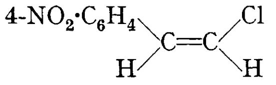
Nucleophilic Reactions in Ethylenic Derivatives. Part XI.[1] Substitution and Elimination in β-Halogenostyrenes

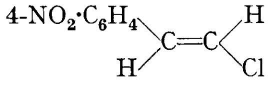
By **G. Marchese** and **F. Naso**, Istituto di Chimica Organica, Università, Bari, Italy
G. Modena,* Istituto di Chimica Organica, Università, Padova, Italy

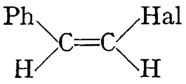
The reactions of *cis*- and *trans*-β-chloro-4-nitrostyrenes with benzenethiolate and methoxide ions in methanol show the usual features of vinylic reactivity: *i.e.*, only in the case of the *cis*-isomer with methoxide ion does elimination compete favourably with direct substitution. Particular care was devoted to the investigation of the elimination mechanism, which was also studied with the unsubstituted *cis*-β-chloro- and -β-bromo-styrenes. The presence of a primary isotope effect (k_H/k_D = 1·6—3) and the absence of any H/D exchange proved that the elimination followed an *E*2-like mechanism with a large carbanionic character.

In recent communications[1] it has been reported that *cis*- and *trans*-β-bromo-nitro- and -dinitro-styrenes give with benzenethiolate ion a clean substitution reaction with retention of configuration, whereas with methoxide ion they give substitution in the case of *trans*-isomers and elimination to acetylenes in the case of *cis*-isomers. The elimination reaction moreover appeared to be, on the basis of the usual isotopic tests, a concerted reaction,[1b] at variance with the opinion [2a,b] that carbanionic intermediates are involved in the elimination leading to acetylenes.

Our interest in this field[3] led us to consider the reactivity of the *cis*- and *trans*-chloronitrostyrenes (I) and (II) and of the unsubstituted bromo- and chloro-styrenes (III) and (IV).


(I)

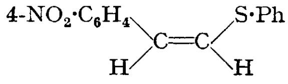

(II)

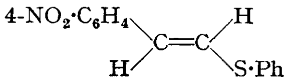

(III) Hal = Br; (IV) Hal = Cl

In fact, the change of the leaving group from bromine to chlorine could shift the balance between substitution and elimination in favour of the former, as was found in the case of arylsulphonylhalogenoethylenes[3], and between *E*2 and *E*1c*B* mechanisms in favour of the latter in the case of elimination. The effects of the nitro-substitution on reactivity and isotope effects were also studied in order to obtain further information on the character of the transition state.

RESULTS

Products of Reaction with Sodium Benzenethiolate.—*cis* and *trans*-β-Chloro-4-nitrostyrene, (I) and (II), yielded with benzenethiolate ion in methanol, *cis*- and *trans*-4-nitrostyryl phenyl sulphide,[1a] (V) and (VI) respectively, as already described for the analogous reaction of the bromonitrostyrenes.[1a]


(V)


(VI)

Also, in this case the *cis*-4-nitrostyryl phenyl sulphide (V) was contaminated by substantial amounts (*ca.* 10%) of the *trans*-isomer (VI) because of the easy isomerisation of (V) to (VI) under the reaction conditions.

Products of Reactions with Sodium Methoxide.—*trans*-β-Chloro-4-nitrostyrene (II) yielded, with methoxide ion, 1,1-dimethoxy-2-(4-nitrophenyl)ethane (VIII) which should be formed, as shown [1a] in the case of the bromostyrene reaction, by addition of methanol to the initially formed 4-nitrophenyl vinyl ether (VII).

cis-β-Halogenostyrenes, (III) and (IV), in the reaction with methoxide ion, gave quantitatively phenylacetylene [2c] (IX) (titration by Hanna and Siggia's method [4]).

$$\text{(II)} \xrightarrow[-\text{Cl}^-]{\text{MeO}^-} \underset{\text{(VII)}}{p\text{-NO}_2\text{·C}_6\text{H}_4\text{·CH=CH(OMe)}} \xrightarrow{\text{MeO}^-/\text{MeOH}} \underset{\text{(VIII)}}{4\text{-NO}_2\text{·C}_6\text{H}_4\text{·CH}_2\text{·CH(OMe)}_2}$$

$$\text{(I)} \xrightarrow[-\text{Cl}^-]{\text{MeO}^-} \underset{\text{(X)}}{4\text{-NO}_2\text{·C}_6\text{H}_4\text{·C}\equiv\text{CH}} + \text{(VIII)}$$

cis-β-Chloro-4-nitrostyrene (I) yielded 4-nitrophenylacetylene (X),[1a] but in this case the yields were not quantitative and the product was contaminated by 1,1-dimethoxy-2-(*p*-nitrophenyl)ethane (VIII). This point was analysed in detail (see later) since it could have meant that there was competition between substitution and elimination–addition mechanisms, as observed in another system.[3] In fact, (VIII) could have originated by direct substitution, as in the case of the *trans*-isomer (II), or by base-catalysed addition of methanol to the initially formed 4-nitrophenylacetylene (X).

The kinetic analysis (see below) showed that the elimination process is the main reaction path, and that the direct substitution accounted for only 10% of the reaction. Therefore it may be ignored in the first approximation.

Kinetic Results.—The rates of the reactions of halogeno-

---

[1] (*a*) Part X, G. Marchese, G. Modena, and F. Naso, *Tetrahedron*, 1968, **24**, 663; (*b*) G. Marchese, G. Modena, and F. Naso, *Chem. Comm.*, 1966, 492.

[2] (*a*) G. Köbrich, *Angew. Chem. Internat. Edn.*, 1965, **4**, 49; (*b*) J. Hine, 'Physical Organic Chemistry,' 2nd edn., McGraw-Hill, New York, 1962, ch. 8. Cf. (*c*) S. J. Cristol and W. P. Norris, *J. Amer. Chem. Soc.*, 1954, **76**, 3005; (*d*) S. I. Miller and W. G. Lee, *ibid.*, 1959, **81**, 6313.

[3] (*a*) L. Di Nunno, G. Modena, and G. Scorrano, *J. Chem. Soc.* (*B*), 1966, 1186; (*b*) S. Ghersetti, G. Modena, P. E. Todesco, and P. Vivarelli, *Gazzetta*, 1961, **91**, 620, and earlier papers of the series.

[4] J. G. Hanna and S. Siggia, *Analyt. Chem.*, 1949, **21**, 1469.

styrenes (I)—(IV) with benzenethiolate and methoxide ions in methanol were measured at various temperatures. They always followed second-order kinetics, and the rate coefficients (average of two or more runs usually at different initial base concentrations), with the derived energies and entropies of activation, are in Tables 1 and 2.

TABLE 1

Rate coefficients and activation parameters [a] for the reactions of various β-halogenostyrenes (~1·5 × 10^{-2}M) with benzenethiolate ion (0·2—2 × 10^{-1}M) in methanol

	10^4k (l. mole^{-1} sec.$^{-1}$)				E_a (kcal./mole)	$\Delta S^‡$ (45°) (e.u.)
	15°	21°	30°	45°		
cis-4-$NO_2\cdot C_6H_4\cdot CH{=}CHCl$		1·32	3·62	13·5	17·8	−17·8
trans-4-$NO_2\cdot C_6H_4\cdot CH{=}CHCl$	3·78	—	15·8	68·1	17·6	−15·2
cis-4-$NO_2\cdot C_6H_4\cdot CH{=}CHBr$				50 [b]	18·9 [c]	−11·8
trans-4-$NO_2\cdot C_6H_4\cdot CH{=}CHBr$				150 [b]	18·2 [c]	−11·8

[a] Probable errors are 2% for k, ±0·5 kcal./mole for E_a, and ±1·5 e.u. for $\Delta S^‡$. [b] Extrapolated from the data at lower temperatures reported in ref. 1*a*. [c] Data taken from ref. 1*a*.

TABLE 2

Rate coefficients and activation parameters [a] for the reactions of various β-halogenostyrenes (~1·5 × 10^{-2}M) with methoxide ion (0·3—4 × 10^{-1}M) in methanol

	10^4k (l. mole^{-1} sec.$^{-1}$)						E_a (kcal./mole)	$\Delta S^‡$ (60°) (e.u.)
	45°	50°	60°	78·25°	90°	100°		
cis-4-$NO_2\cdot C_6H_4\cdot CH{=}CHBr$			600 [b]	4200 [b]			25·0 [c]	+8·9
cis-4-$NO_2\cdot C_6H_4\cdot CH{=}CHCl$	0·76 [d]	—	5·48 [d]	56·7 [d]			29·0 [e]	+11·6 [e]
trans-4-$NO_2\cdot C_6H_4\cdot CH{=}CHBr$			1·45 [c]	9·70 [c]			25·1 [c]	−3·0
trans-4-$NO_2\cdot C_6H_4\cdot CH{=}CHCl$		0·59	1·65	11·5			23·8	−6·7
cis-$C_6H_5\cdot CH{=}CHBr$		1·34	4·77	43·5			28·0	+7·9
cis-$C_6H_5\cdot CH{=}CHCl$			0·025 [f]	0·33	1·22	4·56	31·6	+8·7

[a,b,c] As in Table 1. [d] k_t values (see text). Apparent values calculated by using k_t values. [f] Extrapolated from the data at higher temperatures.

Isotopic Experiments.—α-Deuteriated *cis*-halogenostyrenes (Ia), (IIIa), and (IVa) were prepared by an independent synthesis (see Experimental), the rates of reaction with methoxide ion were measured, and the k_H/k_D ratios evaluated (see Table 3).

TABLE 3

Deuterium isotope effects in the reactions of various *cis*-β-halogenostyrenes with methoxide ion

	Temp.	k_H/k_D
$C_6H_5\cdot CH{=}CHBr$	50°	2·9
4-$NO_2\cdot C_6H_4\cdot CH{=}CHBr$	45	2·2
$C_6H_5\cdot CH{=}CHCl$	78·2	2·2
4-$NO_2\cdot C_6H_4\cdot CH{=}CHCl$	45	1·6 *

* Calculated taking into account the substitution reaction.

Also, experiments to detect H/D exchange at the α-position were performed using the reaction of *cis*-β-chloro-4-nitrostyrene in MeOD or the corresponding deuteriated styrene in MeOH. No exchange was observed. In fact, the infrared spectra of the unreacted materials (at 50% reaction completion) were superposable on those of the starting substrates.

Kinetic Analysis of the Reaction of β-*Chloro*-4-*nitrostyrene with* MeO^-.—As shown previously,[3a] the rates of elimination and of substitution may be evaluated by the equations (1)—(3).

$$[D']/[D] = k_t/k_e \qquad (1)$$

$$k_t = k_s + k_e \qquad (2)$$

$$[D'] = \frac{A_0[(A_0k_tt + 1)^{k_a/k_t - 1} - 1]}{(k_a/k_t - 1)(A_0k_tt + 1)^{k_a/k_t}} \qquad (3)$$

where k_t is the overall reaction rate coefficient; k_e and k_s are the rate coefficients of elimination and substitution respectively; $[D']$ is the concentration of the acetylenic intermediate at a given time (t) calculated with the aid of the rate of methoxide-catalysed addition of methanol to the acetylene [equation (3), k_a] with the assumption that the reaction occurred only by an elimination–addition mechanism; $[D]$ is the directly measured concentration of the acetylene at a given time; A_0 is the concentration of methoxide ion and styrene in the actual reaction solution (the concentration is the same for both reagents). The results are in table 4.

TABLE 4

Experimental and calculated [equation (3)] values for the concentration of 4-nitrophenylacetylene at times of maximum concentration in the reacting solution of *cis*-β-chloro-4-nitrostyrene and methoxide ion in methanol at 45° (A_0 = 0·173M; $k_a = 2·2 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$; $k_t = 7·60 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$)

Time (hr.)	[−C≡C−] (10^{-2} M) [calc., eqn. (3)]	(exp.)	10^5k_e (l. mole^{-1} sec.$^{-1}$)	10^5k_e
26·2	8·3	7·4	6·78	0·82
45	9·7	8·7	6·81	0·79
64·6	10·2	9·1	6·78	0·82
114	10·4	9·2	6·72	0·88

DISCUSSION

The problems discussed are the general reactivities of the halogenostyrenes toward nucleophiles (say the vinylic reactivity), and particular aspects of the mechanism of the elimination reaction. The two points will be dealt with separately.

Vinylic Reactivity.—The general features of the reactivity of chloronitrostyrenes are very similar to those of the bromonitrostyrenes,[1a] and of other vinylic substrates previously studied.[3,5] The highly polarisable, feebly basic ('soft'[6]) benzenethiolate ion gives substitution with both isomers whereas the feebly polarisable, strongly basic ('hard'[6]) methoxide ion gives direct substitution with the *trans*-isomer but elimination with the *cis*-isomer because of the favourable steric arrangement.

As discussed elsewhere,[3] the mechanism of direct substitution is not very sensitive to the configuration of the reagents or to the nature of the leaving group. Accordingly, the rate constants of the reactions of benzenethiolate ion with *cis*- and *trans*-bromo- and -chlorostyrenes are all included within a factor of 10. Also, in the reactivity of *trans*-halogenonitrostyrenes with methoxide ion, there is no significant difference between chloro- and bromo-derivatives. Indeed, in this case the chloro- reacts a little faster than the bromo-compound.

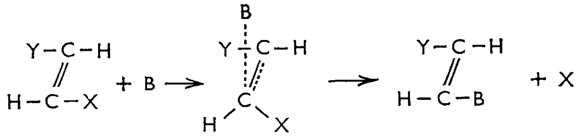
On the other hand, the *cis*-bromostyrenes react with methoxide ion much faster than the chloro-derivatives, as expected for elimination in vinylic systems.[3,7]

However, a simple comparison of rates of reactions could be misleading. In fact, *cis*- and *trans*-chloronitrostyrenes with methoxide ion react at similar rates, but in this case the Arrhenius parameters are significantly different whereas in the other reactions the similarities in rates were due to similarities in the energies and entropies of activation. A very similar situation was found in the reaction of arylsulphonylhalogenoethylenes,[3] although in that case substitution accounted for about 50% of the overall reaction.

In this respect it should be noted that the substitution reactions always have negative entropies of activation, as is normally found,[8,1a] whereas the eliminations seem to be characterised by having positive entropy values (see Tables 1 and 2).

A minor but distinctive feature of the reactions of halogenonitrostyrenes with benzenethiolate ion is the greater reactivity of the *trans*- than the *cis*-isomers, whereas in other systems the reverse was found.[3,5]

Apart from minor details, the direct substitution mechanism may be represented as shown in the Scheme, which requires that the β-carbon atom becomes almost tetrahedral in the transition state.



According to this hypothesis, the transition states from *cis*- and *trans*-isomers would be very similar, and, other things being equal, the energies of activation would depend on the energy content of the ground states. It follows that the less thermodynamically stable isomer (usually the *cis*) should react faster than the more stable one. Such a hypothesis is still valid when the transition states are removed from the tetrahedral structure but they still differ in energy less than in the initial states.

However, when the differences in the initial states are such that they more directly affect the reactivity, as, for instance, different degrees of interaction of the activating group and the reaction centre, such a hypothesis can no longer be valid.

This might be the case with nitrostyrenes, where the *trans*- react faster than *cis*-isomers, since the efficient transmission of the effect of the nitro-group requires coplanarity of the molecule, which is more easily obtained in the *trans*- than in the *cis*-isomers. Accordingly, we found[1a] that the ratio of *trans*- to *cis*-reactivity is much greater in the case of the β-bromo-2,4-dinitrostyrenes, where the steric hindrance to coplanarity in the *cis*-isomer is certainly more severe.

In conclusion, the general aspects of the reactivity of halogenonitrostyrenes fit into the scheme proposed for the vinylic reaction, characterised by competition between direct substitution and elimination. Such competition is controlled by the specific properties of the nucleophile and by the geometrical configuration of the substrate.

In contrast, the detailed mechanism of elimination from halogenostyrenes has characteristics completely different from those of other investigated eliminations leading to acetylenes.

Elimination Mechanism.—To our knowledge, two examples of elimination leading to acetylenes have been studied in detail: the dehydrohalogenation of 1,2-dihalogenoethylenes[2d] and that of arylsulphonylhalogenoethylenes.[3b] In both cases, fast hydrogen–deuterium exchange, which suggested the occurrence of an $E1cB$ mechanism, was observed.

At variance with these results, we find that eliminations from halogenostyrenes occur by a concerted mechanism, since no hydrogen–deuterium exchange was observed and isotope effects larger than 1 were measured.* However, the k_H/k_D values are too small (see Table 3) for a synchronous $E2$ process, and they suggest that the transition states have high carbanionic character.[10] Therefore, a mechanism intermediate between the synchronous $E2$ and the $E1cB$ has to be considered.

The opposite hypothesis, of a mechanism with some

---

* Similar results have been observed[9] in the base-catalysed elimination from halogenocrotonic esters and nitriles.

[5] S. Patai and Z. Rappoport, in 'The Chemistry of Alkenes,' ed. S. Patai, Interscience, London, 1964, ch. 8.

[6] R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, 1967, **89**, 1827.

[7] S. I. Miller and R. M. Noyes, *J. Amer. Chem. Soc.*, 1952, **74**, 629.

[8] G. Kohnstam, *Adv. Phys. Org. Chem.*, 1967, **5**.

[9] F. Theron, Thesis (S.E. No. 79), University of Clermont-Ferrand, 1967.

[10] C. K. Ingold, *Proc. Chem. Soc.*, 1962, 265; J. F. Bunnett, *Angew. Chem. Internat. Edn.*, 1962, **1**, 225; D. V. Banthorpe, 'Elimination Reactions,' Elsevier, Amsterdam, 1963; D. V. Banthorpe, in 'Studies on Chemical Structure and Reactivity,' ed. J. H. Ridd, Methuen, London, 1966, ch. 3; W. H. Saunders, ref. 5, ch. 2.

*E*1 character, which could also explain the low isotope effects, is very improbable in such systems, and it is not consistent with the general features of the reaction. In fact, nitro-substitution, which increases the acidity of the hydrogens and stabilises the developing negative charge, greatly increases the rates. The above factors, perhaps combined with a hindering effect on the C–Hal bond-breaking, favour more C–H bond-breaking in the transition state, and consequently a decrease in k_H/k_D is observed.

Also consistent with the above hypothesis is the effect of changing the leaving group from bromine to chlorine. In fact, with the better leaving group are associated higher rates, smaller nitro-activation, and greater isotope effects, as expected in view of the smaller need for nucleophilic assistance to the leaving group by the developing negative charge, and consequently for a smaller carbanionic character of the transition state.

Some aspects of our findings could also be explained by an *E*1*cB*-like mechanism in which the C–H bond breaking is rate-determining and the halide ion is removed in a fast subsequent step ($k_{-1} \ll k_2$)

$$\mathrm{ArCH{=}CHX} + \mathrm{B}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ar\text{-}\overset{-}{C}{=}CHX} + \mathrm{BH} \xrightarrow{k_2} \mathrm{ArC{\equiv}CH} + \mathrm{BH} + \mathrm{X}^-$$

However, such mechanism would require no, or a very small, effect of the leaving group on the rates, contrary to what has been found.

In conclusion, our results suggest that a continuous gradation of mechanisms from typical *E*1*cB* to *E*2 is operating in the elimination leading to acetylenes. The shift of the mechanism certainly depends on the degree of activation, as shown by the present results. However, the kind of activation is even more important in this respect, as shown by the results with dihalogenoethylenes,[2d] which are less reactive than halogenonitrostyrenes, and with arylsulphonylhalogenoethylenes,[3] which have similar reactivity, both reacting through an *E*1*cB* mechanism.

EXPERIMENTAL

The i.r. spectra were recorded with a Beckman I.R. ×8 instrument.

Substrates.—*cis*-β-Bromo-4-nitrostyrene, m.p. 50—51° [from light petroleum (b.p. 80—120°)],[2c] *cis*-β-bromostyrene (III), m.p. −7 to −6° (from methanol),[2c] and *cis*-β-chlorostyrene (IV), b.p. 54—55°/2 mm.,[11,12] were prepared by known methods. cis-β-*Chloro*-4-*nitrostyrene* (I), m.p. 50—51° [from light petroleum (b.p. 80—120°)] (Found: C, 52·35; H, 3·25; Cl, 19·2; N, 7·55. $C_8H_6ClNO_2$ requires C, 52·3; H, 3·3; Cl, 19·3; N, 7·6%), was prepared by decarboxylative dehalogenation of *trans*-*p*-nitrocinnamic acid dichloride, m.p. 187—188°,[13] as described for the corresponding bromo-derivatives. *trans*-β-Chloro-4-nitrostyrene (II), m.p. 127—128° (from ethanol),[11,14] was prepared by heating the corresponding *cis*-isomer under nitrogen for 10 hr. at 150° in the presence of traces of Iodine.

The purity of the above compounds, particularly with regard to the presence of stereoisomers, was checked by t.l.c. and i.r.

Deuteriated Substrates.—[^{2}H]Benzaldehyde was prepared by the Stephen reduction of benzonitrile with DCl and dry stannous chloride.[15] It reacted with acetic anhydride and sodium acetate under the usual conditions, giving deuteriocinnamic acid which, by chlorination in carbon disulphide in the presence of light, gave in good yield the corresponding deuteriocinnamic acid dichloride, m.p. 169—170°.[16] The dichloride yielded, by decarboxylative dehalogenation in boiling acetone in the presence of sodium hydrogen carbonate, cis-β-*chloro*-α-*deuteriostyrene* (IVa), b.p. 54—55°/2 mm. cis-β-*Chloro*-α-*deuterio*-4-*nitrostyrene* (Ia), m.p. 50—51° [from light petroleum (b.p. 80—120°)], was obtained by nitration of the deuteriocinnammic acid dichloride and reaction of the *p*-nitrodeuteriocinnamic acid dichloride, m.p. 187—188°,[13] with sodium hydrogen carbonate following the usual procedure.[1a,2c] cis-β-*Bromo*-α-*deuteriostyrene* (IIIa), m.p. −7 to −6° (from methanol),[2c] was prepared by decarboxylative dehalogenation of the deuteriocinnamic acid dibromide, m.p. 198—199°,[17] obtained by bromination of the deuteriocinnamic acid. *cis*-β-Bromo-α-deuterio-4-nitrostyrene,[1a] m.p. 50—51° [from light petroleum (b.p. 80—120°)], was prepared by nitration of the deuteriocinnamic acid dibromide and decarboxylative dehalogenation of the resulting *p*-nitrodeuteriocinnamic acid dibromide, m.p. 216—217°.[18]

All the above deuteriostyrenes had melting points corresponding to those of the protio-compounds and showed characteristic modifications in the region 650—1000 cm.$^{-1}$. The deuterium content at the α-position was in the range 0·7—0·9 atom per molecule, and was determined in each sample by n.m.r. spectroscopy.

Kinetic Methods.—The reactions of the halogenostyrenes with methoxide and benzenethiolate ions were followed as previously described.[1a]

Isotope effects were evaluated by experiments performed under pseudo-unimolecular conditions and by taking into account the contents of deuterium in each sample as measured by n.m.r. The data are in Table 3; the estimated error is ±5%.

The rate of addition of methanol to *p*-nitrophenylacetylene was measured at 45° by titration of the unreacted acetylene by Hanna and Siggia's method.[4] Concentrations of 0·7—1·4 × 10^{-1}M of *p*-nitrophenylacetylene and 0·1—0·2M of methoxide ion were used.

Determination of k_e *and* k_s.—The curve of *p*-nitrophenylacetylene concentration as a function of time was calculated, as previously described,[3a] by use of equation (3) with the experimental values of k_a and k_t for the initial concentration used in the experiment. This was performed by treating *cis*-β-*chloro*-4-*nitrostyrene* with methoxide ion at

---

[11] A. T. Dann, A. Howard, and W. Davies, *J. Chem. Soc.*, 1928, 605.

[12] M. Schlosser, *Chem. Ber.*, 1964, **97**, 3219.

[13] P. Pfeiffer, G. Birencweig, A. Hofmann, and C. Windheuser, *Ber.*, 1914, **47**, 1580.

[14] L. M. Yagupol'skiĭ and A. S. Shtepanek, *Zhur. obshchei Khim.*, 1959, **29**, 3086.

[15] A. Streitwieser, jun., and J. R. Wolfe, jun., *J. Amer. Chem. Soc.*, 1957, **79**, 903.

[16] C. Liebermann and H. Finkenbeiner, *Ber.*, 1895, **28**, 2235.

[17] J. J. Sudborough and K. J. Thompson, *J. Chem. Soc.*, 1903, **83**, 666.

[18] E. R. Trumbull, R. T. Finn, K. M. Ibne-Rasa, and C. K. Sauers, *J. Org. Chem.*, 1962, **27**, 2339.

45° and measuring the acetylene concentration at various times in the region of its calculated maximum concentration (see Table 4).

Hydrogen–Deuterium Exchange Experiments.—The exchange was thoroughly investigated with the 4-nitro-β-bromo- and -β-chloro-styrenes. Solutions of reagents at concentrations comparable to those used in the kinetics experiments were prepared by using deuteriated styrenes in MeOH or protio-compounds in deuteriated methanol (MeOD). The reactions were allowed to reach 40—50% completion and then quenched by neutralisation with acetic acid. Alcoholic silver nitrate was added and the precipitated material was filtered off. The solvent was evaporated and the pure *cis*-isomer obtained from the residue by preparative t.l.c. on silica gel (HF_{254} according to Sthal) developed with light petroleum (b.p. 80—120°)–ethyl acetate (9 : 1).

The i.r. spectra of the unreacted halogenostyrenes were superposable on the spectra of the starting substrates. On the other hand, the spectra of the deuteriated styrenes were markedly different from those of their isotopically normal counterparts, and it was confirmed that, particularly in the case of reactions of protio-compounds in MeOD, 2—3% of exchange could easily have been revealed.

We thank Professor F. Taddei, Istituto di Chimica Organica e di Chimica Industriale, Bologna, for the n.m.r. analyses. This work was supported by a grant from the Consiglio Nazionale delle Ricerche, Rome.

[7/1663 *Received, December 19th, 1967*]