6. *Allenes. Part II.*[1] *Reactions of Prop-2-yn-1-ols with Thionyl Chloride.*

By Y. R. Bhatia, Phyllis D. Landor, and S. R. Landor.

Tertiary acetylenic carbinols are shown to react with thionyl chloride to give 1-chloroallenes and alkenynes, whereas secondary and primary acetylenic carbinols give mainly the normal acetylenic chlorides. Good yields of chloroallenes are obtained from α-polysubstituted and sterically hindered tertiary acetylenic carbinols. The mechanism of these reactions is discussed.

It has been shown [1] that pyrolysis of prop-2-ynyl acetates yields allenic acetates, probably through a cyclic transition state. A similar mechanism might afford allenic chlorides by reaction of thionyl chloride with prop-2-yn-1-ols, the unstable chlorosulphite being formed as a short-lived intermediate.

The literature showed that the products from this reaction could roughly be divided into two classes: (*a*) the expected 3-chloroprop-1-ynes [2] and (*b*) rearrangement products, often inadequately identified, for which varying structures had been put forward. Since the latter products might well have contained allenic halides some of this earlier work was repeated and the products were examined for allenic groups.

For instance, Sobotka and Chanley [3] reported that treatment of 1-ethynyl-2 : 2 : 6-trimethyl*cyclo*hexanol with thionyl chloride in the presence of excess of pyridine gave a 54% yield of a chlorine-containing compound (b. p. 96°/14 mm., n_D^{20} 1·5030) which was not the expected 1-ethynyl-2 : 2 : 6-trimethyl*cyclo*hexyl chloride. They rejected an allenic structure for this compound on the grounds of its reaction with alcoholic silver nitrate

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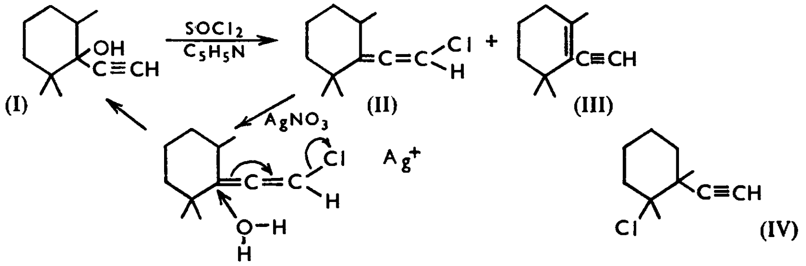
[1] Part I, *J.*, 1956, 1015.

[2] *E.g.*, Hennion and Sheehan, *J. Amer. Chem. Soc.*, 1949, **71**, 1964; Bailey and Fujuwara, *ibid.*, 1955, **77**, 165.

[3] Sobotka and Chanley, *ibid.*, 1949, **71**, 4136.

and suggested structure (IV), resulting from Wagner–Meerwein rearrangement of a prop-1-ynyl carbonium ion. In our hands comparable conditions to those used by Sobotka and Chanley gave a 60% yield of a chloride with similar physical constants, as well as some 1-ethynyl-2 : 6 : 6-trimethyl*cyclo*hexene (III). A strong allene C=C stretching band at 1950 cm.$^{-1}$ as well as an exceptionally intense band at 730 cm.$^{-1}$ (cf. C–Cl stretching for vinyl chloride [4]) showed the presence of an allenic chloride (II), which was corroborated by the absence of any acetylenic CH stretching band from the 3300 cm.$^{-1}$ region and of any maximum from the ultraviolet spectrum. No immediate reaction was observed with alcoholic silver nitrate but prolonged heating gave over 90% of the theoretical quantity of silver chloride. The organic material isolated consisted mainly of an acetylenic carbinol (as shown by the infrared spectrum) similar in properties to the original carbinol, but the quantities obtained were insufficient for rigorous identification. A mechanism can be put forward in which a S_N2' attack by a water molecule follows co-ordination of the chlorine with the silver ion, giving the original acetylenic carbinol (I): removal of the halide ion is facilitated by the ready access of the terminal carbon atom to the π-electrons of the 2 : 3-double bond of the allene, making it more reactive than a normal vinyl chloride.



Hurd and Jones,[5] treating ethynyl*cyclo*hexanol in pyridine with thionyl chloride at 50—60°, obtained an inert chloride which was sufficiently identified as 1-1′-chlorovinyl-*cyclo*hexene, probably formed from ethynyl*cyclo*hexene (which was also isolated) by addition of hydrogen chloride. We repeated this reaction at 0° and –80° as at these temperatures pyridine hydrochloride would be unlikely to react with the acetylene group. The product was mainly ethynyl*cyclo*hexene, but it contained up to 25% of allenic chloride as shown by the infrared spectra. Separation was achieved by treating the mixture with alcoholic silver acetate, which removes the ethynyl compounds as their silver salts but leaves the allenic chloride largely unaffected; it does, however, introduce a small amount of carbonyl-containing impurity into the product.

1-Ethynyl-2 : 2 : 6 : 6-tetramethyl*cyclo*hexanol, which cannot give the corresponding ethynyl*cyclo*hexene, gave an 83% yield of allenic chloride. Similarly, in the aliphatic field, 3-*tert.*-butyl-4 : 4-dimethylpent-1-yn-3-ol gave 3-*tert.*-butyl-1-chloro-4 : 4-dimethyl-penta-1 : 2-diene in 74% yield; again no α-hydrogen atom is available for elimination.

The same experimental conditions gave (*a*) 25% of 1-chloro-4-methyl-3-*iso*propyl-penta-1 : 2-diene from 4-methyl-3-*iso*propylpent-1-yn-3-ol, and (*b*) 35% of 1-chloro-3 : 4 : 4-trimethylpenta-1 : 2-diene from 3 : 4 : 4-trimethylpent-1-yn-3-ol. Other tertiary ethynyl carbinols, *e.g.*, $CH{\vdots}C{\cdot}CR_2{\cdot}OH$ where R = Et, Pr^n, or Bu^i, gave approximately 10% of the corresponding 1-chloroallenes. The principal by-product isolated was alkenyne resulting from the indirect dehydration of the acetylenic carbinol. No acetylenic chlorides could by detected. It is evident that the proportion of alkenyne in the product increases as the number of α-hydrogen atoms increases and as the steric hindrance at those hydrogen atoms decreases.

The formation of allenic chlorides from sterically hindered tertiary ethynylcarbinols

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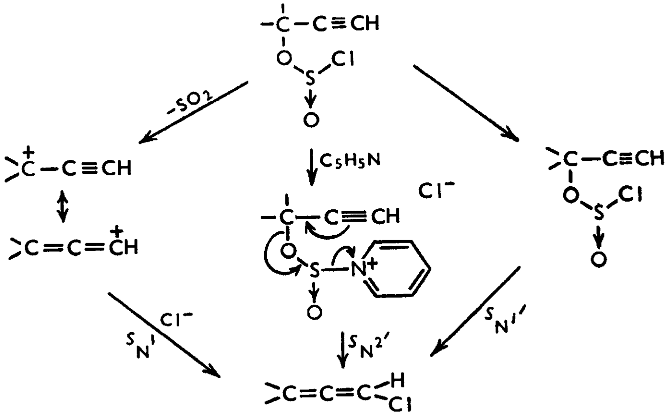
[4] Thompson and Torkington, *Proc. Roy. Soc.*, 1945, *A*, **184**, 21; Torkington, *ibid.*, 1951, *A*, **206**, 17.

[5] Hurd and Jones, *J. Amer. Chem. Soc.*, 1934, **56**, 1924.

could be the result of an S_N1, S_N2', or S_Ni' reaction of the unstable, unisolatable chlorosulphite (as shown). No precise information is available regarding the mechanism of the reaction of thionyl chloride with tertiary alcohols. In the presence of excess of pyridine optically active secondary alcohols give chlorides with predominantly inverted configuration,[6] and allylic alcohols give mainly the unrearranged normal allylic chlorides,[7]



indicating an S_N2 type mechanism. By analogy an S_N2' mechanism would be expected to be responsible for the formation of allenic chlorides under these conditions. Clearly an S_Ni' mechanism would be more favourable to the formation of allenic halide and if realised should give higher yields. The best conditions for an S_Ni' mechanism are dilution in a nucleophilic solvent, such as ether or dioxan, and absence of an added base, such as pyridine.[8] Unfortunately, the reaction of tertiary alcohols in the absence of a base is very slow, particularly so when hindered ethynylcarbinols are used. Thus, 1-ethynyl-2 : 2 : 6-trimethyl*cyclo*hexan-1-ol was recovered substantially unchanged after reaction with thionyl chloride in dry ether at room temperature or under reflux. Reasonable yields of allenic chlorides, however, were obtained from most of these alcohols by raising the temperature of the reaction mixture either by evaporating most of the ether at the end of the experiment and heating the residue under reflux, or by the use of dry dioxan as solvent. Small quantities of rearranged products which could not be separated from the allenic chlorides by fractionation (as shown by the persistence of weak twin bands between 1600 and 1650 cm.$^{-1}$, absent in the pure allenic chloride) contaminated these allenes, and owed their formation to the acidic conditions developing during the experiment in the absence of pyridine. Less alkenyne was always isolated in the absence than in the presence of a base, suggesting a base-catalysed elimination mechanism of the *E*2 type for the formation of alkenyne in the presence of pyridine.

Reaction of secondary ethynylcarbinols (prepared from aldehydes) with thionyl chloride gave mainly the normal acetylenic chlorides. *E.g.*, hex-1-yn-3-ol gave 3-chlorohex-1-yne containing approximately 10% of the allenic chloride and the normal chloride obtained in dioxan contained about 20% of allene. Jacobs, Teach, and Weiss,[9] in work on the dehalogenation of allenic halides, claimed to have obtained a 44% yield of 1-chlorohexa-1 : 2-diene by using a mixture of diethyl and di*iso*propyl ether as solvent, but gave no further experimental details. 1-Phenylprop-2-yn-1-ol gave 3-chloro-3-phenylprop-1-yne in good yield, but no trace of allenic material was detected by infrared analysis. In this case the well-known stability of the benzyl carbonium ion suggests a S_N1 mechanism.

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[6] Cowdrey, Hughes, Ingold, Masterman, and Scott, *J.*, 1937, 1252 and references quoted; Gerrard, *J.*, 1944, 85.

[7] De Wolfe and Young, *Chem. Rev.*, 1956, **56**, 753 and references quoted.

[8] Boozer and Lewis, *J. Amer. Chem. Soc.*, 1953, **75**, 3182.

[9] Jacobs, Teach, and Weiss, *ibid.*, 1955, **77**, 6254.

1-Chloroallenes have previously been prepared by the action of concentrated hydrochloric acid, in the presence of cuprous and ammonium chlorides, on 3-chloroacetylenes or directly on ethynylcarbinols.[9,10] After lengthy reactions the yields obtained by this method have been variable and in many instances infrared data were not available as a criterion of the purity of the allenic product.

EXPERIMENTAL

Ultraviolet spectra were determined for 95% EtOH ethanolic solutions by using a Unicam S.P. 500 spectrophotometer, and infrared spectra with a Hilger H 800 or a Grubb-Parsons instrument. The acetylenic alcohols were purified until there were no carbonyl bands in the infrared spectra.

2 : 2 : 6-*Trimethyl*cyclo*hexylidenevinyl Chloride* (II).—(*a*) 1-Ethynyl-2 : 2 : 6-trimethyl*cyclo*hexanol (8·3 g.) was mixed with dry redistilled pyridine (6 g.) and cooled in ice. Thionyl chloride (3·6 ml.) was added during 1 hr. with rapid stirring. The stirred mixture was allowed to warm to room temperature, pyridine hydrochloride filtered off, and the product washed with dilute hydrochloric acid, water, and aqueous sodium hydrogen carbonate, and distilled through a 6″ column of Fenske rings to give two main fractions; the first, b. p. 82°/15 mm., rapidly becoming pink in the air, was 1-ethynyl-2 : 6 : 6-trimethyl*cyclo*hexene (III) (1·4 g., 19%), $\lambda_{\text{max.}}$ 227 mμ (ε 11,000); the second, b. p. 92—94°/15 mm., n_D^{20} 1·4998, was 2 : 2 : 6-*trimethyl*cyclo*hexylidenevinyl chloride* (II) (5·5 g., 60%), $\nu_{\text{max.}}$ 3275 w (trace C≡CH), 1950 m (C=C=C), and 730 s cm.$^{-1}$ (C=C=CHCl). Refractionation gave material of b. p. 96°/15 mm., n_D^{20} 1·5020 (Found: C, 72·6; H, 9·7. $C_{11}H_{17}Cl$ requires C, 71·5; H, 9·2%) (cf. Sobotka and Chanley [3] give b. p. 96°/14 mm., n_D^{20} 1·5030, analysis C, 72·4; H, 9·7%).

(*b*) 1-Ethynyl-2 : 2 : 6-trimethyl*cyclo*hexanol (16·6 g.) in dry ether (100 ml.) was treated with thionyl chloride (9·0 ml.) and stirred at room temperature for 1 hr. The solvent was distilled off, and the residue heated for 3 hr. on a steam-bath and washed with aqueous sodium hydrogen carbonate. Distillation gave two main fractions, (i) b. p. 86—92°/15 mm., (ii) b. p. 92—94°/15 mm., which were the chloride (II) (5·5 g., 30%) and this mixed with the unchanged alcohol (9·0 g.) respectively, as shown by infrared bands at 3580 s (OH), 3270 s (C≡CH), 1950 m (C=C=C), and 730 s cm.$^{-1}$ (C=C=CHCl). A similar experiment in which the product was directly distilled from the reaction mixture without washing the allene (96%) contained only a trace of alcohol (from infrared data) and had b. p. 104—105°/17—20 mm. (Found: C, 70·9; H, 9·4%).

(*c*) 1-Ethynyl-2 : 2 : 6-trimethyl*cyclo*hexanol (16·6 g.) in anhydrous ether (200 ml.) was treated with thionyl chloride (11·9 g.) in ether (200 ml.) and stirred for 2 hr. at room temperature. Working up as in (*b*) and distillation gave one main fraction, b. p. 88—91°/16 mm., identified as the unchanged alcohol by infrared bands at 3580 s (OH) and 3270 s cm.$^{-1}$ (C≡CH) and the absence of a band at 1950 cm.$^{-1}$ (C=C=C).

In general, experiments using pyridine gave high analytical figures for carbon and hydrogen owing to the presence of alkenyne, and experiments in the absence of pyridine gave low values owing to traces of addition compound, indicated by infrared bands of varying intensity in the C=C stretching region between 1600 and 1650 cm.$^{-1}$.

The allenic chloride (II) (6·15 g.) and silver nitrate (5·7 g.) in 75% ethanol (70 ml.) were heated under reflux for 2 hr. Silver chloride (4·3 g., 91%) was filtered off and the filtrate neutralised with sodium hydrogen carbonate, evaporated to a small volume, diluted with water, and extracted into ether. Fractionation of the extract gave 1-ethynyl-2 : 2 : 6-trimethyl*cyclo*hexanol (2·8 g.), b. p. 96—98°/18 mm., identified by comparing its infrared spectrum with that of an authentic specimen.

2 : 2 : 6 : 6-*Tetramethyl*cyclo*hexylidenevinyl Chloride.*—1-Ethynyl-2 : 2 : 6 : 6-tetramethyl*cyclo*hexanol (9 g.) in anhydrous ether (50 ml.) gave, by method (*a*), after distillation 2 : 2 : 6 : 6-*tetramethyl*cyclo*hexylidenevinyl chloride* (8·2 g., 83%), b. p. 82—84°/20 mm. (Found: C, 72·5; H, 9·7; Cl, 18·0. $C_{12}H_{19}Cl$ requires C, 72·5; H, 9·6; Cl, 17·9%), $\nu_{\text{max.}}$ 1955 m (C=C=C) and 730 s cm.$^{-1}$ (C=C=CHCl) (no maximum in the ultraviolet region).

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[10] (*a*) I. A. Favorskaya, *Zhur. obshchei Khim.*, 1948, **18**, 52; (*b*) T. A. Favorskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **9**, 386; (*c*) T. A. Favorskaya and Zakharova, *ibid.*, 1940, **10**, 446; (*d*) T. A. Favorskaya, *ibid.*, 1942, **12**, 638; (*e*) Nagibina, *Zhur. obshchei Khim.*, 1940, **10**, 427; (*f*) Jacobs and Brill, *J. Amer. Chem. Soc.*, 1953, **75**, 1314.

2 : 2 : 4 : *4-Tetramethylpent-3-one.*—This was prepared by Whitmore and Stahly.[11] In our variation of the method di*iso*propyl ketone (57 g.) was added in 10 min. to sodamide (23 g.) in anhydrous benzene (200 ml.) at room temperature, then the mixture was heated under reflux (2·5 hr.). Methyl iodide (78 g.) was added dropwise (15 min.) to the cooled mixture, and the whole heated under reflux (15 min.) and set aside overnight. This procedure was repeated twice more, with the same quantities of sodamide and methyl iodide; the mixture was finally altered, dried, and distilled, to give 2 : 2 : 4 : 4-tetramethylpent-3-one (44 g., 62%), b. p. 48—50°/17 mm., n_D^{20} 1·4200 (Found: C, 76·1; H, 12·4. Calc. for $C_9H_{18}O$: C, 76·0; H, 12·6%) (lit.,[11] b. p. 144—150°/740 mm., n_D^{20} 1·4197).

3-tert.-*Butyl-4 : 4-dimethylpent-1-yn-3-ol.*—2 : 2 : 4 : 4-Tetramethylpent-3-one was treated in the usual way with sodium acetylide in liquid ammonia, to give the crude ethynylcarbinol, b. p. 60—72°/12 mm. (21·5 g., 77%), $\nu_{max.}$ 3232 s (C≡CH), 3441 s (OH), and 1685 w cm.$^{-1}$ (CO), indicating that about 30% of ketonic material was present. One repetition of the ethynylation with lithium acetylide in liquid ammonia gave 3-tert.-*butyl-4 : 4-dimethylpent-1-yn-3-ol* (17 g., 61%), b. p. 71—73°/10 mm. (Found: C, 78·5; H, 12·1. $C_{11}H_{20}O$ requires C, 78·6; H, 11·9%) [no infrared band at 1685 cm.$^{-1}$ (CO)].

3-tert.-*Butyl-1-chloro-4 : 4-dimethylpenta-1 : 2-diene.*—*Method* (*a*). The foregoing pentynol (2·8 g.) in anhydrous ether (20 ml.) gave, after fractionation, 3-tert.-*butyl-1-chloro-4 : 4-dimethylpenta-1 : 2-diene* (2·3 g., 74%), b. p. 72—74°/15 mm. (Found: C, 71·0; H, 10·1; Cl, 18·3. $C_{11}H_{19}Cl$ requires C, 70·8; H, 10·2; Cl, 19·0%), $\nu_{max.}$ 1930 m (C=C=C) and 738 s cm.$^{-1}$ (C=C=CHCl) (no ultraviolet maximum).

Method (*b*). This gave the allene (79%), b. p. 98—104°/32 mm., identified by comparison of the infrared spectrum with that of the previous pure sample.

*Action of Thionyl Chloride on 1-Ethynyl*cyclo*hexanol* (12·4 g.).—(*a*) Distillation gave fractions covering a wide range of b. p.s: (i) b. p. 30—60°/15 mm. (3·9 g., 38%), identified, by an infrared band at 3285 s cm.$^{-1}$ (C≡CH) and absence of a band at 3580 cm.$^{-1}$ (OH), as mainly 1-ethynyl*cyclo*hexene; (ii), b. p. 60—62°/15 mm. (4·2 g.), had infrared bands at 3580 m (OH), 3285 m (C≡CH), 1970 m (C=C=C), and 750 s cm.$^{-1}$ (C=C=CHCl), indicating a mixture of unchanged alcohol and *cyclo*hexylidenevinyl chloride. A substantially pure sample of the allene was prepared by shaking fraction (ii) (3·9 g.) with silver acetate (4 g.) in ethanol (120 ml.) at room temperature for 15 min. The mixture was filtered, diluted with light petroleum, washed, dried, and evaporated, to give the allene chloride, identified by the infrared spectrum which also showed that a small carbonyl impurity had now been introduced (weak band at 1720 cm.$^{-1}$).

Similar results were obtained by using methods (*b*) and (*c*), and additional infrared bands in the C=C stretching region between 1600 and 1650 cm.$^{-1}$ suggested the presence of a rearrangement product.

*1-Chloro-4-methyl-3-*iso*propylpenta-1 : 2-diene.*—(*a*) 4-Methyl-3-*iso*propylpent-1-yn-3-ol (84 g.) on distillation gave the following fractions: (i) b. p. 45—56°/760 mm., largely ether containing some alkenyne; (ii) b. p. 134—155°/760 mm. (31·5 g.), identified as the alkenyne mixed with about 40% of allene from infrared bands at 3230 s (C≡CH) and 1938 w cm.$^{-1}$ (C=C=C) and the absence of a band at 3510 cm.$^{-1}$ (OH), and an ultraviolet maximum at 225 mμ (ε 6200); (iii) b. p. 155—167°/760 mm. (15·0 g.), identified as the allene mixed with about 20% of enyne from the infrared spectrum. Fractions (ii) and (iii) were combined and refractionated through a 9″ column of Fenske rings to give fractions: (i) b. p. up to 147°/760 mm. (17 g., 23%), identified as *4-methyl-3-*iso*propylpent-3-en-1-yne* by the infrared spectrum and ultraviolet absorption [$\lambda_{max.}$ 226 mμ (ε 10,000)]; (ii) b. p. 147—170°/760 mm. (24 g., 25%), which was again fractionated to give material of b. p. 168—170°/760 mm., n_D^{20} 1·4629, identified as *1-chloro-4-methyl-3-*iso*propylpenta-1 : 2-diene* (Found: C, 68·4; H, 9·7. $C_9H_{15}Cl$ requires C, 68·1; H, 9·5%) by infrared bands at 1938 m (C=C=C) and 740 s cm.$^{-1}$ (C=C=CHCl) and the absence of ultraviolet light absorption maxima.

(*b*) 4-Methyl-3-*iso*propylpent-1-yn-3-ol (28 g.) gave a product, b. p. 50—52°/10 mm. (24 g.), identified by the infrared spectrum as the allene mixed with about 30% of unchanged alcohol.

(*d*) In this method the alcohol (28 g.) was treated with thionyl chloride in the presence of 2% of pyridine. Distillation gave a product, b. p. 51—57°/11 mm. (27 g.), shown by infrared bands at 1938 m (C=C=C) and 3232 w cm.$^{-1}$ (C≡CH) and no band at 3580 cm.$^{-1}$ (OH) to be a mixture of the allene and enyne.

(*e*) In this method the alcohol (28 g.) and thionyl chloride (24 g.) were added dropwise and

[11] Whitmore and Stanly, *J. Amer. Chem. Soc.*, 1933, **55**, 4155.

simultaneously to boiling dioxan (100 ml.). When half the liquid had been added a copious evolution of hydrogen chloride began; the product was refluxed for 1 hr. at the end of the addition, by which time evolution of hydrogen chloride had ceased, and then taken up in light petroleum, washed, dried, and distilled to give a main fraction, b. p. 65—66°/17 mm. (23 g.) (72·0%), identified as the allene by infrared bands at 1938 s (C=C=C) and 740 s cm.$^{-1}$ (C=C=CHCl).

1-*Chloro*-3 : 4 : 4-*trimethylpenta*-1 : 2-*diene*.[10a]—(*a*) 3 : 4 : 4-Trimethylpent-1-yn-3-ol (6·3 g.) gave on distillation one main fraction, b. p. 60°/25 mm. (2·5 g., 35%), identified as 1-chloro-3 : 4 : 4-trimethylpenta-1 : 2-diene by bands at 1950 m (C=C=C) and 730 s cm.$^{-1}$ (C=C=CCl), containing about 10% of acetylenic impurities (band at 3300 w cm.$^{-1}$).

(*c*) Unchanged alcohol was obtained.

(*e*) By this method, but with the addition of pyridine (8 g.), when the dioxan became saturated with hydrogen chloride, the alcohol (12·6 g.) gave three fractions on distillation: (i) b. p. 56—60°/16 mm. (1·0 g.), 3-*tert*.-butylbut-3-en-1-yne containing some allene, having $\nu_{max.}$ 3270 m (C≡CH), 1945 w (C=C=C), and 906 s cm.$^{-1}$ (C=CH_2) and no band at 3580 cm.$^{-1}$ (OH); (ii) b. p. 62—63°/15 mm., 1-*chloro*-3 : 4 : 4-*trimethylpenta*-1 : 2-*diene* (6·8 g., 47%), $\nu_{max.}$ 1945 m (C=C=C) and 735 s cm.$^{-1}$ (C=C=CCl) (Found: C, 65·9; H, 8·9. $C_8H_{13}Cl$ requires C, 66·4; H, 9·0%); and (iii) b. p. 63—70°/15 mm. (1·3 g.), allene mixed with some rearrangement product, giving infrared bands between 1600 and 1650 cm.$^{-1}$.

3-iso*Butyl*-1-*chloro*-5-*methylhexa*-1 : 2-*diene*.—(*a*) 3-*iso*Butyl-5-methylhex-1-yn-3-ol (33·6 g.), on distillation, gave two main fractions: (i) b. p. up to 91°/16 mm. (21·5 g.), 3-*iso*butyl-5-methylhex-3-en-1-yne containing about 30% of the allene, $\lambda_{max.}$ 224 mμ (ε 8700), $\nu_{max.}$ 3250 s (C≡CH), 1950 w (C=C=C), and 735 w cm.$^{-1}$ (C=C=CCl) and no peak at 3400 cm.$^{-1}$ (OH); (ii) b. p. 94—100°/20 mm. (3·0 g., 8·0%), 3-iso*butyl*-1-*chloro*-5-*methylhexa*-1 : 2-*diene* (Found: C, 71·0; H, 10·1. $C_{11}H_{19}Cl$ requires C, 70·8; H, 10·2%), $\nu_{max.}$ 1950 m (C=C=C) and 835 s cm.$^{-1}$ (C=C=CCl).

(*b*) Distillation gave fractions, b. p. 59—92°/17 mm., which were identified by infrared and ultraviolet spectra as various mixtures of alkenyne, allene, and unchanged alcohol.

(*d*) These conditions gave similar results to (*b*).

3-*Chloro*-3-*phenylprop*-1-*yne*.—(*a*) 1-Phenylprop-2-yn-1-ol (6·5 g.) in anhydrous ether (20 ml.) afforded on distillation a main fraction, b. p. 76—78°/15 mm. (4·1 g., 54%), identified by an infrared band at 3290 s cm.$^{-1}$ (C≡CH) and the absence of a band at 3580 cm.$^{-1}$ (OH), and the absence of a maximum in the ultraviolet spectrum, as 3-chloro-3-phenylprop-1-yne.

(*b*) By this method 1-phenylprop-2-yn-1-ol (13·2 g.) in anhydrous ether (100 ml.) gave two fractions: (i) b. p. 68°/5 mm. (8·9 g., 59%), $\nu_{max.}$ 3290 s cm.$^{-1}$ (C≡CH), no band at 3580 cm.$^{-1}$ (OH), 3-chloro-3-phenylprop-1-yne; (ii) b. p. 68—70°/5 mm. (1·8 g.), the normal chloride contaminated with cinnamaldehyde as shown by a new infrared band at 1675 w cm.$^{-1}$ (C=C·CHO) and formation of a 2 : 4-dinitrophenylhydrazone (from chloroform–methanol), m. p. 254° (lit., 255°).

(*c*) This method gave the unchanged alcohol, identified by its infrared spectrum.

(*d*) Distillation gave one main fraction, b. p. 64—66°/4 mm. (67%), identified by infrared spectrum as 3-*chloro*-3-*phenylprop*-1-*yne* (Found: C, 71·4; H, 4·8. C_9H_7Cl requires C, 71·8; H, 4·6%).

1-*Chlorohexa*-1 : 2-*diene*.[9]—(*a*) Hex-1-yn-3-ol (19·6 g.) gave the two main fractions: (i) b. p. 65°/20 mm. (6 g.), unchanged alcohol, identified by the infrared spectrum; (ii) b. p. 152—153°/20 mm. (9·5 g., 39%), containing sulphur (about 11·5%), $\nu_{max.}$ 3300 s (C≡CH) and 1206 cm.$^{-1}$ (SO_3) indicating that this material was di-(1-propylpropynyl) sulphite.

(*b*) Hex-1-yn-3-ol (9·8 g.) gave a main fraction, b. p. 38—40°/23 mm., identified by infrared bands at 3170 s (C≡H) and 1939 w cm.$^{-1}$ (C=C=C) and the absence of an ultraviolet maximum as 3-chlorohex-1-yne containing about 10% of 1-chlorohexa-1 : 2-diene.

(*e*) This method gave a similar result to (*b*), but the yield of allene increased to 20%, as estimated from the infrared spectrum.

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