mole) of p-nitrobenzaldehyde, 75 ml. of anhydrous benzene and a catalytic amount of p-toluenesulfonic acid. The solution was refluxed for 2 hours and then 30 ml. of benzene was distilled off. Cooling and crystallization gave 1.0 g. of the starting diol.

Preparation of the Monoacetates of Diols A and B.—To 1.26 g. (0.01 mole) of diol was added 2 ml. of anhydrous pyridine and 1.02 g. (0.01 mole) of acetic anhydride. The solution was heated on a steam bath for 5 minutes and cooled. Vapor phase chromatography (Silicone column, 180°) of the crude reaction mixture was then carried out and the fractions were collected and infrared spectra were taken.

Diol A gave two peaks on v.p.c. analysis which were shown to be due to the diacetate and monoacetate of the diol by their infrared spectra.

Diol B gave an almost identical v.p.c. pattern with the important exception that the monoacetate fraction was split into a distinct doublet. From these data it follows that A must be 3-*exo*-5-*exo*-tricyclo[2.2.1^{2,6}]heptane diol, and that B must be 3-*exo*-5-*endo*-tricyclo[2.2.1^{2,6}]heptane diol.

3-Keto-nortricyclene.—To 100 ml. of glacial acetic acid was added 55.0 g. (0.5 mole) of 3-hydroxynortricyclene and the solution was heated to 50°. To this was added 40.0 g. (0.4 mole) of chromium trioxide in 15 ml. of water at such a rate that the temperature did not exceed 55°. After the addition was completed, the solution was kept at 50° for 18 hours and then poured into 1 liter of water. The aqueous solution was then extracted five times with 100-ml. portions of ether and discarded. The ether extracts were neutralized with aqueous potassium carbonate, dried, and concentrated. Distillation gave 44 g. of the desired ketone, b.p. 50–55° (6 mm.). The material immediately solidified on cooling to a hard white solid. Upon exposure to the air the crystals soon became soggy and melted. A pure sample of the ketone was prepared by vapor phase chromatography (silicone–stearic acid column, 150°). The carbonyl maximum of a pure sample of the ketone was at 1753 cm.$^{-1}$ ($CHCl_3$).

3-Hydroxy-3-tricyclo[2.2.1.0^{2,6}]heptyl Formate (V).—To 1.0 g. of 3-keto-nortricyclene was added 2.0 ml. of 98–100% formic acid. Vapor phase chromatography (silicone–stearic acid column, 158°) indicated a new compound had been formed. This fraction was collected and exhibited infrared maxima at 3500 (broad), 1724 and 812 cm.$^{-1}$ in carbon tetrachloride. Since this material could not be obtained completely free from the starting ketone, a mixture of it and 3-keto-nortricyclene was collected and purified by several distillations on the silicone–stearic acid column. The composition of the mixture was calculated to be 64.2% 3-ketonortricyclene and 35.8% VI using a planimeter to measure the areas of the two peaks.

Anal. Calcd. for 64.2% C_7H_8O and 35.8% $C_8H_{10}O_3$: C, 72.24; H, 7.07. Found: C, 71.94; H, 7.24.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Reaction of Propargyl Alcohols with Thionyl Chloride[1]

BY THOMAS L. JACOBS, WALTER L. PETTY AND EUGENE G. TEACH

RECEIVED DECEMBER 22, 1959

The reaction of secondary propargyl alcohols, RCHOHC≡CH, with thionyl chloride in the presence of ethers yields larger proportions of the related chloroallenes, RCH=C=CHCl, than does the reaction in the presence of pyridine. Both the chloroallene and the propargyl chloride were usually formed. 2-Methyl-3-butyn-2-ol and 2-propyn-1-ol were also studied.

The specificity of the SNi′ mechanism which permits clean conversion of a number of allylic alcohols to rearranged allylic chlorides by formation with thionyl chloride and decomposition of chlorosulfinates in ether[2–5] suggested that chloroallenes might be formed similarly from propargyl alcohols. A preliminary report of the application of this method to 1-hexyn-3-ol has appeared.[6]

Thionyl chloride has been used by a number of workers to convert propargyl alcohols to chloride, but in most instances pyridine was present which favors production of the propargyl chloride rather than the chloroallene. Recently several t-propargyl alcohols, RR′COHC≡CH, were treated with thionyl chloride under a variety of conditions and unrearranged propargyl chlorides were never isolated.[7] Chloroallenes were the major products from highly hindered t-propargyl alcohols incapable of elimination to form enynes, but in other instances enynes were produced (especially in the presence of pyridine) and the yields of chloroallenes were reduced. Other products were also found but not identified. Two secondary propargyl alcohols were also examined.

In the conversion of allylic chlorosulfinates to rearranged allylic chlorides, the solvent diethyl ether is believed[2–5,8] to minimize competition from SN2 processes which yield unrearranged chlorides because it forms a hydrogen-bonded, non-ionic complex with hydrogen chloride.[9–11] This solvent was not convenient to use for propargyl chlorosulfinates because higher temperatures are required for their decomposition. We have therefore used higher boiling ethers as solvents and have succeeded in increasing considerably the yield of chloroallenes relative to propargyl chlorides. The results are presented in Table I. This work is incomplete, but is presented at this time in view of work in another laboratory.[7]

Diisopropyl ether was used first, but the chlorosulfinate from 1-hexyn-3-ol decomposed only slowly at the boiling point of this solvent (68°). In bis-(2-ethoxyethyl) ether (diethyl Carbitol) at 100–120° this chlorosulfinate gave about the same pro-

---

(1) Most of this work was carried out under a contract with the office of Ordnance Research, U. S. Army. Reproduction in whole or in part is permitted for any purpose of the United States Government. Much of the material is taken from the Ph.D. thesis of Walter L. Petty, May, 1958.

(2) W. G. Young, F. F. Caserio, Jr., and D. Brandon, Jr., *Science*, **117**, 473 (1953).

(3) F. F. Caserio, Jr., G. E. Dennis, R. H. De Wolfe and W. G. Young, THIS JOURNAL, **77**, 4182 (1955).

(4) R. H. De Wolfe and W. G. Young, *Chem. Revs.*, **56**, 813 (1956).

(5) F. F. Caserio, Jr., Ph.D. Dissertation, University of California, Los Angeles, 1954.

(6) T. L. Jacobs, E. G. Teach and D. Weiss, THIS JOURNAL, **77**, 6254 (1955).

(7) Y. R. Bhatia, P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 24 (1959).

(8) S. H. Sharman, F. F. Caserio, Jr., R. F. Nystrom, J. C. Leak and W. G. Young, THIS JOURNAL, **80**, 5965 (1958).

(9) A. M. Buswell, W. H. Rodebush and M. F. Roy, *ibid.*, **60**, 2528 (1938).

(10) D. R. Chesterman, *J. Chem. Soc.*, 906 (1935).

(11) T. Mounajed, *Compt. rend.*, **197**, 44 (1933).

TABLE I

REACTIONS OF PROPARGYL ALCOHOLS WITH THIONYL CHLORIDE

Alcohol	Solvent[a]	Yield of chlorides,[b] %	Allenic chloride in prod., %
n-$C_3H_7CHOHC\equiv CH$	i-Pr_2O[c]	45	~69
	DEC[a]	40	67
	Dioxane	32	52
	THF[a,d]	49	Trace
	None[c,d]	55	22
$C_2H_5CHOHC\equiv CH$	DEC[a]	38	54
	None[d]	70	21
$CH_3CHOHC\equiv CH$[e]	DEC[a]	26	59
	None[d]	80	8
$CH_2OHC\equiv CH$	n-Bu_2O[c]	49	0
$(CH_3)_2COHC\equiv CH$	DEC[a]	14	73

[a] DEC represents diethyl Carbitol, THF represents tetrahydrofuran. [b] In experiments where products were analyzed by gas chromatography yields of chlorides were usually determined from such data. [c] These experiments were carried out before gas chromatography was available. The percentage of chloroallene in the product was estimated by assuming a linear refractive index relationship for mixtures with the propargyl chloride. [d] Pyridine was present in these runs. [e] Experiments with this compound were carried out by Mr. Robert N. Johnson.

portions of allenic and acetylenic derivatives in comparable total yield more rapidly. A single run in dioxane gave a higher proportion of 3-chloro-1-hexyne in lower over-all yield, but the concentration of chlorosulfinate was slightly higher (1 M instead of 0.75 M) which makes the evaluation less certain because with allylic alcohols it was shown[5] that higher concentrations favor the unrearranged chlorides. In the presence of pyridine both the over-all yield and the acetylene/allene ratio increased.

The yields of allenic plus propargylic chlorides ranged from 32 to 45% in the absence of pyridine. The remainder of the product seemed to consist of enynes, dichlorides, colored polymeric materials and possibly conjugated dienic chlorides, but these were not examined carefully.

It is not possible at present to assess the importance for increasing the allene/acetylene ratio of complexing of hydrogen chloride with the ethers used as solvents because no information on such complexes was found. Dioxane was reported[5] to be somewhat less effective than diethyl ether in promoting rearrangement during replacement of the hydroxyl by chlorine in α- and γ-methylallyl alcohols, and the diethyl ether of ethylene glycol is intermediate in this respect. It is interesting that the last-mentioned ether gave the same specificity within experimental error at 54° as at 5°. Dioxane was reported[8] to lead to much more unrearranged chloride than other ethers in the thermal decomposition of allyl chlorosulfinate-1-C^{14}, a result attributed to a special solvent effect. Our results indicate that dioxane is not the solvent of choice for chloroallene production. As yet we have not found any combination of solvent and conditions which permits the clean formation of rearranged product that was attained with the allylic compounds.

It was important to show that the allenyl chlorides were not formed by rearrangement of the propargyl chlorides in the reaction mixture, because such a rearrangement is well known under other conditions. To this end cyclohexanol was allowed to react with thionyl chloride under the conditions used and in the presence of 3-chloro-1-hexyne. This propargyl chloride was recovered in 68% yield from the reaction mixture, and no 1-chloro-1,2-hexadiene was found. In this reaction cyclohexanol gave only 11% of cyclohexyl chloride along with cyclohexene in 58% yield.

The relative amounts of propargyl and allenyl chlorides reported in Table I represent the amounts isolated rather than the amounts formed in the reactions. It was therefore of interest to determine the relative stabilities of the two isomers under the reaction conditions. 1-Hexanol was allowed to react with thionyl chloride in diethyl Carbitol in the presence of a mixture of chlorides containing 42% of 1-chloro-1,2-pentadiene and 47% of 3-chloro-1-pentyne (the remainder being 1-chloro-1,3-pentadiene). The resulting chloride mixture contained n-hexyl chloride (85% yield), 1-chloro-1,2-pentadiene (50% recovery), 3-chloro-1-pentyne (83% recovery) and 1-chloro-1,3-pentadiene (100% recovery). The lower stability of the chloroallene suggests that the amounts of chloroallenes recorded in Table I are actually lower than the amounts formed in the reactions.

It is hoped that further increase in the chloroallene/propargyl chloride ratio can be realized and that the over-all yield of chlorides can also be increased. At present however, it is probably preferable to prepare a mixture of the desired chloroallene and its isomer by whatever method gives the maximum total yield of chlorides (*e.g.*, by reaction of the alcohol with thionyl chloride in the presence of pyridine), to rearrange this mixture by reaction with cuprous salts[6] and to remove the propargyl chloride by reaction with diethylamine[6] or by careful fractional distillation when the boiling points of the isomers are sufficiently far apart.

Most of the work was concentrated on secondary propargyl alcohols, $RCHOHC\equiv CH$, because a single early run indicated that propargyl alcohol itself did not give rearrangement, and yields with simple tertiary propargyl alcohols were very low. A result with 2-methyl-3-butyn-2-ol is reported in Table I. The chlorosulfinate of 3-methyl-1-pentyn-3-ol was also prepared and decomposed in dioxane, but a gas chromatogram indicated that sixteen compounds were produced and that the chloroallene was formed in very low yield.

It is not possible at this time to give a precise picture of the S_Ni mechanism believed responsible for the formation of chloroallenes from propargyl chlorosulfinates. The careful work of Young and his collaborators[2-5,8] with allylic compounds makes it appear probable that alkyl-oxygen ionization to an intermediate ion pair is the rate-determining step in all of the reactions of allylic chlorosulfinates and that the rearranged chlorides arise by collapse of a rigidly-oriented ion pair. A concerted cyclic process is even less likely with the propargyl esters because in the allyl chlorosulfinates the chlorine can be brought within easy bonding distance of the γ-carbon of the allylic system if "normal" bond angles and distances are preserved, but in propargyl chlorosulfinates the chlorine cannot be brought closer than the center of the carbon–carbon triple bond in this way. Furthermore the marked change in the acetylene/allene ratio as the carbinol carbon is varied from primary to secondary to tertiary suggests an ion-pair process rather than a cyclic one, although the data are far from sufficient to establish this with certainty.

Recent work by Landor and Taylor-Smith[12] established that the rearrangement of a *t*-propargyl chlorosulfinate is stereospecific, but the extent of the stereospecificity is uncertain. As with the allylic compounds, this can be explained on the basis of either the concerted cyclic mechanism or the rigidly-oriented ion-pair mechanism. It is not surprising that the propargyl chlorosulfinates are more stable than the corresponding allylic esters because acetylenic groups are far less electron donating than olefinic groups and should make the alkyl–oxygen ionization less facile.

Further work is planned to examine the mechanism of the reaction and to attempt to increase both the yield and the allene/acetylene ratio. It is expected that the greater stability of chlorosulfinates of propargyl alcohols as compared with the corresponding allylic derivatives will permit a study of these chlorosulfinates in the absence of hydrogen chloride.

Experimental Part

The distilling columns used in this work were two glass helix-packed, total-condensation, Whitmore–Fenske columns (1.4 × 45 cm. and 2.0 × 75 cm.) and a Trubore concentric tube type, 9.5 mm. i.d., 85 cm. in length. All boiling points are uncorrected unless otherwise stated. Infrared spectra were determined with a Perkin–Elmer model 21 spectrophotometer using a sodium chloride cell and prism, cell thickness of 0.03 mm. and neat sample unless otherwise stated.

Propargyl alcohol was obtained from the General Aniline and Film Corporation and distilled through the 45-cm. column in the presence of about 1% of succinic acid[13] before use.

1-Hexyn-3-ol was prepared by the addition of *n*-butyraldehyde to sodium acetylide in liquid ammonia in 50–55% yield.[14] The product was distilled through the 45-cm. column, b.p. 73–74° at 50 mm., $n^{25}\mathrm{D}$ 1.4340 (material used in earlier work) and after 3.5 years redried and redistilled through the same column, b.p. 56° at 15 mm., $n^{26}\mathrm{D}$ 1.4352.

1-Pentyn-3-ol was prepared similarly from propionaldehyde and sodium acetylide in 48% yield, b.p. 52.4–52.6° at 35 mm. (45-cm. column), $n^{25}\mathrm{D}$ 1.4320, d^{25}_4 0.8834, $MR\mathrm{D}$ (obsd.) 24.69, $MR\mathrm{D}$ (calcd.) 24.81; reported[15,16] b.p. 121–124° at 750 mm., 124–126°, $n^{20}\mathrm{D}$ 1.43447, d^{20} 0.8851.

3-Butyn-2-ol[17] was carefully redistilled through the 75-cm. column in the presence of a little succinic acid. After a small forerun which contained a little water, the bulk of the material came over sharply at 47.5° (51 mm.).

2-Methyl-3-butyn-2-ol and 3-methyl-1-pentyn-3-ol[18] were dried over Drierite and distilled through the 45-cm. column, b.p. 103.5–103.6° (750 mm.), $n^{25}\mathrm{D}$ 1.4198, and b.p. 121.2–121.4°, $n^{25}\mathrm{D}$ 1.4298, respectively.

Solvents and Reagents.—Thionyl chloride (Eastman Kodak Co., white label) was distilled through the 45-cm. column, b.p. 76.2° (755 mm.), sealed under reduced pressure in glass in amounts needed for each reaction, and stored in the refrigerator. Pyridine (Eastman Kodak Co. white label, Karl Fischer grade) was used without further purification. 1-Hexanol (Eastman Kodak Co. pract.) was distilled through the 45-cm. column, b.p. 155.8–156.0° (747 mm.), $n^{25}\mathrm{D}$ 1.4168. Cyclohexanol (Eastman Kodak Co. white label) was used without further purification. Mallinckrodt anhydrous ethyl ether (analytical reagent grade) was used without further purification. Technical grade isopropyl ether was refluxed for 10 hours over lithium aluminum hydride and distilled through the 75-cm. column, b.p. 68.4–68.5°, $n^{27}\mathrm{D}$ 1.3657, and stored over sodium wire. Technical grade dioxane was purified by the method of Fieser,[19] then refluxed 3 days over sodium and distilled through the 75-cm. column, b.p. 101.4° (754 mm.), $n^{25}\mathrm{D}$ 1.4217. Technical grade bis-(2-ethoxyethyl) ether (diethyl-Carbitol, Carbide and Carbon Chemicals Co.) was treated like dioxane. Sodium metal attacks this ether at its boiling point and it was necessary to redistil the material that had been distilled from sodium to remove a low-boiling ingredient. The material used had b.p. 188.2–188.3° (751 mm.). Tetrahydrofuran (Eastman Kodak Co. white label) was dried with lithium aluminum hydride overnight and distilled from an all-glass apparatus with careful exclusion of moisture. *n*-Butyl ether (Eastman Kodak Co. practical grade) was dried over calcium chloride and distilled from an ordinary flask, b.p. 140–142°.

Analytical Method.—All products from the thionyl chloride reactions except those obtained before gas chromatography was available were analyzed as follows: A sample of the volatile material, after washing as described in the next section, was chromatographed on a 2-meter column packed with didecyl phthalate-on-fire-brick, using helium as the carrier gas. The components were separated cleanly on this column and the peaks were triangular, so peak areas were obtained by multiplying the height by the width at half-peak height. These widths were proportional to retention times, and with the very narrow peaks it was more accurate to use the retention times to calculate areas. Known mixtures were used to establish the validity of the method. The average relative error was about 3%. In most experiments, after the gas chromatogram was completed, the bulk of the crude product was fractionally distilled and the individual components identified by their infrared spectra.

The Reaction of 1-Hexyn-3-ol with Thionyl Chloride.—A mixture of 45.5 g. (0.382 mole) of thionyl chloride and 440 ml. of diethyl Carbitol was cooled to 2° and treated with stirring with 34.0 g. (0.347 mole) of 1-hexyn-3-ol diluted with 60 ml. of solvent during 40 minutes. No rise in temperature was observed. The reaction mixture was stirred at 0° for an additional hour and then raised to room temperature during 1 hour. Ice-water was circulated through the reflux condenser and the reaction mixture was raised to 90° during 50 minutes. At this point the mixture was quite dark and began to evolve sulfur dioxide. The temperature was maintained between 100° and 120° for 1.5 hours. The system was then slowly put under aspirator pressure *via* a Dry Ice trap, and water at 40–50° was circulated through the reflux condenser. In this way the volatile chlorides passed through the condenser while the diethyl Carbitol refluxed into the reaction vessel. After all of the volatile material had been collected it was washed twice with sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and analyzed by gas chromatography as described above, which indicated that the combined yield of 1-chloro-1,2-hexadiene and 3-chloro-1-hexyne was 40% and that 67% of this was the allene. Fractional distillation of the mixture through the 45-cm. column gave a series of fractions boiling from 32–36° (120 mm.) (mainly enyne) to 52–56° (40 mm.) (mainly 1-chloro-1,2-hexadiene). These fractions were analyzed for the chloroallene and propargyl chloride by an infrared spectral method which indicated that the ratio of total allene to total acetylene was approximately 64/36, in good agreement with the gas chromatography values. The

---

[12] S. R. Landor and R. Taylor-Smith, *Proc. Chem. Soc. London*, 154 (1959).

[13] J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, p. 106.

[14] G. F. Hennion and J. J. Sheehan, THIS JOURNAL, **71**, 1964 (1949).

[15] F. C. McGrew and R. Adams, *ibid.*, **59**, 1497 (1937).

[16] Yu. S. Zal'kind and I. M. Gverdtsiteli, *Zhur. Obshcheĭ Khim.*, **9**, 971 (1939); *C. A.*, **33**, 8569 (1939).

[17] We wish to thank the Badische Anilin and Soda-Fabrik A. G. for the gift of a generous supply of this alcohol.

[18] We wish to thank the Air Reduction Co. for the gift of generous samples of these alcohols.

[19] L. F. Fieser, "Experiments in Organic Chemistry," third edition, D. C. Heath and Co., New York, N. Y., 1955, pp. 284–285; K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938); E. Eigenberger, *J. prakt. Chem.*, **130**, 75 (1931).

composition of a fraction containing only the chloroallene and the propargyl chloride as determined by these methods or by assuming a linear relationship between the refractive indices was the same within 5%. Separation of pure 1-chloro-1,2-hexadiene from these fractions by further distillation was difficult and the diethylamine treatment described earlier[6] is preferable. The fraction b.p. 52–56° (40 mm.) was found by gas chromatography to contain 8% 3-chloro-1-hexyne, 83% 1-chloro-1,2-hexadiene and 9% of a third material tentatively identified as 1-chloro-1,3-hexadiene on the basis of spectral data.

A similar run was carried out with 53.0 g. (0.445 mole) of thionyl chloride, 36.3 g. (0.37 mole) of 1-hexyn-3-ol and 300 ml. of dioxane, addition time 1 hr. (no further stirring at 0° or room temp.), slow heating to reflux during 2 hr., and refluxing for 5 hr. The reaction mixture was poured onto 500 ml. of ice and extracted with three 50-ml. portions of methylene chloride. The methylene chloride solution was washed with sodium bicarbonate solution, dried, concentrated and the product analyzed as described, to give the results reported in Table I.

To 34.0 g. (0.347 mole) of 1-hexyn-3-ol and 27 g. (0.34 mole) of pyridine in 250 ml. of tetrahydrofuran was added during 30 minutes 45.5 g. (0.382 mole) of thionyl chloride with stirring and cooling in an ice-bath. The reaction mixture was allowed to come to room temp. during 21 hr. with stirring, refluxed 3.5 hr., the solvent removed through a Vigreux column and the residue poured onto ice. The mixture was extracted with methylene chloride, the extract washed thoroughly with water and sodium bicarbonate solution, dried and distilled to give 16.3 g. (40%) of 3-chloro-1-hexyne, b.p. 45.3–46.5° (48–49 mm.) (45-cm. column) and an additional 3.7 g. (9%) containing small amounts of 1-chloro-1,2-hexadiene. The largest fraction (13.9 g.) was collected at 46.2–46.5° (48 mm.), n^{25}_{D} 1.4358. The infrared spectrum was reported earlier.[8]

The reaction of 1-pentyn-3-ol with thionyl chloride in diethyl Carbitol was carried out as described for the 6-carbon alcohol. After analysis by gas chromatography (Table I), the product was distilled through the 45-cm. column to give a series of fractions boiling from 58° (195 mm.) to 82° (100 mm.). Three fractionations through the 85-cm. column gave a low yield of pure 1-chloro-1,2-pentadiene, b.p. 50.0–50.2° (95 mm.), n^{25}_{D} 1.4625, d^{25}_{4} 0.9636, MR_{D} (obsd.) 29.29, MR_{D} (calcd.) 29.66.[20]

Anal. Calcd. for C_5H_7Cl: C, 58.54; H, 6.88; Cl, 34.57. Found: C, 58.65; H, 7.16; Cl, 34.15.

The infrared spectrum of 1-chloro-1,2-pentadiene showed a strong band at 1957 cm.$^{-1}$, and no absorption at 3280 where the strong acetylenic hydrogen stretching frequency is observed for 3-chloro-1-pentyne, nor at 2130 ($C{\equiv}C$ stretching). Very weak, broad absorption in the 1700 region suggests that the sample may have undergone slight oxidation during manipulation.

1-Pentyn-3-ol (118 g., 1.4 moles) was added dropwise at 0° with stirring during 1 hr. to 177 g. (1.48 moles) of thionyl chloride containing 10 g. of pyridine; the mixture was stirred for 0.5 hr. at 0°, allowed to warm during 1.5 hr. to room temp., heated on a steam-bath for 2 hr., and vacuum transferred into a Dry Ice trap. The product was washed with satd. sodium bicarbonate solution, and dried over calcium chloride yielding 122 g. (86%) of crude product. Distillation through the 45-cm. column gave 4 fractions, the main one (71 g.), b.p. 41.0–43.3° (104 mm.), containing 86% 3-chloro-1-pentyne. On the basis of gas chromatography this run gave 55.7% of the theoretical yield of 3-chloro-1-pentyne, 14.6% of 1-chloro-1,2-pentadiene, 0.5% of a conjugated diene (probably 1-chloro-1,3-pentadiene), 0.6% of 3-penten-1-yne and 1.6% of a fraction believed to be a dichloride. Thus the yield of propargyl plus allenyl chlorides is 70.3% and the allene/acetylene ratio is 21/79. Careful refractionation of the main fraction through the 85-cm. column gave good recovery of pure 3-chloro-1-pentyne, b.p. 40.8–40.9° (94 mm.), n^{25}_{D} 1.4330, d^{25}_{4} 0.9511, MR_{D} (obsd.) 28.03, MR_{D} (calcd.) 28.16.

Anal. Calcd. for C_5H_7Cl: C, 58.54; H, 6.88; Cl, 34.57. Found: C, 58.33; H, 6.83; Cl, 34.16.

The infrared spectrum showed a characteristic strong band at 3280 cm.$^{-1}$ (acetylenic C–H stretching), a weak but very sharp band at 2130 ($C{\equiv}C$ stretching) and no absorption at 1957; the absence of carbonyl impurities was indicated by the absence of absorption between 1700 and 1800.

The reaction of 3-butyn-2-ol with thionyl chloride in diethyl Carbitol was carried out as described for the 6-carbon alcohol except that the reaction mixture was heated on a steam-bath for 135 min. instead of 100–120°. The chlorosulfinate of this alcohol appears to decompose at a lower temperature than the 5- or 6-carbon esters, and the temperature of the vapors was not observed to rise above 66°. The crude yield was only 32% and the gas chromatogram indicated that 1-chloro-1,2-butadiene and 3-chloro-1-butyne made up only 80% of the mixture; these were present in the ratio 58.5/41.5 Only one small run was made with this alcohol under these conditions, and isolation of pure 1-chloro-1,2-butadiene was not successful. The infrared spectrum of the mixture showed a medium band at 1960 cm.$^{-1}$, the correct position for allenic stretching.

The reaction of 3-butyn-2-ol with thionyl chloride in the presence of pyridine was carried out as for 1-pentyn-3-ol but on a 4.25-mole scale. Addition of the carbinol required 1 hr. and gas (a mixture of hydrogen chloride and sulfur dioxide) was evolved during most of this time. Gas evolution was complete after additional stirring for 30 minutes, warming to room temp. and stirring for 2 hr. and finally heating on the steam-bath for 30 minutes. The product after vacuum transfer and drying over anhydrous potassium carbonate weighed 290 g. (80%). Gas chromatography indicated only two components in the mixture: the propargyl chloride (92%) and chloroallene (8%). The infrared spectrum was in agreement for such a mixture, and also indicated by a very weak band at 1730 cm.$^{-1}$, the presence of a trace of carbonyl-containing impurity which was probably the result of air oxidation. The crude product was distilled through the 45-cm. column; no forerun appeared, but separation of the isomers was very poor. The allenic chloride appears to have a slightly higher boiling point than the propargyl chloride. Careful redistillation through the 85-cm. column of a fraction containing 95% 3-chloro-1-butyne gave a product that appeared to be pure on the basis of gas chromatography and infrared spectrum, b.p. 69.1° (747 mm.), n^{25}_{D} 1.4219, d^{25}_{4} 0.955, MR_{D} (obsd.) 23.65, MR_{D} (calcd.) 23.54; reported[21] b.p. 68.5°, n^{25}_{D} 1.4218, d^{25}_{4} 0.9466.

Anal. Calcd. for C_4H_5Cl: C, 54.26; H, 5.69; Cl, 40.05. Found: C, 54.03; H, 5.81; Cl, 39.58.

The infrared spectrum showed a medium band at 2120 cm.$^{-1}$ and a strong band at 3280 cm.$^{-1}$; there was no absorption at 1960 cm.$^{-1}$ nor in the 1700 region. In addition to the usual C–H absorption at 2960, 2910 and 2850, strong bands were observed at 1450, 1377, 1310, 1225, 1095, 1070, 990 and 885.

The reaction of 2-methyl-3-butyn-2-ol with thionyl chloride in diethyl Carbitol was carried out as described for 1-hexyn-3-ol. In the vacuum transfer of the volatile chlorides at the end of the reaction about half of the product proved to be non-volatile; this residue was not examined. Gas chromatography of the volatile material indicated the composition (the structural assignments are tentative except for the chloroallene and propargyl chloride): enyne, 2.5%; 3-chloro-3-methyl-1-butyne, 12.6%; conjugated chlorodiene I, 3.8%; conjugated chlorodiene II, 4.6%; 1-chloro-3-methyl-1,2-butadiene, 34.7%; dichloride, 41.5%. Distillation of the crude product through the 45-cm. column at reduced pressure gave poor separation; the supposed dichloride came over in 2 fractions boiling at 52–60° (80 mm.) and 60–63° (75 mm.) (total only 28% of crude product taken). The infrared spectrum of the 60–63° fraction suggested the presence of a terminal methylene group, possibly in $(CH_3)_2CClCCl{=}CH_2$. However a chlorine analysis indicated the impurity of the material. Calcd. for $C_5H_8Cl_2$: Cl, 51.01. Found: Cl, 46.41. This dichloride gave n^{25}_{D} 1.4580.

LOS ANGELES 24, CALIF.

---

[20] This value was obtained using a value of 3.9 for the allene system; T. L. Jacobs and W. F. Brill, THIS JOURNAL, **75**, 1314 (1953), note 23. If the value for 2 double bonds is used (3.466), MR_{D} (calcd.) is 29.22.

[21] G. F. Hennion and J. M. Campbell, *J. Org. Chem.*, **21**, 791 (1956).