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.

Acknowledgment.—The authors gratefully acknowledge a grant (919-A1) from the Petroleum Research Fund of the American Chemical Society which made this work possible and the assistance of Miss B. Stevenson for all microanalyses recorded.

Determination of the Hammett σ-Constants for the Picryl Group

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Received September 28, 1964

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] 1.70×10^{-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 ρ 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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(1) To whom further correspondence should be addressed.

(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).

The observed difference between $\sigma_{m\text{-Pi}}$ and $\sigma_{p\text{-Pi}}$ is essentially within the experimental error in the average values of the rate constant k_2. However, if there is resonance interaction between the picryl group and the benzene ring to which it is attached, $\sigma_{p\text{-Pi}}$ should be considerably *more* positive than $\sigma_{m\text{-Pi}}$. Therefore, it may be concluded that the planes of the two benzene rings are essentially normal to each other. Although perhaps within the experimental error, the observed *decrease* in σ-values, about 5% on moving the picryl group from the *meta* to the *para* position, is about that expected for the fall off in inductive effect of a substituent on moving it one sp^2-carbon distance further from the reaction site.[4]

Experimental

Preparation of Reagents.—Diphenyldiazomethane was prepared by the previously described procedure[5] using commercially available benzophenone hydrazone (Aldrich Chemical Co.). After removing the mercury by filtration, the dark red-violet pentane solution was stored under refrigeration. Stock solutions were prepared in commercial absolute ethanol by evaporating the pentane from a suitable aliquot of the stock solution under reduced pressure, taking up the residue in ethanol, and diluting to volume with absolute ethanol.

Methyl *m*-picrylbenzoate was prepared by adding 0.05 mole (12.4 g.) of picryl chloride to a melt of 0.15 mole (39.3 g.) of methyl *m*-iodobenzoate at 80 to 100°. The resulting clear melt was heated to 170–180° and, while stirring, 0.2 mole (12.7 g.) of copper powder (Venus Natural Copper, Fine 44-F, U. S. Bronze Powder Works, Flemington, N. J.) was added in 1-g. portions at such a rate that the temperature of the reaction maintained itself at 220–240°. One to two minutes after all of the copper had been added, the temperature began to fall. The thick melt was allowed to cool slowly on the hot plate to 150°, then was returned to ambient temperatures by cooling in water. Acetone (100 ml.) was added to dissolve the organic components. The acetone solution was filtered to remove copper and copper halides. The solids were washed with 100 ml. of acetone and the combined acetone filtrates were treated twice with 10-g. portions of Darco G-60 charcoal. The acetone was removed on the steam bath and 150 ml. of ether was added to the residue. A yellow-brown solid separated which was collected on a Büchner funnel. This product, 10 g., melted at 141.5–144°. Recrystallization from acetone–methanol with charcoal treatment gave a pale yellow solid, m.p. 143.5–144.5°.

Anal. Calcd. for $C_{14}H_9N_3O_8$: C, 48.4; H, 2.6; N, 12.1. Found: C, 48.4, 48.7; H, 2.5, 2.3; N, 12.1, 12.6.

***m*-Picrylbenzoic acid** was prepared by adding 0.04 mole (14 g.) of the methyl ester to a mixture of 125 ml. of glacial acetic acid and 20 ml. of concentrated hydrochloric acid. The resulting mixture was heated on the steam bath at 90–100° for 5 hr. The yellow solution was poured onto ice and the solid that separated was collected on a Büchner funnel and washed thoroughly with water. The crude acid was taken up in methylene chloride and extracted thoroughly with saturated sodium bicarbonate. Evaporation of the methylene chloride on the steam bath left less than 1 g. of nonacidic material.

The combined bicarbonate extracts were run into an excess of 3 *M* hydrochloric acid and the precipitated picrylbenzoic acid was collected on a Büchner funnel, washed thoroughly with water, and dried. The product, 11.4 g. of an off-white solid, melted at 209–211°. Recrystallization from 50% ethanol gave a microcrystalline, pale yellow solid, m.p. 209.8–211°.

Anal. Calcd. for $C_{13}H_7N_3O_8$: C, 46.8; H, 2.1; N, 12.6; mol. wt., 333. Found: C, 47.0, 46.9; H, 1.9, 1.9; N, 12.4, 13.0; neut. equiv., 342.

Methyl *p*-picrylbenzoate was similarly prepared from picryl chloride and methyl *p*-iodobenzoate using nitrobenzene as a solvent and a reaction temperature of 160–180°. Following removal of the nitrobenzene *in vacuo*, the organic residue was taken up in acetone and treated with charcoal. The yellow-orange solid obtained on evaporation of the acetone was recrystallized from aqueous ethanol to give the methyl ester, m.p. 110.8–112.2°.

Anal. Calcd. for $C_{14}H_9N_3O_8$: C, 48.4; H, 2.6; N, 12.1; mol. wt., 347. Found: C, 48.0, 49.0; H, 2.6, 2.5; N, 12.4, 12.7; mol. wt., 348 (osmometer, chloroform solution).

The methyl ester was hydrolyzed in an acetic–hydrochloric acid mixture as described above. The crude product, precipitated from the bicarbonate extracts with 3 *M* hydrochloric acid, was recrystallized from aqueous acetic acid. The recrystallized *p*-picrylbenzoic acid was obtained as glistening yellow plates melting at 188–190°.

Anal. Calcd. for $C_{13}H_7N_3O_8$: C, 46.8; H, 2.1; N, 12.6; mol. wt., 333. Found: C, 47.2, 46.8; H, 2.0, 2.1; N, 12.3, 12.5; neut. equiv., 345.

Kinetic Studies.—In a typical run, 2.14×10^{-3} mole (0.7123 g.) of *m*-picrylbenzoic acid were transferred to a 100-ml. volumetric flask with about 65 ml. of absolute ethanol. The flask was placed in a thermostat at 30 ± 0.05° together with a flask containing 4×10^{-3} *M* DDM stock solution for at least 30 min. A 25-ml. aliquot of the DDM stock solution was then added to the carboxylic acid solution as rapidly as possible; the solution was diluted to volume with thermostated ethanol and mixed by shaking. A 10-cm. quartz cell was then filled with the reaction mixture after rinsing twice with the reaction mixture. The cell was placed in the thermostated cell compartment of a Cary Model 14 spectrophotometer at 30 ± 0.05°. This entire operation generally took about 2 min.

The decrease in optical density of the reaction mixture at 525 mμ was followed with time. Infinity values were obtained by measuring the optical density of the reaction mixture after at least ten half-lives. The pseudo-first-order constant, k_1, was calculated from the slope of the plot of log $[\text{O.D.}_t - \text{O.D.}_\infty]$ *vs.* time.

Acknowledgment.—This work was supported by the Foundational Research Fund of the U. S. Naval Ordnance Laboratory, Task FR-44. The experimental Ullmann procedures were suggested by Dr. J. C. Dacons of this laboratory.

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[5] L. I. Smith and K. L. Howard, *Org. Syn.*, **24**, 53 (1944).