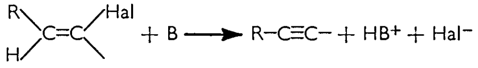
397. *Nucleophilic Reactions in Ethylenic Derivatives. Part VIII.* Mechanisms of the Reactions of Primary and Secondary Amines with Arylsulphonylhalogenoethylenes*

By S. Ghersetti, G. Lugli, G. Melloni, G. Modena, P. E. Todesco,
and P. Vivarelli

The reactions of arylsulphonylhalogenoethylenes with primary and secondary amines in methanol, ethanol, and propan-2-ol have been studied. *cis*-1-Arylsulphonyl-2-bromoethylene and *cis*-1-arylsulphonyl-2-bromo- and -2-chloro-prop-1-ene, show irregular kinetic behaviour, sensitivity to the salt of the reacting base in methanol and ethanol (but not in propan-2-ol), whilst the others behave regularly in all the solvents. In the lower alcohols, but not in propan-2-ol, hydrogen–deuterium exchange at carbon 1 is faster than the substitution.

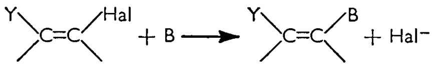
A detailed analysis of the results in the light of previous research on nucleophilic substitution at an ethylenic centre indicates that primary and secondary amines react by " direct substitution." In methanol and ethanol an elimination–addition mechanism involving alkoxide ions is also observed.

Vinylic halides (I) are known to be very unreactive towards nucleophilic substitution; elimination, on the other hand, when it is possible, often occurs rather readily.[1]



(I) (II)

It is also known that " activated " vinylic halides (III) are much more generally reactive and that they give mainly substitution products (IV).[2-4]



(III) (IV)

Activation occurs with strong electron-withdrawing groups such as COR, CO_2R, SOR, and SO_2R, which by inductive and/or mesomeric effects facilitate nucleophilic attack by the reagent at the carbon bonded to the halogen. However, it has also been shown [3] that elimination is accelerated by electron-withdrawing groups and that a formal substitution

* Part VII, *Gazzetta*, 1961, **91**, 620.

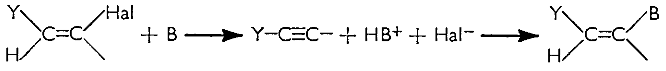
[1] S. I. Miller, *J. Org. Chem.*, 1961, **26**, 2619; *J. Amer. Chem. Soc.*, 1959, **81**, 6313; E. D. Hughes, *Trans. Faraday Soc.*, 1938, **34**, 185; V. Gold, *J.*, 1951, 1430; J. F. Bunnet in " Theoretical Organic Chemistry," Butterworth, London, 1959, p. 144.

[2] S. I. Miller and P. K. Yonan, *J. Amer. Chem. Soc.*, 1957, **79**, 5931; F. Montanari, *Boll. sci. Fac. Chim. ind. Bologna*, 1958, **16**, 31; D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *J.*, 1960, 2349.

[3] S. Ghersetti, G. Modena, P. E. Todesco, and P. Vivarelli. *Gazzetta*, 1961, **91**, 620, and earlier Papers of the series.

[4] S. Patai and Z. Rappoport, " The Chemistry of Alkenes," ed. Patai, Interscience Publ., London, 1964, ch. 8.

reaction may occur *via* an " elimination–addition " path in which addition is so fast that the intermediate acetylenic derivative (V) is not easily detected.



(III) (V) (IV)

The mechanism of the overall reactions in terms of the competition between direct substitution and elimination–addition has been recently elucidated, and generally discussed for the case where the reagent is an anionic nucleophile.[3] It has been shown that the true substitution is normally stereospecific [2,3] and that elimination may prevail over substitution only when hydrogen and halogen are *trans*-related. Under these conditions, the relative ease of the two reaction paths depends on the leaving group and, more strongly, on the nature of the nucleophile: bromo-derivatives give more ready elimination than the chloro-analogues, and basic anions (RO^-) are much more effective than less basic and polarisable anions (RS^-) in favouring elimination over substitution.

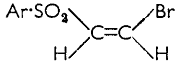
The reactions with amines have been much less thoroughly studied: [5] in this case the reaction is not stereospecific and, to the first approximation, it seems that the behaviour of neutral reagents is intermediate between that of thiophenoxide and of alkoxide ions. However, there are some ill-defined points and the present study was carried out to gain a more detailed picture of the reactions with primary and secondary amines.

As in our previous studies, *p*-tolylsulphonylhalogenoethylenes (VI) were chosen as substrates.

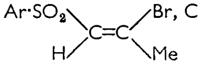
$p\text{-Me}\cdot C_6H_4\cdot SO_2\cdot CR{=}CR'\cdot Hal$ (VI) R, R′ = H, Me
Hal = Cl, Br

Results

Salt effect. Most of the reactions of arylsulphonylhalogenoethylenes with primary and secondary amines (cyclohexylamine, dibutylamine, dimethylamine) in methanol followed regular second-order kinetics but, when the substrate was very susceptible to elimination, as with compounds (VII) and (VIII), irregular kinetic behaviour was observed; [6] the second-order rate coefficent, particularly in the first stages of the reaction, decreasing with time.



(VII)



(VIII)

However, simple second-order kinetic behaviour was observed when the perchlorate of the amine was added, even at low concentration (1—2 × 10^{-2} mole/l.): *i.e.*, at a concentration of the same order of magnitude as that of the halogenoethylene. The initial rate was, under these circumstances, reduced (Table 1).

Table 1

Effect of the perchlorate of the base on the reaction of *cis*-2-bromo-1-*p*-tolylsulphonylprop-1-ene (~1·20 × 10^{-2}M) with cyclohexylamine and dimethylamine in methanol at 25·0°

	Cyclohexylamine (~5·8 × 10^{-2}M)								
[$C_6H_{11}NH_3^+$] (10^{-2}M)	—	0·18	0·53	1·76	2·50	5·28	7·75	8·05	11·04
10^3k (sec.$^{-1}$ mole^{-1} l.)	36 *	26 *	12·6 *	9·3	7·52	5·50	5·08	4·60	4·06
	Dimethylamine (~6 × 10^{-2}M)								
[$(CH_3)_2NH_2^+$] (10^{-2}M)	—	0·9	1·8	3·6	5·0	5·99			
10^3k (sec.$^{-1}$ mole^{-1} l.)	49 *	9·34	8·31	7·56	7·71	7·55			

* Initial rate.

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[5] G. Modena *et al.*, *Gazzetta*, 1959, **89**, 878; 1960, **90**, 694; *Ricerca sci.*, 1960, **30**, 894; *Boll. sci. Fac. Chim. ind. Bologna*, 1960, **18** 66; F. Montanari, *Gazzetta*, 1956, **86**, 415; see also ref. 2.

[6] L. Maioli, G. Modena, and P. E. Todesco, *Boll. sci. Fac. Chim. ind. Bologna*, 1960, **18**, 66; see also ref. 5.

The effect of the salt, which was very large at the beginning, tended to level off at higher concentration; at constant salt concentration the rate coefficient was not very sensitive to change in amine concentration (Table 2) but a small decrease in rate was observable for the higher values.

TABLE 2

Effect of the amine concentration at constant salt concentration $[C_6H_{11}NH_3^+ClO_4^-] = 1{\cdot}76 \times 10^{-2}$M) in the reaction of *cis*-2-bromo-1-*p*-tolylsulphonylprop-1-ene ($1{\cdot}20 \times 10^{-2}$M) with cyclohexylamine in methanol at 25·0°

$[C_6H_{11}NH_2]$ (10^{-2}M)	4·44	5·70	5·81	7·12	7·76	10·0
10^3k	9·32	9·52	9·30	8·75	8·84	8·02

The other halogenoethylenes studied did not show these effects: the rate coefficents were constant with time and not significantly altered by the addition of the salt of the reacting base. A summary of the results obtained with various halogenoethylenes is given in Table 3.

The effect of lithium perchlorate on the reactions was studied (Table 4). A normal positive salt effect was observed, as expected, for reactions between neutral molecules, leading to ionic products. The magnitude of the salt effect does not appear to depend on whether or not the reaction is sensitive to the conjugate acid of the nucleophile.

Hydrogen–deuterium exchange. All the compounds here considered, when allowed to react completely with primary and secondary amines in deuteromethanol (CH_3OD), yielded products which contained substantial amounts of deuterium at C-1 (deduced by infrared analysis, see Experimental section).

TABLE 3

Effect of amine perchlorate on the rate of reaction (10^3k) of halogeno-alkenes with amines in methanol

	Cyclohexylamine		Dibutylamine		
Compound	No perchlorate	[Perchlorate] = $1{\cdot}8 \times 10^{-2}$M	No perchlorate	[Perchlorate] = $1{\cdot}8 \times 10^{-2}$M	Temp.
cis-*p*-Me·C_6H_4·SO_2·CH:CHCl	0·46 *	0·43	2·38 *	2·50	0·0°
trans-*p*-Me·C_6H_4·SO_2·CH:CHCl	0·23 *	0·21	2·85 *	3·08	0·0
cis-*p*-Me·C_6H_4·SO_2·CH:CHBr	16 † ‡	4·25	11 † ‡	4·8	0·0
trans-*p*-Me·C_6H_4·SO_2·CH:CHBr	0·22 †	0·23	3·06 †	3·15	0·0
cis-*p*-Me·C_6H_4·SO_2·CH:CCl·Me	0·40 ‡	0·15	0·30 ‡	0·16	25·0
cis-*p*-Me·C_6H_4·SO_2·CH:CBr·Me	40 ‡	9·6	40 ‡	6·4	25·0

* See ref. 16. † See ref. 14; the values for the *cis*-compounds are somewhat higher than those previously reported for a better evaluation of the initial rate. ‡ Initial rate.

TABLE 4

Effect of lithium perchlorate on reaction of halogeno-alkenes with cyclohexylamine (6×10^{-2}M) in methanol at 25·0°

cis-2-Bromo-1-*p*-tolylsulphonylprop-1-ene ($1{\cdot}20 \times 10^{-2}$M); $[C_6H_{11}NH_3^+ClO_4^-]$ — $1{\cdot}80 \times 10^{-2}$M.

$[LiClO_4]$ (10^{-2}M)	—	1·45	2·87	4·31	6·03	10·06
10^3k	9·3 *	9·83	11·2	12·5	13·7	16·3

trans-2-Chloro-1-*p*-tolylsulphonylethylene ($1{\cdot}2 \times 10^{-2}$M).

$[LiClO_4]$ (10^{-2}M)	—	1·48	4·30	6·96	10·86	14·75
10^3k	1·78 †	1·93	2·14	2·21	2·34	2·45

* See Table 1. † See ref. 16.

Consistently, the *cis*- and *trans*-deutero-compounds (VI; R = D, R′ = H, Hal = Cl or Br), on reaction with cyclohexylamine in methanol, yielded products containing no deuterium; the exchange at C-1 was, in this case, complete. With secondary amines, on the other hand, exchange was not complete since some deuterium remained in the final product.

The interpretation of these results is made difficult by the observation that the cyclohexylaminoethylene itself under goes hydrogen exchange at carbon-1 in presence of an excess of base, whilst this does not occur with the products derived from the secondary amines. The exchange reaction of the cyclohexylamine derivative is not due to addition–elimination of the base across the double bond: indeed with the aid of isotopically labelled cyclohexylamine it was shown that the exchange does not involve the cyclohexylamino-residue (see Experimental section).

The exchange may arise from the tautomeric equilibrium $-CH{:}CH{\cdot}NHR \rightleftharpoons -CH_2{\cdot}CH{:}NR$ (which is impossible with the derivatives of secondary amines).

The hydrogen–deuterium exchange in the substrate was investigated directly by measuring the decrease in deuterium content of unreacted substrate isolated from the reaction mixtures at various times. A summary of the results is given in Table 5. The data show a quite evident decrease in the percentage of exchange when the salt of the reacting base is present.

A clearer indication of the velocity of hydrogen exchange is given by the data in Table 6 where the percentages of exchange of the four typical compounds at a fixed time are reported. Rough values of the rate of the exchange were calculated using the expression

$$k = 2{\cdot}303/t \,.\, \log\{100/(100 - x)\}.$$

These values are, of course, approximate since they have been calculated using only one time value and also because, as shown in Table 5, the rates of exchange are quite sensitive to, and slowed down by, the presence of the salt of the reacting base. They are considered to be correct within a factor of two.

Spectroscopic identification of the acetylenic intermediate. Infrared analysis (1 mm. CaF_2 cell) of solutions from the reactions of *cis*-2-bromo-1-*p*-tolylsulphonylprop-1-ene (VI; $R = H$, $R' = Me$, $Hal = Br$) ($\sim 3 \times 10^{-2}$M) with cyclohexylamine and dibutylamine ($\sim 15 \times 10^{-2}$M) in methanol and in ethanol showed the presence of 1-p-tolylsulphonylpropyne (sharp band at 2210 cm.$^{-1}$). However, in propan-2-ol no evidence of the acetylenic intermediate was detectable.

TABLE 5

Reaction of 2-halogeno-1-*p*-tolylsulphonyl [1-^{2}H]ethylenes ($1{\cdot}20 \times 10^{-2}$M) with amines ($6 \times 10^{-2}$M) in methanol

Compound	Amine	Temp.	Time (min.)	Reaction (%)	Perchlorate concn. (10^{-2}M)	Exchange (%) *
trans-2-Chloro	Cyclohexylamine	25°	90	50	—	88
trans-2-Chloro	Dibutylamine	25	8	50	—	28
cis-2-Chloro	Cyclohexylamine	25	45	50	—	100
trans-2-Bromo	Cyclohexylamine	25	100	50	—	94
trans-2-Bromo	Cyclohexylamine	25	100	—	1·8	91
trans-2-Bromo	Cyclohexylamine	25	30	16	—	83
trans-2-Bromo	Cyclohexylamine	25	30	—	1·8	43·5
trans-2-Bromo	Dibutylamine	0	45	50	—	28
cis-2-Bromo	Cyclohexylamine	0	16	50	—	34·5
cis-2-Bromo	Cyclohexylamine	0	16	—	1·8	20·5
cis-2-Bromo	Dibutylamine	0	23	50	—	40·5
cis-2-Bromo	Dibutylamine	0	23	—	1·8	17·5

* To ±3%.

TABLE 6

Percentage of exchange at 10 min., rates of exchange (k_e) and of substitution (k_s) for reaction of 2-halogeno-1-*p*-tolylsulphonyl[1-^{2}H]ethylene with amines in methanol at 0°

	Cyclohexylamine			Dibutylamine		
Compound	Exchange (%)	10^3k_e	10^3k_s	Exchange (%)	10^3k_e	10^3k_s
cis-2-Chloro	23	5·9	0·46	9	2·2	2·38
trans-2-Chloro	11	2·6	0·23	6·5	1·6	2·70
cis-2-Bromo	31	8·4	4·30 *	26	6·8	4·8 *
trans-2-Bromo	20	5·0	0·22	10	2·3	3·06

* In the presence of the perchlorate of the base ($1{\cdot}8 \times 10^{-2}$M).

Solvent effect. Change of solvent from methanol to ethanol and to propan-2-ol had little effect in some cases and a fairly large one in others (Table 7). The compounds which showed good second-order kinetic behaviour and were not sensitive to the presence of the conjugate acid of the base were also not very sensitive to solvent change. On the other hand, those compounds for which decreasing second-order rate coefficients and sensitivity to the conjugate acid of the base were observed showed rates which decreased markedly with change of solvent from methanol to propan-2-ol.

Another aspect of the solvent effect is illustrated in Table 8. The salt sensitivity is clearly dependent upon the solvent since it is almost absent in propan-2-ol but present in ethanol and in methanol.

The rate of hydrogen exchange is also affected by the solvent (Table 9). The percentage of exchange at equal times is much greater in methanol than in propan-2-ol, where it is extremely slow. The behaviour of ethanol is intermediate.

TABLE 7

Effect of solvent on the rate of reaction (10^3k) of 2-halogeno-1-*p*-tolylsulphonylalkenes with amines at 25·0°

	Cyclohexylamine			Dibutylamine		
Compound	MeOH	96% EtOH	Pr^{i}OH	MeOH	96% EtOH	Pr^{i}OH
cis-p-Me·C$_6$H$_4$·SO$_2$·CH:CHCl	3·94 *	5·98	8·10	16·2 *	22·3	28·7
trans-p-Me·C$_6$H$_4$·SO$_2$·CH:CHCl ...	1·78 *	2·65 †	3·30	20·6 *	31·7	39
cis-p-Me·C$_6$H$_4$·SO$_2$·CH:CHBr	68 ‡	47 ‡	13	66 ‡	46 ‡	33
trans-p-Me·C$_6$H$_4$·SO$_2$·CH:CHBr ...	1·98	2·35	3·67	24·7	34·8	42·1
cis-p-Me·C$_6$H$_4$·SO$_2$·CH:CCl·Me	0·40 ‡	0·42	0·16	0·30 ‡	0·20	0·17
cis-p-Me·C$_6$H$_4$·SO$_2$·CH:CBr·Me......	40 ‡	11	1·20	40 ‡	6·60	0·92

* See ref. 16. † 10^3k = 2·9 in absolute ethanol. ‡ Initial rate.

TABLE 8

Effect of cyclohexylamine perchlorate on the rates of reaction (10^3k) of halogenoalkenes with cyclohexylamine in various solvents at 25·0°

	trans-p-Me·C$_6$H$_4$·SO$_2$·CH:CHBr			*cis-p*-Me·C$_6$H$_4$·SO$_2$·CH:CHBr			*cis-p*-Me·C$_6$H$_4$·SO$_2$·CH:CBr·Me		
	MeOH	EtOH	Pr^{i}OH	MeOH	EtOH	Pr^{i}OH	MeOH	EtOH	Pr^{i}OH
No perchlorate	**1·78**	2·40	**3·67**	68 *	47 *	**13**	**36** *	11 *	1·20
[Perchlorate] = $1·8 \times 10^{-2}$ M	1·67	2·70	3·85	30	17	12·5	9·6	3·40	1·04

* Initial rate.

TABLE 9

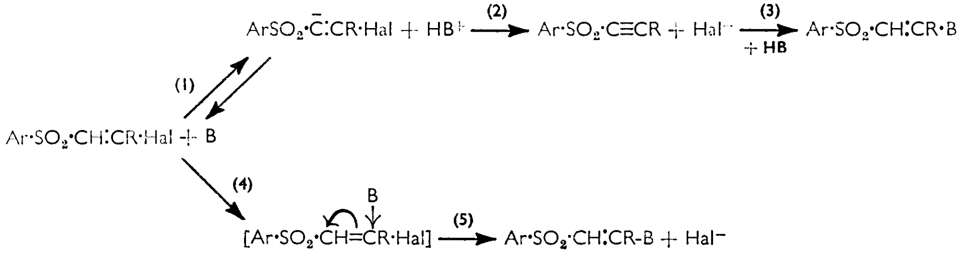
Solvent effect on the hydrogen exchange of 2-bromo-1-*p*-tolylsulphonylethylene with cyclohexylamine at 0·0° after 10 min.

Isomer		Methanol	Ethanol	Propan-2-ol *
cis	Exchange (%)	31	9	0
trans	Exchange (%)	19·5	10	—

* The exchange after 50 min. was 4%.

DISCUSSION

The mechanism of the reactions of arylsulphonylhalogenoethylenes with anionic nucleophiles, previously discussed,[3] may be summarised as follows:



The reactions of amines should fit the same picture, but might be complicated, however, because the acid–base equilibria of amines in hydroxylic solvents could lead to the presence of a second reagent (RO$^-$) in the system.

From the results given above it appears that primary and secondary amines behave quite similarly, apart from minor differences in velocity, and therefore, they will be discussed together. On the other hand, in methanol and ethanol, the halogenoethylenes, as already pointed out and later discussed in detail, may be subdivided into two groups, differing in kinetic behaviour, whilst in propan-2-ol the reactions of all the compounds show the same features.

Two main factors, therefore, appear to affect the reactions: the solvent and the nature of the substrate.

Reactions in propan-2-ol. All the compounds follow regular second-order kinetic behaviour, the salt of the reacting base does not affect the rate, *cis*- and *trans*-chloro- and -bromo-derivatives all react at almost the same rate * and hydrogen exchange is very slow compared with substitution. Indeed there is no evidence for the participation of the elimination–addition mechanism and the general picture is very similar to that found for the thiophenoxide reactions.[3]

The substitution with primary and secondary amines is, therefore, in this solvent " true " direct substitution. However, the reactions differ from those with thiophenoxide in that they are not stereospecific. This presumably reflects a greater stability of amino-adducts whose lifetime must be sufficiently long for rotation to lead to the thermodynamically stable product. This seems reasonable since the initial amino-adducts are dipolar ions whereas the adducts formed with mercaptide ions carry a full negative charge.

Reactions in methanol and ethanol. In these solvents the general picture resembles that found for the methoxide-ion reactions: [3] extensive hydrogen exchange accompanies the substitution, different behaviour between *cis*- and *trans*-derivatives is observed, and a definite sensitivity to the salt of the reacting base affects the kinetic behaviour of the *cis*-compounds; moreover in some reactions the acetylenic intermediate can be detected.

All these facts may be rationalised on the basis of the relatively fast reaction (1) (see Scheme) and with the participation of the elimination–addition mechanism.

The equilibrium (1) assumes the form (6) when the nucleophile is an amine:

$$\text{Ar}\cdot\text{SO}_2\cdot\text{CH}{:}\text{CH}\cdot\text{Hal} + \text{R}\cdot\text{NH}_2 \rightleftharpoons \text{Ar}\cdot\text{SO}_2\cdot\overset{-}{\text{C}}{:}\text{CH}\cdot\text{Hal} + \text{R}\cdot\text{NH}_3^+ \quad (6)$$

The hydrogen exchange in the unreacted halogenoethylenes is consistent with the existence of such an equilibrium or of a similar one involving alkoxide ion [see (7) below]; the depression of the exchange by the salt of the reacting base is strictly correlated with it because an increase in the concentration of $\text{R}\cdot\text{NH}_3^+$ shifts the equilibrium to the left.

As in the reaction with methoxide ion the formation of the carbanion is not in itself a sufficient condition for the occurrence of the elimination–addition path, since reaction (2) may still be slower than reaction (4) (see Scheme) as discussed above and elsewhere.[3] This is the case of the reactions of *trans*-derivatives and also of *cis*-2-chloro-1-*p*-tolylsulphonylethylene (VI; $R = R' = H$; $\text{Hal} = \text{Cl}$). The general features of these reactions are, indeed, very similar to those in propan-2-ol and it seems very likely that, notwithstanding the hydrogen exchange, they react by direct substitution. In fact, the same picture was found for the reactions of *trans*-derivatives with methoxide ion in methanol and the same conclusions were reached.[3]

On the other hand, the other group of compounds (*i.e.*, *cis*-derivatives in general), which have previously been shown to undergo elimination–addition with methoxide ion, show, with the hydrogen exchange, falling second-order rate coefficients and sensitivity to the salt of the reacting base.

This suggests that the carbanion is a necessary intermediate in the reaction path leading to the final products. The falling second-order rate coefficients now receive a natural explanation; *i.e.*, progressive increase in the conjugate acid of the amine displaces

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* This is not strictly true for the 2-methyl compounds, though in this case the difference between the bromo- and chloro-derivatives are still significantly smaller than in other solvents.

equilibrium (6) to the left, and the concentration of the intermediate carbanion is consequently reduced. Consistently, when enough salt is added at the beginning, so that the total concentration of the salt does not significantly change during the reaction, simple second-order kinetics are observed.

Therefore, it may be safely stated that the second group of compounds react, at least partly, by elimination–addition and that the participation of this mechanism in the overall reaction is responsible for the kinetic complications observed, which, in turn, assume a diagnostic character.

However, the complete absence of elimination–addition in propan-2-ol suggests that equilibrium (6) is not a complete description of the system and that the acid–base equilibria of the amines with the solvents must be taken into consideration:

$$\mathrm{RNH_2 + ROH \rightleftharpoons RNH_3^+ + RO^-}$$

$$\mathrm{Ar{\cdot}SO_2{\cdot}CH{=}CH{\cdot}Hal + RO^- \rightleftharpoons Ar{\cdot}SO_2{\cdot}C^-{=}CH{\cdot}Hal + ROH} \quad (7)$$

The acidity of the alcohols, and therefore the concentrations of RO^-, decreases steadily from methanol to propan-2-ol.[7] It is quite clear from our results that in the system here considered, the concentration of RO^- is high enough to participate significantly as reagent only in methanol and ethanol but not in propan-2-ol.

Moreover, the competition of RO^- with amines for the substrate is not at all significant in the direct substitution as shown by the constancy of the second-order rate coefficients and the absence of any particular salt effect in the reactions of *trans*-derivatives.*

The effect of RO^-, when present in significant amount, would be, therefore, only in reaction (1) in agreement with the known high rate of this reaction with alkoxide ions,[3] thus producing both the hydrogen exchange reaction and, when the stereochemical conditions are fulfilled, the elimination–addition mechanism.

It seems, therefore, that amine nucleophiles react completely by direct substitution and that the participation of elimination–addition is due to the intervention of the alkoxide ion.†

Solvent effect. The effect of the solvent on the reactions is complicated by the intervention of alkoxide ions, which depends on the acidity of the alcohol, and therefore on the equilibrium concentration of RO^- and on the high efficiency of this reagent in promoting elimination. On the other hand, when the reactions are true direct substitutions and the active nucleophiles are only the amines, a definite increase in rate is observed in changing the solvent from methanol to propan-2-ol. Such variation is in the reverse order to that predicted by simple theories, since a decrease in polarity would decrease the rates. However, other reactions are known which behave similarly and a more detailed study is needed to understand which factors cause the observed trend. Data on solvent effects of this kind are quite poor,[8,9] but it appears that reactions with amines 1-halogeno-2,4-dinitrobenzenes follow the same trend [10] whereas in other cases the rates increase in the expected order.[11]

EXPERIMENTAL

Solvents. Methanol and propan-2-ol were dried by distillation from magnesium in the usual way. Ethanol containing 4% water was used for most of the experiments. The use of absolute ethanol made no significant difference to either the rate coefficients or the products.

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* In nucleophilic substitution of activated aromatic compounds in methanol and ethanol solvents, competition between amines and the lyate ion of the solvent has been detected on several occasions. However in other cases it seems to be absent.[8]

† On simple kinetic grounds the participation of equilibrium 6 aside the equilibrium 7 in methanol and ethanol solvents cannot be rigorously ruled out. However, the absence of any significant hydrogen–deuterium exchange in propan-2-ol makes this hypothesis improbable since it should be assumed a too strong and specific solvent effect on reaction (1).

[7] P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, 1960, **82**, 795; J. Hine and M. Hine, *ibid.*, 1952, **74**, 5266.

[8] J. F. Bunnett and R. Zahler, *Chem. Rev.*, 1951, **49**, 273.

[9] J. F. Bunnett, *Quart. Rev.*, 1958, **12**, 1.

[10] G. Modena, unpublished results.

[11] P. E. Todesco and P. Vivarelli, unpublished results.

Products. The following arylsulphonylhalogenoethylenes were prepared as previously described: *trans*-,[12] m. p. 50—51°, and *cis*-2-chloro-1-*p*-tolylsulphonylethylene,[13] m. p. 45—46°; *trans*-,[14] m. p. 72—73°, and *cis*-2-bromo-1-*p*-tolylsulphonylethylene,[14] m. p. 56—57°; *cis*-2-Cl-,[3] m. p. 65—66°, and *cis*-2-bromo-1-*p*-tolylsulphonylprop-1-ene,[6] m. p. 59—60°. *cis*-2-Chloro- and -2-bromo-1-*p*-tolylsulphonyl[^{2}H]ethylene were prepared by addition of ^{2}HCl or ^{2}HBr to *p*-tolylsulphonylacetylene.[3, 15] The *trans*-isomers were obtained by thermal isomerisation of the *cis*-derivatives.[3] The deuterium content, measured by infrared spectroscopy [3] was 70—90%.

Reaction products. In earlier Papers [3] the stoicheiometry of the reactions here studied was established: *cis*- and *trans*-2-halogeno-1-*p*-tolylsulphonylethylenes on reaction with cyclohexylamine give 2-cyclohexylamino-1-*p*-tolylsulphonylethylene, m. p. 131·5—132·5°,[16] and with dibutylamine give 2-dibutylamino-1-*p*-tolylsulphonylethylene, m. p. 54—55°,[16] *cis*-2-halogeno-1-*p*-tolylsulphonylprop-1-enes give the corresponding cyclohexylamino-,[6] m. p. 126—127°, and dibutylamino-derivatives,[6] m. p. 56—57°.

2-Dimethylamino-1-*p*-tolylsulphonylethylene was obtaind by reaction of the *cis*- and *trans*-1-*p*-tolylsulphonyl-2-halo-ethylenes with dimethylamine in alcoholic solution. The same product was also obtained by addition of dimethylamine to 1-*p*-tolylsulphonylacetylene in alcoholic solution at room temperature. It was recrystallised from ethanol, m. p. 134—135° (Found: N, 6·15; S, 14·3. Calc. for $C_{11}H_{15}NO_2S$: N, 6·2; S, 14·25%).

2-Dimethylamino-1-*p*-tolylsulphonylprop-1-ene was similarly obtained by reaction of 2-halogeno-1-*p*-tolylsulphonylprop-1-enes with dimethylamine or by addition of dimethylamine to 1-*p*-tolylsulphonylprop-1-yne, m. p. 143—144° (from ethanol) (Found: N, 5·85; S, 13·2. Calc. for $C_{12}H_{17}NO_2S$: N, 5·85; S, 13·4%).

2-Amino-1-*p*-tolylsulphonyl[1-^{2}H]ethylenes were obtained by reaction of halogenoethylenes or by addition of amines to *p*-tolylsulphonylacetylene in deuterated methanol. The products so obtained were indistinguishable from the normal compounds but the infrared spectra show a characteristic band at 770 cm.$^{-1}$ indicative of the presence of deuterium.

Deuterated cyclohexylamine. Cyclohexanone (5 g.) was dissolved in deuteromethanol (CH_3OD) containing sodium methoxide (0·01M). The isotopic concentration was *ca.* 90%. After 24 hr. the solution was neutralised with hydrochloric acid (0·05N) and most of the methanol was removed by fractional distillation. The residue was diluted with water, extracted with ether, and the extract dried (Na_2SO_4). After elimination of solvent the cyclohexanone was distilled through a Vigreaux column (16 cm.) (yield 4 g.).

The deuterated cyclohexanone showed an infrared spectrum very similar to the normal compound but with some modification in the range of the in-plane and out-of-plane C–H bending vibration (1200 cm.$^{-1}$, respectively). This is indicative of deuteration at the cyclohexanone carbons (probably the α-carbons).

The cyclohexanone was reacted with hydroxylamine in the usual way and the oxime [2·6 g., m. p. 87—90 [17]] was then reduced with lithium aluminium hydride (2·2 g.) in boiling dry ether (~100 ml.) for about 3 hr. After decomposition of the excess of the reducing agent, the ether was almost completely removed and the residue dissolved in dilute sulphuric acid. The aqueous solution was extracted with ether and made alkaline with excess of sodium hydroxide. Extraction with ether followed by drying and removal of solvent gave the cyclohexylamine (2 g.), b. p. 127—130°.

The infrared spectrum of the compound has a band at 2155 cm.$^{-1}$ (C–D stretching), thus showing the presence of deuterium in the cyclohexane ring (probably at the α-position).

The deuterated cyclohexylamine reacted with *cis*- and *trans*-2-bromo-1-*p*-tolylsulphonylethylenes yielding 2-cyclohexylamino-1-*p*-tolylsulphonylethylene which was indistinguishable from the normal compound (see above) except for a new infrared band at 2170 cm.$^{-1}$ (C–D stretching).

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[12] G. Leandri, G. Modena, and F. Montanari, *Boll. sci. fac. Chim. ind. Bologna*, 1954, **12**, 170; F. Montanari, *Gazzetta*, 1956, **86**, 406.

[13] L. Maioli and G. Modena, *Boll. sci. Fac. Chim ind. Bologna*, 1958, **16**, 86.

[14] A. Campagni, G. Modena, and P. E. Todeseo, *Gazzetta*, 1960, **60**, 694, reported incorrectly 62—63°; see also E. Angeletti, F. Montanari, and A. Negrini, *Gazzetta*, 1957, **87**, 1086.

[15] L. Maioli and G. Modena, *Ricerca sci.*, 1959, **29**, 1931.

[16] G. Modena, P. F. Todesco, and S. Tonti, *Gazzetta*, 1959, **89**, 878.

[17] Bayer, *Annalen*, 1894, **278**, 102.

Amines. AnalaR grade products were purified by conventional methods and used throughout.

Salts. The perchlorates of cyclohexylamine, dibutylamine, and dimethylamine were prepared by neutralisation of the base dissolved in alcohol, evaporation to dryness *in vacuo*, and crystallisation from ethanol–ether.

Lithium perchlorate. AnalaR grade commercial product was purified by crystallisation in the usual way.

Deuteromethanol. This was prepared by hydrolysis of dimethylphthalate with deuterium oxide or by decomposition of magnesium methoxide with deuterium oxide.

Reactions.—Hydrogen exchange in the aminoethylenes. The course of the reaction was followed by two methods:

(*a*) Deuterated halogenoethylenes in methanol were allowed to react for *ca.* 3—4 half-lives with the various amines under conditions similar to those used in the kinetic experiments (see below). The solution was then neutralised with dilute hydrochloric acid and the solvent removed at reduced pressure. The residue was diluted with water, the amino-derivative was filtered off, and, after crystallisation, analysed spectroscopically for deuterium content.

(*b*) Normal halogenoethylenes were reacted with the same amines in deuteromethanol. The solution was worked up as described above and the product analysed.

The infrared spectra were always compared with those of the pure products.

*Hydrogen exchange in 2-cyclohexylamino-*1-p-*tolylsulphonyl*[1-^{2}H]*ethylene.* The deuterated cyclohexylamino-derivative, prepared as described above, was dissolved in methanol (2—5 × 10^{-2} mole/l.) and two equivalents of cyclohexylamine added. After *ca.* 2—3 hr. the solution was neutralised with dilute hydrochloric acid and evaporated to dryness at reduced pressure. The amino-derivative was filtered and crystallised, and the infrared spectrum recorded. The spectrum was identical to that of the undeuterated compound. Test experiments showed that no exchange occurred in the absence of the base.

On the other hand, under the same and also under more drastic conditions no exchange was observable when the dibutylamino- or the dimethylamino-ethylene were reacted with excess of base.

When cyclohexylaminoethylene prepared with deuterated cyclohexylamine (see above) was used, the compound was recovered unchanged after reaction with two equivalents of cyclohexylamine for up to 24 hr. at room temperature. The infrared spectra of the compounds before and after reaction were identical.

Kinetics.—The reactions were followed by argentometric titration of the halide ion and the rate coefficients were calculated by conventional methods as previously described.[3] Usually a 1 : 6 molar ratio of halogenoethylene to amine was used except where otherwise stated, and the values referred to in the Tables are average values from two or more runs. The standard deviation is about ±3% or better.

When necessary initial rates were evaluated graphically and in these cases the errors are something greater (~10%).

Percentage of hydrogen–deuterium exchange. Solutions of 1-deuterated halogenoethylenes and amine in the chosen alcohol were prepared in the usual way and at fixed time quenched by pouring into dilute hydrochloric acid (~250 ml. for 70 ml. alcoholic solution). The solutions were extracted with ether, the ethereal extracts were washed with water and dried, and the unreacted halogenoethylene and the products were recovered. The mixtures were fractionated by chromatography on a short alumina column, where the retention times of the halogenoethylenes were much shorter than those of the aminoethylenes.

The almost pure halogenoethylenes were crystallised and the deuterium contents before and after reaction were measured spectroscopically.[3]

Infrared analyses were carried out with a Beckman IR4 spectrometer equipped with either sodium chloride or, when necessary, calcium fluoride calibrated cells.

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(S. G., P. E. T., P. V.) ISTITUTO DI CHIMICA INDUSTRIALE DELL'UNIVERSITÀ,
V LABORATORIO DI RICERCA DEL C.N.R., BOLOGNA, ITALY.
(G. L., G. M., G. M.) ISTITUTO DI CHIMICA ORGANICA DELL'UNIVERSITÀ,
BARI, ITALY.

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