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PARTICIPATION AND REARRANGEMENT IN THE GAS-PHASE ELIMINATION KINETICS OF 3-(*o*-METHOXYPHENYL)PROPYL-1-METHANESULPHONATE AND 4-(*p*-METHOXYPHENYL)BUTYL-1-METHANESULPHONATE

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The gas-phase unimolecular elimination of the methanesulphonates in the temperature range 289·0–331·4 °C and pressure range 18–152·5 Torr follows a first-order rate law. The rate coefficients for the homogeneous reactions are expressed by the following equations: for 3-(*o*-methoxyphenyl)propyl-1-methanesulphonate $\log[k_1(s^{-1})] = (12{\cdot}04 \pm 0{\cdot}32) - [(167{\cdot}8 \pm 3{\cdot}6)\ kJ\ mol^{-1}](2{\cdot}303RT)^{-1}$ and for 4-(*p*-methoxyphenyl)butyl-1-methanesulphonate $\log[k_1(s^{-1})] = (12{\cdot}82 \pm 0{\cdot}30) - [(175{\cdot}1 \pm 3{\cdot}4)\ kJ\ mol^{-1}](2{\cdot}303RT)^{-1}$. The oxygen atom of the CH_3O substituent in 3-(*o*-methoxyphenyl)propyl-1-methanesulphonate appears to participate directly in the C—O bond polarization in order to produce some of the cyclic product dihydrobenzopyran. A parallel reaction occurs with 4-(*p*-methoxyphenyl)butyl-1-methanesulphonate where the *p*-anisyl substituent participates in the elimination process through a five-membered spiro intermediate for the formation of the cyclic product 6-methoxy-1,2,3,4-tetrahydronaphthalene. The second pathway of this elimination takes place via normal formation of the corresponding unsaturated aromatic hydrocarbons. These reactions are interpreted in terms of an intimate ion-pair type of mechanism.

INTRODUCTION

The phenyl substituent at the 2- or 4-position to the C—O bond in $C_6H_5(CH_2)_nOSO_2CH_3$ ($n = 2, 3, 4$) was found to assist in the rate of pyrolysis.[1] Moreover, because of the favourable five-membered structure for anchimeric assistance of the benzene ring when $n = 4$, an interesting cyclic product, tetralin, was also obtained. In view of these results, the presence of *o*- and *p*-CH_3O substitutents in the aromatic nuclei in phenylalkylmethanesulphonates was considered to be of interest in studying whether the resonance effect ($+R$) of this group strengthens the C_6H_5 assistance. In addition, even though the nucleophilicity of the *o*-CH_3O group is reduced by resonance interaction with the aromatic ring, it is plausible that the proximity of the p-electrons of the oxygen atom may favour direct participation of the C—O bond in the transition state, thus forming the corresponding cyclic product. This type of phenomenon has been observed in solvolytic reactions of closely related compounds.[2] In this context, this work was aimed at examining the kinetics and mechanisms of the gas-phase elimination of 2-(*o*-methoxyphenyl)ethyl-1-methanesulphonate, 2-(*p*-methoxyphenyl))ethyl-1-methanesulphonate, 3-(*o*-methoxyphenyl)propyl-1-methanesulphonate and 4-(*p*-methoxyphenyl)butyl-1-methanesulphonate.

RESULTS AND DISCUSSION

The rate of elimination of 2-(*o*-methoxyphenyl)ethyl-1-methanesulphonate, even in seasoned vessels and in the presence of the inhibitor cyclohexene, was difficult to determine. The pyrolysis products detected were benzodihydrofuran and anisole in a ratio of 3 : 1. Similarly, attempts to determine the *k*-values for 2-(*p*-methoxyphenyl)ethyl-1-methanesulphonate pyrolysis failed owing to the polymerization of the primary product *p*-methoxystyrene.

3-(*o*-Methoxyphenyl)propyl-1-methanesulphonate

The products of the gas-phase pyrolysis of 3-(*o*-methoxyphenyl)propyl-1-methanesulphonate, in a static system with vessels seasoned with allyl bromide and in the presence of the inhibitor cyclohexene, are described

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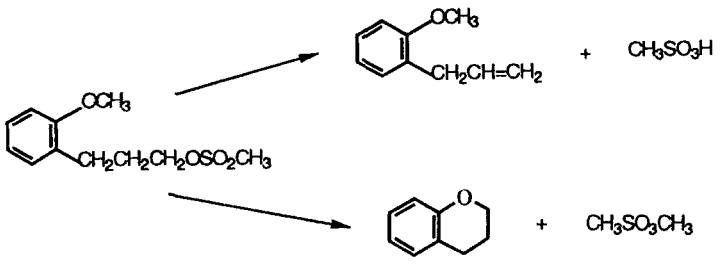
by the reaction



(1)

The stoichiometry represented by equation (1) was examined in the following manner. A series of reaction times of ten half-lives and four different temperatures gave an average experimental value of $P_f/P_0 = 1{\cdot}60$. The theoretical stoichiometry of equation (1) indicates that the final pressure, P_f, should be twice the initial pressure, P_0. The observed $P_f/P_0 < 2$ from the parallel elimination may be due to the polymerization of the product 3-(*o*-methoxyphenyl)prop-1-ene and its corresponding styrene isomer derivative.

The verification of the stoichiometry was possible by comparing, up to 50% reaction, the percentage decomposition of the substrate from pressure measurements with the sum of chromatographic analysis of dihydrobenzopyran and 3-(*o*-methoxyphenyl)prop-1-ene (Table 1).

The analyses of the elimination products of the methoxyphenylpropylmethanesulphonate, in seasoned vessels and in the presence of the free radical suppressor

Table 1. Stochiometry of the pyrolysis reactions

Compound parameter	Values			
3-(*o*-Methoxyphenyl)propyl-1-methanesulphonate at 310·0 °C				
Time (min)	2·5	5	10	15
Reaction (%) (pressure)	16·5	28·3	43·8	56·2
Dihydrobenzopyran (%) (chromatography)	10·5	17·8	22·6	31·4
3-(*o*-methoxyphenyl)prop-1-ene (%) (chromatography)	6·8	12·6	21·2	24·4
4-(Methoxyphenyl)butyl-1-methanesulphonate at 321·2 °C				
Time (min)	2	4	6	8
Reaction (%) (pressure)	28·9	49·0	62·5	72·5
p-Methoxyphenylbutenes (%) (chromatography)	28·0	44·3	53·4	57·4
6-Methoxy-1,2,3,4-tetrahydronaphthalene (%) (chromatography)	5·5	7·2	8·1	10·7

Table 2. Product distribution from pyrolysis of 3-(*o*-methoxyphenyl)propyl-1-methanesulphonate at different percentages of reaction at 310·0 °C

Reaction (%)	3-(*o*-Methoxyphenyl) prop-1-ene	Dihydrobenzopyran
17·3	39·1	60·7
30·4	41·5	58·6
43·8	48·5	51·5
55·8	43·7	56·3

Table 3. Product distribution from pyrolysis of 3-(*o*-methoxyphenyl)propylmethanesulphonate at different temperatures and 50% reaction

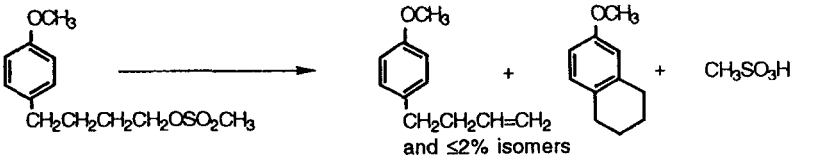
Temperature (°C)	3-(*o*-Methoxyphenyl) prop-1-ene	Dihydrobenzopyran
290	38·4	61·6
300·1	37·9	62·1
310·1	44·2	55·8
320·2	55·3	44·7
330·2	64·6	35·4

cyclohexene, are shown in Table 2. Within the limits of experimental error, the distribution of products appears to be invariant as the reaction progresses at the working temperature.

Further examination of the product distribution at different temperatures (Table 3) shows that the cyclic product dihydrobenzopyran tends to decrease whereas the corresponding aromatic alkene increases as the temperature increases.

4-(*p*-Methoxyphenyl)butyl-1-methanesulphonate

The pyrolysis products of this compound are described by the equation



(2)

Table 4. Distribution of products from pyrolysis of 4-(*p*-methoxyphenyl)butyl-1-methanesulphonate at different percentages of reaction at 321·0 °C

Reaction (%)	4-(*p*-Methoxyphenyl) but-1-ene[a]	6-Methoxy-1,2,3,4-tetrahydronaphthalene
28·1	83·7	16·3
49·0	85·7	14·3
62·5	82·0	18·0
72·5	83·4	16·6
80·0	83·5	16·5

[a] Yields of 4-(*p*-methoxyphenyl)but-2-ene and 1-(*p*-methoxyphenyl)-but-1-ene at about 2% are included.

The stoichiometry of reaction (2) indicates that $P_f = 2P_0$. The average experimental results of P_f/P_0 at five different temperatures and ten half-lives was 1·81. The fact that $P_f/P_0 < 2$ appears to be due to slight polymerization of the alkene products during pyrolysis.

Further examination of the stoichiometry of reaction (2), up to 70% reaction, showed that the extent of decomposition as predicted from pressure measurements was in good agreement with that determined by the sum of the chromatographic analyses of the products *p*-methoxyphenylbutenes and 6-methoxy-1,2,3,4-tetrahydronaphthalene (Table 1).

The yield of products of the methanesulphonate described in Table 4 shows, within experimental error, no variations with increasing percentage of reaction at a particular temperature. However, Table 5 indicates that up to about 50% reaction and at several different temperatures, an increase in the arylbutene and a decrease in the tetralin derivative occur as the temperature increases.

The effect of surface on the rate of pyrolysis of the two methanesulphonates was investigated by using a vessel packed with glass tubing in which the surface-to-volume ratio has been increased by a factor of 6 compared with the unpacked clean Pyrex vessel. When the packed and unpacked vessels were seasoned with the product of decomposition of allyl bromide, no significant effect on the rate coefficients was observed for either substrate (Table 6). However, the packed and unpacked clean Pyrex vessel had a marked effect on the rate of both methanesulphonate decompositions.

The effect of different proportions of the free radical suppressor cyclohexene in these reactions is shown in Table 7. The results indicate that cyclohexene does not affect the rates of elimination of 4-(*p*-methoxyphenyl)butyl-1-methanesulphonate. However, the rate coefficient for the elimination of 3-(*o*-methoxyphenyl)propyl-1-methanesulphonate was determined in the presence of a twofold excess of cyclohexene in order to inhibit any possible radical chain process of the substrate and/or products, and no induction period was observed. The rate coefficients are reproducible with a relative standard deviation not greater than 5% at a given temperature.

Table 5. Distribution of products from pyrolysis of 4-(*p*-methoxyphenyl)butyl-1-methanesulphonate at different temperatures at 50% reaction

Temperature (°C)	4-(*p*-Methoxyphenyl) but-1-ene[a]	6-Methoxy-1,2,3,4-tetrahydronaphthalene
289	64·7	35·3
300	66·6	33·4
310	74·0	26·0
314·5	81·9	18·1
321	85·7	14·3
331·4	89·1	10·9

[a] Including 2% yield of the two isomers 4-(*p*-methoxyphenyl)but-2-ene and 1-(*p*-methoxyphenyl)but-1-ene.

Table 6. Homogeneity of the reaction

	$10^4 k_1$ (s^{-1})	
Compound S/V (cm^{-1})[a]	A[b]	B[c]
3-(*o*-Methoxyphenyl)propyl-1-methanesulphonate at 310·0 °C		
1	–[d]	10·24
6	–[d]	10·42
4-(*p*-Methoxyphenyl)butyl-1-methanesulphonate at 310·0 °C		
1	–[d]	14·02
6	–[d]	13·96

[a] S = surface; V = volume.
[b] Clean Pyrex vessel.
[c] Vessel seasoned with allyl bromide.
[d] *k*-values are very high and irreproducible.

Table 7. Effect of cyclohexene inhibitor on rates

Compound P_0 (Torr)[a]	P_i (Torr)[a]	P_i/P_0	$10^4 k_1$ (s^{-1})
3-(*o*-Methoxyphenyl)propyl-1-methanesulphonate at 310·0 °C			
67·5	–	–	21·14
49·5	38	0·8	16·74
113·5	156·5	1·4	12·11
152·5	262	1·7	10·42
104	264	2·5	10·09
64	221·5	3·5	10·47
46	261·5	5·7	10·31
4-(*p*-Methoxyphenyl)butyl-1-methanesulphonate at 321·0 °C			
53	–	–	27·22
70	37	0·5	26·76
66	108·5	1·6	27·11
41·5	83	2·0	27·25
39	120·5	3·1	27·10

[a] P_0 = pressure of the substrate; P_i = pressure of cyclohexene inhibitor. 1 Torr = 133·3 Pa.

Table 8. Invariability of rate coefficients with initial pressure

Compound parameter	Values				
3-(*o*-Methoxyphenyl)propyl-1-methanesulphonate at 310·1 °C					
P_0 (Torr)[a]	46	64	91·5	104	152·5
$10^4 k_1$ (s^{-1})	10·31	10·47	10·06	10·09	10·42
4-(*p*-Methoxyphenyl)butyl-1-methanesulphonate at 314·5 °C					
P_0 (Torr)[a]	18	23·5	47	65	81	99
$10^4 k_1$ (s^{-1})	18·63	18·11	18·00	18·54	18·45	18·44

[a] 1 Torr = 133·3 Pa.

Table 9. Temperature dependence of rate coefficients

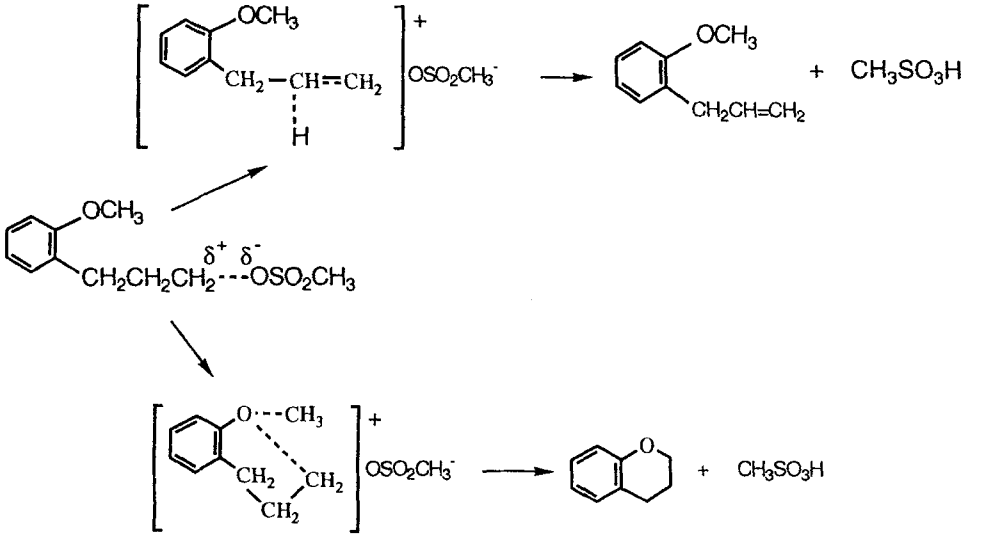
Compound parameter	Values					
3-(*o*-Methoxyphenyl)propyl-1-methanesulphonate						
Temperature (°C)	290·0	300·1	310·1	320·2	330·2	
$10^4 k_1$ (s^{-1})[a]	3·06	5·67	10·24	18·23	33·54	
4-(*p*-Methoxyphenyl)butyl-1-methanesulphonate						
Temperature (°C)	289·0	300·0	310·0	314·5	321·0	331·4
$10^4 k_1$ (s^{-1})[b]	3·60	7·12	14·02	18·36	27·10	48·80

[a] $\text{Log}[k_1\ (s)^{-1})] = (12·04 \pm 0·32) - [(167·8 \pm 3·6)\ \text{kJ mol}^{-1}]\ (2·303RT)^{-1}$.
[b] $\text{Log}[k_1\ (s)^{-1})] = (12·82 \pm 0·30) - [(175·1 \pm 3·4)\ \text{kJ mol}^{-1}]\ (2·303RT)^{-1}$.

The rate coefficients for the pyrolytic elimination of these methanesulphonates were found to be invariant with their initial pressure (Table 8). The logarithmic plots are linear up to 50% decomposition for 3-(*o*-methoxyphenyl)propyl-1-methanesulphonate and up to 70% for 4-(*p*-methoxyphenyl)butyl-1-methanesulphonate. The variation of the rate coefficients of the methanesulphonates with temperature, in seasoned vessels and in the presence of the inhibitor cyclohexene, is shown in Table 9. The data were fitted to the Arrhenius equation where 90% confidence limits from a least-squares procedure are quoted.

Efforts to determine the pyrolyses kinetics of 2-(*o*-methoxyphenyl)ethyl-1-methanesulphonate for anchimeric assistance of the phenyl group and oxygen participation for a five-membered conformation were very complex with erratic product analysis. The only products detected were benzodihydrofuran and anisole in the ratio 3:1. Similarly, determination of the rate coefficients for 2-(*p*-methoxyphenyl)ethyl-1-methanesulphonate was found to be unreliable and irreproducible at any working temperature. After a slow pressure decrease up to 25% decomposition, the reaction tends to stop completely thereafter. This effect may be due to the rapid polymerization of the product *p*-methoxystyrene. Because of this, it is not possible to assess whether the *p*-anisyl substituent assists the rate of CH_3SO_3H elimination during the pyrolysis of *p*-$CH_3OC_6H_4CH_2CH_2OSO_2CH_3$.

The pyrolysis of 3-(*o*-methoxyphenyl)propyl-1-methanesulphonate, with a possible six-membered conformation of oxygen participation, yielded, in addition to the normal elimination product 3-(*o*-methoxyphenyl)prop-1-ene, the cyclic product dihydrobenzopyran. This result suggests the mechanism of a parallel reaction in terms of an intimate ion-pair intermediate by intramolecular solvation or autosolvation of the leaving methanesulphonate ion [equation (3)].



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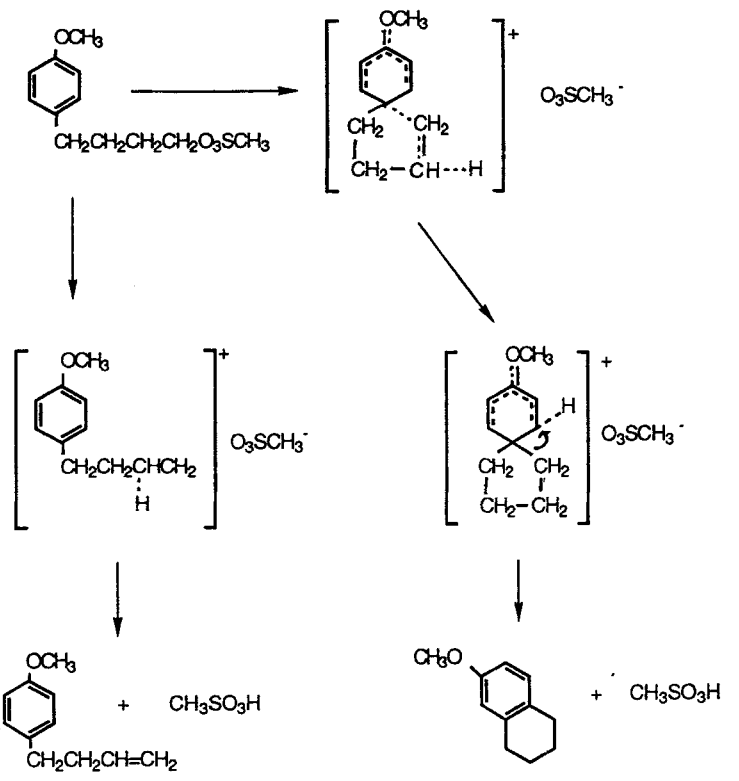

(4)

Table 10. Arrhenius parameters for $ZCH_2CH_2OSO_2CH_3$ at 320·0 °C

Z	10^4k_1 (s^{-1})	10^4k_H (s^{-1})[a]	E_a (kJ mol^{-1})	Log[A (s^{-1})]
o-$CH_3OC_6H_4CH_2$	18·20	9·10	167·8 ± 3·6	12·04 ± 0·32
p-$CH_3OC_6H_4CH_2CH_2$	25·12	12·56	175·1 ± 3·4	12·82 ± 0·30

[a] k_H = Rate per β-hydrogen.

In the case of the elimination kinetics of 4-(*p*-methoxyphenyl)butyl-1-methanesulphonate, the resonance effect (+ *R* or + *M*) of the methoxy substituent towards the aromatic nuclei led to a significant increase in the formation of the corresponding cyclic derivative of tetralin (6-methoxy-1,2,3,4-tetrahydronaphthalene) when compared with the production of tetralin from 4-phenylbutyl-1-methanesulphonate pyrolysis.[1] According to the present results, the mechanism for methoxyphenylbutylmethanesulphonate proceeds via two pathways leading through normal elimination to the formation of the corresponding unsaturated aromatic hydrocarbon and to some extent, owing to the anchimeric assistance of the *p*-anisyl substituent, a rearrangement with ring expansion to give 6-methoxy-1,2,3,4-tetrahydronaphthalene [equation (4)].

The above mechanism is also rationalized in terms of an intimate ion-pair intermediate by intramolecular solvation of the leaving $CH_3SO_3^-$ group.

Table 10 gives the Arrhenius parameters of the methoxyphenylmethanesulphonates at 320·0 °C. The fact that the formation of dihydrobenzopyran and methoxytetrahydronaphthalene (Tables 3 and 5) tends to decrease with increasing temperature may be due to a decrease in the polar or ionic nature of the elimination process.

EXPERIMENTAL

3-(o-Methoxyphenyl)propyl-1-methanesulphonate. This substrate was obtained by treating the corresponding alcohol (Aldrich) in diethyl ether with CH_3SO_2Cl.[3] The methanesulphonate product decom-

poses on distillation; it was purified in an alumina chromatographic column using hexane–diethyl ether (9 : 1) as solvent. The purity of the substrate was 99·8% as determined by GLC (3% OV-17 on Chromosorb QII, 80–100 mesh). NMR: δ 2·00 (m, 2H), 2·85 (m, 2H), 2·95 (s, 3H), 3·80 (s, 3H), 4·20 (t, 2H), 7·10 (m, 4H). Quantative analysis of the products was effected in the same OV-17 column. 3-(*o*-Methoxyphenyl)prop-1-ene: MS, *m/z* 148 (M^+), 133 ($M^+ - CH_3$), 105 ($M^+ - C_2H_4$), 91 ($C_7H_7^+$). Dihydrobenzopyran: MS, *m/z* 134 (M^+), 115 ($C_9H_7^+$), 106 ($M^+ - C_2H_4$), 91 ($C_7H_7^+$), 78 ($C_6H_6^+$).

4-(p-Methoxyphenyl)butyl-1-methanesulphonate. This compound was prepared by adding CH_3SO_2Cl to the corresponding alcohol (Aldrich) in diethyl ether as reported.[3] The reaction product had to be purified as above in an alumina chromatographic column using hexane–diethyl ether (1 : 1) as solvent. The purity of the methanesulphonate substrate was >95% as determined by NMR: δ 1·60 (m, 4H), 2·55 (m, 2H), 2·90 (s, 3H), 3·75 (s, 3H), 4·20 (m, 2H), 6·95 (dd, 4H). Quantitative analysis of the pyrolysis products was effected in a 6 ft column of 10% Dow Corning 200/100 on Chromosorb W AW DMCS (80–100 mesh). 6-Methoxy-1,2,3,4-tetrahydronaphthalene: MS, *m/z* 162 (M^+), 134 ($M^+ - C_2H_4$), 91 ($C_7H_7^+$), 131 ($M^+ - CH_3O$). 4-(*p*-Methoxyphenyl)but-1-ene: MS, *m/z* 162 (M^+), 121 ($M^+ - C_3H_6$), 91 ($C_7H_7^+$). 4-(*p*-Methoxyphenyl)but-2-ene: MS, *m/z* 162 (M^+), 121 ($M^+ - C_3H_6$), 91 ($C_7H_7^+$). 1-(*p*-Methoxyphenyl)but-1-ene: MS, *m/z* 162 (M^+), 147 ($C_{10}H_{11}O^+$), 91 ($C_7H_7^+$).

The kinetic runs were performed in a static system[4,5] seasoned with allyl bromide, and the rates were followed by measuring the pressure increase and/or by chromatographic analyses of the products. The temperature was kept to better than ±0·2 °C and measured with a calibrated platinum–platinum–13% rhodium thermocouple. Different points along the reaction vessel showed no temperature gradient. The substrate were injected into the reaction vessel with a syringe through a silicone-rubber injection system and the reaction walls were reconditioned with allyl bromide pyrolysis after each group of 2–3 kinetic runs on the substrate.

Other compounds. Similar procedures to the above were applied for the syntheses of 2-(*o*-methoxyphenyl)ethyl-1-methanesulphonate [NMR: δ 2·85 (s, 3H), 3·05 (t, 2H), 3·85 (s, 3H), 4·40 (t, 2H), 6·90 (t, 2H), 7·20 (m, 2H). MS: *m/z* 230 (M^+), 121 ($M^+ - C_8H_9O$), 134 ($M^+ - CH_3SO_3H$), 91 ($C_7H_7^+$)] and 2-(*p*-methoxyphenyl)ethyl-1-methanesulphonate[1] [NMR: δ 2·90 (s, 3H), 3·00 (t, 2H), 3·80 (s, 3H), 4·40, (t, 2H), 7·05 (m, 4H)] and their purifications.

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REFERENCES

1. G. Chuchani, R. M. Domínguez, A. Rotinov, I. Martín and J. Alvarez, *G. J. Phys. Chem.* **99**, 3341 (1990).
2. B. Capon and S. P. McManus, *Neighboring Group Participation*, Vol. 1, Chapt. 4. Plenum Press, New York (1976).
3. W. C. Ross, *J. Chem. Soc.* 2420 (1957).
4. A. Maccoll, in *Techniques of Organic Chemistry*, edited by A. Weissberger, Vol. VIII, Part I, Chapt. X, p. 435. Interscience, New York (1961).
5. A. Maccoll, *Chem. Rev.* **69**, 33 (1969).