monohydrate, m.p. 213.5–214.5°. Repeating with 14.0 g. of III afforded 11.5 g. of II monohydrate, m.p. 213–214°. The total yield of II monohydrate was 31.3 g. (83%) from 50.3 g. of III. The samples of II were all homogeneous on paper in solvents A ($R_f$ 0.70), B ($R_f$ 0.51, streaky), and C ($R_f$ 0.65), and were identical in all respects to authentic II.[2a]

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# The Organic Chemistry of a New Weak Field Tridentate Chelating Agent. 3,5-Di(2-pyridyl)-1,2,4-triazole

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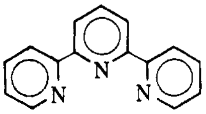
As a result of an interest in tridentate chelating agents of the terpyridine [2,6-di(2-pyridyl)pyridine, I] type, we have synthesized a new ligand, 3,5-di(2-pyridyl)-1,2,4-triazole (II), by the methods shown in Chart I. Hydrazine hydrate and 2-cyanopyridine were heated together under reflux; the product was 3,6-di(2-pyridyl)-1,2-dihydro-1,2,4,5-tetrazine (III).[2] III was rearranged to 3,5-di(2-pyridyl)-4-amino-1,2,4-triazole (VI) essentially by the method of Dallacker[2] but again without Raney nickel. We were unable to convert VI to bis(2-picolinoyl)hydrazide to any appreciable degree by further treatment with acid.[2,3]



I

Nitrous acid attacked VI with difficulty giving the desired triazole II. The infrared spectrum of VI shows substantial hydrogen bonding of the amine protons. VI does not form a stable salicylidene derivative and its resistance to attack by nitrous acid appears to be a consequence of this bonding.

Treatment of III with nitrous acid gives one of two products depending of the pH of the reaction medium. In almost neutral solutions, nitrous acid oxidizes III to 3,5-di(2-pyridyl)-1,2,4,5-tetrazine (IV). The same reaction has been reported using nitric acid as the oxidant.[2] In acidic media, nitrous acid converts III to 2,5-di(2-pyridyl)-1,3,4-oxadiazole (V). Elemental analysis, the mass spectrum, and spectroscopic data establish unambiguously the identity of V. V and VI are probably produced *via* a common intermediate. It is obvious that III does not first rearrange to VI during formation of V because nitrous acid attack on VI gives the triazole II. A suggested mechanism is given by the scheme shown in Chart II.

CHART I
($R = 2C_5H_4N$)

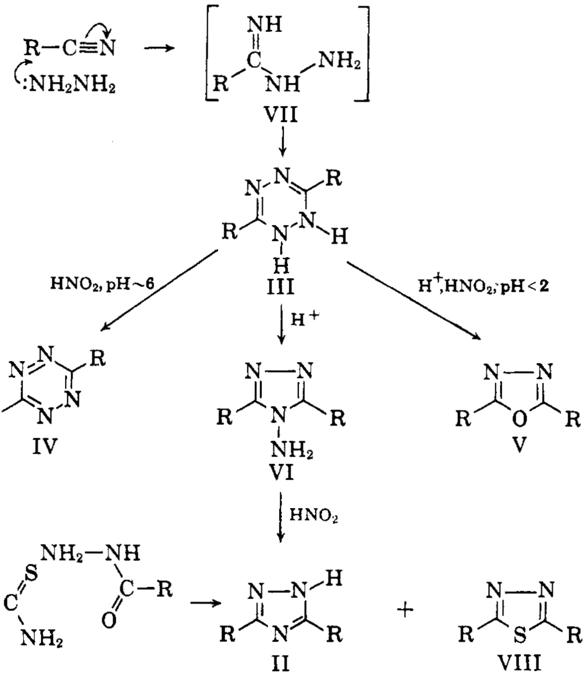
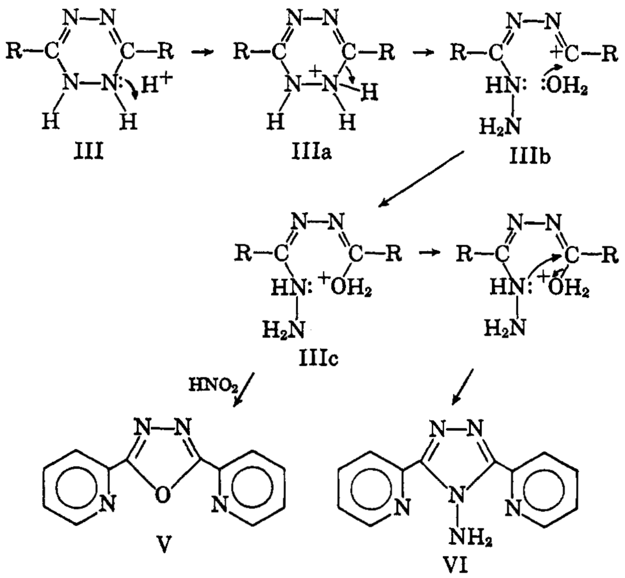


CHART II



It is reasonable to postulate the conversion of III to IIIc by acid attack. IIIc can then cyclize to VI by elimination of water or to V by the attack of nitrous acid. IIIc is constituted similarly to compounds known to give oxadiazoles when treated with nitrous acid.[4]

The triazole II was also prepared by heating together equimolecular amounts of 2-picolinthionamide and 2-picolinoylhydrazide at 160°. Sodium hydroxide extracted II from the mixture of products. The alkali-insoluble material proved to be 2,5-di(2-pyridyl)-1,3,4-thiadiazole (VIII).

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(1) Petroleum Research Fund Fellow of the University of Sydney; Department of Chemistry, University of Illinois, Urbana, Ill.

(2) F. Dallacker [*Monatsh.*, **91**, 294 (1960)] reports the use of Raney nickel in this condensation.

(3) D. D. Libman and R. Slack, *J. Chem. Soc.*, 2253 (1956).

(4) A. Pinner, *Ann.*, **297**, 221 (1897); **298**, 16 (1897); A. Pinner and N. Caro, *Chem. Ber.*, **27**, 3288 (1894).

The coordination chemistry of II will be reported elsewhere.

### Experimental

**3,6-Di(2-pyridyl)-1,2-dihydro-1,2,4,5-tetrazine (III).** A.—A mixture of 2-cyanopyridine (20 g.) and an excess of hydrazine hydrate (20 ml.) was warmed on a water bath for 3 hr. The solid was collected and crystallized from pyridine in orange needles, m.p. 197-198°. The yield was 13.4 g. A further 4 g. of product was recovered from the mother liquor by evaporation.

B.—III was formed almost quantitatively when 2-picolinic amidrazone was heated in aqueous or ethanolic solution for 2 hr.

*Anal.* Calcd. for $C_{12}H_{10}N_6$: C, 60.5; H, 4.2; N, 35.3. Found: C, 60.3; H, 4.4; N, 35.1.

**3,6-Di(2-pyridyl)-1,2,4,5-tetrazine (IV).**—Compound III (7.0 g.) was dissolved in a mixture of glacial acetic acid (600 ml.) and water (400 ml.) and the solution was cooled to 0°. Sodium nitrite (18.4 g.) in cold water (50 ml.) was then added slowly with vigorous stirring; the reaction mixture turned red-violet in color. The mixture was neutralized with ammonia solution (*d* 0.88) and the product was collected. It crystallized from benzene in red-violet plates, m.p. 229–230°. The yield was 4.1 g.

*Anal.* Calcd. for $C_{12}H_8N_6$: C, 61.0; H, 3.4; N, 35.6. Found: C, 61.1; H, 3.5; N, 35.3.

**3,5-Di(2-pyridyl)-4-amino-1,2,4-triazole (VI).**—III (11.1 g.) was suspended in aqueous hydrochloric acid (110 ml., 2 *N*) and the mixture was boiled for 10 min. The initially brown solution turned light yellow in color. The mixture was cooled and made alkaline with ammonia solution (*d* 0.88). The thick precipitate was collected and crystallized from aqueous ethanol in colorless needles, m.p. 186°. The yield was 9.9 g.

*Anal.* Calcd. for $C_{12}H_{10}N_6$: C, 60.5; H, 4.2. Found: C, 60.4; H, 4.3.

**3,5-Di(2-pyridyl)-1,2,4-triazole (II).** A.—VI (1 g.) was dissolved in aqueous nitric acid (10 ml., 5 *N*) by boiling. The solution was cooled to 0° and an aqueous sodium nitrite solution (2 g. in 4 ml.) added. The reaction mixture was allowed to stand for 0.25 hr., and was then boiled for 5 min. After cooling, the solution was made alkaline with ammonium hydroxide solution (3 *N*) and the precipitated product was collected. It crystallized from benzene, m.p. 217–218°.

B.—2-Picolinthionamide (4.8 g.) and 2-picolinoylhydrazide (4.7 g.) were heated together for 2.5 hr. at 160–170°. The oil was cooled; the solid was broken up and extracted several times with 10 *N* sodium hydroxide solution. The filtered extract was neutralized with 2 *N* acetic acid and cooled. The yellow precipitate was collected and recrystallized from benzene until colorless, m.p. 218–218.5°. The yield was 2 g.

*Anal.* Calcd. for $C_{12}H_9N_5$: C, 64.6; H, 4.1; N, 31.4. Found (A): C, 64.4; H, 4.2; N, 30.7. Found (B): C, 64.4; H, 4.0; N, 29.7.

The residue left after the extraction with sodium hydroxide was recrystallized from ethanol until colorless. The yield of **2,5-di(2-pyridyl)-1,3,4-thiadiazole** (VIII), m.p. 221–222°, was 1.5 g.

*Anal.* Calcd. for $C_{12}H_8N_4S$: C, 60.0; H, 3.4; N, 23.3; S, 13.3. Found: C, 60.3; H, 3.5; N, 22.9; S, 13.4.

**2,5-Di(2-pyridyl)-1,3,4-oxadiazole (V).**—III (13.4 g.) was dissolved in hot aqueous hydrochloric acid (120 ml., 2.5 *N*) and the mixture was cooled to 0°. A solution of sodium nitrite in water (11 g. in 50 ml.) was slowly added and the slightly violet solution was boiled until colorless. The solution was concentrated *in vacuo*, made strongly alkaline with sodium hydroxide solution, and extracted with ether several times. The ether was removed from the dried extracts by distillation and the residue was recrystallized from benzene–petroleum ether as white needles, m.p. 155–156°. The yield of V was 5 g.

*Anal.* Calcd. for $C_{12}H_8N_4O$: C, 64.3; H, 3.6; N, 25.0; O, 7.1. Found: C, 64.7; H, 4.0; N, 24.8; O, 7.4.

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## Determination of the Hammett $\sigma$-Constants for the Picryl Group

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In connection with other studies of the reactions of picryl-substituted benzenes, it was desirable to have a quantitative measure of the inductive and resonance effect, if any, of a picryl substituent attached to a benzene ring. The simplest procedure was to measure the rates of reaction of the *m*- and *p*-picrylbenzoic acids with diphenyldiazomethane (DDM) and, from these data, calculate the values of $\sigma_{m\text{-Pi}}$ and $\sigma_{p\text{-Pi}}$ for the picryl group. Although not reported previously, these acids were conveniently obtained by hydrolysis of their methyl esters which were in turn prepared by coupling picryl chloride with the appropriate methyl halobenzoate under Ullmann conditions. The *m*- and *p*-picrylbenzoic acids are crystalline solids melting at 209.8–211 and 188–190°, respectively.

Measurements of the rates of reaction of these acids with diphenyldiazomethane were made under pseudo-first-order conditions in absolute ethanol at 30° with at least a tenfold excess of the carboxylic acid. The pseudo-first-order rate constants, $k_1$, were calculated from the slopes of the straight-line plots of the log [DDM] *vs.* time. The second-order constant, $k_2$, was obtained from $k_1$ by dividing by the formal concentration of carboxylic acid used in each run. These rate constants are summarized in Table I.

TABLE I

RATE CONSTANTS FOR PICRYLBENZOIC ACIDS WITH DIPHENYLDIAZOMETHANE IN ETHANOL AT 30°

| $RCO_2H$, R[a] | $10^2$ [acid] | $10^3$ $k_1$, sec.$^{-1}$ | $10^2$ $k_2$, l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|---|
| $C_6H_5$ | 9.97 | 1.65 | 1.66 |
| *m*-$PiC_6H_4$ | 2.14 | 9.21 | 4.31 |
| *m*-$PiC_6H_4$ | 1.61 | 6.64 | 4.13 |
| *m*-$PiC_6H_4$ | 1.61 | 7.00 | 4.32 |
| *m*-$PiC_6H_4$ | 2.58 | 10.6 | 4.10 |
| *p*-$PiC_6H_4$ | 2.17 | 8.96 | 4.13 |
| *p*-$PiC_6H_4$ | 3.23 | 12.9 | 3.99 |
| *p*-$PiC_6H_4$ | 2.11 | 8.44 | 4.00 |

[a] Pi = 2,4,6-trinitrophenyl.

In order to calibrate the procedure, an initial run was made with benzoic acid. The value of $k_2$ obtained (Table I) was found to be in good agreement with the average of the literature values,[2] $1.70 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$. Averaging the data for the picrylbenzoic acids gives values of $k_2$ equal to $4.21 \pm 0.10 \times 10^{-2}$ and $4.04 \pm 0.06 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$ for the *m*- and *p*-picrylbenzoic acids. Taking the value of $\rho$ for the reaction of substituted benzoic acids with diphenyldiazomethane as 0.940[3] and $k_0$ the value of $k_2$ for benzoic acid listed in Table I, $\sigma_{m\text{-Pi}}$ and $\sigma_{p\text{-Pi}}$ were found to be 0.430 and 0.412, respectively.

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(2) R. M. O'Ferrall and S. I. Miller, *J. Am. Chem. Soc.*, **85**, 2440 (1963).

(3) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).