

Anal. Calcd. for $C_{22}H_{16}$: C, 94.2; H, 5.7. Found: C, 94.4; H, 5.7.

The compound forms a yellow picrate, m.p. 125°.

9-Methyl-1,2,7,8-dibenzfluorene (IV).— β,β -(1,1'-Dinaphthyl)-ethylene¹⁷ (1 g.) was thoroughly mixed with anhydrous stannic chloride (1 g.). The complex, which formed readily, was a viscous gum of dark-green color. The mixture was stirred at room temperature for 2 minutes whereupon it turned brown. The complex was at once decomposed by the addition of dilute hydrochloric acid. The hydrocarbon was taken up in ether and the extract was shaken with more dilute acid to remove all stannic chloride. After evaporation of the solvent, the hydrocarbon (0.82 g.) crystallized from the solution. It was purified by dissolving in a saturated alcoholic solution of picric acid, from which deep-red needles of the picrate, m.p. 151°, were obtained. The picrate was recrystallized several times from alcohol in presence of some excess of picric acid and decomposed by passing an alcoholic solution of it through a column of alumina. The colorless solid obtained from the eluate was sublimed at 160° (0.1 mm.). The sublimate, 9-methyl-1,2,7,8-dibenzfluorene crystallized from ligroin in large, lustrous plates, m.p. 173°.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.2; H, 5.7. Found: C, 93.9; H, 5.7.

The compound turns deep-green in concentrated sulfuric acid. With *s*-trinitrobenzene it forms a di-*s*-trinitrobenzoate which crystallized from alcohol in presence of some excess of trinitrobenzene and was obtained in clusters of yellow needles, m.p. 154°.

Anal. Calcd. for $C_{24}H_{22}O_6N_6$: C, 58.2; H, 3.1; N, 11.9. Found: C, 58.7; H, 3.1; N, 11.8.

9-Methyl-1,2,5,6-dibenzfluorene (III).—To β,β -(1,2'-dinaphthyl)-ethylene (1.3 g.) was added anhydrous stannic

chloride (0.75 g.) and the resulting oily mixture stirred vigorously for 1 minute, while the color changed from deep-green to deep-purple. The complex was then decomposed by dilute hydrochloric acid, the hydrocarbon taken up in ether and shaken with more acid, the solvent partially removed and alcohol added. An amorphous, colorless solid precipitated from the solution, presumably a polymer of dinaphthylethylene. This compound could not be crystallized or sublimed; it did not form a complex with picric acid. It was removed by filtration and from the filtrate was obtained 9-methyl-1,2,5,6-dibenzfluorene (0.8 g. or 62%). This compound was purified by recrystallization of the deep-red picrate, m.p. 148°, which was decomposed by passing its alcoholic solution through a column of alumina. The solid obtained from the eluate was sublimed at 120° (0.3 mm.). The sublimate, after crystallization from alcohol, was obtained in colorless plates, m.p. 144° (Cook and Preston⁴ report a m.p. 144–145°).

Anal. Calcd. for $C_{22}H_{16}$: C, 94.2; H, 5.7. Found: C, 94.2; H, 5.5.

Dimerization.— β,β -(2,2'-Dinaphthyl)-ethylene (1 g.), when mixed with anhydrous stannic chloride (1 g.) for 1 minute at room temperature, and decomposed with dilute hydrochloric acid, extracted with ether, washed with acid and precipitated with alcohol, gave a colorless, amorphous powder, which could be reprecipitated by alcohol from a solution in benzene, giving a m.p. 165–169°.

Anal. Calcd. for $C_{44}H_{32}$: C, 94.2; H, 5.7; mol. wt., 560. Found: C, 93.9; H, 5.8; mol. wt., 521.

The hydrocarbon is soluble in benzene, sparingly soluble in alcohol and ether and does not sublime when heated *in vacuo*. It does not form a complex with picric acid or *s*-trinitrobenzene.

OXFORD, ENGLAND

[CONTRIBUTION FROM ELECTROCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

The Reactions of Vinyl Acetate with Aliphatic Hydroxy Compounds. A New Synthesis of Vinyl Ethers¹

BY ROBERT L. ADELMAN

RECEIVED NOVEMBER 25, 1952

A new reaction of vinyl acetate with primary hydroxy compounds is described. At low temperatures in the presence of mercuric salts of strong acids, vinyl ethers and acetic acid are formed. A mechanism is suggested for this reaction which postulates that vinyl acetate dissociates to give an acetylene-mercury complex and acetic acid. This mechanism satisfactorily accounts for other mercuric salt-catalyzed reactions of vinyl acetate and alcohols.

The known reactions of vinyl acetate with aliphatic hydroxy compounds may be summarized as follows: (A) In the presence of alkaline catalysts, vinyl acetate is known to be an acetylating agent for aliphatic hydroxy compounds.² (B) With strong acids as catalysts, mixtures of acetals and transesterification products are formed in low conversions.³ (C) With strong acids plus mercuric salts of strong acids as catalysts, the conversions and yields of acetals from primary aliphatic alcohols are markedly improved^{3,4} and traces of acetoxyacetals are also produced.

The acetoxyacetal was postulated as the intermediate to acetal formation.³

Our findings demonstrate that when the reaction of primary aliphatic alcohols and vinyl acetate is

(1) This work was presented at the Atlantic City Meeting of the American Chemical Society, September, 1952. See also U.S.P. 2,579,411.

(2) V. L. Hansley, U. S. Patent 2,342,612 (1944); 2,355,971 (1944).

(3) W. J. Croxall, F. J. Glavis and H. T. Neher, *THIS JOURNAL*, **70**, 2805 (1948).

(4) (a) D. D. Coffman, G. H. Kalb and A. B. Ness, *J. Org. Chem.*, **13**, 223 (1948); (b) D. T. Mowry, W. H. Yanko and E. L. Ringwald, *THIS JOURNAL*, **69**, 2358 (1947).

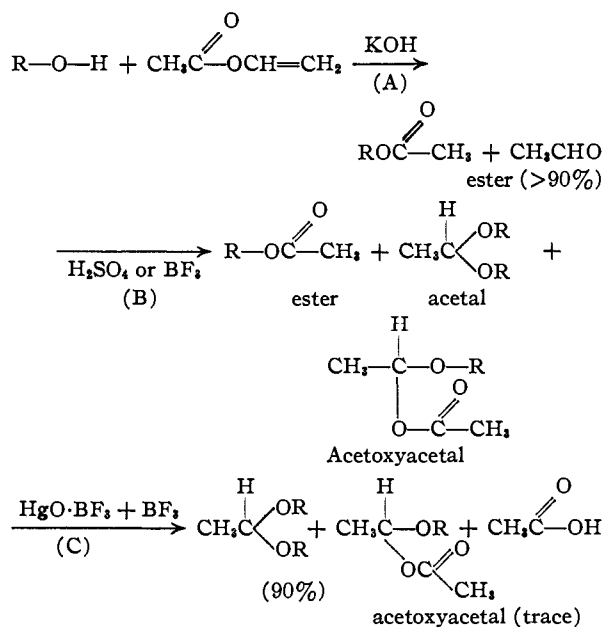
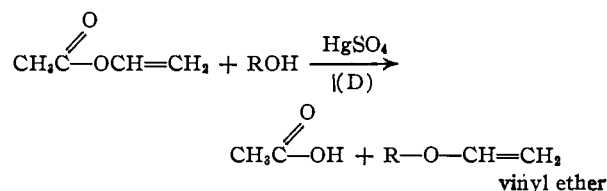


TABLE I
VINYL ETHERS FORMED BY INTERCHANGE OF HYDROXY COMPOUNDS AND VINYL ACETATE

Vinyl ethers of	Exptl. conditions ^a Temp., °C.	Time, hr.	Acetic acid formation (% when reaction stopped)	Conv., %	Yield, %	B.p., °C./ (mm.)	Refrac. index
(1) Ethanol	-22	1.75	60	8	8	35-37 (750)	1.3768 ^{20D}
	-14	0.17					
(2) Tetrahydrofurfuryl alcohol	-20	2.5	55 ^c	25	25	80-81 (45)	1.4480 ^{20D}
(3) Methyl glycolate	-22	2.5	60	40	>90	80-84 (82)	1.4236 ^{20D}
(4) 1,5-Pentanediol	-25	3 ^d	44	25	>85	92-95 (9)	1.4461 ^{21D}
						118-119 (35)	
(5) 1,5-Pentanediol (monovinyl ether)	-25	6 ^d	55	>30 ^b	..	100-101 (35)	1.4425 ^{20D}

^a The mole ratio of vinyl acetate/hydroxy compound was 6/1. The weight ratio of copper resinate/mercuric acetate/sulfuric acid was 0.006/1.8/0.5. ^b The reaction mixture was not completely worked up. ^c Actually 60% of the theoretical acetic acid by vinyl interchange had been formed after 1.5 hours at -20°. ^d Two liquid phases were present. One phase was formed as the reaction proceeded. The monovinyl ether was formed in (4), the divinyl ether in (5). 1,5-Pentanediol was the starting material in both cases.

carried out in the presence of mercuric sulfate at low temperatures (-60 to -10°) for 0.25-3.5 hours, the vinyl ether of the alcohol and acetic acid are formed. In the case of methyl glycolate, conditions were found in which these were the only reaction products formed (reaction D, also Table III, reaction (1)).



Several primary hydroxy compounds have been investigated and all those soluble in vinyl acetate were found to undergo the vinyl interchange.

In Table I are listed the vinyl ethers prepared by the interchange reaction with vinyl acetate.

In the experiments of Table I, no attempt was made to obtain maximum yields, for which considerably lower temperatures would be desirable. Acetals were often found to be by-products at -20°, and it was generally observed that the formation of acetal and acetoxyacetal compared to vinyl ether was decreased as the temperature was lowered.

This new method of preparing vinyl ethers may prove to be a useful alternative to the Reppe methods of using alcohols and acetylene, for the latter methods usually require very strong basic catalysts or the use of zinc or cadmium salts at elevated temperatures and pressures.⁵ Thus many vinyl ethers containing alkali-sensitive or heat sensitive groups may become available.

An approximate measure of the relative speed of reaction of several types of alcohols with vinyl acetate is shown in Table II. These data were obtained by shaking the alcohol with vinyl acetate, stabilizer, and catalyst at -30° in glass-stoppered flasks. The catalyst dissolved to form a homogeneous solution within ten minutes. The extent of reaction was measured by taking samples at regular intervals and measuring acetic acid formation by titration to a pH of 8.0 with dilute standard alkali. This also served as an indirect meas-

ure of vinyl ether formation. The reaction products were not isolated. However, the temperature of the reaction was low enough to consider the vinyl interchange reaction as the predominant one.⁶

TABLE II
COMPARISON OF EXTENT OF REACTION; LOW TEMPERATURE INTERCHANGE OF VINYL ACETATE WITH VARIOUS ALCOHOLS (MERCURIC SULFATE CATALYST)

Reactant ^a	Conv., ^b %	Time, hr.	Temp., °C.
<i>n</i> -Butyl alcohol	80	2	-30
Isopropyl alcohol	66	3	-30
<i>t</i> -Butyl alcohol	12	3	-30
Ethylene chlorohydrin	90	0.6	-30
Ethylene cyanohydrin	<5	4	-30
	42 ^c	60	+30
Tetramethylene cyanohydrin	34	3	-30

^a All reactants were distilled center cuts. The mole ratio of vinyl acetate/alcohol was 6/1. The weight ratio of stabilizer/mercuric acetate/sulfuric acid was 0.001/0.3/0.1. ^b Conversion was estimated by extent of acetic acid formation. ^c This value is probably a measure of acetal formation rather than vinyl ether due to the elevated temperature.

The results indicate that reaction proceeds more rapidly with a primary alcohol than with a secondary, and much more rapidly with a secondary alcohol than with tertiary. The presence of a chlorine atom in the molecule appears to increase the rapidity of reaction, while a nitrile group tends to decrease the reaction rate.

In order to determine whether the interchange was reversible the reaction of an excess of vinyl butyl ether with acetic acid in the presence of mercuric sulfate catalyst at -20° was carried out. A slow steady drop in acetic acid concentration was observed, and an approximately 50% yield of a higher boiling product, probably 1-acetoxyethyl butyl ether, was formed. Unchanged vinyl butyl ether and acetic acid were recovered from the reaction, but no vinyl acetate was found (expt. 6).

If vinyl interchange took place, some vinyl acetate should have been found, since the possibly consecutive reaction of vinyl acetate with acetic acid to form ethylidene diacetate is negligible under

(6) Lack of side reaction under these conditions was evidenced by measuring the maximum acetic acid formation at -30°, with a 6:1 ratio of vinyl acetate to methyl glycolate. As high as 92% of the theoretical amount of acetic acid for reaction D was found in the reaction solution.

(5) Brit. Patent 369,297, U. S. Patent 2,017,355; 2,017,347; 2,157,348; 2,021,869; 2,404,700.

TABLE III
 SUMMARY OF VINYL ACETATE-METHYL GLYCOLATE REACTIONS^a

Reaction conditions Temp., °C.	Time, hr.	Methyl glyco- late reco- vered, g.	Reaction products, g. ^d				Hold- up and resi- due	Remarks
			Acetic acid	Vinyl ether	Acet- oxy- acetal	Acetal		
(1) -22	2.5 ^b	50	36	35	<2	<2	8	Vinyl ether of methyl glycolate formed at low temp. Acetic acid was only other product
(2) +38	0.16 ^b	24	29	0	4	74	6	Acetal formed after short reaction period at room temperature
(3) 25	8 ^b	10	20	0	103	27	6	Acetoxyacetal formed after long reaction periods
(4) 30	16 ^c	48 ^e	..	0	15	39	9	Reaction was slow and led to mixtures with sulfuric acid alone as catalyst

^a In all cases, 90 g. (1 mole) of methyl glycolate, 516 g. (6 moles) vinyl acetate and 0.005 g. copper resinate were reactants used. ^b The catalyst was 2 g. of mercuric acetate plus 0.7 g. of sulfuric acid. ^c The catalyst was 0.7 g. of sulfuric acid only. ^d The extent of acetic acid formation was determined by titration of an aliquot of the final reaction solution with standard 0.2 *N* alkali to the phenolphthalein end-point (ice-water). The extent that other products were formed was determined by actual isolation of the pure products. ^e An undetermined amount of the acetate of methyl glycolate is also present in this fraction.

these conditions.⁷ The absence of vinyl acetate indicates that if the vinyl ester-alcohol interchange reaction (D) is reversible, the equilibrium point for (D) is far in the direction of vinyl ether formation.

The yield in grams of products under varying conditions is illustrated for methyl glycolate in Table III. The primary reaction of vinyl interchange occurs in high yields at -22° (reaction (1)).

At somewhat higher temperatures (-10 to +80°) or with longer reaction periods, the results of Croxall, Glavin and Neher³ were verified, and acetals were readily formed from vinyl acetate and alcohols in the presence of mercuric sulfate (Table III, reaction 2).

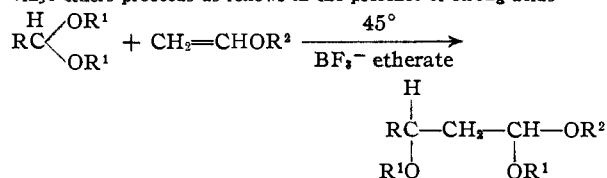
It also has been demonstrated that acetals are rapidly formed from vinyl ethers with alcohols in the presence of traces of acids at 0°.³ These data, therefore, indicate that the vinyl ether is the reaction intermediate for acetal formation.

Contrary to previous hypotheses,³ we have found that acetoxyacetal formation occurs more slowly than acetal formation under these conditions (Table III, reaction 3).⁸ This parallels the observation that the rate of addition of carboxylic acids to vinyl ethers is considerably slower than the rate of addition of simple primary alcohols to vinyl ethers.

It was also verified that the presence of mercuric sulfate (or mercuric oxide-boron trifluoride complex) is essential if acetal formation is to occur rapidly and in high yields.³ Mercuric acetate alone, or sulfuric acid alone leads to low rates and low yields of acetal under these experimental conditions (see Table III, reaction 4).

(7) R. L. Adelman, *J. Org. Chem.*, **14**, 1067 (1949).

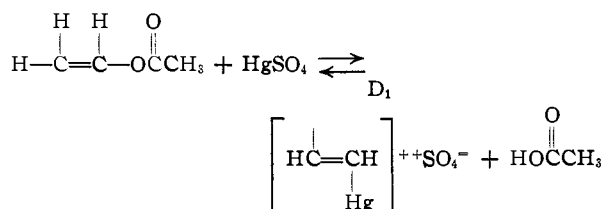
(8) According to Hoaglin and Hirsch⁹ the reaction of acetals with vinyl ethers proceeds as follows in the presence of strong acids



This reaction probably does not compete significantly with the reactions described in this paper, because of (a) the negligible free mineral acid concentration, and (b) the very low concentration of vinyl ether present at any time at temperatures above 0°.

(9) Hoaglin and Hirsch, *THIS JOURNAL*, **71**, 3468 (1949).

Proposed Mechanism.—A mechanism which readily accounts for the above data is based on the hypothesis that vinyl acetate dissociates into an acetylene-mercury complex ion and acetic acid (reaction D₁). This mechanism also appears to



explain the mercuric sulfate-catalyzed reactions of vinyloxy compounds in general.

Reaction (D₁) was originally offered to describe the course of the interchange reaction of vinyl acetate with carboxylic acids to form vinyl esters.⁷

The structure of the acetylene-mercury complex is difficult to postulate. Compounds of acetylene and mercuric chloride have been isolated and apparently identified as chlorovinyl mercuric chloride.¹⁰ However, compounds of acetylene with other mercuric salts are more unstable, not as well defined,¹¹ and considerably more active catalysts than the acetylene-mercuric chloride complex.

In reactions of acetylene with alcohols which are catalyzed by mercuric salts of strong acids, an acetylene-mercury complex¹² and vinyl ethers¹³ have also been postulated as intermediates to the formation of acetals.

For the reactions of vinyl acetate with alcohols in the presence of mercuric salts of strong acids (reactions C and D), we first assume a dissociation

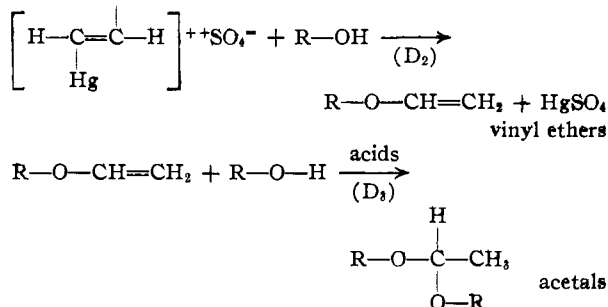
(10) P. Biginelli, *Ann. Farm. Chem.*, **16** (1898); J. S. S. Brame, *J. Chem. Soc.*, **87**, 427 (1905); D. L. Chapman and W. J. Jenkins, *ibid.*, **115**, 847 (1919); P. D. Bartlett, H. J. Dauben and L. J. Rosen, U. S. Patent 2,465,834 (1949).

(11) J. A. Nieuwland and J. A. Maguire, *J. Chem. Soc.*, **28**, 1025 (1906); K. A. Hofmann, *Ber.*, **38**, 1999 (1905).

(12) G. F. Hennion, R. R. Vogt and J. A. Nieuwland, *J. Org. Chem.*, **1**, 159 (1936); H. S. Hill and H. Hibbert, *THIS JOURNAL*, **45**, 3124 (1923); J. S. Reichert, J. H. Bailey and J. A. Nieuwland, *ibid.*, **48**, 1552 (1923).

(13) H. S. Hill and L. M. Pidgeon, *ibid.*, **50**, 2718 (1928); H. Plauson, U. S. Patent 1,436,288 (1921); Consortium für Electrochemische Industrie G.m.b.H., British Patent 231,841 (1924); H. Plauson and J. A. Vielle, British Patent 156,117 (1920).

of the vinyl acetate to form an acetylene-mercury complex and acetic acid (reaction D₁). Then analogous conditions to the acetylene-mercuric salt-alcohol reactions exist, and the acetylene-mercury complex should react with alcohols plus mercuric salts to form vinyl ethers (reaction D₂) and then acetals (reaction D₃). Thus, a series of consecutive steps would be involved in the vinyl acetate-alcohol reaction. The ex-



perimental results justify this hypothesis, and are enumerated below.

(a) The vinyl ether of methyl glycolate is formed under the mildest reaction conditions, the acetal with more difficulty,¹⁴ and the acetoxyacetal after extended reaction periods.

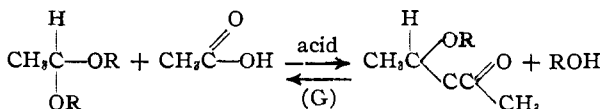
(b) The typical acid-catalyzed alcohol-ester interchange reaction does not occur readily with primary alcohols and vinyl acetate. This tends to eliminate a bimolecular acid-catalyzed interchange mechanism involving acyl-oxygen fission.¹⁵

(c) The catalyst and conditions for the alcohol-vinyl acetate interchange, followed by acetal formation are the same as those found effective for the acetylene-alcohol reaction to form acetals. This suggests that the reaction proceeds as indicated in steps D₁ and D₂. The role of mercuric sulfate is thus more readily understood in this mechanism.

(d) If a bimolecular alkyl-oxygen fission mechanism was involved in the primary step under these conditions, it would be expected that a vinyl ester-ester interchange would occur with esters capable of interchange at the alkyl-oxygen bond. Esters of inorganic acids are known to interchange by alkyl-oxygen fission, as evidenced by their ability to alkylate alcohols to form ethers. However, practically no reaction was observed between vinyl acetate and dimethyl sulfate or tributyl phosphate in the presence of mercuric sulfate under extended periods of reflux.

There are at least two possible reactions for the formation of acetoxyacetal in these systems.

One probable course for acetoxyacetal formation is an acid-catalyzed reaction between the acetal and acetic acid (reaction G).



(14) The acid-catalyzed thermal dissociation of acetals to form vinyl ethers occurs only at a much higher temperature (250-500°) (P. L. Bramwyche and M. Mugdan, U. S. Patent 2,482,725 (1949); C. E. Schildknecht, A. O. Zoss and C. McKinley, *Ind. Eng. Chem.*, **39**, 180 (1947)).

(15) I. Roberts and H. C. Urey, *THIS JOURNAL*, **60**, 2391 (1938).

This course was indicated by the decrease in acetic acid concentration during the vinyl acetate-methyl glycolate reaction, as the amount of acetal decreases, and the acetoxyacetal is formed (expt. 5, also Table III, reaction (2) *vs.* reaction (3)). Further, it was found possible to treat the acetal of methyl glycolate with acetic acid in the presence of a trace of sulfuric acid to form the acetoxyacetal of methyl glycolate in appreciable conversions (20-50%) plus the free alcohol (methyl glycolate, see expt. 4). The reaction is apparently reversible.³

Probably some acetoxyacetal is also formed by the acid-catalyzed addition of acetic acid to the vinyl ether (see expt. 6).

The facts that low yields of acetals and relatively high percentages of transesterification and olefinic by-products result from the reaction of tertiary alcohols with vinyl acetate³ may be readily explained by the existence of the vinyl ether intermediate. As shown in Table II, the rates of vinyl interchange of tertiary alcohols with vinyl acetate are very slow as compared to those of primary or secondary alcohols with vinyl acetate. If vinyl ether formation is involved in the rate-determining step for acetal formation, then it would be expected that acetals of tertiary alcohols would form more slowly than acetals of primary or secondary alcohols. Competing reactions may then become significant. A similar explanation can be offered for the formation of by-products, along with low yields of acetals, when sulfuric acid alone is used as the catalyst for the reaction of vinyl esters with alcohols (see Table II, reaction (4)).

The greater activity of primary alcohols as compared to tertiary alcohols may be understood, as this mechanism postulates the breaking of the hydrogen-oxygen bond in the alcohol.

The greater reactivity of vinyl acetate (*via* the acetylene-mercury complex) with alcohols than with carboxylic acids, which is illustrated by (a) the milder conditions for reaction (D) than for carboxylic acid-vinyl acetate interchanges,⁷ and (b) the apparent irreversibility of (D), is rather difficult to explain. However, it should be noted that the mercuric salt-catalyzed reactions of acetylene also occur more readily with alcohols than with acids.¹⁶ This parallel reactivity of acetylene and vinyl acetate is expected from the hypothesis that the acetylene-mercury complex is the intermediate for both acetylene and vinyl acetate reactions.

Experimental

The hydroxy compound studied most intensively was methyl glycolate, as considerable work on the acetal and vinyl ether of this compound has been reported previously.¹⁴ Also, the presence of the methyl ester group facilitates identification of the reaction products. The other vinyl ethers were prepared similarly to the technique used for the methyl glycolate-vinyl acetate reaction. The infrared

(16) Acetylene and alcohols (HgSO₄) form acetals, with vinyl ethers as intermediates at 10 to 80°, while acetylene and carboxylic acids (HgSO₄) form vinyl esters at 20 to 60°. Ethylidene diester formation occurs at even a higher temperature range or under more vigorous reaction conditions. (Nieuwland and Vogt, "The Chemistry of Acetylene," Reinhold Publ. Corp., New York, N. Y., 1948, pp. 126-127, 129-131). Another example in which a primary alcohol is more effective than a carboxylic acid as a hydrogen donor is the well known bimolecular acid-catalyzed esterification reaction.¹¹

spectra and physical constants of vinyl ethers (1), (2), (4), (5), listed in Table I were found to be identical with the spectra of the vinyl ethers prepared from the alcohol and acetylene using strong caustic as catalyst.

1. **The Vinyl Ether of Methyl Glycolate.**—Methyl glycolate (obtained from the du Pont Co. Polychemicals Dept., b.p. 71° (41 mm.), n_D^{20} 1.4177) 90 g. (1 mole), vinyl acetate (redistilled) 516 g. (6 moles), copper resinate 0.005 g., mercuric acetate (reagent) 1.8 g. and sulfuric acid 0.2 g., were added in the above order, with vigorous stirring, to a one-liter flask cooled to -22°. After 10 minutes, the catalyst had completely dissolved to form a homogeneous solution. After 1.5 hours, with occasional stirring, the homogeneous solution contained 0.46 equivalent water-soluble acid (acetic acid). This was determined by withdrawing a 5-ml. sample, adding crushed ice and titrating to the phenolphthalein end-point with standard 0.2 *N* sodium hydroxide. After 2.5 hours at -22°, the solution contained 0.6 equivalent acetic acid. The reaction solution was poured rapidly into a solution of 53 g. (0.5 mole) of sodium carbonate in one liter of ice-water. Unchanged methyl glycolate was soluble in the aqueous layer. The mixture was shaken well and the organic layer was separated, dried with sodium sulfate, and distilled under reduced pressure through a 3-foot packed column. The following fractions were obtained: (a) cold trap (-78°), 425 g. of vinyl acetate; (b) b.p. 80-84° (82 mm.), 35.5 g. (35% conversion) of vinyl ether of methyl glycolate; (c) holdup and residue—8 g.

The unchanged methyl glycolate is more easily recovered if the water-wash step is eliminated, and the reaction mixture, neutralized with a base, is distilled directly. A more careful fractionation is required, however, than in the above procedure.

The characteristics of a redistilled sample of the vinyl ether of methyl glycolate (fraction b) were as follows: b.p. 91-91.5° (93 mm.), n_D^{20} 1.4236, d_4^{20} 1.05. (The published constants for this compound are b.p. 76.7° (49.5 mm.), n_D^{20} 1.4232, d_4^{20} 1.0531.^{4a}) The infrared spectrum indicated the loss of an hydroxyl group, and the presence of a vinyl ether group (no band at 2.92 μ , new bands at 6.15, 6.20, 8.65, 10.00, 11.25, 12.20 μ).

The redistilled product rapidly reacted with bromine in carbon tetrachloride at 25° to give a bromine-equivalent weight of 115 (theory is 116).

The theoretical amount of hydrogen was also absorbed at 3 atmospheres pressure at 30° using Raney nickel catalyst in tetrahydrofuran solvent. The hydrogenated product had the boiling point and refractive index of ethoxyacetic acid methyl ester.

2. **Preparation of the Acetal of Methyl Glycolate.**—Methyl glycolate 90 g. (1 mole), vinyl acetate 516 g. (6 moles) and copper resinate 0.005 g., were mixed at +28°. No acetic acid was formed in the reaction solution after 10 minutes as indicated by titration of an aliquot with standard alkali. Mercuric acetate 1.8 g. (0.2%), was added, and the mixture was stirred for 10 minutes. No appreciable solution of the mercuric salt occurred, and less than 0.02 mole of acetic acid had formed. Concentrated sulfuric acid 0.7 g., was then added drop by drop to the stirred mixture. A temperature rise of over 10° (+38°) occurred almost immediately, and the mercuric acetate dissolved to form a homogeneous reaction medium. After 10 minutes, 0.64 mole of acetic acid was present in solution. After 20 minutes, the amount of acetic acid present had dropped to 0.49 mole. Five grams of sodium acetate was stirred into the reaction solution for 10 minutes, and the mixture was distilled rapidly under reduced pressure in a small 1-foot packed column with the following results: (a) cold trap (-78°), 509 g. (vinyl acetate plus acetic acid); (b) b.p. 50-58° (12 mm.), 24 g. (crude recovered methyl glycolate); (c) b.p. 80-102° (4 mm.), 4 g.; (d) b.p. 110-113° (3 mm.), 74 g. (71% conversion, 97% yield of acetal of methylglycolate) n_D^{20} 1.4297, saponification equivalent 95 (theory is 103). Acetaldehyde was liberated on acidification with hydrochloric acid. The infrared spectrum indicated the presence of acetal and ester groups in the molecule. The literature values for the physical constants of this compound are: b.p. 114-116° (2 mm.), n_D^{20} 1.4308, d_4^{25} 1.1652³; (e) holdup and residue—6 g.

3. **Preparation of the Acetoxyacetal of Methyl Glycolate.**—Methyl glycolate 90 g. (1 mole), vinyl acetate 516 g. (6 moles), copper resinate 0.01 g., mercuric acetate 1.8 g. and

sulfuric acid 0.8 g., were added in the above order to a reaction flask with stirring at 25°. After 10 minutes, 0.66 mole of acetic acid had formed in the reaction solution, which had turned black. After 20 hours, an aliquot indicated 0.40 mole of acetic acid and after 85 hours, an aliquot indicated 0.34 mole of acetic acid. Five grams of sodium acetate was then stirred into the reaction solution, and the mixture was rapidly vacuum distilled through a 1-foot packed column with the following results: (a) trap (-78°), 434 g. (vinyl acetate and uncombined acetic acid); (b) b.p. 30-50° (10 mm.), 10 g. (crude recovered methyl glycolate); (c) b.p. 83-85° (4 mm.), 103 g. (59% conversion to the acetoxyacetal of methyl glycolate); (d) b.p. 115-120° (6 mm.), 27 g. (26% conversion to acetal of methyl glycolate); (e) holdup and residue—6 g.

The identity of fraction (c) as the acetoxyacetal of methyl glycolate, a new compound, was established by its physical constants and chemical properties. A redistilled sample had a b.p. 88.5-89.5° (9 mm.), n_D^{20} 1.4158; C, 47.92, 47.95; H, 6.58, 6.72 (theory, C, 47.73; H, 6.83), saponification equivalent of 84 (theory 88), and liberated acetaldehyde in aqueous acids and alkalis. Infrared spectra data also supported the existence of the expected groups in the molecule.

4. **Reaction of the Acetal of Methyl Glycolate with Acetic Acid in the Presence of Mercuric Sulfate.**—The acetal of methyl glycolate 59 g. (0.28 mole), acetic acid 30 g. (0.5 mole), and mercuric sulfate 1.8 g., were added in the above order with stirring to a reaction flask at +25°. After 16 hours at 20° 5 g. of sodium acetate was added, the mixture was stirred for 3 hours, and then distilled under reduced pressure through a 1-foot packed column: (a) trap (-80°), 18 g. (acetic acid); (b) b.p. <35° (35 mm.), 8 g. (acetic acid); (c) b.p. 65-70° (40 mm.), 14 g. (methyl glycolate plus acetic acid); (d) b.p. 113-117° (35 mm.), 11 g. (acetoxyacetal of methyl glycolate); (e) b.p. 130° (10 mm.), 34 g. (acetal of methyl glycolate); (f) holdup and residue—6 g.

Similar equilibrium values were obtained with sulfuric acid as catalysts, whereas no reaction occurred in the absence of a catalyst.

Although it is not possible to get quantitative data from the above experiment, it can be seen that the acetic acid loss roughly corresponds to the acetoxyacetal formed. Apparently, some degradation of the acetal also took place.

5. **Demonstration of the Peak in Acetic Acid Concentration which Occurs During the Vinyl Acetate-Methyl Glycolate Reaction.**—Methyl glycolate 9.0 g. (0.1 mole), vinyl acetate 51.6 g. (0.6 mole), mercuric acetate 0.18 g. (4%) and 1 drop of sulfuric acid were added in the above order to a flask, cooled to -22°, and shaken vigorously every 30 minutes. After six hours, a total of 0.08 mole of acetic acid had developed in the solution. This amount is 80% of the theoretically possible acetic acid formation if the primary interchange reaction (D) occurred exclusively. On raising the temperature to 20° for six hours, the acetic acid present dropped to 0.04 mole, indicating acetoxyacetal and acetal formation had largely occurred.

The addition of methyl glycolate to the vinyl ether of methyl glycolate to form the acetal thus appears to occur quite slowly at -22° (much more rapidly at -10°) and acetic acid adds to the vinyl ether even more slowly (expt. 2 vs. expt. 3).

6. **Reaction of Vinyl Butyl Ether with Acetic Acid.**—Vinyl butyl ether (b.p. 92-93°, n_D^{20} 1.3995) 90 g. (1 mole), glacial acetic acid 15 g. (0.25 mole), mercuric acetate 0.6 g., and one drop of sulfuric acid were added in the above order with stirring to a reaction flask at -22°. Immediate discoloration occurred on the addition of the sulfuric acid. After ten minutes, an aliquot indicated 0.21 mole of acetic acid in the solution. After one hour, 0.19 mole of acetic acid was present and after 2 hours, 0.15 mole; 3 hours, 0.13 mole; 4 hours, 0.12 mole; 6 hours, 0.10 mole. The acetic acid remaining in solution was removed with two washings of 0.1 mole of ice cold Na₂CO₃ solution, the organic layer was dried over sodium sulfate, and distilled (72 g.). No vinyl acetate was found. The following fractions were obtained: (a) 29 g., b.p. 92-93° of vinyl butyl ether recovered; (b) 42 g. of non-viscous residue, not distilled (probably contains 1-acetoxyethyl butyl ether), n_D^{20} 1.4098. Approximately 10 g. of distillable products was used up in taking aliquots.

NIAGARA FALLS, N. Y.