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

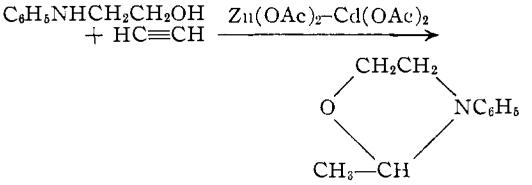
The Preparation of 2-Methyloxazolidines and 2-Methyltetrahydro-1,3-oxazines from Acetylene and Aminoalcohols

BY WARREN H. WATANABE AND LAWRENCE E. CONLON

RECEIVED NOVEMBER 2, 1956

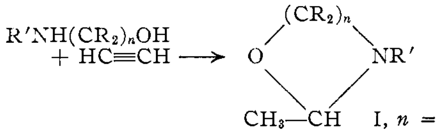
In the absence of any added catalyst acetylene reacts with aminoalcohols, $RNH(CR_2)_nOH$, where R is H or an alkyl group and n is 2 or 3, at pressures of 400–500 p.s.i. and temperatures of 100 to 200°, to form 2-methyloxazolidines (I, $n = 2$) and 2-methyltetrahydro-1,3-oxazines (I, $n = 3$). No vinyl ether is formed in this reaction. Owing to the instability of these products at reaction temperatures, the reactions are best carried out to 10–30% conversions. Yields based on unrecovered aminoalcohol then range from 30 to 75%. The theoretical implications of this new reaction are discussed and a possible mechanism proposed.

When acetylene is treated with an alcohol in the presence of a strong base, there is formed in good yield a vinyl ether. As one example, aminoalcohols are thus readily converted to aminoalkyl vinyl ethers.[1] Reppe has reported, moreover, that when N-phenylethanolamine is treated with acetylene, with zinc and cadmium acetates as catalyst, the isolated product is N-phenyloxazolidine[2] (whether exclusively or in mixture with the vinyl ether is not stated)



(1)

We now have found that even in the absence of any added catalyst, aminoalcohols containing primary or secondary amino groups beta or gamma to the hydroxyl group are converted by acetylene exclusively to 2-methyloxazolidines and 2-methyltetrahydro-1,3-oxazines



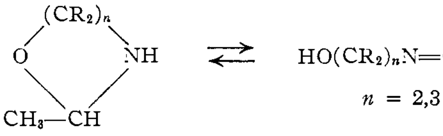
(2)

I, $n = 2,3$

Under these new conditions, aminoalcohols in which R′ is H, alkyl or substituted alkyl, but not aryl (N-phenyl ethanolamine does not undergo this reaction), are transformed to compounds I in yields ranging from about 5 to 75%, with conversions on the order of 13–30%.

A short study of reaction variables showed that yields were determined by a balance of reaction conditions, the major factors being the opposing ones of stability of the products and the reactivity of the aminoalcohols in the acetylene–aminoalcohol reaction. Calculations of very crude rate "constants" from weight gain and time of reaction data, assuming a first-order consumption of aminoalcohol, showed that the highest rate was obtained with N-methylethanolamine. Less rapid were the reactions of ethanolamine and 3-aminopropanol-1, both aminoalcohols with primary amino groups but with no substituents on the carbon chain, and least reactive were the aminoalcohols containing primary amino groups and alkyl substituents alpha or beta to the amino group.

Identification and Stability of Products.—Boiling points, physical constants, analyses and chemical reactions were not sufficient to provide clear-cut characterizations of the products. It was particularly desirable to show that these were actually the cyclic compounds and not the isomeric vinyl ethers. Fortunately there is in the infrared spectra of vinyl ethers a multiplicity of quite characteristic bands (1637, 1615, 960 and 810 cm.$^{-1}$)[3] which makes it possible to determine with certainty the presence or absence of vinyl ether. In none of the compounds prepared was any vinyl ether detected. Positive identification of the ring structure was, however, less satisfactory, although a pattern of peaks at longer wave lengths is claimed to be associated with O–C–N of the ring.[4] In those compounds (I) which have R′ = H, a further aid to identification is provided in the ring-chain tautomerism



(3)

$n = 2,3$

The Schiff base form could be characterized by —C═N— absorption at 1650–1680 cm.$^{-1}$ and, after dilution with a non-polar solvent, non-bonded -OH at 3570 cm.$^{-1}$.[5] All compounds prepared in this work capable of existing in the Schiff base form, except one, showed —C═N— absorption, indicating that at least some Schiff base was present. The exception was 2,4,4-trimethyloxazolidine, which had no absorption at all in the double bond region, thus unambiguously eliminating the vinyl ether form as well as the Schiff base.

The products, immediately after purification by fractional distillation, gave molecular refraction values only slightly lower than those calculated for the cyclic structure but higher by about 1.8

---

[1] (a) W. Reppe, U. S. Patent 1,959,927 (May 22, 1934); (b) W. Reppe and O. Hecht, U. S. Patent 2,157,347 (May 9, 1939); (c) M. F. Shostakovskii, I. A. Chekulaeva and N. A. Gershtein, *Izvest. Akad. Nauk. S.S.S.R., Otdel Khim. Nauk*, 328 (1951); *C. A.*, **46**, 897i (1952).

[2] Quoted in J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949, p. 36.

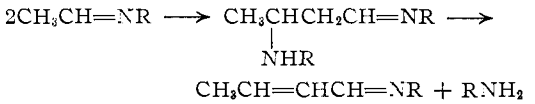
[3] J. D. Stroupe, personal communication; G. D. Meakins, *J. Chem. Soc.*, 4170 (1953).

[4] E. D. Bergmann, E. Zimkin and S. Pinchas, *Rec. trav. chim.*, **71**, 168 (1952); E. D. Bergmann, E. Gil-Av and S. Pinchas, THIS JOURNAL, **75**, 358 (1953).

[5] L. Kahovec, *Acta Phys. Austriaca*, **1**, 307 (1948); *C. A.* **42**, 6665c (1948); L. W. Daasch and U. E. Hanninen, THIS JOURNAL, **72**, 3673 (1950); L. W. Daasch, *ibid.*, **73**, 4523 (1951).

units than values calculated for the Schiff base form. In the case of 2,4,4,-trimethyloxazolidine, which is, from infrared measurements, entirely in the cyclic form, the difference [M_D (theor. cyclic) $- M_D$ (exptl.)] was 0.27. This difference for three of the other four products ranged from 0.21 to 0.31. Thus if there is any validity to the claim that the proportion of the two forms in equilibrium 3 can be determined from the M_D value of the mixture, it must be concluded that these three products initially contained very little, if any, Schiff base. On subsequent warming of these compounds to room temperature there were rapid but measurable increases in both refractive index and density, which may have reflected the approach to an equilibrium state. Infrared curves were taken at least a day after the compounds were prepared, and it is thus not surprising that absorption bands for the Schiff base forms were found in these measurements.

There was also observed a non-reversible condensation of all our products to higher-boiling materials upon standing at room temperature, or upon short heating at higher temperatures. For those compounds (I) with R′ = H, Nace and Goldberg[6] have suggested that this conversion is most probably an aldol condensation proceeding through the Schiff base form



$$2CH_3CH{=}NR \longrightarrow CH_3\underset{NHR}{CH}CH_2CH{=}NR \longrightarrow CH_3CH{=}CHCH{=}NR + RNH_2 \quad (4)$$

$$R = (CR_2)_nOH,\ n = 2 \text{ or } 3$$

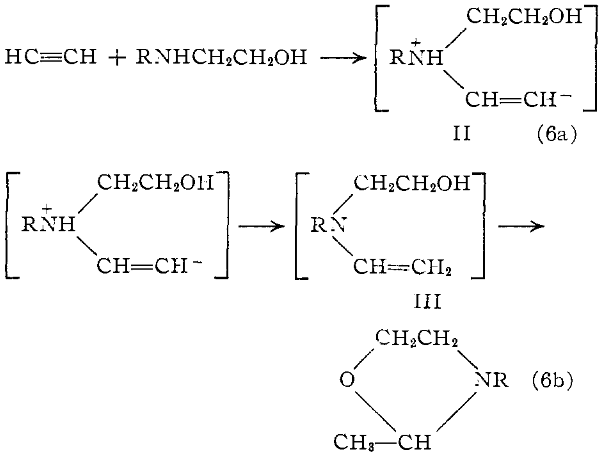
This condensation also contributes to changes in refractive index, density and infrared spectrum, measurements of which therefore must be used with caution if it is intended to draw conclusions as to proportions of oxazolidine and Schiff base. Since 2,3-dimethyloxazolidine cannot exist in Schiff base form, its mode of conversion to higher-boiling compounds is considerably more obscure.

Possible Mechanism.—It is probable that the present reaction is a special instance of vinylation, in which the reaction of acetylene is on the amine nitrogen rather than on the oxygen. It would then be analogous to the reaction of tertiary amines in aqueous solution with acetylene to form vinyl trialkylammonium hydroxide.[7] The general mechanism for such nucleophilic reactions on acetylene has been written as[8]

$$HC{\equiv}CH + N:^- \longrightarrow [HC{=}CHN]^- \text{ rate determining} \quad (5a)$$

$$[HC{=}CHN]^- + HN \longrightarrow CH_2{=}CHN + N:^- \text{ fast} \quad (5b)$$

where $N:^-$ is a nucleophilic species. The present reaction could then proceed in the steps



II (6a)

III

(6b)

The intermediate II may go directly to product or proceed through a transitory N-vinylamine III, which then cyclizes. We have no positive proof of the existence of III, and since there are a number of other likely paths through which II may cyclize, we wish only to emphasize the probability of (6a) as the first step in the mechanism of reaction 2. Evidence supporting (6a) is our observation that acid reduces the rate of reaction 2.[9]

The possibility that (2) proceeds by O-vinylation to a vinyl ether, followed by cyclization, is excluded since O-vinylation requires a strongly basic catalyst. Moreover, it was not found possible to cyclize a representative aminoalkyl vinyl ether, obtained by base-catalyzed O-vinylation, to an oxazolidine under conditions in which reaction 2 occurs readily. A further possibility is that water acts as a catalyst, generating OH^- by hydrolysis of the amine, which reacts with acetylene to form acetaldehyde. The acetaldehyde would then form the oxazolidine from the aminoalcohol, regenerating water. However, deliberately added water neither increased the rate of reaction nor improved the conversion to product; the reverse was rather the case.

Since reaction 1 is catalyzed by metal salts, it might be conceived that the apparently uncatalyzed reaction 2 was actually catalyzed by trace amounts of metal salts dissolved from the metal reactor. We do not believe this to be the case since sulfur, a mercaptan and a sequestering agent, all effective poisons for metal-catalyzed reactions, do not inhibit reaction 2. If, however, reaction 2 is indeed catalyzed by metal salts, then it no longer becomes possible to eliminate a two-step mechanism in which a vinyl ether is first formed, then cyclized. This is so since each step is independently known. Zinc and cadmium salts are stated to be catalysts for the vinylation of alcohols,[10] and we have shown that these same salts will catalyze

---

[6] H. R. Nace and E. P. Goldberg, This Journal, **75**, 3646 (1953); the adlol condensation of an aldimine has been demonstrated by W. S. Emerson, S. H. Hess and F. G. Uhle, *ibid.*, **63**, 872 (1941).

[7] (a) W. Reppe, German Patent Appln. I-37, 024 (IVe/12o); B.I.O.S. Final Report No. 359, Item No. 22; (b) C. Gardner, V. Kerrigan, J. D. Rose and B. C. L. Weedon, *J. Chem. Soc.*, 789 (1949).

[8] R. Rigamonti and L. Bernardi, *Chimica e industria*, **34**, 561 (1952); S. I. Miller and G. Shkapenko, This Journal, **77**, 5038 (1955).

[9] *Cf.* W. H. Watanabe and L. R. DeFonso, *ibid.*, **78**, 4542 (1956), in which it is shown that acid sharply reduces the rate of an aminolysis reaction. The aminolysis is therefore proposed to proceed largely through the amine anion, RNH^-. Since aminolysis and reaction 6a are both nucleophilic reactions of amines, it could be considered that the retarding action of acid on (6a) argues for $HOCH_2CH_2\overset{-}{N}R$ as the actual reacting species.

[10] W. Reppe and O. Hecht, U. S. Patent 2,157,348 (May 9, 1939); T. H. Insinger, British Patent 656,556 (August 29, 1951).

the cyclization of aminoalkyl vinyl ethers to 2-methyloxazolidines.[11]

Acknowledgments.—We thank Mr. O. H. Loeffler for his constant advice and encouragement during the course of this work and acknowledge with pleasure many stimulating discussions held with Dr. H. J. Schneider. Mr. Benjamin C. Wilbur provided technical assistance in a portion of this work.

Experimental

Materials, Apparatus and General Procedure.—The aminoalcohols were all commercially available compounds and were redistilled before use. As reactors there were used a 250-ml. magnetically-stirred stainless steel autoclave, heated with high-pressure steam, and a 300-ml. stainless steel rocking bomb, heated with a liquid heat transfer agent. The general procedure for all runs was as follows: The aminoalcohol was charged to the reactor, the reactor then sealed and pressure-tested, swept twice with nitrogen and twice with acetylene and finally cut off under about 50 p.s.i. acetylene. Heat was then applied to bring the reactor up to reaction temperature and the temperature maintained by suitable controls. Temperatures were in the range 100–180°. Acetylene was then pressed in to 400–500 p.s.i. and this pressure maintained by replenishing the acetylene as required. At the end of the reaction period the reactor was cooled, vented and drained. The raw product was in most instances directly fractionated under nitrogen to obtain the pure material. The product fractions were collected in receivers cooled with ice-water and every attempt was made to measure the density and refractive index of these materials within 5 min. of the time when the product was removed from the distilling column. It should nevertheless again be emphasized that some of the products, notably those with R′ = H in I, increased rapidly in these constants as the compounds aged, and our values may therefore not be entirely reliable. The neutralization equivalents of the products, as reported below, were obtained from potentiometric titration of the compounds in water with standard hydrochloric acid. Yield and conversion data for the reactions studied are given in Table I.

Preparation of 2-Methyloxazolidine.—About 175 g. of ethanolamine was dissolved in 60 g. of benzene and the solution distilled to remove any benzene–water azeotrope. Most of the benzene was then boiled off and the residue (169.0 g.) was charged to the magnetically-stirred autoclave. Since 10 g. of benzene was recovered later from the products, the charge therefore consisted of 159 g. (2.60 moles) of ethanolamine. Reaction with acetylene was then carried out according to the above general procedure at 145–150° for 2.5 hr. The material drained from the reactor weighed 180 g., the gain in weight of 11 g. corresponding to an acetylene uptake of 0.42 mole. Fractionation of this reaction mixture gave 26.0 g. of crude 2-methyloxazolidine, b.p. 50–56° (60 mm.), and 107.0 g. of recovered ethanolamine, b.p. 100° (90 mm.) –92° (40 mm.). The crude oxazolidine was therefore obtained in 12% conversion and 36% yield, based on unrecovered aminoalcohol. This material immediately was sealed in an ampoule under nitrogen and stored in the refrigerator. After storage for 13 days, it was found to have yellowed and become quite viscous. It was, however, combined with the crude product from another preparation of 2-methyloxazolidine and refractionated. Since the residue from this distillation amounted to 17.2 g. (largely column hold-up), it was clear that a large proportion of the 26 g. of apparently polymerized 2-methyloxazolidine had been regenerated in the distillation. The pure compound had b.p. 51–52° (60 mm.), $n^{25}{}_{D}$ 1.4338, $d^{25}{}_{4}$ 0.9651, M_D 23.50 (theor. 23.71), neut. equiv. 90.13 (theor. 87.12). These constants do not agree with those reported by Knorr and Matthes[12] and Doughty, *et al.*[13]

Anal.[14] Calcd. for C_4H_9ON: C, 55.14; H, 10.41; N, 16.08. Found: C, 55.29; H, 10.38; N, 15.92.

TABLE I

THE EFFECT OF TEMPERATURE AND REACTION TIME ON YIELDS

Temp., °C.	Reacn. time, hr.	Conversion[a] %	Yield,[b] %
N-Methylethanolamine to 2,3-dimethyloxazolidine			
112	0.6	25	54
149	1.5	42	..
144	2.5	35	57
1-Aminopropanol-2 to 2,5-dimethyloxazolidine			
151	2.6	14	50
147	5.1	13	39
150	6.3	10	35
Ethanolamine to 2-methyloxazolidine			
111	5.0	8	..
147	2.5	12	36
151	4.2	18	..
180	3.2	3	5
2-Amino-2-methylpropanol-1 to 2,4,4-trimethyloxazolidine			
148	1.8	4	..
145	2.6	6	30
150	5.7	10	72
175	10.5	31	73
2-Aminobutanol-1 to 2-methyl-4-ethyloxazolidine			
180	2.3	23	56
3-Aminopropanol-1 to 2-methyltetrahydro-1,3-oxazine			
152	3.9	12	31

[a] Per cent. (by mole) of total aminoalcohol converted to pure product. [b] Per cent, (by mole) of unrecovered aminoalcohol converted to pure product.

Preparation of 2,5-Dimethyloxazolidine.—A charge of 141.0 g. (1.88 moles) of 1-aminopropanol-1 was treated with acetylene in the magnetically-stirred autoclave for 2.6 hr. at 136–152°. Fractionation of the reaction mixture gave 27.5 g. of 2,5-dimethyloxazolidine (14% conversion, 50% yield) b.p. 68–69° (120 mm.), $n^{25}{}_{D}$ 1.4304, $d^{25}{}_{4}$ 0.9246, M_D 28.28 (theor. 28.33), neut. equiv. 101.3 (theor. 101.15), and 100 g. of recovered 1-aminopropanol-2, b.p. 97–100° (80 mm.).

Anal. Calcd. for $C_5H_{11}ON$: C, 59.37; H, 10.96; N, 13.85. Found: C, 59.63; H, 10.99; N, 13.90.

Preparation of 2-Methyl-4-ethyloxazolidine.—2-Aminobutanol-1 (139.0 g., 1.56 moles) was treated in a similar fashion with acetylene. Fractional distillation of the product gave 41.5 g. of 2-methyl-4-ethyloxazolidine, b.p. 83° (105 mm.) to 81° (86 mm.) (mainly at 81.5° (86 mm.)), and 82.0 g. of recovered 2-aminobutanol-1, b.p. 113–115° (76–72 mm.) (23% conversion, 56% yield). Redistillation of this product gave pure 2-methyl-4-ethyloxazolidine, b.p. 84° (100 mm.), $n^{25}{}_{D}$ 1.4302, $d^{25}{}_{4}$ 0.9119, M_D 32.64 (theor. 32.95), neut. equiv. 115.7 (theor. 115.17).

Anal. Calcd. for $C_6H_{13}ON$: C, 62.57; N, 12.16; H, 11.38. Found: C, 62.80; N, 11.94; H, 11.22.

Preparation of 2,4,4-Trimethyloxazolidine.—2-Amino-2-methylpropanol-1 was dried by azeotropic distillation with benzene, and 122 g. of a mixture consisting of 114 g. (1.28 moles) of the aminoalcohol and 8 g. of benzene was allowed to react at 175° for 10.5 hr. The reaction mixture was fractionated into 46.0 g. of crude 2,4,4-trimethyloxazolidine, b.p. 62–75° (120 mm.), and 66.0 g. of recovered 2-amino-2-methylpropanol-1, b.p. 102° (120 mm.) to 97° (55 mm.) (31% conversion, 73% yield). This product was redistilled to give the pure oxazolidine, b.p. 72° (125 mm.), $n^{25}{}_{D}$ 1.4215, $d^{25}{}_{4}$ 0.8946, M_D 32.68 (theor. 32.95), neut. equiv., 118.6 (theor. 115.2).

Anal. Calcd. for $C_6H_{13}ON$: C, 62.57; H, 11.38; N, 12.16. Found: C, 62.59; H, 11.20; N, 11.91.

Another reaction carried out at 150° for 5.7 hr. gave a 10% conversion and 72% yield. When 3% by weight of water was added to the aminoalcohol before reaction, the conversion dropped to 4% and the yield to 22%.

---

[11] This work will be described in a later communication.

[12] L. Knorr and H. Matthes, *Ber.*, **34**, 3484 (1901).

[13] J. B. Doughty, C. L. Lazzell and A. R. Collett, THIS JOURNAL, **72**, 2866 (1950).

[14] All microanalyses by Mr. C. W. Nash and associates.

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}_{D} 1.4200, d^{25}_{4} 0.8991, M_{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}_{D} 1.4382, d^{25}_{4} 0.9480, M_{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}_{D} 1.4390; 9.5 g., b.p. 65–68° (100 mm.), n^{25}_{D} 1.4389; 55.0 g., b.p. 68–70° (100 mm.), n^{25}_{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).