Nucleophilic Attack on Halogeno(phenyl)acetylenes by Halide Ions

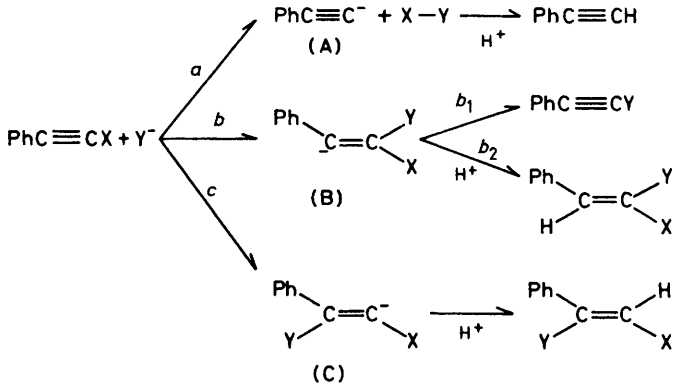
By **Ryuichi Tanaka,* Shì-Qín Zhèng, Kenji Kawaguchi,** and **Takehide Tanaka,** Department of Materials Science and Technology, Kyushu University, Fukuoka, Japan 812

Nucleophilic reactions between halogeno(phenyl)acetylenes and halide ions, ArC≡CX + Y^-, where Ar = C_6H_5 or p-ClC_6H_4, X = Cl or Br, and Y = Cl or Br, have been examined. Halogen exchange of the Finkelstein type was observed for the first time in acetylene halides in anhydrous dimethyl sulphoxide when X = Br and Y = Cl. This exchange did not occur with other X–Y combinations. In the presence of up to 20% water in dimethyl sulphoxide, or under aqueous–organic phase-transfer catalytic conditions, nucleophilic addition (formally of HY) took place for all the X–Y combinations studied. In the additions, the nucleophile Y^- invariably attacked the carbon to which the phenyl group was bound. The mode of HY addition was stereospecifically *trans*; accordingly, the resulting dihalogenostyrenes always had the (*Z*)-1,2-dihalogeno-configuration.

THE list of successful nucleophilic substitutions on halogenoethynes has been growing, but is much less exhaustive than the corresponding examples for halogeno-alkanes, -alkenes, or -benzenes.[1,2] For example, halogen exchange reactions of the Finkelstein type have not been reported for halogenoalkynes, although iodide ion was tried without success on 1-chloro-2-phenylethyne (1) in dry acetone,[3] and on 1-bromo-2-phenylethyne (4) in a dimethyl sulphoxide–water mixture.[4] In the latter case, phenylethyne (5), rather than 1-iodo-2-phenylethyne, was the only product. Our previous experience of the reactions of 1-halogeno-2-phenylethynes with sodium methoxide told us that we would have to choose nearly aprotic conditions and that we might be better off with substrate (1) than with (4) to obviate path *a* in Scheme 1 and to effect path $b \longrightarrow b_1$.[5] Path *c*, which leads to another 'wrong' product, still remains as a possibility. The present study deals with regio- and stereo-selectivity in the reactions of 1-aryl-2-halogenoethynes with halide nucleophiles in anhydrous dimethyl sulphoxide (DMSO), DMSO–H_2O, and heterogeneous systems under phase-transfer catalytic conditions.

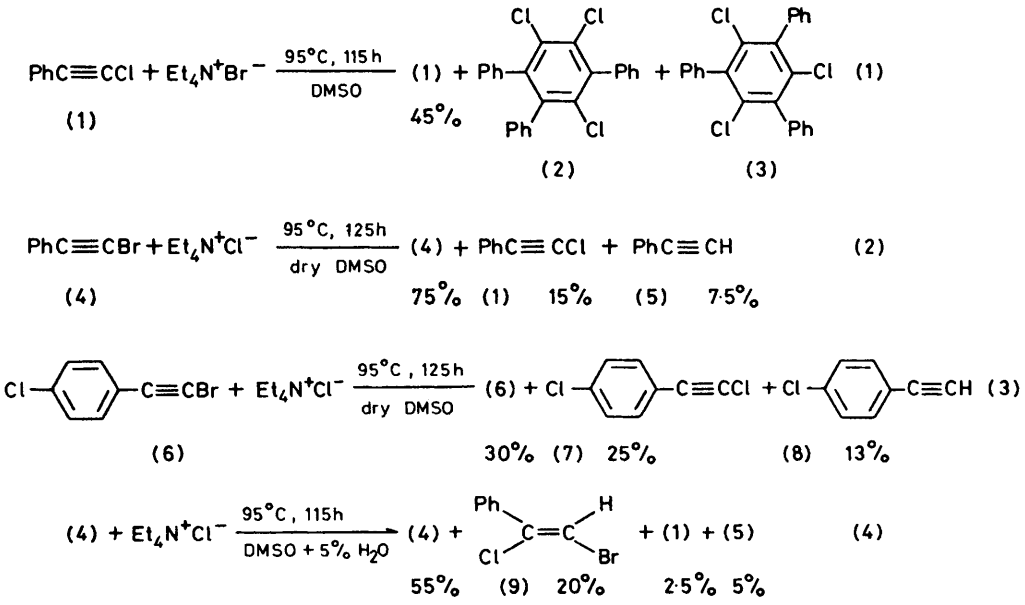
RESULTS AND DISCUSSION

Halogen Exchange in Anhydrous DMSO.—In search of reaction conditions under which halogen exchange (Scheme 1, path $b \longrightarrow b_1$) would occur, we heated



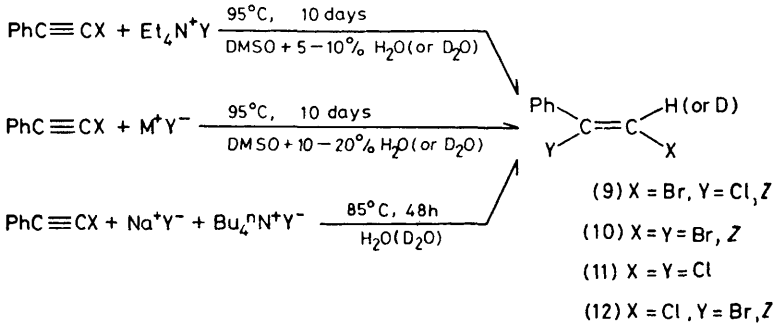
SCHEME 1 X = Cl, Br; Y = F, Cl, Br, I

1-aryl-2-halogenoethynes (ArC≡CX) with tetraethylammonium halides ($Et_4N^+Y^-$) in thoroughly dried DMSO.



In the reaction of 1-chloro-2-phenylethyne (1) with an excess of tetraethylammonium bromide (TEAB), *i.e.*, when X = Cl and Y = Br, the chlorine of (1) was not displaced by bromide ion. While *ca.* 45% of the starting material (1) was recovered, the rest was a tar due to thermal polymerisation of (1), from which the cyclic trimers (2) and (3) were isolated.

As shown in Scheme 2, not only the combination of substrate (4) with TEAC but also the (1)–TEAC, (1)–TEAB, and (4)–TEAB combinations gave rise to the formation of (*Z*)-αβ-dihalogenostyrenes in DMSO containing up to 10% water. Moreover, sodium chloride



SCHEME 2 X = Cl, Br; Y = Cl, Br; M = Na, K

or potassium bromide could take the place of TEAC or TEAB, if as much as 20% water was added to DMSO. Replacement of the water added to DMSO with D_2O enabled the synthesis of the deuteriated homologues of the dihalogenostyrenes. The results are summarised in Table 1.

In contrast, when 1-bromo-2-phenylethyne (4) and 1-bromo-2-(4-chlorophenyl)ethyne (6) were heated with tetraethylammonium chloride (TEAC), *i.e.*, when X = Br and Y = Cl, the desired substitution of chloride for the bromines of (4) and (6) did occur: 1-chloro-2-phenylethyne (1) and 1-chloro-2-(4-chlorophenyl)ethyne (7) were formed in yields of 15 and 25%, respectively. Though the concomitant formation of arylethynes (5) and (8), presumably *via* path *a* in Scheme 1, could not completely be suppressed, the present results provide the first examples of the Finkelstein reactions in halogenoacetylene systems.

Nucleophilic Additions in Wet DMSO, or in Water under Phase-transfer Catalysis.—If 5% water was added to DMSO, halogen exchange still took place when X = Br and Y = Cl [substrate (4) and TEAC]. But the main product turned out not to be (1) but (*Z*)-(2-bromo-1-chlorovinyl)benzene (9). Formally, product (9) may be regarded as resulting from the *trans*-addition of

Scheme 2 also illustrates that the same additions were brought about under somewhat milder conditions by suspending substrates (1) or (4) in an aqueous solution of a sodium halide in the presence of a phase-transfer catalyst such as tetrabutylammonium halide. In the absence of the catalyst, addition did not occur at all. The results of the phase-transfer reactions are also included in Table 1.

The most remarkable feature of these reactions was that in each substrate–nucleophile pair given in Scheme 2, only a single geometrical isomer [(*Z*)-αβ-dihalogeno-configuration] among the three (X = Y) or six (X ≠ Y) possible isomers of the dihalogenostyrene was formed.

TABLE 1

Reaction of halide ions with 1-halogeno-2-phenylethynes under protic conditions [a]

Reactants [c]	Medium	Temperature (°C)	Time (h)	Product(s) (%) [b]
(1) + TEAC	DMSO + 5% H_2O	95	264	(11) 31, (5) trace
(1) + NaCl	DMSO + 20% H_2O	95	288	(11) 19 [c]
(1) + NaCl	H_2O + $Bu^n_4N^+Cl^-$	85	48	(11) 27
(1) + TEAB	DMSO + 5% H_2O	95	240	(12) 35, (5) trace
(1) + TEAB	DMSO + 10% H_2O	95	240	(12) 43
(1) + KBr	DMSO + 10% H_2O	95	240	(12) 32 [c]
(1) + KBr	DMSO + 10% D_2O	95	240	[^{2}H]-(12) 35 [c]
(1) + NaBr	H_2O + $Bu^n_4N^+Br^-$	85	96	(12) 38
(4) + TEAC	DMSO + 5% H_2O	95	115	(9) 20, (1) 2.5 (5) 5
(4) + TEAC	DMSO + 10% H_2O	95	264	(9) 41
(4) + TEAC	DMSO + 20% H_2O	95	288	(9) 33
(4) + NaCl	DMSO + 10% H_2O	95	240	(9) 34 [c]
(4) + NaCl	DMSO + 7% D_2O	95	240	[^{2}H]-(9) 34 [c]
(4) + NaCl	DMSO + 20% H_2O	95	288	(9) 19
(4) + NaCl	H_2O + $Bu^n_4N^+Cl^-$	85	115	(9) 34
(4) + TEAB	DMSO + 5% H_2O	95	288	(10) 42, (5) trace
(4) + NaBr	H_2O + $Bu^n_4N^+Br^-$	85	72	(10) 58

[a] For amounts of reagents and media, see Experimental section. [b] Yields are based on g.l.c. peak ratios unless otherwise stated. [c] Yields are based on the amounts of isolated products on the preparative scale.

TABLE 2

G.l.c. retention times and n.m.r. chemical shifts of dihalogenostyrenes

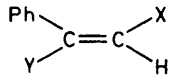
Dihalogenostyrene	Retention time (min) [b]	$\delta_{obs.}$ [c] (p.p.m.)	$\delta_{lit.}$ [d] (p.p.m.)	$\delta_{calc.}$ [e] (p.p.m.)
(9) [a]	15.1	6.81	6.81 [f]	6.81
(10) [a]	22.1	6.93	6.95,[g] 6.98 [h] 7.00 [i]	7.23
(11) [a]	9.65	6.63	6.63,[j,k] 6.62 [l]	6.82
(12) [a]	13.8	6.76		7.24
(13)	8.3	6.50	6.55 [f]	6.44 [q]
(14)	11.6	6.69	6.70,[g] 6.75 [h,i]	6.69 [q]
(15)	5.4	6.45	6.45,[k] 6.46 [j] 6.49 [l]	6.44
(16)				6.58
(17)	9.9	7.18	6.95 or 7.05 [m]	7.07 [q]
(18)		7.50	7.40,[h] 7.45 [n] 7.43 [o]	7.34
(19)	4.94	6.73	6.72,[p] 6.48 [n]	6.94
(20)	11.0	7.09	6.95 or 7.05 [l]	7.21

[a] Dihalogenostryrenes that were confirmed to be formed in PhC≡CX + Y^- reactions. [b] G.l.c. column: 20% QF-1 on fire brick, 5 mm × 1 m, 110 °C, He 30 cm^3 min^{-1}. [c] Chemical shift of vinyl proton singlet; solvent is CCl_4. [d] Chemical shift of vinyl proton singlet reported in the literature. Solvent is CCl_4 unless otherwise stated. [e] Estimated from an additivity rule according to U. E. Mater, C. Pascual, E. Pretsch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, 1969, **25**, 691. [f] S. Uemura, H. Okazaki, A. Onoe, and M. Okano, *J.C.S. Perkin I*, 1979, 548. [g] G. D. Mel'nikov and S. P. Mel'nikova, *J. Org. Chem. U.S.S.R.*, 1977, **13**, 625. [h] Ref. 22. [i] S. Uemura, H. Okazaki, and M. Okano, *J.C.S. Perkin I*, 1978, 1278. [j] A. Debon, S. Masson, and A. Thuiller, *Bull. Soc. chim. France*, 1975, 2493. [k] Ref. 23. [l] S. Ueumura, H. Okazaki, A. Onoe, and M. Okano, *J.C.S. Perkin I*, 1977, 676 ($CDCl_3$). [m] Ref. 16. [n] S. Takano K. Ogasawara I. Nagayama and T. Katsuma, *Synth. Comm.*, 1976, **6** 349. [o] C. Wesdemoitis and H. Schwarz, *Annalen*, 1976, 1889. [p] E. Kiehlmann, R. J. Bianchi, and W. Reeve, *Canad. J. Chem.*, 1969, **47**, 1521; G. K. Rudnev, I. G. Khaskin, and B. A. Geller, *J. Org. Chem. U.S.S.R.*, 1976, **12**, 1740. [q] When bromine is *cis* to the phenyl group, corrections were made according to S. W. Tobey, *J. Org. Chem.*, 1969, **34**, 1281.

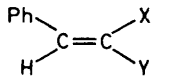
This was easily recognized from the n.m.r. spectra of the crude product mixtures; each spectrum showed only one peak in the region for vinyl proton signals. Nevertheless, this did not mean that these reaction systems as a whole were clean. The thermal polymerisation of 1-aryl-2-halogenoethynes, which was the sole reaction of (1) in anhydrous DMSO in the presence of TEAB, was still a serious competing process in every system we studied. In fact, some 20—60% of the starting materials were liable to polymerise after such prolonged heating under the reaction conditions. With this reservation in mind, we may state that the nucleophilic addition of halide ions to 1-aryl-2-halogenoethynes proceeded regio- and stereo-specifically.

Characterisation of Addition Products.—The simplest clues to the identity of the dihalogenostyrenes were the n.m.r. chemical shifts of the vinyl proton singlets and the g.l.c. retention times. For comparison, we prepared, mostly *via* the known synthetic routes, ten isomers among the 12 possible dihalogenostyrenes (9)—(20).

From the n.m.r. and g.l.c. data of all the possible dihalogenostyrenes bar two [(9) and (16)] in Table 2, we were able to establish that chloride as well as bromide ion invariably added to 1-aryl-2-halogenoethynes in accord with Scheme 2 under protic conditions. In no case, were geminal digalogenostyrenes such as (17)—(20) detected in the crude product mixtures of the reactions listed in Table 1.

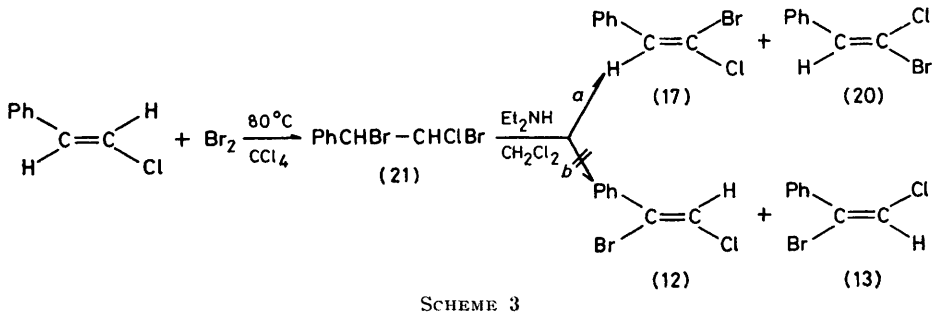


(13) X = Br, Y = Cl
(14) X = Y = Br
(15) X = Y = Cl
(16) X = Cl, Y = Br



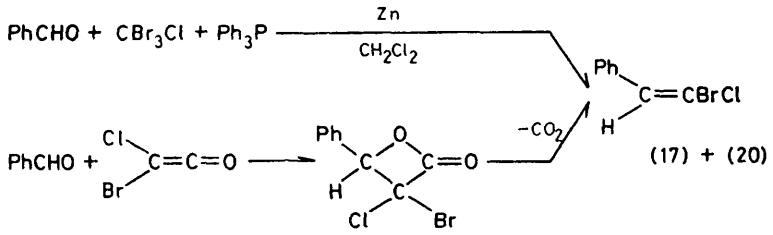
(17) X = Br, Y = Cl
(18) X = Y = Br
(19) X = Y = Cl
(20) X = Cl, Y = Br

The preparation of (*Z*)- and (*E*)-(2-bromo-2-chlorovinyl)benzenes, (17) and (20), which are included in Table 2, is noteworthy. This isomeric pair was first reported to be formed *via* path *a* in Scheme 3 by Schlosser and Ladenberger.[6] Since these workers gave no spectral data, we were unable to rule out the possibility that the second pathway *b* leading to (12) and/or (13) might have been operating. It was only after we prepared compounds (17) and (20) by the two alternative, less equi-



SCHEME 3

vocal methods [7,8] given in Scheme 4 that the dehydrobromination of (1,2-dibromo-2-chloroethyl)benzene (21) turned out to proceed, in fact, exclusively *via* path *a* in Scheme 3, because the product distributions of the three reactions were practically the same.



SCHEME 4

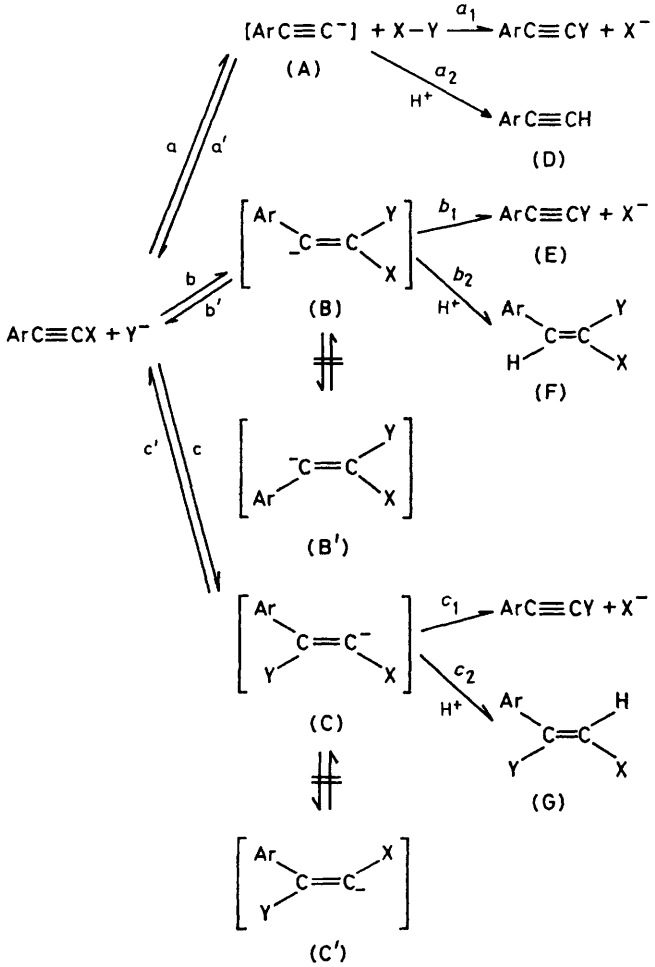
Mechanisms.—To understand the reaction paths in the nucleophilic reactions of 1-aryl-2-halogenoethynes, we have re-examined Scheme 1 in the more elaborate form of Scheme 5.

At present, we have very few theories to answer the question as to which site of 1-aryl-2-halogenoethyne is preferentially attacked by a nucleophile. Beltrame examined the choice made by nucleophile HS^- between the halogen and C-1 in 1-halogeno-2-phenylethynes in terms of the potential energy surfaces based on the extended Hückel calculations. Attack at C-1 was predicted when X = Cl or F. Halogen attack was favoured when X = I, and a borderline case was encountered when X = Br.[9] So far as only these two routes are involved, the predictions agree very well with experience. Unfortunately, the third possibility, *i.e.*, attack on C-2 was not considered by Beltrame. Hence, we must have recourse to the rather qualitative arguments which follow.

In Scheme 5, if anion (B) is formed as the result of attack on C-1, the aryl group becomes the α-substituent of the vinyl anion. On the other hand, attack on C-2 to form anion (C) puts the halogen at the α-position to the anionic centre. The ability of α-halogens to stabilise carbanions have been well documented for saturated,[10,11] and unsaturated systems; [12] in most cases, the stabilising power is in the order I > Br > Cl > F. The remaining question is whether this α-effect of the halogens in the unsaturated anion (C) is superior to the stabilisation by the α-phenyl group in anion (B).

A partial answer to this comes from the exclusive formation of dihalogenostyrenes (17) and (20) (Scheme 3); this indicates that, of the two aliphatic protons of substrate (21), the one adjacent to bromine and chlorine was abstracted by the base in preference to the one adjacent to bromine and phenyl, *i.e.* chlorine is more effective than phenyl in stabilising the sp^3-hybridised carbanionic, or carbanion-like intermediate in this particular reaction. Judging from the close parallelism between saturated and unsaturated systems for the anion stabilising effect of halogens, we expect anion (C) to be more stable than anion (B) in Scheme 5 so far as X = Cl or Br.

In principle, anion (B) could invert to anion (B′) *via* the flipping of the lone-pair electrons at the anionic centre. But the barriers to the inversion of vinyl anions are usually very high. A MINDO calculation for the unsubstituted vinyl anion predicts a barrier of *ca.* 130 kJ mol^{-1}.[13] The introduction of phenyl group(s) as substituent(s) reduces the barrier height considerably,[14] but it still amounts to *ca.* 38 kJ mol^{-1} in 1,2-diphenylvinyl anion.[15] The reversion of (B) to the starting materials (path *b*′) may be roughly approximated by the second half of the reaction co-ordinate of a hypothetical *E*2-CB elimination of HY from dihalogenostyrene (F); carbanion (B) lies past the transition state, and path *b*′ should be mostly downhill. It is, therefore,



SCHEME 5 X = Cl, Br; Y = nucleophile

unlikely that the anion inversion (B) $\rightleftharpoons$ (B′) which requires a considerable activation energy, can compete favourably with path b'. By the same token, carbanion (C) cannot isomerise to (C′) when faced with the option of path c'.

In our systems, nucleophilic substitution took place in anhydrous DMSO when X = Br and Y = Cl, whereas it did not occur at all when X = Cl and Y = Br. The ionic intermediate responsible for the transformation of 1-bromo- to 1-chloro-2-phenylethyne [(4) $\longrightarrow$ (1)] now appears to be the vinylic carbanion (B) for the following reasons: (a) if path a_1 were operating, it would involve an unlikely attack of the phenylvinyl anion (A) at the 'positive' chlorine in bromine chloride (X–Y in Scheme 5); anion (A) is probably responsible only for the formation of the traces of phenylethyne (5); (b) path $c \longrightarrow c_1$ through the Fritsch–Buttenberg–Wiechel type rearrangement is highly improbable in the absence of a strong base.[1,2,16]

Suppose carbanion (B) is formed under aprotic conditions. The forward reaction b_1 requires the elimination of the leaving group X situated *cis* to the lone pair electrons of vinyl anion (B). The reverse reaction b' involves the ejection of Y which is *trans* to the negative lobe. So far as the geometrical dispositions are concerned, the *trans*-elimination mode in the reverse path b' is probably much more favourable than the *cis*-elimination mode of the forward path b_1. For path b_1 to be able to compete with path b' favourably, or at least to an appreciable extent, therefore, X has to be a sufficiently better leaving group than Y. This requirement appears to be met without exception in the successful cases of nucleophilic substitutions on 1-aryl-2-halogenoethynes reported in the literature.[1,2] Also in the present systems, path b_1 is open when X = Br and Y = Cl, but it is closed when the roles of X and Y are reversed, in agreement with above requirement.

When water was added, the structure of the dihalogenostyrenes, the addition products, was always (G) rather than (F) in Scheme 5, as stated in the previous section. This was true even when the substitution (path b_1; X = Br, Y = Cl) was still concurrently occurring to some extent in DMSO containing 5% water. It follows, therefore, that the protonation of anion (B) *via* path b_2 has to be much slower or negligible relative to paths b_1 and b' even when protons are available. Though this may sound a little peculiar, we can cite at least two precedents in which protonation of a carbanion is overwhelmed by elimination of the α-halogen: (a) when X = Br and Y = CH_3O, the formation of (E) was faster than that of (F);[5] (b) when X = Cl or Br and Y = p-$CH_3C_6H_4S$, only (E) was obtained, and the presence of ethanol did not cause the protonation of (B) at all.[17]

A consistent rationale for our present findings may be given, if we assume that the formation of anion (C) is much faster than that of anion (B). So far as path c_1 is non-existent and path c_2 is closed in the absence of proton donors, intermediate (C) has no choice but to revert *via* path c'. This phase of the reaction thus becomes latent, and the net result is the occurrence of substitution *via* the much slower path $b \longrightarrow b_1$. Under protic conditions, on the other hand, path c_2 is now unlocked and the formation of adduct (G) becomes predominant or even exclusive. The rate of formation of dihalogenostyrenes (G), however, is not very great, probably because path c_2 has to compete with path c' which must be very fast.

EXPERIMENTAL

N.m.r. spectra were recorded on a JEOL JNM MH-60 instrument. Mass spectra were taken on a JEOL JMS-07 mass spectrometer. When necessary, the spectrometer was operated in g.l.c.–m.s. mode in conjunction with a JEOL JGC-20K gas chromatograph.

Materials.—Reagent grade dimethyl sulphoxide was distilled under reduced pressure, dried first over Linde molecular sieves 4X, then over calcium hydride, and finally re-distilled under reduced pressure directly into a reservoir, from which the solvent could be delivered into the reaction vessels by dry nitrogen pressure. The quaternary ammonium salts (TEAC, TEAB, $Bu^n_4N^+Cl^-$, and $Bu^n_4N^+Br^-$) were purchased and recrystallised from ethanol before use.

1-Chloro-2-phenylethyne (1),[18] 1-bromo-2-phenylethyne (4),[18] and 1-bromo-2-(4-chlorophenyl)ethyne (6)[19] were prepared by the conventional methods. They were stored in a refrigerator below −20 °C and vacuum-distilled immediately prior to use.

Tribromochloromethane was prepared by refluxing aluminium bromide (0.7 mol) with carbon tetrachloride (0.7 mol) for 8 h.[20] The crude product solidified when brought to room temperature. The solid was crushed with a spatula. After fresh carbon tetrachloride (*ca.* 50 ml) was added, the mixture was heated to 50 °C and filtered under suction. Carbon tetrachloride and bromotrichloromethane, b.p. 102—106 °C, were stripped off from the filtrate by simple distillation. The residue was distilled under reduced pressure. After dibromodichloromethane, b.p. 45—50 °C at 30 mmHg, had been removed, the desired tribromochoromethane fraction, b.p. 55 °C at 18 mmHg, was collected in 12% yield. The product was recrystallised from 1 : 1 water–ethanol, m.p. 54 °C.

The isomeric pair of (*Z*)- and (*E*)-(2-bromo-1-chlorovinyl)-benzenes (9) and (13) was obtained by heating α-bromoacetophenone with phosphorus pentachloride at 100 °C and distilling the resulting melt under vacuum, b.p. 60 °C at 0.1 mmHg.[21] (*Z*)- and (*E*)-(1,2-dibromovinyl)benzenes (10) and (14) were obtained as an isomeric mixture by brominating phenylethyne (5) in chloroform at 0 °C. Treatment of the product mixture with zinc powder and zinc chloride in ethanol gave isomer (10).[22] Isomer (14) was prepared by carrying out the bromination of phenylethyne in glacial acetic acid in the presence of lithium bromide.[22] (*Z*)- and (*E*)-(1,2-dichlorovinyl)benzenes (11) and (15) were made from α-chloroacetophenone and phosphorus pentachloride.[21,23] An attempted synthesis of (*Z*)- and (*E*)-(1-bromo-2-chlorovinyl)benzenes (12) and (16) from α-chloroacetophenone and phosphorus pentabromide[24] was unsuccessful. (2,2-Dibromovinyl)benzene (18) was prepared from benzaldehyde, carbon tetrabromide, and triphenylphosphine according to the procedure reported by Corey and Fuchs.[7] (2,2-Dichlorovinyl)benzene (19) was obtained *via* decarboxylation of 3,3-dichloro-4-phenyl-

oxetan-2-one, which was prepared from benzaldehyde and dichloroketen.[25]

(*Z*)- and (*E*)-(2-bromo-2-chlorovinyl)benzenes (17) and (20) were prepared in three different ways. (a) (*E*)-(2-Chlorovinyl)benzene was brominated and dehydrobrominated according to Schlosser and Ladenberger.[6] (b) Corey's procedure for the preparation of dibromostyrene (18) was modified by using tribromochloromethane in place of carbon tetrabromide.[7] (c) 3-Bromo-3-chloro-4-phenyloxetan-2-one was prepared from benzaldehyde and bromochloroacetyl chloride [26] in the presence of triethylamine.[8] The oxetanone was pyrolysed by simply distilling it under vacuum. All three methods gave practically the same product mixture, b.p. 54 °C at 0.5 mmHg; not only the n.m.r. peak positions but also the g.l.c. retention times of the products agreed very well. To distinguish the (*Z*)- from the (*E*)-isomer, the mixture was dissolved in dichloromethane containing an excess of diethylamine and left at room temperature for 30 min. After the solvent and the amine were removed under reduced pressure, the residue was examined by n.m.r. and g.l.c. The isomer which diminished faster was tentatively assumed to have (*Z*)-configuration (17), as, in this instance, the proton at C-1 is in a *trans*-relationship with the bromine at C-2. Since in these dihalogenostyrenes, there seem to be no structural complications which might direct otherwise, we believe that *trans*-dehydrobromination from (17) is more facile than *cis*-dehydrobromination or *trans*-dehydrochlorination from (20).

Reaction of 1-*Bromo*-2-*phenylethyne* (4) *with Tetraethylammonium Chloride* (*TEAC*) *in Anhydrous DMSO*.—Since the experiments for other reactant–nucleophile combinations were conducted similarly, we here give only a representative procedure. Reactant (4) (0.02 mol), TEAC (0.06 mol), and t-butylbenzene (0.005 mol; g.l.c. internal standard) were dissolved in anhydrous DMSO; the total volume was adjusted to 100 ml. Nine 10-ml portions were pipetted into separate ampoules, purged with dry nitrogen, sealed, and dipped in an oil-bath thermostatted at 95 °C. The ampoules were withdrawn at intervals and the contents were worked-up with ice-water and extracted with ether (2 ml). After most of the ether had evaporated under normal pressure, the extract was analysed by g.l.c. (for conditions, see footnote *b* in Table 2).

Two peaks (1.2 and 3.0 min) were noticeable in addition to those of the starting material (4) and the internal standard, in the product mixture obtained after reaction for 24 h; both peaks grew larger in product mixtures worked-up thereafter. The retention time of the former peak (1.2 min) corresponded to that of phenylethyne (5), *m/e* 102 ($M^{+\bullet}$). The retention time of the latter peak (3.0 min) agreed with that of 1-chloro-2-phenylethyne (1), *m/e* 136 (M^{+}) and 138 (36% in intensity).

Formation of the substitution product (1) was established by carrying out the reaction on a preparative scale followed by fractional distillation under reduced pressure. The product boiled at 70—74 °C at 15 mmHg, $\nu_{max.}$ (neat) 2 220 cm^{-1} (C≡C), in agreement with an authentic sample of (1).

Reaction of 1-*Bromo*-2-*phenylethyne* (4) *with TEAC in DMSO containing* 5% *Water*.—The procedure as above was followed except 5% water was added to DMSO beforehand. In addition to products (5) and (1), g.l.c. showed another peak at 15.4 min. The same compound was isolated (34%) from a preparative run: reactant (4) (*ca.* 10 g) and an excess of NaCl (*ca.* 100 g) was stirred in DMSO (500 ml) containing 10% water at 95 °C for 10 days. The solution was worked-up with ice–water and ether; the extract was distilled under reduced pressure. The yellow, pungent oil, was (Z)-(2-*bromo*-1-*chlorovinyl*)*benzene* (9) (Found: C, 44.25; H, 2.95. C_8H_6BrCl requires C, 44.2; H, 2.8%), *m/e* 216 and 218 (25, 28%, $M^{+\bullet}$), 180 and 182 (100, 98, $M - HCl^{+\bullet}$), 137 (22, $M - Br^{+\bullet}$), 102 (87), and 101 (83), $\nu_{max.}$ 1 600, 908, 760, and 738 cm^{-1}; δ(60 MHz; CCl_4) 6.81 (1 H, s, vinylic) and 7.17—7.58 (5 H, m, phenyl).

Reaction of 1-*Chloro*-2-*phenylethyne* (1) *with Tetraethylammonium Bromide* (*TEAB*) *in DMSO containing Water*.—The conditions employed were comparable with those for the (4)–TEAC combination. The main product had a g.l.c. retention time of 14.3 min. On a preparative scale, reactant (1) (10 g) was stirred with KBr (200 g) in DMSO containing 5% water at 95 °C for 10 days. Vacuum distillation of the worked-up product mixture gave a yellow oil (42%), b.p. 75 °C at 0.5 mmHg; *m/e* 216 and 218 (19, 22.5%, $M^{+\bullet}$); 137 and 139 (93, 30, $M - Br^{+\bullet}$), 102 (100, $C_8H_6^{+\bullet}$) and 101 (47%); $\nu_{max.}$ 1 600, 920, 905, and 830 cm^{-1}; δ(60 MHz; CCl_4) 6.76 (1 H, s, vinylic) and 7.17—7.60 (5 H, m, phenyl).

This compound was obviously one of the six geometrical isomers of bromochlorostyrene, but its spectral properties did not agree with those of isomers (9), (13), (17), and (20), which we were able to prepare by other methods. Moreover, the product was transformed back to the starting material (1) by allowing it to stand in ethylene glycol containing KOH at 60 °C. Although we are still not completely certain whether this compound is isomer (12) or (16), we prefer the (*Z*)-structure (12) by analogy with our other results.

Reaction of 1-*Aryl*-1-*halogenoethynes with Halide Ions under Phase-transfer Catalytic Conditions*.—Typically, reactant (4) (0.03 mol) was suspended in water (90 ml) containing tetrabutylammonium bromide (0.01 mol) and NaBr (0.027 mol) The system was vigorously stirred for 72 h at 85 °C. The organic layer was separated and analysed by g.l.c.; the main peak appeared at a retention time of 20.9 min and amounted to 58% of the initial feed. The g.l.c. as well as the spectral properties were identical with those of the authentic samples of (*Z*)-(1,2-dibromovinyl)benzene (10).

[0/339 *Received*, 3*rd March*, 1980]

REFERENCES

[1] S. I. Miller and J. I. Dickstein, *Accounts Chem. Res.*, 1976, **9**, 358.
[2] J. I. Dickstein and S. I. Miller, 'The Chemistry of the Carbon–Carbon Triple Bond,' ed. S. Patai, Wiley, New York, 1978, ch. 19.
[3] M. J. Murray, *J. Amer. Chem. Soc.*, 1938, **60**, 2662.
[4] M. C. Verplough, L. Donk, H. J. T. Bos, and W. Drenth, *Rec. Trav. chim.*, 1971, **90**, 765.
[5] (*a*) R. Tanaka and S. I. Miller, *Tetrahedron Letters*, 1971, 1753; (*b*) R. Tanaka, M. Rodgers, R. Simonaitis, and S. I. Miller, *Tetrahedron*, 1971, **27**, 2651.
[6] M. Schlosser and V. Ladenberger, *Chem. Ber.*, 1967, **100**, 3893.
[7] E. J. Corey and P. L. Fuchs, *Tetrahedron Letters*, 1972, 3769.
[8] W. T. Brady and A. D. Patel, *J. Org. Chem.*, 1972, **37**, 3536.
[9] P. Beltrame, A. Gavezzotti, and M. Simonetta, *J.C.S. Perkin II*, 1974, 502.
[10] J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Amer. Chem. Soc.*, 1957, **79**, 1406.
[11] J. D. Park, J. R. Lacher, and J. R. Dick, *J. Org. Chem.*, 1966, **31**, 1116.

[12] D. Daloze, H. G. Viehe, and G. Chiurdoglu, *Tetrahedron Letters*, 1969, **3945**.
[13] M. J. S. Dewar and M. Shanshal, *J. Amer. Chem. Soc.*, 1969, **91**, 365.
[14] D. Y. Curtin and J. W. Crump, *J. Amer. Chem. Soc.*, 1958, **80**, 1922.
[15] D. H. Hunter and D. J. Cram, *J. Amer. Chem. Soc.*, 1964, **86**, 5478.
[16] H. G. Viehe and S. Y. Delvarenne, *Chem. Ber.*, 1970, **103**, 1216.
[17] P. Beltrame, P. L. Beltrame, M. G. Cattania, and M. Simonetta, *J.C.S. Perkin II*, 1973, 63.
[18] S. I. Miller, G. R. Ziegler, and R. Wielseck, *Org. Synth.*, 1965, **45**, 86.
[19] D. Woodcock, *J. Chem. Soc.*, 1949, 203.
[20] G. Lehmann and B. Lucke, *J. prakt. Chem.*, 1963, **22**, 230.
[21] R. Dyckeroff, *Ber.*, 1877, **10**, 119.
[22] J. König and V. Wolf, *Tetrahedron Letters*, 1962, 1629.
[23] R-R. Lii and S. I. Miller, *J. Amer. Chem. Soc.*, 1973, **95**, 1602.
[24] C. E. Kaslow and M. M. Marsl, *J. Org. Chem.*, 1947, **12**, 456.
[25] (*a*) D. Borrmann and R. Wegler, *Chem. Ber.*, 1969, **102**, 64; (*b*) H. O. Krabbenhoft, *J. Org. Chem.*, 1978, **43**, 1305.
[26] H. Crompton and P. M. Triffitt, *J. Chem. Soc.*, 1922, **119**, 230.