid at 100° for 1 h gave the *bis-sulphone*, m.p. 163–164° (from acetone) (Found: C, 57.7; H, 4.3. C<sub>16</sub>H<sub>14</sub>S<sub>2</sub>O<sub>4</sub> requires C, 57.5; H, 4.2%).

**1,6-Bis(phenylsulphonyl)hexa-2,4-diyne (27).**—Phenyl prop-2-ynyl sulphone<sup>24</sup> was obtained by oxidation of the sulphide.<sup>25</sup> The sulphone (2 g) in saturated ethanol, was added to ammonium chloride (9 g), copper(I) chloride (3 g), and concentrated hydrochloric acid (0.45 ml) in water (45 ml). The clear solution was shaken in an atmosphere of oxygen and, when absorption was complete after 2.5 h (227 ml absorbed), the heterogeneous mixture was acidified with 2M-HCl (100 ml) and extracted with dichloromethane. Evaporation of the extracts gave a residue (1.97 g) of the *bis-sulphone*, m.p. 125–130°, raised on crystallisation from acetone to 198–200° (0.71 g) (Found: C, 60.5; H, 4.0. C<sub>18</sub>H<sub>14</sub>O<sub>4</sub>S<sub>2</sub> requires C, 60.4; H, 3.9%). Hydrogenation of the *bis-sulphone* (250 mg) in suspension in ethanol over 5% palladium-charcoal (200 mg) gave 1,6-bis(phenylsulphonyl)hexane<sup>26</sup> (215 mg), m.p. and mixed m.p. 112–113°.

**1,6-Bis(phenylsulphonyl)hex-4-en-2-yne (28).**—Phenyl prop-2-ynyl sulphone (2 g) was added to a boiling suspension of copper(I) oxide (200 mg) in acetic acid (40 ml). The mixture was boiled for 2 min after addition was complete (4 min in all), poured into water (200 ml), and after the addition of 2M-HCl (10 ml) was extracted with dichloromethane. Evaporation gave the *bis-sulphone*, m.p. 165–166° (from methanol) (Found: C, 59.4; H, 4.5. C<sub>18</sub>H<sub>16</sub>O<sub>4</sub>S<sub>2</sub> requires C, 60.0; H, 4.4%). Hydrogenation of the *disulphone* over palladised charcoal as before gave 1,6-bis(phenylsulphonyl)hexane, m.p. and mixed m.p. 113–114°.

**trans-1,4-Bis-(*p*-tolylsulphonyl)but-2-ene (22).**—(with A. T. KADER) *trans*-1,4-Dibromobut-2-ene (10 g) was added to a solution of toluene-*p*-thiol (11.05 g) and sodium ethoxide (7.687 g) in ethanol (100 ml). The mixture was set aside at room temperature for 1 h when extraction gave the *bis-sulphide* (10.23 g), m.p. 50–51° (from methanol) (Found:

<sup>19</sup> G. Smith and C. J. M. Stirling, *J. Chem. Soc. (C)*, 1971, 1530.

<sup>20</sup> P. Lauger, M. Prost, and R. Charlier, *Helv. Chim. Acta*, 1959, **42**, 2379.

<sup>21</sup> G. D. Appleyard and C. J. M. Stirling, *J. Chem. Soc. (C)*, 1967, 2686.

<sup>22</sup> R. C. Krug, J. A. Rigney, and G. R. Tichelaar, *J. Org. Chem.*, 1962, **27**, 1305.

<sup>23</sup> G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 1950, 3650.

<sup>24</sup> G. Pourcelot, P. Cadot, and A. Willemart, *Compt. rend.*, 1961, **252**, 1630.

<sup>25</sup> K. Sato and O. Mujamoto, *J. Chem. Soc. Japan*, 1956, **77**, 1409.

<sup>26</sup> F. G. Bordwell, H. M. Andersen, and B. M. Pitt, *J. Amer. Chem. Soc.*, 1954, **76**, 1082.

C, 72.5; H, 6.5.  $C_{18}H_{20}S_2$  requires C, 72.1; H, 6.7%. Oxidation of the bis-sulphide (20.38 g) as before gave the *bis-sulphone* (23.95 g), m.p. 192—194° (from ethanol) (Found: C, 59.5; H, 5.2.  $C_{18}H_{20}O_4S_2$  requires C, 59.3; H, 5.5%).

*Benzyl trans-Buta-1,3-dienyl Sulphone* (25).—The *cis*-diene, obtained by benzylation of the anion of butadiene-1-sulphinic acid<sup>22</sup> (250 mg), dissolved in a mixture of diethyl ether (10 ml) and benzene (20 ml), was treated with iodine (2.5 mg). After 16 h in daylight, the solvent was removed and a solution of the residue in dichloromethane was washed with aqueous sodium thiosulphate. Evaporation gave a residue of the *sulphone*, m.p. 50—51°, raised to 54—55° [from isopropyl ether—light petroleum (b.p. 40—60°)]. This material depressed the m.p. of the *cis*-isomer previously obtained (Found: C, 62.7; H, 5.4.  $C_{11}H_{12}O_2S$  requires C, 63.3; H, 5.7%).

*Dimethyl-(2-methoxyprop-2-enyl)sulphonium Bromide* (19).—Dimethyl(prop-2-ynyl)sulphonium bromide (517 mg) in methanol (25 ml) was added to a solution of tetramethylammonium bromide (0.1M) in methanol (50 ml). After 4 days, the solvent was removed under reduced pressure and the residue was crystallised from ethanol—ethyl acetate to give the *methoxy-compound*, m.p. 96—98° (Found: C, 33.5; H, 6.1.  $C_6H_{13}BrOS$  requires C, 33.8; H, 6.1%). The <sup>1</sup>H n.m.r. spectrum showed vinyl protons and a methoxy-group in addition to the methyl sulphonium protons ( $\tau$  7.0).

*Controlled Potential Electrolysis of Allenyl p-Tolyl Sulphone* (8).—The allene (200 mg) in a potassium dihydrogen phosphate—potassium hydroxide buffer (50 ml), pH (nominal) 6.55, in methanol, was electrolysed at -1.40 V for 7 days. Removal of solvent and extraction with a mixture of water and dichloromethane gave, in the organic extracts, a 99.5% yield of material, m.p. 35—40°, raised to 45—48° [from isopropyl ether—petroleum ether (b.p. 40—60°)] alone or mixed with an authentic specimen of allyl *p*-tolyl sulphone. I.r. analysis of solutions of the whole crude product showed that the actual yield of allylic sulphone was 84%.

*Addition of Methanol to Prop-2-ynyl p-Tolyl Sulphone* (cf. ref. 4).—(i) *Formation of 2-methoxyprop-2-enyl p-tolyl sulphone* (29). The sulphone (7) (1 g) in dry methanol (10 ml) was treated with 0.02M-methanolic sodium methoxide (10 ml). After 10 min, addition of ether and water with subsequent separation of the ethereal extract yielded the *sulphone* (29) (86%), m.p. 71—72°, raised to 78.7° (from isopropyl ether) (Found: C, 58.3; H, 6.25.  $C_{11}H_{14}O_3S$  requires C, 58.4; H, 6.2%),  $\tau$  2.3 (4H, m), 5.77 (2H, s), 6.08 (2H, s), 6.54 (3H, s), and 7.5 (3H, s).

(ii) *Formation of trans-2-methoxyprop-1-enyl p-tolyl sulphone*. Prop-2-ynyl *p*-tolyl sulphone (1.9 g), suspended in methanol (2 ml), was treated with 0.25M-methanolic sodium methoxide (10 ml) dropwise with cooling. After 90 min ether (100 ml) was added, together with water (50 ml), and the ether layer was separated and washed twice with water. Evaporation gave the *methoxy-sulphone* (90%), m.p. 62—63° raised to 71.5° (from isopropyl ether) (Found: C, 58.2; H, 6.3.  $C_{11}H_{14}O_3S$  requires C, 58.4; H, 6.2%),  $\tau$  2.3 (4H, m), 4.35 (1H, s), 6.48 (3H, s), 7.58 (3H, s), and 7.79 (3H, s).

*Isomerisation of Prop-2-ynyl p-Tolyl Sulphone*.—The sulphone ( $5 \times 10^{-4}M$ ) in a 0.2M- $KH_2PO_4$ -KOH buffer (pH 6.6) made up in 7:3 water-methanol (v/v at 25°) gave no initial wave. Subsequent measurements of half-wave

potential and diffusion current are given in Table 2. The half-wave potential determined under these conditions was -1.10 V. It was confirmed that addition of allenyl *p*-tolyl sulphone increased the wave height indicating that the appearance of the wave was due to the isomerisation of terminal acetylene to the allene.

TABLE 2

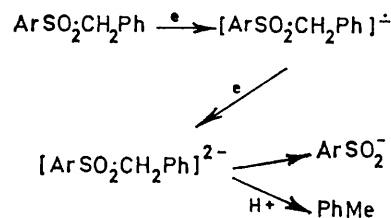
Variations of diffusion current with time for the isomerisation of prop-2-ynyl *p*-tolyl sulphone (7)

<i>t</i> /min	<i>i</i> <sub>d</sub> /μA
0	0
14	0.16
87	0.24
1140	0.76
1506	0.80

## DISCUSSION

A number of previous investigations of the electroactivity of sulphones, sulphoxides, and sulphonium salts have been made, and the present results will be considered against the background of previous work.

It can be seen from Table 1 that simple saturated sulphones have very negative half-wave reduction potentials and that, for methyl *p*-tolyl sulphone, for example, the reduction potential corresponds to the cleavage of the carbon-sulphur bond [*ca.* -2 V (below)]. This potential becomes less negative when a methyl group is replaced by a benzyl group. Other work<sup>27,28</sup> indicates two-electron processes, the nature of which probably varies with the proton-donating capacity of the solvent.<sup>27</sup> A simple representation, *e.g.* for the sulphone (2) (Scheme 2) is consistent with previous results. A



SCHEME 2

lower reduction potential for the sulphone is expected irrespective of whether the alkyl group is lost from the intermediate as an anion or a radical. The half-wave reduction potential of the second wave (*ca.* -2 V) was determined only for a few sulphones which were electroactive at less negative potentials. No detailed studies of the more negative reduction waves were made.

Simple alkenes such as ethylene have very negative reduction potentials in the range not normally accessible. Attachment of an electronegative group and particularly one capable of stabilising either a radical or a carbanionic centre markedly lowers the half-wave potential.<sup>1</sup> The effect is seen in the half-wave potential of *p*-tolyl vinyl sulphone (3), a type of substrate previously investigated.<sup>29</sup>

<sup>28</sup> R. C. Bowers and H. D. Russell, *Analyt. Chem.*, 1960, **32**, 405.

<sup>27</sup> G. Geminet and J. Simonet, *Compt. rend. (C)*, 1971, **272**, 661, and references therein.

<sup>29</sup> P. Carsky, P. Zuman, and V. Horak, *Coll. Czech. Chem. Comm.*, 1965, **30**, 4316.

The importance of conjugation with the electro-negative group is shown for allyl *p*-tolyl sulphone (5) where the very negative reduction potential again corresponds to C-S cleavage giving a relatively stable allyl group [cf. the benzyl sulphone (2)].

Allylic sulphones are subject to prototropy under basic conditions,<sup>30</sup> but under the present polarographic conditions (pH 9.2) isomerisation does not appear to occur as the half-wave potential of *trans*-propenyl *p*-tolyl sulphone, into which it would be converted, is even more negative. The allylic sulphones (20) and (21) bearing acyloxy-groups attached to the carbon-carbon double bond are also electroinactive at potentials less negative than that required for C-S bond fission.

The importance of stabilisation of radical anion intermediates is shown by the more negative half-wave potential of *p*-tolyl vinyl sulphoxide (6). The sulphanyl group is less well able, than the sulphonyl group, to stabilise carbanionic centres,<sup>31</sup> and sulphoxides are, in any case, subject to reduction at the sulphanyl group<sup>28</sup> with  $E_{\frac{1}{2}}$  ca.  $-2.1$  V.

The acetylenic, (7) and (9) and allenic isomers (8) make an interesting comparison in terms of the relationship of their electroactivity with their other prototropic reactions such as nucleophilic addition which, of course, in many respects parallels polarographic reduction. The terminal acetylenic sulphone (7) at pH 9.2 gives a half-wave reduction potential ( $-1.32$  V) much lower than could possibly be accounted for by C-S bond cleavage. Isolated carbon-carbon triple bonds have very much more negative reduction potentials,<sup>1</sup> and it is clear that direct reduction of this group is not occurring. At pH 6.6, the sulphone is electroinactive but electroactivity gradually develops at a somewhat more positive potential than in the conditions operative for experiments carried out at pH 9.2. At this latter pH, the half-wave potential is the same within experimental error as that obtained for the allenic sulphone (8) and is considerably more positive than the half-wave potential of the internal acetylenic isomer (9). Previous work<sup>4,5</sup> established that sulphones of type (7) are susceptible to nucleophilic addition only after prototropic isomerisation to the allene. Direct nucleophilic addition<sup>5</sup> to the conjugated acetylene (9) occurs under suitable conditions, but it is less reactive than the allene (8).

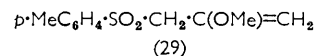
The important characteristic of these three isomers is that the thermodynamic stabilities are in the order (8) > (7) > (9) shown by heat of combustion<sup>32</sup> measurements, entirely in accord with reactivity considerations.<sup>4,5</sup> It is clear that at pH 9.2, sulphone (7) rapidly isomerises to sulphone (8) and thus shows the same half-wave potential. By contrast, sulphone (9) albeit the least thermodynamically stable of the series, isomerises much more slowly to the allene and hence shows a different half-wave potential which is attributable to the conjugated acetylene itself.

<sup>30</sup> A. T. Kader and C. J. M. Stirling, *J. Chem. Soc.*, 1962, 3686.

<sup>31</sup> J. Crosby and C. J. M. Stirling, *J. Chem. Soc. (B)*, 1970, 671.

The allenic sulphone (8) has been submitted to controlled potential ( $-1.4$  V) electrolysis in order to check on the nature of the process producing the wave at  $-1.36$  V. The product, obtained in high yield, was allyl *p*-tolyl sulphone. This confirms that the sequence of electron addition and protonation is analogous to that involved in nucleophilic addition which produces adducts of the type (29). Electroreduction of conjugated allenic ketones<sup>33</sup> is similarly considered to give the  $\beta\gamma$ -unsaturated ketone as the primary product although isomerisation is believed to occur under the reaction conditions.

It was established in earlier work<sup>34</sup> that nucleophiles such as methoxide ion added rapidly to sulphone (8) and, in confirmation of the above conclusions, addition of methoxide ion to the medium rendered the sulphones electroinactive at potentials near  $-1.4$  V. Addition produces the sulphone (29) which, as expected by com-



parison with the allyl sulphone (5) and sulphones (20) and (21), is electroinactive. Only under much more strongly basic conditions is the conjugated methoxy-adduct, *trans*-2-methoxyprop-1-enyl *p*-tolyl sulphone obtained (see Experimental section).

The behaviour of the acetylenic sulphide (11) shows that replacement of the powerful carbanion-stabilising arylsulphonyl group by an arylthio-group raises the reduction potential to inaccessibly high negative values and it is improbable that isomerisation to the allenyl sulphide occurs under these conditions in accordance with earlier experience<sup>25,34</sup> of the isomerisation of terminal acetylenic sulphides which requires strongly basic conditions.

The electroactivity of the sulphoxide (10) is clearly due to isomerisation to the allene as for the sulphone (7) and reduction occurs at a somewhat more positive potential than for the vinyl sulphoxide (6). This observation is in line with the relative reduction potentials of the vinyl sulphone (3) and the allene (8).

*Polarographic Reduction of 'Onium Salts.*—The electrolytic behaviour of acetylenic and allenic sulphonium salts has been investigated in parallel with the study of nucleophilic additions to these substrates.<sup>18,35</sup>

The reduction wave at  $-1.00$  V observed for the salt (12) is attributable to isomerisation of the terminal acetylene to the allenic sulphonium salt, a process which occurs rapidly even in neutral methanol.<sup>18</sup> The reduction of simple sulphonium salts occurs at much more negative potentials<sup>36</sup> (e.g.  $\text{Me}_3\text{S}^+\text{SO}_4\text{Me}^-$  at  $-1.95$  V) and

<sup>32</sup> H. Mackle and W. V. Steele, *Trans. Faraday Soc.*, 1969, 65, 2073.

<sup>33</sup> P. Martinet, J. Simonet, and M. Morenas, *Bull. Soc. chim. France*, 1970, 814.

<sup>34</sup> C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5863.

<sup>35</sup> J. W. Batty, P. D. Howes, and C. J. M. Stirling, *Chem. Comm.*, 1971, 543.

<sup>36</sup> E. L. Colichman and D. L. Love, *J. Org. Chem.*, 1953, 18, 40.

it is not conceivable that the prop-2-ynyl group lowers the reduction potential to this extent. When the electroactivity of the sulphonium salt was checked at pH 7.0 in aqueous methanolic phosphate buffer, the half-wave potential was  $-1.15$  V. Addition of methanolic sodium methoxide to a methanolic solution of sulphonium salt (12) caused a shift of the half-wave potential to the more negative value of  $-1.40$  V. This change corresponds to addition of methoxide ion to the sulphonium salt, producing a methoxy-salt (19) which may be isolated direct from the mixture, provided that the concentration of methoxide ion is kept very low (*ca.*  $10^{-3}$ M). When the concentration of methoxide ion is increased, the wave with  $E_{\frac{1}{2}} -1.40$  V disappears. This change corresponds to dealkylation of the sulphonium salt as found in synthetic work with alkoxide and other nucleophiles.<sup>37</sup>

The related phosphonium salt (13) is also electroactive at a potential less negative than that of simple alkyl phosphonium salts. Methyltriphenylphosphonium bromide for example, shows  $E_{\frac{1}{2}} -2.23$  V under comparable conditions.<sup>38</sup> Again we attribute this observation of electroactivity to isomerisation to the conjugated allenic phosphonium salt which occurs under the mildly basic conditions of the medium. The salt (13) readily undergoes nucleophilic addition<sup>18</sup> *via* isomerisation to the allene in accordance with the conjugative stabilisation of carbanionic intermediates by phosphonium groups.<sup>39</sup>

The interesting contrast is with the acetylenic ammonium salt (14) which shows no reduction wave at potentials more positive than  $-2$  V. Isomerisation of this salt does not occur because of the very much lower acidity of the  $\alpha$ -methylene protons, which is due to the unavailability of *d*-orbital stabilisation<sup>40</sup> of the anionic intermediate involved in the prototropy of the second row 'onium salts (12) and (13). An electroactive system cannot, therefore, be generated and no wave is observed.

*The Four-carbon Acetylene-Allene Prototropic System.*—In connection with another investigation,<sup>19</sup> we had occasion to examine the reactivity of the sulphones (15)—(17) in terms of their tendency towards prototropic isomerisation and their relative thermodynamic stabilities. This system makes an interesting contrast to the three-carbon system as exemplified by the sulphones (7)—(9), as it is found that, under the standard conditions (pH 9.2), only sulphone (15) is electroactive at potentials less negative than that required for C-S bond fission<sup>27,28</sup> (*ca.*  $-2.1$  V). The failure of the sulphone (16) to show electroactivity is not surprising as removal of the most acidic proton, from the methylene group adjacent to the sulphonyl group, does not produce an anion capable of prototropy and formation of a conjugated system is not favoured. On the other hand, for the sulphone (17) removal of an  $\alpha$ -methylene proton could readily form the conjugated allene (15) in the same way that the terminal acetylenic sulphone (7) isomerises

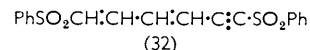
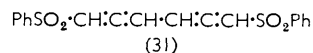
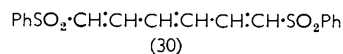
to the allene (8). The failure of this sulphone to give a wave at *ca.*  $-1.4$  V indicates that the process does not occur and this is entirely consistent with the observation<sup>19</sup> that chromatography of the conjugated allene (15) on basic alumina produces the non-conjugated, non-terminal acetylene (17) by prototropic rearrangement. In this case, therefore, it is the non-conjugated, non-terminal acetylene that is the most stable isomer and the free energy difference between compounds (17) and (15) is clearly great enough to prevent the existence of an adequate equilibrium concentration of the conjugated allene for the observation of a cathodic wave.

The oxygen analogue (18) of the four-carbon terminal acetylene (16) is electroactive, the reduction potential in this case corresponding to O-C bond fission,<sup>41</sup> which produces sulphonate ion.

*Electroactivity of Poly-unsaturated Sulphones.*—In the four-carbon sulphone system, compounds (22)—(24), it is clear that the behaviour of the non-conjugated butenyl sulphone (22) is consistent with that of the propenyl (4) and allyl (5) sulphones. If formation of a conjugated system bearing an alkyl group occurs, the effect in lowering the reduction potential is counterbalanced by the destabilising effect of the  $\beta$ -substituent.

The behaviour of the four-carbon isomers (23) and (24) is consistent with prototropic isomerisation of the former. The reduction potential is much more positive than for the simple vinyl sulphone (3) consistent with greater stabilisation in the radical anion produced by initial electron addition. It is interesting that the reduction potential obtained for the bis-sulphone (24) is also very much less negative than that for the isomers (25) and (26) indicating a rather modest degree of stabilisation in the radical anion obtained from these substrates. The observation is, however, consistent with the rather low reactivity of these systems towards nucleophilic addition.<sup>42</sup> The reason for the apparent low degree of stabilisation in the case of the butadienyl sulphones is not, at present, clear.

In the six-carbon systems (27) and (28), an interesting comparison is available between the en-yne and the di-yne isomers. For the en-yne isomer, prototropic isomerisation produces the conjugated triene (30) which, upon reduction, evidently produces a radical-anion intermediate of great stability as indicated by the low ( $-0.89$  V) reduction potential. By contrast, for the di-yne sulphone (27) prototropy can lead only to the formation of either a diallene system (31) or a dienyne system (32). In the former, there is not full conjugation



<sup>37</sup> P. D. Howes and C. J. M. Stirling, to be published.

<sup>38</sup> L. Horner, F. Röttger, and H. Fuchs, *Chem. Ber.*, 1963, **96**, 3141.

<sup>39</sup> R. F. Hudson, 'Structure and Mechanism in Organophosphorus Chemistry,' Academic Press, London, 1965.

<sup>40</sup> K. A. R. Mitchell, *Chem. Rev.*, 1969, **69**, 157.

<sup>41</sup> S. G. Mairanovskii and M. B. Neiman, *Doklady Akad. Nauk S.S.S.R.*, 1952, **87**, 805.

<sup>42</sup> R. W. Howsam and C. J. M. Stirling, to be published.

with and between the sulphonyl groups. For isomer (32) conjugation is complete but evidently the presence of the triple bond raises the energy difference between the ground state and the radical anion.

It is clear from the foregoing considerations that polarographic examination of unsaturated substrates yields valuable information on the prototropic behaviour and conjugation in unsaturated systems bearing electro-

negative sulphur substituents which correlates extremely well with studies of nucleophilic addition reactions.

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