

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Synthesis of 1-Alkenyl Alkyl Ethers

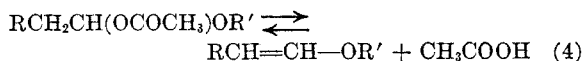
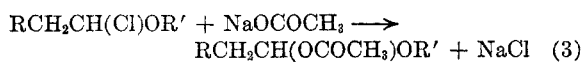
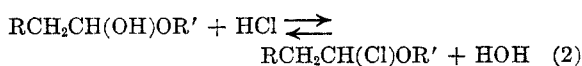
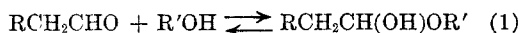
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A new method is presented for the preparation of 1-alkenyl alkyl ethers.

The synthesis of 1-alkenyl alkyl ethers has been reported by several investigators. Sigmund and Uchann¹ pyrolyzed acetals using a nickel catalyst. Voronkov² heated acetals with sodium bisulfate or sulfanilic acid. Deschamps, Paty, and Pineau³ decomposed acetals by passing them over kaolin at 300°.

In this investigation it is shown that 1-alkenyl alkyl ethers may be prepared from the corresponding hemiacetals according to the following sequence of reactions.



When equimolar quantities of an aldehyde and an alcohol are mixed, it has been shown that equilibrium (1) results.^{4,5} The preparation of α -chloroalkyl alkyl ethers (Reaction 2), by saturating a cooled, equimolar mixture of an aldehyde and an alcohol with dry hydrogen chloride, was first reported by Wurtz and Frapolli⁶ and the procedure was later modified and used by a number of workers.⁷ Hurd and Green⁸ reported the synthesis of various 1-alkoxyalkyl acetates by shaking α -chloro ethers with sodium acetate, and Bauer and Neher⁹ prepared the acrylic esters of a number of hemiacetals by reacting α -halo ethers with salts of acrylic and methacrylic acid (Reaction 3).

In this work six new 1-alkoxyalkyl acetates (Ia to VIa) were synthesized and their physical constants and analyses are listed in Table I. These acetates were pyrolyzed (Reaction 4) to yield the corresponding ethers (Ib to VIb) shown in Table II. The acetates corresponding to ethers VIIb and VIIIb are not reported due to the ease of decomposition of these two acetates upon heating. Purification by distillation, therefore, was not accomplished, and the crude acetates were pyrolyzed directly.

The pyrolysis of 1-alkoxyalkyl acetates apparently has not been applied to the preparation of 1-alkenyl alkyl ethers, and it became of interest to determine the general applicability of the reaction. Consequently, there was prepared a number of ethers, of which IIb, IIIb, VIb, and VIIb have not been reported previously. This method appears to have several advantages over methods using acetals. It is necessary to use only one mole of alcohol per mole of aldehyde. The pyrolysis temperature is relatively low and decomposition is readily accomplished without the use of a catalyst. Finally, the isolation of pure intermediate products is not mandatory, and it is possible, therefore, to start with an aldehyde and an alcohol and proceed directly to the unsaturated ether.

The 1-alkoxyalkyl acetates and 1-alkenyl alkyl ethers were prepared from the following aldehyde-alcohol mixtures: I, isobutyraldehyde and ethyl alcohol; II, valeraldehyde and ethyl alcohol; III, hexanal and ethyl alcohol; IV, heptanal and ethyl alcohol; V, *n*-butyraldehyde and *n*-butyl alcohol; VI, isobutyraldehyde and isobutyl alcohol; VII, 2-ethylbutanal and 2-ethylbutanol; VIII, 2-ethylhexanal and 2-ethylhexanol.

EXPERIMENTAL

General method of preparation of 1-alkenyl alkyl ethers. *α -Chloroalkyl alkyl ethers.* These compounds were prepared by passing dry hydrogen chloride into a cooled, equimolar mixture of the aldehyde and alcohol according to known methods.⁷ The chloro ethers were not distilled before using them due to large losses by decomposition. The yields of crude chloro ethers ranged from 67% to 95%.

1-Alkoxyalkyl acetates. The procedure of Hurd and Green⁸ was used with the following modification. Prior to separation of the product from the solid material, the mixture of anhydrous sodium acetate and the α -chloro ether was stirred for two hours, and then heated just below the boiling point, with stirring, for two hours more to complete the reaction. Heating temperatures ranged from 70° for the lowest

(1) F. Sigmund and R. Uchann, *Monatsh.*, **51**, 234 (1929).

(2) M. G. Voronkov, *J. Gen. Chem. (U.S.S.R.)*, **20**, 2060 (1950).

(3) J. Deschamps, M. Paty, and P. Pineau, *Compt. rend.*, **238**, 2006 (1954).

(4) Anon, *Ann. Rept. Schimmel and Co.*, **71** (1933).

(5) W. Herold, *Z. Elektrochem.*, **39**, 566 (1933).

(6) A. Wurtz and A. Frapolli, *Ann.*, **108**, 226 (1858).

(7) (a) D. Gauthier, *Ann. chim. et phys.*, [8] **16**, 311 (1909); (b) B. H. Shoemaker and C. E. Boord, *J. Am. Chem. Soc.*, **53**, 1505 (1931); (c) H. R. Henze and J. T. Murchison, *J. Am. Chem. Soc.*, **53**, 4077 (1931).

(8) C. D. Hurd and F. O. Green, *J. Am. Chem. Soc.*, **63**, 2201 (1941).

(9) L. N. Bauer and H. T. Neher, U. S. Pat. Appl. **773,922**.

TABLE I
 1-ALKOXYALKYL ACETATES

Acetate	No.	Yield, % ^a	B.P., °C. ^b	Mm.	n_D^{25}	d_4^{25}	Analyses ^c					
							MR _D		Carbon		Hydrogen	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
1-Ethoxy-2-methylpropyl	Ia	50.0	49.5-52	10	1.3991	0.9125	42.42	42.42	59.98	60.37	10.07	10.40
1-Ethoxypropyl	IIa	50.5	62.4-62.8	6	1.4063	0.9057	47.22	47.04	62.04	61.93	10.41	10.29
1-Ethoxyhexyl	IIIa	58.0	70.5-71.5	4	1.4108	0.9041	51.61	51.66	63.79	64.22	10.71	10.96
1-Ethoxyheptyl	IVa	53.4	84-85	4	1.4150	0.8993	56.20	56.30	65.31	64.66	10.96	10.84
1-Butoxybutyl	Va	46.81	69-72	4	1.4102	0.9016	51.68	51.66	63.79	63.61	10.71	10.68
1-Isobutoxy-2-methylpropyl	VIa	63.30	55-56.5	4	1.4058	0.8833	52.26	51.66	63.79	63.53	10.71	10.62

^a Based on aldehyde. ^b Boiling points are uncorrected. ^c Analyses by Drs. Weiler and Strauss, Oxford, England.

 TABLE II
 1-ALKENYL ALKYL ETHERS

Ether	No.	Yield, % ^a	Yield, % ^b	B.P., °C. ^c	n_D^{25}	d_4^{25}	Analyses					
							MR _D		Carbon		Hydrogen	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
2-Methyl-1-propenyl ethyl ^d	Ib	70.5	33.0	92-94	1.4060	0.7772	31.59	31.10				
1-Pentenyl ethyl	IIb	72.5	36.7	118-119	1.4107	0.7884	35.85	35.70	73.63	73.15	12.36	12.20
1-Hexenyl ethyl	IIIb	84.4	49.0	144-147	1.4160	0.7915	40.57	40.31	74.94	74.67	12.58	12.63
1-Heptenyl ethyl ^e	IVb	65.5	35.0	165-168	1.4236	0.8033	45.07	44.93				
1-Butenyl butyl ^f	Vb	73.4	42.2	64-66 (40 mm.)	1.4151	0.7898	40.62	40.31				
2-Methyl-1-propenyl isobutyl	VIb	71.3	56.3	131-132	1.4138	0.7825	40.86	40.32	74.94	75.05	12.58	12.38
2-Ethyl-1-butenyl 2-ethylbutyl	VIIb	— ^g	51	90-90.5 (11 mm.)	1.4350	0.8150	58.90	58.79	78.19	77.77	13.13	13.34
2-Ethyl-1-hexenyl 2-ethylhexyl ^h	VIIIb	— ^g	40	135-136 (10 mm.)	1.4434	0.8199	77.65	77.26				

^a Based on 1-alkoxyalkyl acetate. ^b Based on aldehyde. ^c Boiling points are uncorrected. ^d Lit.² b.p. 94°, n_D^{20} 1.4053, d_4^{20} 0.7757. ^e Lit.¹⁰ b.p. 60-61° (12 mm.), n_D^{21} 1.4250, d_4^{21} 0.802. ^f Lit.¹¹ b.p. 35.5° (10 mm.), n_D^{20} 1.4179. ^g No corresponding pure acetate prepared. ^h Lit.¹² b.p. 137-139° (10 mm.).

molecular weight acetate to 130° for the highest molecular weight compound investigated. The infrared spectra of these acetates showed strong carbonyl absorption at 5.72 μ and strong C—O—C absorption at 8.0-8.2 μ .

1-Alkenyl alkyl ethers. The 1-alkoxyalkyl acetates were heated to temperatures sufficient for decomposition, usually 150-250°, for at least two hours and then were distilled slowly through a 30-cm. fractionating column packed with glass pearls. The distillate, a mixture of acetic acid and unsaturated ether, was washed with an excess of sodium hydroxide or sodium carbonate solution; dried over anhydrous sodium carbonate or potassium hydroxide, and distilled over potassium hydroxide. It was then fractionated to yield the 1-alkenyl alkyl ether. The yields ranged from 65.5% to 81.4%. The infrared spectra of these ethers showed strong ether absorption between 8.1-9.0 μ and strong double bond absorption at 5.9-6.1 μ .

The following examples will illustrate the general procedures employed in this synthetic process.

α -Chlorohexyl ethyl ether. Dry hydrogen chloride was passed into a cold mixture of 100 g. (1.0 mole) of freshly distilled hexanal and 46 g. (1.0 mole) of absolute ethanol

until 40 g. (1.09 moles) of hydrogen chloride was absorbed. The lower (aqueous) layer was discarded and the upper layer was dried over anhydrous calcium chloride for two hours. The liquid was then kept under partial vacuum for two hours to remove any excess hydrogen chloride. Purification by distillation results in considerable losses and is unnecessary. The yield of crude α -chlorohexyl ethyl ether was 151 g. (0.915 mole, 91.5%), and it is pure enough for use in the next step of the process.

1-Ethoxyhexyl acetate (IIIa). To 82 g. (1.0 mole) of anhydrous sodium acetate in a 300-ml. three-necked flask, fitted with a mechanical stirrer and a reflux condenser protected by a drying tube, was added, all at once, 158 g. (0.915 mole) of crude α -chlorohexyl ethyl ether which had been cooled to 10°. The mixture was stirred and heat was evolved. Stirring was continued for two hours and then the mixture was warmed to 120° and stirring was continued an additional two hours. After cooling to room temperature, 50 ml. of anhydrous ethyl ether was added to the mixture. The product was then separated from the solid material by filtration, and the solid was washed with another 50 ml. of ether. The ether was removed by evaporation and the residue was distilled under reduced pressure. The distillate was fractionated to yield 109 g. (0.58 mole) of 1-ethoxyhexyl acetate, b.p. 70-71° (4 mm.), n_D^{25} 1.4108, d_4^{25} 0.9041. The yield was 58% based on hexanal and 63.7% based on α -chlorohexyl ethyl ether.

1-Hexenyl ethyl ether (IIIb). Ninety-four grams (0.5 mole) of 1-ethoxyhexyl acetate was heated at 200-230° for two

(10) J. Ficini and H. Normant, *Compt. rend.*, **237**, 731 (1953).

(11) R. H. Hall, A. R. Philpotts, and E. S. Stern, *J. Chem. Soc.*, 3341 (1951).

(12) J. K. Mertzweiler, U. S. Patent **2,578,724**.

hours, and then distilled slowly to yield 90 g. of a liquid, b.p. 115–145°. This distillate was washed once with 130 ml. of 20% sodium carbonate solution and twice with 25-ml. portions of the same solution. After being dried over anhydrous sodium carbonate, the remaining 60.1 g. of liquid was distilled over solid potassium hydroxide to yield 57 g. of liquid, b.p. 138–148°, which when fractionated gave 54 g. of 1-hexenyl ethyl ether, b.p. 144–147°, n_D^{25} 1.4160, d_4^{25}

0.7915. The yield was 84.4% based on 1-ethoxyhexyl acetate and 49% based on hexanal.

The infrared spectrum of compound (IIIb) exhibited prominent absorption bands at 3.46(s), 6.02(s), 6.83(m), 7.22(s), 7.34(m), 7.67(m), 7.94(m), 8.07(m), 8.26(s), 8.49(s), 9.02(s), 10.71(m), 12.67(s) microns.

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[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

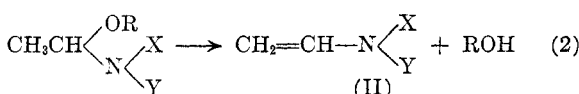
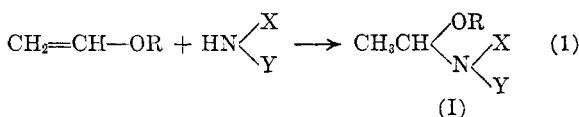
Reaction of Vinyl Ethers with Acidic Imino Compounds. A New Synthesis of Some *N*-Vinyl Imides

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By heating vinyl ethers with dicarboxylic acid imides, there were formed addition products which were proved to be α -imidoethers. With *N*-methyl-*p*-toluenesulfonamide as a reactant, the adduct formation did not occur until an acidic catalyst was added to the reaction system. *N*-Vinylimides were prepared by elimination of alcohol, with the aid of an acidic catalyst, from the corresponding α -imidoethers. In the case of *N*- α -butoxyethyl-*N*-methyl-*p*-toluenesulfonamide, the elimination took place without any added catalyst to give *N*-methyl-*N*-vinyl-*p*-toluenesulfonamide.

In the course of our studies on organic syntheses with vinyl ethers as starting materials, these compounds were found to react readily with some acidic imides to give α -imidoethers (I), from which *N*-vinylimides (II) could be prepared by elimination of alcohol with the aid of acidic catalysts.

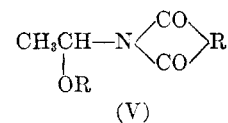
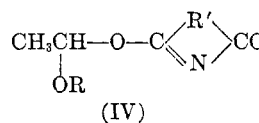
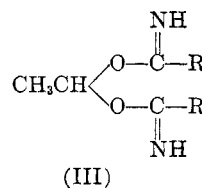


This paper examines the reactivity of these imides and certain amides in the addition reaction. Details of methods for preparing *N*-vinylimides are also reported.

The addition reaction. With dicarboxylic acid imides, the addition reaction (1) was done by heating the reaction mixture without any added catalysts. Under similar reaction conditions, benzamide¹ or *p*-toluenesulfonamide also reacted with vinyl ethers to give ethylidenediamides. *N*-Methyl-*p*-toluenesulfonamide, on the other hand, gave an imidoether (I), provided a small quantity of hydrochloric acid was added. Products, yields, and physical properties are given in Table I.

The adducts were readily hydrolyzed by 1:1 hydrochloric acid to give acetaldehyde, the corresponding alcohol, and the dicarboxylic acid, its imide, or the amide. The addition products therefore have α -imido-ether and ethylidenebisamide

structures, since β -adducts would not give acetaldehyde on hydrolysis. Since Voronkov¹ reported that ethylidenediacylamides have the structure (III), the alkoxyethyl dicarboxylic imides could have a similar structure (IV). However, as will be described later, *N*-vinylphthalimide was formed by the elimination of alcohol from α -ethoxyethylphthalimide. Thus, structure (IV) can be eliminated² in favor of V.



From experiments to determine the optimum condition for the preparation of *N*- α -butoxyethylsuccinimide, it was found that the optimum condition (100% conversion and 94–95% yield) is as follows: reaction temperature, 195°; reaction time, 3–5 hours; and the molar ratio of succinimide to vinyl ether, 1:2 or 3:4. Results as to the other *N*- α -alkoxyethyldicarboxylic acid imides are listed in Table II.

In the reaction of butyl vinyl ether with benzamide, we observed that benzamide crystals gradually disappeared on heating, and finally resulted in a clear solution; but, on prolonged heating,

(1) Voronkov reported addition reactions between vinyl ether and some acylamides. M. G. Voronkov, *J. Gen. Chem. (U.S.S.R.)*, 21, 1631 (1951); *Chem. Abstr.*, 46, 8002 (1952).

(2) Ethylidenedibenzamide, $(\text{C}_6\text{H}_5\text{CONH})_2\text{CHCH}_3$, is also reported. British Patent 710,468; *Chem. Abstr.*, 49, 11709 (1955).