

Electrophilic Additions to Acetylenes. Part II.¹ Addition of Alkyl Chlorides to Diphenylacetylene

By Roberto Maroni, Giovanni Melloni,* and Giorgio Modena, Centro ' Meccanismi di Reazioni Organiche ' del C.N.R., Istituto di Chimica Organica, Università di Padova, 35100 Padova, Italy

The addition of *t*-butyl, diphenylmethyl, and benzyl chlorides to diphenylacetylene in dichloromethane in the presence of a Lewis acid has been investigated. With *t*-butyl chloride the expected 1:1 addition products are formed, while with diphenylmethyl chloride cyclisation to indene derivatives is observed. In the case of benzyl chloride both addition and cyclisation products are obtained. The configuration of the 1:1 addition products, assigned by ¹H n.m.r. spectroscopy, shows that in the case of *t*-butyl chloride the *anti* addition product is predominant, while with benzyl chloride the *syn* addition product is preferentially formed. The results are discussed in terms of linear vinyl cation intermediates, which may give either the cyclisation or addition products. The apparent contradiction between the results with *t*-butyl chloride and with benzyl chloride is resolved by considering preferential attack of the nucleophile Cl⁻ from the less hindered side of the cationic intermediate.

In our previous paper¹ we showed that the Lewis acid-catalysed addition of *t*-butyl, benzyl, and diphenylmethyl chlorides to phenylacetylene gives the products of 1:1 addition. The stereochemistry of the reaction was rationalised in terms of an open linear vinyl cation intermediate, which is attacked by the nucleophile Cl⁻ from the less hindered side. The large difference in size between the hydrogen and the various alkyl groups in the cationic intermediate made the system quite unbalanced; accordingly, the isomer formed in larger amount (in the case of the addition of *t*-butyl chloride the only isomer) had a configuration corresponding to the attack of the nucleophile from the side bearing the hydrogen.

In order to test the behaviour of a more balanced system we have studied the addition of the same alkyl chlorides to diphenylacetylene. However, particularly in the case of the addition of diphenylmethyl chloride, cyclisation to indene derivatives was observed. This result limited the possibility of a stereochemical comparison between the addition reactions in the two systems, but showed the occurrence of an interaction between the positive centre of a vinyl cation intermediate and a γ -phenyl residue, and led to the discovery of a new synthetic route to the indene system.²

RESULTS

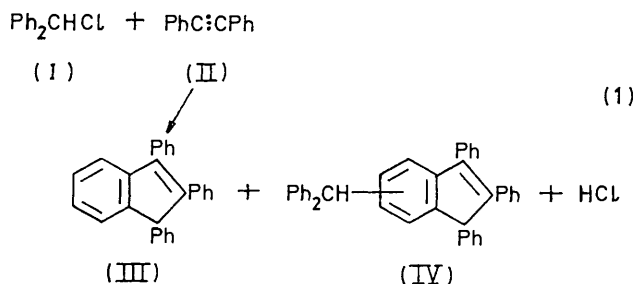
The addition reactions described here were all carried out in boiling anhydrous dichloromethane, in the presence of a catalytic amount of anhydrous zinc chloride or aluminium chloride. In the case of *t*-butyl and benzyl chlorides no reaction was observed in the absence of catalyst even after prolonged reflux; in the case of diphenylmethyl chloride a 32% yield of cyclisation products was obtained after refluxing for 1 week. No isomerisation of the addition products, both of (*E*)- and (*Z*)-configuration, under the reaction conditions was observed.

Addition of Diphenylmethyl Chloride.—This reaction was carried out with various molar ratios of the reagents for 3 h. The chromatography of the crude reaction mixtures afforded, besides some unchanged diphenylacetylene (II), 1,2,3-triphenylindene (III) and a diphenylmethyl derivative (IV) [equation (1)].

Compound (IV) was probably formed by a subsequent reaction of diphenylmethyl chloride (I) with compound (III),

¹ Part I, R. Maroni, G. Melloni, and G. Modena, *J.C.S. Perkin I*, 1973, 2491.

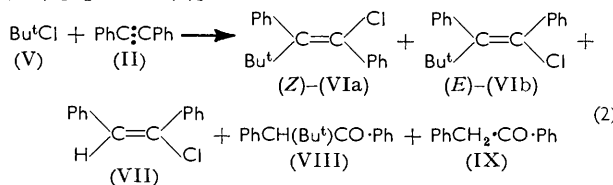
as indicated by an independent reaction carried out with equivalent amounts of the two compounds under the same conditions as the addition reaction. The position of the



diphenylmethyl residue in compound (IV) was not established.

The results obtained under different reaction conditions are reported in the Table.

Addition of *t*-Butyl Chloride.—This reaction was carried out using a five-fold excess of *t*-butyl chloride (V) in the presence of zinc chloride for 15 h, and afforded a mixture of the 1:1 addition products (VIa and b), together with minor amounts of (*E*)- α -chlorostilbene (VII), 3,3-dimethyl-1,2-diphenylbutanone (VIII), and benzyl phenyl ketone (IX) [equation (2)].



The mixture of the two isomeric addition products (VI) could not be resolved; a pure sample of the major (*Z*)-isomer (VIa) could however be obtained by fractional recrystallisation. The configuration was then assigned on the basis of the ¹H n.m.r. spectrum of the mixture, by comparison with spectra of similar compounds, obtained in the previous study.¹ The (*Z*):(*E*) ratio, evaluated by integration to the ¹H n.m.r. signals corresponding to the *t*-butyl protons, was 95:5.

(*E*)- α -Chlorostilbene (VII) was probably formed by addition to diphenylacetylene (II) of hydrogen chloride, formed by dehydrochlorination of *t*-butyl chloride (V) under the

² Preliminary communication, R. Maroni and G. Melloni, *Tetrahedron Letters*, 1972, 2869.

reaction conditions.¹ An independent experiment confirmed that hydrogen chloride in dichloromethane in the presence of zinc chloride reacts with diphenylacetylene in an exclusive *syn*-fashion.

The formation of ketones (VIII) and (IX) was not investigated in detail. They are probably the products of hydrolysis during the work-up procedures of the corresponding dichloro-derivatives which are formed by addition of hydrogen chloride to the products (VI) and (VII) under the reaction conditions.

Addition reactions carried out with smaller (V):(II) ratios or in the presence of aluminium chloride gave very low yields of addition products and were therefore not studied in detail.

Addition of Benzyl Chloride.—This reaction was carried out with various molar ratios of the two reagents for 10 h.

latter were then assigned on the basis of the ¹H n.m.r. spectrum of the mixture, by comparison with an authentic mixture of the two isomers prepared by independent synthesis, and also by comparison with the spectra of similar compounds, obtained previously.¹ The (*Z*):(*E*) ratio, evaluated by integration of the ¹H n.m.r. signals of the benzylic protons, was *ca.* 15:85 under all the reaction conditions examined.

The results are reported in the Table.

DISCUSSION

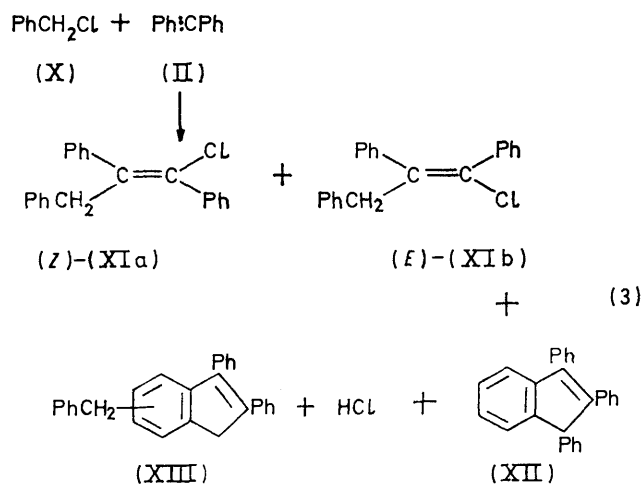
Stereochemistry of the Addition Reactions.—Viewed formally, *t*-butyl chloride gives predominant *anti* addition to diphenylacetylene whereas benzyl chloride gives predominant *syn* addition. This apparent contradiction

Addition of alkyl chlorides (I) and (X) to diphenylacetylene (II)

Alkyl chloride	Catalyst	Reagent ratio *	Reaction time (h)	Products (yield/%)		
				1:1 Adducts	Indene	Alkyl-substituted indene
(I)	AlCl ₃	1:1	3	None	(III) (61)	(IV) (5)
(I)	ZnCl ₂	1:1	3	None	(III) (15)	(IV) (32)
(I)	ZnCl ₂	1:5	3	None	(III) (53)	(IV) (22)
(I)	None	1:4	168	None	(III) (27)	(IV) (5)
(X)	AlCl ₃	1:5	10	(XIa and b) (13)	(XII) (3)	(XIII) (<i>ca.</i> 1)
(X)	ZnCl ₂	1:1	10	(XIa and b) (16)	(XII) (4)	(XIII) (5)
(X)	ZnCl ₂	1:5	10	(XIa and b) (59)	(XII) (12)	(XIII) (2)
(X)	ZnCl ₂	1:10	10	(XIa and b) (68)	(XII) (14)	(XIII) (trace)
(X)	None	1:5	168	None	None	None

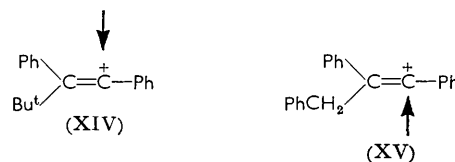
* Ratio alkyl chloride : diphenylacetylene.

Complex mixtures of products were obtained, complicated also by the presence of benzylic polymers. Chromatography on silica gel of the reaction mixtures permitted isolation of a fraction containing the isomeric 1:1 addition products (XIa and b) and a cyclisation product, the 2,3-diphenylindene (XII). Also isolated was a small amount of the hydrocarbon (XIII), which was shown to arise from a subsequent reaction of benzyl chloride (X) with the indene derivative (XII) [equation (3)].



The mixture of the three compounds (XIa), (XIb), and (XII) could not be satisfactorily resolved by adsorption chromatography. Preparative g.l.c. separated fairly pure samples of the indene (XII) and of the mixture of the (*Z*),(*E*)-isomers (XI). The structure and the configuration of the

may easily be resolved by assuming that both reactions proceed *via* a linear free vinyl cation, which then undergoes addition of the nucleophile. The steric requirements of the β-groups in such a cationic intermediate are clearly in the order: *t*-butyl > phenyl > benzyl. Consequently, the phenyl side is more accessible in the vinyl cation (XIV) whereas the benzyl side is more accessible in the vinyl cation (XV).

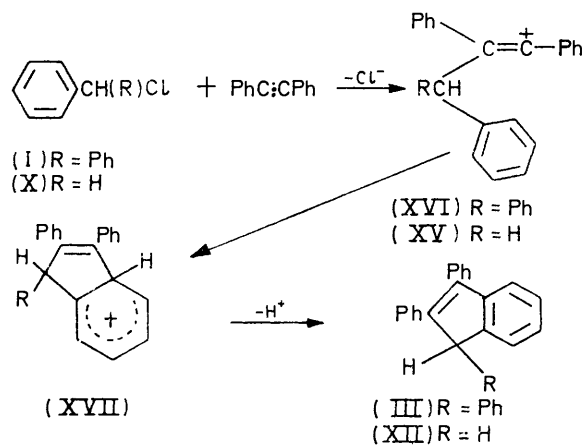


The trend observed is in qualitative agreement with the results obtained in the addition of the same alkyl chlorides to phenylacetylene.¹ Although a quantitative analysis of the steric requirements of the various groups would be highly speculative and beyond the scope of this work, the present results further support the hypothesis¹ that a vinyl cation is an intermediate in these addition reactions and that vinyl cations stabilised by an α-phenyl group have linear structure.

Fate of the Vinyl Cation.—The formation of an indene derivative in the addition of diphenylmethyl and benzyl chloride to diphenylacetylene is readily rationalised by assuming a Friedel-Crafts-like attack by the positive centre of a vinyl cation intermediate on a γ-phenyl residue, followed by loss of a proton (Scheme).

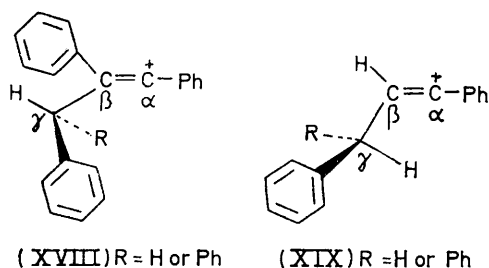
Other cases of internal electrophilic attack by a vinyl

cation on a suitably located π -system have been reported by us³ and by other authors.⁴ This is however the first case where a phenyl ring isolated from the vinyl system by a methylene (or methine) group is involved.



SCHEME

The question whether the phenyl ring is attacked by the electrophilic centre after the formation of a free cation or whether it anchimerically assists the formation of the cation warrants consideration. Examination of models of the possible conformations of the intermediate vinyl cations involved both in the addition of diphenylmethyl and benzyl chlorides to diphenylacetylene (dis-



cussed here) and in the addition of the same alkyl chlorides to phenylacetylene (previously reported¹) in which no cyclisation product was formed show that in the first case the minimum energy conformations are those having the γ -phenyl (or phenyls) of the benzyl (or diphenylmethyl) group as far as possible from the phenyl bonded to the β -carbon atom (XVIII). This corresponds to having a γ -phenyl close to the positive centre, and therefore in an appropriate position to undergo cyclisation. In the case of the additions to phenylacetylene the minimum energy conformations are those having the γ -phenyl (or phenyls) as far as possible from the positive centre (XIX), and therefore in a position unfavourable for cyclisation.

³ G. Melloni and G. Modena, *J.C.S. Perkin I*, 1972, 218, and references therein; *ibid.*, p. 1355; G. Capozzi and G. Modena, *ibid.*, p. 216; G. Capozzi, G. Modena, and L. Ronzini, *ibid.*, p. 1136.

⁴ H. Martens and G. Hoornaert, *Tetrahedron Letters*, 1970, 1821; *Synth. Comm.*, 1972, 2, 147; T. C. Clarke and R. G. Bergman, *J. Amer. Chem. Soc.*, 1972, 94, 3627.

It appears therefore that the formation of cyclisation products in these systems largely reflects the presence of a bulky group in the β -position forcing a γ -phenyl toward the positive centre by steric interaction, rather than a positive interaction between the aromatic π -system and the developing positive charge. In this complex balance between inter- and intra-molecular nucleophilic attack, the considerable effect exerted by a bulky β -group on the rate of attack of the external nucleophile should not be neglected, as shown by the stereoselectivity observed in these reactions.

EXPERIMENTAL

The general experimental details are as described in Part I,¹ except the g.l.c. nitrogen flow rate (120 ml min⁻¹).

Addition of Diphenylmethyl Chloride (I) to Diphenylacetylene (II).—A typical run was as follows. To a suspension of anhydrous aluminium chloride (0.13 g, 1 mmol) in a solution of diphenylacetylene (II) (1.78 g, 10 mmol) in dichloromethane (30 ml) at room temperature was added a solution of diphenylmethyl chloride (I) (2.03 g, 10 mmol) in the same solvent (10 ml). After a few min of stirring at room temperature the mixture was refluxed for 3 h. After cooling, the mixture was filtered, and the solvent was evaporated to give a dark green residue which was chromatographed on silica gel. Elution with light petroleum gave a small amount of unchanged diphenylacetylene (II). Elution with light petroleum-benzene (6:1) gave 1,2,3-triphenylindene (III) (2.1 g, 61%), m.p. 134–135° (from ethanol) (lit.,⁵ 134–136°, τ 2.55–3.10 (19H, m) and 5.05 (1H, s). Further elution with light petroleum-benzene (3:1) gave a diphenylmethyl-1,2,3-triphenylindene (IV) [0.25 g, 5% (yield based on diphenylacetylene)], m.p. 165–166° (from absolute ethanol) (Found: C, 93.8; H, 6.1. Calc. for C₄₀H₃₀: C, 94.1; H, 5.9%); m/e 510 (M^+); λ_{max} (EtOH) 210 (ϵ 17,500), 243 (9200), and 310 nm (7000); τ 2.55–3.10 (28H, m), 4.55 (1H, s), and 5.05 (1H, s). Elution with other eluants gave only tarry products.

Compound (IV) was readily prepared in 92% yield by the reaction of diphenylmethyl chloride (I) (5 mmol) with 1,2,3-triphenylindene (III) (5 mmol) in boiling dichloromethane (30 ml) in the presence of anhydrous aluminium chloride (or zinc chloride) (0.5 mmol) for 1 h.

The results obtained with other reaction conditions are reported in the Table.

Addition of *t*-Butyl Chloride (V) to Diphenylacetylene (II).—To a suspension of anhydrous zinc chloride (1.36 g, 10 mmol) in a solution of diphenylacetylene (II) (3.56 g, 20 mmol) in boiling dichloromethane (35 ml) was added a solution of *t*-butyl chloride (V) (9.26 g, 100 mmol) in the same solvent (20 ml). The mixture was then refluxed for 15 h. After cooling, the catalyst was filtered off and the solvent was evaporated to give a brownish residue which was chromatographed on a column of silica gel (1.5 m long). Elution with light petroleum afforded a small amount of unchanged diphenylacetylene (II), (*E*)- α -chlorostilbene (VII) (0.17 g, 4%), identical by u.v. and ¹H n.m.r. spectra with an authentic sample,⁶ and a mixture of (*Z*)- and (*E*)-1-chloro-

⁵ M. Vaillant, *Ann. Chim. (France)*, 1954, 9, 5; J. E. Hodgkins and M. P. Hughes, *J. Org. Chem.*, 1962, 27, 4187; L. L. Miller and R. F. Boyer, *J. Amer. Chem. Soc.*, 1971, 93, 650, and references cited therein.

⁶ D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *J. Amer. Chem. Soc.*, 1965, 87, 863; G. Favini, S. Trovato, and A. Gamba, *Theor. Chim. Acta*, 1967, 7, 305, and references therein.

3,3-dimethyl-1,2-diphenylbutene (VIa and b) (3.68 g, 68%). Further elution with light petroleum-benzene (2 : 1) gave 3,3-dimethyl-1,2-diphenylbutanone (VIII) (0.3 g, 6%). Further elution gave tarry substances and a small amount (30 mg) of benzyl phenyl ketone.

The α -chlorostilbene (VII) was synthesised by addition of gaseous hydrogen chloride (as a saturated dichloromethane solution) (0.36 g, 10 mmol) to diphenylacetylene (II) (1.96 g, 11 mmol) in dichloromethane (30 ml) in the presence of zinc chloride (0.14 g, 1 mmol) at 40° for 21 h. Chromatography of the reaction mixture on silica gel with light petroleum as eluant, afforded 1.78 g (83%) of the (*E*)-isomer (VII). No evidence was found of the presence of the (*Z*)-isomer.

The two isomeric 1-chloro-3,3-dimethyl-1,2-diphenylbutenes (VIa and b), low-melting colourless crystals (Found: C, 79.55; H, 7.15; Cl, 12.95. Calc. for C₁₈H₁₉Cl: C, 79.8; H, 7.1; Cl, 13.1%) could not be satisfactorily separated by adsorption chromatography. Preparative g.l.c. led to decomposition. They were therefore identified on the basis of the ¹H n.m.r. spectrum of their mixture, by comparison with spectra of similar compounds prepared in a previous work,¹ and also by comparison with an authentic mixture of (VIa and b) synthesised independently. The ¹H n.m.r. spectrum of the mixture showed, besides bands at τ 2.55—3.05 (m), a signal at τ 8.67, attributable to the (*E*)-isomer (VIb), and a signal at τ 9.09, attributable to the (*Z*)-isomer (VIa) (s of integral ratio 1 : 19). By fractional recrystallisation from ethanol a pure sample of (*Z*)-1-chloro-3,3-dimethyl-1,2-diphenylbutene (VIa) was obtained, m.p. 60—61° (Found: C, 79.65; H, 6.9; Cl, 12.85%), τ 2.55—3.05 (10H, m) and 9.09 (9H, s).

3,3-Dimethyl-1,2-diphenylbutanone (VIII) was identified by comparison with an authentic sample, prepared by the Friedel-Crafts reaction of 3,3-dimethyl-2-phenylbutanoyl chloride⁷ with benzene in the presence of aluminium chloride (62% yield), m.p. 55—56° (from ethanol) (lit.,⁸ 76.0—76.5°) (Found: C, 85.45; H, 8.1. Calc. for C₁₈H₂₀O: C, 85.65; H, 8.0%; τ 2.00—2.90 (10H, m), 5.56 (1H, s), and 8.95 (9H, s); ν_{\max} (KBr) 1675 cm⁻¹ (C=O).

Synthesis of (*Z*)- and (*E*)-1-Chloro-3,3-dimethyl-1,2-diphenylbutene (VIa) and (VIb).—A solution of 3,3-dimethyl-1,2-diphenylbutanone (VIII) (5.05 g, 20 mmol) in benzene (80 ml) was slowly added to phosphorus pentachloride (4.16 g, 20 mmol) at room temperature, and the mixture was refluxed with vigorous stirring for 4 h. The phosphoryl chloride formed and the solvent were then distilled off under reduced pressure. To the crude 1,1-dichloro-3,3-dimethyl-1,2-diphenylbutane thus formed was added a large excess of triethylamine (10.12 g, 0.1 mol) in carbon tetrachloride, and the mixture was refluxed for 12 h. The hot mixture was poured into concentrated hydrochloric acid containing cracked ice, and the organic layer was separated, washed with water, and dried (CaCl₂). Evaporation of the solvent gave a yellow residue, which was chromatographed on silica gel. Elution with light petroleum gave a mixture (ca. 1 : 1) of (*Z*)- and (*E*)-1-chloro-3,3-dimethyl-1,2-diphenylbutene (VIa and b) (3.52 g, 65%), as a high-boiling liquid (Found: C, 80.2; H, 7.15; Cl, 13.0%). The ¹H n.m.r. spectrum of the mixture showed, besides bands at

τ 2.55—3.05 (m), signals at 8.67 and 9.09 (s of integral ratio ca. 1 : 1).

Addition of Benzyl Chloride (X) to Diphenylacetylene (II).—This reaction was carried out as described for the corresponding addition of diphenylmethyl chloride (I) to diphenylacetylene (II). The reaction conditions and the yields of the products are reported in the Table.

Chromatography of the crude reaction mixtures on silica gel with light petroleum as eluant afforded unchanged diphenylacetylene (II) and a small amount of (*E*)- α -chlorostilbene (VII). Elution with light petroleum-benzene (9 : 1) gave a complex mixture of products, among which could be identified 2,3-diphenylindene (XII), m.p. 107—108° [from petroleum (b.p. 75—120°)] (lit.,⁹ 108°), τ 2.45—3.10 (14H, m) and 6.15 (2H, s), and (*Z*)- and (*E*)-1-chloro-1,2,3-triphenylpropene (XIa and b). Further elution with light petroleum-benzene (6 : 1) afforded a benzyl-2,3-diphenylindene (XIII), m.p. 125—126° (from ethanol) (Found: C, 93.6; H, 6.15. Calc. for C₂₈H₂₂: C, 93.8; H, 6.2%; *m/e* 358 (*M*⁺); τ 2.55—3.15 (18H, m), 6.10 (2H, s), and 6.32 (2H, s). Considerable amounts of benzylic polymers were also isolated by chromatography.

Fairly pure samples of the indene (XII) and of the mixture of the chloropropenes (XI) could be obtained only by preparative g.l.c. [*t*_R (XII), 28 min; mixture of (XIa and b), 24 min], where, however, some decomposition occurred. The ¹H n.m.r. spectrum of the mixture of (*Z*)- and (*E*)-1-chloro-1,2,3-triphenylpropene (XIa and b), a high-boiling liquid (Found: C, 82.55; H, 5.6; Cl, 11.5. Calc. for C₂₁H₁₇Cl: C, 82.75; H, 5.6; Cl, 11.65%), showed, besides bands at τ 2.45—3.10 (m), a signal at 5.9, attributable to the (*E*)-isomer (XIb), and a signal at 6.3, attributable to the (*Z*)-isomer (XIa) (s of integral ratio ca. 7 : 1).

Compound (XIII) was readily prepared in 90% yield by the reaction of benzyl chloride (X) (4 mmol) with 2,3-diphenylindene (XII) (4 mmol) in boiling dichloromethane (25 ml) in the presence of zinc chloride (0.4 mmol) for 2 h.

Synthesis of (*Z*)- and (*E*)-1-Chloro-1,2,3-triphenylpropene (XIa) and (XIb).—This reaction was carried out as described for the synthesis of the isomeric 1-chloro-3,3-dimethyl-1,2-diphenylbutenes (VI), *i.e.*, by the reaction of 2,3-diphenylpropionophenone¹⁰ with phosphorus pentachloride in refluxing benzene and subsequent dehydrochlorination of 1,1-dichloro-1,2,3-triphenylpropane in the presence of triethylamine.

Chromatography on silica gel of the crude reaction mixture, with light petroleum-benzene (9 : 1) as eluant, gave a mixture (ca. 1 : 4) of (*Z*)- and (*E*)-1-chloro-1,2,3-triphenylpropene (XIa and b) (45% yield), as a high-boiling liquid. By fractional recrystallisation from ethanol a small amount of pure (*E*)-1-chloro-1,2,3-triphenylpropene (XIb) could be obtained, m.p. 105—106° (Found: C, 82.7; H, 5.6; Cl, 11.4. C₂₁H₁₇Cl requires: C, 82.75; H, 5.6; Cl, 11.65%); τ 2.45—3.10 (15H, m) and 5.90 (2H, s).

We thank Mr. Roberto Salmaso for technical assistance in recording the high-resolution n.m.r. spectra.

[3/1778 Received, 24th August, 1973]

⁷ C. Aaron, D. Dull, J. L. Schmiegel, D. Jaeger, Y. Ohashi, and H. S. Mosher, *J. Org. Chem.*, 1967, **32**, 2797.

⁸ A. K. Mills and A. E. Wilder Smith, *Helv. Chim. Acta*, 1960, **43**, 1915.

⁹ J. J. McCullough, *Canad. J. Chem.*, 1968, **46**, 43.

¹⁰ S. Miyano and Y. Sako, *Chem. and Pharm. Bull. (Tokyo)*, 1965, **13**, 1372 (*Chem. Abs.*, 1966, **64**, 6545).