

## Chlorination and Interhalogenation of Alkylphenylacetylenes with Antimony Pentachloride

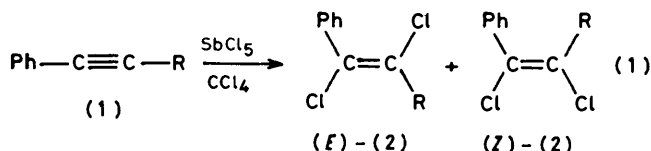
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Reactions of alkylphenylacetylenes with antimony pentachloride in carbon tetrachloride give the corresponding dichloroalkenes in 20–55% yields, (*Z*)-addition predominating. In the presence of iodine or lead(II) thiocyanate, interhalogenation occurs to give the chloriodo- or chlorothiocyanato-alkenes respectively as the sole or the main products in fair to good yields, the (*E*)-isomer being predominant except the case of phenylacetylenes where the stereospecificity is low. A concerted or near-concerted molecular addition of antimony pentachloride or its dimer to triple bond is postulated for the chlorination with very high (*Z*)-stereospecificity, and the stepwise (*E*)-attack of iodine monochloride or chlorothiocyanogen activated by antimony pentachloride is proposed for the interhalogenation. Replacement of an iodine, a bromine, or a chlorine atom in *vic*-dihalogenoalkenes by a chlorine atom of antimony pentachloride has been shown to occur through a vinyl cation intermediate by product analysis as well as a study of the isomerization of the starting dihalogenoalkenes.

It is known that antimony pentachloride reacts with acyclic and cyclic olefins to give unexpected dichloroalkanes.<sup>1</sup> However, the only report on its reaction with acetylenes is that by Nesmeyanov *et al.*<sup>2</sup> which describes the formation of stereoisomeric tris-(2-chlorovinyl)-antimony dichloride in the reaction of acetylene with antimony pentachloride. We have now found that alkylphenylacetylenes react with antimony pentachloride to give mainly (*Z*)-dichloroalkenes instead of vinylantimony compounds. It was also found that, if iodine or lead(II) thiocyanate is present, interhalogenation occurred to give the chloriodo- or chlorothiocyanato-alkenes respectively as in reactions with olefins.<sup>3,4</sup> We describe here the details of these reactions,<sup>5</sup> as part of our current studies on the halogenation of acetylenes.<sup>6</sup>

### RESULTS AND DISCUSSION

When the alkylphenylacetylene (1) was slowly added to a carbon tetrachloride solution of antimony pentachloride at 25–30 °C and the mixture was stirred for 0.1–1 h, an isomeric mixture of the corresponding dichloroalkenes, (*E*)-(2) and (*Z*)-(2), was obtained in 20–30% yields together with resinous products (reaction 1), the (*Z*)-isomer being predominant irrespective



of the alkyl group. In the case of phenyl-*t*-butylacetylene (1; R = Bu<sup>t</sup>) (*Z*)-(2; R = Bu<sup>t</sup>) was formed stereospecifically. In some cases the (*E*) HCl addition products, (*E*)-Ph(Cl)C=CHR, were also formed, especially when an excess of (1) was used with respect to antimony pentachloride. A possible source of this hydrogen chloride seems to be hydride ion abstraction by antimony pentachloride from (1) as has been proposed in the case of olefins.<sup>1a</sup> The chlorination also proceeded in dichloromethane, chloroform, or 1,2-dichloroethane, but a significant improvement in the (*Z*)-selectivity or the yield was not observed. When the reaction was carried

out at higher temperatures, the yield often increased (up to 55%), but the (*Z*)-stereospecificity decreased. Reverse addition, namely the addition of antimony pentachloride to a carbon tetrachloride solution of (1), appeared to have no effect on the yields and the isomer ratios of the products. Typical results are shown in Table 1. Since prolonged reaction time had little effect

TABLE 1  
Chlorination of alkylphenylacetylenes with antimony pentachloride

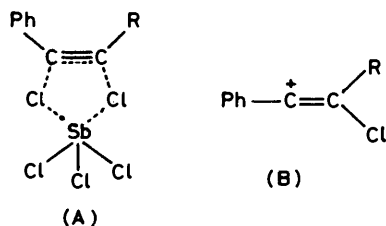
| R               | (1)<br>mmol | SbCl <sub>5</sub><br>mmol | Solvent<br>(ml)                        | Temp.<br>°C | Time<br>min | Yield (%) <sup>a</sup><br>of (2) ( <i>E</i> : <i>Z</i> ) |
|-----------------|-------------|---------------------------|--|-------------|-------------|--|
| Me              | 1.3         | 1.6                       | CCl <sub>4</sub> (5)                   | 25          | 10          | 28 (13 : 87)   |
| Me              | 1.3         | 1.6                       | CCl <sub>4</sub> (5)                   | 30          | 60          | 27 (17 : 83)   |
| Me              | 2.4         | 2.9                       | CCl <sub>4</sub> (10)                  | 76          | 10          | 25 (22 : 78)   |
| Me              | 1.3         | 1.6 <sup>b</sup>          | CCl <sub>4</sub> (5)                   | 76          | 10          | 27 (28 : 72)   |
| Me              | 4.4         | 4.9                       | CH <sub>2</sub> Cl <sub>2</sub> (50)   | 40          | 30          | 21 (12 : 88)   |
| Me              | 4.4         | 5.1                       | (CH <sub>2</sub> Cl) <sub>2</sub> (50) | 25          | 60          | 25 (13 : 87)   |
| Me              | 4.5         | 5.3                       | (CH <sub>2</sub> Cl) <sub>2</sub> (50) | 82          | 60          | 45 (35 : 65)   |
| Me              | 1.8         | 1.0                       | CCl <sub>4</sub> (5)                   | 76          | 10          | 8 (40 : 60) <sup>c</sup>                                 |
| Et              | 1.3         | 1.4                       | CCl <sub>4</sub> (5)                   | 25          | 10          | 32 (16 : 84)   |
| Et              | 10.1        | 10.2                      | CCl <sub>4</sub> (100)                 | 76          | 120         | 51 (67 : 33) <sup>d</sup>                                |
| Pr <sup>n</sup> | 1.1         | 1.4                       | CCl <sub>4</sub> (5)                   | 25          | 10          | 24 (7 : 93)  |
| Bu <sup>n</sup> | 1.1         | 1.4                       | CCl <sub>4</sub> (5)                   | 25          | 10          | 17 (10 : 90)   |
| Bu <sup>t</sup> | 2.5         | 2.7                       | CCl <sub>4</sub> (25)                  | 25          | 10          | 25 (0 : 100) <sup>e</sup>                                |
| Bu <sup>t</sup> | 5.1         | 5.3                       | CCl <sub>4</sub> (50)                  | 76          | 120         | 55 (0 : 100) <sup>f</sup>                                |

<sup>a</sup> Based on amount of (1) and determined by g.l.c. analysis. <sup>b</sup> Inverse addition, *i.e.*, SbCl<sub>5</sub> was slowly added to (1)-CCl<sub>4</sub>. <sup>c</sup> Based on amount of SbCl<sub>5</sub>. Other product, (*E*)- and (*Z*)-1-chloro-1-phenylprop-1-ene (0.70 mmol) (*E* : *Z* 54 : 46). <sup>d</sup> Other product, (*E*)- and (*Z*)-1-chloro-1-phenylbut-1-ene (0.94 mmol) (*E* : *Z* 88 : 12). <sup>e</sup> Other product, (*E*)-1-chloro-3,3-dimethyl-1-phenylbut-1-ene (0.85 mmol). <sup>f</sup> Other product, (*E*)-1-chloro-3,3-dimethyl-1-phenylbut-1-ene (1.08 mmol). For reference to these other products, see F. Marcuzzi and G. Melloni, *J. Amer. Chem. Soc.*, 1976, **98**, 3295.

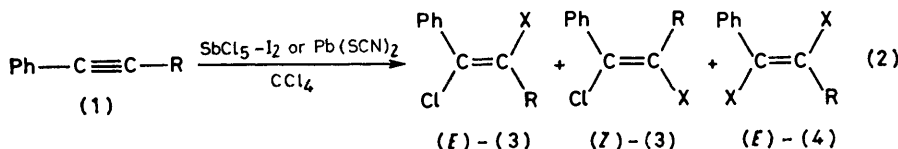
on the isomer ratios of the products, the reactions must be almost entirely kinetically controlled. We confirmed independently that interconversion between the isomers of (2; R = Me) (*E* : *Z* 12 : 88 or 54 : 46) did not occur in carbon tetrachloride at reflux temperature for 0.2–2 h in the presence of 3 equiv. of antimony pentachloride. Treatment of phenylacetylene (1; R = H) with antimony pentachloride resulted in rapid formation of polymeric tars under various conditions. Since (2; R = H) is reasonably stable (see data in Table 3) in refluxing carbon tetrachloride containing antimony pentachloride, it is clear that the tars are formed before (2; R = H).

Although polymerization of (1; R = H) by antimony pentachloride is apparently not yet known, its ready polymerization by molybdenum pentachloride or tungsten hexachloride as catalyst has been reported.<sup>7</sup>

Chlorination of (1; R = Me) and (1; R = Bu<sup>t</sup>) with chlorine in carbon tetrachloride at -60 °C for 0.2 h<sup>6b</sup> or under reflux for 2 h<sup>6a</sup> gave a mixture of (*E*)- and (*Z*)-(2; R = Me) (67—73 : 27—33) and a mixture of (*E*)- and (*Z*)-(2; R = Bu<sup>t</sup>) (4—14 : 86—96) in >80% yield, respectively. Reaction with copper(II) chloride in acetonitrile at 82 °C for 24—48 h afforded the corresponding dichloro-compounds (2) almost quantitatively, with isomer ratios (*E*:*Z*) of 95 : 5 for the reaction of (1; R = Me) and 21 : 79 for (1; R = Bu<sup>t</sup>). These results show that the (*Z*)-stereospecificity in chlorination with chlorine or copper(II) chloride is much lower than that with



antimony pentachloride. The very high (*Z*)-stereospecificity for antimony pentachloride can be explained by assuming a concerted or near-concerted molecular addition of antimony pentachloride or its dimer to the triple bond as shown in (A); a similar mechanism has been suggested for the (*Z*)-chlorination of simple olefins.<sup>1a</sup> To some extent the reaction may proceed through a vinyl cation intermediate such as (B) to give both the (*Z*)- and (*E*)-isomers. When R is sterically large, it would hinder the attack of SbCl<sub>6</sub><sup>-</sup> on its own side of (B) leading to the (*Z*)-isomer.



Treatment of the acetylenes (1; R = alkyl or H) with a mixture of antimony pentachloride and iodine or lead(II) thiocyanate gave smoothly the chloriodoalkenes (3; X = I) or the chlorothiocyanoalkenes (3; X = SCN) respectively, the (*E*)-isomer being predominant except in the case of (1; R = H) [reaction (2)]. The reactions were usually accompanied by formation of small amounts of the dichloro-, di-iodo-, and/or bis-thiocyanato-alkenes (4; X = Cl, I, or SCN). In contrast to chloriodination of (1; R = H) with copper(II) chloride-iodine where the (*E*)-isomer is almost the sole product,<sup>6a</sup> the stereospecificity was quite low in this chloriodination and the isomer ratios (*E*:*Z*) of (3; R = H, X = I) are not reproducible; for example, ratios varying from 57 : 43 to 18 : 82 were obtained under almost the same conditions. Similar non-reproducibility in the isomer ratios was also observed in

the chlorothiocyanoation of (1; R = H). When antimony trichloride was used instead of the pentachloride in the chloriodination of (1; R = H), the yield of (3; R = H, X = I) was low but the specificity for formation of the (*E*)-isomer was very high. In this case the main product was the di-iodoalkene, (*E*)-(4; R = H, X = I), which can be obtained in better yield without the addition of antimony trichloride. These results are shown in Table 2. The reactive species in these reaction systems seem to be iodine monochloride and chlorothiocyanoanogen which are activated by antimony pentachloride, as has already been shown in reactions with olefins<sup>3,4</sup> and arenes<sup>4</sup>; *i.e.*, I<sup>+</sup> and SCN<sup>+</sup> are the initial attacking species. In fact the chloriodination of (1; R = Bu<sup>t</sup>) with commercial iodine monochloride in refluxing carbon tetrachloride in the presence of antimony pentachloride (acetylene : ICl : SbCl<sub>5</sub> = 1 : 1.5 : 0.36) afforded an 84% yield of (3; R = Bu<sup>t</sup>, X = I) (*E*:*Z* 64 : 36) after 30 min, this isomer ratio being almost the same as that obtained in the chloriodination with antimony pentachloride-iodine. Reaction in the absence of antimony pentachloride, under otherwise identical conditions, gave only a 34% yield of (3; R = Bu<sup>t</sup>, X = I) (*E*:*Z* 63 : 37) together with a considerable amount of (2; R = Bu<sup>t</sup>). This result clearly shows that antimony pentachloride activates iodine monochloride by functioning as a Lewis acid. Antimony trichloride also accelerates the reaction; probably the antimony(III) species is partly oxidized to antimony(V) by the excess of iodine monochloride present.

As just described above, the stereospecificity was quite low in the interhalogenation of (1; R = H) with antimony pentachloride. Since the isomer ratios of (3; R = H) were not reproducible and the reaction with antimony trichloride gave the (*E*)-isomer with high stereospecificity, one of the reasons for this low selectivity

seems to be the isomerization of the initial product by the action of antimony pentachloride, the extent of which depends on the amount of the free pentachloride under the actual conditions. In order to investigate this isomerization, we treated (*E*)-(3; R = H, X = I) with antimony pentachloride in refluxing carbon tetrachloride. The (*E*)-isomer was partially converted into the (*Z*)-isomer to give a mixture of both isomers, though the recovered yield of (3) was low especially with longer reaction times and/or a high molar ratio of SbCl<sub>5</sub> to (*E*)-(3; R = H, X = I). In contrast, (*E*)-(3; R = Me, X = I) was more stable than (*E*)-(3; R = H, X = I) and its isomerization was much slower under similar conditions, this result being consistent with both a high yield and a high (*E*)-stereospecificity in the chloriodination of (1; R = Me) with antimony pentachloride-iodine. It is worth noting that dichloro-

alkenes (2; R = H or Me) were always formed in these experiments, as a result of exchange of iodine for chlorine at the  $\beta$ -carbon atom. A similar halogen exchange

abstraction of the halogen on the  $\alpha$ -carbon atom by antimony pentachloride [reaction (3)]. The formation of such an intermediate might also explain the isomeriz-

TABLE 2

Chloriodination and chlorothiocyanoation of alkylphenylacetylenes with antimony pentachloride and iodine or lead(II) thiocyanate

| (1)<br>R mmol       | SbCl <sub>5</sub><br>mmol | Halogens<br>or Pb(SCN) <sub>2</sub><br>(mmol) | CCl <sub>4</sub><br>ml | Temp.<br>°C | Time<br>min | Yield (%) <sup>a</sup>    |                 |       |
|---------------------|---------------------------|---|------------------------|-------------|-------------|---------------------------|-----------------|-------|
|                     |                           |   |                        |             |             | (3) (E : Z)               | (2)<br>X = I    | E-(4) |
| H 2.5               | 1.5                       | I <sub>2</sub> (5)                            | 25                     | 76          | 3           | 87 (62 : 38)              | 1               | Trace |
| H 5                 | 3                         | I <sub>2</sub> (10)                           | 50                     | 76          | 30          | 55 (57 : 43) <sup>b</sup> | 2               | Trace |
| H 2.5               | 1.5                       | I <sub>2</sub> (5)                            | 25                     | 25          | 30          | 50 (53 : 47)              | 2               | Trace |
| H 2.5               | 1.5                       | I <sub>2</sub> (5)                            | 25                     | 0           | 30          | 14 (64 : 36)              | 3               | Trace |
| Me 5                | 3                         | I <sub>2</sub> (10)                           | 50                     | 76          | 30          | 82 (100 : 0)              | 5               | 0     |
| Et 5                | 3                         | I <sub>2</sub> (10)                           | 50                     | 76          | 30          | 68 (100 : 0)              | 5               | 0     |
| Pr <sup>t</sup> 2.5 | 1.5                       | I <sub>2</sub> (5)                            | 25                     | 76          | 30          | 84 (98 : 2)               | 0               | 0     |
| Bu <sup>t</sup> 5   | 3                         | I <sub>2</sub> (10)                           | 50                     | 76          | 30          | 92 (66 : 34)              | 0               | 0     |
| Bu <sup>t</sup> 1   | 0.6                       | I <sub>2</sub> (2)                            | 10                     | 76          | 300         | 72 (66 : 34)              | Trace           | 0     |
| H 2.5               | SbCl <sub>3</sub> 5       | I <sub>2</sub> (5)                            | 25                     | 76          | 30          | 8 (92 : 8)                | 0               | 57    |
| H 2.5               | 0                         | I <sub>2</sub> (5)                            | 25                     | 76          | 30          |                           |                 | 76    |
| Bu <sup>t</sup> 1   | 0                         | ICl (1.5)                                     | 10                     | 76          | 30          | 34 (63 : 37)              | 29 <sup>c</sup> | 0     |
| Bu <sup>t</sup> 1   | 0.36                      | ICl (1.5)                                     | 10                     | 76          | 30          | 84 (64 : 36)              | 0               | 0     |
| Bu <sup>t</sup> 1   | SbCl <sub>3</sub> 0.75    | ICl (1.5)                                     | 10                     | 76          | 30          | 90 (63 : 37)              | 0               | 0     |
|                     |                           |   |                        |             |             | X = SCN                   |                 |       |
| H 10                | 20                        | Pb(SCN) <sub>2</sub> (20)                     | 100                    | 76          | 10          | 39 (27 : 73)              | 0               | d     |
| H 10                | 20                        | Pb(SCN) <sub>2</sub> (20)                     | 100                    | 76          | 120         | 34 (18 : 82) <sup>e</sup> | 0               | d     |
| Me 5                | 10                        | Pb(SCN) <sub>2</sub> (10)                     | 50                     | 76          | 120         | 31 (79 : 21)              | Trace           | d     |

<sup>a</sup> Based on amount of (1) and determined by g.l.c. analysis. <sup>b</sup> Yield 55% and E : Z 35 : 65 and 58% 18 : 82 in two other runs carried out under similar conditions. <sup>c</sup> E : Z = 25 : 75. A small amount of an unidentified compound was also produced. <sup>d</sup> Identified by mass spectroscopy, but the stereospecificity and yield were not determined. <sup>e</sup> In another run the yield was 39% (E : Z 48 : 52).

reaction was also observed at the  $\alpha$ -carbon atom for  $\alpha\beta$ -dibromo- or  $\alpha\beta$ -di-iodo-styrene (4; R = H, X = Br or I), which afforded (3; R = H, X = Br) or (3;

and the ready halogen exchange for (4; R = H, X = I) of (4; R = H, X = Cl)\*. A slower isomerization of (4; R = H, X = Cl)\* than (4; R = H, X = Br)

TABLE 3

Isomerization and halogen exchange reaction of dihalogenoalkenes with antimony pentachloride in carbon tetrachloride<sup>a</sup>

| Starting dihalogenoalkene<br>(E : Z) | Molar ratio<br>SbCl <sub>5</sub> /<br>dihalogenoalkene | Time<br>min | Product and yield (%) <sup>b</sup><br>(E : Z) |                           |
|--------------------------------------|--|-------------|---|---------------------------|
|                                      |  |             | Isomerized                                    | Exchanged                 |
| (3; R = H, X = I)                    |  |             | (3; R = H, X = I)                             | (2; R = H)                |
| (100 : 0)                            | 0.1  | 30          | 62 (89 : 11)                                  | 2 (76 : 24)               |
| (100 : 0)                            | 0.5  | 2           | 80 (89 : 11)                                  | 2 (74 : 26)               |
| (100 : 0)                            | 0.5  | 30          | 52 (40 : 60)                                  | 2 (28 : 72)               |
| (100 : 0)                            | 1.0  | 30          | 29 (47 : 53)                                  | 8 (37 : 63)               |
| (3; R = Me, X = I)                   |  |             | (3; R = Me, X = I)                            | (2; R = Me)               |
| (100 : 0)                            | 0.5  | 30          | 86 (94 : 6)                                   | 2 (87 : 13)               |
| (4; R = H, X = I)                    |  |             | (4; R = H, X = I)                             | (3; R = H, X = I)         |
| (100 : 0)                            | 0.5  | 30          | 45 (100 : 0)                                  | 26 (99 : 1) <sup>c</sup>  |
| (100 : 0)                            | 1.0  | 10          | 46 (100 : 0)                                  | 9 (85 : 15) <sup>c</sup>  |
| (100 : 0)                            | 1.0  | 120         | 7 (100 : 0)                                   | 34 (57 : 43) <sup>c</sup> |
| (4; R = H, X = Br)                   |  |             | (4; R = H, X = Br)                            | (3; R = H, X = Br)        |
| (62 : 38)                            | 0.5  | 30          | 87 (43 : 57)                                  | 5 (80 : 20)               |
| (62 : 38)                            | 1.0  | 10          | 67 (77 : 23)                                  | 7 (79 : 21)               |
| (78 : 22)                            | 1.0  | 120         | 31 (30 : 70)                                  | 12 (42 : 58)              |
| (2; R = H)                           |  |             | (2; R = H)                                    |                           |
| (93 : 7)                             | 0.5  | 30          | 85 (82 : 18)                                  |                           |
| (93 : 7)                             | 1.0  | 120         | 33 (70 : 30)                                  |                           |
| (2; R = Me)                          |  |             | (2; R = Me)                                   |                           |
| (97 : 3)                             | 0.5  | 30          | 60 (96 : 4)                                   |                           |

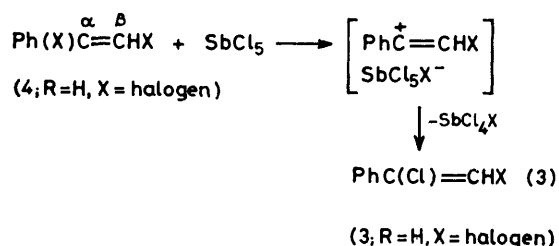
<sup>a</sup> Dihalogenoalkene (0.5—1 mmol), SbCl<sub>5</sub> (0.1—1 mmol), and CCl<sub>4</sub> (25 ml), at 76 °C. <sup>b</sup> Determined by g.l.c. analysis. Based on dihalogenoalkene. <sup>c</sup> In addition, a trace of (2; R = H) was produced.

R = H, X = I) respectively in moderate yield. Typical results are shown in Table 3. The  $\alpha$ -halogen exchange reaction of (4; R = H, X = Br or I) and the isomerization of (4; R = H, X = Br) seem to proceed through a vinyl cation intermediate which could be formed by

agree with the usually accepted concept that the halogen in alkyl or aryl halides is abstracted in the following order: I > Br > Cl. Several instances of halogen abstraction from alkyl halides by antimony penta-

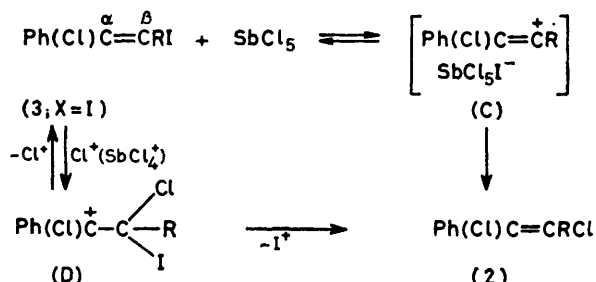
\* Corresponds to (2; R = H).

chloride have been reported<sup>1b,8,9</sup> and it is also known that chlorine<sup>10a</sup> or fluorine<sup>10b</sup> in  $\text{Ar(X)C}=\text{CR}_2$  is



abstracted quite readily by antimony pentafluoride in  $\text{SO}_2\text{ClF}$ . In the case of (4; R = H, X = I) iodine participation in the intermediate may prevent the formation of (*Z*)-(4; R = H, X = I), corresponding to no isomerization of the starting di-iodide, and also to form only (*E*)-(3; R = H, X = I) as the initial exchange product which then isomerizes under these reaction conditions as already described.

For the isomerization of (*E*)-(3; R = H, X = I), which is accompanied by formation of a small amount of the  $\beta$ -halogen exchanged product (2; R = H), the two pathways in the Scheme are two of the possibilities; these involve either the abstraction of iodine from the  $\beta$ -carbon to give the intermediate (C) or the addition-elimination of a cationic chlorine on the  $\beta$ -carbon atom



SCHEME

affording (D). However, if the reaction proceeds through (C), the isomerization of (3; R = Me, X = I) should be faster than that of (3; R = H, X = I) from a consideration of the difference in the stability of (C) in these cases. On the other hand, in the addition-elimination scheme substantial interaction between iodine and the positive  $\alpha$ -carbon atom may cause the departure of the iodine cation yielding (2) to be difficult, but the difference between the isomerization rates for (3; R = H, X = I) and (3; R = Me, X = I) cannot be so easily explained unless the rate of attack of a cationic chlorine species or  $\text{SbCl}_4^+$  on the  $\beta$ -carbon atom of (3; R = Me, X = I) is slower than that of (3; R = H, X = I) because of the larger steric hindrance of methyl than hydrogen. Although we prefer the latter scheme at the moment, more work is necessary to clarify the mechanism.

#### EXPERIMENTAL

Alkylphenylacetylenes were prepared as previously described.<sup>6a</sup> Other organic and inorganic materials were

commercial products and used without further purification. I.r. and mass spectra were recorded with a Hitachi EPI-S2 and a JEOL JMS-01SG spectrometer, respectively. <sup>1</sup>H N.m.r. spectra were taken with a JEOL MH-100 instrument for solutions in  $\text{CCl}_4$  with  $\text{Me}_4\text{Si}$  as internal standard (with an external lock). <sup>13</sup>C N.m.r. spectra were obtained at 25.1 MHz with a JEOL FX-100 instrument in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  as internal standard (with an internal deuterium lock). G.l.c. analyses were carried out with a Shimadzu 4BMPF apparatus [EGSS-X (15%)–Chromosorb W (1 or 3 m) and Apiezon-L (30%)–Celite (1 m) columns;  $\text{N}_2$  as carrier gas; ethyl cinnamate or styrene dibromide as internal standard]; all compounds prepared by the reported method<sup>6</sup> were used as authentic samples for g.l.c. analyses except (3; X = SCN) and (3; R = H, X = Br).

**Chlorination.**—A typical procedure is as follows. A solution of phenyl-*t*-butylacetylene (1; R = Bu<sup>t</sup>) (0.80 g, 5.1 mmol) in carbon tetrachloride (5 ml) was slowly added to carbon tetrachloride (45 ml) containing antimony pentachloride (1.6 g, 5.3 mmol) at 76 °C, and the mixture was stirred at that temperature for 2 h. After cooling, aqueous sodium hydroxide was added and the organic layer was separated, washed with water, and dried over magnesium sulphate. G.l.c. analysis of the organic layer showed the presence of 2.81 mmol of (*Z*)-(2; R = Bu<sup>t</sup>). Distillation gave pure (*Z*)-(2; R = Bu<sup>t</sup>) (0.52 g, 2.3 mmol, 45%); b.p. 137–140 °C at 17 mmHg, m.p. 66–67 °C (from EtOH).

**Chloroiodination.**—Methylphenylacetylene (1; R = Me) (0.58 g, 5 mmol) was added to a carbon tetrachloride (50 ml) solution containing antimony pentachloride (0.90 g, 3 mmol) and iodine (2.54 g, 10 mmol) at reflux temperature; the mixture was then stirred for 0.5 h. After cooling, aqueous sodium thiosulphate was added to remove the excess of iodine and then the mixture was filtered. The organic layer of the filtrate was washed with aqueous sodium hydrogen carbonate and dried ( $\text{MgSO}_4$ ). G.l.c. analysis showed the presence of 4.09 mmol (82%) of (*E*)-(3; R = Me, X = I) and 0.15 mmol (5%) of (*Z*)-(2; R = Me.) Distillation gave pure (*E*)-(3; R = Me, X = I)<sup>6a</sup> (0.66 g, 2.4 mmol, 48%).

Similar treatment of phenylacetylene (1; R = H) afforded a mixture of (*E*)-<sup>6a</sup> and (*Z*)-(3; R = H, X = I) (*E*:*Z* 36:64) (0.42 g, 1.6 mmol, 32%); b.p. 97–99 °C at 3 mmHg;  $\delta$  6.63 (1 H, s, vinyl of *E*-isomer) and 6.96 (1 H, s, vinyl of *Z*-isomer) (Found: C, 36.9; H, 2.25. Calc. for  $\text{C}_8\text{H}_6\text{ClI}$ : C, 36.3; H, 2.3%).

**Chlorothiocyanylation.**—Phenylacetylene (1; R = H) (1.02 g, 10 mmol) was added to a stirred heterogeneous mixture of a carbon tetrachloride (100 ml) solution containing antimony pentachloride (6.0 g, 20 mmol) and lead(II) thiocyanate (6.5 g, 20 mmol) at 60–65 °C; the mixture was then heated under reflux for 2 h. The cooled mixture was added to water and then filtered, and the filtrate was treated as just described. G.l.c. analysis showed the presence of 3.43 mmol of a mixture of (*E*)- and (*Z*)-(3; R = H, X = SCN) (*E*:*Z* 18:82); the peak of lower retention time was assigned to the (*E*)-isomer as for the dichloro- and dibromo-analogues;<sup>6</sup> <sup>1</sup>H n.m.r. spectroscopy also supported this assignment. Distillation gave an almost pure mixture of (*E*)- and (*Z*)-(3; R = H, X = SCN) [(*E*:*Z* 20:80), 0.35 g, 1.79 mmol, 18%], b.p. 122–123 °C at 5 mmHg;  $\delta$  6.73 (1 H, s, vinyl of *E*-isomer), 6.96 (1 H, s, vinyl of *Z*-isomer), and 7.6–7.9 (5 H, m, Ph) *m/e* 195 ( $M^+$ ) and 197 ( $M^+ + 2$ ); a small peak at *m/e* 218

corresponding to  $\text{PhC}(\text{SCN})=\text{C}(\text{H})\text{SCN}$  was also present; i.r. 2 150 ( $\nu_{\text{SCN}}$ )  $\text{cm}^{-1}$ ;  $^{13}\text{C}$  n.m.r.  $\delta$  (from  $\text{Me}_4\text{Si}$ ) for (*Z*)-isomer: 109.4 (s, SCN), 111.8 (d, =CSCN), 126.0 (d, *para*-C), 128.6 (d, *ortho*-C), 130.0 (d, *meta*-C), 134.6 (s, =CPh) and 136.7 (s, quaternary phenyl C) p.p.m.; for (*E*)-isomer, 109.4 (s, SCN), 110.0 (d, =CSCN), 126.0 (d, *para*-C), 128.1 (d, *ortho*-C), 130.5 (d, *meta*-C), 134.0 (s, =CPh), and 138.0 (s, quaternary phenyl C) p.p.m. (Found: C, 55.4; H, 3.1; N, 8.0. Calc. for  $\text{C}_9\text{H}_6\text{ClNS}$ : C, 55.2; H, 3.1; N, 7.2%).

Similar treatment of methylphenylacetylene (1; R = Me) afforded a mixture of (*E*)- and (*Z*)-(**3**; R = Me, X = SCN) (*E*:*Z* 80:20); b.p. 95–96 °C at 4 mmHg;  $\delta$  2.35 (3 H, s, Me of *Z*-isomer), 2.59 (3 H, s, Me of *E*-isomer), and 7.4–7.8 (5 H, m, Ph); *m/e* 209 ( $M^+$ ) and 211 ( $M^+ + 2$ ); a small peak at *m/e* 232 corresponding to  $\text{PhC}(\text{SCN})=\text{C}(\text{Me})\text{SCN}$  was also present: i.r. 2 150 ( $\nu_{\text{SCN}}$ )  $\text{cm}^{-1}$  (Found: C, 57.2; H, 3.5; N, 8.3. Calc. for  $\text{C}_{10}\text{H}_8\text{ClNS}$ : C, 57.3; H, 3.8; N, 6.7%).

**Preparation of (3; R = H, X = Br).**—Phenylacetylene (1; R = H) (0.51 g, 5 mmol) was added to a mixture of copper(II) chloride (1.34 g, 10 mmol) and bromine (0.40 g, 2.5 mmol) in refluxing acetonitrile (50 ml); the stirred mixture was heated under reflux for 2 h. The cooled mixture was then added to water (200 ml) and extracted with benzene. Distillation gave 0.32 g of an oil (b.p. 82–96 °C at 4 mmHg) which was shown to contain two unidentified compounds (61% from g.l.c. peak areas) together with (**4**; R = H, X = Br) (*E*:*Z* 78:22) (33%) and (*E*)-(**2**; R = H) (6%) by g.l.c. analysis. From  $^1\text{H}$  n.m.r. and mass spectral analysis these compounds were assigned the structures (**3**; R = H, X = Br) (*E*:*Z* 91:9);  $\delta$  6.55 (1 H, s, vinyl of *E*-isomer) and 6.81 (1 H, s, vinyl of *Z*-isomer); *m/e* ( $M^+$ ) 215.931 3 ( $\text{C}_9\text{H}_6\text{BrCl}$  requires 215.934 2), the ratio  $M^+ : M^+ + 2 : M^+ + 4$  being 100:126:32.9 (required 100:130:31.9).

**Isomerization and Halogen Exchange Reactions.**—The general procedure is as follows. A carbon tetrachloride (5 ml) solution of the dihalogenoalkene (0.5–1 mmol) was

slowly added (*ca.* 3 min) to a stirred carbon tetrachloride (20 ml) solution of antimony pentachloride (0.1–1 mmol) at 76 °C. The stirred mixture was kept at this temperature for the appropriate time, and then cooled and treated as already described. For the di-iodo- or chloriodo-alkenes the mixture was treated with aqueous sodium thiosulphate to remove the free iodine which was always formed during the reaction. The products in the organic layer were then analysed by g.l.c. The reactions at 20–25 °C were very slow.

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