Anal. Calcd. for $C_6H_8O_4$: C, 49.98; H, 5.60; neutral equivalent, 72. Found: C, 49.18; H, 5.65; neutral equivalent, 72.

The oil (above) completely freed of crystals was perhaps a hydroxycyclobutanecarboxylic acid.

Anal. Calcd. for $C_5H_8O_3$: C, 51.72; H, 6.95; neutral equivalent, 116. Found: C, 50.48; H, 6.95; neutral equivalent, 116.8.

The oil was converted into its dry sodium salt and heated with *p*-bromophenacyl bromide. The product, crystallized from 95% alcohol, melted at 145°. Its composition agreed with that calculated for a bromophenacyl ester of a hydroxycyclobutanecarboxylic acid.

Anal. Calcd. for $C_{12}H_{13}O_4Br$: C, 49.84; H, 4.15. Found: C, 49.45, 49.53; H, 3.85, 3.95.

(7) **Hydrogenation of Alcohol-Soluble Polymers.**—Crude polymer in absolute alcohol was hydrogenated (using PtO_2), distilled, and rehydrogenated until no further absorption occurred.

A fraction corresponding to hydrogenated dimer was washed with sulfuric acid, dried over sodium and separated into fractions by distillation through a good column. Physical properties and composition were determined for the first (A, 38 g.) and last (B, 25 g.) fractions as shown below.

(A) B. p. 36–38° at *ca.* 0.1 mm.; d_4^{20} 0.7858; n_D^{20} 1.4342.

(B) B. p. 38–40° at *ca.* 0.1 mm.; d_4^{20} 0.8045; n_D^{20} 1.4432.

Anal. Calcd. for $C_{12}H_{24}$: C, 85.62; H, 14.38; mol. wt., 168.2. Found: (A) C, 85.69, 85.44; H, 14.63, 14.52; mol. wt. (freezing benzene), 170.6, 171. (B): C, 85.80, 85.96; H, 14.18, 14.51; mol. wt. (freezing benzene), 172, 171.

The difference in physical properties between (A) and (B) is sufficient to suggest the presence of stereoisomers in the original dimer.

Further distillation of hydrogenated polymer gave higher boiling fractions, and a fairly sharp cut (7.5 g.) separated at 111–113° under 1–1.5 mm. had d_4^{20} 0.8537; n_D^{20} 1.4682. Analysis showed that it was hydrogenated trimer.

Anal. Calcd. for $C_{18}H_{24}$: C, 86.31; H, 13.48; mol. wt., 250.3. Found: C, 86.23, 85.75; H, 13.48, 13.52; mol. wt. (freezing benzene), 255, 251.

The hydrogenated dimer and trimer both absorbed bromine rapidly with the liberation of hydrogen bromide, and were oxidized slowly by hot alkaline permanganate.

Summary

The thermal polymerization of divinylacetylene yields an oily polymeric mixture, from which the dimer has been isolated and identified as *trans*-1,2-divinylethynyl-cyclobutane. The trimer is probably similarly a *bis*-vinylethynylcyclobutylacetylene. The isolated hydrogenated (saturated) derivatives of the dimer and trimer are described.

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The Addition of Alcohols to Vinylacetylene[1]

BY RALPH A. JACOBSON, H. B. DYKSTRA AND WALLACE H. CAROTHERS

Both acetylenic and ethylenic linkages are activated by conjugation with certain polar groups (*e. g.*, carbonyl) in such a manner that they react readily directly with alcohols. Consideration of the formula of vinylacetylene (III) suggested that the acetylenic linkage might here be similarly activated by the vinyl group or conversely the ethylenic linkage by the ethynyl group. Vinylacetylene was accordingly heated at about 105° with methanol and a little sodium methylate. Reaction occurred smoothly and a product having the composition $C_4H_4{\cdot}CH_3OH$ was obtained. In view of its origin this material might be expected to have the formula I or II.

$$\underset{\text{(I)}}{CH_2{=}C(OCH_3)CH{=}CH_2} \qquad \underset{\text{(II)}}{CH{\equiv}C{-}CH(OCH_3)CH_3}$$

Examination of its reactions showed, however, that it was V. Hydrogenation converted it to methyl *n*-butyl ether and oxidation gave a mixture of acetic and methoxyacetic acids.

$$\underset{\text{(III)}}{CH{\equiv}C{-}CH{=}CH_2} \longrightarrow \underset{\text{(IV)}}{[CH_2{=}C{=}CHCH_2OCH_3]} \longrightarrow \underset{\text{(V)}}{CH_3C{\equiv}CCH_2OCH_3}$$

The course of the reaction must therefore be interpreted as follows. The alcohol adds 1,4 to the conjugated system, giving rise to the intermediate IV, which is then rearranged by the sodium alcoholate to the acetylenic ether V. It may be recalled that hydrogen chloride similarly adds to vinylacetylene at the ends of the conjugated system, giving rise to a product analogous to IV, but this is capable of being isolated, and subsequent rearrangement follows an entirely different course involving an α,γ-shift.[2] As a matter of observation α,γ-shifts in compounds of

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[1] Paper XX in the series "Acetylene Polymers and their Derivatives." Paper XIX, THIS JOURNAL, **56**, 1167 (1934).

[2] Carothers, Berchet and Collins, *ibid.*, **54**, 4066 (1932).

type IV occur only if the terminal group (instead of OCH_3) is halogen.[3] The present case may be compared with observations recorded by Favorski:[4] monosubstituted allenes and acetylenes are rearranged to disubstituted acetylenes by heating with sodium alcoholates.

In the present reaction yields based on unrecovered vinylacetylene are good. Side reactions are not extensive; the major one consists in conversion of some vinylacetylene to resinous polymers. In some experiments a very small lower-boiling fraction of the primary product gave positive tests for acetylenic hydrogen, indicating that traces of an isomeric ether were present. There was also obtained a very small amount of product resulting from the addition of two moles of alcohol to one of vinylacetylene.

The addition of alcohols to vinylacetylene appears to be a quite general reaction. Compounds obtained in this manner are listed in Table I. The primary alcohols for the most part reacted at a good rate and gave good results. *i*-Propyl alcohol reacted quite slowly (4% conversion in six hours at 105°) while *t*-butyl alcohol was still slower. In these cases the polymerization of the vinylacetylene becomes an important competing reaction affecting the yield. With the exception of the first one all of the compounds of Table I are new. They are colorless liquids having highly characteristic odors.

TABLE I

PROPERTIES OF ALKOXY-4-BUTYNES-2

Alkoxy group	B. p., °C.	d_4^{20}	n_D^{20}	M_R Calcd.	M_R Found
CH_3O-	99.5–100	0.8496	1.4262	24.52	25.36
C_2H_5O-	119–120	.8363	1.4290	29.12	30.23
i-C_3H_7O-	132–134	.8334	1.4244	34.17	34.34
n-C_4H_9O-	161–162	.8366	1.4362	38.32	39.43
t-C_4H_9O-	125–135	.8474	1.4347	38.79	38.81
cyclo-$C_6H_{11}O-$	64 at 2 mm.	.9254	1.4745	45.82	46.24
$C_6H_5CH_2O-$	94–96 at 3 mm.	.9943	1.5271	49.04	49.51
$HOCH_2CH_2O-$	71–73 at 4 mm.	1.0152	1.4802	31.19	31.93
$CH_3OCH_2CH_2O-$	84–87 at 30 mm.	0.9294	1.4462	35.81	36.77

TABLE II

ANALYSES OF ALKOXY-4-BUTYNES-2

Alkoxy group	Empirical formula	Calcd., % C	Calcd., % H	Found, % C	Found, % H
CH_3O-	C_5H_8O	71.43	9.52	71.08	9.60
C_2H_5O-	$C_6H_{10}O$	73.57	10.20	73.80	10.38
i-C_3H_7O-	$C_7H_{12}O$	74.94	10.79	73.77	10.43
n-C_4H_9O-	$C_8H_{14}O$	76.12	11.19	75.64	11.15
t-C_4H_9O-	$C_8H_{14}O$	76.12	11.19	75.12	10.63
cyclo-$C_6H_{11}O-$	$C_{10}H_{16}O$	78.88	10.52	78.79	10.85
$C_6H_5CH_2O-$	$C_{11}H_{12}O$	82.46	7.55	82.26	7.24
$HOCH_2CH_2O-$	$C_6H_{10}O_2$	63.11	8.84	61.52	8.95
$CH_3OCH_2CH_2O-$	$C_7H_{12}O_2$	65.58	9.44	65.14	9.77

Experimental Part

Action of Methanol on Vinylacetylene.—The reaction as carried out in steel bombs involved 268 g. (5.2 moles) of vinylacetylene, 132 g. (4 moles) of methanol and 56 g. (1 mole) of sodium methylate heated for seven hours at 105°. Distillation then gave 42 g. (0.8 mole) of vinylacetylene, 33 g. (1 mole) of methanol, 227 g. of product A boiling at 99.5–100° and 2 g. of a fraction B boiling at 137–140°. The residue (127 g.) was water soluble (mostly sodium methylate) except for 58 g. of resinous polymer. The yield of fraction A (methoxy-4-butyne-2) was 61% based on unrecovered vinylacetylene and 90% on unrecovered methanol.

Fraction B apparently resulted from the addition of two moles of methanol to one of vinylacetylene: b. p. 137–140°; d_4^{20} 0.9159; n_D^{20} 1.4392.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.01; H, 10.42. Found: C, 64.23; H, 9.94.

Proof of Structure of Methoxy-4-butyne-2.—Hydrogenation of the ether in acetic acid using PtO_2 gave a quantitative yield of methyl *n*-butyl ether, b. p. 70.5–71°; d_4^{20} 0.7455; n_D^{20} 1.3728. These constants are in good agreement with those accepted by "International Critical Tables" for methyl *n*-butyl ether but quite different from those reported for methyl *s*-butyl ether.

The ether (21 g.) when oxidized with alkaline permanganate at 35–40° gave 7 g. of acetic acid and 3 g. of methoxyacetic acid. The former was identified by its boiling point and its *p*-toluidide (mixed m. p.), the latter by its boiling point (190–197°).

Methoxy-4-butyne-2 has already been described and the properties recorded[5] are in good agreement with those indicated in Table I.

Hydrogenation of Ethoxy-4-butyne-2.—This gave ethyl *n*-butyl ether of b. p. (760 mm.) 92.5–93°; d_4^{20} 0.7505; n_D^{20} 1.3820.

Summary

In the presence of sodium alcoholates alcohols add smoothly to vinylacetylene at about 100° giving ethers of the general formula $CH_3C\equiv CCH_2OR$. Nine such ethers are described.

WILMINGTON, DEL.

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(3) Carothers and Berchet, THIS JOURNAL, **55**, 2808 (1933).

(4) Favorski, *J. Russ. Phys.-Chem. Soc.*, **19**, I, 414, 553 (1887); *J. prakt. Chem.*, [2] **37**, 531 (1888); *ibid.*, **44**, 208 (1891); *Chem. Zentr.*, 1540 (1887); 242 (1888); 1201 (1888); II, 615 (1891).

(5) Yvon, *Compt. rend.*, **180**, 748 (1925); Bourguel, *Ann. chim.*, [10] **3**, 325 (1925).