N alcoholic sodium hydroxide for 15 hours at room temperature. The material was recovered by the use of an IR-120 column and the resulting white powder was assayed using an *Escherichia coli* mutant 81–3 which requires shikimic acid and it was found to be active. The infrared spectra of *dl*-shikimic acid and natural *l*-shikimic acid taken in KBr were compared and found to be almost identical. The melting point of *dl*-shikimic acid was found to be 193–195° and *l*-shikimic 190–191°. On mixed melt of the *dl* and *l* acids the melting point was 188–190°.

Acknowledgment.—We are indebted to Dr. Max E. Rafelson, Department of Biochemistry, University of Illinois Medical School, for the biological assays and comparison of our final product with natural shikimic acid.

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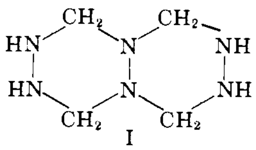
RECEIVED DECEMBER 6, 1958

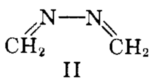
MONOMERIC FORMALDAZINE—SYNTHESIS OF 1,3,4-THIADIAZOLIDINE—A NEW HETEROCYCLE

Sir:

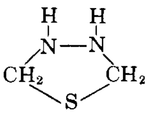
The reaction of aqueous formaldehyde with hydrazine leads only to "tetraformaltrisazine" I[1] or a white amorphous polymer[2] instead of the expected formaldazine II.



I



II



III

However, by thermally decomposing[3] the polymer over a small flame in a nitrogen atmosphere (5–20 mm. pressure) and collecting the distillate in a Dry Ice trap we have isolated (50% yield), purified by low temperature distillation and characterized monomeric formaldazine II.

The redistilled product collected as large colorless or white crystals, m.p. −48 ± 3°, soluble in the cold in common polar organic solvents. On warming to room temperature (either neat or in solution) the material polymerized spontaneously, first to a viscous liquid and eventually to a white solid, *anal.*[4] Found: C, 42.61; H, 7.40; N, 50.06.

From the ratio of the intensities of the isotopic 57 to the parent 56 peak in the mass spectrometer (observed 3.05), the molecular formula was determined to be $C_2H_4N_2$ (theoretical 3.04).[5]

Of the many possible structures, the infrared spectrum in the vapor phase (52 mm., 10-cm. cell) was compatible only with structure II (bands at 3.26(m), 3.41(ms), 4.93(mw), 6.04(w), 6.12(w), 7.08(w), 7.16(m), 8.47(m), 8.64(w) and 9.81(s) microns). The n.m.r. spectrum (in carbon tetrachloride) showed four peaks (two doublets) centered at about +1 parts per ten million from benzene. Using the shift charts[6] one predicts +3 p.p.t.m. for the terminal methylene hydrogens.

The only non-polymeric derivative prepared to date has been assigned the interesting 1,3,4-thiadiazolidine structure III. Mixing ether solutions of an excess of hydrogen sulfide and formaldazine at −70° gave a precipitate which was sublimed at room temperature yielding beautiful white crystals with a slight sulfide-like odor, m.p. 86–91° (dependent on rate of heating, slight decomposition), *anal.* Found: C, 26.93; H, 6.85; N, 31.09; S, 35.63; mol. wt. 90 (mass spectrometer); 117 (Menzies).[4] The infrared spectrum showed the N–H band; the n.m.r. spectrum (in deuterated chloroform) showed two types of hydrogens in the ratio of 2.25 to 1 (theory 2 to 1). The methylene hydrogen resonance was at +30 p.p.t.m. from benzene (predicted[6] +33) and the amine hydrogen resonance was a broad band centered at +37.5 p.p.t.m. The material was stable in the cold under nitrogen, but decomposed slowly at room temperature with the release of hydrogen sulfide (odor). Other reactions of formaldazine are under investigation.

The kind assistance of F. C. Stehling, D. E. Nicholson, N. F. Chamberlain and O. G. Weir of the Humble Oil and Refining Company is gratefully acknowledged.

[1] K. A. Hofmann and D. Storm, *Ber.*, **45**, 1728 (1912).

[2] G. Pulvermacher, *ibid.*, **26**, 2360 (1893).

[3] The conversion was later found to be similar in principle to the method for preparing N-alkylmethylenimines, J. L. Anderson, U. S. Patent No. 2,729,679; see *C. A.*, **50**, P12097d (1956).

[4] Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

[5] Method described by H. E. Lumpkin, Meeting of Gulf Coast Spectroscopic Group, Corpus Christi, March, 1959.

[6] See N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959).

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RECEIVED MARCH 25, 1959

IONIC POLYMERIZATION. THE EFFECT OF SOLVENTS ON THE COPOLYMER COMPOSITION IN CATIONIC CATALYZED POLYMERIZATION

Sir:

We wish to report an interesting and new observation in homogeneous cationic catalyzed polymerization. The object of this work was to study the effects of some reaction variables, particularly catalyst and solvent, on the monomer reactivity ratios in the *p*-chlorostyrene-isobutylene copolymer system catalyzed by cationic initiators. Such studies offer an effective method of obtaining the relative reactivities of monomers toward carbonium ions, and the system studied in this work is of particular value in this respect because of the differences in the reactivity and structure of the carbonium ions derived from the two monomers, and of the monomers themselves. This might be expected to lead to changes in reactivity ratios as the polarity of the solvent changes. In previous work,[1] only minor effects on monomer reactivity ratios were observed with monomer pairs of similar types (styrene, *p*-chlorostyrene) in homogeneous cases with mixed solvent system (CCl_4, $C_6H_5NO_2$). Here localized solvent effects from one of the solvents may play a role. With styrene and 3,4-

[1] C. G. Overberger, R. J. Ehrig and D. Tanner, THIS JOURNAL, **76**, 772 (1954).