

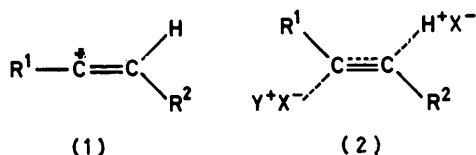
## Ionic Additions to Unsaturated Systems. Part 2.† Triethylammonium Hydrogendichloride as Reagent in the Addition of Hydrogen Chloride to Alkynes

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Addition of hydrogen chloride to the carbon-carbon triple bond may easily be performed by means of triethylammonium hydrogendichloride ( $\text{Et}_3\text{NH}^+\text{HCl}_2^-$ ): an equimolar mixture of this reagent with an alkyne, either neat or dissolved in an aprotic medium, affords the 1 : 1 addition product in high yield, without a catalyst. This method has been applied to dimethyl but-2-ynedioate, 3-chloropropyne, phenylacetylene, 1-phenylpropyne, and 3,3-dimethyl-1-phenylbut-1-yne. The reaction proceeds essentially through *anti*-addition of hydrogen chloride; predominant but non-exclusive *syn*-addition is only observed with 3,3-dimethyl-1-phenylbut-1-yne. The results are discussed in terms of the ambivalent character of the  $\text{HCl}_2^-$  ion, which acts both as a precursor of hydrogen chloride and as a powerful nucleophilic reagent, and prevents to some extent the formation of vinyl cation intermediates that normally are easily generated by protonation of alkylphenylacetylenes; the results also provide new evidence of the importance of the nucleophilic character of the species involved in the C-Cl bond formation in controlling the stereochemical course of the electrophilic addition of hydrogen chloride to alkynes.

MANY workers have already studied the ionic additions of the protic acids HX to alkynes;<sup>1-3</sup> this topic, however, still merits further investigation. These reactions may proceed by various mechanisms, and the outcome depends markedly upon many experimental factors. Recent reports deal with the addition of hydrogen chloride to acetylenecarboxylic acids and derivatives in water or water-dioxan,<sup>4</sup> and to various alkynes  $\text{R}^1\text{C}\equiv\text{CR}^2$  ( $\text{R}^1, \text{R}^2 = \text{H}$ , alkyl, or phenyl) in acetic acid<sup>5</sup> or in dichloromethane,<sup>6</sup> and with the addition of trifluoroacetic acid<sup>7</sup> and of fluorosulphuric acid in sulphuryl chloride fluoride or sulphur dioxide at low temperature<sup>8</sup> to similar alkynes.

These reactions involve two main processes, a choice between which depends upon the nature of the reagent attacking the triple bond in the rate-determining step, *i.e.* the attack may be nucleophilic, by an anion  $\text{X}^-$  when the triple bond bears electron-withdrawing groups,<sup>3,4</sup> or electrophilic, by  $\text{H}^+$ .<sup>1,2,5-8</sup> The latter process has held the attention of most workers, and two mechanisms are currently recognized: a bimolecular one (*AdE2*) proceeding through a vinyl cation intermediate (1) which can lead after incorporation of the



anion  $\text{X}^-$  to both *syn*- and *anti*-adducts in proportions depending mainly on the structure of the initial alkyne, and a trimolecular one (*AdE3*) proceeding through a transition state such as (2) which leads exclusively to

the product of *anti*-addition. The nature of the reagents and the experimental conditions deeply affect the course of the addition: it has been pointed out that use of a substituted phenylacetylene<sup>6</sup> or a highly polar and strongly acidic but weakly nucleophilic solvent<sup>7-9</sup> favours the *AdE2* mechanism, whereas a not very polar medium and, especially, a high nucleophilic power of the species  $\text{Y}^+\text{X}^-$  involved in C-X bond formation<sup>5</sup> favour the *AdE3* mechanism.

In our previous studies on the reaction between hydrogen chloride and various acetylenic tertiary amines  $\text{R}^1_2\text{N}\cdot[\text{CH}_2]_n\cdot\text{C}\equiv\text{CR}^2$  ( $\text{R}^1 = \text{alkyl}$ ;  $\text{R}^2 = \text{H}$  or alkyl,  $n = 1, 2$ , or 3) in anhydrous media, the following points have emerged: (i) isolation of the corresponding ammonium hydrogendichloride salts ( $\text{R}^1_2\text{NH}^+\cdot[\text{CH}_2]_n\cdot\text{C}\equiv\text{C}-\text{R}^2, \text{HCl}_2^-$ ) is possible;<sup>10</sup> (ii) gently heating these salts, in the pure state or dissolved in aprotic media ( $\text{CHCl}_3$ , MeCN, or  $\text{PhNO}_2$ ), and in the absence of catalyst, induces the addition of 1 equiv. of hydrogen chloride to the carbon-carbon triple bond in high yield, according to an exclusive *anti*-process.<sup>11</sup>

The two characteristic features of this reaction, *i.e.* the stereospecificity of the addition of hydrogen chloride and the use of the  $\text{HCl}_2^-$  ion as a reagent (this ion has been considered as a possible intermediate in the addition of hydrogen chloride to isobutene in nitromethane<sup>12</sup>), induced us to study its extension to various alkynes which do not bear an amino-group. Triethylammonium hydrogendichloride (3) has been used as reagent, for its  $\text{HCl}_2^-$  anion offers the same dissymmetric structure as in the salts  $\text{R}^1_2\text{NH}^+\cdot[\text{CH}_2]_n\cdot\text{C}\equiv\text{CR}^2, \text{HCl}_2^-$ .<sup>10,13</sup> The alkynes (4)–(8) have been chosen from

<sup>7</sup> R. H. Summerville and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1974, **96**, 1110.

<sup>8</sup> G. A. Olah and R. J. Spear, *J. Amer. Chem. Soc.*, 1975, **97**, 1845.

<sup>9</sup> P. J. Stang, *Progr. Phys. Org. Chem.*, 1973, **10**, 276.

<sup>10</sup> J. Cousseau and L. Gouin, *Compt. rend.*, 1973, **277C**, 351; *Bull. Soc. chim. France*, 1974, 2955.

<sup>11</sup> J. Cousseau and L. Gouin, *Tetrahedron Letters*, 1974, 2889; *Bull. Soc. chim. France*, 1976, 244.

<sup>12</sup> Y. Pocker, *J. Chem. Soc.*, 1960, 1292.

<sup>13</sup> J. Cousseau, L. Gouin, L. V. Jones, G. Jugie, and J. A. S. Smith, *J.C.S. Faraday II*, 1973, 1821.

† Part 1, ref. 11.

<sup>1</sup> R. C. Fahey, *Topics Stereochem.*, 1968, **3**, 237.

<sup>2</sup> E. Winterfeldt, in 'Chemistry of Acetylenes,' ed. H. G. Viehe, Dekker, New York, 1969.

<sup>3</sup> E. Winterfeldt, *Angew. Chem. Internat. Edn.*, 1967, **6**, 423.

<sup>4</sup> K. Bowden and M. J. Price, *J. Chem. Soc. (B)*, 1970, 1466.

<sup>5</sup> R. C. Fahey, M. T. Payne, and D. J. Lee, *J. Org. Chem.*, 1974, **39**, 1124.

<sup>6</sup> F. Marcuzzi and G. Melloni, *J. Amer. Chem. Soc.*, 1976, **98**, 3295.

those whose reaction with hydrogen chloride has been reported already under other conditions.

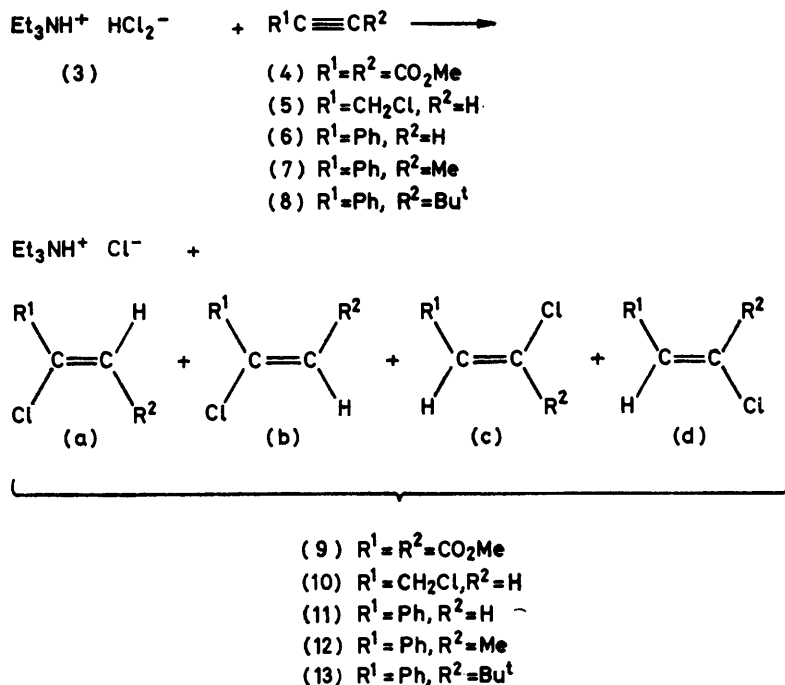
The present work is not a kinetic study, but the experiments have been followed under kinetic control, and the stereochemistry of the addition has been deduced from the number and the structure of the chloro-adducts obtained.

## RESULTS

Equimolar quantities (0.1 mol) of triethylammonium hydrogendichloride (3) and the alkyne [(4)—(8)] were heated either neat or dissolved in chloroform, acetonitrile, nitromethane, or nitrobenzene (concentration of 1M in each reagent).

To maintain a convenient degree of stability of the salt (3), the experimental conditions were carefully selected, and the behaviour of the salt was checked in control experiments in the absence of alkyne. When

mol<sup>-1</sup>.<sup>12,14-16</sup> The behaviour of the salt (3) in the above solvents was followed by comparison of the <sup>1</sup>H n.m.r. singlet due to the HCl<sub>2</sub><sup>-</sup> ion in a fresh solution (Table 1) with that observed after heating the solution (50 °C in chloroform, 80 °C in the other solvents). It was thus shown that the salt (3) does not undergo any serious degradation in chloroform or nitrobenzene media. In acetonitrile, however, the HCl<sub>2</sub><sup>-</sup> signal, originally sharp, is slowly broadened and flattened while its position and its intensity remain constant. This can be interpreted as the result of interaction between hydrogen chloride and the weakly basic nitrile group, which is likely to shift equilibrium (i) towards the left. Such an interaction would lead to MeC≡NH<sup>+</sup>Cl<sup>-</sup> or to MeCCl=NH<sub>2</sub><sup>+</sup>Cl<sup>-</sup>,<sup>17,18</sup> which would be expected to provide a broad <sup>1</sup>H n.m.r. signal.<sup>19</sup> In nitromethane, a reaction between the salt (3) and the solvent was observed, although the stability of the ion HCl<sub>2</sub><sup>-</sup> has been previ-



SCHEME 1

neat, it loses hydrogen chloride and slowly decomposes to triethylamine hydrochloride on heating in a dry atmosphere; ca. 40 h are necessary for conversion of 0.1 mol of the salt (3) in this manner. On the other hand, it is known that the ion HCl<sub>2</sub><sup>-</sup> is stable at room temperature in dipolar aprotic medium, the equilibrium constant for its formation (*K*) being 1.6—6 × 10<sup>2</sup> l



\* Neither the percentage of ionic chlorine, determined by titration with silver nitrate as 57.1%, nor the results of elemental analysis (Found: H, 6.8; Cl, 58.6; N, 22.85%) agree with the formula NH<sub>2</sub>OH·2HCl (Calc.: H, 4.7; Cl, 67.0; N, 13.2%) assigned by Pocker to the solid resulting from prolonged reaction between hydrogen chloride and nitromethane.<sup>12</sup> Possibly NH<sub>2</sub>OH·HCl is also formed; this point is under investigation.

ously considered as high in this solvent;<sup>12</sup> as well as triethylamine hydrochloride another white solid product is formed after 5—6 h. The structure of this latter product has not yet been elucidated.\*

The course of the reactions between the salt (3) and the alkynes (4)—(8) was followed by g.l.c. and <sup>1</sup>H n.m.r. spectroscopy and can be represented as in Scheme 1.

<sup>14</sup> H. F. Herbrandson, R. T. Dickerson, jun., and J. Weinstein, *J. Amer. Chem. Soc.*, 1954, **76**, 4046.

<sup>15</sup> J. F. Coetzee, *Progr. Phys. Org. Chem.*, 1967, **4**, 45.

<sup>16</sup> F. Y. Fujiwara and J. S. Martin, *J. Chem. Phys.*, 1972, **56**, 4091.

<sup>17</sup> G. J. Janz and S. S. Danyluk, *J. Amer. Chem. Soc.*, 1959, **81**, 3850.

<sup>18</sup> G. Simchen and G. Entenmann, *Angew. Chem. Internat. Edn.*, 1973, **12**, 119.

<sup>19</sup> R. M. Lynden-Bell and R. K. Harris, 'Nuclear Magnetic Resonance Spectroscopy, Nelson, London, 1971, p. 136.

TABLE 1  
<sup>1</sup>H Chemical shifts of HCl<sub>2</sub><sup>-</sup> in aprotic media <sup>a</sup>

Solvent	CHCl <sub>3</sub>	MeCN	MeNO <sub>2</sub>	PhNO <sub>2</sub>
δ	9.6	10.4	9.4	9.9

<sup>a</sup> Data for fresh 1M-solutions of the salt (3).

The results are listed in Table 2. The use of acetonitrile was restricted to the alkynes (4) and (6) because the other alkynes showed too low a reactivity in this

notable in the case of 3-chloropropyne (5), which scarcely reacts under other conditions.<sup>24,25</sup>

Most of the chloro-adducts result from *anti*-addition. In order to interpret the results, we can reasonably use the mechanistic classification drawn from studies on the addition of hydrogen chloride to the same alkynes under other experimental conditions: Shilov and Shilov have established that dimethyl but-2-ynedioate (4) undergoes

TABLE 2  
 Addition of hydrogen chloride to alkynes (4)—(8)

Runs	Alkyne	Solvent	Temp. (°C)	Reaction time (h)	Overall yield (%)	Ethylenic chloro-adducts			
						Compd.	Ratios (%) *		
						(a)	(b)	(c)	
1	(4)	None	40	1	68	(9)	74	26	
2		CHCl <sub>3</sub>	50	7	97		75	25	
3		MeCN	60	2	86		78	22	
4		MeNO <sub>2</sub>	60	2.5	98		80	20	
5	(5)	None	50	74	55	(10)	75		25
6		CHCl <sub>3</sub>	50	100	†				
7	(6)	None	70	19	73	(11)	73		
8		CHCl <sub>3</sub>	50	26	50		50		
9		MeCN	80	51.5	60		60		
10	(7)	None	65	27	65	(12)	50	6	44
11		CHCl <sub>3</sub>	50	115	33		50	6	44
12	(8)	None	75	24	70	(13)	12.5	87.5	
13		CHCl <sub>3</sub>	50	100	30		12	88	

\* Determined by g.l.c.; estimated error ≤ 2%. † Negligible.

solvent. Because of the side reaction mentioned above between the salt (3) and nitromethane, only the fast reaction of dimethyl but-2-ynedioate (4) was investigated in this medium. Finally, although nitrobenzene is a good solvent for the salt (3), its high b.p. does not permit a good separation of the reaction products, nor a clear interpretation of the results; therefore no data for reactions in nitrobenzene are reported in Table 2.

The structures of the ethylenic chloro-adducts were established mainly from their <sup>1</sup>H n.m.r. spectra (Table 3). The identifications are unambiguous for compounds (9a and b),<sup>20</sup> (10a and c),<sup>21,22</sup> and (11a),<sup>23</sup> whose n.m.r. data agreed with those reported. When such identifications were doubtful, as in the case of compounds (12a—c) and (13a and b), authentic samples were prepared by established methods (see Experimental section), for comparison. Our results show that no isomerisation of the ethylenic chloro-adducts occurs under the reaction conditions, and that no chloro-adduct of type (d) is produced {if we except the case of the compounds (9) [(9a) ≡ (9c) and (9b) ≡ (9d)]}.

#### DISCUSSION

Our results show that addition of hydrogen chloride to the alkynes (4)—(8) is easily achieved in mild conditions by use of the salt (3), although the reaction mixture contains no additional catalyst; this feature is especially

<sup>20</sup> M. Brink and E. Larsson, *Acta Univ. Lund.*, 1967, Sect. 2, no. 23.

<sup>21</sup> A. D. Cohen and N. Sheppard, *Proc. Roy. Soc.*, 1959, **252A**, 488.

<sup>22</sup> F. S. Mortimer, *J. Mol. Spectroscopy*, 1959, **3**, 335.

<sup>23</sup> R. Maroni, G. Melloni, and G. Modena, *J. C. S. Perkin I*, 1973, 2491.

<sup>24</sup> W. Kirmse and M. Kapps, *Chem. Ber.*, 1966, **99**, 2869.

nucleophilic addition in the medium lithium chloride-acetic acid,<sup>26</sup> whereas the other alkynes (5),<sup>24,25</sup> (6),<sup>27</sup>

TABLE 3

<sup>1</sup>H N.m.r. data for the ethylenic chloro-adducts (δ values; Me<sub>4</sub>Si as internal reference; solvent CCl<sub>4</sub>)

Compound	Data
MeO <sub>2</sub> C·CH·CCl·CO <sub>2</sub> Me	
Z-isomer (9a)	=CH 7.07 (s), CH <sub>2</sub> 3.8 (s), and 3.9 (s)
E-isomer (9b)	=CH 6.28 (s), CH <sub>2</sub> 3.73 (s), and 3.88 (s)
ClCH <sub>2</sub> ·CCl·CH <sub>2</sub> (10a)	=CH <sub>2</sub> 5.37 (m) and 5.57 (m), ClCH <sub>2</sub> 4.12 (m)
ClCH <sub>2</sub> ·CH·CHCl (10c)	=CH 6.00 (m) and 6.22 (m) ( <sup>3</sup> J <sub>cis</sub> 7 Hz), ClCH <sub>2</sub> 4.2 (m)
PhCCl·CH <sub>2</sub> (11a)	=CH <sub>2</sub> 5.45 (d) and 5.67 (d) ( <sup>2</sup> J 1.8 Hz), Ph 7—7.5 (m)
PhCCl·CH·CH <sub>3</sub>	
Z-isomer (12a)	=CH 6.03 (q), CH <sub>3</sub> 1.9 (d) ( <sup>3</sup> J 6.8 Hz), Ph 7.1—7.7 (m)
E-isomer (12b)	=CH 5.95 (q), CH <sub>3</sub> 1.7 (d) ( <sup>3</sup> J 7.2 Hz), Ph 7.2 (s)
PhCH·CCl·CH <sub>3</sub>	
Z-isomer (12c)	=CH 6.35br (s), CH <sub>3</sub> 2.17 (d) ( <sup>4</sup> J 1.2 Hz), Ph 7.1—7.7 (m)
PhCCl·CHBu <sup>t</sup>	
Z-isomer (13a)	=CH 6.02 (s), Bu <sup>t</sup> 1.29 (s), Ph 7.1—7.6 (m)
E-isomer (13b)	=CH 5.92 (s), Bu <sup>t</sup> 0.89 (s), Ph 7.2 (s)

(7),<sup>5,6</sup> and (8)<sup>6</sup> are known to undergo electrophilic addition.

From the acetylenic diester (4) both dimethyl chloromaleate (9b) and dimethyl chlorofumarate (9a) are obtained, whereas only the latter product was reported

<sup>25</sup> R. Gelin and D. Pigasse, *Bull. Soc. chim. France*, 1971, 1840.

<sup>26</sup> E. A. Shilov and A. E. Shilov, *Doklady Akad. Nauk S.S.S.R.*, 1953, **91**, 873.

<sup>27</sup> F. Marcuzzi, G. Melloni, and G. Modena, *Tetrahedron Letters*, 1974, 413.



Berliner *et al.* in order to account for the third-order iodination reaction of propiolic acid derivatives in aqueous medium involving the tri-iodide ion  $I_3^-$ .<sup>31</sup>

3,3-Dimethyl-1-phenylbut-1-yne (8) is likely to react mainly through the *AdE2* mechanism, in view of the formation of (*E*)-2-chloro-3,3-dimethyl-1-phenylbut-1-ene (13b) as major product. However, we further observed the formation of a significant proportion of the *Z*-isomer (13a) which was not reported previously;<sup>6,23</sup> in agreement with these other studies the formation of compound (13a) is to be ascribed to the *AdE3* mechanism, and this result supports our interpretation of the action of the  $HCl_2^-$  ion.

*Conclusion.*—This work emphasizes the extent to which the stereochemistry and regioselectivity of the addition of hydrogen chloride to a carbon-carbon triple bond depend upon the reaction conditions, and illustrates the importance of the nucleophilic power of the species involved in C-Cl bond formation. In this respect, the  $HCl_2^-$  ion exhibits unusual properties on account of its ambivalent character and reveals a marked tendency to favour *anti*-addition, even to alkynes such as alkyl-phenylacetylenes; moreover, this addition is possible without a catalyst.

#### EXPERIMENTAL

Triethylammonium hydrogendichloride (3) was prepared as previously described.<sup>13</sup> The alkynes (4)–(7) are commercially available, and were distilled under reduced pressure before use; their purity was checked by g.l.c. and n.m.r. analysis. 3,3-Dimethyl-1-phenylbut-1-yne (8) was

<sup>31</sup> M. H. Wilson and E. Berliner, *J. Amer. Chem. Soc.*, 1971, **93**, 208; E. Mauger and E. Berliner, *ibid.*, 1972, **94**, 194; V. L. Cunningham and E. Berliner, *J. Org. Chem.*, 1974, **39**, 3731.

<sup>32</sup> A. Mortreux and M. Blanchard, *Bull. Soc. chim. France*, 1970, 4035.

prepared according to a reported procedure.<sup>32</sup> Solvents were carefully purified according to the usual methods.<sup>33</sup>

In a typical experiment, 0.1 mol each of alkyne and triethylammonium hydrogendichloride (3) were mixed in a flask provided with stirrer, thermometer, and reflux condenser fitted with  $CaCl_2$  tube, and the mixture was heated in a thermostatted bath; when a solvent was used, the concentration of both reactants was 1M.

For product analysis, samples were withdrawn, mixed with water, and extracted with diethyl ether; the extracts were dried ( $Na_2SO_4$ ) and analysed by g.l.c. on a Carlo-Erba GI gas-chromatograph [2 m × 4 mm column packed with 10% SE 30 on Chromosorb W (80–100 mesh); nitrogen flow rate *ca.* 100 ml min<sup>-1</sup>].

When the reactions were stopped, the mixtures were worked up similarly. The extracts were evaporated and the residues analysed (g.l.c. and <sup>1</sup>H n.m.r.) and then distilled. <sup>1</sup>H N.m.r. spectra were recorded for solutions in carbon tetrachloride, with tetramethylsilane as internal standard, on a Varian T-60 spectrometer.

The ethylenic chloro-adducts from the alkynes (4)–(6) were identified by comparison of their n.m.r. spectra (Table 3) with those reported<sup>20-23</sup> (see above); the adducts from 1-phenylpropyne (7) and 3,3-dimethyl-1-phenylbut-1-yne (8) were identified from comparison of n.m.r. spectra and g.l.c. data with those of authentic samples prepared according to reported methods. (*Z*)- and (*E*)-1-Chloro-1-phenylpropene (12a and b) and (*Z*)- and (*E*)-2-chloro-1-phenylpropene (12c and d) were obtained by the procedure of Fahey and Schubert;<sup>34</sup> compound (12d) showed <sup>1</sup>H n.m.r. signals at  $\delta$  2.23 (3 H, d, <sup>4</sup>J 1.2 Hz), 6.63br (1 H, s), and 7.15 (5 H, s). (*Z*)- and (*E*)-1-Chloro-3,3-dimethyl-1-phenylbut-1-ene (13a and b) were made by the procedure of Maroni *et al.*<sup>23</sup>

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<sup>33</sup> J. A. Riddick and W. B. Bunger, in *Techniques of Chemistry*, vol. 2, ed. A. Weissberger, Wiley, New York, 1970.

<sup>34</sup> R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, 1965, **87**, 5172.