

material from ethyl acetate-hexane gave 4.0 g. (6.4%) of tan solid, m.p. 131–132°. Two additional recrystallizations of this solid from ethyl acetate-hexane gave pure VII as white needles: m.p. 132–133°; $\nu_{\text{N-H}}$ 3108 (N–H) and 1665 cm^{-1} (amide carbonyl); $\lambda_{\text{max}}^{\text{EtOH}}$ 215 $\text{m}\mu$ (ϵ 14,850) and 296 $\text{m}\mu$ (ϵ 9250).

Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{F}_6\text{NO}$: C, 49.84; H, 4.18; F, 36.39; N, 4.47; mol. wt., 313. Found: C, 49.99; H, 4.35; F, 38.67; N, 4.23; mol. wt., 322.¹³

Further elution of the column with ether afforded 2.4 g. of recovered I, m.p. 129–130° (from ethyl acetate-hexane). The remainder of all fractions were intractable tars.

Acknowledgment.—The author is indebted to M. A. Rebenstorf for carrying out the autoclave reaction and to the Physical and Analytical Chemistry Department of The Upjohn Company for the microanalytical and spectral determinations.

(13) The molecular weight was determined ebullioscopically in chloroform.

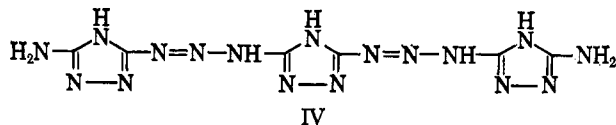
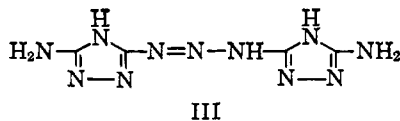
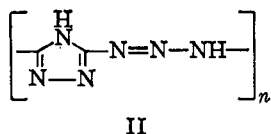
The Diazotization and Autocoupling of Guanazole¹

M. HAUSER

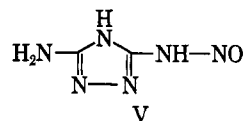
Central Research Division, American Cyanamid Company,
Stamford, Connecticut

Received June 12, 1964

As part of a program directed toward the preparation of novel heteroaromatic monomers and polymers of high nitrogen content, we were interested in studying some aspects of the chemistry of guanazole (I, 3,5-diamino-1,2,4-triazole). Particular emphasis was placed on means of "connecting" two or more molecules of I. Stolle and Dietrich² had reported that I could be diazotized or tetrazotized and the diazonium salts then coupled with phenol to give the corresponding mono- and bisazo compounds. We felt that tetrazotized I when treated with additional I could give polymer II as well as the analogous dimer III and trimer IV.



The work of Stolle and Dietrich had indicated that it would be difficult to obtain a diazonium solution free of tetrazotized material and *vice versa* by direct diazotization. However, they had also reported that treatment of 3-amino-5-nitrosamino-1,2,4-triazole (V), prepared from I and sodium nitrite in dilute acetic



acid,³ with concentrated hydrochloric acid gave a diazonium solution capable of coupling. This appeared a logical starting point for the synthesis of II–IV.

When a diazonium solution prepared from V was added to an aqueous solution of an equivalent amount of I, 1,3-bis[3-(5-amino-1,2,4-triazolyl)]triazene (III) was obtained as the dihydrochloride. Dimer III on diazotization with an equivalent of nitrous acid and coupling with an equivalent of I was converted to the trimer 3,5-bis[3-(5-amino-1,2,4-triazolyl)]triazenyl-1,2,4-triazole (IV).

The known⁴ pH dependence of coupling reactions led us to believe that at higher pH the diazonium solution prepared from V might undergo a self-coupling reaction. Accordingly, V was treated with hydrochloric acid and the solution was then neutralized. The precipitate obtained proved to be II. Polymer II was also obtained by tetrazotization of III and coupling with I.

The direct diazotization and autocoupling of I proceeded readily, but, as expected, some difficulties were encountered in separation and determination of yields of the products obtained. Treatment of I with 1 mole of nitrous acid, followed by coupling with an additional mole of I, yielded 31% of III and 11% of II. These two materials were separated by treating the reaction precipitate with boiling water. The insoluble II was removed by filtration and III was then recovered by concentration of the aqueous extract. Under these conditions no IV was isolated, probably due to the fact that IV merely represents a specialized case of II and has similar solubility characteristics. The primary differentiation between III and the higher homologs is that III is amphoteric while II and IV are acidic.

As the ratio of nitrous acid to I was increased, the expected increase in the ratio of yields of II and III was observed (Table I). At large excesses of nitrous

TABLE I
DIAZOTIZATION AND COUPLING OF I

Mole ratio of NaNO_2 -I	Yield of III, %	Yield of IV, %	Yield of II, %
1	31	...	11
2	22	...	30
3	6	3	49
4	10	4	34

acid, the yield of II was diminished but the yield of III was increased. This increase may be a function of excess nitrous acid diazotizing the guanazole used in the coupling step. During the course of some of these reactions, particularly those at three-to-one or higher excess, it was noted that on standing the reaction filtrates deposited additional material. These proved to be mixtures of III and IV. Evidently, IV is some-

(1) This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by the Bureau of Naval Weapons, RMMP, under Contract NOrd 18728.

(2) R. Stolle and W. Dietrich, *J. prakt. Chem.*, [2] **139**, 193 (1934).

(3) R. Stolle and K. Krauch, *ibid.*, [2] **88**, 311 (1913).

(4) K. H. Saunders, "The Aromatic Diazo Compounds and Their Technical Applications," 2nd Ed., Edward Arnold and Co., London, 1949, p. 194 ff.

what more acid soluble than II and tends to precipitate more slowly. These observations were not, however, strictly reproducible and there was considerable variation in the amount and composition of the mixtures from run to run even under apparently "identical" conditions. The figures given in Table I represent the average of several runs.

A brief investigation was also made of the effect on product distribution of varying the amount of I used for coupling. It was found that above the stoichiometric amount there was essentially no variation in the yields of II, III, and IV, but that the rate of coupling appeared to be more rapid with excess I present.

In analogy to the preparation of II by neutralization of an acid solution of V, neutralization of the diazonium solution prepared from equivalent amounts of I and sodium nitrate also gave II.

Experimental⁵

1,3-Bis[3-(5-amino-1,2,4-triazolyl)]triazene (III).—A mixture of 2.0 g. (0.016 mole) of V and 50 ml. of concentrated hydrochloric acid was stirred 1 hr. at 25°. The chilled solution was then added to a cold solution of 1.6 g. (0.016 mole) of I in 50 ml. of water. After 1 hr., the precipitate was filtered, dried, and recrystallized from methanol to give 2.1 g. (46.5%) of bright yellow needles, m.p. 187° dec. (explosive). This material was the dihydrochloride of III⁶ (IIIa).

Anal. Calcd. for $C_4H_7N_{11} \cdot 2HCl$: C, 17.0; H, 3.2; Cl, 25.2; N, 54.6. Found: C, 16.7; H, 3.5; Cl, 24.8; N, 54.5.

Infrared (Nujol mull): 3290 (m), 3210 (m), 3175 (s), 2700 (s), 2550 (m), 1690 (s), 1650 (s), 1485 (m), 1260 (s), 1115 (m), 1055 (m), 920 (s), 800 (m), 715 (s).

3,5-Bis[3-(5-amino-1,2,4-triazolyl)]triazene-1,2,4-triazole (IV).—A solution of 0.69 g. (0.01 mole) of sodium nitrite in 10 ml. of water at 5° was slowly added to a cold slurry of 2.8 g. (0.01 mole) of IIIa in 100 ml. of 10% hydrochloric acid. A clear solution was rapidly obtained. To this solution was added 1.0 g. (0.01 mole) of I in 20 ml. of water. The resulting precipitate was filtered and washed thoroughly with boiling water to give 1.8 g. (56%) of IV, an orange-red solid, m.p. >300°. A recrystallization solvent could not be found and microanalysis⁷ was performed on the crude, washed material.

Anal. Calcd. for $C_6H_9N_{17}$: C, 22.6; H, 2.8; N, 74.6. Found: C, 22.7; H, 2.8; N, 74.6.

Infrared (Nujol mull): 3320 (m), 3160 (s), 1640 (s), 1560 (m), 1330 (m), 1210 (m), 1080 (m), 925 (m), 720 (m).

Poly(3-diazoamino-1,2,4-triazole) (II). **A. From V.**—A mixture of 2.0 g. (0.016 mole) of V and 50 ml. of concentrated hydrochloric acid was stirred 1 hr. at 25°, then chilled to 10° and neutralized with 5 N sodium hydroxide. The resulting precipitate was filtered, washed with boiling water, and dried to give 0.78 g. (45%) of II, a dark red, amorphous solid, m.p. >300°.

B. From IIIa.—A solution of 1.73 g. (0.025 mole) of sodium nitrite in 20 ml. of water at 5° was slowly added to a cold slurry of 2.8 g. (0.01 mole) of IIIa in 100 ml. of 10% hydrochloric acid. A cold solution of 1.0 g. (0.01 mole) of I in 20 ml. of water was then added to this solution. The precipitate was washed with boiling water to give 1.0 g. (31%) of II.

The infrared spectra of the products from A and B above were identical. They were also identical with that of IV except for a broadening and loss of sharpness of the various bands.

Microanalyses of II varied with the molecular weight (see below) of the polymer but were in a range.

Anal. Calcd. for $C_6H_9N_9$: C, 21.8; H, 1.8; N, 76.4. Found: C, 21.5–22.5; H, 2.0–2.5; N, 75–76.

(5) Melting points were taken on a calibrated Fisher-Johns apparatus. Infrared spectra were taken on a Perkin-Elmer Infracord spectrophotometer.

(6) Compound IIIa was often obtained as a hemihydrate; note the following analysis: Calcd. for $C_4H_7N_{11} \cdot 2HCl \cdot 0.5H_2O$: C, 16.5; H, 3.4; Cl, 24.4; N, 52.9; neut. equiv., 291. Found: C, 16.4; H, 3.3; Cl, 23.9; N, 52.7; neut. equiv., 293. Drying at 130° (1 mm.) was required for complete dehydration.

(7) Compound IV was often obtained as a hydrate. Calcd. for $C_6H_9N_{17} \cdot H_2O$: C, 21.4; H, 3.3; N, 70.6. Found: C, 21.6; H, 3.2; N, 70.1. Drying at 130° (1 mm.) was required for dehydration.

Extreme insolubility of II made accurate determinations of molecular weight impossible, but estimates of 1000–2000 were obtained by nonaqueous titration.

Diazotization and Coupling of I.—Data on this reaction is summarized in Table I. A typical experiment was run as follows. A finely powdered, dry mixture of 5.0 g. (0.05 mole) of I and 10.4 g. (0.15 mole) of sodium nitrite was flooded with 100 ml. of concentrated hydrochloric acid. The mixture was stirred several minutes, chilled for 0.5 hr., and filtered. The cold filtrate was added, with vigorous stirring, to 7.5 g. (0.075 mole) of I in 100 ml. of water. The precipitate was filtered, dried, and extracted with three 200-ml. portions of boiling water. The water-insoluble material was II. Concentration and chilling of the aqueous extracts gave a precipitate of IIIa.

The reaction filtrate on standing overnight deposited additional solid. This material was filtered, dried, and extracted with two 25-ml. portions of boiling water. The insoluble material was IV. Concentration and chilling of the extracts gave more of IIIa.

Preparation of II from a Diazonium Solution.—A mixture of 2.0 g. (0.02 mole) of I and 1.4 g. (0.02 mole) of sodium nitrite was flooded with 50 ml. of concentrated hydrochloric acid. The mixture was chilled 0.5 hr. and filtered. The chilled filtrate was then carefully neutralized with 5 N sodium hydroxide. The precipitate was filtered and washed with boiling water to give 0.77 g. (35%) of II.

Acknowledgment.—The author is indebted to Miss Oksana Logush for technical assistance and to the Research Service Department, Stamford Laboratories, for microanalyses and aid in the interpretation of infrared spectra.

Some Merocyanines with Chelating Properties

J. W. FALLER, A. MUELLER, AND J. P. PHILLIPS

Department of Chemistry, University of Louisville,
Louisville, Kentucky

Received June 8, 1964

We have prepared several merocyanines in which the oxygen-containing ring of the merocyanine function is also a chelating center (of the 8-quinolinol type) for metals, a class of compounds believed to be novel solvatochromic reagents for metal ions.

Solvatochromic compounds are substances that change color in solution as a function of solvent polarity; large effects, shifts of absorption maxima of 50–100 mμ or more in going from aqueous to nonpolar solvents, are shown by merocyanines¹ as well as several other kinds of compounds.² In our previous studies of solvatochromic chelating agents we have examined reagents in which the solvatochromism was (in principle) not affected by the chelation and others in which solvatochromism was impaired to some extent by chelation.^{3,4} Here we consider reagents in which the solvatochromism is supplied by a merocyanine function that is eliminated through employment of its phenolic oxygen in the chelation; thus the reagents may be solvatochromic but not the chelates.

5-[β-(N-Methyl-5-ethyl-2-pyridyl)vinyl]-8-hydroxyquinoline iodide (I) and related compounds (see Table I) were prepared in 65–85% yields by piperidine-catalyzed condensations of 5-formyl-8-quinolinols with

(1) J. P. Phillips and J. T. Leach, *J. Org. Chem.*, **27**, 3309 (1962).

(2) J. P. Saxena, W. H. Stafford, and W. L. Stafford, *J. Chem. Soc.*, 1579 (1959); S. Hünig and O. Rosenthal, *Ann.*, **682**, 161 (1955).

(3) A. Mueller, J. T. Leach, and J. P. Phillips, *Talanta*, **10**, 1087 (1963).

(4) J. W. Faller and J. P. Phillips, *ibid.*, **11**, 641 (1964).