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ELECTROORGANIC CHEMISTRY–XV

ELECTROREDUCTION OF SULFONIUM AND AMMONIUM SALTS. FORMATION OF SULFONIUM YLIDS

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Abstract—In the electroreduction of sulfonium and ammonium salts, sulfonium ylid was generated from the sulfonium salt, whereas in the case of the ammonium salt, nitrogen ylid was not formed but the N^+—C bond was reductively cleaved. On the basis of the controlled potential electrolysis, it seems acceptable that the mechanism of formation of sulfonium ylid involves the direct electron transfer to the sulfonium salt as the initiation step.

INTRODUCTION

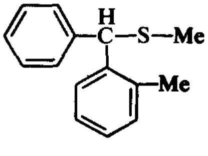
The formation of a cross-coupling product in the electroreduction of dimethylbenzylsulfonium *p*-toluenesulfonate under the existence of acrylonitrile has been reported and elucidated by an anionic mechanism, in which the anion is formed by the reductive cleavage of the sulfonium salt.[1] Furthermore, the cleavage of N^+-alkyl bond has been observed in the electroreduction of various ammonium salts.[2] However, no mechanism of these electrochemical reductions of sulfonium and ammonium salts has been established. The fact that the electrochemical half-wave reduction potentials of sulfonium salts are in the range of −1·5 to −2·0 volt *vs* SCE,[1,3] whereas those of the corresponding ammonium salts are more negative than −2·2 volt *vs* SCE would suggest the important role of the vacant d-orbital of sulfur in the electroreduction of a sulfonium salt. One role of the vacant d-orbital of sulfur would be the stabilization of a sulfonium ylid, which may be formed in the electroreduction as an intermediate. Thus, the electroreduction of some sulfonium and ammonium salts was investigated from this point of view.

RESULTS

The electrochemical reduction of an aqueous solution of 2-nitrofluorenyl-9-dimethylsulfonium bromide (**1**) using a carbon rod electrode gave immediately a purple solid on the surface of cathode. This product was identified as dimethylsulfonium 9-(2-nitrofluorenylidide) (**2**) by comparison with authentic material.[4]

In a cylindrical cell equipped with a ceramic diaphragm, benzyldimethylsulfonium fluoroborate (**3**), *p*-methylbenzyldimethylsulfonium fluoroborate (**4**), trimethylsulfonium iodide (**5**) or ethyldiphenylsulfonium fluoroborate (**6**) was electrolysed at the cathode potential of −1·6 to −2·1 volt *vs* SCE using a carbon electrode. Dimethylsulfoxide, benzaldehyde or a solution of an ylid acceptor, such as carbonyl compounds or α,β-unsaturated olefinic compounds in DMSO was used as the reaction solvent. As shown in Table 1, epoxy compounds, cyclopropane derivatives or rearranged products were obtained suggesting that sulfonium ylids were intermediately generated in the electroreduction of sulfonium salts.

It was previously reported[5] that by the treatment with a base, dibenzylmethylsulfonium fluoroborate (**18**) gave **19** and **20** *via* sulfonium ylid, and the ratio of these rearranged products (**19**/**20**) varied over a wide range by changing the base concentration. The corresponding ratio observed in the electroreduction of **18** in DMSO at the cathode potential of −1·6 volt *vs* SCE was 3·6, suggesting that the electroreduction corresponds to using 5% methanolic solution of Na.



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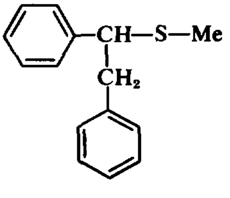

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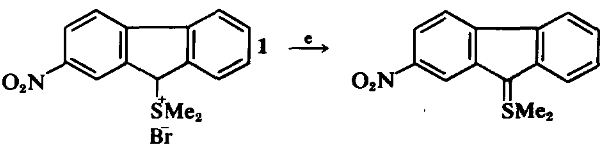
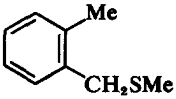
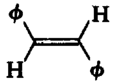
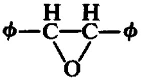
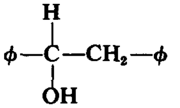
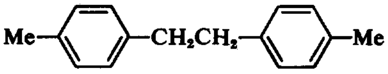
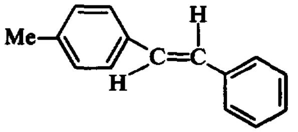
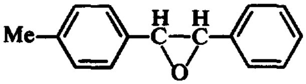
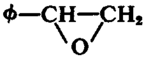
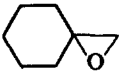
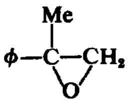
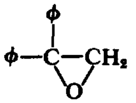
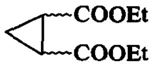
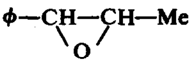


Table 1. Electroreduction of some sulfonium salts in various solvents

Sulfonium salt	Solvent	Product	Yield[a,b] %
3	DMSO	$\phi-CH_2CH_2-\phi$ (**7**)	4
		 (**8**)	17
3	benzaldehyde		7
		 (**9**)	12
		 $\phi-\overset{H}{C}-\overset{H}{C}-\phi$ (*cis*) (**10**)	30
		 $\phi-\overset{H}{\underset{OH}{C}}-CH_2-\phi$ (**11**)	19
4	benzaldehyde	 (**12**)	8
		 (**13**)	14
		 (*cis*) (**14**)	13
5	benzaldehyde	 $\phi-CH-CH_2$ (**15**)	28
5	benzaldehyde +DMSO	**15**	32
5	cyclohexanone +DMSO	 (**16**)	10
5	acetophenone +DMSO	 $\phi-\overset{Me}{C}-CH_2$	7
5	benzophenone +DMSO	 $\phi-\overset{\phi}{C}-CH_2$	7
5	ethyl maleate +DMSO	 (**17**)	10 (*trans*) 6 (*cis*)
	ethyl fumarate +DMSO		6 (*trans*) 6 (cis)
6	benzaldehyde	 $\phi-CH-CH-Me$	10

[a] Analysed by VPC

[b] Based on the sulfonium salt.

Some ammonium salts such as benzyltrimethylammonium bromide (**21**), trimethyl-n-butoxymethylammonium bromide (**22**) or cyclohexylmethyltrimethylammonium iodide (**23**) were electrochemically reduced in various solvents. The products originated in the reductive cleavage of the N^+—C bond were obtained. These results are shown in Table 2.

Table 2. Electroreduction of ammonium salts in various solvents

Ammonium salt	Solvent	Product	Yield,[a,b] (%)
21	DMSO	toluene	43
22	cyclohexene + acetonitrile	n-butyl methyl ether	28
23	acetonitrile	cyclohexylmethyl-dimethylamine	38

[a] Analysed by VPC

[b] Based on the ammonium salt

DISCUSSION

Two different routes could be implied for the mechanism of the electrochemical ylid formation from sulfonium salts. (i) A carbanion species formed from electroreduction of solvent abstracts a proton from the sulfonium salt to yield the ylid. (ii) A sulfonium ylid is generated by the direct electron transfer to the sulfonium salt.

The relationship between current density and cathode potential measured in DMSO clearly demonstrated that trimethylsulfonium iodide (**5**) was the most easily reducible of the three compounds (cyclohexanone, TEAT and V) shown in Fig 1. The oxirane compounds (**16**) was obtained in the controlled potential reduction of a mixture of **5** and cyclohexanone at −1·95 volt *vs* SCE where **5** is the exclusively reducible component as shown in Fig 1. In view of these facts, route (ii) seems acceptable as the mechanism of the ylid formation. Three possible paths could be suggested in route (ii).

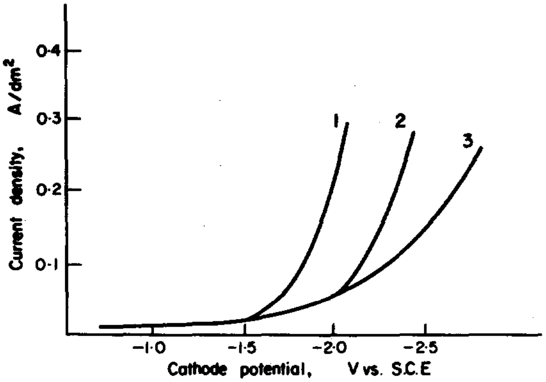


Fig 1. *Catholyte*: 1; DMSO (80 ml), cyclohexanone (30 g) and V (6 g). 2; DMSO (80 ml), cyclohexanone (30 g) and tetraethylammonium p-toluenesulfonate (TEAT) (4 g). 3; DMSO (80 ml) and TEAT (4 g). *Anolyte*: DMSO (10 ml) and TEAT (0·5 g).

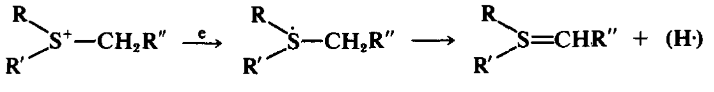
(a) The sulfonium ylid is formed by elimination of hydrogen after the electron is transfered to the vacant d-orbital of sulfur.

(b) The ylid is generated in one step by electrolytic reductive cleavage of the α C—H bond.

(c) The alkyl anion produced by reductive cleavage of the S^+-alkyl bond abstracts a proton from a sulfonium salt to yield an ylid.

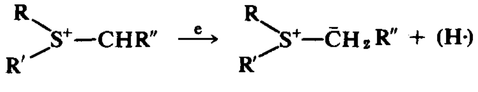
However, the quantity of toluene (trace) formed in the electroreduction of **3** in DMSO or benzaldehyde was too small to accept the path (c). Although the data obtained in the present study may not necessarily be sufficient to establish the propriety of path (a) or (b), the reasonable explanation of the mechanism of hydrogen ejection in the path (a) seems rather difficult.

When **3** was electrochemically reduced in benzaldehyde, **7**, **9** and **11** were also formed together with the usual product **10** of a sulfonium ylid with a carbon group. Compound **7** may be formed by a coupling reaction of the benzyl moiety of **3** *via* the reductive cleavage of the S^+-benzyl bond, since *p,p'*-dimethyl substituted compound **12** was pro-



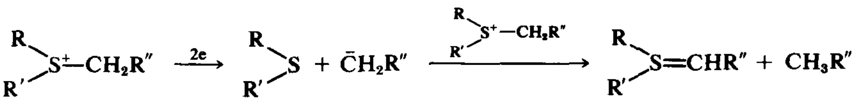
$$\mathrm{RR'S^+{-}CH_2R''} \xrightarrow{e} \mathrm{RR'\dot{S}{-}CH_2R''} \longrightarrow \mathrm{RR'S{=}CHR''} + (\mathrm{H}\cdot)$$

(a)



$$\mathrm{RR'S^+{-}CHR''} \xrightarrow{e} \mathrm{RR'S^+{-}\bar{C}H_2R''} + (\mathrm{H}\cdot)$$

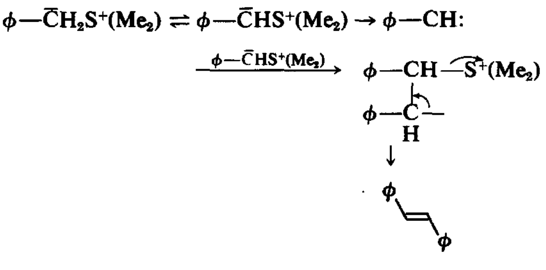
(b)



$$\mathrm{RR'S^+{-}CH_2R''} \xrightarrow{2e} \mathrm{RR'S} + \mathrm{\bar{C}H_2R''} \xrightarrow{\mathrm{RR'S^+{-}CH_2R''}} \mathrm{RR'S{=}CHR''} + \mathrm{CH_3R''}$$

(c)

duced in electroreduction of **4**. Compound **11** seems to be a secondary reduction product derived from **10**, as the independent electroreduction of **10** gave **11**. Previously, Yoshimine and Hatch[6] obtained **9** by the treatment of benzyldimethylsulfonium chloride with aqueous NaOH, and postulated a reaction of a sulfonium ylid with phenyl carbene generated from the ylid intermediate.



If this mechanism is supposed to be applicable to the electro-chemical formation of **9**, the electroreduction of **4** in benzaldehyde should give *trans-p,p′*-dimethylstilbene. The product actually formed was, however, a monomethyl substituted stilbene (**13**). Thus, the product **9** is certainly obtained from **3** and benzaldehyde, and not a secondary reduction product, because the independent electrolysis of **10** or **11** did not give **9**. On the basis of these facts, the formation of **9** may be attributable to an unusual reactivity of sulfonium ylid generated on the surface of the electrode.

When nitrogen ylids are generated intermediately from ammonium salts by base, 1-phenylethyldimethylamine[7] or *o*-methylbenzyldimethylamine[8] should be obtained from **21**, and 7-(n-butoxy)-norcarane must be formed from **22** in the presence of cyclohexene,[9] and **23** has to give methylenecyclohexane.[10] On the other hand, in the electroreduction of **21**, **22** or **23**, the formation of these products, which suggest the intermediary of nitrogen ylid were not observed, but the reductive cleavage of the N^+—C bond was confirmed. Accordingly it is concluded that, in the electroreduction sulfonium ylids are generated from sulfonium salts, whereas ammonium salts do not give ammonium ylids.

EXPERIMENTAL

Benzyldimethylsulfonium fluoroborate (**3**). A mixture of benzylchloride (45 g), dimethylsulfide (20 g) and water (10 g) was stirred at 30–40° until homogeneous. After fluoroboric acid (42%, 76 g) was added to the mixture, a ppt was formed by cooling. This was filtered off and recrystallized from EtOH-water as white crystals (72 g), m.p. 94–95°. (Found: C, 45·09; H, 5·17; Calcd. for $C_9H_{13}B_1F_4$; C, 45·02; H, 5·46%).

p-*Methylbenzyldimethylsulfonium fluoroborate* (**4**). Compound **4** was prepared by the same operation as for **3**, m.p. 164–165°. (Found: C, 47·04; H, 5·92. Calcd. for $C_{10}H_{15}B_1F_4$; C, 47·26; H, 5·95%).

Electroreduction of sulfonium salts in DMSO. In a 150 ml cylindrical cell, equipped with a reflux condenser, carbon electrodes and a reference electrode, was placed a solution of **3** or **18** (0·05 mole) in DMSO (80 ml). A ceramic cylinder was used to separate the cathodic and anodic chambers. The soln was electrochemically reduced at a cathode potential of −1·6 to −1·7 volt *vs* SCE and a current of 0·15 amp (0·42 amp/dm²) with a magnetic stirring until the current was decreased to about zero (*ca* 24 hr). The mixture was poured into excess water and extracted with ether. The ethereal soln was dried over $MgSO_4$ and distilled to remove ether. The residue was evaporated under reduced pressure. The product was isolated by preparative VPC and identified by comparison with an authentic material (IR, NMR, VPC). The yield was determined by VPC analysis of the original mixture.

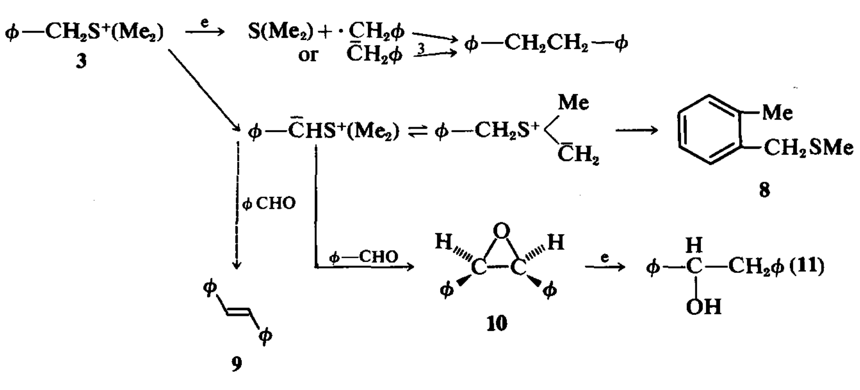
Electroreduction of sulfonium salts in benzaldehyde. A soln of a sulfonium salt (**3–6**) (0·03 mole) in benzaldehyde (130 ml) was electrolysed at a cathode potential of −1·6 to −2·1 volt *vs* SCE and the product was isolated according to the above method. Identification of products from (**3**), (**5**) and (**6**) was performed by comparison with authentic material.

Spectroscopic and analytical data of the products from **4** were as follows.

12: IR (nujol) 3050(w), 2950(s), 2860(s), 1510(m), 1460(s), 1380(s), 1218(m), 1140(m), 1100(m), 1040(m), 940(m), 810(s) 710(s) cm⁻¹; NMR (CCl_4) τ 2·93 (s, 8H), 7·13 (s, 4H), 7·70 (s, 6H). (Found: C, 91·21; H, 8·53. Calcd. for $C_{16}H_{18}$; C, 91·36; H, 8·64%).

13: IR (nujol) 3040(w), 2975(m), 2950(s), 2860(s), 1600(m), 1500(m), 1460(s), 1380(s), 965(s), 800(s), 745(s), 700(s) cm⁻¹; NMR (CCl_4) τ 2·35 ~ 2·98 (m, 11H), 7·65 (s, 3H). (Found: C, 92·67; H, 7·36. Calcd. for $C_{15}H_{14}$; C, 92·74; H, 7·25%.

(**14**): IR (nujol) 3040(w), 2975(m), 2950(s), 2860(s), 1500(w), 1460(s), 1380(s), 1150(m), 872(m), 860(m), 818(s), 790(m),



765(s), 740(s), 698(s) cm^{-1}; NMR (CCl_4) τ 2·64 (s, 5H), 2·79 (s, 4H), 6·16 (s, 2H). 7·63 (s, 3H). (Found: C, 85·64; H, 6·76. Calcd. for $C_{15}H_{14}O$: C, 85·68; H, 6·71%).

Electroreduction of (**5**) *in mixed solvents of DMSO and various ylid acceptors.* A soln of (**5**) (0·03 mole) and an ylid acceptor (0·3 mole) in DMSO (80 ml) was electrochemically reduced at a cathode potential of −2·0 to −2·1 volt *vs* SCE. Isolation and identification of products was performed according to the method described.

Electroreduction of ammonium salts (**21** ~ **23**). Compounds **21**, **22** and **23** (0·03 mole) were electrolysed in DMSO, a mixed solvent of acetonitrile and cyclohexene, and acetonitrile respectively. The products were isolated by preparative VPC and identified by comparison with authentic samples.

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