972. *The Preparation of* 1-*Chloroalkyl and Vinyl Ethers*

By D. K. Black and S. R. Landor

A new general method for the preparation of 1-chloroalkyl ethers and vinyl ethers is described. Boron trichloride with acetals or mixtures of alcohols and aldehydes gives excellent yields of 1-chloroalkyl ethers, which are converted into vinyl ethers with trimethylamine. A number of new prop-2-ynyl vinyl ethers have been prepared by this method.

Vinyl ethers have been prepared by dehydrobromination of alkyl 2-bromoethyl ethers or by pyrolysis of acetals between 150 and 300°.[1,2] Duhamel[3] made butyl vinyl ether by the acid-catalysed elimination of butanol from acetaldehyde dibutyl acetal, and Brannock[4] obtained allyl vinyl ether in 48% yield by distilling acetaldehyde diallyl acetal from a small amount of phosphoric acid. However, isobutyraldehyde diallyl acetal gave only the rearrangement product, 2,2-dimethylpent-4-enal.

The new general method described here employs boron trichloride at —10° for the elimination of a molecule of alcohol from an acetal * and gives 1-chloroalkyl ethers in excellent yields. Alternatively, the alcohol and aldehyde can be converted directly into the 1-chloroalkyl ethers with excess of boron trichloride. This method has three main advantages over earlier procedures: (i) low-temperature conversion; (ii) azeotropic mixtures of ether and alcohol are not formed, the alcohol being removed as the alkyl borate; (iii) the yields of 1-chloroalkyl ethers by the direct conversion method are hardly affected by increased substitution of the reactants, whereas the yields of acetals decrease rapidly, and acetals of sterically hindered alcohols are not therefore readily accessible.

The general procedure is as follows. Either the acetal (3 equiv.) or a mixture of aldehyde (1 equiv.) and alcohol (2 equiv.) is added dropwise with stirring, under anhydrous conditions, to cooled boron trichloride (2 and 1·3 equiv., respectively, stirred for 2 hr. at 0° and at room temperature for 1—3 days), and the chloro-ether distilled *in vacuo* from the reaction mixture into a cooled trap. After fractionation the 1-chloro-ethers given in Table 1 were obtained.

Co-ordination of the acetal oxygen with the boron trichloride, followed by a four-centre rearrangement, and repeating with a second and then a third acetal molecule gives one molecule of triallyl borate and three molecules of allyl 1-chloroethyl ether. The mechanism for the direct conversion of aldehyde and alcohol into chloro-ether involves co-ordination of boron trichloride and aldehyde oxygen, followed by nucleophilic addition of alcohol and a four-centre rearrangement.

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* A number of new prop-2-ynyl acetals are described in the Experimental section.

[1] L. Claisen, *Ber.*, 1912, **45**, 3157.

[2] C. D. Hurd and M. A. Pollack, *J. Amer. Chem. Soc.*, 1938, **60**, 1905.

[3] A. Duhamel, *Bull. Soc. chim. France*, 1956, 156.

[4] K. C. Brannock, *J. Amer. Chem. Soc.*, 1959, **81**, 3379.

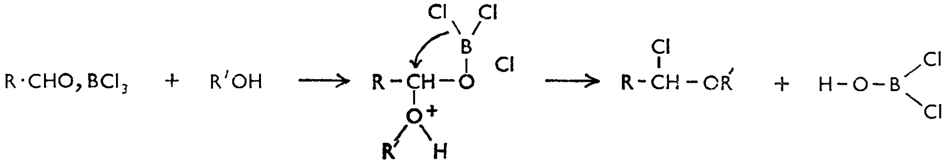
TABLE 1

Chloro-ethers

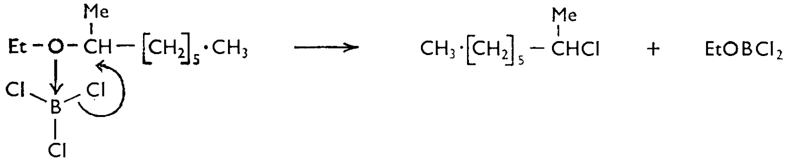
R	R′	B. p./mm.	Yield (%)	R	R′	B. p./mm.	Yield (%)
$CHCl{\cdot}Me$	Bu	80°/140	73	$CHCl{\cdot}Me$	$CMe_2{\cdot}C{\equiv}CH$	43—44°/145	37
$CHCl{\cdot}Me$	$CH_2{\cdot}CH{:}CH_2$	114—116/760	79	$CHCl{\cdot}CHMe_2$	$CHMe{\cdot}C{\equiv}CH$	86—88/130	73
$CHCl{\cdot}CHMe_2$	$CH_2{\cdot}CH{:}CH_2$	69—70/48	84	$CHCl{\cdot}CHMe_2$	$CMe_2{\cdot}C{\equiv}CH$	47—48/150	66
$CHCl{\cdot}Me$	$CH_2{\cdot}C{\equiv}CH$ *	54—55/70	71	$CHCl{\cdot}CH_2Cl$	$CH_2{\cdot}C{\equiv}CH$ *	58—59/7.6	73
$CHCl{\cdot}CHMe$	$CH_2{\cdot}C{\equiv}CH$ *	74/60	47	$CHCl{\cdot}CHCl_2$	$CH_2{\cdot}C{\equiv}CH$	50—51/5·2	66
$CHCl{\cdot}CHMe_2$	$CH_2{\cdot}C{\equiv}CH$ *	52—54/10	70	$CHCl{\cdot}CHMe_2$	$CHPr{\cdot}C{\equiv}CH$	49—50/1·7	42
$CHCl{\cdot}Me$	$CHMe{\cdot}C{\equiv}CH$	67—68/110	84				

* All prop-2-ynyl ethers contained slight impurities which could not be separated by fractional distillation, and this resulted in low carbon values in the analysis possibly caused by some addition of HCl or BCl_3 to the acetylene. However, they all gave pure vinyl ethers on elimination of HCl.

Gerrard, Lappert, and Silver [5a] found that both alkyl and allyl ethers reacted readily with boron trichloride to give fission products. They postulated co-ordination of the



ether molecule with boron trichloride followed by fission of the C–O bond in the ether–boron trichloride complex, this being favoured by electron ascession to that bond:



Fission of the 1-chloro-ethers was not observed during this work, and this can be ascribed to the presence of the α-chlorine atom. The strong electron attraction of the chlorine atom decreases the nucleophilic properties of the oxygen which are now much weaker than those of the acetal; therefore the latter co-ordinates preferentially with boron trichloride. However, Edwards, Gerrard, and Lappert [5b] have shown that prolonged pyrolysis of chloromethyl methyl ether under more extreme conditions (sealed tube, 100°, 85 hr.) than used here gives methyl chloride and di(chloromethyl) ether as fission products. However, vinyl ethers gave fission products with boron trichloride similar to those obtained by Gerrard.

Treatment of the chloro-ethers in dry diethyl ether solution at 0° with excess of anhydrous trimethylamine gave the corresponding quaternary ammonium salts as hygroscopic solids. These were decomposed by heating at 100—120° *in vacuo*, to give the vinyl ethers (Table 2) and trimethylamine hydrochloride.

TABLE 2

Vinyl ethers

R	R′	B. p./mm.	Yield (%)	R	R′	B. p./mm.	Yield (%)
$CH{:}CH_2$	$CH_2{\cdot}CH{:}CH_2$	66—68°/760	39	$CH{:}CH_2$	$CHMe{\cdot}C{\equiv}CH$	30—32°/3·2	27
	(ref. 4)			$CH{:}CH_2$	$CMe_2{\cdot}C{\equiv}CH$	78—80/760	81
$CH{:}CMe_2$	$CH_2{\cdot}CH{:}CH_2$	100/260	60	$CH{:}CMe_2$	$CMe_2{\cdot}C{\equiv}CH$	100—105/755	—
$CH{:}CH_2$	$CH_2{\cdot}C{\equiv}CH$	90—92/760	68	$CH{:}CHCl$	$CH_2{\cdot}C{\equiv}CH$	48/4·7	43
$CH{:}CHMe$	$CH_2{\cdot}C{\equiv}CH$	48—50/64	36	$CH{:}CCl_2$	$CH_2{\cdot}C{\equiv}CH$	62—63/12	42
$CH{:}CMe_2$	$CH_2{\cdot}C{\equiv}CH$	50/10	75				

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[5] (*a*) W. Gerrard, M. F. Lappert, and Silver, *J.*, 1956, 3285; (*b*) J. D. Edwards, W. Gerrard, and M. F. Lappert, *J.*, 1957, 377.

The ethers were identified by elemental analysis and infrared data. Vinyl ethers showed a C=C doublet at approximately 1620 and 1640 cm.$^{-1}$. 2-Monosubstituted-vinyl ethers show a singlet at 1680 cm.$^{-1}$ and 2,2-disubstituted-vinyl ethers a singlet in the region of 1700 cm.$^{-1}$. The characteristic C=C doublet may originate from *cis*- and *trans*-forms of the substituent R about the conjugated C–O bond; *cis*–*trans* isomerism is sterically and electronically less favoured for 2-substituted ethers. Some alkyl chloro-ethers have previously been prepared by treating mixtures of aldehydes and alcohols at 0° with dry hydrogen chloride.[6] Frazer, Gerrard, and Lappert [7a] obtained di-(1-chloroalkyl) ethers by the action of boron trichloride on a number of aldehydes. Di-(1-chloroalkyl) ethers did not react further with boron trichloride,[5b] which was ascribed to their low basic strength.

Bonner, Bourne, and McNally [7b] used the product formed from methyl α-D-glucoside and boron trichloride as a glucosylating agent. By analogy with the reaction of acyclic acetals and boron trichloride described in this Paper, methyl α-D-glucoside would be expected to form α-glucosyl chloride which then exhibits the glucosylating properties observed and which, under aqueous conditions, is hydrolysed to the parent sugar.

EXPERIMENTAL

Infrared spectra were determined on a Perkin-Elmer Infracord spectrometer for liquid films, and n.m.r. spectra on a Perkin-Elmer 40 Mc. spectrometer for 20% solutions in carbon tetrachloride with tetramethylsilane as internal standard.

n-Butyl 1-*Chloroethyl Ether*.—A mixture of n-butanol (14·8 g., 0·2 mole) and acetaldehyde (4·4 g., 0·1 mole) was added dropwise during 1 hr. to boron trichloride (11·7 g., 0·1 mole) at −10°. After stirring at 0° for 4 hr., filtration and distillation gave: (i) *n-butyl* 1-*chloroethyl ether* (3·1 g., 22·3%) (Found: C, 52·9; H, 9·5; Cl, 25·9. $C_6H_{13}ClO$ requires C, 52·8; H, 9·5; Cl, 26·0%), b. p. 80°/140 mm., $\nu_{max.}$ 1140vs (C–O–C), 1370m (*C*-Me), and no C=C bands; a 1 : 3 : 3 : 1 quartet at τ 4·35 (–CHO–), a doublet at τ 8·3 (CH_3–C), a multiplet at τ 8·3—8·8 (alkyl-chain methylenes), and a singlet at τ 9·05 (–CH_3); (ii) tributyl borate (4·4 g., 19%).

Allyl 1-*Chloroethyl Ether*.—Acetaldehyde diallyl acetal (20 g., 0·14 mole) was added dropwise with stirring to boron trichloride (10·9 g., 0·094 mole) at −10°. After leaving at −10° for 2 hr. and at room temperature for 2 days, distillation (2 mm.) gave a trap fraction (16 g.) and a polymeric residue. Distillation of the trap fraction gave *allyl* 1-*chloroethyl ether* (13·4 g., 79%), b. p. 114—116°/760 mm. (Found: C, 49·0; H, 7·5; Cl, 29·0. C_5H_9ClO requires C, 49·8; H, 7·5; Cl, 29·5%), $\nu_{max.}$ 1650s (allyl C=C).

Allyl Vinyl Ether.—Anhydrous trimethylamine (25 ml.) was added to a solution of allyl 1-chloroethyl ether (13·4 g., 0·11 mole) in dry ether (100 ml.) at 0°. After leaving at 0° for 1 hr. and at room temperature for 5 hr., filtration and washing with dry ether (50 ml.) gave a white hygroscopic solid which, when heated at 100°/2 mm., gave the impure ether (4·8 g.) collected in a trap cooled at −60°. Distillation gave allyl vinyl ether (3·6 g., 39%), b. p. 66—68°/760 mm. (lit.,[2] 65°/733mm.), $\nu_{max.}$ 1650m (allyl C=C), 1620m (vinyl C=C), and 1100vs cm.$^{-1}$ (C–O–C).

Allyl 1-*Chloro*-2-*methylpropyl Ether*.—Isobutyraldehyde diallyl acetal (28 g., 0·165 mole) and boron trichloride (12·7 g., 0·11 mole), at −10° for 3 hr. and at 20° for 1 day, gave the *product* (20·6 g., 84%), b. p. 69—70°/48 mm. (Found: C, 56·6; H, 8·2; Cl, 23·9. $C_7H_{13}ClO$ requires C, 56·6; H, 8·7; Cl, 23·9%), $\nu_{max.}$ 1650s (allyl C=C), 1100vs (C–O–C), 1360m. and 1380m (CMe_2 doublet), and 700vs cm.$^{-1}$ (C–Cl).

Allyl 2,2-*Dimethylvinyl Ether*.—Anhydrous trimethylamine (35 g.) and allyl 1-chloro-2-methylpropyl ether (20·0 g., 0·135 mole), in dry ether (100 ml.) at 0° for 3 hr. and at 20° overnight, gave a white solid (19·0 g., 82%). Heating the solid (18·0 g.) at 120°/2 mm. for 2 hr. gave the *product* (9·0 g., 60%), b. p. 100°/260 mm. (Found: C, 74·7; H, 10·6. $C_7H_{12}O$ requires C, 75·0; H, 10·7%), $\nu_{max.}$ 1650m (allyl C=C), 1700m (substituted vinyl C=C), and 1200s cm.$^{-1}$ (C–O–C).

1-*Chloroethyl Prop*-2-*ynyl Ether*.—Prop-2-ynol (324 g., 5·6 moles), anhydrous calcium chloride (40 g.), acetaldehyde (66 g., 1·5 moles) gave, after 2 days, acetaldehyde diprop-2-ynyl

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[6] H. R. Henze and J. T. Murchison, *J. Amer. Chem. Soc.*, 1931, **53**, 4077; B. H. Shoemaker and C. E. Boord, *ibid.*, 1505.

[7] (*a*) M. J. Frazer, W. Gerrard, and M. F. Lappert, *J.*, 1957, 739; (*b*) T. G. Bonner, E. J. Bourne, and S. McNally, *J.*, 1962, 761.

acetal (124 g., 81%), b. p. 60°/5 mm., $\nu_{\text{max.}}$ 3260s ($C\equiv CH$), 2110m ($C\equiv C$), and 1000—1100 cm.$^{-1}$ (C–O–C). The acetal (43·8 g., 0·32 mole) and boron trichloride (25 g., 0·21 mole), at −10° for 2 hr. and at room temperature for 2 days, gave the *product* (27 g., 71%), b. p. 54—55°/70 mm., $\nu_{\text{max.}}$ 3290s ($C\equiv CH$), 2120m ($C\equiv C$), 1110—1135vs (C–O–C), and 650—670vs cm.$^{-1}$ (C=Cl) (Found: C, 49·7; H, 6·0; Cl, 30·4. C_5H_7ClO requires C, 50·9; H, 5·9; Cl, 30·1%); a triplet at τ 7·55 and 7·65 (C=C–H), a doublet centred at τ 6·65 and 5·85 ($-CH_2C=C$), a doublet at τ 8·2 and 8·7 (*C*-Me) and a quartet at τ 4·1 and 5·0 (CH_3CH-), and triprop-2-ynyl borate (9·2 g., 50%), b. p. 65—67°/1·1 mm., $\nu_{\text{max.}}$ 3270s ($C\equiv CH$), 2120m ($C\equiv C$), 1350vs cm.$^{-1}$ (B–O stretching) (Found: C, 60·5; H, 5·2. Calc. for C_9H_9BO: C, 61·4; H, 5·1%).

Prop-2-ynyl Vinyl Ether.—Anhydrous trimethylamine (30 g.) and 1-chloroethyl prop-2-ynyl ether (12·8 g., 0·108 mole) in dry ether (100 ml.), at 0° for 5 hr. and at room temperature overnight, gave a white hygroscopic solid (14·2 g., 81%), m. p. 278—280°, $\nu_{\text{max.}}$ 3200s ($C\equiv CH$), 2110s cm.$^{-1}$ ($C\equiv C$). The solid (13·0 g., 0·003 mole), heated at 150°/2 mm. for 90 min., gave the *product*, b. p. 90—92°/760 mm. (4·4 g., 50%) (Found: C, 73·1; H, 7·2. C_5H_6O requires C, 73·2; H, 7·3%), $\nu_{\text{max.}}$ 3300s ($C\equiv CH$), 2110m ($C\equiv C$), 1620m and 1640m (C=C doublet), and 1100vs cm.$^{-1}$ (C–O–C). G.l.c. (dinonyl phthalate; 77°; nitrogen 2·0 l./hr.) gave a single peak (*t*, 7 min.).

1-*Chloropropyl Prop-2-ynyl Ether.*—Prop-2-ynol (112 g., 2·0 moles) and anhydrous calcium chloride (25 g.) (58·1 g., 1·0 mole) after shaking for 6 days, gave propionaldehyde diprop-2-ynyl acetal (36 g., 24%), b. p. 72—73°/8 mm., $\nu_{\text{max.}}$ 3280vs ($C\equiv CH$), 2110s ($C\equiv C$), 1100vs cm.$^{-1}$ (C–O–C). The acetal (36 g., 0·24 mole) and boron trichloride (18·6 g., 0·16 mole), at −10° for 1 hr. and at 18° for 24 hr., gave 1-chloropropyl prop-2-ynyl ether (15 g., 47%), b. p. 76°/60 mm.

Propenyl Prop-2-ynyl Ether.—1-Chloropropyl prop-2-ynyl ether (26·4 g., 0·2 mole) dissolved in dry ether (100 ml.) and anhydrous trimethylamine (30 ml.), at 0° for 6 hr. and at room temperature for 2 days, gave a white hygroscopic solid (32 g., 64%) which, heated at 150°/2 mm., gave the *product* (Found: C, 74·7; H, 8·3. C_6H_8O requires C, 75·0; H, 8·3%), $\nu_{\text{max.}}$ 3290vs ($C\equiv CH$), 2120m ($C\equiv C$), 1680 (C=C), and 1020s cm.$^{-1}$ (C–O–C).

1-*Chloro-2-methylpropyl Prop-2-ynyl Ether.*—Anhydrous calcium chloride (20 g.), prop-2-ynol (112 g., 2·0 moles), and isobutyraldehyde (60 g., 0·83 mole), after shaking for 12 hr. and occasionally during 3 days, gave isobutyraldehyde diprop-2-ynyl acetal[8] (91·6 g., 67%), b. p. 63—64°/3·2 mm., $\nu_{\text{max.}}$ 3300vs ($C\equiv CH$), 2120m ($C\equiv C$), 1050vs (C–O–C), and a doublet at 1360m and 1380m cm.$^{-1}$ ($-CMe_2$). The acetal (46·6 g., 0·28 mole) and boron trichloride (22 g., 0·188 mole), at 10° for 2 hr. and at room temperature for 3 days, gave: (i) the *product* (29 g., 70%), b. p. 52—54°/10 mm., $\nu_{\text{max.}}$ 3290s ($C\equiv CH$), 2120m ($C\equiv C$), 1080—1120vs (C–O–C), and 700s cm.$^{-1}$ (C–Cl) (Found: C, 56·3; H, 6·8; Cl, 23·7. $C_7H_{11}ClO$ requires C, 57·3; H, 7·51; Cl, 24·2%); (ii) triprop-2-ynyl borate (11·5 g., 70%), b. p. 75—76°/2·0 mm.

2,2-*Dimethylvinyl Prop-2-ynyl Ether.*—Anhydrous trimethylamine (35 ml.) and 1-chloro-2-methylpropyl prop-2-ynyl ether (10 g., 0·068 mole) in dry ether (100 ml.), at 0° for 6 hr. and overnight at room temperature, gave a white hygroscopic solid (10 g., 72%). Heating this solid at 160—170°/2 mm. for 1 hr. gave the *produt*, b. p. 50°/10 mm. (5·7 g., 84%) (Found: C, 76·3; H, 9·0. $C_7H_{10}O$ requires C, 76·4; H, 9·1%), $\nu_{\text{max.}}$ 3300vs ($C\equiv CH$), 2110m ($C\equiv C$), 1090vs (C–O–C), and a doublet at 1670m and 1690m (substituted C=C). G.l.c. (dinonyl phthalate; 61°; N_2 2·2 l./hr.; *t* 18 min.).

1-*Chloroethyl* 1-*Methylprop-2-ynyl Ether.*—But-3-yn-2-ol (50·0 g., 0·72 mole), calcium chloride (20 g.), and acetaldehyde (15·8 g., 0·36 mole), shaken for 4 days, gave acetaldehyde di-1-methylprop-2-ynyl acetal,[8] b. p. 45—46°/1·4 mm. (18·7 g., 31·6%), $\nu_{\text{max.}}$ 3260s ($C\equiv CH$), 2110m ($C\equiv C$), and 1880vs cm.$^{-1}$ (C–O–C). The acetal (13·0 g., 0·078 mole) and boron trichloride (6·0 g., 0·052 mole), at −10° for 3 hr. and at room temperature for 3 days, gave the *product* (8·8 g., 84%), b. p. 67—68°/110 mm. (Found: C, 53·8; H, 6·7; Cl, 26·2. C_6H_9ClO requires C, 54·3; H, 6·8; Cl, 26·8%), $\nu_{\text{max.}}$ 3300s ($C\equiv CH$), 2120m ($C\equiv C$), and 1130s (C–O–C); doublets at τ 7·55 and 7·85 (C=C–H), at τ 8·25 coupled with the 1 : 3 : 3 : 1 quartet centred at τ 4·0 (CH_3-CH-); a 1 : 1 doublet at τ 8·55 prop-2-ynyl methyl resonance, and *tri*-1-*methylprop*-2-*ynyl borate* (Found: C, 60·0; H, 6·6. $C_{12}H_{15}BO$ requires C, 60·1; H, 6·3%), $\nu_{\text{max.}}$ 3260s ($C\equiv CH$), 2100w ($C\equiv C$), and 1320vs cm.$^{-1}$ (B–O stretching).

1-*Methylprop-2-ynyl Vinyl Ether.*—Trimethylamine (20 ml.) and 1-chloroethyl 1-methylprop-2-ynyl ether (6·2 g., 0·047 mole) in dry ether (100 ml.), at 0° for 4 hr. and overnight at

[8] E. R. H. Jones, J. D. Loder, and M. C. Whiting, *Proc. Chem. Soc.*, 1960, 180.

room temperature, gave a white hygroscopic solid (6·8 g., 79%). Heating this solid at 150°/5 mm. for 1 hr. gave the *product* (1·2 g., 27%), b. p. 30—32°/3·2 mm. (Found: C, 74·9; H, 8·2. C_6H_8O requires C, 75·0; H, 8·3%), $\nu_{\text{max.}}$ 3300s (C≡CH), 2110w (C≡C), 1620m and 1640m (C=C doublet), and 1080vs cm.$^{-1}$ (C–O–C). G.l.c. (dinonyl phthalate; 85°; N_2 2·1 l./hr.) gave one main peak (*t*, 11 min.) with a single impurity (*t*, 9 min.; 2%).

1-*Chloro*-2-*methylpropyl* 1-*Methylprop*-2-*ynyl Ether*.—But-3-yn-2-ol (93 g., 1·33 moles), anhydrous calcium chloride (30 g.), and isobutyraldehyde (47·5 g., 0·66 mole), shaken for 5 days at room temperature, gave isobutyraldehyde di-1-methylprop-2-ynyl acetal[8] (34 g., 27%), b. p. 45—48°/5·0 mm., $\nu_{\text{max.}}$ 3290s (C≡CH), 2100m (C≡C), and 1100vs cm.$^{-1}$ (C–O–C). The acetal (30 g., 0·155 mole) and boron trichloride (12·1 g., 0·10 mole), at −10° for 3 hr. and at 20° for 3 days, gave the *product* (18·4 g., 74%), b. p. 86—88°/130 mm. (Found: C, 58·7; H, 7·4; Cl, 21·8. $C_8H_{13}ClO$ requires C, 59·1; H, 8·1; Cl, 22·1%), $\nu_{\text{max.}}$ 3300s (C≡CH), 2110w (C≡C), 1360m and 1380m (–CMe$_2$), and 1090s cm.$^{-1}$ (C–O–C), and tri-1-methylprop-2-ynyl borate (8·0 g., 71%).

1-*Chloroethyl* 1,1-*Dimethylprop*-2-*ynyl Ether*.—(a) *From acetaldehyde di*-1,1-*dimethylprop*-2-*ynyl acetal*. 1,1-Dimethylprop-2-ynol (100 g., 1·2 moles), with anhydrous calcium chloride (30 g.) and acetaldehyde (24·2 g., 0·55 mole), at 20° for 7 days, gave acetaldehyde di-1,1-dimethylprop-2-ynyl acetal, b. p. 64—65°/0·5 mm. (2·8 g., 3%), $\nu_{\text{max.}}$ 3280s (C≡CH), 2100m (C≡C), and 1050 cm.$^{-1}$ (C–O–C). Boron trichloride (1·2 g., 0·01 mole) in n-hexane (10 ml.) and the acetal (2·8 g., 0·0145 mole), at 0° for 30 min. and at 20° for 1 hr., gave the *product*, b. p. 38—42°/130 mm. (0·6 g., 28%), $\nu_{\text{max.}}$ 3280vs (C≡CH), 2120s (C≡CH), 1140vs (C–O–C), 650vs cm.$^{-1}$ (C–Cl), and a doublet at 1360, 1380s (CMe$_2$).

(b) *From ethyl* 1,1-*dimethylprop*-2-*ynyl acetal*. Hydrochloric acid (0·02 ml.; 30%) was added to a mixture of 1,1-dimethylprop-2-ynol (42 g., 0·5 mole) and ethyl vinyl ether (72 g., 1·0 mole) and allowed to stand at 20° for 18 hr. After treatment with anhydrous potassium carbonate and drying ($MgSO_4$), distillation gave the acetal[9] (60 g., 77%), b. p. 40°/14 mm. The acetal (23·4 g., 0·15 mole) and boron trichloride (11·7 g., 0·10 mole), at 0° for 1 hr. and at 20° for 3 hr., gave the *product* (8·1 g., 37%), b. p. 43—44°/145 mm. (Found: C, 56·9; H, 7·7; Cl, 23·9. $C_7H_{11}ClO$ requires C, 57·3; H, 7·5; Cl, 24·2%), g.l.c. (silicone oil; 50°; N_2 2·2 l./hr.) showed a main component (*t*, 8 min.; 95%) and two impurities (*t*, 2·5 and *t*, 3·5 min.), and two fractions believed to be triethyl borate, b. p. 34—44°/1·6 mm. (6 g.) and tri-1,1-dimethylprop-2-ynyl) borate, b. p. 54—56°/1·6 mm. (6·2 g.).

1,1-*Dimethylprop*-2-*ynyl Vinyl Ether*.—1-Chloroethyl 1,1-dimethylprop-2-ynyl ether (8·0 g., 0·055 mole) in dry ether (100 ml.) and anhydrous trimethylamine (30 ml.), for 2 hr. at 0° and at room temperature for 1 day, gave a white hygroscopic solid which on heating at 150°/2 mm. gave the *product* (4·9 g., 81%), b. p. 78—80°/760 mm. (Found: C, 75·8; H, 9·2. $C_7H_{10}O$ requires C, 76·4; H, 9·1%), $\nu_{\text{max.}}$ 3300s (C≡CH), 2110w (C≡C), 1110s (C–O–C), and a doublet at 1620/1640w cm.$^{-1}$ (C=C). G.l.c. (silicone oil; 54°; N_2 2·5 l./hr.) showed a major component (*t*, 10 min.) and an impurity (*t*, 11·5 min., 5%).

1-*Chloro*-2-*methylpropyl* 1,1-*Dimethylprop*-2-*ynyl Ether*.—Isobutyraldehyde (7·2 g., 0·1 mole) and 1,1-dimethylprop-2-ynol (16·8 g., 0·2 mole) with boron trichloride (11·7 g. 0·1 mole), for 3 hr. at −10° and at 20° for 12 hr., gave isobutyraldehyde di-(1,1-dimethylprop-2-ynyl) *acetal* (Found: C, 75·2; H, 9·8. $C_{14}H_{22}O_2$ requires C, 75·7; H, 9·9%), $\nu_{\text{max.}}$ 3300vs, (C≡CH), 2110m (C≡C), 1080vs (C–O–C), and a doublet at 1360/1380s cm.$^{-1}$ (CMe$_2$), and tri-(1,1-dimethylprop-2-ynyl borate (4·2 g., 49%), b. p. 106—108°/1·8 mm. The acetal (5·0 g., 0·0225 mole) and boron trichloride (1·8 g., 0·015 mole), at −10° for 3 hr. and at room temperature overnight, gave the *product*, b. p. 47—48°/150 mm. (2·6 g., 66%) (Found: C, 62·3; H, 7·7; Cl, 20·0 $C_9H_{15}ClO$ requires C, 61·9; H, 8·6; Cl, 20·4%), $\nu_{\text{max.}}$ 3300vs (C≡CH), 2110m (C≡C), 1110vs (C–O–C) 690vs (C=Cl), and a doublet at 1360/1380s cm.$^{-1}$ (–CMe$_2$). G.l.c. (silicone oil; 84°; N_2, 2·0 l./hr.) showed a single peak (*t*, 15 min.).

1-*Chloro*-2-*methylpropyl* 1-*Propylprop*-2-*ynyl Ether*.—1-Propylprop-2-ynol (16·8 g., 0·2 mole and isobutyraldehyde (7·2 g., 0·1 mole) with boron trichloride (11·7 g., 0·1 mole), at −10° for 3 hr., gave the *product* (Found: C, 64·7; H, 9·5; Cl, 18·7. $C_{10}H_{17}ClO$ requires C, 63·7; H, 9·2; Cl, 18·8%), $\nu_{\text{max.}}$ 3300vs (C≡C), 2110w (C≡C), 1090vs (C–O–C), and a doublet at 1360—1380m cm.$^{-1}$ (–CMe$_2$–). G.l.c. (silicone oil; 150°; N_2, 2·1 l./hr.) showed a major peak (95%) (*t*, 12 min.) and an impurity (*t*, 7·5 min.), and *tri*-(1-*propylprop*-2-*ynyl*) *borate* (Found: C, 72·1;

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[9] M. F. Shostakovsky and I. A. Shikhiev, *Bull. Acad. Sci. U.S.S.R.*, 1953, **6**, 1061.

H, 8·8; B, 3·8. $C_{18}H_{27}BO_3$ requires C, 71·6; H, 8·8; B, 3·6%), $\nu_{max.}$ 3300vs (C≡CH), 2110m (C≡C), and 1345vs cm.$^{-1}$ (B–O stretching).

1,2,2-*Trichloroethyl Prop-2-ynyl Ether.*—2,2-Dichloroacetaldehyde diethyl acetal (100 g., 0·545 mole),[10] prop-2-ynol (61 g., 1·09 mole), and concentrated sulphuric acid (0·1 ml.) were slowly distilled until ethanol (50 g.) had been collected. The mixture was cooled, neutralised with anhydrous potassium carbonate, and distilled, giving 2,2-dichloroacetaldehyde diprop-2-ynyl acetal (57·4 g., 38%), b. p. 60—62°/0·3 mm., $\nu_{max.}$ 3300s (C≡CH), 2120m (C≡C), 1040—1070vs (C–O–C), and 790 cm.$^{-1}$ (C–Cl). The acetal (57·4 g., 0·277 mole) and boron trichloride (21·3 g., 0·184 mole), at −10° for 2 hr. and at 20° for 24 hr., gave the *product* (34·5 g., 66%), b. p. 50—51°/5·2 mm. (Found: C, 31·6; H, 3·0; Cl, 56·1. $C_5H_5Cl_3O$ requires C, 32·1; H, 2·7; Cl, 56·6%), $\nu_{max.}$ 3280s (C≡CH), 210w (C≡C), 1120vs (C–O–C), and 790 cm.$^{-1}$ (C–Cl).

2,2-*Dichlorovinyl Prop-2-ynyl Ether.*—Anhydrous trimethylamine (50 ml.) and 1,2,2- trichloroethyl prop-2-ynyl ether (31·2 g., 0·167 mole) in dry ether (100 ml.), at 0° for 2 hr. and at room temperature for 12 hr., gave a white solid which on heating at 200°/2 mm. gave the *product* (10·6 g., 42%), b. p. 62—63°/12 mm. (Found: C, 39·1; H, 2·4; Cl, 45·4. $C_5H_4Cl_2O$ requires C, 40·0; H, 2·7; Cl, 46·6%), $\nu_{max.}$ 3300s (C≡CH), 2110w (C≡C), 740vs (C=Cl), and 1115 cm.$^{-1}$ (C–O–C).

1,2-*Dichloroethyl Prop-2-ynyl Ether.*—Prop-2-ynol (112 g., 2·0 moles), 2-chloroacetaldehyde diethyl acetal (152·5 g., 2·0 moles), and concentrated sulphuric acid (0·12 ml.) distilled for 13 hr. gave ethanol (92 ml.). Addition of anhydrous potassium carbonate and distillation gave 2-chloroacetaldehyde diprop-2-ynyl acetal (90·5 g., 52%), b. p. 124—125°/10 mm. (Found: C, 55·55; H, 5·1; Cl, 20·65. $C_8H_9ClO_2$ requires C, 55·65; H, 5·2; Cl, 20·6%), $\nu_{max.}$ 3280s (C≡CH), 2120w (C≡C), 1050vs (C–O–C), and 675 cm.$^{-1}$ (C–Cl). The acetal (56·1 g., 0·324 mole) and boron trichloride (25 g., 0·216 mole), at −10° for 2 hr. and at room temperature overnight, gave the *product*, b. p. 58—59°/7·6 mm. (Found: C, 39·85; H, 5·3, Cl, 47·4. $C_5H_6Cl_2O$ requires C, 39·2; H, 4·0; Cl, 46·4%), $\nu_{max.}$ 3290vs (C=CH), 2120s (C=C), 755s (C–Cl), 1120vs (C–O–C).

2-*Chlorovinyl Prop-2-ynyl Ether.*—Anhydrous trimethylamine (30 ml.) and 1,2-dichloroethyl prop-2-ynyl ether (36·4 g., 0·238 mole) in dry ether (150 ml.), at 0° for 3 hr. and overnight at room temperature, gave a white solid, which on heating at 150°/1 mm. for 1 hr. gave the *product* (12 g., 43%), b. p. 48°/4·7 mm. (Found: C, 51·5; H, 4·8; Cl, 30·9. C_5H_5ClO requires C, 51·55; H, 4·3; Cl, 30·45%), $\nu_{max.}$ 3300s (C≡CH), 2110m (C≡C), 1120vs (C–O–C), and 750vs cm.$^{-1}$ (C–Cl).

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WOOLWICH POLYTECHNIC, LONDON S.E.18.
[Present address (S. R. L.): FOURAH BAY COLLEGE,
THE UNIVERSITY COLLEGE OF SIERRA LEONE.]

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[10] G. Eglington, E. R. H. Jones, B. L. Shaw, and M. C. Whiting, *J.*, 1954, 1860.