Kinetics and Mechanism of the Nucleophilic Substitution of Arylhalogenoacetylenes by Sodium Toluene-*p*-thiolate in *NN*-Dimethylformamide

By **P. Beltrame,*** Istituto Chimico, Università, Cagliari, Italy
P. L. Beltrame, M. G. Cattania, and **M. Simonetta,** Istituto di Chimica Fisica, Università, Milano, Italy

The title reaction of 1-chloro- and 1-bromo-2-phenylacetylenes and of their *p*-Me and *p*-Cl substituted derivatives has been kinetically studied. Only 1-*p*-tolylthio-2-arylacetylenes are obtained. provided an excess of thiolate is avoided. By use of excess of thiolate. an addition reaction takes place on the substitution product. Ratios $k_{RCl}:k_{RBr}$ in the range 2·5—4·2 have been found for the substitution at −25 °C. Hammett ρ values of 3·4 and 3·9 are calculated for chloro- and bromo-acetylenes. respectively. In agreement with these results. p-NO_2·C_6H_4·$C\equiv CBr$ gives a fast substitution even at −50 °C. Results are interpreted on the basis of the α-addition–elimination mechanism for substitution at an acetylenic carbon atom.

KINETIC studies have been reported for the reactions of nucleophiles with halogenoacetylenes.[1,2] However, data are still scarce, particularly for the substituent effect and for the dependence of the rate on solvents. We planned to collect more data and chose the reaction of arylhalogenoacetylenes (I)—(V) with sodium toluene-*p*-thiolate in *NN*-dimethylformamide. Several arylhalogenoacetylenes have been found to give the corresponding arylacetylenes by reaction with sulphur nucleophiles in alcoholic solvents.[2,3] The present study with dimethylformamide as solvent offers an opportunity to compare different reaction conditions. Partial reports have been given.[4]

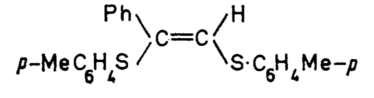
$$p\text{-}Z\cdot C_6H_4C\equiv CX \qquad \left.\begin{array}{r}\text{(I)}\ Z = H\\ \text{(II)}\ Z = Me\\ \text{(III)}\ Z = Cl\\ \text{(IV)}\ Z = NO_2\\ \text{(V)}\ Z = OMe\end{array}\right\}\ \begin{array}{l}a;\ X = Cl\\ b;\ X = Br\\ c;\ X = p\text{-}MeC_6H_4S\end{array}$$

RESULTS AND DISCUSSION

Products from arylhalogenoacetylenes (I)—(V) (X = Cl or Br) were the corresponding *p*-tolylthio-derivatives (Ic)—(Vc), provided an excess of thiolate was avoided. Experiments with excess of thiolate were done on (Ia), (IIb), and (IIIb): the substitution was followed by an addition reaction, to give the corresponding aryldi(*p*-tolylthio)ethylenes. Evidence was obtained by elemental analysis, molecular weight determinations, and n.m.r. spectra.

Additional evidence as to the structure of the ethylenic product from (Ia) was mainly obtained by ozonolysis, which gave $PhCO\cdot SC_6H_4Me$-*p*, proving that the *p*-tolylthio-groups are in vicinal positions. A test for keten dithioacetals[5] gave a negative result.

In the n.m.r. spectrum of this product the ethylenic proton appears to be strongly deshielded ($\tau < 3{\cdot}1$). Shifts evaluated by empirical correlations[6,7] are: τ 3·4 for *cis*-1,2-di(arylthio)-2-phenylethylene and τ 4·0—4·1 for the *trans*-isomer. Formula (VI) is therefore suggested for the product. The n.m.r. spectra of the ethylenic products from (IIb) and (IIIb) along the same lines[7] suggest analogous structures. *trans*-Addition is usual for nucleophilic thiol addition to acetylenes.[8]



(VI)

Reactions of the bromoacetylenes (Ib), (IIIb), and (Vb) with toluene-*p*-thiolate in dimethylformamide containing 1M-ethanol gave the same products as in the standard solvent. Therefore the presence of a small amount of protic impurity in the aprotic solvent is not critical.

Kinetic measurements for the substitution were possible for compounds (I)—(III) only. Runs were carried out at −25 °C in the case of reactants (I) and (III) (Table 1), and from −17 to +5 °C for reactants (II) (Table 2). Second-order rate coefficients were calculated.[1a] Values of the activation parameters

TABLE 1

Rate coefficients for substitution at −25 °C

X	Z		[RX]/M initial	[Nucleophile]/M initial	$\frac{10^2k}{\text{l mol}^{-1}\text{ s}^{-1}}$
Cl	H	(Ia)	0·047	0·015	6·63 [a]
Cl	Cl	(IIIa)	0·032	0·012	37·4
			0·031	0·012	39·8
Br	H	(Ib)	0·050	0·014	2·23
			0·122	0·012	2·08
Br	Cl	(IIIb)	0·045	0·011	16·6
			0·055	0·011	14·4

[a] Lit.,[1a] 6·12 (average).

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for 1-halogeno-2-(*p*-tolyl)acetylenes (Table 2) are comparable with those for the reaction of 1-chloro-2-phenylacetylene[1a] ($\Delta E^\ddagger = 12{\cdot}3$ kcal mol^{-1}; $\Delta S^\ddagger = -16{\cdot}8$ cal mol^{-1} K^{-1}).

TABLE 2

Rate coefficients and activation parameters for the reaction of *p*-$MeC_6H_4{\cdot}C{\equiv}CX$. Initial concentrations: [RX] = 0·04—0·06M; [Nucleophile] = 0·011—0·016M

X	t/°C	10^2k / l mol^{-1} s^{-1}	log A	$\Delta E^\ddagger$ / (kcal mol^{-1})	$\Delta S^\ddagger$ / (cal mol^{-1} K^{-1})
Cl (IIa)	−15·0	4·39			
	−5·0	10·61	8·86	12·1	−19·8
	+5·0	23·8	±0·45	±0·5	±2·0
Br (IIb)	−17·0	0·985			
	−10·0	1·88			
	−5·0	3·67	10·18	14·3	−13·7
	−2·0	5·82	±0·54	±0·7	±2·5
	+5·0	8·54 [a]			

[a] $10^2k = 6{\cdot}12$ l mol^{-1} s^{-1} in dimethylformamide containing 1M-ethanol.

TABLE 3

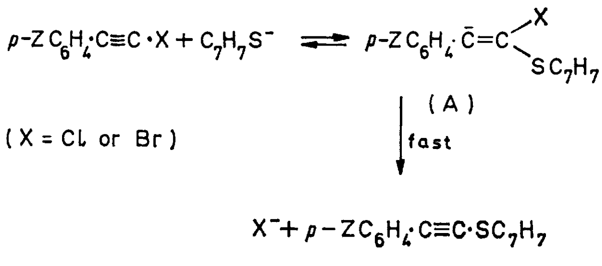
Leaving-group effect on the nucleophilic substitution at −25 °C

Z	Me	H	Cl
10^2k_{RCl}/l mol^{-1} s^{-1}	1·70 [a]	6·63	38·6 [b]
10^2k_{RBr}/l mol^{-1} s^{-1}	0·403 [a]	2·15 [b]	15·5 [b]
$k_{\mathrm{RCl}} : k_{\mathrm{RBr}}$	4·22	3·08	2·49

[a] From Arrhenius equation. [b] Average values.

As a leaving group, chloride is slightly favoured over bromide (Table 3). The substituent effect, when expressed by the Hammett correlation, corresponds to $\rho = 3{\cdot}41 \pm 0{\cdot}03$ (X = Cl) and $\rho = 3{\cdot}94 \pm 0{\cdot}08$ (X = Br). Accordingly, the reaction rate of 1-bromo-2-(*p*-nitrophenyl)acetylene was too large to be measured. A lower limit of 3·6 l mol^{-1} s^{-1} was evaluated by experiments at −50 °C.

These results are in agreement with a mechanism of addition of the nucleophile to the α-carbon atom followed by fast elimination of the halide ion, as first suggested by Miller *et al.*[1a] (Scheme). The intermediate anion (A) apparently does not capture a proton from added ethanol, but evolves by losing X^-. This is justified, since halide ions are good leaving groups, even in dimethylformamide.



SCHEME

Alternative mechanisms for the nucleophilic substitution of halogenoacetylenes were suggested by Arens[3b] and by Viehe *et al.*,[9] and have been discussed,[10] but do not fit the present results either for chloro- or for bromo-derivatives. In fact, reactions of arylacetylenic derivatives $ArC{\equiv}CX$ with nucleophiles attacking X[3b] are reported to have a leaving-group effect in the sense $k(X = Br) \gg k(X = Cl)$,[2] and ρ values around unity;[2,11] moreover, the intermediate acetylide anion easily captures a proton from alcohols.[1c,12] Also the anion produced by rate-determining addition to the β-carbon atom[9] should be trapped by alcohols. Since such a carbanion does not carry a charge on the carbon atom adjacent to the substituted benzene ring, a low ρ value would be expected, although a value as high as 2·58 has been reported for the β-addition of *p*-nitrothiophenoxide to arylpropiolates.[13]

The observed substituent and leaving-group effects are similar to those for aromatic and ethylenic nucleophilic substitution. A typical Hammett ρ value for attack by thiophenoxide on substituted 1-chloro-2-nitrobenzenes is 5·1 (methanol; 35 °C).[14] For attack by toluene-*p*-thiolate on 2-chloro-1,1-diarylethylenes a ρ value of 4·32 ($Me_2N{\cdot}CHO$; 24 °C) was found.[15] Values of ρ measured in dimethylformamide should be lower than the corresponding values in methanol since ρ values usually decrease with increasing dielectric constant of the solvent[16] unless specific interactions are present.[17] As to the leaving-group effect, the literature[18] shows that, for substitution at an sp^2 carbon atom by different nucleophiles, the ratio $k(\mathrm{Cl}) : k(\mathrm{Br})$ is usually within the range 0·1—4.

A few reactions of arylhalogenoacetylenes with nucleophiles gave $k(\mathrm{Cl}) : k(\mathrm{Br})$ ratios similar to those reported here. A value of 1·25 has been found[1c] for the Arbuzov reaction of 1-chloro- and 1-bromo-2-phenylacetylene with triethyl phosphite in tetrahydrofuran at 79 °C; a value of *ca.* 1·9 has been reported[1d] for attack on the α-carbon atom of the same acetylenes by sodium methoxide in methanol at 78 °C.

The relative stability of vinyl anions like (A) that contain two orthogonal π electron systems, together with other considerations,[19] can explain the high reactivity observed. The rate of the reaction of 1-chloro-2-phenylacetylene (Table 1) is much higher than that of an analogous ethylene (2-chloro-1,1-diphenylethylene) with the same nucleophile–solvent system ($k =$

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$1{\cdot}74 \times 10^{-7}$ l mol^{-1} s^{-1} at −25 °C, from the Arrhenius equation).[20]

An order-of-magnitude evaluation of solvent effects can be done as follows. Extrapolation of published data [2] allows us to attribute a value of the order of 10^{-4} l mol^{-1} s^{-1} to the rate coefficient for halogen abstraction from 1-bromo-2-phenylacetylene by toluene-*p*-thiolate in methanol at −25 °C. Since attack on the α-carbon atom was not observed in methanol, a much smaller rate coefficient should be attributed to such a reaction. If the mechanism of attack on α-carbon is accepted for the same reaction in dimethylformamide, a value $\leqslant 2{\cdot}15 \times 10^{-2}$ l mol^{-1} s^{-1} should be attributed to the hypothetical rate coefficient for the non-observed attack on bromine in this solvent. As a consequence the solvent effect on the nucleophilic addition to carbon would be expressed by the ratio $k(\mathrm{Me_2N{\cdot}CHO}) : k(\mathrm{MeOH}) \gg 10^2$, while the same ratio would be $\ll 10^2$ for bromine abstraction. Although this is only qualitative reasoning, the conclusion does not conflict with published values of $k(\mathrm{Me_2N{\cdot}CHO}) : k(\mathrm{MeOH})$ ratio for the two types of reaction. By use of tetra-alkylammonium iodides as nucleophiles, that ratio was found to be 400 for attack at carbon (1-bromo-2,4-dinitrobenzene) [21] and *ca.* 45 for attack at bromine (*meso*-1,2-dibromo-1,2-diphenylethane).[22,23]

EXPERIMENTAL

Purity was checked by g.l.c. on SE-30 5—20% columns at 110—180 °C with a C. Erba Fractovap GT chromatograph (flame ionisation detector). Molecular weights were determined by vapour-pressure osmometry (in benzene) with a Perkin-Elmer 115 instrument. The remaining equipment has been described.[15,24] Tetramethylsilane was used as standard and $\mathrm{CDCl_3}$ as solvent for n.m.r. spectroscopy.

Arylhalogenoacetylenes.—These were prepared by direct halogenation [25,26] of the corresponding acetylenes,[27] unless otherwise stated. The products showed little or no i.r. absorption at 3300 cm^{-1} [ν(≡C–H)].

1-Chloro-2-phenylacetylene (Ia), prepared from commercial phenylacetylene through the sodium acetylide,[28] had b.p. 74—75 °C at 25 mmHg; n_{D}^{18} 1·578 (lit.,[28] 71 °C at 16 mmHg; 1·576); $\lambda_{\mathrm{max.}}$ (95% ethanol) 239 (ε 18,400) and 251 nm (16,900). 1-Bromo-2-phenylacetylene (Ib) was 99·9% pure by g.l.c.; $\lambda_{\mathrm{max.}}$ (n-hexane) 242 (ε 18,600) and 253 nm (18,200). 1-Chloro-2-(*p*-tolyl)acetylene (IIa) was obtained both by Truchet's method [28] and by direct chlorination, and purified by repeated distillation or column chromatography on alumina; n_{D}^{25} 1·5695 (lit.,[28] 1·5700) (Found: Cl, 23·0. Calc. for $\mathrm{C_9H_7Cl}$: 23·5%). The compound was 95% pure by g.l.c. and n.m.r. 1-Bromo-2-(*p*-tolyl)acetylene (IIb) was obtained with the same purity (Found: Br, 40·2%; *M*, 207. Calc. for $\mathrm{C_9H_7Br}$: Br, 41·0%; *M*, 195·06); τ 2·5—3·0 (4H, m) and 7·68 (3H, s).

1-Chloro-2-(*p*-chlorophenyl)acetylene (IIIa), prepared by a known procedure,[29] had m.p. 77—78 °C (lit.,[29] 77—78) (Found: Cl, 40·6. Calc. for $\mathrm{C_8H_4Cl_2}$: Cl, 41·5%); τ 2·69 (s). 1-Bromo-2-(*p*-chlorophenyl)acetylene (IIIb) was obtained as a solid, m.p. 83—85 °C (lit.,[2] 80—82·5) (Found: C, 44·6; H, 1·9%; *M*, 221. Calc. for $\mathrm{C_8H_4BrCl}$: C, 44·6; H, 1·85%; *M*, 215·5); $\lambda_{\mathrm{max.}}$ (n-hexane) 251 (ε 23,000) and 262 nm (22,250); τ 2·67 (s). 1-Bromo-2-(*p*-nitrophenyl)acetylene (IVb) had m.p. 172 °C (from ethanol) [lit.,[2] 170 (decomp.)] (Found: C, 42·3; H, 1·7; N, 5·85. Calc. for $\mathrm{C_8H_4BrNO_2}$: C, 42·5; H, 1·8; N, 6·2%); $\lambda_{\mathrm{max.}}$ (methanol) 217 (ε 9900) and 296 nm (18,300); τ 1·7—2·5 (m). 1-Bromo-2-(*p*-methoxyphenyl)acetylene (Vb), after being purified by column chromatography on alumina, was ⩾98% pure by g.l.c.; τ 2·6—3·4 (4H, m) and 6·26 (3H, s).

Aryl-(p*-tolylthio)acetylenes.*—These were prepared from arylhalogenoacetylenes (0·06—0·16M) and toluene-*p*-thiolate (0·05—0·15M) in 'standard' dimethylformamide under nitrogen, mostly at −25 °C during a few minutes. Yields were 30—40% after purification. 1-Bromo-2-(*p*-methoxyphenyl)acetylene (Vb) gave (Vc) after 40 h at 40 °C.

1-Phenyl-2-(*p*-tolylthio)acetylene (Ic) had m.p. 45—46 °C (lit.,[30] 45·5—46·5) (Found: S, 13·9%; *M*, 228. Calc. for $\mathrm{C_{15}H_{12}S}$: S, 14·3%; *M*, 224·3); $\lambda_{\mathrm{max.}}$ (95% ethanol) 251 (ε 30,200) and 300—315br nm (12,900). 1-p-*Tolyl*-2-(p-*tolylthio*)*acetylene* (IIc) had m.p. 66—67 °C (from light petroleum) (Found: C, 79·6; H, 5·9%; *M*, 250. $\mathrm{C_{16}H_{14}S}$ requires C, 80·6; H, 5·9%; *M*, 238·35). 1-(p-*Chlorophenyl*)-2-(p-*tolylthio*)*acetylene* (IIIc) was obtained from (IIIa) and (IIIb) as large prisms, m.p. 92 °C (from light petroleum) (Found: C, 70·2; H, 4·15%; *M*, 266. $\mathrm{C_{15}H_{11}ClS}$ requires C, 69·6; H, 4·15%; *M*, 258·8); τ 2·5—2·9 (8H, m) and 7·67 (3H, s). 1-(p-*Nitrophenyl*)-2-(p-*tolylthio*)*acetylene* (IVc) was obtained as a yellow solid, m.p. 106 °C (from methanol) (Found: C, 66·4; H, 3·8; N, 5·05. $\mathrm{C_{15}H_{11}NO_2S}$ requires C, 66·9; H, 4·1; N, 5·2%); $\lambda_{\mathrm{max.}}$ (methanol) 220sh (ε 14,500), 249 (16,700), 284 (10,400), and 360 nm (15,100); τ 1·7—2·9 (8H, m), and 7·64 (3H, s). 1-(p-*Methoxyphenyl*)-2-(p-*tolylthio*)*acetylene* (Vc) was an oil, b.p. *ca.* 200 °C at 2 mmHg (Found: C, 76·1; H, 5·7. $\mathrm{C_{16}H_{14}OS}$ requires C, 75·55; H, 5·55%); τ 2·4—3·3 (8H, m), 6·19 (3H, s), and 7·68 (3H, s).

1,2-*Di*-(p-*tolylthio*)-2-*arylethylenes.*—They were prepared from the corresponding arylhalogenoacetylenes (0·15M) and sodium toluene-*p*-thiolate (0·45M) in 'standard' dimethylformamide under nitrogen, during 36 h at room temperature.

1,2-*Di*-(p-*tolylthio*)-2-*phenylethylene* (VI), obtained from (Ia) in 58% yield, was pure by g.l.c., m.p. 84 °C (from n-heptane) (Found: C, 74·7; H, 5·6%; *M*, 339. $\mathrm{C_{22}H_{20}S_2}$ requires C, 75·8; H, 5·8%; *M*, 348·53); $\lambda_{\mathrm{max.}}$ (95% ethanol) 257 (ε 15,000), 295 (16,100), and 315 nm (16,200); τ 2·4—3·1 (14H, m), 7·67 (3H, s), and 7·80 (3H, s); μ (benzene; 25 °C) 2·50 D. Compound (VI) was ozonised in methylene dichloride; after being shaken with aqueous sodium hydrogen carbonate, the organic layer gave crystals, m.p. 75 °C (from ethanol), which were shown to be *S*-(*p*-tolyl) thiobenzoate (lit.,[31] m.p. 75 °C) (Found: C, 73·1;

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H, 5·15; S, 14·1. Calc. for $C_{14}H_{12}OS$: C, 73·65; H, 5·3; S, 14·05%); $\nu_{max.}$ 1670s cm^{-1}; τ 2—3 (9H, m) and 7·63 (3H,s).

Refluxing of (VI) during 4 h in aqueous-alcoholic mercuric chloride [5] gave no phenylacetic acid.

Di-(p-*tolylthio*)-(p-*tolyl*)*ethylene*.—This *compound*, obtained in 22% yield from (IIb), was pure by g.l.c., m.p. 73—74 °C (from methanol) (Found: C, 77·8; H, 6·05%; *M*, 354. $C_{23}H_{22}S_2$ requires C, 75·8; H, 5·8%; *M* 362·53); τ 2·5—3·2 (13H, m), 7·65 (3H, s), 7·73 (3H, s), and 7·77 (3H, s). *Di-*(p-*tolylthio*)-(p-*chlorophenyl*)*ethylene* [yield (from IIIb) 40%] had m.p. 69 °C (Found: C, 68·5; H, 4·85. $C_{22}H_{19}ClS_2$ requires C, 69·0; H, 4·85%), τ 2·4—2·9 (13H, m), 7·63 (3H, s), and 7·74 (3H, s); μ (benzene; 25 °C) 2·63 D.

*Sodium Toluene-*p-*thiolate*.—Toluene-*p*-thiol (B.D.H. reagent grade) was treated with sodium in toluene; the salt was filtered off, thoroughly washed with toluene, dried, and kept *in vacuo* under phosphoric oxide. Solutions were iodometrically titrated (purity was generally *ca.* 95%).

'*Standard Dimethylformamide*.'—Dimethylformamide (RS Carlo Erba) was purified in two ways: (*a*) by passage over alumina under nitrogen, after drying on molecular sieves 4A; and (*b*) by distillation over calcium hydride, under nitrogen, after treatment on BaO overnight. After these treatments, dimethylformamide was analysed by g.l.c. on 0·8 m Porapak P columns (thermal conductivity detector, carrier H_2). Column temperature was raised from 90 (3 min) to 200 °C during 11 min. Water content was *ca.* 0·05% (w/w) in both cases. Kinetic runs and product preparations in solvents purified by methods (*a*) or (*b*) showed no difference.

Kinetics.—Substrates were weighed and thiolate was titrated. Aliquot portions of reactants were introduced under nitrogen in the two arms of a Y-tube with screw cap, and thermostatted ±0·1 °C. After fast mixing, solution was left to react (0·3—12 min), then poured into a solution of nitric acid in dimethylformamide at −50 °C. Organic compounds were extracted with carbon tetrachloride. In the aqueous phase halide ion was titrated with 0·02M-$AgNO_3$ by use of a Metrohm E 436 potentiograph. Most reactions were followed up to 60% completion. Rate coefficients (*k*) were calculated by least-squares fitting to the second-order rate equation. A typical kinetic run is described for 0·0445M-(IIIb) + 0·0113M-p-$C_7H_7S^-Na^+$ at −25·0 °C. Time (s) and Br$^-$ concentration (mol l^{-1}): 22, 0·00228; 45, 0·00403; 60, 0·00437; 104, 0·00551; 119, 0·00685; 159, 0·00769. Rate coefficient *k* = 0·1662 ± 0·0103 l mol^{-1} s^{-1}.

Reaction of (IVb) is too fast to be followed as described. An attempt to follow the reaction by direct spectrophotometric analysis failed because of formation of coloured complexes between substrate and solvent. The reactivity of (Vb) was too irregular for kinetic measurements.

Reactions in Dimethylformamide containing 1M-*Ethanol*.—Substitutions were studied by use of *ca.* 0·05M-(Ib) or -(Vb) and *ca.* 0·015M-toluene-*p*-thiolate at −25 °C for (Ib) and at room temperature for (Vb), up to completion. Organic compounds, extracted with carbon tetrachloride, were examined by g.l.c. Only traces of arylacetylenes, already present in the reactants, were revealed.

The process of substitution followed by addition was studied by use of 0·08M-(IIIb) and 0·23M-toluene-*p*-thiolate at room temperature. The same product as in 'standard' dimethylformamide was obtained (mixed m.p., n.m.r. spectrum).

We thank Consiglio Nazionale delle Ricerche (Rome) for financial support.

[2/1267 *Received, 5th June*, 1972]