

Electrophilic Additions to Acetylenes. Part I. Addition of Some Alkyl Chlorides to Phenylacetylene

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The addition of *t*-butyl, benzyl, and diphenylmethyl chlorides to phenylacetylene in dichloromethane with a Lewis acid as catalyst afford high yields of the 1 : 1 addition products, mainly of the (*E*)-configuration, corresponding to predominant *anti*-addition. Products with (*E*)-configuration also result predominantly from the addition of hydrogen chloride to 3,3-dimethyl-1-phenylbutyne, 1,3-diphenylpropyne, and 1,3,3-triphenylpropyne under the same reaction conditions; this corresponds to predominant *syn*-addition. The structure and the configuration of the addition products are assigned by independent synthesis and by ¹H n.m.r. spectroscopy. The results are discussed in terms of the intermediacy of linear vinyl cations, which are preferentially attacked by the nucleophile Cl⁻ from the less hindered side.

THE existence of vinyl cations has been indicated by the results of studies on electrophilic addition to acetylenes and allenes and on the unimolecular solvolyses of appropriate vinyl substrates.¹ However, only a few data are available for the addition of carbonium ions to acetylenes,^{2,3} concerning the stereochemistry of the reaction and the relative reactivity towards double and triple bonds, properties which characterise the behaviour of different electrophiles in additions to unsaturated systems. Indeed, previous studies have shown that halogens and sulphenyl derivatives react faster with double bonds than with triple bonds with a high degree of stereoselectivity to give preferentially products of *anti*-addition,^{1,4,5} whereas the rates of addition of the proton to double and triple bonds are comparable and the reactions are less stereoselective.^{1,4,6} We report here the results obtained in the Lewis acid-catalysed addition of *t*-butyl, benzyl, and diphenylmethyl chlorides to phenylacetylene.⁷

RESULTS

The addition reactions described here were all carried out in boiling anhydrous dichloromethane, usually in the

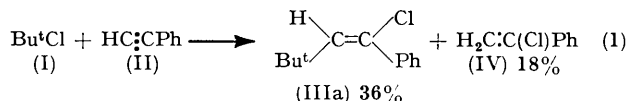
¹ H. G. Richey, jun., and J. M. Richey in 'Carbonium Ions,' eds. G. A. Olah and P. v. R. Schleyer, Interscience, New York, 1970, vol. 1, p. 899; M. Hanack, *Accounts Chem. Res.*, 1970, **3**, 209; G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, 1971, **9**, 185; P. J. Stang, *Progr. Phys. Org. Chem.*, 1973, **10**, 276.

² T. Sasaki, S. Eguchi, and T. Toru, *Chem. Comm.*, 1968, 780; K. Bott, *Tetrahedron Letters*, 1969, 1747; K. Bott, *Chem. Comm.*, 1969, 1349; D. R. Kell and F. J. McQuillin, *ibid.*, 1970, 599.

³ H. Schlubach and V. Franzen, *Annalen*, 1953, **583**, 93; P. Chini, M. Corbellini, C. Vacca, and M. De Maldè, *Chem. Ind. (Milan)*, 1963, **45**, 701; L. Bindacz and A. Balog, *Chem. Ber.*, 1960, **63**, 1716, 1722; D. Martin and A. Weise, *Annalen*, 1967, **702**, 86.

presence of a catalytic amount of anhydrous zinc chloride, and afforded as main products the 1 : 1 addition products of the two reagents. Several experiments were also carried out in the presence of aluminum chloride. A few additions of alkyl arenesulphonates to phenylacetylene were preliminarily investigated. No isomerisation of the addition products, both of (*E*)- and (*Z*)-configuration, in the reaction conditions was observed. In the addition of alkyl chlorides, no reaction was observed in the absence of catalyst, even after prolonged reflux.

Addition of t-Butyl Chloride.—Addition of *t*-butyl chloride (I) to phenylacetylene (II) (molar ratio *ca.* 1 : 3) in the presence of zinc chloride for 4–5 h afforded (*E*)-1-chloro-3,3-dimethyl-1-phenylbut-1-ene (IIIa) and α -chlorostyrene (IV). No evidence was found of the formation of the (*Z*)-isomer (IIIb) [equation (1)].



α -Chlorostyrene (IV) probably arose from the addition to phenylacetylene (II) of hydrogen chloride formed by the concomitant dehydrochlorination of *t*-butyl chloride

⁴ K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H.-W. Leung, and R. McDonald, *J. Amer. Chem. Soc.*, 1973, **95**, 160, and references therein.

⁵ D. R. Hogg and J. H. Smith, *Mech. Reactions Sulfur Comp.*, 1968, **3**, 63; G. Modena and G. Scorrano, *ibid.*, 1968, **3**, 115, and references therein.

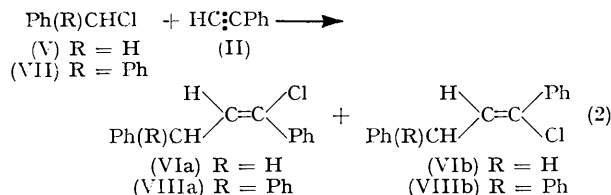
⁶ R. C. Fahey and D. J. Lee, *J. Amer. Chem. Soc.*, 1966, **88**, 5555; 1967, **89**, 2780; P. E. Peterson and J. E. Dudley, *ibid.*, 1966, **88**, 4990; Z. Rappoport and M. Atidia, *Tetrahedron Letters*, 1970, 4085.

⁷ Preliminary account, R. Maroni, G. Melloni, and G. Modena, *J.C.S. Chem. Comm.*, 1972, 857.

in the presence of the Lewis acid. Correspondingly, considerable amounts of polymeric substances were also formed.

Experiments carried out with smaller (II) : (I) ratios gave the same products, although in lower yields.

Addition of Benzyl and Diphenylmethyl Chlorides.—The main products in all the reactions examined were (*E*)- and (*Z*)-1-chloro-1,3-diphenylprop-1-ene (VIa) and (VIb) in the ratio 80 : 20 in the case of the addition of benzyl chloride (V), and (*E*)- and (*Z*)-1-chloro-1,3,3-triphenylprop-1-ene (VIIIa) and (VIIIb) in the ratio 90 : 10 in the case of the addition of diphenylmethyl chloride (VII) [equation (2)].



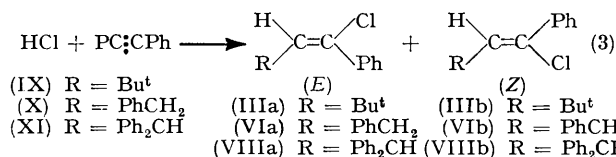
The results obtained using various (V) : (II) and (VII) : (II) ratios and different catalysts are reported in Table 1. The (*E*) : (*Z*) ratio in the addition products did not vary with the reaction conditions.

TABLE 1
Addition of alkyl chlorides (V) and (VII) to phenylacetylene (II)

Alkyl chloride	Catalyst	Re-agent ratio *	Reaction time (h)	Products	Yields (%)
(V)	ZnCl ₂	1 : 1	12	(VIa) + (VIb)	15
(V)	ZnCl ₂	1 : 5	12	(VIa) + (VIb)	55
(V)	ZnCl ₂	1 : 10	12	(VIa) + (VIb)	95
(V)	AlCl ₃	1 : 1	12	(VIa) + (VIb)	12
(V)	AlCl ₃	1 : 5	12	(VIa) + (VIb)	25
(V)	None	1 : 5	168	None	
(VII)	ZnCl ₂	1 : 1	6	(VIIIa) + (VIIIb)	76
(VII)	ZnCl ₂	1 : 5	6	(VIIIa) + (VIIIb)	92
(VII)	AlCl ₃	1 : 1	6	(VIIIa) + (VIIIb)	62
(VII)	None	1 : 5	168	None	

* Ratio alkyl chloride : phenylacetylene.

Addition of Hydrogen Chloride to Substituted Phenylacetylenes RC:CPh (R = *t*-Butyl, Benzyl, and Diphenylmethyl).—These reactions were carried out in dichloromethane saturated with dry hydrogen chloride in the presence of zinc chloride in tightly stoppered flasks maintained at 40°, *i.e.*, in conditions similar to those used in the addition reactions of alkyl chlorides (I), (V), and (VII), and afforded high yields (60–80%) of the expected 1 : 1 addition products [equation (3)].



The (*E*) : (*Z*) ratios in the addition products obtained both in these reactions and in the corresponding addition

reactions of alkyl chlorides (I), (V), and (VII) to phenylacetylene (II) are reported in Table 2.

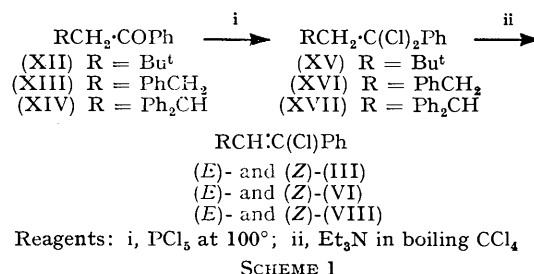
TABLE 2

Isomer ratio in the products of the addition reactions

Reaction	Products	Isomer ratio (%) *	
		(<i>E</i>)	(<i>Z</i>)
(I) + (II)	(III)	100	
(V) + (II)	(VI)	80	20
(VII) + (II)	(VIII)	90	10
HCl + (IX)	(III)	100	
HCl + (X)	(VI)	85	15
HCl + (XI)	(VIII)	95	5

* Calculated by integration of ¹H n.m.r. signals (estimated error: ±5%).

Structure and Configuration of the Addition Products.—The structure of the addition products was assigned on the basis of their elemental analysis and spectral data, and also by comparison with authentic samples synthesised independently. This synthesis was performed by dehydrochlorination in the presence of triethylamine of the dichloro-derivatives (XV), (XVI), and (XVII), obtained by treatment with phosphorus pentachloride of the corresponding ketones (XII), (XIII), and (XIV) respectively (Scheme 1), and afforded (*E*),(*Z*)-mixtures



SCHEME 1

of the addition products (III), (IV), and (VIII), and in particular the (*Z*)-1-chloro-3,3-dimethyl-1-phenylbut-1-ene (IIIb), which was not formed in the addition reaction.

The configurations to the three pairs of isomers were assigned by ¹H n.m.r. spectroscopy, and were based on the deshielding effect caused by a phenyl group on a β-*cis*-olefinic proton relative to a *trans*-proton, feature which has been tested previously and found characteristic of a number of styrene derivatives.⁸⁻¹⁰ Thus, we assigned the (*Z*)-configuration to the compounds having the vinyl proton signal at lowest field. This assignment was confirmed by the relative chemical shift of the *t*-butyl, methylene, and methine protons in each pair of isomers. It has been shown that in styrene derivatives the phenyl group has a shielding effect on β- and γ-*cis*-methyl and -methylene protons relative to *trans*-protons.^{9,10} The (*Z*)-isomers are the compounds having the signals of such protons at lowest field.

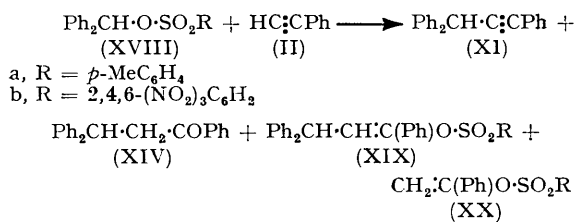
Addition of Diphenylmethyl Arenesulphonates to Phenylacetylene.—Diphenylmethyl toluene-*p*-sulphonate (XVIIIa) and 2,4,6-trinitrobenzenesulphonate (XVIIIb), prepared *in situ* by the reaction of diphenylmethyl

⁸ M. Barbieux, N. Defay, J. Pecher, and R. H. Martin, *Bull. Soc. chim. belges*, 1964, **73**, 716.

¹⁰ R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, 1965, **87**, 5172; G. H. Schmid and M. Heinola, *ibid.*, 1968, **90**, 3466.

⁹ C. N. Banwell and N. Sheppard, *Mol. Phys.*, 1960, **3**, 351; L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 1960, 2881.

chloride (VII) with the appropriate silver arene-sulphonate, were allowed to react with phenylacetylene (II) in boiling dichloromethane for 4–10 h. The results obtained in the two reactions are reported in Scheme 2 and in Table 3.



SCHEME 2

TABLE 3

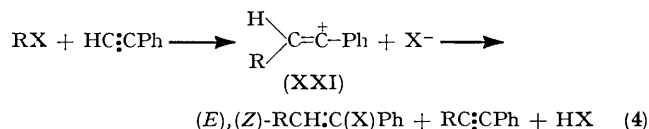
Addition of diphenylmethyl sulphonates (XVIII) to phenylacetylene (II)

Sulphonate (XVIIIa) (XVIIIb)	Yields (%)			
	(XI)	(XIV)	(XIX)	(XX)
(XVIIIa)	9	4	46	10
(XVIIIb)	18	37	None	None

Among the products obtained, the ketone (XIV) is probably not a primary product, but derives from hydrolysis of the vinyl sulphonate (XIX) during the reaction or the work-up procedures. Products derived from thermal decomposition of sulphonates (XVIII) and some unchanged phenylacetylene were also isolated. The configuration of the 1,3,3-triphenylprop-1-enyl toluene-*p*-sulphonate (XIXa), the 1:1 addition product of the reagents (XVIIIa) and (II), has not, as yet, been defined.

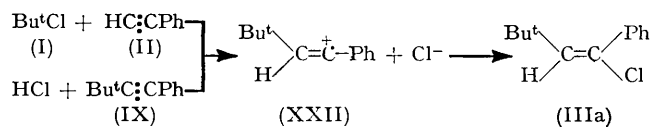
DISCUSSION

The smooth reaction observed in the addition of *t*-butyl, benzyl, and diphenylmethyl chlorides to phenylacetylene under Friedel–Crafts conditions and with a rather weak catalyst emphasises once more^{1,4} the ease of electrophilic additions to the triple bond. The more complex range of products obtained in the addition of diphenylmethyl sulphonates (XVIII) to phenylacetylene (II) emphasises the role of the chloride ion, either free or complexed by the catalyst, in quenching the reactive cationic intermediate with formation of the addition products. In the reactions of sulphonates (XVIII) a significant amount of the acetylene (XI), an addition–elimination product, was formed, while with alkyl chlorides (I), (V), and (VII) only the addition products were obtained. These results can be rationalised assuming that all these reactions proceed through the formation of a vinyl cation intermediate (XXI), which may either co-ordinate the nucleophile at the positive carbon or suffer proton loss [equation (4)].



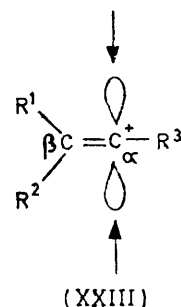
Regarding the stereochemistry of the addition, the different stereoselectivity observed in the three reactions

of alkyl chlorides is particularly relevant to the geometry of the vinyl cation intermediate (XXI). Both the addition of *t*-butyl chloride (I) to phenylacetylene (II) and the corresponding addition of hydrogen chloride to *t*-butylphenylacetylene (IX) afforded the same product, the vinyl chloro-derivative of (*E*)-configuration (IIIa). This corresponds to 100% *anti*-addition in the case of the alkyl chloride and to 100% *syn*-addition in the case of hydrogen chloride. Moreover, the isomer (IIIa), having the two bulkiest groups *cis* to each other, is reasonably the less thermodynamically stable of the two isomers. It seems unlikely that this kind of result may be explained on the basis of concerted *anti*- and *syn*-additions. Rather, the course of these additions may be properly explained assuming that both proceed through the formation of the same intermediate, the linear vinyl cation (XXII), which is subsequently attacked by the chloride ion to give the same product (IIIa) in both cases (Scheme 3).



SCHEME 3

The stereospecificity observed agrees with the intrinsic low symmetry of linear vinyl cations, which are not cylindrically symmetric, but have a planar geometry, with the two lobes of the empty *p*-orbital lying in the plane of the molecule (XXIII). Consequently, the attack of a nucleophile on the positive centre should occur in this plane and in the two opposite directions



along the axis of the empty *p*-orbital. The two sides of the cation, and hence the two directions of attack, are equivalent only when the groups bonded to the adjacent carbon atom [*R*¹ and *R*² in (XXIII)] are equal. In the case under discussion *R*¹ and *R*² represent hydrogen and *t*-butyl, and on simple steric grounds one would predict that the hydrogen side would be more accessible for the approaching nucleophile than the *t*-butyl side. This has been experimentally observed.

A corollary of the above arguments is that reducing the difference between *R*¹ and *R*² would cause a decrease in the stereoselectivity of the attack by the nucleophile. This is what has been observed in the addition of diphenylmethyl and benzyl chlorides (VII) and (V) to phenylacetylene (II), where decreased crowding around

the β -carbon atom results in a decrease in stereoselectivity. Also in these reactions the stereochemical results of the addition of the alkyl chlorides to phenylacetylene agree well with the results of the addition of hydrogen chloride to the corresponding substituted phenylacetylenes (X) and (XI).

It may be noticed in Table 2, however, that the addition of hydrogen chloride to the acetylenic derivatives (X) and (XI) gave slightly larger amounts of the (*E*)-isomers than those expected on the basis of schemes analogous to Scheme 3. These small differences, at the limit of the experimental errors, could be due to a minor participation of a mechanism of *syn*-addition of hydrogen chloride. This hypothesis is supported by results recently obtained in this laboratory on the addition of deuterium chloride to phenylacetylene,¹¹ where a *syn*-pathway seems to intervene.

EXPERIMENTAL

Anhydrous dichloromethane and light petroleum (b.p. 40–70°) were used. ¹H N.m.r. spectra were recorded in carbon tetrachloride solution, with tetramethylsilane as internal standard, on a Perkin-Elmer model R 12 spectrometer operating at 60 MHz, and in some cases on a Bruker model HFX high-resolution spectrometer operating at 90 MHz. Preparative g.l.c. separations were performed on an Aerograph Autoprep model 705 gas-chromatograph equipped with a 2 m \times 10 mm column packed with 30% Carbowax 20M on Chromosorb P (mesh size 60–80) at 180°, with a nitrogen flow of about 180 ml min⁻¹.

Addition of *t*-Butyl Chloride (I) to Phenylacetylene (II).—To a suspension of anhydrous zinc chloride (0.4 g, 3 mmol) in a solution of phenylacetylene (II) (9.19 g, 90 mmol) in dichloromethane (30 ml) at room temperature was added a solution of *t*-butyl chloride (I) (2.78 g, 30 mmol) in the same solvent (10 ml). After a few min of stirring at room temperature, the mixture was refluxed for 6 h. After cooling, the mixture was filtered, and the solvent was evaporated to give a brown residue which was chromatographed on silica gel. Elution with light petroleum gave first some unchanged phenylacetylene (II) and subsequently a mixture of α -chlorostyrene (IV) [0.75 g, 18% (yield based on the *t*-butyl chloride)] and of (*E*)-1-chloro-3,3-dimethyl-1-phenylbut-1-ene (IIIa) (2.1 g, 36%), which were separated by g.l.c. [*t*_R (IV), 11 min; (IIIa), 24 min]. No evidence was found of the presence of the (*Z*)-isomer (IIIb).

The α -chlorostyrene (IV) was identified by comparison with an authentic sample prepared as described in the literature.¹² The ¹H n.m.r. spectrum showed bands at τ 2.42–3.00 (5H, m), 4.49 (1H, d, *J* 1.8 Hz), and 4.58 (1H, d, *J* 1.8 Hz).

The vinyl chloro-derivative (IIIa) (Found: C, 73.65; H, 7.8; Cl, 18.1. C₁₂H₁₅Cl requires: C, 74.0; H, 7.75; Cl, 18.2%) was identified by comparison with authentic samples of both isomers (*E*) (IIIa) and (*Z*) (IIIb) synthesised independently. The ¹H n.m.r. spectrum showed bands at τ 2.78 (5H, s), 4.05 (1H, s), and 9.12 (9H, s).

* A mixture of 1-chloro-1,3-diphenylprop-1-enes in a similar (*E*):(*Z*) ratio (2.5:1) was obtained in the Friedel-Crafts reaction of 3-chloro-1-phenylprop-1-ene with benzene.¹⁴

¹¹ F. Marcuzzi, G. Melloni, and G. Modena, unpublished results.

¹² C. Dufraisse and J. E. Viel, *Bull. Soc. chim. France*, 1925, **37**, 874.

(*E*)- and (*Z*)-1-Chloro-3,3-dimethyl-1-phenylbut-1-ene (IIIa) and (IIIb).—3,3-Dimethyl-1-phenylbutan-1-one¹³ (XII) (8.81 g, 50 mmol) was slowly added to phosphorus pentachloride (10.41 g, 50 mmol) at room temperature, and the mixture was heated on a steam-bath with stirring for 2 h. The phosphoryl chloride formed was then distilled off under reduced pressure. To the crude 1,1-dichloro-3,3-dimethyl-1-phenylbutane (XV) thus formed was added a large excess of triethylamine (20.24 g, 0.2 mol) in carbon tetrachloride (80 ml), 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. 1:4) of (*E*) and (*Z*)-1-chloro-3,3-dimethyl-1-phenylbut-1-ene (IIIa) and (IIIb) (7.0 g, 72%), which were separated by g.l.c. [*t*_R (IIIa), 24 min; (IIIb), 20 min]. The ¹H n.m.r. spectrum of the (*Z*)-isomer (IIIb) (Found: C, 73.7; H, 7.6; Cl, 18.15. C₁₂H₁₅Cl requires: C, 74.0; H, 7.75; Cl, 18.2%) showed bands at τ 2.40–2.88 (5H, m), 3.98 (1H, s), and 8.71 (9H, s).

Addition of Benzyl Chloride (V) to Phenylacetylene (II).—This reaction was carried out as described for the corresponding addition of *t*-butyl chloride (I) to phenylacetylene (II), using various ratios of reagents and also two different catalysts. The reaction conditions and the yields of products obtained are reported in Table 1.

Chromatography of the crude reaction mixtures on silica gel, with light petroleum as eluant, afforded a mixture of unchanged phenylacetylene and benzyl chloride. Further elution with light petroleum–benzene (9:1) gave a mixture (4:1 in all the cases examined) of (*E*)- and (*Z*)-1-chloro-1,3-diphenylprop-1-ene* (VIa) and (VIb), b.p. 238–245 at 1 \times 10⁻³ mmHg (Found: C, 78.3; H, 5.8; Cl, 15.2. C₁₅H₁₃Cl requires: C, 78.75; H, 5.75; Cl, 15.5%).

The two isomeric chloropropenes (VIa) and (VIb) could not be satisfactorily separated either by adsorption chromatography or by g.l.c. They were therefore identified on the basis of the ¹H n.m.r. spectrum of their mixture, and also by comparison with an authentic mixture of (VIa) and (VIb) synthesised independently. The ¹H n.m.r. spectrum of the mixture showed, besides bands at τ 2.46–3.05 (m), signals at τ 3.78 (1H, t, *J* 6 Hz) and 6.33 (2H, d, *J* 6 Hz) attributable to the (*Z*)-isomer (VIb), and signals at τ 3.89 (1H, t, *J* 8 Hz) and 6.65 (2H, d, *J* 8 Hz) attributable to the (*E*)-isomer (VIa).

(*E*)- and (*Z*)-1-Chloro-1,3-diphenylprop-1-ene (VIa) and (VIb).—This reaction was carried out as described for the isomeric 1-chloro-3,3-dimethyl-1-phenylbut-1-enes (III), *i.e.*, by reaction of 3-phenylpropiophenone¹⁵ (XIII) with phosphorus pentachloride and subsequent dehydrochlorination of 1,1-dichloro-1,3-diphenylpropane (XVI) in the presence of triethylamine. Chromatography on silica gel of the crude mixture, with light petroleum–benzene (9:1) as eluant, gave a mixture (ca. 1:4) of (*E*)- and (*Z*)-1-chloro-1,3-diphenylprop-1-ene (VIa) and (VIb) (75%), b.p. 240–245° at 2 \times 10⁻³ mmHg (Found: C, 78.45; H, 5.8; Cl, 15.6. C₁₅H₁₃Cl requires: C, 78.75; H, 5.75; Cl, 15.5%).

Addition of Diphenylmethyl Chloride (VII) to Phenyl-

¹³ B. S. Kupin and A. A. Petrov, *Zhur. obschei Khim.*, 1961, **31**, 2958.

¹⁴ R. Gelin, S. Gelin, and D. Pigasse, *Compt. rend. (C)*, 1970, **270**, 1875.

¹⁵ S. Miyano and Y. Sako, *Chem. Pharm. Bull. (Tokyo)*, 1965, **13**, 1372.

acetylene (II).—This reaction was carried out as described for the corresponding addition of *t*-butyl chloride (I) to phenylacetylene (II), using various ratios of reagents and two different catalysts. The reaction conditions and the yields of products obtained are reported in Table 1.

Chromatography on silica gel of the crude mixtures, with light petroleum–benzene (9 : 1) as eluant, afforded, besides some unchanged phenylacetylene, a mixture (9 : 1 in all the cases examined) of (*E*)- and (*Z*)-1-chloro-1,3,3-triphenylprop-1-ene (VIIIa) and (VIIIb) (low-melting crystals) (Found: C, 83.4; H, 5.5; Cl, 11.3. $C_{21}H_{17}Cl$ requires: C, 82.75; H, 5.6; Cl, 11.65%). The two isomeric chloropropenes (VIIIa) and (VIIIb) could not be satisfactorily separated by absorption chromatography. They were therefore identified on the basis of the 1H n.m.r. spectrum of their mixture, and also by comparison with an authentic mixture of (VIIIa) and (VIIIb) synthesised independently. The 1H n.m.r. spectrum of the mixture showed, besides bands at τ 2.55–3.10 (m), signals at τ 3.49 (1H, d, J 9.5 Hz) and 4.61 (1H, d, J 9.5 Hz) attributable to the (*Z*)-isomer (VIIIb), and signals at τ 3.61 (1H, d, J 11 Hz) and 5.26 (1H, d, J 11 Hz) attributable to the (*E*)-isomer (VIIIa).

By fractional recrystallisation from ethanol a pure sample of (*E*)-1-chloro-1,3,3-triphenylprop-1-ene (VIIIa) was obtained, m.p. 65–66° (Found: C, 83.25; H, 5.5; Cl, 11.6. $C_{21}H_{17}Cl$ requires: C, 82.75; H, 5.6; Cl, 11.65%), τ 2.65–3.05 (15H, m), 3.61 (1H, d, J 11 Hz), and 5.26 (1H, d, J 11 Hz).

(*E*)- and (*Z*)-1-Chloro-1,3,3-triphenylprop-1-ene (VIIIa) and (VIIIb).—This reaction was carried out as described for the isomeric 1-chloro-3,3-dimethyl-1-phenylbut-1-enes (IIIa) and (IIIb), *i.e.*, by reaction of 3,3-diphenylpropiofenone¹⁶ (XIV) with phosphorus pentachloride in refluxing benzene and subsequent dehydrochlorination of 1,1-dichloro-1,3,3-triphenylpropane (XVII) 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 : 6) of (*E*)- and (*Z*)-1-chloro-1,3,3-triphenylprop-1-ene (VIIIa) and (VIIIb) (81% yield), as an oil.

Addition of Hydrogen Chloride to 3,3-Dimethyl-1-phenylbutyne (IX), 1,3-Diphenylpropyne (X), and 1,3,3-Triphenylpropyne (XI).—To a solution of the appropriate acetylenic compound (20 mmol) in dichloromethane (30 ml) were added anhydrous zinc chloride (0.54 g, 4 mmol) and a saturated solution of dry hydrogen chloride (40 mmol) in dichloromethane (*ca.* 80 ml). The flask was tightly stoppered, and the mixture was heated at 40° for 48 h. The catalyst was filtered off, the solvent and the excess of hydrogen chloride were removed under reduced pressure, and the residue was chromatographed on silica gel.

In the addition to 3,3-dimethyl-1-phenylbutyne¹³ (IX), chromatography with light petroleum as eluant afforded, besides a trace of unchanged acetylene (IX), (*E*)-1-chloro-3,3-dimethyl-1-phenylbut-1-ene (IIIa) (3.35 g, 86%). No evidence of the formation of the (*Z*)-isomer (IIIb) was found. Further elution with light petroleum–benzene (4 : 1) gave a small amount of 3,3-dimethyl-1-phenylbutan-1-one (XII) (0.14 g, 4%), which was identified by comparison with an authentic sample.¹³

In the addition to 1,3-diphenylpropyne¹⁷ (X)

chromatography of the reaction residue, with light petroleum–benzene (9 : 1) as eluant, afforded a mixture (*ca.* 6 : 1) of (*E*)- and (*Z*)-1-chloro-1,3-diphenylprop-1-ene (VIa) and (VIb) (2.93 g, 64%). Further elution with light petroleum–benzene (6 : 1) and (4 : 1) gave unchanged 1,3-diphenylpropyne (X) (0.84 g, 22%) and a small amount of 3-phenylpropiofenone (XIII) (84 mg, 2%), which was identified by comparison with an authentic sample,¹⁵ respectively.

In the addition to 1,3,3-triphenylpropyne¹⁸ (XI) the chromatography of the reaction residue, with light petroleum–benzene (9 : 1) as eluant, afforded a mixture (*ca.* 19 : 1) of (*E*)- and (*Z*)-1-chloro-1,3,3-triphenylprop-1-ene (VIIIa) and (VIIIb) (4.45 g, 73%). Further elution with light petroleum–benzene (6 : 1) and (4 : 1) gave unchanged 1,3,3-triphenylpropyne (XI) (0.64 g, 12%) and 3,3-diphenylpropiofenone (XIV) (0.23 g, 9%), identified by comparison with authentic samples,^{16,18} respectively.

Addition of Diphenylmethyl Sulphonates (XVIIIa) and (XVIIIb) to Phenylacetylene (II).—To a well stirred suspension of silver toluene-*p*-sulphonate¹⁹ or, correspondingly, silver 2,4,6-trinitrobenzenesulphonate²⁰ (as the acetonitrile complex, 15 mmol) in a solution of phenylacetylene (II) (1.53 g, 15 mmol) in dichloromethane (80 ml) was added dropwise a solution of diphenylmethyl chloride (VII) (3.04 g, 15 mmol) in the same solvent (30 ml) at room temperature. After a few min stirring, the mixture was heated to reflux for 4 h in the case of the addition of (XVIIIb) and for 10 h in the case of (XVIIIa). After cooling, the mixture was filtered and the solvent was evaporated off to give a dark green residue, which was chromatographed on silica gel.

In the addition of diphenylmethyl toluene-*p*-sulphonate (XVIIIa), chromatography with light petroleum as eluant afforded some unchanged phenylacetylene and a small amount of diphenylmethane. The following products were also obtained (the corresponding eluants are indicated in parentheses): 1,3,3-triphenylpropyne (XI) (0.36 g, 9%) [light petroleum–benzene (6 : 1)]; 3,3-diphenylpropiofenone (XIV) (0.17 g, 4%) [light petroleum–benzene (4 : 1)]; 1-phenylvinyl toluene-*p*-sulphonate (XX; R = *p*-MeC₆H₄) (0.41 g, 10%), and 1,3,3-triphenylprop-1-enyl toluene-*p*-sulphonate (XIX; R = *p*-MeC₆H₄) (3.04 g, 46%) [light petroleum–benzene (1 : 1)]. Finally, the chromatography afforded small amounts of benzophenone and of diphenylmethanol, and uncharacterisable tarry products.

1,3,3-Triphenylpropyne¹⁸ (XI), m.p. 78–79° (from ethanol) and 3,3-diphenylpropiofenone¹⁶ (XIV), m.p. 91–92° (from ethanol) were identified by comparison with authentic samples synthesised independently. 1-Phenylvinyl toluene-*p*-sulphonate (XX), m.p. 47–49° (from dichloromethane–pentane) (lit.,²¹ 49–50°) was identified by comparison of the u.v. and 1H n.m.r. spectra with those reported in the literature.²¹ 1,3,3-Triphenylprop-1-enyl toluene-*p*-sulphonate (XIX), m.p. 110–111° (from ethanol) (Found: C, 76.45; H, 5.6; S, 7.2. $C_{28}H_{24}O_3S$ requires: C, 76.3; H, 5.5; S, 7.3%) was identified on the basis of the i.r. spectrum (KBr), which showed bands at ν_{max} 1350 and 1175 cm^{-1} (covalent O–SO₂), and 1H n.m.r. spectrum, which showed signals at τ 2.3–3.0 (19H, m), 3.97 (1H, d, J 11 Hz), 5.28 (1H, d, J 11 Hz), and 7.67 (3H, s). The configuration

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of the vinyl sulphonate (XIX) was not established. Solvolysis in aqueous ethanol at 150° for 24 h afforded 3,3-diphenylpropiophenone (XIV). Diphenylmethane, benzophenone, and diphenylmethanol were shown by an independent test to arise from thermal decomposition of diphenylmethyl toluene-*p*-sulphonate²² (XVIIIa).

In the addition of diphenylmethyl 2,4,6-trinitrobenzenesulphonate (XVIIIb) chromatography of the reaction mixture afforded, besides unchanged phenylacetylene (I) and products derived from thermal decomposition of sulphonate (XVIIIb), 1,3,3-triphenylpropyne (XI) (0.72

g, 18%), 3,3-diphenylpropiophenone (XIV) (1.59 g, 37%), and a small amount of acetophenone. Quite a lot of tarry products were also isolated. Attempts to purify the reaction mixture by other means than column chromatography have failed.

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

[3/1099 Received, 30th May, 1973]

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