(5) H_1 of pyridine-4-carboxaldehyde is a triplet with $J = 0.35$ c.p.s. $J_{H_1H_4}$ of pyridine-2-carboxaldehyde is 0.60 c.p.s. in dimethyl sulfoxide and 0.50 c.p.s. in carbon tetrachloride. $J_{H_1H_6}$ of pyridine-3-carboxaldehyde is 0.44 c.p.s. in carbon tetrachloride[8]; we find it to be 0.50 c.p.s. in dimethyl sulfoxide. If these aldehydes are planar, then pyridine-2-carboxaldehyde exists 70-85% as XIII and 15-30% as XIV. Similarly, pyridine-3-
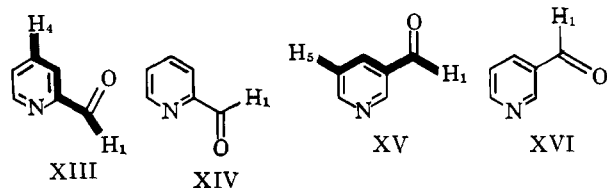
carboxaldehyde exists approximately 70% as XV and 30% as XVI.

The preference of certain conformations over others can be readily explained in terms of competitive hydrogen bonding and dipole, electrostatic, and resonance interactions.

Acknowledgment.—We thank the United States Atomic Energy Commission for financial support, Grant AT(11-1)-1189.

(8) V. J. Kowalewski and D. G. de Kowalewski, *J. Chem. Phys.*, **36**, 266 (1962).

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Preparation of Solutions of Pure Nitrous Acid

Sir:

The existence of solutions of pure nitrous acid has not been previously reported in the literature and the following technique for their production has been developed. Solutions of sodium nitrite in mixtures of water and ethylene glycol dimethyl ether (glyme) are ion exchanged at $-30°$ to produce effluent solutions of relatively pure nitrous acid.

The process was originally used for the preparation of pure polyamine nitrites by direct neutralization, but can also be used to prepare the nitrites of other cations or for nitrosation and diazotization reactions.

Following is a typical example of the generation of nitrous acid solutions: A 1×16-cm. column of acid form Dowex 50W-X4 was equilibrated at $-30°$ with a 66% solution of glyme in water. Through this column at $-30°$ was passed 0.284 g. (4.12 mequiv.) of $NaNO_2$ as a 3% solution in 66% glyme-water. Flow rate was 12 ml./min. which gave a column residence time of about 24 sec. The nitrite solution was followed by 30 ml. of glyme-water.

Column effluent was collected in water containing 5.57 mequiv. of KOH, and back titration of the effluent solution showed a recovery of 97% of theoretical acidity.

Recovery of NO_2^- was determined by the following methods. The neutralized effluent was purged with N_2 through a gas diffusion tube to eliminate the possible presence of dissolved nitrogen oxide gases. A sample of neutralized and purged effluent was then titrated with ceric sulfate which showed a recovery of 94% of the NO_2^-. Evaporation of a portion of the neutralized effluent gave a weight balance which also corresponded to a 94% recovery of HNO_2. Less than 4 p.p.m. of sodium was found in the effluent solution (about 0.01 mequiv.). These results indicate that the production of nitrous acid is nearly quantitative, allowing for a

small amount of column holdup and analytical inaccuracies. If the difference between 97% acidity recovery and 94% nitrite recovery is real, then this may represent decomposition of HNO_2 to HNO_3 and NO. However, the solids recovered are entirely accountable for as KNO_2, which refutes the decomposition. The fate of about 3% of the HNO_2 therefore remained uncertain.

Yost and Russell[1] report the rate of decomposition of nitrous acid as being proportional to the fourth power of nitrous acid concentration, and very temperature dependent. This extreme dependence of rate on concentration and temperature showed the importance of operating at low temperatures and concentrations in order to prepare pure HNO_2.

The effect of concentration is illustrated by the 98% recovery of nitrous acid at as high a temperature as $0°$ when the $NaNO_2$ concentration was reduced to 1.17%.

The applicability of this technique is limited mainly by the need for a nonreactive solvent system which will hold usable amounts of nitrite salts at low temperature. In this work, the glyme–water system was found most useful, although three-component freezing-point diagrams were also explored for $NaNO_2$–water with dimethyl ether, dimethyl sulfoxide, acetone, and methanol. It is quite possible that the reactivities of the last three toward HNO_2 would limit their usefulness. Temperatures of phase separation for the $NaNO_2$–glyme–water system are shown in Table I.

TABLE I

| | Composition, % | | Temperature of |
$NaNO_2$	Glyme	Water	phase separation, °C.
7	45	48	-35
8	60	32	-5
8.68	41.3	50	-34
10	50	40	-26
10	40	50	-29
14	30	56	-20

For those interested in extremely low temperatures, the following may be useful: A $-44°$ freezing point is achieved with 12% $NaNO_2$, 40% dimethyl sulfoxide, and 48% water. A $-50°$ freezing point is achieved with 12% $NaNO_2$, 38% methanol, and 50% water.

(1) D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, New York, N. Y., 1946, pp. 58-61.

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Optically Active Vinyl Polymers. X. Synthesis of Optically Active Poly-α-olefins from Racemic Monomers by Asymmetric Catalysts

Sir:

Although the resolution of the polymers of some racemic α-olefins in fractions having optical activity of opposite sign[1] seems to indicate that the polymerization rate of the two antipodes on a single catalytic center is remarkably different, no asymmetric catalyst which electively polymerizes one of the two antipodes of racemic α-olefins has been described.[2]

The polymerization of racemic 3,7-dimethyl-1-octene and 3-methyl-1-pentene has been investigated now using catalysts prepared from $TiCl_4$ and bis[(S)-2-methylbutyl]zinc having $[\alpha]^{25}D +9.93°$ (optical purity 96%).[3]

(1) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Natta, *J. Am. Chem. Soc.*, **84**, 1487 (1962).

(2) P. Pino, F. Ciardelli, and G. P. Lorenzi, paper presented at the International Symposium of Macromolecular Chemistry, Paris, July 1-6, 1963.