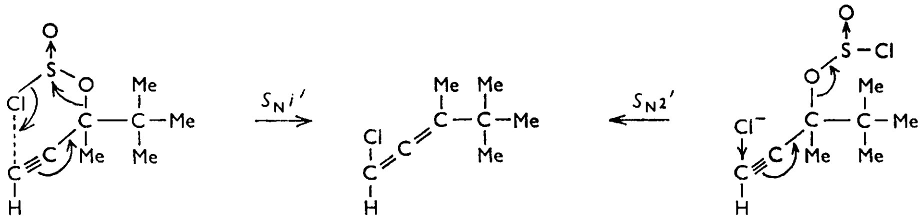
283. *Allenes. Part IV.*[1] *The Synthesis of an Optically Active Allenic Chloride.*

By R. J. D. Evans, S. R. Landor, and R. Taylor Smith.

The resolution of 3,4,4-trimethylpent-1-yn-3-ol *via* the brucine salt of the hydrogen phthalate and its reduction to the ethylenic and the saturated alcohol are described. The (+)- and (—)-acetylenic alcohols are converted into the (+)- and the (—)-allenic chloride (1-chloro-3,4,4-trimethylpenta-1,2-diene), respectively, by thionyl chloride under various conditions. Details of the mechanism of the reaction are discussed.

In a previous paper[2] we reported that 2-polysubstituted tertiary acetylenic alcohols react with thionyl chloride to give chloroallenes. Mechanistic considerations indicated that this reaction probably proceeds by an S_Ni' or S_N2' mechanism and we reasoned that by starting with an optically active acetylenic alcohol an optically active allenic chloride should result. 3,4,4-Trimethylpent-1-yn-3-ol (I), which is readily available by ethynylation of pinacolone, was chosen as it had previously been converted into the corresponding chloroallene in 47% yield,[2] under conditions which favour the S_Ni' mechanism.[3]



The pure alcohol (I), free from carbonyl bands in the infrared spectrum, was essential for resolution and was obtained by recycling the product from the first ethynylation of pinacolone through a second ethynylation. Attempts to convert it into the hydrogen phthalate by Kenyon and Hickman's method[4] by using (*a*) pyridine or (*b*) triethylamine gave 20% and 30% yields, respectively, of dark products which we found difficult to purify. However, the crystalline hydrogen phthalate was obtained in about 70% yield by treating the Grignard reagent from ethylmagnesium bromide and the alcohol (1) with pure phthalic anhydride, the whole operation being carried out in dry tetrahydrofuran.* The less soluble brucine salt (after debasification, $[\alpha]_D^{20}$ +40 to +60°) crystallised rapidly from hot acetone in which it is only sparingly soluble. From the mother-liquors the more soluble brucine salt (hydrogen phthalate, $[\alpha]_D^{20}$ —40° to —60° after removal of base) was isolated. Repeated fractional crystallisation of the brucine salts gave, after removal of base, small quantities of hydrogen phthalates, m. p. 120—123°, of maximum $[\alpha]_D^{15}$ +72° and —74°.

Similarly repeated fractional crystallisation of the (+)- and the (—)-hydrogen phthalate from chloroform–light petroleum gave small quantities of material having $[\alpha]_D^{20} > 70°$. As it was impracticable to convert such small quantities of the hydrogen phthalate into the optically pure alcohol (I) material of 55—65% optical purity was used. The optically active alcohol was obtained from the acid ester by reduction with less than one equivalent of lithium aluminium hydride at 0° (the hydrogen phthalate requires 5 H per mole; only

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* Doering and Zeiss[5] treated the Grignard derivative of the tertiary alcohol, 3,5-dimethylhexan-3-ol with phthalic anhydride, apparently in ether, without success.

[1] Part III, *J.*, 1962, 2298; for a preliminary report of some of the present work, see Landor and Taylor-Smith, *Proc. Chem. Soc.*, 1959, 154.

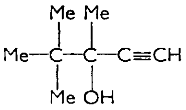
[2] Bhatia, Landor, and Landor, *J.*, 1956, 1015.

[3] De Wolf and Young, *Chem. Rev.*, 1956, **56**, 753; Young, Caserio, and Brandon, *J. Amer. Chem. Soc.*, 1960, **82**, 6163.

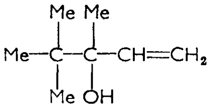
[4] Kenyon and Hickmann, *J.*, 1955, 2051; 1957, 4677.

[5] Doering and Zeiss, *J. Amer. Chem. Soc.*, 1950, **72**, 147.

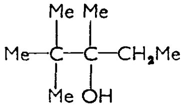
4 were used but the ester group is attacked in preference to the acid and no decrease in yield results; partial deactivation of an excess of lithium aluminium hydride with water or alcohol, leaving 4 H per mole of hydrogen phthalate gave similar results). This method


$\mathrm{Me{-}\overset{Me}{\underset{Me}{C}}{-}\overset{Me}{\underset{OH}{C}}{-}C{\equiv}CH}$

(I)


$\mathrm{Me{-}\overset{Me}{\underset{Me}{C}}{-}\overset{Me}{\underset{OH}{C}}{-}CH{=}CH_2}$

(II)


$\mathrm{Me{-}\overset{Me}{\underset{Me}{C}}{-}\overset{Me}{\underset{OH}{C}}{-}CH_2Me}$

(III)

avoids alkyl-oxygen fission and under carefully controlled conditions the triple bond is not reduced. Thus hydrogen phthalate of $[\alpha]_D^{20}$ ±50° gives the acetylenic alcohol (I) of $[\alpha]_D^{20}$ ±0·81°. However, if the temperature is allowed to rise or an excess of reagent used, some reduction to the ethylenic alcohol (II) takes place. This has $[\alpha]_D^{20}$ —2·41° and cannot be separated from the acetylenic alcohol, $[\alpha]_D^{20}$ —0·73°, by fractionation or by vapour-phase chromatography on dinonyl phthalate (one sharp band only) and it shows only weak absorption in the 1650 cm.$^{-1}$ region of the infrared spectrum. Resolution is achieved on a G.E.O. 100 stationary phase † and this, together with abnormally high values of the rotation, indicated that earlier samples [1] of the acetylenic alcohol [8] (I) were contaminated with the ethylenic alcohol. The ethylenic (II) and the saturated alcohol (III) and their corresponding hydrogen phthalates were prepared by reducing the acetylenic compounds in the presence of a Lindlar and a platinum oxide catalyst, respectively. Hydrogenation of the phthalates was accompanied by 20—30% of hydrogenolysis occurred in both cases. Lithium aluminium hydride and the saturated hydrogen phthalate gave the alcohol (III) of 40% lower rotation than was obtained by direct reduction of the acetylenic alcohol, indicating racemisation during hydrogenation or stereospecific hydrogenolysis.

TABLE 1.

Conversion of (+)- and (—)-acetylenic alcohols into allenic chlorides.*

Expt.	Solvent	Reflux time after completion of addition (min.)	Hydrogen phthalate $[\alpha]_D^{20}$	Acetylenic alcohol $[\alpha]_D^{20}$	Allenic chloride	
					$[\alpha]_D^{20}$	$[\alpha]_D^{20}$ (adjd.) ¶
1	Dry dioxan ‡	60	+50·8°		+23·88°	+23·50°
2	Dry dioxan ‡	60	—39·2		—17·71	—23·57
3	Dry dioxan §	60	—50·0	—0·76°	—33·18	—33·18
4	Dry dioxan §	60	—50·0	—0·76	—33·63	—33·63
5	Dry dioxan §	30	+49·6		+41·44	+41·62
6	Dry dioxan §	30	+52·5		+42·25	+40·35
7	Dry dioxan §	5	+55·5		+52·53	+47·46
8	Dry dioxan §	2	—50·0	—0·76	—48·11	—48·11
9	Dry dioxan §	2	—52·6	—0·83	—53·10	—50·50
10	Dry dioxan §	2	—47·3	—0·70	—48·15	—51·92
11	Dry dioxan §	2	—44·7	—0·72	—44·28	—49·48
12	Commercial dioxan	3	+47·6		+6·82	+7·15
13	Dry ether, NBu_3 §	—	+50·4	+0·78	+32·80	+32·60
14	Dry ether, NBu_3 §	—	—52·6	—0·83	—35·92	—34·13
15	Dry ether, pyridine	—	—40·0		—19·13	—24·88

* As the acetylenic alcohol has a very low specific rotation small amounts of impurity of higher rotation have a disproportionately large effect on the values obtained. We have, therefore, given only the rotation of alcohol samples which were known to be free from impurity as shown by spectra and vapour-phase chromatography. The best correlation is obtained by comparing the specific rotations of the hydrogen phthalate and allene chloride. An excess of thionyl chloride had to be used in all the experiments listed to avoid contamination of allenic chloride by recovered acetylenic alcohol from which it cannot readily be separated.

¶ For direct comparison, the rotations of allenic chloride have been adjusted to correspond to a standard rotation of hydrogen phthalate of $[\alpha]_D^{20}$ ± 50·0°.

‡ 50% excess of commercial redistilled thionyl chloride.

§ 20% excess of thionyl chloride purified by the Cottle process.[6]

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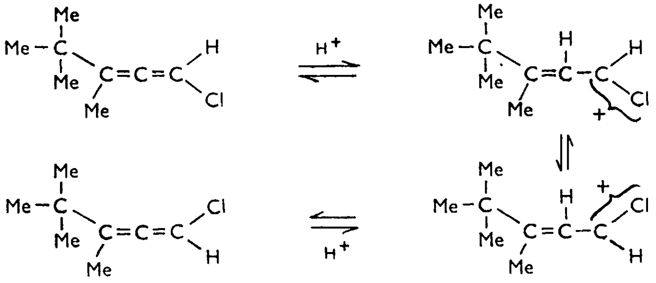
† Glycerol–ethylene oxide polymer. We thank Dr. M. C. Whiting for drawing our attention to this most useful stationary phase and presenting us with a sample.

[6] Cottle, *J. Amer. Chem. Soc.*, 1946, **68**, 1380.

The acetylenic alcohol was converted into 1-chloro-3,4,4-trimethylpenta-1,2-diene with thionyl chloride under the conditions summarised in Table 1.

The following conclusions may be drawn: (1) Impurities in the thionyl chloride lower the stereospecificity (Expts. 1, 2). (2) Impurities in the dioxan (mainly water) largely destroy stereospecificity and give at least 85% racemic product (Expt. 12). (3) Refluxing after completion of the addition of reactants leads to racemisation (Expts. 1—6). (4) Reaction in ether in the presence of a base lowers the stereospecificity (Expts. 13, 14, 15). (In ethereal solution without a base the reaction is too slow to be suitable for the preparation of optically active allene chloride; cf. ref. 2.)

The action of hydrogen chloride on the allenic chloride could account for racemisation when refluxing is continued after addition or when the " wet " commercial dioxan is used. This was confirmed by refluxing the allenic chloride in dry dioxan saturated with hydrogen chloride for 1 hr., which resulted in the loss of 18% of its optical activity. Protonation of the allene chloride at C-2, followed by rotation of the terminal carbon atom and deprotonation, leads to racemic allene chloride. Protonation should be facilitated in the more polar medium such as the " wet " commercial dioxan and this explains the more extensive racemisation in that medium (Expt. 12). Addition products have not been found (cf. Jacobs and Johnson [7]), but some isomerisation accompanies racemisation and this is under investigation.



In the presence of tributylamine, allene chloride of the same sign but lower magnitude of rotation was produced. As these conditions favour the S_N2' reaction (cf. ref. 3) it is suggested that the S_N2' mechanism mainly gives double inversion with propargyl–allene rearrangements as it does with allylic rearrangements [8] but is less stereospecific than the S_Ni' mechanism and that in refluxing dioxan allene chloride is mainly formed by the S_Ni' mechanism.

If the hydrogen phthalate, $[\alpha]_D^{20}$ ±50°, of the acetylenic alcohol is taken to be 65—70% optically pure, the optical purity of the allenic chloride, $[\alpha]_D^{20}$ ±50°, is estimated to be 50—60%.

EXPERIMENTAL

Rotations of hydrogen phthalates were determined for acetone solutions (*c* 2—5%); rotations of alcohols and chloroallenes were determined for the pure liquids.

3,4,4-*Trimethylpent*-1-*yn*-3-*ol*.—3,3-Dimethylbutan-2-one (200 g., 2 moles) was added dropwise to sodium acetylide (sodium, 52 g., 2·25 g.-atoms and cryst. ferric nitrate, 0·1 g.) in liquid ammonia (2 l.); acetylene was passed into the mixture with stirring for 4 hr. The sodium salt was then decomposed with ammonium chloride (117 g., 2·27 moles), and the products were extracted with ether and dried ($MgSO_4$). Ethynylation was repeated on this ethereal solution. The products of the second stage were dried, and the ether was removed. Distillation gave three fractions: the first two, b. p. 34—45°/15 mm. (8·1 g., 3%) and 46—47°/15 mm. (2·8 g., 1%), were mixtures of the alcohol and unchanged starting material, as shown by $\nu_{max.}$ 1710w cm.$^{-1}$ (C=O). The third fraction, b. p. 47°/15 mm. (172·4 g., 67%), $\nu_{max.}$ 3450s (OH), 3280s (C≡C), 2100w

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[7] Jacobs and Johnson, *J. Amer. Chem. Soc.*, 1960, **82**, 6397.

[8] Stork and White, *J. Amer. Chem. Soc.*, 1956, **78**, 4609.

($C\equiv CH$), 1390m, 1365s (CMe_3 doublet), and 1225s cm.$^{-1}$ (CMe_3), was the pure carbinol [no peak at 1710 cm.$^{-1}$ ($C=O$)].

Hydrogen Phthalate of 3,4,4-*Trimethylpent*-1-*yn*-3-*ol*.—Ethylmagnesium bromide was prepared from magnesium (10·5 g., 0·437 g.-atom), ethyl bromide (47·5 g., 0·437 mole), and iodine (0·1 g.) in dry tetrahydrofuran (200 ml.). A solution of 3,4,4-trimethylpent-1-yn-3-ol (55 g., 0·437 mole) in dry tetrahydrofuran (150 ml.) was added at 0°, with stirring. The mixture was warmed to 50° for 2 hr., and a warm solution of phthalic anhydride (65 g., 0·438 mole) in dry tetrahydrofuran (700 ml.) added. After a further 2 hr. at 50°, about 250 ml. of tetrahydrofuran were removed under reduced pressure. The mixture was then shaken with dilute hydrochloric acid and ether, and the ether layer extracted several times with aqueous sodium hydroxide. These extracts were combined and acidified with dilute hydrochloric acid, and the hydrogen phthalate was extracted with ether. After drying ($MgSO_4$), and removal of the ether, the crude hydrogen phthalate (91·1 g., 75%) crystallised on being stirred with light petroleum (b. p. 40—60°), and it was then dissolved in hot chloroform. Phthalic acid (11·4 g.), m. p. 208° (decomp.), was filtered off, most of the solvent was removed by evaporation; the hydrogen phthalate (78·0 g., 65%), m. p. 136—138°, crystallised when stirred with light petroleum. Recrystallisation from chloroform–light petroleum gave the pure hydrogen phthalate, m. p. 137—138°, $\nu_{max.}$ (in Nujol) 3250m ($C\equiv C$), 2100w ($C\equiv CH$), 1740s ($C=O$ acid), 1690s ($C=O$ ester), 1595m, 1570s ($C=C$ aromatic), 810m cm.$^{-1}$ ($C\equiv C$). On evaporation of the neutral ether layer and distillation, 8 g. of the alcohol were recovered.

Brucine Phthalate of 3,4,4-*Trimethylpent*-1-*yn*-3-*ol*.—In a typical experiment a warm suspension of anhydrous brucine (151 g., 0·383 mole) in acetone (700 ml.) was added with stirring to a solution of the hydrogen phthalate (105 g., 0·383 mole) in acetone (200 ml.). The mixture was refluxed for ½ hr., giving a clear solution, followed by slow crystallisation of brucine salt (crop 1). After the mixture had cooled to room temperature, brucine salt (crop 1) was filtered off and dried. The filtrate was evaporated down to half its volume and kept for 2 days, and the brucine salt (crop 2) was filtered off, and again one week later (crop 3). Evaporation of the filtrate to dryness gave 0·5 g. of syrup which was discarded. A test sample (5 g.) from each crop was decomposed to the hydrogen phthalate by shaking it with dilute hydrochloric acid and ether until all the solid had gone into solution. The ethereal layer was washed with water, dried, and evaporated. The hydrogen phthalate that crystallised when stirred with light petroleum was filtered off, and the rotation of its acetone solution (5 ml.) was measured. If the rotations were sufficiently high, the remainder of the brucine salt (crops 1 and 2) was similarly decomposed with dilute hydrochloride acid and the hydrogen phthalates crystallised. Crop 3 was found to be of low rotation, so the brucine salt was recycled into the next resolution. Some results are in Table 2. (l = 1 dm.)

TABLE 2.

Brucine salt		Hydrogen phthalate				
Crop	Wt. (g.)	Wt. (g.)	Yield (%)	c (in acetone)	α	$[\alpha]_D^{20}$
1	124·3	45·9	43·7	3·506	+1·74°	+49·6°
2	116·8	39·9	38·0	4·086	−2·24	−54·7
3	11·5	—	—	2·600	−0·18	−6·9

Hydrogen Phthalate of 3,4,4-*Trimethylpentan*-3-*ol*.—The hydrogen phthalate (15·0 g., 0·0547 mole), m. p. 117—120°, $[\alpha]_D^{20}$ +55·4°, of the acetylenic alcohol was shaken in ethyl acetate solution (350 ml.) with hydrogen and platinic oxide, absorbing 2710 ml. of hydrogen (2 mol. = 2450 ml.). Filtration and evaporation gave crystals (11·2 g.), which were extracted with chloroform. The residue of phthalic acid (4·1 g.), m. p. 205—207° (decomp.), was filtered off. Evaporation of the chloroform, followed by stirring with light petroleum, gave the saturated hydrogen phthalate (6·9 g., 46%), m. p. 116—118° (decomp.), $[\alpha]_D^{20}$ +23·1°. The absence of infrared bands at 3300, 2100, 990, 985, 915, and 810 cm.$^{-1}$ showed acetylenic and vinyl impurities to be absent.

Hydrogen Phthalate of 3,4,4-*Trimethylpent*-1-*en*-3-*ol*.—The hydrogen phthalate (1·1 g., 0·040 mole), m. p. 117—121°, $[\alpha]_D^{20}$ +50·1°, of the acetylenic alcohol was shaken in ethyl acetate solution (100 ml.) with hydrogen and a Lindlar palladium catalyst (0·18 g.), absorbing 112 ml. of hydrogen (1 mol. = 95·2 ml.). The catalyst was filtered off and the solvent evaporated. The residual solid was taken up in chloroform and the phthalic acid (0·08 g.), m. p. 207—208° (decomp.), filtered off. Evaporation of the chloroform, followed by stirring with light petroleum gave the hydrogen phthalate (0·65 g., 61%), m. p. 114—115°, $[\alpha]_D^{20}$ +51·9°, of 3,4,4-trimethylpent-1-en-3-ol. The infrared spectrum showed the absence of acetylene bands at 3300, 2100, and 810 cm.$^{-1}$; weak vinyl peaks were present at 990, 985, and 915 cm.$^{-1}$.

(+)- *and* (−)-3,4,4-*Trimethylpent*-1-*yn*-3-*ol*.—(*a*) Water (2·8 g., 0·155 mole) was added cautiously to a stirred suspension of lithium aluminium hydride (9·0 g., 0·238 mole) in dry ether (250 ml.) at 0°. When the reaction was over, the suspension was slowly added to a stirred solution of the hydrogen phthalate (42·5 g., 0·155 mole), $[\alpha]_D^{20}$ −47·3°, in dry ether (250 ml.), cooled by a freezing mixture. After 4½ hr. at 0°, water (50 ml.) was added dropwise to the mixture, which was then allowed to warm to room temperature. The products were shaken with dilute hydrochloric acid, and the ether layer washed with aqueous sodium hydrogen carbonate, dried, and distilled at atmospheric pressure. Distillation of the products under a vacuum gave fractions: (i) b. p. 50—51°/20 mm. (1·1 g., 5%), $[\alpha]_D^{20}$ −0·54°, (ii) b. p. 51—52°/20 mm. (1·2 g., 6%), $[\alpha]_D^{20}$ −0·60°, and (iii) b. p. 52°/20 mm. (9·7 g., 49%), $[\alpha]_D^{20}$ −0·77°. More vigorous heating gave two further fractions, (iv) b. p. 52—53° (0·5 g.), $[\alpha]_D^{20}$ −0·52°, and (v) b. p. 53—65° (0·4 g.), $[\alpha]_D^{20}$ +1·47°, $\nu_{max.}$ 1720vs (C=O) and 1650vs cm.$^{-1}$ (C=C). Infrared spectra showed that fractions (i) and (ii) contained some carbonyl impurity which was absent in the main fraction, (iii). Fractions (i)—(iii) were practically free from olefinic impurity.

(*b*) A suspension of lithium aluminium hydride (5·35 g., 0·141 mole assumed ≈90% pure) in dry ether (250 ml.) was slowly added at 0° to a stirred solution of the hydrogen phthalate (37·6 g., 0·137 mole), $[\alpha]_D^{20}$ −44·7°, in dry ether (250 ml.). After being stirred for 4½ hr. at 0°, the mixture was decomposed with water and the products were extracted and distilled as before, giving a main fraction, b. p. 39°/11 mm. (10·6 g., 61%), $[\alpha]_D^{20}$ −0·72°. The infrared spectrum of this fraction was identical with that of the main fraction obtained by method (*a*).

3,4,4-*Trimethylpentan*-3-*ol*.—(*a*) A suspension of lithium aluminium hydride (1·06 g., 0·028 mole) in dry ether (100 ml.) was added slowly to a stirred solution of the hydrogen phthalate (5·0 g., 0·018 mole), $[\alpha]_D^{20}$ +23·1°, of the saturated alcohol, and stirring was continued for a further 2 hr. at room temperature. The excess of the reagent was decomposed with water, the mixture acidified, and the ether layer separated and dried. Distillation of the products gave 3,4,4-trimethylpentan-3-ol as the main fraction, b. p. 68—69°/32 mm. (1·0 g., 43%), $[\alpha]_D^{20}$ +3·33°, $\nu_{max.}$ 3450s (OH), 1640w (C=C), 1385m, 1365s (doublet, CMe_3) and 1215s cm.$^{-1}$ (CMe_3). There was no band at 3300 or 2100 cm.$^{-1}$. The alcohol was therefore free from acetylenic impurity but contained traces of olefinic compounds.

(*b*) 3,4,4-Trimethylpent-1-yn-3-ol (1·35 g., 0·011 mole), $[\alpha]_D^{20}$ +0·75°, was shaken in ether (70 ml.) with hydrogen and platinic oxide (0·03 g.), absorbing 497 ml. of hydrogen (2 mol. = 485 ml.). After filtration and evaporation, distillation gave 3,4,4-trimethylpentan-3-ol as the main fraction, b. p. 50°/16 mm. (0·9 g., 64%), $[\alpha]_D^{20}$ +4·84°. There was no infrared band at 3300 (C≡C), 2100 (C≡CH), 1860, 1650, 930, 815, or 710 cm.$^{-1}$ (all C=C).

3,4,4-*Trimethylpent*-1-*en*-3-*ol*.—3,4,4-Trimethylpent-1-yn-3-ol (2·0 g., 0·016 mole), $[\alpha]_D^{20}$ −0·73°, was shaken in ether (200 ml.) with hydrogen and a Lindlar palladium catalyst (0·15 g.), absorbing 305 ml. of hydrogen (1 mol. = 358 ml.). After filtration and evaporation, distillation gave 3,4,4-trimethylpent-1-en-3-ol as the main fraction, b. p. 47°/15 mm. (1·2 g., 60%), $[\alpha]_D^{20}$ −2·41°, $\nu_{max.}$ 3500s (OH), 1860m ($CH=CH_2$ overtone), 1660m and 1640m (both $CH=CH_2$), 1390m, 1365s (doublet) and 1220s (CMe_3), and 950s cm.$^{-1}$ ($CH=CH_2$). The alcohol was free from acetylenic impurity, as shown by the absence of bands at 3300 and 2100 cm.$^{-1}$.

1-*Chloro*-3,4,4-*trimethylpenta*-1,2-*diene*.—(*a*) 3,4,4-Trimethylpent-1-yn-3-ol (5·4 g., 0·043 mole), $[\alpha]_D^{20}$ −0·70°, and thionyl chloride (7·1 g., 0·059 mole, purified by Cottle's method [6]), were added slowly and simultaneously, with stirring, to dry dioxan (140 ml.), heated under reflux. Heating was then stopped, and, after 2 min., dry pyridine (7·7 g., 0·097 mole) was added dropwise. The reactants were stirred for another ½ hr., then the products were extracted with ether, washed successively with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water, and dried. Ether was distilled off at atmospheric pressure, then the products were distilled under a vacuum, giving two main fractions: (i) b. p. 60—61°/32 mm. (0·3 g., 5%), $[\alpha]_D^{20}$ −46·20, and (ii) b. p. 61°/32 mm. (1·6 g., 26%), $[\alpha]_D^{20}$ −48·15°. Fraction (ii), the allenic chloride containing only traces of acetylenic chloride, had $\nu_{max.}$ at 3250vw (C≡C), 1940s (C=C=C), 1380m, 1360s, 1245s (CMe_3 bands), 1060m (C=C=C), 828s (C=C=CHCl), and 735s cm.$^{-1}$ (C–Cl). There was no band at 3500 cm.$^{-1}$ (OH). Fraction (i) contained slightly more acetylenic chloride and traces of a vinyl compound, as shown by $\nu_{max.}$ at 3250m (C≡C), 1745vw (overtone $C=CH_2$), 1620vw (C=C) and 877vw cm.$^{-1}$ ($C=CH_2$).

(*b*) Tributylamine (8·84 g., 0·048 mole) was added to a stirred solution of 3,4,4-trimethylpent-1-yn-3-ol (6·0 g., 0·048 mole), $[\alpha]_D^{20}$ −0·83°, in dry ether (100 ml.). The mixture was cooled to 0° and thionyl chloride (7·9 g., 0·066 mole; purified as before) was added dropwise, then the mixture allowed to warm to room temperature. After ½ hr., the products were shaken with dilute hydrochloric acid, and the ether layer was separated, washed with aqueous sodium hydrogen carbonate, and dried. After removal of the ether, distillation gave two main fractions: (i) b. p. 48—49°/18 mm. (0·3 g., 4%), $[\alpha]_D^{20}$ −30·33°, and (ii) b. p. 49°/18 mm. (1·1 g., 16%), $[\alpha]_D^{20}$ −35·91°. Fraction (ii), the allenic chloride containing traces of acetylenic chloride and a vinyl compound, had $\nu_{max.}$ at 3250w ($C{\equiv}C$), 1940s ($C{=}C{=}C$), 1690vw ($C{=}C$), 1660vw ($C{=}CH_2$), 1380m, 1355s, 1245s (CMe_3 bands), 1060m ($C{=}C{=}C$), 828s ($C{=}C{=}CHCl$) and 735s cm.$^{-1}$ (C–Cl). There was no maximum at 3500 cm.$^{-1}$ (OH). Fraction (i) contained slightly more of these impurities as shown by $\nu_{max.}$ at 3250m ($C{\equiv}C$), 1690vw ($C{=}C$), and 1660w ($C{=}CH_2$).

Purification of Allenic Chloride Fractions.—The allenic chloride (2·4 g.), $[\alpha]_D^{20}$ −33·34°, containing acetylenic and olefinic impurities as shown by $\nu_{max.}$ at 3300m ($C{\equiv}C$), 1745vw ($C{=}CH_2$ overtone), 1620vw ($C{=}C$) and 877m cm.$^{-1}$ ($C{=}CH_2$), was shaken for 10 min. with saturated aqueous silver nitrate (30 ml.). The precipitate was filtered off and the filtrate extracted with ether. The ethereal solution of the allenic chloride was dried and distilled, giving pure allene chloride, b. p. 48°/16 mm. (0·7 g.), $[\alpha]_D^{20}$ −34·18°. The infrared spectrum showed no band at 3300 ($C{\equiv}C$), 1750 ($C{=}CH_2$ overtone), or 877 cm.$^{-1}$ ($C{=}CH_2$).

Effect of Hydrogen Chloride on 1-*Chloro*-3,4,4-*trimethylpenta*-1,2-*diene*.—Dry hydrogen chloride was passed for 10 min. through dry dioxan (100 ml.), under reflux. Then 1-chloro-3,4,4-trimethylpenta-1,2-diene (1·5 g., 0·01 mole), $[\alpha]_D^{20}$ −44·28°, was added and the solution was refluxed for 1 hr. The products were worked up in the usual way and distilled, giving the allene chloride as the main fraction, b. p. 35°/12 mm. (0·9 g., 60·1%), $[\alpha]_D^{20}$ −36·48°. Weak bands at 1655, 1625, 880, and 860 cm.$^{-1}$ indicated small amounts of olefinic impurity.

2,2,3-*Trimethylpentane*.—1-Chloro-3,4,4-trimethylpenta-1,2-diene (0·0282 g., 0·0002 mole), $[\alpha]_D^{15}$ +12·1° (*c* 2·738 in hexane), on being shaken for 6 hr. in dry hexane (20 ml.) with hydrogen and platinic oxide (2 mg.), absorbed 14 ml. of hydrogen at 22°/736·7 mm. (3 mol. = 13·9 ml.), and the solution showed $[\alpha]_D^{15}$ 0·01—0·02°, *i.e.*, $\approx$90% loss of optical activity.

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