

Chlorination and Chloriodination of Acetylenes with Copper(II) Chloride¹

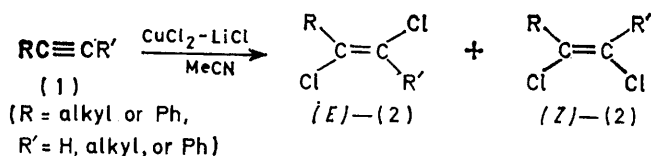
By Sakae Uemura,* Hajime Okazaki, Akira Onoe, and Masaya Okano, Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan

Reactions of acetylenes ($RC\equiv CR'$; R and/or R' = H, alkyl, or phenyl) (1), with copper(II) chloride–lithium chloride in acetonitrile give the corresponding *E*-dichloroalkenes in good yields except in the case of (1; R = Ph, R' = Bu^t) where the *Z*-product is favoured. Reactions with copper(II) chloride–iodine or –potassium iodide proceed more smoothly to afford, completely regiospecifically and highly stereospecifically, *E*-chloroiodoalkenes in high yields. Reactions with iodine chloride also give the same compounds, but the yield and *E*-stereospecificity are low in comparison with those in the copper(II) chloride–iodine case. An open vinyl cation intermediate in which copper(I) co-ordinates weakly with both the double bond and the chlorine atom attached to carbon is postulated for chlorination, and a cyclic iodonium ion intermediate is proposed for chloriodination.

THE liquid-phase chlorination of olefins with copper(II) chloride is well known.² However, there is only one report³ on its application to acetylenes; this describes the trichlorination of prop-2-yn-1-ol and prop-2-ynal and the dichlorination of methyl propiolate. We now report the stereochemistry and the mechanism of the chlorination and chloriodination of various kinds of acetylenes with copper(II) chloride in the presence of lithium chloride or iodine. The chlorination of similar acetylenes with (dichloroiodo)benzene has been reported recently.⁴

RESULTS AND DISCUSSION

Treatment of an acetylene (1) with an equimolar mixture of copper(II) chloride and lithium chloride in acetonitrile at reflux temperature gave a mixture of two isomeric dichloroalkenes (2) in high yield (Scheme 1).



SCHEME 1

The reaction was sluggish at room temperature. Typical results are shown in Table 1. All reactions produced mainly the *E*-isomer, except in the case of *t*-butylphenylacetylene where *cis*-addition, giving the *Z*-isomer, occurred predominantly. The reaction proceeded even without lithium chloride, but both the yield and the selectivity for *trans*-addition appeared to decrease, as shown with compounds (1; R = Ph, R' = Me or Bu^t); the addition of an excess of lithium chloride did not affect the yield or the stereoselectivity. Since prolonged reaction times resulted in improved yields without affecting isomer ratios, the reactions must be almost entirely kinetically controlled. We confirmed in separate

experiments that interconversion between the isomers did not occur under the reaction conditions. However, (*E*)-(2) was isomerized to (*Z*)-(2) when mixture of both isomers was kept for several days at room temperature, especially in cases where R' = H. It has been reported⁴ that a thermodynamic equilibrium mixture of (*E*)- and

TABLE I
Chlorination of acetylenes with copper(II) chloride in acetonitrile^a

(1)		Molar ratio of (CuCl ₂ + LiCl) ^c to (1)	Time (h)	Yield (%) ^b of (2) (<i>E</i> : <i>Z</i>)
Ph	H	20 : 1	2	12 (96 : 4)
Ph	H	5 : 1	12	19 (94 : 6)
Ph	H	20 : 1	12	65 (92 : 8)
Ph	H	20 : 1	24	71 (94 : 6)
Ph	H	40 : 1	24	95 (95 : 5)
Ph	Me	40 : 1	2	22 (97 : 3)
Ph	Me	40 : 1	24	94 (98 : 2)
Ph	Me	40 : 1 ^d	24	68 (91 : 9)
Ph	Et	40 : 1	24	94 (95 : 5)
Ph	Pr ⁿ	40 : 1	48	93 (94 : 6)
Ph	Bu ⁿ	40 : 1	48	93 (93 : 7)
Ph	Pr ^t	40 : 1	48	95 (80 : 20)
Ph	Bu ^t	40 : 1 ^d	2	6 (14 : 86)
Ph	Bu ^t	40 : 1	2	27 (20 : 80)
Ph	Bu ^t	40 : 1	48	95 (21 : 79)
Ph	Bu ^t	80 : 1 ^d	2	35 (11 : 89)
Ph	Ph	40 : 1	48	42 (96 : 4)
<i>n</i> -Hexyl	H	40 : 1	2	73 (88 : 12)
<i>n</i> -Hexyl	H	40 : 1	12	83 (92 : 8)
Pr ⁿ	Pr ⁿ	40 : 1	2	42 (98 : 2)
CH ₂ OH	H	40 : 1	12	69 (100 : 0)

^a Alkyne (1) (5–10 mmol), CuCl₂ and LiCl (100–200 mmol each), and MeCN (50–100 ml) were used; at 82°. ^b Based on the amount of (1) and determined by g.l.c. analysis. ^c CuCl₂ : LiCl 1 : 1. ^d LiCl not added.

(*Z*)-(2) is easily obtained by irradiation in the presence of a trace of bromine, when isomerization of (*E*)-(2) to (*Z*)-(2) takes place.

Chloriodination of acetylenes (1) with an equimolar mixture of copper(II) chloride and iodine⁵ proceeded

¹ Preliminary communication, S. Uemura, A. Onoe, and M. Okano, *J.C.S. Chem. Comm.*, 1975, 925.

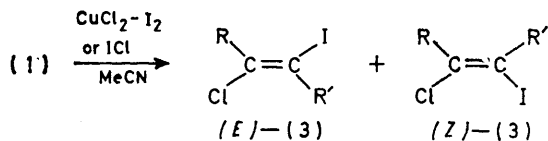
² K. Ichikawa, S. Uemura, Y. Takagaki, and T. Hiramoto, *Bull. Japan Petrol. Inst.*, 1970, **12**, 77, and references therein.

³ C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, 1965, **30**, 587.

⁴ A. Debon, S. Masson, and A. Thuillier, *Bull. Soc. chim. France*, 1975, 2493.

⁵ The chloriodination of olefins by this system has been reported: W. C. Baird, jun., J. H. Surridge, and M. Buza, *J. Org. Chem.*, 1971, **36**, 2088.

more smoothly than the foregoing chlorination and afforded, completely regiospecifically and highly stereospecifically, *E*-chloroiodoalkenes (3) in high yields (Scheme 2 and Table 2). When an excess of copper(II)



SCHEME 2

TABLE 2

Chloriodination of acetylenes with copper(II) chloride and iodine in acetonitrile

(1)		Molar ratio of (CuCl ₂ + I ₂) ^c to (1)	Time ^a (h)	Yield (%) ^b of (3)
R	R'			
Ph	H	1:1	0.25	35
Ph	H	5:1	0.25	54
Ph	H	5:1	5	97
Ph	Me	5:1	0.25	75
Ph	Me	5:1	5	100
Ph	Me	5:1	5 ^d	87
Ph	Me ^e	5:1	5	72
Ph	Et	5:1	0.25	100
Ph	Pr ⁿ	5:1	0.25	100
Ph	Pr ⁱ	5:1	0.25	54 ^f
Ph	Pr ⁱ	5:1	5	76 ^f
Ph	Bu ⁿ	5:1	0.25	88
Ph	Bu ^t	5:1	5	92 ^g
Ph	Et	25:1	5	54 ^h
n-Hexyl	H	5:1	5	84
Pr ⁿ	Pr ⁿ	5:1	5	100
Et	Et	5:1	5	82

^a At 82 °C. ^b Based on the amount of (1) and determined by g.l.c. analysis; only the *E*-isomer was detected except where otherwise stated. ^c CuCl₂:I₂ 1:1. ^d At 18–20 °C. ^e KI used in place of I₂ (CuCl₂:KI 1:1). ^f *E*:*Z* 99:1. ^g *E*:*Z* 89:11. ^h Isolated yield after recrystallization; *E*-isomer only.

chloride (with respect to iodine) was used, dichloroalkenes were produced as by-products. Potassium iodide could be used in place of iodine, but the yield was slightly lower. The reaction of acetylenes (1) with commercial iodine monochloride also proceeded smoothly with high regiospecificity to give chloroiodoalkenes (3), but both the yield and *E*-stereospecificity were low in comparison with the copper(II) chloride-iodine case (Table 3). Here, the addition of copper(II) chloride accelerated the reaction and improved the yield of (3); the reverse was observed on addition of copper(I) chloride.

The configurations of the alkenes (2) were assigned from ¹H n.m.r. spectra and also by comparison with reported data. For (*E*)- and (*Z*)- $\alpha\beta$ -dibromostyrene, the proton chemical shifts have been reported to be δ 6.75 and

6.98, respectively.⁶ Further, it has been known that alkyl protons *cis* to chlorine resonate at lower field than those *trans* to chlorine in both hydrogen chloride addition products of the acetylenes (1; R = Ph, R' = Me⁷ or Bu^t⁸). On the basis of these facts, the configurations

TABLE 3

Chloriodination of acetylenes with iodine chloride in acetonitrile

(1)		Molar ratio of ICl to (1)	Additive [ratio to (1)]	Time ^a (h)	Yield (%) ^b of (3) (<i>E</i> : <i>Z</i>)
R	R'				
Ph	H	1:1		1	52 (95:5)
Ph	H	1.5:1	CuCl ₂ (3:1)	0.5 ^c	85 (98:2)
Ph	Me	1:1		1	76 (99:1)
Ph	Et	1:1		1	74 (99:1)
Ph	Pr ⁱ	1:1		1	49 (97:3)
Ph	Bu ^t	1:1		1	33 (78:22)
Ph	Bu ^t	1.5:1	CuCl ₂ (3:1)	0.5	63 (87:13) ^d
Ph	Bu ^t	1.5:1		5	74 (77:23)
Ph	Bu ^t	1.5:1	CuCl (1.5:1)	5	15 (92:8) ^e
n-Hexyl	H	1:1		1	50 ^f
n-Hexyl	H	1.5:1		5	49 ^f
n-Hexyl	H	5:1		5	36 ^f
Pr ⁿ	Pr ⁿ	1:1		1	47 ^f

^a At 82 °C. ^b Based on the amount of (1) and determined by g.l.c. analysis; a small amount of (2) was always formed. ^c At 25–30 °C. ^d Other product: 15% yield of (2) (*E*:*Z* 5:95). ^e Other product: 4% yield of (2) (*E*:*Z* 72:28). ^f Almost entirely *E*-isomer; *Z*-isomer not identified.

of the alkenes (*E*)- and (*Z*)-(2; R = Ph, R' = H or alkyl) were assigned. For example, the vinyl protons of (*E*)- and (*Z*)-(2; R = Ph, R' = H) resonated at δ 6.46 and 6.62 respectively, and the methyl protons of (*E*)- and (*Z*)-(2; R = Ph, R' = Me) absorbed at δ 2.40^{*} and 2.12, respectively. Several attempts to determine the structures of the chloroiodoalkenes (3) by hydrogenation or hydrodeiodination to known compounds were unsuccessful; we therefore used ¹H and ¹³C n.m.r. spectroscopy for this purpose. In ¹H n.m.r. spectra, a low-field shift of 0.17 p.p.m. in the resonance of the vinyl proton of (*E*)-(3; R = Ph, R' = H) in comparison with (*E*)-(2; R = Ph, R' = H) is consistent with that observed in the cases of 1-chloro- and 1-iodo-propenes (0.12–0.23 p.p.m.).⁹ Similarly, a low-field shift of 0.30 p.p.m. in the methyl proton resonance of (*E*)-(3; R = Ph, R' = Me) in comparison with the dichloro-analogue is reasonably explained by considering the different shielding effects of I and Cl on β -methyl protons in (*Z*)-1-halogenopropenes.¹⁰ More direct evidence for the location of I and Cl in structures (3) was obtained from ¹³C n.m.r. spectra. For (*E*)-(3; R = Ph, R' = H) vinylic carbon atoms α and β to the phenyl group resonate at 133.7 (s) and 73.2 p.p.m. (d, $J_{C,H}$ 194 Hz), respectively. Chemical shifts calculated from substituent parameters for vinyl derivatives¹¹

* Although a resonance at δ 2.98 for this compound was reported,⁴ the reason for the discrepancy is not clear.

⁶ J. König and V. Wolf, *Tetrahedron Letters*, 1970, 1629.

⁷ R. C. Fahey and D. J. Lee, *J. Amer. Chem. Soc.*, 1966, **88**, 5555.

⁸ P. Maroni, G. Melloni, and G. Modena, *J.C.S. Perkin I*, 1973, 2491.

⁹ G. J. Martin and M. L. Martin, *Progr. N.M.R. Spectroscopy*, 1972, **8**, 216.

¹⁰ R. M. Silverstein, C. G. Bassler, and T. C. Morrill, 'Spectrometric Identification of Organic Compounds,' 3rd edn., Wiley, New York, 1974, p. 212.

¹¹ J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972, pp. 71 and 184.

are 147 and 70 p.p.m. respectively, and would be 93 and 123 p.p.m. respectively if iodine and chlorine were *trans*. For (*E*)-(3; R = Ph, R' = Me) α -, β -, and methyl carbon atoms resonate at 128.7 (s), 92 [q, $J_{C,H}$ 8 Hz (coupling with CH_3)], and 31.3 p.p.m. (q, $J_{C,H}$ 130 Hz), respectively; shifts calculated from the observed chemical shifts of (*E*)-(3; R = Ph, R' = H) and the shielding effect of methyl¹¹ are 126 and 84 p.p.m. for α - and β -carbon atoms respectively. This agreement, together with the fact that the high-field carbon signal shows coupling, indicates the structural assignment for (3) to be correct.

It has been reported¹² that the reaction of the acetylene (1; R = Ph, R' = H) with chlorine in dichloromethane gives the alkenes (*E*)- and (*Z*)-(2; R = Ph, R' = H) and chloro(phenyl)acetylene in roughly equal

their simplicity, high yields, and high stereo- (*trans*) and regio-specificities.

Both halogenations were insensitive to radical scavengers such as *m*-dinitrobenzene and oxygen, showing that the reactions are ionic. In the chlorination of the alkyne (1; R = Ph, R' = alkyl) the isomer ratio (*E*:*Z*) decreased markedly on changing the alkyl group from primary to secondary and then to tertiary. This can be explained by assuming that the reaction proceeds through an open vinyl cation intermediate (A) in which Cu^I co-ordinates weakly with both the π -orbital of the double bond¹⁴ and the lone pair of the chlorine atom, the chloride anion co-ordinated to copper being the attacking species. When R' is large, it will hinder attack on its own side in (A) and lead to *Z*-chlorination. Free chloride anion did not seem to play an important role as

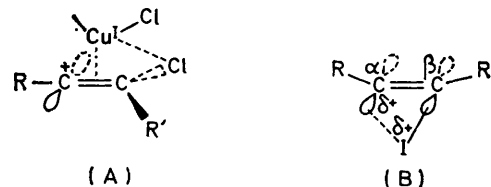
TABLE 4
Characterization of the alkenes (2)

Compound	B.p. (°C) [Torr]	¹ H N.m.r. (δ)	Found (reqd.) (%)		
			C	H	Cl
(<i>E</i>)-(2; R = Ph, R' = H) ^a	103—104 [19]	7.7—7.25 (5 H, m, Ph), 6.62 (1 H, s, vinyl of <i>Z</i> -), 6.46 (1 H, s, vinyl of <i>E</i> -)	55.0 (55.5)	3.3 (3.5)	
(<i>E</i>)-(2; R = Ph, R' = Me)	95—96 [9]	7.5—7.15 (5 H, m, Ph), 2.40 (3 H, s, Me of <i>E</i> -), 2.12 (3 H, s, Me of <i>Z</i> -)	58.0 (57.8)	4.45 (4.3)	37.0 (37.9)
(<i>E</i>)-(2; R = Ph, R' = Et)	113—115 [20]	7.45—7.1 (5 H, m, Ph), 2.70 (2 H, q, CH_2)	60.0 (59.7)	5.2 (5.0)	34.7 (35.3)
(<i>E</i>)-(2; R = Ph, R' = Pr ⁿ)	108—110 [19]	7.55—7.05 (5 H, m, Ph), 2.70 (2 H, t, =C- CH_2)	61.4 (61.4)	5.85 (5.6)	32.9 (33.0)
(<i>E</i>)-(2; R = Ph, R' = Bu ⁿ)	145—146 [19]	7.50—7.05 (5 H, m, Ph), 2.66 (2 H, t, =C- CH_2)	63.1 (62.9)	6.3 (6.15)	30.7 (30.9)
(<i>E</i>)- and (<i>Z</i>)-(2; R = Ph, R' = Pr ⁱ) ^b	121—123 [18]	7.70—7.25 (5 H, m, Ph), 3.65 (1 H, sept, CH of <i>E</i> -), 2.92 (1 H, sept, CH of <i>Z</i> -)	61.7 (61.4)	5.75 (5.6)	
(<i>E</i>)- and (<i>Z</i>)-(2; R = Ph, R' = Bu ^t) ^c	142—144 [19]	7.30 (5 H, s, Ph), 1.48 (9 H, s, Me of <i>E</i> -), 1.05 (9 H, s, Me of <i>Z</i> -)	62.8 (62.9)	6.4 (6.15)	30.0 (30.9)
(<i>E</i>)-(2; R = R' = Ph)	(M.p. 147—148) ^d	7.65—7.15 (m, Ph),	67.6 (67.5)	3.9 (4.05)	
(<i>E</i>)-(2; R = CH_2OH , R' = H)	108—110 [18]	6.46 (1 H, s, vinyl), 4.40 (2 H, s, CH_2)	16.4 (16.5)	1.9 (1.85)	
(<i>E</i>)-(2; R = R' = Pr ⁿ)	78—79 [20]	2.54 (2 H, t, =C- CH_2)	53.0 (53.1)	7.75 (7.8)	
(<i>E</i>)- and (<i>Z</i>)-(2; R = n-Hexyl, R' = H) ^e	80—82 [19]	6.15 (1 H, s, vinyl), 2.76—2.35 (2 H, m, =C- CH_2)	53.1 (53.1)	8.1 (7.8)	

^a Mixture of *E* and *Z* (95 : 5). ^b Mixture of *E* and *Z* (80 : 20). ^c Mixture of *E* and *Z* (20 : 80); *Z*-isomer, m.p. 65—67° (from EtOH). ^d Recryst. from EtOH; lit.,⁴ m.p. 146—147°. ^e Mixture of *E* and *Z* (88 : 12). ^f Vinylic protons of both *E*- and *Z*-isomer had the same chemical shift, as reported.⁴

amounts, and that the acetylene (1; R = Ph, R' = Me) does not undergo homogeneous reaction in carbon tetrachloride. However, we found¹³ that the alkynes (1; R = Ph, R' = Me or Bu^t) react with chlorine in carbon tetrachloride at room temperature or under reflux (0.2—2 h) to give a mixture of (*E*)- and (*Z*)-(2; R = Ph, R' = Me) (63—73 : 27—37) in 50—82% yield and a mixture of (*E*)- and (*Z*)-(2; R = Ph, R' = Bu^t) (12—14 : 86—88) in 62—79% yield, respectively. Similar low *E*-selectivity in the chlorination of (1; R = Ph, R' = H or Et) with chlorine have also been reported recently.⁴ Therefore both chlorination and chloriodination with copper(II) chloride seem synthetically useful, because of

the attacking species, since the presence of an excess of lithium chloride had no effect on yield or isomer ratio. On the other hand, in the chloriodination high *trans*-stereospecificity and the complete regiospecific formation



of (3) are characteristic. This cannot be so easily explained unless the reaction proceeds through a cyclic

¹² R. C. Fahey, *Topics Stereochem.*, 1968, 3, 279.
¹³ Preliminary report, S. Uemura, A. Onoe, and M. Okano, *J.C.S. Chem. Comm.*, 1976, 145.

¹⁴ The co-ordination of Cu^I to olefins and acetylenes is well known; e.g. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd edn., Interscience, New York, 1972, pp. 910—911.

iodonium ion (B) in which the iodine interacts more strongly with the β - than with the α -carbon. The cationic character at the α -carbon atom may be stabilized by overlap with phenyl p -orbitals¹⁵ when R is phenyl and R' is hydrogen or alkyl, or by the inductive effect of an alkyl group when R is alkyl and R' is hydrogen. The attacking species seems to be CuCl_3^- , since the reaction with iodine monochloride in the presence of copper(II) chloride gave (3) in an isomer ratio similar to that obtained with the copper(II) chloride-iodine system (*cf.* data in Tables 2 and 3 for R = Ph, R' = H or Bu^t). The re-

inorganic materials were commercial products. I.r. and mass spectra were recorded with a Hitachi EPI-S2 and a JEOL JMS-01SG spectrometer, respectively. ¹H N.m.r. spectra were taken with a Varian EM-360 instrument for solutions in CCl_4 with Me_4Si as internal standard (with internal lock). ¹³C N.m.r. spectra were obtained at 25.1 MHz with a JEOLCO ¹³C Fourier transform n.m.r. system (JNM-PFT-100) and were recorded after 50–100 pulses with intervals of 3 s. An internal deuterium lock was employed and Me_4Si was used as internal standard. G.l.c. analyses were carried out with a Shimadzu 4BMPF apparatus [EGSS-X (15%)–Chromosorb W (1 or 3 m) and

TABLE 5
Characterization of the alkenes (3)

Compound	B.p. (°C) [Torr]	¹ H N.m.r. (δ)	Found (reqd.) ^a (%)		m/e	
			C	H	M^+	$M^+ + 2$
(E)-(3; R = Ph, R' = H) ^b	112–113 [5]	7.60–7.03 (5 H, m, Ph), 6.63 (1 H, s, vinyl)	35.9 (36.3)	2.15 (2.3)		
(E)-(3; R = Ph, R' = Me) ^c	94–96 [2]	7.22 (5 H, s, Ph), 2.70 (3 H, s, Me)	39.8 (38.8)	2.95 (2.9)	278	280
(E)-(3; R = Ph, R' = Et)	113–115 [20]	7.20 (5 H, s, Ph), 2.82 (2 H, s, CH_2)	42.8 (41.1)	3.9 (3.45)	292	294
(E)-(3; R = Ph, R' = Pr ⁿ)	109–111 [20]	7.20 (5 H, s, Ph), 2.79 (2 H, s, CH_2)	44.3 (43.1)	4.15 (3.95)	306	308
(E)-(3; R = Ph, R' = Pr ^t)	101–103 [19] ^d	7.50–6.90 (5 H, m, Ph), 2.86 (1 H, s, CH)	43.3 (43.1)	3.85 (3.95)		
(E)-(3; R = Ph, R' = Bu ⁿ)	136–138 [20]	7.22 (5 H, s, Ph), 2.77 (2 H, s, CH_2)			320	322
(E)- and (Z)-(3; R = Ph, R' = Bu ^t) ^e	130–132 [5]	7.40–7.06 (5 H, m, Ph), 1.50 (9 H, s, Me of E-), 1.07 (9 H, s, Me of Z-)	46.5 (45.0)	4.65 (4.4)	320	322
(E)-(3; R = Ph, R' = Ph)	(M.p. 193–194) ^f	7.50–7.05 (5 H, m, Ph), 6.26 (1 H, s, vinyl), 2.56 (2 H, m, $=\text{C-CH}_2$)	49.3 (49.4)	2.9 (2.95)		
(E)-(3; R = n-Hexyl, R' = H)	95–97 [6]		34.8 (35.3)	5.15 (5.2)		
(E)-(3; R = R' = Pr ⁿ)	104–106 [18]	2.69 (2 H, t, $=\text{C-CH}_2$)	35.8 (35.3)	5.4 (5.2)		
(E)-(3; R = R' = Et)	78–80 [19]	2.66 and 2.63 (4 H, q, CH_2), 1.12 and 1.05 (6 H, t, Me)	30.0 (29.5)	4.1 (4.1)		

^a In some cases it was difficult to obtain correct analytical data, probably because of decomposition of the product giving iodine. In such cases mass spectra were taken. The intensity of the $M^+ + 2$ peaks was always consistent with the presence of one chlorine atom. ^b ¹³C N.m.r. δ (from Me_4Si) 137.1 (s, quaternary phenyl C), 133.7 (s, $=\text{CPh}$), 129 (d, *meta*-C), 128.6 (d, *ortho*-C), 127.8 (d, *para*-C), and 73.2 (d, $=\text{CI}$). ^c ¹³C N.m.r. δ (from Me_4Si) 141.2 (s, quaternary phenyl C), 128.8 (d, *meta* C), 128.7 (s, $=\text{CPh}$), 128.4 (d, *ortho*-C), 128 (d, *para*-C), 92 (q, $=\text{CI}$), and 31.3 (q, Me). ^d M.p. 66–68° (from MeOH). ^e Mixture of E and Z (90 : 10). ^f Recryst. from EtOH.

giospecific formation of (3) is in sharp contrast with the reaction of the alkynes (1; R = Ph, R' = H or Me) with iodine azide where iodine attacks only the α -carbon atom.¹⁶ The difference in counter-ion thus appears to change the nature of the reaction. The assumption of a cyclic intermediate in the case of iodine and not in the case of chlorine parallels the mechanism of solvolysis of β -halogenovinyl sulphonic esters.¹⁷

EXPERIMENTAL

n-Alkyl,¹⁸ isopropyl,¹⁹ and t-butyl-phenylacetylene²⁰ were prepared by the reported methods. Other organic and

Apiezon-L (30%)–Celite (1 m) columns; N_2 as carrier gas; ethyl cinnamate or styrene dichloride as internal standard]; the E-isomer has a shorter retention time than the Z-isomer in all cases except (2; R = R' = Ph).

Chlorination.—A typical experimental procedure is as follows. Phenylacetylene (1; R = Ph, R' = H) (0.55 g, 5.3 mmol) was added to acetonitrile (100 ml) containing copper(II) chloride (26.8 g, 200 mmol) and lithium chloride (8.4 g, 200 mmol) at room temperature, and the mixture was heated at reflux temperature for 24 h. After cooling, the precipitated copper(I) salt was filtered off and the filtrate was added to water (*ca.* 500 ml) and extracted with benzene. The extract was concentrated to *ca.* 10 ml, then analysed by

¹⁷ P. Bassi and U. Tonellato, *J.C.S. Perkin II*, 1974, 1283.

¹⁸ J. R. Johnson, A. M. Shwarty, and T. L. Jacobs, *J. Amer. Chem. Soc.*, 1938, **60**, 1882.

¹⁹ H. H. Schlubach and K. Repenning, *Annalen*, 1958, **614**, 37.

²⁰ A. Morteux and M. Blanchard, *Bull. Soc. chim. France*, 1970, 4035.

¹⁶ The conjugation of the developing cationic orbital with aromatic π -orbitals in an α -arylvinyl system is well documented, *e.g.*, Z. Rappoport, *Accounts Chem. Res.*, 1976, **9**, 267; G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, 1971, **9**, 264.

¹⁷ A. Hassner, R. J. Isbister, and A. Friederang, *Tetrahedron Letters*, 1969, 2939.

g.l.c. (styrene dichloride as internal standard). Distillation gave the alkene (*E*)-(2; R = Ph, R' = H) (0.62 g, 3.5 mmol, 67%) containing 5% of the *Z*-isomer. Properties of the alkenes (2) are summarized in Table 4.

Chloriodination.—Phenylacetylene (1.0 g, 10 mmol) was added to acetonitrile (100 ml) containing copper(II) chloride (6.7 g, 50 mmol) and iodine (12.7 g, 50 mmol) at room temperature and then the mixture was heated at reflux temperature for 5 h. The cooled mixture was then filtered, and the filtrate was added to aqueous sodium thiosulphate to remove the excess of iodine, and then extracted with benz-

ene. Distillation gave the pure *E*-alkene (3; R = Ph, R' = H) (1.7 g, 6.5 mmol, 65%). Reactions with iodine chloride were carried out similarly [acetylene (2.5—5 mmol), iodine chloride (3.75—5 mmol), and acetonitrile (25—50 ml) in the presence or absence of copper(II) or copper(I) chloride]. Properties of the alkenes (3) are recorded in Table 5.

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