

deuterium occurred when the mandelic acid was dissolved in water. But optically active mandelic acid does not readily racemize in water, and the α -hydrogen atom is therefore not exchanged. In fact, mandelic acid is quite stable in acid solution even at 96°, and racemizes only slowly at that temperature in strong alkali.¹⁰

Reduction of Pyruvic Acid.—The reduction of pyruvic acid by the Hantzsch compound already has been reported.³ The reaction was repeated in ethanol and in glycol dimethyl ether as solvents; low yields (ca. 5%) of lactic acid could be identified, after chromatography, in each case.

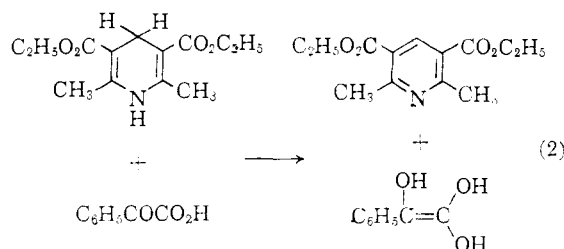
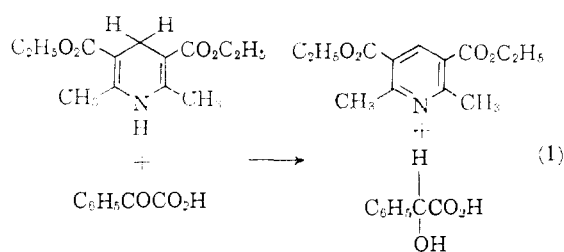
Discussion

The reduction of benzoylformic acid might take place by either of two mechanisms, which are represented schematically as shown.

If the reaction had taken place by way of the enol of mandelic acid (scheme 2) then the hydrogen atoms of the enol would have exchanged with those of the solvent and, in the deuterated solvent, the product would have contained an atom of deuterium per molecule, or at least a large fraction of an atom of deuterium per molecule. Since no appreciable amount of deuterium was in fact transferred to the mandelic acid, the reduction must have taken place by a direct hydrogen transfer from the reducing agent to the α -carbon atom of the benzoylformic acid.

The yield in this reduction is very low, and the reducing agent is not really comparable in structure to reduced diphosphopyridine nucleotide, since the Hantzsch compound has a hydrogen atom,

(10) A. N. Campbell and A. J. R. Campbell, *THIS JOURNAL*, **54**, 4581 (1932).



rather than an alkyl group, attached to the nitrogen atom of the pyridine ring. However, the work does show that a non-enzymatic reduction of a ketoacid by a derivative of 1,4-dihydropyridine can occur with direct hydrogen transfer.

Acknowledgment.—The authors wish to thank the National Institutes of Health for a grant in support of this work.

CAMBRIDGE 38, MASS.

[CONTRIBUTION FROM THE DEVELOPMENT DEPARTMENT, UNION CARBIDE CHEMICALS CO., DIVISION OF UNION CARBIDE CORP.]

The Chemistry of α,β -Unsaturated Ethers. III. Self Condensation¹

BY R. I. HOAGLIN, D. G. KUBLER AND A. E. MONTAGNA

RECEIVED APRIL 23, 1958

The novel self condensation of α,β -unsaturated ethers in the presence of boron trifluoride and mercuric acetate to yield dimers, trimers and tetramers is reported. The primary products are acetals or ketals of β,γ -unsaturated aldehydes or ketones. The higher condensation products are acetals and probably result from the condensation of the lower acetal or ketal products with the starting ether. Attempts to isolate the free vinylacetaldehyde from 1,1-diethoxy-3-butene (dimer of vinyl ethyl ether) were unsuccessful, but this aldehyde was isolated as its 2,4-dinitrophenylhydrazone. The mechanism of the reaction is discussed.

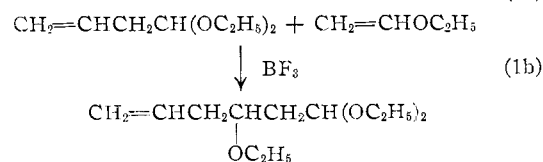
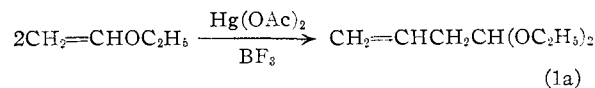
α,β -Unsaturated ethers are polymerized readily by strongly acidic catalysts, particularly those of the Friedel-Crafts type.² Inasmuch as most of the known reactions of these ethers are also acid-catalyzed, this marked tendency to polymerize is often the most important reason for the failure when these ethers do not react well with other compounds.

During our studies of the chemistry of α,β -unsaturated ethers we learned that the catalyst combination of mercuric acetate and boron trifluoride is effective for controlling the polymerization of these ethers to yield dimers, trimers and tetramers. Higher condensation products were formed but in insufficient yields to permit their isolation and identification.

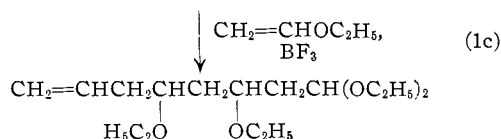
(1) For the previous paper of this series see R. I. Hoaglin, D. G. Kubler and R. E. Leech, *THIS JOURNAL*, **80**, 3069 (1958).

(2) C. E. Schildknecht, A. O. Zoss and C. McKinley, *Ind. Eng. Chem.*, **39**, 180 (1947).

The dimeric products of this reaction are acetals or ketals of β,γ -unsaturated aldehydes or ketones. The trimers and tetramers appear to be the acetal-vinyl ether condensation products of the dimers and trimers, respectively, with the starting ether.³ These may be expressed for the self condensation of vinyl ethyl ether by



(3) R. I. Hoaglin and D. H. Hirst, *THIS JOURNAL*, **71**, 3468 (1949).



Four different α,β -unsaturated ethers have been studied in this reaction. These include vinyl ethyl ether, vinyl 2-ethylhexyl ether, 1-butenyl ethyl ether and isopropenyl ethyl ether. The conditions used and the results obtained are shown in Table I. Vinyl alkyl ethers dimerize with better results than do ethers containing an alkyl group on the α - or the β -carbon atom of the vinyl group.

larger amounts do not appear to be beneficial. The influence of the ratio of acid to mercuric salt was not evaluated.

While other co-catalysts, such as acetate salts of copper(II), nickel(II), silver, lead and zinc, were found to be ineffective, one should expect mercury salts of other organic acids to be effective.⁴

The rate of addition of the unsaturated ether to the reaction mixture or the total residence time or both appear to be critical. While these variables were not studied closely (see footnote *d* of Table III), the rate of addition of the vinyl alkyl ether should be as rapid as possible, commensurate with

TABLE I

Unsaturated ether, moles	BF ₃ , g. ^a	SELF CONDENSATIONS OF α,β -UNSATURATED ETHERS				Products	Yield, %
		Hg(OAc) ₂ , mole %	Reaction temp., °C.	Addition time, min.	Total reacn. time, min.		
Vinyl ethyl, 10.0	7.0	1.0	38-46	19	25	1,1-Diethoxy-3-butene	51
						1,1,3-Triethoxy-5-hexene	14
						1,1,3,5-Tetraethoxy-7-octene	8
Vinyl ethyl, 10.0	7.0	1.5	39-44	14	20	1,1-Diethoxy-3-butene	72
						1,1,3-Triethoxy-5-hexene	7
Vinyl 2-ethylhexyl, 5.3	3.6	1.5	40-47	8	16	1,1-Di-(2-ethylhexoxy)-3-butene	70
						1,1,3-Tri-(2-ethylhexoxy)-5-hexene	10
1-Butenyl ethyl, 4.0	2.7	1.5	40-45	5	56	1,1-Diethoxy-2-ethyl-3-hexene	30
Isopropenyl ethyl, 5.0	3.4	1.5	32-37	8	154	4,4-Diethoxy-2-methyl-1-pentene	11

^a This quantity of BF₃ was added as a 32% solution in diethyl ether.

The dimer of vinyl ethyl ether was identified as 1,1-diethoxy-3-butene on the following evidence: hydrogenation yielded diethylbutyral; mild hydrolysis provided vinylacetaldehyde (isolated as its 2,4-dinitrophenylhydrazone); hydrolysis under reflux with aqueous acid provided crotonaldehyde; the infrared spectrum contained absorption bands at 6.05 and 10.97 μ , characteristic of the CH₂=CH— group (the 10.1 μ band was masked by the acetal absorption); and the mass spectrum had a strong 103 peak characteristic of the —CH(OC₂H₅)₂ fragment, and a molecular weight peak of 144. Finally, 1,1-diethoxy-3-butene was synthesized from allylmagnesium chloride and ethyl orthoformate. The synthetic product contained the starting ester as an impurity, but the infrared spectrum was very similar to that of the dimer of vinyl ethyl ether. Equivalence of the two materials was established by conversion of the synthetic acetal to the 2,4-dinitrophenylhydrazone of vinylacetaldehyde, identical to that obtained from the dimer of vinyl ethyl ether.

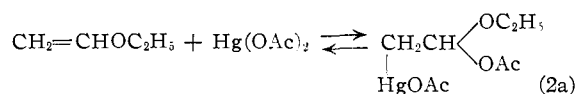
Analytical data, infrared and mass spectral data, and derivatives were used to assign the structures of the other products shown in Table II. This table includes the physical properties, analytical data and derivatives of the products prepared by the self condensation of α,β -unsaturated ethers.

A few experiments were performed to demonstrate the variables which influence the self condensation of vinyl ethyl ether. These experiments are shown in Table III.

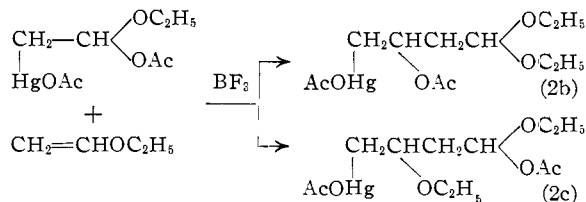
Comparison of the results for the four different acid catalysts which were used shows that boron trifluoride is the preferred catalyst. The concentration of the co-catalyst, mercuric acetate, at a constant concentration of acid directly affects the yield of the dimer up to 1.5 mole per cent. but

the ease of removal of the heat of reaction. For α,β -unsaturated ethers of types other than vinyl alkyl ethers, longer reaction times are needed to effect appreciable conversion (Table II).

The course of the reaction is believed to involve the addition of mercuric acetate to the unsaturated ether followed by the acid-catalyzed condensation of the mercuric derivative with another molecule of the unsaturated ether. The catalysis of vinyl alkyl ether-alcohol exchange by mercuric acetate,⁴ the catalysis of vinyl ester-alcohol exchange by mercuric acetate and boron trifluoride,^{4,5} and the general addition of mercuric acetate to carbon-carbon unsaturation⁶ all suggest that the primary step is



Condensation of this intermediate with vinyl ether can occur in either of two ways



These steps would be followed by exchange of the mercuric acetate (or mercuric ethoxy acetate)

(4) W. H. Watanabe and L. E. Conlon, *THIS JOURNAL*, **79**, 2828 (1957).

(5) R. L. Adelman, *ibid.*, **75**, 2678 (1953); W. J. Croxall, F. J. Glavis and H. T. Neher, *ibid.*, **70**, 2805 (1948); D. H. Hirsh, R. I. Hoaglin and D. G. Kubler, *J. Org. Chem.*, **23**, 1083 (1958).

(6) F. C. Whitmore, "Organic Compounds of Mercury," Chemical Catalogue Co. (Reinhold Publ. Corp.), New York, N. Y., 1921, p. 31; G. F. Wright, *THIS JOURNAL*, **57**, 1993 (1935).

TABLE II
 PROPERTIES OF SELF CONDENSATION PRODUCTS OF α,β -UNSATURATED ETHERS

Compound	°C.	B.p.	Mm.	n_D^{20}	Sp. gr. 20	Carbon, %		Hydrogen, %		Equiv. wt. a		2,4-Dinitrophenylhydrazone, m.p., °C.		Analysis of II Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	I ^b	II ^c	Calcd.	Found
1,1-Diethoxy-3-butene ^{d,e}	66-67	50	1.4087	0.851	66.67	66.27	11.12	11.23	144	143	191 ^f	128-129 ^g	22.39	22.55	
1,1,3-Triethoxy-5-hexene ^{d,e}	94-96	10	1.4247	.893	66.67	66.40	11.12	11.11	216	216	51-51.5	17.38	17.70	
1,1,3,5-Tetraethoxy-7-octene ^d	137-140	1	1.4324	.914	66.67	66.41	11.12	11.19	288	286	189 ^f	126-128 ^g	
1,1-Di-(2-ethylhexoxy)-3-butene ^d	125-126	1	1.4422	.853	76.86	76.64	12.90	13.09	
1,1,3-Tri-(2-ethylhexoxy)-5-hexene ^d	178	0.5	1.4480	.867	76.86	76.54	12.90	13.19	468	473	
1,1-Diethoxy-2-ethyl-3-hexene ^{e,h}	82-85	10	1.4265	.848	71.95	71.42	12.08	11.94	
4,4-Diethoxy-2-methyl-1-pentene ^{e,i}	67-68	10	1.4241	.864	69.72	69.37	11.70	11.72	172	173	
1-Acetoxy-1-ethoxy-3-butene ^e	53-54	10	1.4148	.947	60.73	60.86	8.90	9.01	

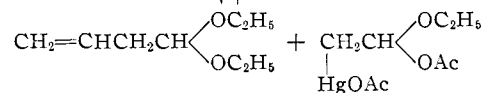
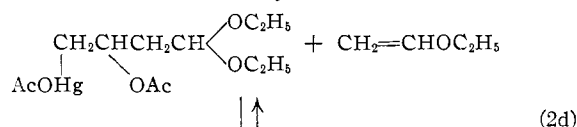
^a These values were determined by oximation. ^b These derivatives are of the α,β -unsaturated carbonyl compounds; see Experimental for the method of preparation. ^c These derivatives are of the β,γ -unsaturated carbonyl compounds; see Experimental for the method of preparation. ^d This material had absorption bands in the infrared at 6.05 and 10.97 μ , characteristic of $\text{CH}_2=\text{CHR}$. ^e This material had mass spectra characteristic of this structure, including the molecular weight. ^f The melting point was not depressed when in admixture with an authentic 2,4-dinitrophenylhydrazone of crotonaldehyde. ^g The melting point was not depressed when in admixture with the 2,4-dinitrophenylhydrazone of vinylacetaldehyde prepared from the synthetic 1,1-dieethoxy-3-butene. ^h This material had absorption bands in the infrared at 10.35 μ , characteristic of *trans*-RCH=CHR. ⁱ The melting point was not depressed when in admixture with an authentic 2,4-dinitrophenylhydrazone of 2-ethyl-2-hexenal. ^j This material had absorption bands in the infrared at 11.3 μ , characteristic of $\text{CH}_2=\text{CR}_2$. ^k The melting point was not depressed when in admixture with an authentic 2,4-dinitrophenylhydrazone of mesityl oxide. ^l This material may be the 2,4-dinitrophenylhydrazone of 2-ethoxy-2-methyl-4-pentanone which could have formed during the hydrolysis of the ketal for the preparation of the derivative in the ethanol-water solution. *Anal.* Calcd. for $\text{C}_{11}\text{H}_{20}\text{N}_4\text{O}_4$: C, 51.85; H, 6.22; N, 17.28. Found: C, 51.87; H, 7.08; N, 17.65.

 TABLE III
 CATALYST EVALUATION FOR THE SELF CONDENSATION OF VINYL ETHYL ETHER^a

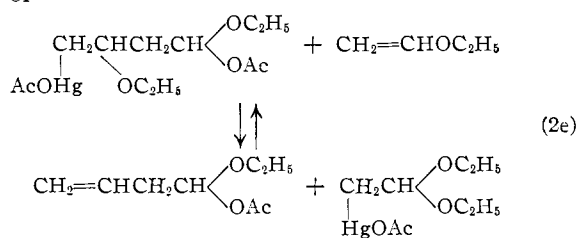
Acid catalyst	Mercuric acetate, mole %	Addition time, min.	Total time, min.	Yield, %		
				Dimer	Trimer	Polymer ^b
BF_3^c	0.0	15	23	0	0	98
BF_3^c	0.5	8	10	16	..	81
BF_3^c, d	1.0	19	25	51	14	16
BF_3^c	1.5	14	20	72	7	5
BF_3^c	2.0	16	22	72	7	3
Super-filtrol						
X-202 ^e	1.5	6	23	33	13	29
ZnCl_2	1.5	16	21	4	10	84
AlCl_3	1.0	18	23	11	20	31

^a These expts. were conducted by adding the vinyl ethyl ether to the catalyst mixture and 10 ml. of diethyl ether for each mole of vinyl ethyl ether. The temperature was moderated at $42 \pm 4^\circ$. For the first two expts., 2 moles of vinyl ethyl ether was used while for the others, 10 moles. The acid catalysts were employed in the amount of 1.0 mole % except for the AlCl_3 expt. (0.5 mole %) and the Super-Filtrol expt. (1.0 wt. %). ^b This number includes the tetramer which was not isolated for these expts. ^c Added as a 32% solution in diethyl ether. ^d This expt. was repeated except that the ether was added over a period of 95 min. and the total time was 125 min. The yield of dimer was 9%, of trimer was 12% and of polymer was 56%. ^e An acid-washed clay. Filtrol Corporation, 3250 East Washington Blvd., Los Angeles, Calif.

from the products to the more strongly polarized unsaturation of the vinyl ether



or



Obviously, 2c (and subsequently 2e) occurs only to a minor extent because of the limited quantity of mercuric acetate used in the reactions. However, it probably occurs because 1-acetoxy-1-ethoxy-3-butene was isolated in very low yield from the dimerization of vinyl ethyl ether.

The formation of the trimer, tetramer and higher condensation products most likely occurs by the acetal-vinyl ether condensation.³

The self-condensation of α,β -unsaturated ethers represent an easy synthesis, in particular, of the acetals of vinylacetaldehyde. It also represents an alternate method of conducting aldol condensations.

The products are hydrolyzed readily to α,β -unsaturated aldehydes or ketones. All attempts to prepare vinylacetaldehyde by hydrolysis of 1,1-diethoxy-3-butene resulted in rearrangement to cro-

tonaldehyde. That vinylacetaldehyde is formed by hydrolysis of 1,1-diethoxy-3-butene was proved by conducting the hydrolysis under mild conditions in the presence of 2,4-dinitrophenylhydrazine and isolating this aldehyde as its derivative.

These products may also be used as starting materials for the synthesis of 1-alkoxy-1,3-butadienes by de-alcoholation, in the same manner as from 1,1,3-trialkoxybutanes or acetals of crotonaldehyde.⁷

Experimental⁸

Self Condensations. General Procedure.—The starting materials were available commercially or were prepared by the vapor-phase de-alcoholation of the acetals. The boron trifluoride was used as a 32% solution in diethyl ether. The mercuric acetate was Mallinckrodt's analytical grade.

The description of experiment 2 of Table I will serve to illustrate the general procedure. Vinyl ethyl ether (720 g., 10 moles) was added with vigorous stirring to a mixture of 21 g. of 32% boron trifluoride in diethyl ether, 47.5 g. (0.15 mole) of mercuric acetate and 100 ml. of diethyl ether over a period of 14 minutes. The temperature was maintained at $42 \pm 3^\circ$ by frequent cooling (ice-water). Six minutes after the ether was added, the temperature started to drop without cooling. The mixture was neutralized with 50 g. of sodium carbonate in 500 ml. of water. The heterogeneous mixture was filtered, and the filter cake was washed with diethyl ether. After removing the water layer, the organic layer was distilled. The fractions obtained and their identity are: fract. 1, b.p. 33–35 (760 mm.), 153 g. of diethyl ether which contained 14.2% vinyl ethyl ether; fract. 2, b.p. 25–62° (50 mm.), 31 g. being mainly diethyl acetal (b.p. 36° (50 mm.)); fract. 3, b.p. 62–68° (50 mm.), 547 g., 1,1-diethoxy-3-butene; fract. 4, b.p. 52–53° (10 mm.), 13 g., 1-acetoxy-1-ethoxy-3-butene; fract. 5, b.p. 53–91° (10 mm.), 20 g. being mainly 1,1,3-triethoxybutane (b.p. 72° (10 mm.)); fract. 6, b.p. 91–93° (10 mm.), 56 g., 1,1,3-triethoxy-5-hexene; and 36 g. of residue.

Hydrolysis of 1,1-Diethoxy-3-butene.—A mixture of 144 g. of 1,1-diethoxy-3-butene, 100 ml. of water and 1 g. of concentrated sulfuric acid was heated under total reflux on a distillation column for 1 hour. The mixture was distilled until the vapor temperature could not be maintained below 80°; 250 ml. of water was added to the distillation kettle and the distillation continued until the distillate was essentially water. The total distillate was 213 g. and contained 30.4% crotonaldehyde (64.7 g., 92.5% yield), 41.8% ethanol (89 g., 96.8% yield) and 26.4% water. The crotonaldehyde was identified as its 2,4-dinitrophenylhydrazone, m.p. 190–192°, and the melting point was not depressed when in a mixture with an authentic sample of the 2,4-dinitrophenylhydrazone of crotonaldehyde.

Hydrogenation of 1,1-Diethoxy-3-butene.—1,1-Diethoxy-3-butene (1440 g., 10 moles) was hydrogenated at 150 p.s.i.g. over 43 g. of Raney nickel catalyst. Distillation of the hydrogenated material provided 208 g. of a fraction distilling at 68 to 114° which contained ethanol and ethyl butyl ether. This fraction gave a positive hydroxyl test and removal of the ethanol by water extraction followed by distillation gave 80 g. of ethyl butyl ether, b.p. 90–91°, n_D^{20} 1.3816, sp. gr. $^{20}_4$ 0.753 (lit.⁹ values are b.p. 92.3°, n_D^{20} 1.3798, d^{20}_4 0.752). The main fraction (1140 g., 78% yield) was diethyl butylal. The purity was 98.9% by oximation and the physical properties were b.p. 146.4° (760 mm.) (cor.), n_D^{20} 1.3959 and sp. gr. $^{20}_4$ 0.8297. The corresponding values for a highly refined sample of diethyl butylal prepared by the reaction of butylaldehyde and ethanol were b.p. 146.2° (760 mm.) (cor.), n_D^{20} 1.3958 and sp. gr. $^{20}_4$ 0.8295.

Synthesis of 1,1-Diethoxy-3-butene from Allylmagnesium Chloride and Ethyl Orthoformate.—1,1-Diethoxy-3-butene

was prepared by the procedure of Tschitschibabin¹⁰ using 95.6 g. (1.25 moles) of allyl chloride, 30 g. (1.25 moles) of magnesium, 148 g. (1.0 mole) of ethyl orthoformate and 500 ml. of anhydrous ethyl ether. There was obtained 95 g. of 1,1-diethoxy-3-butene which distilled at 66–68° (50 mm.), n_D^{20} 1.3995, and which was contaminated with ethyl orthoformate (lit.¹¹ b.p. 145–147° (atm.), 60° (30 mm.), n_D^{20} 1.3922). Comparison of the infrared spectrum for this impure material and the 1,1-diethoxy-3-butene prepared from vinyl ethyl ether demonstrated that the materials were essentially identical except for the ethyl orthoformate contamination.

The material was converted to the 2,4-dinitrophenylhydrazone of vinylacetaldehyde by method II described below. The golden plates melted at 128–129° and the melting point was not depressed when in admixture with the 2,4-dinitrophenylhydrazone prepared by method II from 1,1-diethoxy-3-butene (from vinyl ethyl ether). The infrared spectra confirmed the fact that these materials were equivalent and were the 2,4-dinitrophenylhydrazones of vinylacetaldehyde.

Preparation of 1,1-Diethoxy-2-ethyl-2-hexene.—The diethyl acetal of 2-ethyl-2-hexenal was prepared essentially according to the literature¹² using 144 g. (0.97 mole) of ethyl orthoformate, 99 g. (0.79 mole) of 2-ethyl-2-hexenal, 50 ml. of ethanol and 3 g. of boric acid-oxalic acid.¹ There was obtained 32 g. (20.4% yield) of 1,1-diethoxy-2-ethyl-2-hexene, b.p. 54–55° (1 mm.), n_D^{20} 1.4318; sp. gr. $^{20}_4$ 0.855.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 71.95; H, 12.07. Found: C, 71.7; H, 11.7.

Comparison of the physical properties, and of the infrared and mass spectra of this material to those of the dimer of 1-butenyl ethyl ether definitely established that the latter material did not contain the unsaturation in the 2,3-position.

Identification of 1-Acetoxy-1-ethoxy-3-butene.—The intermediate fractions between 1,1-diethoxy-3-butene and 1,1,3-triethoxybutane from several different dimerizations of vinyl ethyl ether were combined and fractionated to provide one predominant fraction of b.p. 53–54° (10 mm.) which was believed to be 1-acetoxy-1-ethoxy-3-butene.

Complete verification of this structure was obtained from spectral examination. The infrared spectrum contained a large carbonyl band (5.75 μ) and strong unsaturation bands at 6.05, 9.92 and 10.80 μ . The 9.92 and 10.80 bands have apparently shifted from the normal values of 10.10 and 10.97 μ . The ultraviolet spectrum contained no aldehyde or ketone absorption. Finally, the mass spectrum had a large 43

peak ($\text{CH}_3\overset{\text{O}}{\parallel}\text{C}-$), a large 117 peak ($\text{CH}_3\overset{\text{O}}{\parallel}\text{C}\text{CHOC}_2\text{H}_5$) and a molecular weight peak of 158.

The material also was converted to the 2,4-dinitrophenylhydrazone of vinylacetaldehyde by method II; melting point and mixture melting point of 126–128°.

Preparation of 2,4-Dinitrophenylhydrazones. Method I. Derivatives of α,β -Unsaturated Carbonyls.—This method involved refluxing 2–3 g. of the acetal or ketal for 1 hour with 4–6 g. of 50% aqueous acetic acid containing 1 drop of concentrated sulfuric acid. The solution was mixed with 40 ml. of ethanol and the standard 2,4-dinitrophenylhydrazine reagent described in the literature¹³ was added. The derivatives were purified in a standard manner.

Method II. Derivatives of β,γ -Unsaturated Carbonyls were made from the acetals or ketals by a method previously described,¹ except that 250 ml. of ethanol was used in place of the methanol, 150 ml. of water was added, and 2–4 drops of concentrated phosphoric acid was used to catalyze the hydrolysis. The mixtures were warmed on a steam-bath for 1 to 2 hours, allowed to cool to room temperature, and filtered. If the derivatives did not crystallize after standing for 1 to 2 days, sufficient water was added to effect their separation. The materials were then recrystallized from ethanol or ethanol-water mixtures.

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(7) W. Flaig, *Ann.*, **568**, 1 (1950).

(8) All melting points are corrected; boiling points are uncorrected. We wish to thank Mr. J. Bodenschatz of this Laboratory for the elemental analyses which are reported. We particularly wish to thank Dr. V. A. Yarborough, Mr. J. H. Ross and Mr. W. J. Lambdin of this Laboratory for their valuable assistance in the structure determinations by measuring and interpreting the infrared and mass spectra.

(9) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. 2, rev. ed., Oxford University Press, New York, N. Y., 1953, p. 494.

(10) A. E. Tschitschibabin, *Ber.*, **37**, 186 (1904).

(11) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. 4, rev. ed., Oxford University Press, New York, N. Y., 1953, p. 27.

(12) J. A. Van Allan, *Org. Syntheses*, **32**, 5 (1952).

(13) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948 p. 171.