of Corio's tables.[6] A good fit for the AB_2 case for both line position and intensity was found for $J_{AB}/\nu_0\delta$ equal to 0.15. On this basis, the value of $J_{AB} = 2.0$ c.p.s. These data are all consistent with the structure of the condensation product as 2-(1-hydroxy-1-methylethyl)-6,6-dimethylfulvene (IV).[7]

Experimental

Reaction of Acetone with Cyclopentadiene.—The reaction of 181 g. of freshly prepared cyclopentadiene, 160 g. of acetone, and 69 ml. of 20% potassium hydroxide in ethanol was carried out as directed by Crane, Boord, and Henne.[5] After standing overnight in an icebox, the mixture was poured into a large volume of water. The total mixture was then extracted with several portions of ether. The combined extract was dried over magnesium sulfate, and, after filtration, the ether was removed by distillation through a 34-cm. Vigreux column. The residue was then distilled through the same column at 8 mm. yielding the following fractions: 124 g. of dimethylfulvene, b.p. 40–43°; and 9.7 g. of orange oil with $n^{25}\mathrm{D}$ 1.5425, b.p. 118–120°. The remaining material was a nondistillable tar.

Reaction of Dimethylfulvene with Acetone.—Dimethylfulvene (123 g.), 102 g. of acetone, and 100 ml. of 11% potassium hydroxide in ethanol reacted with stirring at 0° overnight. The reaction mixture was worked up as described in the preceding reaction, and the product distilled (8 mm.) as follows: b.p. 110–124° (mostly 118–124°), 4.7 g. of orange oil with $n^{25}\mathrm{D}$ 1.5438. The infrared spectra of this material was identical with that of the material reported in the previous reaction.

Characterization and Degradation of the Orange Oil.—The orange oil, b.p. 118–120° (8 mm.), $n^{25}\mathrm{D}$ 1.5425, showed a strong hydroxyl band in the infrared at 2.98 μ. The hydrogenation equivalent was determined using Adam's platinum catalyst in ethanol: calcd. for $C_{11}H_{16}O$ with three double bonds, 54.8; found, 56.6. The compound in ethanol showed a maximum at 267 mμ (ϵ 2.2 × 10^4). The n.m.r. spectrum was determined in carbon tetrachloride solution (tetramethylsilane as an internal reference) with a Varian A-60 instrument, and the observed absorptions are given in the text.

Anal.[8] Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.59; H, 9.80.

A sample of this material was readily hydrogenated in ethanol using a 5% palladium-on-charcoal catalyst. Work-up of the product in the usual fashion and distillation through a semimicro column gave a colorless oil, b.p. 83–86° (6 mm.), $n^{25}\mathrm{D}$ 1.4670, with a strong band in the infrared at 2.92 μ.

Anal. Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.74; H, 13.13.

The saturated alcohol (6 g. of alcohol mixed with 0.6 g. of piperadine) was dehydrated by slow passage in a stream of nitrogen through a vertical 18-cm. column of 8-mesh alumina heated to *ca.* 355°. The product condensed as a light yellow oil which was taken up in ether, washed with dilute hydrochloric acid, and dried over magnesium sulfate. After filtration, the ether was removed by distillation through a short Vigreux column. The residue was distilled through a semimicro Vigreux column to give a mixture of olefins (2.8 g.), b.p. 146–150°. The strong infrared band at 11.3 μ indicated that the major component contained a terminal double bond and, from subsequent data, was presumably 3-isopropenylisopropylcyclopentane. This component was isomerized to 3-isopropylideneisopropylcyclopentane by treating the olefin mixture on a steam bath for 2 hr. with 0.1 g. of *p*-toluenesulfonic acid. It was noted at this time that the 11.3-μ band had disappeared from the spectrum.

The crude olefin mixture was taken up in 25 ml. of methylene dichloride, washed with diluted sodium bicarbonate, and ozonized in a stream of ozonized air until saturated. Excess ozone was removed in a stream of nitrogen. The ozonide(s) was decomposed by stirring the solution with 3 ml. of 30% hydrogen peroxide in 22 ml. of 10% potassium hydroxide. Water (25 ml.) was added, and the organic layer was removed. The aqueous layer was further extracted with methylene dichloride. The methylene dichloride extracts were combined and dried, and the solvent was removed by distillation.

An authentic sample of 3-isopropylcyclopentanone was prepared by the hydrogenation of 3-isopropenylcyclopentanone[9] using Adam's platinum in ethyl acetate: b.p. 94–97° (34 mm.), $n^{22}\mathrm{D}$ 1.4461; lit.[10] b.p. 183° (761 mm.), $n^{18}\mathrm{D}$ 1.4443. The infrared spectrum of the compound indicated the absence of the unsaturated starting material. Analysis by v.p.c. indicated 95% purity.

The crude ozonization product was fractionated by v.p.c. using a 12-ft. silicone column. In this fashion, it was shown that the reaction mixture consisted of a major band corresponding in retention time to authentic 3-isopropylcyclopentanone plus several smaller bands. The band corresponding in retention time to authentic 3-isopropylcyclopentanone was trapped, $n^{18}\mathrm{D}$ 1.4443. The infrared spectrum of this material was identical with that of the authentic sample; strong bands were observed at 1750, 1475, 1412, 1390, 1375, 1160, and 820 cm.$^{-1}$.

For comparison purposes an authentic sample of 2-isopropylcyclopentanone was prepared by the method of Cornubert and Borrel.[11] The retention time and infrared spectrum were decidedly different from the 3-isopropyl isomer (strong bands at 1750, 1475, 1412, 1390, 1375, 1275, 1195, 1160, 935, and 830 cm.$^{-1}$).

Acknowledgment.—This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is extended to the donors of this fund. We also would like to express our appreciation to the Robert A. Welch Foundation whose generosity made available the Varian A-60.

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[6] P. L. Corio, *Chem. Rev.*, **60**, 363 (1960).

[7] Recently, D. M. Fenton, and M. J. Hurwitz, *J. Org. Chem.*, **28**, 1646 (1963), established that, when dimethylfulvene and acetone are refluxed in methanolic potassium hydroxide, one obtains 3-isopropenyl-6,6-dimethylfulvene, a result in agreement with our findings.

[8] Microanalysis by Galbraith Laboratories, Knoxville, Tenn.

[9] C. Djerassi and B. Tursch, *J. Org. Chem.*, **83**, 4609 (1961).

[10] G. Burger and A. K. Macbeth, *J. Chem. Soc.*, 145 (1946).

[11] R. Cornubert and C. Borrel, *Bull. soc. chim. France*, 958 (1930).

Dipicolinoyl- and Di(6-acetylpicolinoyl)furoxans[1]

M. S. CHANG

Research and Development Department, U. S. Naval Propellant Plant, Indian Head, Maryland

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The reaction of acetophenone and nitric acid has been known since 1887.[2] The formation of dibenzoylfuroxan as the main product by dimerization of benzoylnitrile N-oxide has been proposed,[3] and recently a minor product in this reaction has been assigned the structure of the dibenzoate ester of bis(benzoylformaldoximino)furoxan.[4] In similar work with thiophene derivatives, bis(3-thianaphthenoyl)furoxan[5] and di-(2-thenoyl)furoxan[6] have been prepared. The present work has been directed towards a study of the reaction of nitric acid with acetylpyridine isomers and 2,6-diacetylpyridine.

As weak bases, acetylpyridine isomers form salts with mineral acids. Experimental results indicate that the formation of acetylpyridine nitrates occurs along with nitrosation and oxidation. From either 3- or 4-acetylpyridine and nitric acid, both the formation of the corresponding nitrate salt and oxidation to the cor-

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[1] This work was supported by the Foundational Research Program of the Bureau of Naval Weapons.

[2] A. F. Holleman, *Ber.*, **20**, 3359 (1887).

[3] H. R. Snyder and N. E. Boyer, *J. Am. Chem. Soc.*, **77**, 4233 (1955).

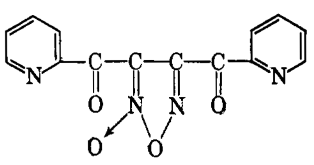
[4] J. H. Boyer and M. S. Chang, *ibid.*, **82**, 2220 (1960).

[5] D. A. Shirley, B. H. Gross, and M. J. Danzig, *J. Org. Chem.*, **23**, 1024 (1958).

[6] M. S. Chang and A. J. Matuszko, *ibid.*, **26**, 5239 (1961).

responding pyridinecarboxylic acid has been detected; presumably furoxans were produced as intermediates. In the absence of suitable conditions for isolation of such intermediates it is assumed that the formation of corresponding acids occurred by hydrolysis. In contrast, 2-acetylpyridine reacts with nitric acid to give the corresponding nitrate salt, picolinic acid, and a colorless solid (I) identified as dipicolinoylfuroxan based on elemental and spectrophotometric[7,8] analyses, molecular weight determination, and the formation of derivatives.

On treatment with phenylhydrazine the colorless solid (I) is transformed into a new colorless solid and a red solid, reminiscent of the formation of colorless benzoyl β-phenylhydrazide and yellow 3-(β-phenylhydrazino)-4-nitroso-5-phenylisoxazole from phenylhydrazine and dibenzoylfuroxan.[9] One of the two products obtained here has been proved to be 1-picolinoyl-2-phenylhydrazine (II) by mixture melting point with an authentic sample which gave no depression. By analogy, the other product is assigned the structure of 3-(β-phenylhydrazino)-4-nitroso-5-α-pyridylisoxazole (III). This assignment is confirmed by elemental and infrared spectrophotometric analyses.



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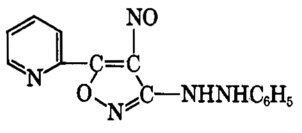
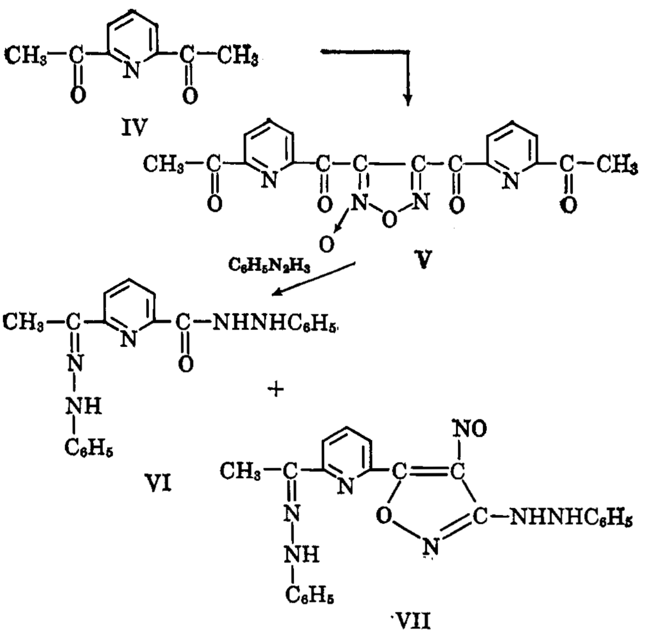


III

Treatment of I with methanol gives a red-black solid of empirical formula, $C_8H_5N_3O_3$, which is converted in acetic acid to an isomeric red solid. The structures of these substances have not been determined.

Under carefully controlled conditions, equimolar quantities of nitric acid and 2,6-diacetylpyridine (IV) at 50–55° react with the formation of di(6-acetylpicolinoyl)furoxan (V) only; equimolar quantities of nitric acid and 2,6-diacetylpyridine (without temperature control) react to give di(6-acetylpicolinoyl)-furoxan (V) along with four additional products. Excess nitric acid and IV (without temperature control) react to give only a high melting unidentified pale yellow solid insoluble in all common solvents.

The structural assignment for the furoxan (V) is supported by elemental analysis, molecular weight determination, and the formation of a bis-2,4-dinitrophenylhydrazone derivative. In agreement with the formation of 1-benzoyl-2-phenylhydrazine and 3-(β-phenylhydrazino)-4-nitroso-5-phenylisoxazole from dibenzoyl furoxan and phenylhydrazine,[10] the combination of the furoxan (V) with phenylhydrazine leads to the formation of the expected 2-(2-phenylhydrazinoformyl)-6-acetylpyridine phenylhydrazone (VI) and 2-[3-(β-phenylhydrazino)-4-nitroso-5-isoxazolyl]-6-acetylpyridine phenylhydrazone (VII).



When equimolar quantities of nitric acid and IV were caused to react without temperature control, a mixture of five solids formed; three were insoluble in the aqueous solution, the other two were soluble in the aqueous solution.

Extraction of the aqueous insoluble solid mixture from benzene, followed by concentration of the benzene extract resulted in the isolation of a solid which was identified as the furoxan (V) by mixture melting point.

Extraction of the remaining aqueous insoluble solid material with methylene chloride followed by concentration resulted in the isolation of a second solid (VIII). Infrared spectra indicate this solid to be another furoxan which reacts with phenylhydrazine to give a red-black solid mixture from which 2-[3-(β-phenylhydrazino)-4-nitroso-5-isoxazolyl]-6-acetylpyridine phenylhydrazine (VII) may be isolated and identified by identical infrared spectra with the product obtained from V and phenylhydrazine. The presence of the (6-acetylpicolinoyl)furoxan group is thus indicated. However, both elemental analysis and molecular weight determination of VIII indicate a complex, apparently polymeric structure of this furoxan which is not yet completely identified.

The third aqueous insoluble solid which was insoluble in common organic solvents was obtained in good yield with a melting point above 300°. Poor solubility limited a thorough investigation; however, spectrophotometric analysis supports the assignment as a furoxan.

One of the two solids from the aqueous solution was orange-red IX. It was found to be soluble in alkali from which it reprecipitates on acidification. Upon warming with phenylhydrazine it is transformed into another red solid. However, the structural assignment of IX is not certain, although the elemental analysis and molecular weight determination indicated that IX has empirical formula, $C_8H_6N_2O_4$.

The last solid obtained from the aqueous solution after concentration was identified as 2,6-pyridinedicarboxylic acid (XI) by comparison with an authentic sample.

Further treatment of di(6-acetylpicolinoyl)furoxan (V) with nitric acid at 50–55° allows recovery of the furoxan in 85% yield; however, at 90–100° the re-

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[7] N. E. Boyer, G. M. Czerniak, H. S. Gutowsky, and H. R. Snyder, *J. Am. Chem. Soc.*, **77**, 4238 (1955).

[8] J. H. Boyer, U. Toggweiler, and G. H. Stoner, *ibid.*, **79**, 1748 (1957).

[9] W. Quist, *Acta Acad. Aboensis, Math. Phys.*, **5**, 16 (1928); *Chem. Zentr.*, **100** (I), 892 (1929).

[10] J. H. Boyer, "Heterocyclic Compounds," Vol. 7, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 491.

action produces another insoluble solid (XII), m.p. above 300°, with infrared absorption bands characteristic of furoxans.[7] Since the solid is insoluble in common organic solvents, a thorough investigation was not undertaken.

Experimental[11]

General Reaction of Acetylpyridine with Nitric Acid. A.—To 12.1 g. (0.1 mole) of 2-acetylpyridine in 10 ml. of glacial acetic at 70°, 13 ml. of 69% nitric acid (*d* 1.42) in 10 ml. of glacial acetic acid was added in one portion with stirring. A small amount of sodium nitrite was immediately added. Stirring was continued for several minutes until the exothermic reaction subsided, and the solution was diluted with 200 ml. of ice water. Extraction of the aqueous solution with benzene followed by concentration of the combined benzene extracts gave a trace amount of picolinic acid, m.p. 125–127°. Evaporation of the aqueous solution under vacuum to dryness, extraction of the residue with benzene, and concentration of the combined benzene extracts gave 5.5 g. (44%) of crude picolinic acid, m.p. 120–127°, which upon sublimation gave picolinic acid, m.p. and m.m.p 135–136° (lit.[12] m.p. 136–137°). A brown residue obtained from reactions at 40° recrystallized from methanol as 2-acetylpyridine nitrate, m.p. 124–125° dec. (lit.[13] m.p. 125° dec.).

Anal. Calcd. for $C_7H_8O_4N_2$: C, 45.65; H, 4.38; N, 15.21. Found: C, 45.88; H, 4.29; N, 15.01.

3-Acetylpyridine in acetic acid was treated in a similar way with nitric acid and sodium nitrite at 90–100°. Nicotinic acid (6.1 g., 49%), m.p. 233–234°, was isolated and identified by infrared absorption which was identical with that obtained from an authentic sample (m.p. 234–236°). 3-Acetylpyridine when treated at 40° with nitric acid and sodium nitrite gave an impure 3-acetylpyridine nitrate. Isolation of the impure 3-acetylpyridine nitrate, m.p. 150–155° dec., was supported by its transformation on treatment with phenylhydrazine to the phenylhydrazone of 3-acetylpyridine, m.p. and m.m.p. 137° (lit.[14] m.p. 137°).

Treatment of 4-acetylpyridine in acetic acid with nitric acid and sodium nitrite at 70° gave isonicotinic acid (7.3 g., 59%), not melting under 300°, sublimation around 270° (lit.[15] m.p. 315° with sublimation, m.p. 325–326° in a sealed tube).

Anal. Calcd. for $C_6H_5O_2N$: C, 58.53; H, 4.09; N, 11.38. Found: C, 58.16; H, 4.43; N, 11.22.

4-Acetylpyridine when treated at 40° with nitric acid and sodium nitrite gave an impure 4-acetylpyridine nitrate. Isolation of the impure 4-acetylpyridine nitrate, m.p. 121–123° dec., was supported by its transformation on treatment with phenyl hydrazine to the phenylhydrazone of 4-acetylpyridine, m.p. and m.m.p. 150° (lit.[16] m.p. 150°).

B.—To 6.05 g. (0.05 mole) of 2-acetylpyridine in 10 ml. of glacial acetic acid at 50°, 3.5 ml. of 69% nitric acid in 5 ml. of glacial acetic acid was added in one portion with stirring. A small amount of sodium nitrite was added immediately. Stirring was continued for several minutes. Before the exothermic reaction subsided, 30 ml. of ice water was added. A precipitate of dipicolinoylfuroxan (I) was washed with water and dried, 2.0 g. (0.007 mole), 28%. It recrystallized from benzene as colorless needles, m.p. 165–166° dec., which turned blue-green on melting. Infrared absorption (cm.$^{-1}$) from a potassium bromide disk is: 675 s, 713 m, 750 s, *820 m*, *940 s*, *1000 s*, 1033 w, 1050 w, 1059 w, *1150 w*, 1225 w, 1245 s, 1278 w, 1280 m, *1300 m*, *1340 s*, *1425 w*, *1450 m*, 1485 m, *1595 s*, 1700 s (the italic values indicate the characteristic of furoxan).

Anal. Calcd. for $C_{14}H_8O_4N_4$: C, 56.76; H, 2.72; N, 18.91; mol. wt., 296. Found: C, 56.98; H, 2.93; N, 18.67; mol. wt. (ebullioscopic in benzene), 287.

Evaporation of the filtrate to dryness under vacuum gave a tarry residue. Upon vacuum sublimation, 2.0 g. (16%) of picolinic acid was obtained, m.p. and m.m.p. 136–137°.

A similar treatment of 2-acetylpyridine nitrate with nitric acid gave a black residue from which picolinic acid, 4.7 g., 38%, m.p. and m.m.p. 136–137°, was isolated by sublimation.

Similar treatment of 3-acetylpyridine with nitric acid gave no exothermic reaction. A solid product, presumably 3-acetylpyridine nitrate, on treatment with phenylhydrazine was transformed into the phenylhydrazone of 3-acetylpyridine, m.p. and m.m.p. 137°.

Similar treatment of 4-acetylpyridine with nitric acid also gave no exothermic reaction. A solid product, presumably 4-acetylpyridine nitrate, on treatment with phenylhydrazine, was transformed into the phenylhydrazone of 4-acetylpyridine, m.p. and m.m.p. 150°.

Treatment of 2,6-diacetylpyridine (IV), 8.05 g. (0.05 mole,) in 10 ml. of glacial acetic acid at 50° with 7 ml. of 69% (*d* 1.42) nitric acid gave di(6-acetylpicolinoyl) furoxan (V) in 81% yield when the temperature was kept between 50–55° by external cooling. V was recrystallized from benzene, m.p. 188–189° dec. Concentration of the combined water washes gave 3.0 g. (0.018 mole) of starting material. Infrared absorption for V from potassium bromide disk (in cm.$^{-1}$) is: 650 w, 660 m, 760 s, 785 w, 812 m, 835 m, 960 s, 1000 s, 1050 m, 1085 w, 1113 m, 1160 m, 1220 m, 1235 m, 1275 w, 1300 s, 1345 w, 1365 s, 1435 m, 1480 m, 1565 w, 1600 s, 1700 s; ultraviolet absorption in ethanol at 266 mμ showed ϵ 27,300.

Anal. Calcd. for $C_{18}H_{12}O_6N_4$: C, 56.84; H, 3.18; N, 14.73; mol. wt., 380. Found: C, 56.77; H, 3.36; N, 15.00; mol. wt., 338 (ebullisocopic in benzene).

In the manner described previously, when di(6-acetylpicolinoyl)furoxan (V) was used, 85% of the starting material was recovered. However, following the same procedure with the exception that the temperature for the addition of nitric acid was at 90–100° (without temperature control after addition), di(6-acetylpicolinoyl)furoxan (V) underwent vigorous reaction to give a solid (XII) which was insoluble in most organic solvents and did not melt under 300° (turned brown around 230°). After washing the solid successively with benzene, ether, chloroform, alcohol, methylene chloride, and petroleum ether, and drying under vacuum, the infrared absorption for XII from potassium bromide disk (in cm.$^{-1}$) is: 650 m, 660 w, 700 m, 750 s, 836 m, 930 m, 955 m, 975 w, 1000 s, 1050 m, 1083 w, 1110 w, 1165 m, 1225 m, 1305 s, 1350 s, 1390 m, 1440 m, 1475 s, 1612 s, 1700 s, 3400 m.

Anal. Calcd. for $C_{26}H_{13}O_{11}N_7$: C, 52.08; H, 2.17; N, 16.36. Found: C, 52.27; H, 2.53; N, 16.96.

In the procedure described before with the exceptions that a twofold amount of nitric acid was used and the temperature for the addition of nitric acid was 90–100° (without temperature control after addition), 2,6-diacetylpyridine underwent a vigorous reaction. A product (A) was isolated with a melting point above 300° (turning brown around 230°) which was insoluble in most organic solvents. The product (A) dissolved in base to give a black solution; acidification changed the solution to a deep red color. Addition of 1 drop of phenylhydrazine to a 1.0 g. of solid A initiated an immediate vigorous reaction with smoking and led to a black rubbery residue. Infrared absorption for product A from potassium bromide disk in cm.$^{-1}$ is: 645 m, 700 m, 750 m, 838 w, 930 m, 955 m, 975 w, 1000 s, 1050 m, 1085 w, 1110 w, 1145 m, 1160 w, 1220 m, 1300 m, 1345 s, 1390 w, 1440 m, 1475 m, 1610 s, 1700 s, 3400 s.

Anal. Calcd. for $C_{35}H_{16}O_{15}N_{10} \cdot H_2O$: C, 50.36; H, 2.16; N, 16.78. Found: C, 50.21; H, 2.71; N, 16.93.

The reaction was repeated with the modification that 2,6-diacetylpyridine was in acetic acid solution at 70–80° when nitric acid in acetic acid solution was added (without temperature control after addition). The reaction became exothermic. Dilution with 100 ml. of ice–water brought about separation of a solid which was washed with a large amount of water to remove any starting material that might exist. After the solid was dried, it weighed 8.5 g. After extraction of the solid with benzene, concentration of the combined benzene extracts gave 0.5 g. (0.0013 mole, 5%) of di(6-acetylpicolinoyl)furoxan (V) (identified by mixture melting point). The benzene-insoluble solid was extracted with a large amount of methylene chloride. Concentration of the combined methylene chloride extracts followed by addition of petroleum ether gave a pink solid, m.p. 220–222° dec. (VIII), 1.2 g. Infrared absorption from potassium bromide disk in cm.$^{-1}$ is: 645 w, 655 w, 700 m, 835 m, 925 m, 950 m, 970 w, 1000 s, 1050 m, 1085 w, 1110 w, 1160 w, 1220 m, 1300 s, 1345 s, 1365 m, 1440 m, 1480 w, 1605 s, 1700 s, 3400 m.

Anal. Calcd. for $(C_{17}H_{10}O_7N_4)_4$: C, 53.40; H, 2.61; N, 14.65;

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(11) Melting points are uncorrected.

(12) I. Heilbron, "Dictonary of Organic Compounds," Vol. IV, Oxford University Press, London 1953, p. 203.

(13) A. Pinner, *Ber.*, **34**, 4240 (1901).

(14) C. Engler and W. Kiby, *ibid.*, **22**, 598 (1889).

(15) I. Heilbron, ref. 12, Vol. III, p. 97.

(16) A. Pinner, *Ber.*, **34**, 4251 (1901).

mol. wt., 1528. Found: C, 53.47; H, 2.50; N, 14.94; mol. wt., 1550 (in dioxane).

The remaining solid (X), with a melting point above 300° (turning brown around 230°), was insoluble in most organic solvents such as alcohol, ether, benzene, methylene chloride, dioxane, etc. The crude material gave the following elemental analysis.

Anal. Calcd. for $C_{26}H_{13}O_{11}N_7$: C, 52.08; H, 2.17; N, 16.36. Found: C, 51.48; H, 3.03; N, 16.14.

Upon cooling the forenamed aqueous solution, 0.5 g. (0.0025 mole, 5%) of an orange-red solid (IX) was isolated. It recrystallized from boiling water as shining red-orange needles, m.p. 249–250° dec. Infrared absorption from potassium bromide disk in cm.$^{-1}$ is: 650 w, 720 w, 732 w, 765 m, 775 m, 782 m, 813 m, 838 m, 845 m, 875 s, 930 s, 950 m, 990 w, 1050 w, 1095 m, 1115 m, 1172 s, 1205 m, 1265 m, 1290 s, 1310 s, 1400 s, 1455 w, 1495 w, 1570 s, 1615 s, 1633 m, 1670 m, 1692 s, 3060 m, 3300 s. The solid (IX) dissolved in 5% potassium hydroxide to give a red solution from which a red-orange solid was reprecipitated on acidification and was identified as IX by identical infrared absorption spectra.

Anal. Calcd. for $C_8H_6O_4N_2$: C, 49.47; H, 3.12; N, 14.43; mol. wt., 194. Found: C, 49.29; H, 3.10; N, 14.34; mol. wt., 197 (in water).

Concentration of the foregoing aqueous solution under vacuum to a small volume gave 2,6-pyridinedicarboxylic acid (XI) as a colorless solid, which recrystallized from water and was dried under vacuum at 100° for a few hours, m.p. 251–252° dec. (lit.[17] m.p. 252° dec.), 1.08 g. (12%), m.m.p. 251–252° dec.

Anal. Calcd. for $C_7H_5O_4N$: C, 50.21; H, 3.02; N, 8.38. Found: C, 50.10; H, 3.25; N, 8.35.

Dipicolinoylfuroxan (I) in Boiling Methanol and Hot Acetic Acid.—Dipicolinoylfuroxan (I) (0.3 g., 0.001 mole) in 50 ml. of boiling methanol gave a red solution from which red-black crystals separated, m.p. 195–196° dec. (pyridine odor). Formation of the product appears to take place more rapidly if the furoxan is initially moist. Infrared absorption of a sample in a potassium bromide disk gave no absorption near 1700 cm.$^{-1}$, the region characteristic of absorption for carbonyl groups. Purification of the product by thorough washing with methanol gave an analytical sample. Suitable solvents for recrystallization were not found; therefore, a molecular weight determination was not obtained.

Anal. Calcd. for $C_8H_5O_3N_3$: C, 50.26; H, 2.64; N, 21.99. Found: C, 50.01; H, 3.10; N, 22.21.

The solid (0.2 g., 0.001 mole) from the previous experiment in 20 ml. of glacial acetic acid was heated to boiling. Upon cooling, a red-brown solid, m.p. 158–160° dec., was separated. Absorption from a potassium bromide disk of the product in the infrared at 1700 cm.$^{-1}$ confirmed the presence of a carbonyl group.

Anal. Calcd. for $C_8H_5O_3N_3$: C, 50.26; H, 2.64; N, 21.99. Found: C, 50.47; H, 3.03; N, 22.32.

Reaction of Dipicolinoylfuroxan (I) with Phenylhydrazine.—One gram (0.003 mole) of I was slowly added to 5 ml. of phenylhydrazine. The mixture was kept around 22° in order to prevent a violent reaction. After the addition was completed, the mixture was allowed to warm to 35° until evolution of gas had ceased. The reaction mixture was poured into a large volume of water. After decanting the water layer, the residue was recrystallized from ethanol in two fractions. One fraction of colorless needles, 0.3 g., m.p. 184–185°, was identified as 1-picolinoyl-2-phenylhydrazine (II) by mixture melting point with an authentic sample with no depression. Infrared absorption from a potassium bromide disk (in cm.$^{-1}$) is: 675 s, 695 s, 750 s, 820 m, 875 m, 920 s, 973 w, 1000 s, 1030 w, 1050 m, 1075 w, 1095 m, 1100 s, 1160 w, 1180 m, 1185 w, 1248 s, 1255 m, 1290 m, 1310 m, 1325 m, 1435 s, 1470 s, 1490 s, 1530 s, 1570 w, 1600 s, 1655 s, 1925 w, 3200 s.

Anal. Calcd. for $C_{12}H_{11}ON_3$: C, 67.59; H, 5.20; N, 19.71. Found: C, 67.80; H, 5.11; N, 19.62.

A second fraction was isolated as a red solid, 0.1 g., m.p. 188–189° dec., and was identified as 3-(β-phenylhydrazino)-4-nitroso-5-α-pyridylisoxazole (III). Infrared absorption from a potassium bromide disk in cm.$^{-1}$ is: 640 m, 680 m, 750 s, 786 s, 880 m, 983 s, 1030 w, 1075 m, 1100 w, 1148 s, 1185 w, 1235 s, 1285 m, 1337 w, 1400 s, 1350 w, 1505 s, 1530 w, 1565 w, 1600 s, 3400 m.

Anal. Calcd. for $C_{14}H_{11}O_2N_5$: C, 59.78; H, 3.94; N, 24.90. Found: C, 59.87; H, 3.63; N, 24.41.

Dipicolinoylfuroxan picrate was obtained from picric acid in methanol. It recrystallized from methanol as yellow needles, m.p. 140–141°.

Anal. Calcd. for $C_{14}H_8O_4N_4 \cdot 2C_6H_3O_7N_3$: C, 41.39; H, 1.87; N, 18.57. Found: C, 40.79; H, 1.87; N, 18.88.

Reaction of Di(6-acetylpicolinoyl)furoxan (V) with Phenylhydrazine.—One gram of the furoxan was suspended in 5 ml. of phenylhydrazine in a small flask and shaken until an exothermic reaction began. This was noted by the evolution of gas. The flask was allowed to cool slowly to room temperature. The reaction mixture was then poured into a large volume of water. After decanting the water layer, the residue was fractionally crystallized from ethanol to yield two fractions, 0.40 g. (0.00096 mole, 37%) which melted at 200–201° dec., and 0.1 g. (0.00028 mole, 11%) which melted at 180–181°.

The red material, melting at 200–201° dec., appears to be 2-[3-(β-phenylhydrazino)-4-nitroso-5-isoxazolyl]-6-acetylpyridine phenylhydrazone (VII), which would be analogous to the product obtained by Quist[9] from the reaction of dibenzoylfuroxan with phenylhydrazine.

Anal. Calcd. for $C_{22}H_{19}O_2N_7$: C, 63.92; H, 4.60; N, 23.72. Found: C, 64.19; H, 4.84; N, 23.42.

The yellow material, melting at 180–181°, appears to be 2-(2-phenylhydrazino-formyl)-6-acetylpyridinephenylhydrazone (VI), which would be analogous to a second product Quist[9] isolated from the reaction of dibenzoylfuroxan with phenylhydrazine.

Anal. Calcd. for $C_{20}H_{19}ON_5$: C, 69.54; H, 5.55; N, 20.28. Found: C, 69.62; H, 5.74; N, 20.63.

Reaction of IX with Phenylhydrazine.—Applying the preceding procedure for the combination of phenylhydrazine with IX with the exception that heating was applied in order to start the reaction, a red solid was obtained which recrystallized from ethanol, m.p. 240–242° (sublimation around 200°).

Anal. Calcd. for $C_{14}H_{11}O_3N_3 \cdot H_2O$: C, 58.33; H, 4.52; N, 14.63. Found: C, 58.46; H, 4.84; N, 14.79.

Reaction of VIII with Phenylhydrazine.—In the same manner as the reaction with IX, the exception that VIII was added slowly to phenylhydrazine, a mixture of solids was obtained. One pure red solid was isolated and identified as 2-[3-(β-phenylhydrazino)-4-nitro-5-isoxazolyl]-6-acetylpyridine phenylhydrazone (VII) by its identical infrared absorption with a product from V and phenylhydrazine.

Reaction of Di(6-acetylpicolinoyl)furoxan (V) with 2,4-Dinitrophenylhydrazine.—A solution of 0.1 g. (0.00026 mole) of V in 25 ml. of methanol was heated to boiling while a solution of 0.25 g. (0.00126 mole) of 2,4-dinitrophenylhydrazine in 25 ml. of methanol was added. Upon addition of a few drops of concentrated hydrochloride, the yellow bis-2,4-dinitrophenylhydrazone derivative precipitated immediately. The solid was separated and recrystallized from nitromethane, m.p. 231–232° dec., 0.15 g. (76%). Infrared absorption from potassium bromide disk (in cm.$^{-1}$) is: 650 w, 725 s, 745 m, 760 m, 835 m, 920 m, 945 m, 995 m, 1055 w, 1100 w, 1135 w, 1160 w, 1220 w, 1240 w, 1265 m, 1310 m, 1335 m, 1378 m, 1460 s, 1500 m, 1570 w, 1590 w, 1610 m, 1695 s, 2895 s.

Anal. Calcd. for $C_{30}H_{20}O_{12}N_{12}$: C, 48.65; H, 2.72; N, 22.70. Found: C, 48.45; H, 3.20; N, 22.41.

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Reaction of Lithium Diphenylphosphide and Carbonyl Compounds

ADAM M. AGUIAR,[1] JACK GIACIN, AND HARRIET J. GREENBERG[2]

Fairleigh Dickinson University, Madison, New Jersey

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Although alkali metal organophosphides are known to react with aldehydes and ketones, in no case has the

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(17) I. Heilbron, ref. 12, Vol. II, p. 436.