Preparation of 2,3-Dimethyloxazolidine.—A solution of 93 g. (1.24 moles) of N-methylethanolamine in 50 g. of benzene was distilled to remove the benzene–water azeotrope, most of the excess benzene distilled off and the residue (101.5 g.) charged to a 250-ml. magnetically-stirred autoclave. Reaction with acetylene was carried out at an average temperature of 144° for 2.5 hr. Fractional distillation of the reaction product yielded 43.5 g. of 2,3-dimethyloxazolidine, b.p. 50–58° (120 mm.), and 36.0 g. of recovered N-methylethanolamine, b.p. 100–102° (100 mm.) (35% conversion, 57% yield). The pure oxazolidine was obtained by redistillation, b.p. 54.5–55° (120 mm.), 109–110° (760 mm.) (lit.[12] 109° (758 mm.)), $n^{25}\text{D}$ 1.4200, d^{25}_4 0.8991, $M\text{D}$ 28.47 (theor. 28.67), neut. equiv. 100.9 (theor. 101.2).

Anal. Calcd. for $C_5H_{11}ON$: C, 59.37; H, 10.96; N, 13.85. Found: C, 59.46; H, 10.73; N, 13.48.

Preparation of 2-Methyltetrahydro-1,3-oxazine.—3-Aminopropanol-1 (161 g., 2.14 moles) was treated with acetylene at an average temperature of 152° for 3.9 hr. to give a product which, after fractionation, yielded 27.0 g. of 2-methyltetrahydro-1,3-oxazine, b.p. 68–70° (100 mm.), $n^{25}\text{D}$ 1.4382, d^{25}_4 0.9480, $M\text{D}$ 28.02 (theor. 28.33), neut. eqiv. 101.3 (theor. 101.2).

Anal. Calcd. for $C_5H_{11}ON$: N, 13.85. Found: N, 13.60.

Recovered 3-aminopropanol-1, b.p. 95° (25 mm.), amounted to 97.0 g. The conversion to product was therefore 12% and the yield 31%.

Preparation of 2-Methyltetrahydro-1,3-oxazine from Acetaldehyde.—A mixture of 75 g. (1.0 mole) of 3-aminopropanol-1 and 30 g. of anhydrous sodium carbonate in 200 ml. of anhydrous ether was placed in a three-neck flask equipped with a stirrer, reflux condenser and dropping funnel. The flask was cooled to 0° and 52 g. (1.2 moles) of acetaldehyde added slowly to the cooled (0–5°) and stirred mixture. After addition was complete, the reaction mixture was allowed to warm to room temperature during an additional 2 hr. of stirring. It was then filtered, most of the low-boiling material distilled from the filtrate under mild water-aspirator vacuum and the residue fractionally distilled. Product cuts were obtained as follows: 3.5 g., b.p. 63–65° (100 mm.), $n^{25}\text{D}$ 1.4390; 9.5 g., b.p. 65–68° (100 mm.), $n^{25}\text{D}$ 1.4389; 55.0 g., b.p. 68–70° (100 mm.), $n^{25}\text{D}$ 1.4389. The yield was therefore 67%. This product was identical in its physical constants with the product from the acetylene–aminoalcohol reaction.

Attempted Cyclization of N-Methylaminoethyl Vinyl Ether under Vinylation Conditions.—When N-methylethanolamine is treated, using strong base catalysis, with acetylene under 400–500 p.s.i. at 140–150° until reaction ceases, there is obtained a mixture containing approximately 25% 2,3-dimethyloxazolidine, b.p. 55–56° (120 mm.), and 50% N-methylaminoethyl vinyl ether, b.p. 65–67° (120 mm.). In order to test whether, under these conditions, the vinyl ether is first formed, then cyclizes to the oxazolidine, the following experiment was performed. A solution of 4.6 g. (0.2 mole) of sodium in 100 g. (1.33 moles) of N-methylethanolamine was mixed with 50 g. (0.49 mole) of N-methylaminoethyl vinyl ether and the resulting solution charged to a 300-ml. stainless steel rocking microbomb. The bomb was pressured to 195 p.s.i. with nitrogen at 23°, heated to 154°, with a resultant increase in pressure to 345–355 p.s.i., and kept at that temperature for 2.5 hr. The mixture was then fractionally distilled. There resulted a 92% recovery of the vinyl ether; no material identifiable as 2,3-dimethyloxazolidine was isolated.

Preparation of 2,3-Dimethyloxazolidine in the Presence of Metal Catalyst Poisons and Acid.—A mixture of 0.5 g. of powdered sulfur and 77.0 g. (1.0 mole) of N-methylethanolamine was treated with acetylene at an average temperature of 140° for 0.5 hr. Uptake of acetylene started immediately and continued vigorously. The crude product, which was homogeneous, had gained 16 g. in weight, corresponding to an acetylene uptake of 0.58 mole. Fractionation of this material gave 25.0 g. of 2,3-dimethyloxazolidine, b.p. 52–54° (120 mm.), and 39.9 g. of recovered N-methylethanolamine, b.p. 55–57° (10 mm.). The conversion to product was therefore 25% and the yield based on unrecovered aminoalcohol, 50%.

The reaction of 89.6 g. (1.2 moles) of N-methylethanolamine with acetylene, within the pressure range 470–400 p.s.i.g. at 117 ± 1° for 0.5 hr. was repeated four times. The first reaction charge (1) contained only the aminoalcohol, the second (2) contained in addition 7.5 g. of the dihydrate of ethylenediaminetetraacetic acid disodium salt, the third (3) contained in addition 2.4 g. of 1,5-pentanedithiol and the fourth (4) contained in addition 5.0 g. of 85% phosphoric acid. Crude rate measurements gave the following rates of absorption of acetylene in the first minute of reaction (in moles per minute): (1) 0.11, (2) 0.10, (3) 0.14, (4) 0.04. The rates during the next 10–20 minutes were: (1) 0.02, (2) 0.01, (3) 0.008, (4) 0.003. The experimental error was such that the rates of (1), (2) and (3) may be considered the same, but the rates in (4) were decidedly lower. Work-up of the reaction products resulted in 14.6 g. of 2,3-dimethyloxazolidine from (1) and 13.7 g. from (3). Most of the product obtained in (2) and (4) polymerized during reaction.

PHILADELPHIA 37, PENNA.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ROHM & HAAS CO.]

Homogeneous Metal Salt Catalysis in Organic Reactions. I. The Preparation of Vinyl Ethers by Vinyl Transetherification

BY WARREN H. WATANABE AND LAWRENCE E. CONLON

RECEIVED NOVEMBER 2, 1956

The interchange reaction $ROCH{=}CH_2 + R'OH \rightleftarrows ROH + R'OCH{=}CH_2$, which is catalyzed by mercuric salts of weak acids, has been studied and found to be of wide scope and utility. It has been found that mercuric salts are specific catalysts for this reaction. A large number of other metal salts, as well as acid and base, were found to be without catalytic activity under conditions in which catalysis by mercuric salts of weak acids was rapid and efficient. As presently developed, the reaction gives yields ranging from relatively poor to excellent, but is nevertheless advantageous in that it provides a simple one-step synthesis of vinyl ethers from alcohols. Some attention has been given to the mechanism of this and related catalytic reactions, and a scheme involving acetoxymercuriacetals as intermediates is proposed.

Among the number of reactions which are specifically catalyzed by mercuric salts, there is an important group in which an olefinic function bonded to oxygen in an ester or ether is transferred to another oxygen atom in another ester or ether. For example, mercuric salts of strong acids catalyze the transfer to carboxylic acids of vinyl[1] or isopropenyl groups[2] from vinyl or isopropenyl esters to form new vinyl or isopropenyl esters. The same type of catalyst has been shown to cause transfer of vinyl groups from vinyl esters to alcohols to form, at low temperatures, vinyl ethers,[3] and to effect transfer of vinyl groups from vinyl ethers to alcohols to give new vinyl ethers, again at low

---

(1) W. O. Herrmann, U. S. Patent 2,079,068 (May 4, 1937); W. T. Toussaint and L. G. MacDowell, U. S. Patent 2,299,862 (October 27, 1942); R. L. Adelman, *J. Org. Chem.*, **14**, 1057 (1949).

(2) J. B. Dickey and T. E. Stanin, U. S. Patent 2,646,437 (July 21, 1953).

(3) R. L. Adelman, THIS JOURNAL, **75**, 2678 (1953).

TABLE I

PREPARATION OF VINYL ETHERS BY VINYL TRANSETHERIFICATION

Alcohol vinylated	Vinylating agent	Method	Yield, %	B.p.,		n^{20}D
				°C.	Mm.	
Ethyl alcohol	*n*-Butyl vinyl ether	A	98	36–37		1.3768
Ethyl alcohol	*n*-Octyl vinyl ether	A	81			
n-Octyl alcohol	Ethyl vinyl ether	B	30	63–64	5	1.4268
Isopropyl alcohol	*n*-Butyl vinyl ether	A	66	54–56		1.3850
t-Butyl alcohol	2-Butoxyethyl vinyl ether	A	43	77–78		1.3987
2-Methoxyethanol	2-Butoxyethyl vinyl ether	A	62	106–108		1.4105
Cyclohexanol	2-Ethylhexyl vinyl ether	A	60	82–83	80	1.4547[6]
Dicyclopentenyl alcohol	*n*-Butyl vinyl ether	B	44	89–91	5	1.5068
Allyl alcohol	*n*-Butyl vinyl ether	A	75	66–67		1.4109
2-Methallyl alcohol	2-Ethoxyethyl vinyl ether	A	75	87–88		1.4204
2-Chloroallyl alcohol	Ethyl vinyl ether	B	18	107–110		1.4502
Benzyl alcohol	*n*-Butyl vinyl ether	B	15	103–104	25	1.5185[6]
Ethylene chlorohydrin	2-Ethylhexyl vinyl ether	A	52	58–59	120	1.4378
Ethylene chlorohydrin	Ethyl vinyl ether	B	37			
Ethylene cyanohydrin	1,2-Divinoxyethane	B	40	79–80	20	1.4335
1-Methyl-1-hydroxy-3-butanone	Ethyl vinyl ether	B	30	55–56	8	1.4316
2-Methyl-2-nitro-1-propanol	Ethyl vinyl ether	B	32	77–78	10	1.4400
2-Nitro-1-butanol	Ethyl vinyl ether	B	27	72–73	5	1.4402
Furfuryl alcohol	Ethyl vinyl ether	B	28	70–71	40	1.4740
N,N-Dimethylaminoethanol	2-Butoxyethyl vinyl ether	A	36	69–71	120	1.4259
2-(*β*-Hydroxyethyl)-pyridine	Ethyl vinyl ether	B	32	87–90	10	1.5118

temperatures.[4] More recently mercuric salts of weak carboxylic acids have been reported to be particularly effective in catalyzing the transfer of vinyl groups from vinyl ethers to alcohols.[5]

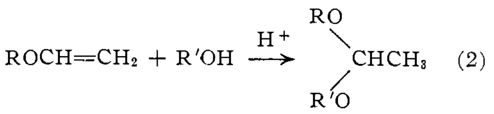
This last reaction, in which weak acid salts of mercury are used to effect vinyl transetherification

$$ROCH{=}CH_2 + R'OH \rightleftarrows ROH + R'OCH{=}CH_2 \quad (1)$$

also was encountered independently in these laboratories several years ago, and it is the purpose of this report to describe our development of this reaction, as well as to suggest a general mechanism for this and the other transfer reactions mentioned above.

Reaction Procedures.—Equation 1 states that vinyl transetherification is reversible, and we have demonstrated that reactions may be made to proceed in either direction by appropriate choice of method. Thus we have prepared *n*-octyl vinyl ether from ethyl vinyl ether and *n*-octyl alcohol, and ethyl vinyl ether from *n*-octyl vinyl ether and ethyl alcohol. The procedure used throughout by the British workers in their disclosure of this new reaction[5] was one in which the desired vinyl ether is directly fractionated out of a solution of catalyst, a high-boiling vinyl ether, and a lower-boiling alcohol which it is desired to vinylate. This is feasible since vinyl ethers generally have boiling points about 10 to 30° below those of the alcohols from which they are derived.[7] We have found this method (method A in Table I) to lead to uniformly good yields of product since the equilibrium in (1) is shifted continuously toward the products, and the newly-formed vinyl ether remains only for a short time in contact with the reaction mixture, thereby minimizing side reactions. Nine examples utilizing this procedure are listed in Table I.

A more general and flexible method, but one in which lower yields are obtained, is the equilibration of a mixture of a vinyl ether, in excess, catalyst and an alcohol which it is desired to vinylate (method B in Table I). The equilibrium is then frozen by flash-stripping the volatile components from the catalyst or by inactivating the catalyst, and the mixture separated. Special advantages of this method are that no restrictions as to boiling point are placed on the vinyl ether serving as vinylating agent (except, of course, that it must ultimately be separable from the product vinyl ether) and that low reaction temperatures may be used, allowing the reaction of thermally-labile materials. The major disadvantage is that low yields (20–40%) are obtained, owing to the occurrence of a side reaction in which acetals are formed by acid-catalyzed addition of alcohol to vinyl ether.[8]



$$ROCH{=}CH_2 + R'OH \xrightarrow{H^+} \begin{matrix} RO \\ \quad\diagdown \\ \quad CHCH_3 \\ \quad\diagup \\ R'O \end{matrix} \quad (2)$$

This side reaction reduces yields to less than half the amount of product to be expected on the basis of an equilibrium constant of one for reaction 1. Table I lists eleven vinyl ethers prepared by method B.

It should be noted that vinyl transetherification provides a one-step synthesis of vinyl ethers directly from alcohols and, thus, in spite of the low yields obtained in reactions carried out by method B, is generally preferable to the common

---

[4] R. L. Adelman, THIS JOURNAL, **77**, 1669 (1955).

[5] G. A. Weeks and W. J. Grant, British Patent 709,106 (May 19, 1954).

[6] M. F. Shostakovskii and N. A. Gershtein, *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik*, **2**, 35 (1952); *C. A.*, **48**, 633f (1954).

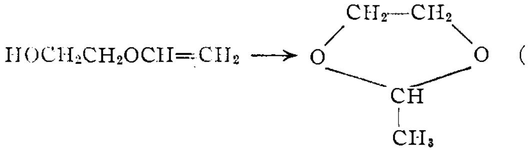
[7] The boiling points of vinyl ethers are usually almost identical with the boiling points of the corresponding ethyl ethers; *cf.* C. E. Schildknecht, A. O. Zoss and C. McKinley, *Ind. Eng. Chem.*, **39**, 180 (1947).

[8] H. S. Hill, THIS JOURNAL, **50**, 2725 (1928); W. Reppe and K. Baur, U. S. Patent 2,000,252 (May 7, 1935). See also more recent papers by M. F. Shostakovskii, *et al.*[9]

[9] M. F. Shostakovskii and E. N. Prilezhaeva, *J. Gen. Chem. (U.S.S.R.)*, **17**, 1129 (1947); *C. A.*, **42**, 3633d (1948).

multi-step procedures (*e.g.*, by cracking of acetals,[10] by dehydrohalogenation of β-haloethyl ethers[11] or by reduction of haloacetals[12]). Base-catalyzed vinylation of alcohols by high pressure acetylene is an alternative one-step method,[13] but vinyl transetherification is of wider application in that it may be used with base-sensitive alcohols which cannot be vinylated with acetylene. Examples of such alcohols which have been converted to vinyl ethers in this work are ethylene chlorohydrin, ethylene cyanohydrin, 1-methyl-1-hydroxy-3-butanone, 2-nitro-1-butanol, 2-methyl-2-nitro-1-propanol, 2-chloroallyl alcohol and 2-(β-hydroxyethyl)-pyridine. Allyl and methallyl alcohols, which are vinylated with difficulty by acetylene,[14] are vinylated by the present method in good yield.

The alcohols listed in Table I indicate a reasonably broad scope for this reaction. Most of these compounds reacted smoothly, but several presented some special aspects which should be mentioned here. Acetal formation was marked in the reaction of ethylene chlorohydrin, even in method A, possibly due to splitting off of HCl with consequent strong acid catalysis of the acetal-forming reaction (2). Some improvement was observed when a salt of a weak acid was added to reduce acidity during the reaction. *t*-Butyl alcohol, ethylene cyanohydrin and N,N-dimethylaminoethanol all reacted very slowly, requiring long reaction times, with resulting losses in yield.[15] A number of other vinyl ethers were tried as vinylating agents for ethylene cyanohydrin, but only with the difunctional 1,2-divinoxyethane was it possible to obtain as high as 40% yield. The vinylation of ethylene glycol also was attempted, but while small amounts of both the monovinyl and divinyl ethers were isolated, the yields were in general low and variable. This is due to the competitive cyclization of 2-hydroxyethyl vinyl ether to 2-methyl-1,3-dioxolane,[12b] which also was isolated from among the reaction products. When amino-alcohols containing primary and secondary amino groups were tried, the reaction was found not to proceed as in (1) but in another direction, which is described in the second paper of this series.[16]


(3)

Catalysts and Catalyst Systems.—Tests made on a variety of metal salts showed that mercuric salts are highly specific catalysts for reaction 1. Inactive salts included those of cobalt, cadmium, copper (cuprous and cupric), iron (ferrous and ferric), lead, silver, nickel and zinc. Of these inactive materials, a number effected the formation of high-boiling products (probably acetals); these salts were mainly halides, although several nitrates also led to this type of reaction.[17]

Adelman already has shown that strong acid salts of mercury will catalyze (1), although vinyl ethers can be isolated only when the reaction is carried out at low temperatures ($-10°$ or lower).[4] We postulate that in the course of the catalysis the acid derived from the anion of the mercuric salt is set free, and it is therefore probable that the strength of this acid will determine the extent of side reaction 2. Our finding that mercuric salts of weak acids, particularly mercuric acetate and mercuric benzoate, are effective catalysts which can be used advantageously at higher temperatures supports this aspect of the catalysis. Thus the specific activity resides in the cation; the acid derived from the anion must take part in some later step of the catalysis but may also be the agent promoting side reactions.

Exceptions to our general observation that strong acid salts of mercury gave acetals at room temperature and above were found in mercuric iodide, mercuric fluoride and chloromercuriacetaldehyde, all of which gave vinyl ether products. These results imply that the extent of dissociation of the mercury salts is also a determining factor in establishing the balance of reactions 1 and 2.

Mechanism of the Reaction.—For those reactions catalyzed by strong acid salts of mercury (*e.g.*, mercuric sulfate), Adelman has postulated a mechanism wherein the vinyl compound first dissociates into an acetylene–mercuric salt complex, which then reacts with alcohol or carboxylic acid to form the product.[3] This mechanism requires that the catalyst for vinyl interchange also be a catalyst for the reaction of acetylene with alcohol or carboxylic acid to give vinyl ether or vinyl ester, and while this is true with mercuric salts of strong acids, it is not the case with mercuric salts of weak acids.[18] We agree with Adelman's proposal that the several mercuric salt-catalyzed vinyl interchange reactions probably proceed through the same general type of mechanism. We consider it more probable, however, that the actual reaction path will more closely correspond to the following scheme, which is written for vinyl transetherification. This mechanism is, in essence, a reversible alkoxymercuration. One of its important aspects is the formation of an intermediate or intermediates which are essentially symmetrical, so that the reverse reactions can lead either to the starting reactants or to the desired products. The anal-

---

[10] K. Baur, U. S. Patent 1,931,858 (October 24, 1933); F. Sigmund and R. Uchann, *Monatsh.*, **51**, 234 (1929).

[11] W. Chalmers, *Can. J. Research*, **7B**, 464 (1932); S. G. Powell and R. Adams, THIS JOURNAL, **42**, 646 (1920).

[12] (a) J. Wislicenus, *Ann.*, **192**, 106 (1878); (b) H. S. Hill and L. M. Pidgeon, THIS JOURNAL, **50**, 2718 (1928).

[13] For references to this work see J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, p. 32, *et seq.*; W. E. Hanford and D. E. Sargent in H. Gilman, ed., "Organic Chemistry," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 1087–1093.

[14] R. Paul, G. Roy, M. Fluchaire and G. Collardeau, *Bull. soc. chim. France*, 121 (1950).

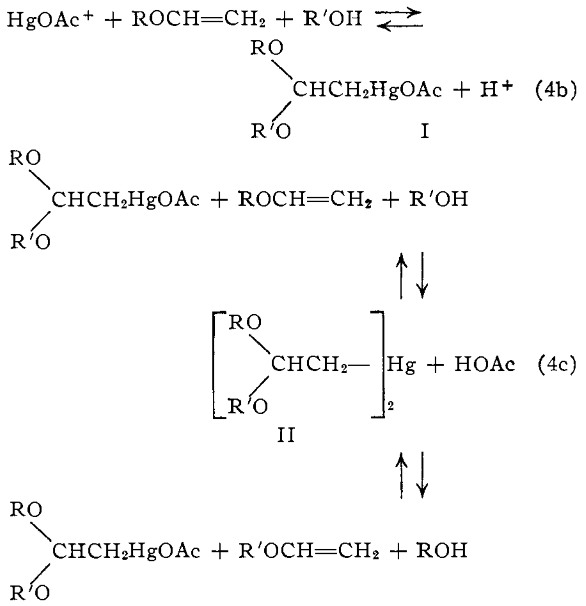
[15] Adelman has reported also that ethylene cyanohydrin reacts very slowly in vinyl acetate–alcohol interchange.[3]

[16] W. H. Watanabe, THIS JOURNAL, **79**, 2833 (1957).

[17] M. F. Shostakovskii and N. A. Gershtein, *J. Gen. Chem. (U.S.S.R.)*, **16**, 937 (1946); *C. A.*, **41**, 1999c (1947), report the use of metal chlorides to catalzye the addition of alcohols to vinyl ethers, forming acetals; see also H. T. Neher and L. N. Bauer, U. S. Patent 2,633,460 (March 31, 1953).

[18] R. R. Vogt and J. A. Nieuwland, THIS JOURNAL, **43**, 2071 (1921).

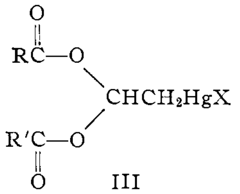
$$Hg(OAc)_2 \rightleftarrows HgOAc^+ + AcO^- \qquad (4a)$$



(4b) I

(4c) II

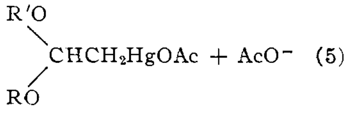
ogous intermediate for vinyl transesterification (III) should also possess the property of reverting either to starting reactants or products, thus explaining the equilibrium character of this reaction.



III

The possibility that intermediates of the structure (I) may in fact be involved in the over-all path of vinyl transetherification is lent some credence by our finding that compounds of structure I readily can be prepared and isolated. Slow addition of sodium ethoxide in ethyl alcohol to mercuric acetate dissolved in ethyl vinyl ether gives a good yield of 2-acetoxymercuri-1,1-diethoxyethane (IV), which can be recrystallized and stored unchanged in the cold for at least several weeks.[19] 2-Acetoxymercuri-1-methoxy-1-ethoxyethane (V) was prepared similarly from sodium methoxide, mercuric acetate and ethyl vinyl ether.

$$R'O^- + ROCH{=}CH_2 + Hg(OAc)_2 \longrightarrow$$



(5)

$$IV,\ R = R' = C_2H_5$$
$$V,\ R' = CH_3\ R = C_2H_5$$

Compound V was kept refrigerated for several months and after this period was found to have decomposed largely into metallic mercury, ethyl vinyl ether and some acetaldehyde.

The 2-acetoxymercuri-1,1-diethoxyethane was found to be decomposed readily by acetic acid to ethyl vinyl ether and ethyl alcohol, thus establishing that such a structure is indeed labile to weak acid. This demonstration is a necessary although not a sufficient condition that structure I be an intermediate in vinyl transetherification. We are led to the proposal of step 4c, in which I reacts further with vinyl ether to give the diacetal II, by our observation that the 2-acetoxymercuriacetals in the absence of added acetic acid (as well as phenyl mercuric acetate, both mercury compounds with a single acid anion) are quite efficient catalysts for vinyl transetherification. This implies that structures $RHgCH_2CH(OR)_2$, where R is phenyl or $(RO)_2CHCH_2$–, may be formed, liberating acetic acid, and may subsequently be decomposed by this acid. As expected, di-*p*-tolylmercury, which is relatively stable to cleavage at the C–Hg bond, has no catalytic activity.

Acknowledgment.—We wish to thank Mr. O. H. Loeffler for much helpful advice and encouragement during the course of this work.

Experimental

Materials.—All vinyl ethers used as vinylating agents, except ethyl vinyl ether and 2-ethylhexyl vinyl ether, which were commercially available, were prepared by base-catalyzed high-pressure vinylation of the alcohols with acetylene[18] and were used either pure or as azeotropes with their precursor alcohols. The commercially obtained vinyl ethers were fractionated before use to remove polymerization inhibitors, which, being amines, inactivate the mercuric salt catalysts. No special effort was made to remove peroxides from the vinyl ethers, other than by distillation; however, these materials were never distilled to less than one-fifth the original pot charge. The alcohols were also purified by distillation. **Dr. P. L.** deBenneville and his associates kindly supplied the 1-methyl-1-hydroxy-3-butanone; all other alcohols were commercially available. All mercuric salts used were the best grade obtainable.

Analytical Methods.—A qualitative test for vinyl ethers which we found most useful in assessing the results of our experiments was as follows: several drops of the compound are placed on a spot plate and a drop of boron trifluoride etherate added with care. If the compound is a vinyl ether, there is an immediate, often violent, reaction with formation of black viscous or solid tars and evolution of fumes. Certain alcohols which are themselves polymerized by acid, such as furfuryl alcohol, also react in this manner to boron trifluoride. Azeotropes of vinyl ethers and alcohols react less violently but still rapidly. Acetals react very slowly, but do darken on standing for several minutes.

Quantitative analyses for the vinyl group were carried out by the method of Siggia, in which the vinyl ether is hydrolyzed in aqueous hydroxylamine hydrochloride, the acetaldehyde thereupon forming the oxime and liberating HCl, and the free HCl then determined by titration.[20]

Catalyst Testing.—The possible catalytic activity of metal salts in effecting reaction 1 was tested by determining whether these salts would convert a solution of ethyl alcohol and *n*-butyl vinyl ether to ethyl vinyl ether and *n*-butyl alcohol, under reflux. By this test the following compounds were found to be active catalysts: mercuric acetate, mercuric benzoate, phenyl mercuric acetate, mercuric citrate, mercuric chromate, mercuric oxalate, mercuric linoleate, mercuric fluoride, mercuric iodide, mercuric lactate, 2-acetoxymercuri-1,1-diethoxyethane, 2-acetoxymercuri-1-ethoxy-1-methoxyethane and chloromercuriacetaldehyde. The fluoride, iodide and lactate were relatively poor catalysts, giving acetals as well as transetherification product. The following compounds led to the formation of high-boiling products, presumably acetals: mercuric sulfate, mercuric nitrate, mercuric chloride, mercuric thiocyanate, mer-

---

(19) A. N. Nesmeyanov, I. F. Lutsenko and N. I. Vereschagina, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 63 (1947); *C. A.*, **41**, 4148i (1948), have prepared chloro- and bromomercuriacetaldehyde in good yield by reaction of an alkyl vinyl ether and mercuric acetate in aqueous solution, followed by addition of KCl or KBr.

(20) S. Siggia, "Quantitative Organic Analysis Via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 63.

curous sulfate, cuprous chloride, nickel bromide, nickel nitrate, nickel iodide, cobalt chloride, antimony trichloride, ferric chloride, bismuth nitrate, arsenic trichloride and sodium bisulfate. Compounds which gave no apparent reaction were mercuric cyanide, mercuric oxide, mercuric sulfide, mercurous chloride, cobalt acetate, cobalt carbonate, cadmium acetate, cadmium carbonate, cadmium oxide, cuprous thiocyanate, cuprous cyanide, cupric carbonate, ferrous sulfate, lead acetate, nickel acetate, nickel cyanide, nickel carbonate, nickel formate, nickel sulfate, thallous bromide, thallous malonate, zinc acetate, zinc bromide, zinc oxide, silver nitrate, silver acetate, ammonium chloride, sodium ethoxide and sodium hydroxide.

Preparation of Ethyl Vinyl Ether. Method A.—This and the following procedure are representative examples of method A. Mercuric acetate (5 g., 0.016 mole) was dissolved in a mixture of dry ethyl alcohol (50 g., 1.08 moles) and *n*-butyl vinyl ether (100 g., 1.0 mole) and the resulting solution placed on a short distilling column fitted with a total condensation partial take-off head. The distillation was first kept at total reflux until the vapor temperature settled at 36–37°, and the rate of distillation was thereafter adjusted so as to keep the boiling point within this range. There was distilled off 71 g. (0.98 mole) pure ethyl vinyl ether, b.p. 36-37°, a yield on the vinyl ether of 98%. Water was then added to the distilling flask, and an azeotrope of *n*-butyl alcohol and water, b.p. 93°, was distilled off and separated to give 71.2 g. (0.97 mole) of *n*-butyl alcohol.

Preparation of Allyl Vinyl Ether. Method A.—A solution of 5 g. of mercuric acetate in 602 g. of *n*-butyl alcohol–*n*-butyl vinyl ether azeotrope (90% vinyl ether, 5.4 moles) and 231 g. (3.98 moles) of dry allyl alcohol was distilled slowly through an efficient distilling column. The reflux ratio was so controlled as to remove distillate at 66–68°. After 6 hr., an additional 5 g. of mercuric acetate was added and distillation continued. An additional 14 hr. of distillation was required to carry the reaction to completion. The pot residue was distilled to recover excess *n*-butyl vinyl ether and the *n*-butyl alcohol formed. The product, 282.5 g., b.p. 66–68°, was an azeotrope of allyl alcohol with allyl vinyl ether, containing about 90% by weight of allyl vinyl ether. This azeotrope was stripped of allyl alcohol by washing with water and redistilling, giving allyl vinyl ether of greater than 98% purity, b.p. 67.5°, n^{20}_D 1.4109. *n*-Butyl vinyl ether (azeotrope with *n*-butyl alcohol) recovered amounted to 125 g.; *n*-butyl alcohol formed amounted to 339.5 g. The yield of pure allyl vinyl ether based on total alcohol was therefore 75%.

Removal of the last traces of allyl alcohol should not be attempted by distillation out of sodium since allyl vinyl ether reacts with sodium and, to an appreciable degree, rearranges to propenyl vinyl ether, $CH_3CH{=}CHOCH{=}CH_2$, b.p. 61–62°, which is very difficult to remove from allyl vinyl ether.[14]

Preparation of *n*-Octyl Vinyl Ether. Method B.—This and the following three procedures are representative of method B. A solution of 3 g. of mercuric acetate in 65 g. (0.5 mole) of *n*-octyl alcohol and 216 g. (3.0 moles) of ethyl vinyl ether was refluxed for 6 hr. During this period, the liquid temperature of the refluxing solution rose from 39.5 to 42°. Several grams of anhydrous potassium carbonate were then added to the cooled reaction mixture and excess ethyl vinyl ether and ethyl alcohol formed in the reaction were removed at reduced pressure. Distillation of this residue directly out of the carbonate gave 28 g. of crude product, b.p. 64–65° (5 mm.), and 30 g. of recovered *n*-octyl alcohol, b.p. 75–77° (5 mm.). The product, which by analysis was shown to contain 83% by weight of *n*-octyl vinyl ether, was distilled out of sodium to give the pure vinyl ether, b.p. 63–64° (5 mm.), n^{20}_D 1.4268. The yield based on total alcohol was 30%, the yield on unrecovered alcohol, 64%.

Preparation of 2-Nitro-2-methylpropyl Vinyl Ether. Method B.—A solution of 5 g. of mercuric acetate and 59.6 g. (0.5 mole) of 2-methyl-2-nitro-1-propanol in 146.2 g. (2.0 moles) of ethyl vinyl ether was heated under reflux for 6 hr. The reaction mixture was then cooled and washed with five 100-cc. portions of water, dried over anhydrous sodium sulfate and flash-distilled at less than 1 mm. pressure into a receiver chilled with Dry Ice until the distillate began to crystallize on the sides of the distilling apparatus. This distillate was fractionated and three cuts totaling 24.9 g., boiling over the range 71–80° (10 mm.), n^{20}_D 1.4404–1.4402, were obtained. These cuts were combined and by analysis found to contain 91.4% 2-nitro-2-methylpropyl vinyl ether. The yield was therefore 32%. Purification of the crude product was carried out by heating it with 50% aqueous sodium hydroxide on the steam-bath, diluting with ether, separating and redistilling to give 99.7% pure vinyl ether, b.p. 77-78° (10 mm.), n^{20}_D 1.4400.

Anal.[21] Calcd. for $C_6H_{11}O_3N$: C, 49.64; H, 7.64; N, 9.65. Found: C. 49.85; H, 7.55; N, 9.52.

Preparation of 2-(β-Vinoxyethyl)-pyridine. Method B.—A solution of 5 g. of mercuric acetate in 61.5 g. (0.5 mole) of 2-(β-hydroxyethyl)-pyridine (redistilled, b.p. 72° (0.35 mm.)) and 288 g. (4.0 moles) of ethyl vinyl ether was refluxed for 7 hr. The reaction mixture was freed of volatile material at 1 mm. pressure at room temperature and the residue from this process then fractionated to give 29.5 g. of crude product, b.p. 98–110° (22 mm.), active to boron trifluoride. Analysis showed this fraction to contain 80% by weight of 2-(β-vinoxyethyl)-pyridine, representing a 32% yield. This material was dissolved in 50 cc. of ether, washed with seven 10-cc. portions of water, dried and redistilled. The pure vinyl ether distilled at 87–89.5° (10 mm.), n^{20}_D 1.5118, d^{26}_4 1.0035, and was 98.4% pure by analysis.

Anal. Calcd. for $C_9H_{11}ON$: C, 72.45; H. 7.43; N, 9.39. Found: C, 72.84; H, 7.44; N, 9.25.

Preparation of 2-Cyanoethyl Vinyl Ether. Method B.—A mixture of 114.1 g. (1.0 mole) of 1,2 divinoxyethane, 35.5 g. (0.5 mole) of ethylene cyanohydrin, 2.0 g. of sodium acetate and 5.0 g. of mercuric acetate was heated under reflux for 2.5 hr. The reaction mixture was cooled and flash-distilled and the distillate fractionated to give several major fractions: 2-methyl-1,3-dioxolane, b.p. 43–44° (180 mm.), 15 g.; recovered 1,2-divinoxyethane, b.p. 71–85° (120 mm.), 42.5 g.; 2-cyanoethyl vinyl ether (95% pure), b.p. 75–85° (20 mm.), 20.5 g. (40% yield). There is no azeotrope formed with this vinyl ether and the alcohol, and it can therefore be purified by refractionation. The 95% crude product from another run in which ethyl vinyl ether was used as the vinylating agent was refractionated to give 100% 2-cyanoethyl vinyl ether, b.p. 79–80° (20 mm.), n^{20}_D 1.4335, d^{22}_4 0.9540.

Anal. Calcd. for C_5H_7ON: C, 61.83; H, 7.27; N, 14.44. Found: C, 61.75; H, 7.23; N, 14.37.

A sample of this product was hydrogenated in heptane with Raney nickel catalyst for 3 hr. under 1500 p.s.i. hydrogen at 100–105°.[22] Approximately three moles of hydrogen was absorbed per mole of compound. Fractionation gave material, b.p. 79° (120 mm.), neutralization equivalent by potentiometric titration with standard base, 103.4 (calculated as 3-ethoxypropylamine, 103.2). To purify this product, it was dissolved in 5% hydrochloric acid, extracted with ether, the acid solution made basic with 5% sodium hydroxide and again extracted with ether. The ether extract of the basic solution was dried over anhydrous sodium sulfate, calcium hydride and calcium oxide added and ether distilled off. The residue was put over fresh calcium hydride and fractionated, yielding material, b.p. 74–75° (120 mm.), n^{20}_D 1.4186, n^{25}_D 1.4166, d^{25}_4 0.8516 (lit.[23] for 3-ethoxypropylamine, n^{20}_D 1.4201, d^{20}_{20} 0.8613).

Anal. Calcd. for $C_5H_{13}ON$: C, 58.21; H, 12.70; N, 13.58. Found: C, 58.11; H, 12.65; N, 13.45.

Preparation of 2-Acetoxymercuri-1,1-diethoxyethane.—A slurry of 180 g. (0.565 mole) of mercuric acetate in 550 cc. of absolute ethyl alcohol was prepared, and to this was added 40 g. (0.538 mole) of ethyl vinyl ether with vigorous stirring. The mercuric acetate dissolved immediately, with an accompanying temperature rise to 40°. The solution was cooled to 20°, and a solution of 0.565 mole of sodium ethoxide in 200 cc. of absolute ethyl alcohol was added at such a rate as to keep the reaction temperature below 21°. The reaction mixture was stirred for 1 hr. and filtered and evaporated to dryness under a nitrogen atmosphere. The residue was then taken up in chloroform, filtered and again evaporated, leaving a mass of white fibrous crystals. Recrystallization from hot 30–60° petroleum ether gave 130 g. of product, m.p. 151–154° dec., a yield of 64% based on ethyl vinyl ether and 61% based on mercuric acetate. This

---

(21) Microanalyses by Mr. C. W. Nash and associates.

(22) We thank Dr. J. LoCicero for performing this hydrogenation.

(23) W. P. Utermohlen, THIS JOURNAL, **67**, 1505 (1945).

material was stored in a vacuum desiccator over potassium hydroxide pellets.

Anal. Calcd. for $C_8H_{16}O_4Hg$: C, 25.50; H, 4.28; Hg, 53.24. Found: C, 25.3; H, 4.5; Hg, 54.0.

Preparation of 2-Acetoxymercuri-1-methoxy-1-ethoxyethane.—A solution of 4 g. (0.174 mole) of sodium in 100 cc. of dry methyl alcohol was added dropwise to a solution of 20 g. (0.063 mole) of mercuric acetate in 250 cc. of dry methyl alcohol until a reddish-orange precipitate of the basic salt began to appear. Ethyl vinyl ether was then added dropwise until this precipitate just dissolved. Alternate additions of sodium methoxide and ethyl vinyl ether were made in this manner until further addition of sodium methoxide failed to precipitate the basic salt. The solution was then evaporated to dryness under vacuum. The residue was taken up in chloroform, filtered to remove sodium acetate and the chloroform solution again evaporated under vacuum. The crystalline residue was recrystallized from 30–60° petroleum ether. About 0.5 g. of this product was tested for catalytic activity, and another small portion was dried in vacuum over phosphoric anhydride, m.p. 56–57°.

Anal. Calcd. for $C_7H_{14}O_4Hg$: Hg, 55.30. Found: Hg, 55.97.

The remainder of the product was stored in a tightly-capped bottle in the refrigerator. Examination of this material after about 7 months showed that it had decomposed largely into free mercury and a colorless two-phase liquid. Fractionation of the liquid gave 2 g., b.p. 31–36°, which had a slight odor of acetaldehyde but was mostly wet ethyl vinyl ether, and 6 g., b.p. 46.5–62°, which probably contained dimethyl acetal.

Decomposition of 2-Acetoxymercuri-1,1-diethoxyethane.—A slurry of 60 g. (0.16 mole) of this compound in 300 cc. of *n*-heptane was brought to gentle reflux on an efficient distilling column. An equimolar amount of glacial acetic acid was then added dropwise to this refluxing slurry over a 45-minute period. The solids in the pot turned from a white to a cream color after this addition, and after 1.5 hr. of reflux, the vapor temperature settled at 36°. Slow fractionation gave 3 g. of 94% pure ethyl vinyl ether. Further fractionation gave 22 g. over the range 40–98°, containing 16.5% ethyl vinyl ether and including a large amount of distillate, b.p. 69–70°, which was the azeotrope of ethyl alcohol with *n*-heptane. The total yield of ethyl vinyl ether was therefore 56%. No free mercury appeared during this distillation until the vapor temperature had reached 70°. All attempts to determine the form in which mercury was present in the distillation residue were unsuccessful, but it appeared that no simple salts of mercury were formed.

PHILADELPHIA 37, PENNA.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ROHM & HAAS CO.]

Homogeneous Metal Salt Catalysis in Organic Reactions. II. The Reaction of Vinyl Ethers with Aminoalcohols and 1,2-Diamines

BY WARREN H. WATANABE

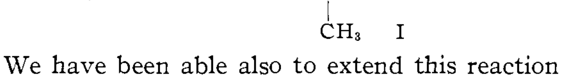
RECEIVED NOVEMBER 2, 1956

When aminoalcohols, $RNH(CR_2)_nOH$, in which R is H, alkyl or aryl and *n* is 2 or 3, are treated with alkyl vinyl ethers in the presence of mercuric salts of weak acids or silver salts such as silver nitrate or silver acetate, there are formed in good yield 2-methyloxazolidines (I, $n = 2$) or 2-methyltetrahydro-1,3-oxazines (I, $n = 3$). Similarly, 1,2-diamines, treated with alkyl vinyl ethers with the same catalysts, give 2-methylimidazolidines (II). These new reactions are improved methods of preparation of these relatively unstable compounds. The relation of these reactions to vinyl transetherification[1] is discussed and a mechanism is proposed.

In a previous publication we have described a method of preparation of vinyl ethers by the reaction

$$ROCH{=}CH_2 + R'OH \rightleftarrows ROH + R'OCH{=}CH_2 \quad (1)$$

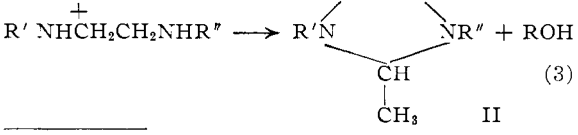
which is catalyzed by mercuric salts of weak acids.[1] We have now found that when the alcohol R'OH is an aminoalcohol, $RNH(CR_2)_nOH$, in which R is H, alkyl or aryl group and *n* is 2 or 3, reaction 1 takes a quite different course. The products in these instances are 2-methyloxazolidines (I, $n = 2$) or 2-methyltetrahydro-1,3-oxazines (I, $n = 3$) rather than the vinyl ethers



(2)

I

We have been able also to extend this reaction to 1,2-diamines, whereby 2-methylimidazolidines are formed



(3)

II

The yields of the cyclic compounds prepared by this method range from about 40 to greater than 80% and are limited largely by the stability of these compounds. This new reaction thus is a simple, useful and generally preferable alternative to the standard method of preparation of I and II, which is by reaction of the aminoalcohols[2] or diamines[3] with acetaldehyde.

Catalysts.—The same catalysts found to be effective in our previous study of vinyl transetherification (*i.e.*, mercuric salts of carboxylic acids[1]) were also the most efficient catalysts for the present reaction. It was of interest that mercuric sulfate, which is a very active catalyst for vinyl transetherification at very low temperatures,[4] had no activity for reaction 2 and, probably due to the strongly basic nature of the reaction mixture, had no effect at all on the vinyl ether. Moreover, in contrast to the vinyl transfer reaction 1, for which mercuric salts are highly specific catalysts, the present reaction also was found to be catalyzed by silver nitrate and silver acetate. Zinc acetate,

---

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

[2] (a) E. D. Bergmann, *Chem. Revs.*, **53**, 309 (1953); (b) L. Knorr and H. Matthes, *Ber.*, **34**, 3484 (1901); (c) A. I. Kiprianov and B. A. Rashkovan, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 1026 (1937); *C. A.*, **31**, 5356 (1937); (d) N. K. Ushenko, *C. A.*, **37**, 4395 (1943); (e) E. Zimkin and E. D. Bergmann, *Rec. trav. chim.*, **71**, 229 (1952).

[3] (a) J. Th. L. B. Rameau, *ibid.*, **57**, 192 (1938); (b) G. Lob, *ibid.*, **55**, 859 (1936); (c) V. S. Salvin and J. R. Adams, U. S. Patent 2,546,169 (March 27, 1951).

[4] R. L. Adelman, THIS JOURNAL, **77**, 1669 (1955).