Reactions of Phosphorus Pentachloride with Ethyl-, Vinyl-, and Ethynyl(trichloromethyl)carbinol and with 1,1,1-Trichloro-3-nonyn-2-ol¹

E. WILKINS REEVE AND THOMAS F. STECKEL

Chemistry Department, University of Maryland, College Park, Maryland 20742 Received July 20, 1972²

Reactions of phosphorus pentachloride with ethyl(trichloromethyl)carbinol (2), (trichloromethyl)vinylcarbinol (7), ethynyl(trichloromethyl)carbinol (11a), and 1,1,1-trichloro-3-nonyn-2-ol (11b) have been studied. Whereas the reaction of phenyl(trichloromethyl)carbinol with phosphorus pentachloride leads to a nearly quantitative replacement of the hydroxyl group by chlorine, the reactions of the aliphatic (trichloromethyl)carbinols are more complicated. Thus the reaction of 2 with phosphorus pentachloride gave 18% of the normal product, 1,1,1,2-tetrachlorobutane (3), 13% of 1,1,2-trichloro-1-butene (4) from a dehydrohalogenation, and a higher boiling phosphate ester – acid chloride mixture. The alkynylcarbinols (11) gave tetrachlorobutynes (12) as well as tetrachloroallenes (13) by allylic rearrangement. A crystalline phosphate ester of 11a was also isolated. Several examples are given of catalytic rearrangements in the vapor phase of 1,1,1-trichloro-2-alkenes to 1,1,3-trichloro-1-alkenes.

On a étudié les réactions du pentachlorure de phosphore avec l'éthyl (trichlorométhyl) carbinol (2), le (trichlorométhyl) vinylcarbinol (7), l'éthènyl (trichlorométhyl) carbinol (11a) et le trichloro-1,1,1 nonyn-3 ol-2 (11b). Alors que la réaction du phényl (trichlorométhyl) carbinol avec le pentachlorure de phosphore conduit pratiquement quantitativement à la substitution du groupe hydroxyle par un chlore, la réaction avec les (trichlorométhyl) carbinols aliphatiques semble être beaucoup plus compliquée. Ainsi, la réaction de 2 avec le pentachlorure de phosphore conduit à la formation du produit normal (18%), tétrachloro-1,1,1,2 butane, (3) ainsi qu'à la formation du trichloro-1,1,2 butène-1 (4) (13%), provenant d'une déhydrohalogénation, et d'un mélange phosphate d'ester – chlorure d'acide ayant un point d'ébullition plus élevé. Les carbinols possèdant des groupes alcynes (11) produisent des tétrachlorobutynes (12) de même que des tétrachloroallènes (13) selon un mécanisme impliquant un réarrangement allylique. Un phosphate d'ester cristallin de 11a a aussi été isolé. Plusieurs exemples de réarrangements catalytiques en phase vapeur sont rapportés pour les trichloro-1,1,1 alcènes-2 entraînant la formation de trichloro-1,1,3 alcènes-1. [Traduit par le journal]

Can. J. Chem., 51, 2017 (1973)

Can. J. Chem. Downloaded from www.nrcresearchpress.com by WA STATE UNIV LIBRARIES on 11/21/14 For personal use only.

The reaction of phosphorus pentachloride with phenyl(trichloromethyl)carbinol is known to give the corresponding chloride in 87% yield (1). When phenyl is replaced by an aliphatic group, a more complicated set of reactions occurs. The purpose of this work was to study the reactions of the compounds R-CHOH-CCl₃, where R is ethyl, vinyl, ethynyl, and nonynyl, with phosphorus pentachloride to determine the products formed in these reactions. These reactions are of importance because the hydroxyl group in trichloromethylcarbinols cannot be replaced by chlorine by treatment of the carbinol with concentrated hydrochloric acid; the presence of the trichloromethyl group prevents the usual displacement reaction from occurring, even when the alcohol is of the benzylic or allylic type.

The reaction of phosphorus pentachloride with

alcohols has been used for over a century to replace the hydroxyl group with chlorine, but the mechanism by which this occurs is even now only imperfectly understood. Several facts are known. First, phosphorus pentachloride is $(PCl_4)^+$ $(PCl_6)^-$ in the crystalline state (2) and in solvents such as phosphorus oxychloride, nitrobenzene, acetonitrile, and benzoyl chloride (3). The reaction occurs with initial stepwise replacement by alkoxy of the chlorines bound to phosphorus but no one has been able to isolate the pentacoordinate chloro ester, ROPCl₄ (4). This agrees with the observation that, while many pentacoordinate compounds of phosphorus are known, (5) they appear to be uncommon intermediates in nucleophilic displacements at tetracoordinate phosphorus (6). The reaction products include the alkyl chloride, always with inversion of configuration in the case of saturated alcohols (7); mono-, di-, and triphosphate esters, particularly from primary alcohols (4); and olefins from secondary alcohols, often accompanied by *trans*

¹Taken in part from the doctoral thesis of Thomas F. Steckel, University of Maryland, 1970.

²Revision received March 6, 1973.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by WA STATE UNIV LIBRARIES on 11/21/14 For personal use only.



Scheme 1

addition of chlorine to the double bond (8). Scheme 1 is consistent with the above experimental facts.

The above scheme incorporates the ideas of Gerrard (4) but assumes tetracoordinate intermediates. Independent evidence for the existence of 1 has been obtained from studies of the variation of electrical conductivity during the reaction of alcohols with phosphorus pentachloride in benzene (9).

In our work with vinyl and acetylenic carbinols (Schemes 3 and 4) the reaction intermediates must have a high degree of carbonium ion character to account for the allylic rearrangements observed, and the incipient carbonium ion could be formed by the heterolysis of the alkyl-oxygen bond of 1. 1 can also react with excess carbinol with the replacement of two more of the phosphorus chlorines.

The reaction of ethyl(trichloromethyl)carbinol (2) with phosphorus pentachloride, which has not been studied previously, was found to yield four chlorinated hydrocarbons and ethyl α -chlorobutyrate (Scheme 2). The structures of the products were deduced from their spectra. Compound 5 rearranged completely to 6 during g.l.p.c. analysis.

With benzene instead of ether as the solvent, compounds 3, 4, and 5 + 6 were obtained in yields of 4, 2, and 8% respectively, ethyl α chlorobutyrate was absent, and the major product consisted of another mixture distilling about 100° higher. This contained phosphorus, exhibited strong i.r. absorption at 1295 cm⁻¹ characteristic of P=O, and showed splitting of the carbinyl proton attributable to phosphorus. It was concluded to be a mixture of mono- and dichlorophosphate esters of the starting carbinol. The residue appeared to be mostly the triphosphate ester.

As is the case with many unsubstituted alcohols (4), it is clear there is competition between phosphate ester formation and replacement of the hydroxyl group by chlorine. During the latter reaction, dehydrohalogenation occurs to 4 and 5. Compound 4 is stable, but 5 is thermally unstable; on heating a mixture of 3, 4, and 5 at 135° for 2 h, about 50% of 5 is converted to 6.

The tertiary alcohol, dimethyl(trichloromethyl)carbinol, does not react with phosphorus pentachloride under the above conditions. Others have found that the conversion of this carbinol to the chloride requires several hours heating at 80° with phosphorus pentachloride (10).

Colonge and Lartigau report that (trichloromethyl)vinylcarbinol and phosphorus pentachloride give *trans*-1,1,1,4-tetrachloro-2-butene (9) in 48% yield using ether as a solvent (11) (see Scheme 3). We duplicated their results and in addition found that, using benzene as the solvent, 9 was obtained in 34% yield and, based on i.r. and n.m.r. spectra, was contaminated with substituted vinylbenzenes. Unlike most allyl alcohols, (trichloromethyl)vinylcarbinol does not react with concentrated hydrochloric acid containing zinc chloride even after standing for 24 h at room temperature.

Compound 8 could not be isolated; only its allylic isomer 9 was obtained. Colonge and Ducarre (12) reported, on the basis of spectral evidence only, that 9 was stable to heat but was partially converted to 10 by light. We have found that this isomerization occurs quantitatively at 125° during g.l.p.c., and can be carried out catalytically on a preparative scale in 81% conversion by a single pass of the vapors of 9 over copper metal beads at 220°. The driving force for this reaction is probably the resonance stabilization afforded by the vinylidene chloride structure as compared to the unconjugated trichloromethyl group. Over alumina, 9 underwent decomposition.

The reaction of ethynyl(trichloromethyl)carbinol with phosphorus pentachloride has not been studied previously. As with the (trichloromethyl)vinylcarbinol, the reaction is unusual in that the expected chloride (12a) is a minor product; the major component of the volatile





Scheme 2



SCHEME 3

fraction of the reaction products is the allene 13a formed by an allylic rearrangement accompanying the displacement of the hydroxyl group (see Scheme 4). This presumably occurs by an S_Ni' mechanism.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by WA STATE UNIV LIBRARIES on 11/21/14 For personal use only.

The phosphate ester 14 could be isolated only when the reaction was carried out by adding phosphorus pentachloride, suspended in benzene, to a benzene solution of the starting carbinol 11a. The phosphate ester crystallized from the residue after the volatile fraction had been distilled. Products 12a and 13a are best obtained by adding the carbinol to the phosphorus pentachloride; thus a 7% yield of the alkyne 12a was obtained versus 1% by the reverse addition, but no phosphate ester could be isolated from the non-volatile portion. It seems likely that the triester was not formed with this mode of addition because the phosphorus pentachloride was in excess at all times during the reaction. This might give the monoalkyl chlorophosphate time to react to form the chlorinated hydrocarbons.

The alkyne 12a was a stable compound, not isomerized by distillation, by passage through a g.l.p.c. apparatus, or by passage over various catalysts in the vapor phase at 218°. In contrast, the allene 13a isomerized quantitatively to the butadiene 15a during g.l.p.c. regardless of the chromatographic column employed. The allene did not isomerize during distillation. Since chemical methods of separating the alkyne and allene isomers were unsuccessful, our best sample of 13a was an 85% pure (by n.m.r.) fraction, obtained by distillation, with the balance being the alkyne 12a together with minor impurities.

The rearrangement of the allene 13a to the butadiene 15a was found to occur quantitatively during a single pass of the allene in the vapor state over alumina at 218°. Copper beads were also effective in catalyzing the isomerization at this temperature, but two passes were necessary to obtain a 90% conversion. Glass wool, sand, and stainless steel wire loops had no catalytic effect. All attempts to carry out the isomerization

2020

CAN. J. CHEM. VOL. 51, 1973



SCHEME 4

in the liquid phase over catalysts such as metallic copper, cupric chloride, copper chromite hydrogenation catalyst, and silica gel were unsuccessful.

To eliminate whatever effect the acetylenic proton might have on the above reactions, namylacetylene was prepared and converted to 1,1,1-trichloro-3-nonyn-2-ol (11b) by reaction with chloral. The reaction of 11b with phosphorus pentachloride was studied by adding the phosphorus pentachloride to the carbinol using benzene as solvent. The crude product containing 12b (major component) and its allylic rearrangement product (13b) was obtained in 84% yield (before distillation; 35% after distillation). The undistilled and the distilled materials gave identical n.m.r. spectra. Compound 12b was the major fraction formed; this involved a normal replacement of the hydroxyl group. The product 13b from the allylic rearrangement was the minor product.

The allene 13b rearranged to the diene 15b on g.l.p.c., and thus 13b could not be obtained pure. This rearrangement could also be carried out as before in the vapor phase at 225° over a variety of substances including alumina, sand mixed with copper powder, and sand alone. Since sand, which is considered to have no catalytic activity, seemed to be best, it appears that the conversion is thermal rather than catalytic. *cis* and *trans* isomers of 15b are possible and evidence for their existence was seen in the n.m.r. spectrum where two signals in the ratio of 3.5:1 were observed

for the vinyl proton. The isomers were not separated by the g.l.p.c. columns used.

The allene 13b was unstable in the liquid phase. After 2 months at room temperature or 30 min at 150°, it was changed to a polymeric material. On heating 13b at 150° with finely divided copper metal for 10 min, a dark brown mixture was formed which contained some diene 15b. Thus in this case, copper has a limited catalytic effect in the liquid phase.

The alkyne 12b, in contrast to the allene 13b, was stable in the liquid phase, even when heated either alone or in the presence of copper metal or alumina. It was unaffected by passage of the vapor at 225° over sand or a 1:1 sand and copper powder mixture. However, over alumina at 225°, 12b lost two chlorine atoms to give 1,1-dichloro-1-nonen-3-yne (16) in about 10% yield, and no starting material could be recovered. During g.l.p.c. analysis at 195°, 12b also gave 16 in 5 to 10% yield, but most of the 12b could be recovered.

Experimental

Melting points and boiling points are corrected. The i.r. spectra were recorded on a Perkin–Elmer instrument Model 337, using thin films for liquid samples and potassium bromide pellets for solid samples. The mass spectra were recorded on a Varian M-66 mass spectrometer, and the n.m.r. spectra with a Varian A60A instrument. Chemical-shift values are expressed as δ values (p.p.m.) downfield from tetramethylsilane internal standard. Vapor phase chromatographic analyses were carried out on an F & M Model 300 with a helium flow

Can. J. Chem. Downloaded from www.nrcresearchpress.com by WA STATE UNIV LIBRARIES on 11/21/14 For personal use only.

rate of 50 ml/min. The percentage composition figures given for the various fractions are g.l.p.c. percentages. The following chromatographic columns were used: Apiezon (10% Apiezon-L on 60/80 mesh silanized diatomaceous earth (Diatoport-S) packed in a 2 m × 6.35 mm copper tube), silicon fluid (20% Dow-Corning Silicon Fluid #710 on 30/60 mesh Chromosorb P packed in a 2 m × 6.35 mm copper tube), silicon gum rubber (F & M silicon gum rubber on Chromosorb P packed in a 0.7 m × 6.35 mm stainless steel tube).

Elemental microanalyses were performed by Dr. Franz J. Kasler.

Ethynyl(trichloromethyl)carbinol (11a)

This was prepared by a modification of Shapiro's method (13) in 51% yield from the reaction of sodium acetylide (14) and commercial anhydrous chloral at 0° for 2 h; b.p. 74-82° (14 mm) (lit. (13) 77-81° (16 mm)); n.m.r. (CDCl₃) δ 4.90 (1 H, d, J = 2.1 Hz, —CHOH—), 3.96 (1 H, broad s, —OH), 2.78 (1 H, d, J = 2.1 Hz, HC=).

1,1,1-Trichloro-3-nonyn-2-ol (11b)

1-Heptyne (15) (32 g, 0.33 mol) in an equal volume of anhydrous ether was added over a 45-min period to 0.3 mol of ethylmagnesium bromide in refluxing ether. After refluxing 2 h, the reaction mixture was cooled in an ice bath under a nitrogen atmosphere and 49 g (0.33 mol) of chloral in an equal volume of ether was added over 1 h; the mixture was then stirred for an additional hour at room temperature. There was obtained 62 g (76%) of the carbinol **11***b*; b.p. 144–149° (16 mm) (lit. (16) 106–110° (4 mm) and 141–142° (12 mm)); n.m.r. (CCl₄) & 4.69 (1 H, m, -CHOH-), 3.44 (1 H, s, OH), 2.26 (2 H, m, -CH₂C=), 1.41 (6 H, m, (-CH₂-)₃), 0.91 (t, 3, CH₃-).

(Trichloromethyl)vinylcarbinol (7)

Can. J. Chem. Downloaded from www.nrcresearchpress.com by WA STATE UNIV LIBRARIES on 11/21/14 For personal use only.

Twenty-six grams (0.15 mol) of ethynyl(trichloromethyl)carbinol (11*a*) dissolved in 150 ml ethanol was hydrogenated at room temperature over 1.2 g of 10% palladium-on-carbon catalyst (17) until 0.15 mol of hydrogen had been absorbed. Distillation of the product combined from three such runs gave 61 g (78%) of the carbinol 7; b.p. 84–87° (30 mm) (lit. 68–69° (12 mm) (13) and 75° (17 mm) (18)); n.m.r. (CDCl₃) δ 6.35–5.35 (3 H, m, $H_2C=CH-$), 4.54 (1 H, doublet with some long range splitting, J = 4.8 Hz, J' = 2.4 Hz, -CHOH-), 3.6 (1 H, s, -OH). The n.m.r. spectra showed the product to be 90–92% pure. Also present were peaks corresponding to the presence of approximately 5% each of 2 and 11*a*.

Ethyl(trichloromethyl)carbinol (2)

The ethynyl carbinol **11***a* was hydrogenated as above, but the reaction was allowed to go to completion. This took about 20 min, and shaking was continued for another 10 min. From 104 g of **11***a*, there was obtained on distillation 78 g (74%) of the carbinol 2; b.p. 79-84° (28 mm) (lit. (13) 67° (13 mm)); n.m.r. (CCl₄) δ 3.98 (1 H, d of d, J = 9.1, J' = 2.1 Hz, --CHOH---), 3.3 (1 H, s, --OH), 2.54-1.33 (2 H, m, --CH₂---), 1.12 (3 H, t, J = 7.2 Hz, CH_3 ---).

Reaction of Ethyl(trichloromethyl)carbinol (2) with Phosphorus Pentachloride

To 4.4 g (0.025 mol) of **2** dissolved in 16 ml of ether, stirred with a magnetic stirrer and cooled with an ice bath, was added a slurry of 10.4 g (0.05 mol) of phosphorus

pentachloride in ether over a period of 10 min. The reaction mixture was stirred for 2 h at room temperature and then decomposed by pouring into ice and water. To this was added 20% potassium hydroxide solution in small portions until the water layer was just basic to litmus; the organic layer was separated, washed twice with 5% sodium carbonate solution, twice with water, dried (MgSO₄), concentrated, and distilled giving 1.7 g of a mixture (b.p. 61-76° (34 mm); lit. for 4: (19) 58° (46 mm), for 6: (20) 64° (50 mm)). G.l.p.c. analysis (silicon fluid column at 100°) showed the mixture to consist of 49%1,1,1,2-tetrachlorobutane (3) (18%), 30% 1,1,2-trichloro-1-butene (4) (13%), 10% 1,1,3-trichloro-1-butene (6) (4%), and 11% ethyl a-chlorobutyrate (12%). These compounds had retention times of 42, 15, 17, and 28 min respectively. The presence of 1,1,1-trichloro-2-butene (5) was shown by the n.m.r. spectrum of the distilled mixture of chlorinated hydrocarbons prior to g.l.p.c. analysis; it rearranged to 6 during g.l.p.c. analysis.

Spectral data on 3 purified by g.l.p.c.: i.r. of stronger bands (neat) 2970, 2935, 2875, 1450, 1090, 1015, 830, 790-770 (s), 680, and 610 cm⁻¹; n.m.r. (CCl₄) δ 4.25 (1 H, d of d, J = 10.3, J' = 2.3 Hz, --CHCl---, 2.7-1.5 (2 H, m, CH₃CH₂---), 1.2 (3 H, t, J = 7.3 Hz, CH₃---).

Data on 4 purified by g.l.p.c.: i.r. of stronger bands (neat) 2975, 2930, 2875, 1600, 1455, 1425, 1130, 1045, 955, 900 (s), 810 (s), and 735 cm⁻¹; n.m.r. (CCl₄) δ 2.64 (2 H, quartet, J = 7.4 Hz, CH₃CH₂—), 1.18 (3 H, t, J = 7.4 Hz, CH₃—).

Data on 6 purified by g.l.p.c.: i.r. of stronger bands (neat) 2980, 2920, 1620 (s), 1445, 1375, 1260, 1215 (s), 1140 (s), 1010 (s), 925, 885 (s), 835, 670, and 620 (s) cm⁻¹; n.m.r. (CCl₄) δ 6.02 (1 H, d, J = 9.8 Hz, —CH=), 4.77 (1 H, m, —CHCl—), 1.62 (3 H, d, J = 6.7 Hz, CH₃).

Identification of ethyl α -chlorobutyrate was based on spectral data obtained on the sample purified by g.l.p.c.: i.r. (neat) 1750 cm⁻¹ (ester C=O) (lit. (21) 1750 cm⁻¹; n.m.r. (CCl₄) δ 4.18 (3 H, m, -CHCl- and -CH₂O--), 1.99 (2 H, m, -CH₂CHCl--), 1.32 (3 H, t, J = 7.1 Hz, CH₃--), 1.03 (3 H, t, J = 7.4, CH₃).

Spectral data on 5 was obtained on a sample prepared from 2 and phosphorus pentachloride using benzene as solvent. The reaction mixture was distilled and the major component comprising 47% of the volatile fraction was identified as 1,1,1-trichloro-2-butene (5) from the n.m.r. spectrum of the mixture. It rearranged to 6 on g.l.p.c. analysis and so its spectral data were measured using the 47% mixture: i.r. (neat) 1655 cm⁻¹ (C=C); n.m.r. (CCl₄) δ 6.03 (2 H, m, -CH=CH-), 1.87 (3 H, d, J = 4.9 Hz, CH₃-).

In a separate experiment, the reaction mixture, after pouring into ice and water, was separated and washed with water ten times, stirred with water for 45 min, and washed twice more. Even though no alkali was used in the work-up, the composition of the undistilled product was nearly the same as above; by g.l.p.c.: 53%3, 11%4, 14%5plus 6, and 18% ethyl α -chlorobutyrate; by n.m.r.: 60%3 + ethyl α -chlorobutyrate, 21%4, 9%5, and 6%6.

Reaction of (Trichloromethyl)vinylcarbinol (7) with Phosphorus Pentachloride

To 3.5 g (0.02 mol) of 7 in 13 ml of dry ether at 0° was

added a slurry of 8.3 g (0.04 mol) of phosphorus pentachloride suspended in 12 ml of dry ether over a 30 min period under the same conditions as in the reaction of 2 above. There was obtained 2.4 g (60% yield) of material prior to distillation, and its n.m.r. spectrum showed it to be 97% trans-1,1,1,4-tetrachloro-2-butene (9). Distillation gave 1.8 g (48%) of 9: b.p. $85-88^{\circ}$ (21 mm) (lit. (11) b.p. 76-78° (15 mm)). The i.r. was identical with that in the literature (11). The n.m.r. (CCl₄) spectrum showed two narrow complex multiplets at δ 6.42 and 4.15 in the ratio of 1:1 (lit. (12) δ 6.4 (s), 4.1 (m)). The material gave proper elemental analyses for carbon, hydrogen, and chlorine.

Catalytic Rearrangement of 9 to 10

A small amount of 9 was injected through a septum into an 8 mm glass U tube packed with copper beads (2 mm diameter) and immersed in a Wood's metal bath (220°). Using nitrogen as a carrier gas, 81% of 10 was collected. No isomerization occurred with sand (Fisher Scientific sea sand) replacing copper. An analytical sample of 10, 1,1,3,4-tetrachloro-1-butene, was obtained by collection from the Apiezon g.l.p.c. column. The retention time was 8 min at 125°. Spectral data: i.r. of stronger bands (neat) 3040-2940 (w), 1615 (s), 1440, 1425, 1285, 1205, 1165, 1040, 930, 905 (s), 885 (s), 835 (s), 750, 710, and 625 cm⁻¹; n.m.r. (CCl₄) δ 6.02 (1 H, d, J = 9.7 Hz, --CH=), 5.05-4.65 (1 H, m, -CHCl-), multiplet of four peaks at 3.79, 3.77, 3.71, and 3.64 (2 H, m, ClCH₂-). The n.m.r. spectrum is essentially the same as that reported by Colonge and Ducarre (12) for their 60% pure sample of 10.

Anal. Calcd. for $C_4H_4Cl_4$: C, 24.77; H, 2.08; Cl, 73.15. Found: C, 24.91; H, 1.97; Cl, 73.04.

Reaction of Ethynyl(trichloromethyl)carbinol (11a)

with Phosphorus Pentachloride

To 19.2 g ($\overline{0}$.11 mol) of 11*a* dissolved in 60 ml of benzene (stirred and cooled in ice) was added (1 h) a slurry of 47 g (0.225 mol) of phosphorus pentachloride in 40 ml of benzene. After 1 h stirring at 25°, the mixture was poured into ice and the benzene layer was washed (10% sodium carbonate solution, then water), dried (MgSO₄), concentrated, and distilled (b.p. 76-81° (26 mm)) giving 4.5 g of a mixture consisting of 5% 3,4,4,4-tetrachloro-1.2butyne (12*a*) (1% yield), 85% 1,4,4,4-tetrachloro-1,2butadiene (13*a*) (17% yield), and 10% of other compounds (by g.l.p.c. analysis (silicon fluid column at 140°) and n.m.r.). Compounds 12*a* and 13*a* had apparent retention times of 10.7 and 12.3 min respectively; the latter retention time was that of 15*a*, isomerization having occurred. The residue from the distillation of the crude material solidified on cooling, and after recrystallization from cyclohexane, 3.4 g (16%) of tris(1,1,1-trichloro-3-butyne-2-ol) phosphate (14) was obtained, m.p. 79-80°.

Adding 13 g (0.075 mol) of the carbinol 11*a*, dissolved in 10 ml of benzene, to 31.2 g (0.15 mol) of phosphorus pentachloride suspended in 30 ml of benzene under the above conditions gave 4.6 g of volatile material, b.p. 85–90° (28 mm). G.I.p.c. and n.m.r. analyses showed it to be a mixture of 12*a* (7% yield) and 13*a* (21% yield) with about 10% of impurities. The sample of 12*a* for analysis was prepared by this procedure. No phosphate ester (14) could be obtained from the residue.

Spectral and analytical data on 3,4,4,4-tetrachloro-1butyne (12a) purified by g.l.p.c.: i.r. of stronger bands (neat) 3300, 2940, 2130, 1210, 965, 815, 735, 665, and 610 cm⁻¹; n.m.r. (CDCl₃) δ 5.17 (1 H, d, J = 2.3 Hz, --CHCl---), 2.84 (1 H, d, J = 2.3 Hz, HC==); mass spectrum (70 eV), M/e very weak molecular ion peaks at 190 and 192.

Anal. Calcd. for $C_4H_2Cl_4$: C, 25.03; H, 1.05; Cl, 73.92. Found: C, 25.06; H, 1.11; Cl, 73.65.

Spectral and analytical data on 1,4,4,4-tetrachloro-1,2butadiene (13a) of 85% purity obtained by distillation: i.r. of stronger bands (neat) 3290, 3145, 1955, 1345, 1225, 1130, 1110, 850, 805, 775, 755, 695, and 600 cm⁻¹; n.m.r. (CCl₄) δ 6.59 (1 H, d, J = 5.5 Hz, ClCH=), 6.21 (1 H, d, J = 5.5 Hz, =CH--CCl₃); the mass spectrum (70 eV) showed the molecular ion isotopes as a cluster at M/e(relative intensity) 190 (100), 192 (125), 194 (52), 196 (13), and 198 (1). Molecular ion peaks for this compound are much stronger than for 12a, but not as strong as for 15a.

Anal. Calcd. for $C_4H_2Cl_4$: C, 25.03; H, 1.05; Cl, 73.92. Found: C, 25.30; H, 1.22; Cl, 73.64.

Spectral and analytical data on *tris*(1,1,1-*trichloro-3-butyne-2-ol*)*phosphate* (14): i.r. of stronger bands (KBr) 3290, 2935, 2135, 1280, 1070, 1030, 970, 910, 825, 800, and 670 cm⁻¹; n.m.r. (CCl₄) δ 5.50 (1 H, d of d, J = 8.2 Hz, J' = 2.1 Hz, > CH—CCl₃), 2.83 (1 H, d of d, J = 1 Hz, J' = 2.1 Hz, HC=).

Anal. Calcd. for C₁₂H₆Cl₉O₄P: C, 25.54; H, 1.07; Cl, 56.55. Found: C, 25.30; H, 1.10; Cl, 56.35.

Rearrangement of 13a to 15a

This occurred quantitatively during g.l.p.c. analyses regardless of the column employed. It was accomplished on a preparative scale over an alumina catalyst (Fisher activated alumina, 8–14 mesh) at 218° using the glass U tube apparatus described above for the isomerization of 9 to 10. The isomerization was nearly 100%. The analytical sample of 1,1,3,4-tetrachloro-1,3-butadiene (15a) was purified by g.l.p.c. (silicon fluid column at 140°); i.r. of stronger bands (neat) 3080, 3035, 1615, 1585, 1255, 1115, 935, 905, 825, and 660 cm⁻¹; n.m.r. (CDCl₃) δ 6.60 (1 H, s), 6.36 (1 H, s); the mass spectrum (70 eV) showed the molecular ion isotopes as a cluster at *M/e* (relative intensity) 190 (100), 192 (126), 194 (62), 196 (12), 198 (1). Anal. Calcd. for C₄H₂Cl₄: C, 25.03; H, 1.05; Cl, 73.92.

Found: C, 25.30; H, 1.15, Cl, 74.10.

Reaction of 1,1,1-Trichloro-3-nonyn-2-ol (11b)

with Phosphorus Pentachloride

To 7.3 g (0.03 mol) of 11b dissolved in 25 ml of benzene (stirred and cooled in ice) was added (30 min) a slurry of 12.5 g (0.06 mol) of phosphorus pentachloride in 15 ml of benzene. After 1 h stirring at 25°, the mixture was poured into ice and neutralized with 20% potassium hydroxide solution. The benzene layer was washed, dried and concentrated as before to yield 6.6 g of a crude product. Distillation was difficult because the material foamed, but was accomplished using Dow defoamers A and Q. There was obtained 2.9 g of a mixture distilling between 147-149° (22 mm). G.l.p.c. analysis (silicon fluid column at 195°) and its n.m.r. spectrum showed the mixture to consist of 60% 1,1,1,2-tetrachloro-3-nonyne (12b) (22% yield) and 35% 1,1,1,4-tetrachloro-2,3-nonadiene (13b) (13% yield). 12b and 13b had apparent retention times of 27 and 21 min respectively; the latter retention time was that of 15b, isomerization having occurred.

Spectral and analytical data on 1,1,1,2-tetrachloro-3nonyne (12b) purified by g.l.p.c., first on the silicon fluid column at 195° (some decomposition), then on silicon gum rubber at 155°; i.r. of stronger bands (neat) 2960,

Can. J. Chem. Downloaded from www.nrcresearchpress.com by WA STATE UNIV LIBRARIES on 11/21/14 For personal use only.

2022

2935, 2860, 2240, 1460, 1285, 1210, 845, 815, 780, 750, 730, and 612 cm^{-1} ; n.m.r. (CCl₄) δ 5.05 (1 H, t, J = 2 Hz, -CHCl-), 2.30 (2 H, m, $-CH_2C\equiv$), 1.43 (6 H, m, CH_3 — CH_2 — CH_2 — CH_2 —), 0.92 (3 H, poorly resolved triplet, CH_3 —); the mass spectrum (70 eV) showed the molecular ion isotopes as a cluster at M/e (relative intensity) 260 (100), 262 (136), 264 (68), 266 (14), and 268 (1).

Anal. Calcd. for C9H12Cl4: C, 41.26; H, 4.62; Cl, 54.12. Found: C, 41.50; H, 4.47; Cl, 53.85.

Spectral data on 1,1,1,4-tetrachloro-2,3-nonadiene (13b) obtained on a distilled sample consisting of 35% 13b and 60% 12b: i.r. (neat) 1970 cm⁻¹ (allene); n.m.r. (CCl₄) δ 6.16 (1 H, t, J = 2.6 Hz, =C=CH-).

Rearrangement of 13b to 15b

This could be carried out at 220-225° over sand (preferred), a sand-copper powder mixture, or alumina using the glass U tube apparatus described above for the isomerization of 9 to 10. The analytical sample of 1,1,3,4-tetrachloro-1,3-nonadiene (15b) was prepared and purified by g.l.p.c., first on the silicon fluid column at 195° (retention time = 21 min), and then reinjected on the Apiezon column at 170° (retention time = 19 min); i.r. of stronger bands (neat) 3030, 2960, 2930, 2860, 1590, 1460, 1370, 1265, 1110, 930-910, 850, 820, 750, and 675-655 cm^{-1} ; n.m.r. (CCl₄) δ 6.50 and 6.34 (1 H, singlets in ratio of 3.5:1, *cis* and *trans* -CH=?), 2.53 (2 H, m, $-CH_2-CCI=$), 1.43 (6 H, m, $-CH_2-CH_2-CH_2-$), 0.92 (3 H, poorly resolved triplet, CH_3); the mass spectrum (70 eV) showed the molecular ion isotopes as a cluster at M/e (relative intensity) 260 (100), 262 (129), 264 (57), 266 (12), and 268 (1).

Anal. Calcd. for C9H12Cl4: C, 41.26; H, 4.62; Cl, 54.12. Found: C, 41.48; H, 4.40; Cl, 53.93.

1,1-Dichloro-1-nonen-3-yne (16)

Can. J. Chem. Downloaded from www.nrcresearchpress.com by WA STATE UNIV LIBRARIES on 11/21/14 For personal use only.

This was formed in 5% yield during g.l.p.c. of 12b on the silicon fluid column at 195°. The column effluent was collected and reinjected on the Apiezon column at 170°; the retention times of 12b and 16 on this latter column were 18 and 6 min respectively. Spectral and analytical data on 16: i.r. (neat) 3030, 2960, 2930, 2850, 2210, 1580, 1460, 1275, 1170, 940–925, 825, 725, and 655 cm⁻¹; n.m.r. (CCl₄) δ 5.85 (1 H, t, J = 2 Hz, \equiv C–CH=), 2.33 (2 H, m, $-CH_2-C\equiv$), 1.43 (6 H, m, $-CH_2-CH_2 CH_2$ —), 0.93 (3 H, poorly resolved triplet, CH_3 —); the mass spectrum (70 eV) showed the molecular ion isotopes as a cluster at M/e (relative intensity) 190 (100), 192 (58), 194 (8).

Anal. Calcd. for CyH12Cl2: C, 56.57; H, 6.33; Cl, 37.10. Found: C, 56.30; H, 6.06; Cl, 36.80.

Compound 16 was also obtained in about 10% yield by passage of the vapors of 12b over alumina at 225°.

- 1. SH. MAMEDOV, G. YA. LERNER, and D. N. KHYDYROV. Zh. Obshch. Khim. 34, 53 (1964); Chem. Abstr. 60, 13172 (1964).
- D. CLARK, H. M. POWELL, and A. F. WELLS. J. Chem. Soc. 642 (1942).
- 3.
- D. S. PAYNE. J. Chem. Soc. 1052 (1953). W. GERRARD and R. J. PHILLIPS. Chem. Ind. 4. (London), 540 (1952).
- E. L. MUETTERTIES and R. A. SCHUNN. Quart. Rev. 5. Chem. Soc. 20, 245 (1966).
- R. D. COOK, P. C. TURLEY, C. E. DIEBERT, A. H. 6. FIERMAN, and P. HAAKE, J. Am. Chem. Soc. 94, 9260 (1972).
- C. K. INGOLD. Structure and mechanism in organic chemistry. Cornell University Press, Ithaca, N.Y. 1953. p. 392.
- H. L. GOERING and F. H. MCCARRON. J. Am. Chem. Soc. 78, 2270 (1956).
- M. MURAKAMI and Y. SASAKI. Mem. Inst. Sci. Ind. 9. Research, Osaka Univ. 10, 181 (1953); Chem. Abstr. 49, 6864 (1955).
- 10. S. M. MCELVAIN and C. L. STEVENS. J. Am. Chem. Soc. 69, 2667 (1947); W. GERRARD and P. L. WYVILL. Res. Appl. Ind. 2, 536 (1949); Chem. Abstr. 44, 2440 (1950).
- 11. J. COLONGE and G. LARTIGAU. JUSTUS Liebigs Ann. Chem. 684, 10 (1965).
- J. COLONGE and M. DUCARRE. C.R. Acad. Sci. 261, 5141 (1965).
- S. L. SHAPIRO, H. SOLOWAY, and L. FREEDMAN. J. 13. Am. Chem. Soc. 77, 4874 (1955); D. C. BISHOP, S. C. R. MEACOCK, and W. R. N. WILLIAMSON. J. Chem. Soc. C, 670 (1966).
- 14. J. H. SAUNDERS. Organic syntheses. Coll. Vol. III. Wiley, New York, N.Y. 1955. p. 416; also ref. 15.
- 15. K. N. CAMPBELL and B. K. CAMPBELL. Organic syntheses. Coll. Vol. IV. Wiley, New York, N.Y. 1963. p. 119, note 7.
- N. E. KOLOGRIVONA and V. N. BELOV. Zh. Obshch. 16. Khim. 28, 3105 (1958), from Chem. Abstr. 53, 10027 (1959); C. MOUREU and H. DESMOTS. Bull. Soc. Chim. Fr. [3], 27, 369 (1902).
- R. MOZINGO. Organic syntheses. Coll. Vol. III. Wiley, New York, N.Y. 1955. p. 687, preparation D.
- 18. H. NORMANT and J. FICINI. Bull. Soc. Chim. Fr. 1441 (1956).
- 19. A. T. MORSE and L. C. LEITCH. Can. J. Chem. 33, 6 (1955).
- 20. E. C. KOOYMAN and W. M. WAGNER. Rec. Trav. Chim. Pays-Bas, 77, 923 (1958).
- A. KIRRMANN and F. DRUESNE. Bull. Soc. Chim. Fr. 21. 1098 (1964).