

4-Phenyl-4*H*-pyrazolo[3,4-*c*]furazans.
The Reactions of 3,4-Diacylfuroxans with Phenylhydrazine and with Aniline.

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Three different 3,4-diacylfuroxans (**1**) are shown to give 3-substituted-1-phenyl-4,5-dioximino-2-pyrazolines (**2**) upon reaction with phenylhydrazine. The compounds **2** were dehydrated to 6-substituted-4-phenyl-4*H*-pyrazolo[3,4-*c*]furazans (**3**) and thermally converted to 3-substituted 5-imino-4-oximino-1-phenyl-2-pyrazolines (**6**). The compounds **1** react with aniline to give 3-anilino-4-acylfurazans (**10**).

Perkin (1) treated methyl dimethylacetoacetate with nitric acid to obtain a "glyoxime peroxide" that with phenylhydrazine gave "methyl phenylaminoisotriazoxole-dimethylmalonylate"; this in turn upon treatment with aqueous base gave an acid of semi-empirical constitution $C_6H_5 [C_3N_4O]CMe_2CO_2H$ to which it was "difficult to assign a satisfactory formula". Perkin suggested a structure containing a 1,5-dehydro (valence-bridged)-1,2-dihydro-1,2,3,4-tetrazine nucleus, whose improbability has previously been noted (2).

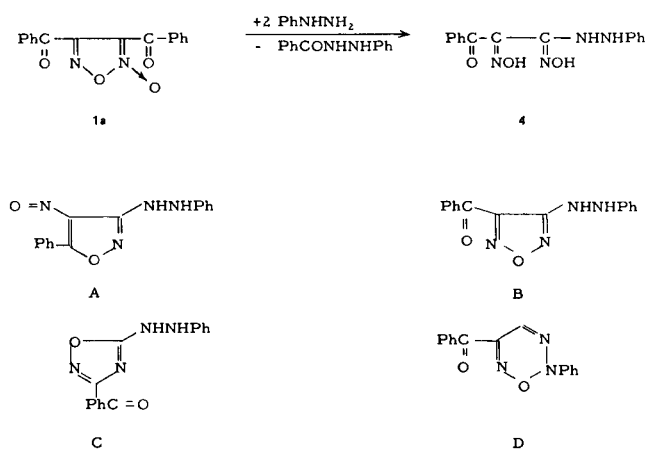
Our curiosity as to the structure of the acid led us to reinvestigate these and related reactions. We assumed that the "glyoxime peroxide" was in fact **1c**, a 3,4-diacylfuroxan (3), and thus for comparison purposes we began by re-examining the reported reactions of the diacetyl and dibenzoyl furoxans.

Diacetyl furoxan (**1b**) has been reported (4) to give with limited or excess phenylhydrazine merely the monophenylhydrazone (m.p. 161-162°) or the diphenylhydrazone (m.p. 176°), respectively. However, neither elemental analyses nor any chemical evidence for these assignments were given.

Dibenzoyl furoxan (**1a**) reportedly reacts with phenylhydrazine to give benzoylphenylhydrazine and a yellow material (**2a**) of empirical formula $C_{15}H_{12}N_4O_2$, which upon heating in acetic acid or acetic anhydride affords a different substance (**3a**) heretofore formulated as an isomer of **2a** (5) on the basis of a single nitrogen analysis. Formulas A, B, and C have been proposed as structures for **2a** and **3a**, and there has been extensive discussion as to which formula should be assigned to which compound (5-8).

The initial unstable reaction product of **1a** and phenyl-

hydrazine was presumed to have structure **4** (5,8). This formula, which implies addition of one molecule of phenylhydrazine to a carbonyl group and one to the ring $C=N \rightarrow O$ function, could readily give A and B, and lead to C after a single Beckmann rearrangement.



Entirely analogous series of formulas and reactions, and in addition formula D, have been proposed for the products from **1a** and anilines, substituted anilines, and ammonia (6,9-16). In these cases also, much controversy exists regarding the correct assignment of structures.

In our opinion, all these structural questions were still open, for no spectral data on these reaction products were available, and the chemical evidence previously used for the structural assignments did not seem entirely conclusive. We doubted some of these assignments because com-

pounds assigned analogous structures did not undergo analogous reactions or were markedly different in color. Rearrangements caused by ring opening and reclosure in a different direction could have occurred during the reactions used.

We herein show that the structures and chemistry involved in the reactions of three 3,4-diacetylfuroxans with phenylhydrazine and with aniline are different from those previously reported.

The following chemical and IR spectral evidence demonstrate that **2a** is in fact 4,5-dioximino-1,3-diphenyl-2-pyrazoline. The IR spectrum of **2a** shows no carbonyl absorption and exhibits strong bands at 990 and 970 cm^{-1} , the latter absorbing more strongly, attributable to the N-O stretchings of oxime groups (17,18). The bands in these regions were more useful for identifying oxime functions than the C=N stretching in the 1600-1650 cm^{-1} region, for the materials encountered in this research have several types of functionalities which absorb in this latter region.

Compound **3a** was prepared from **2a** by heating in acetic anhydride, and found not to be an isomer of **2a**, but to be formed from it by loss of water. The IR spectrum of **3a** shows no carbonyl absorption in the 1650-1750 cm^{-1} region. When **2a** was treated with acetic anhydride under very mild conditions, a bright red diacetate **5a** was formed, which was converted to **3a** upon heating in acetic acid or acetic anhydride, or upon treatment with aqueous base. Solid **5a** was converted to **3a** with loss of acetic anhydride, rapidly upon heating just below its melting point and slowly upon storage at room temperature. The IR spectrum of **5a** shows strong absorptions at 1793 and 1777 cm^{-1} ; these high C=O stretching frequencies suggest oxime acetate groups (19). The ready loss of water from **2a** and of acetic anhydride from **5a** suggest that the oxime functions are on adjacent carbon atoms.

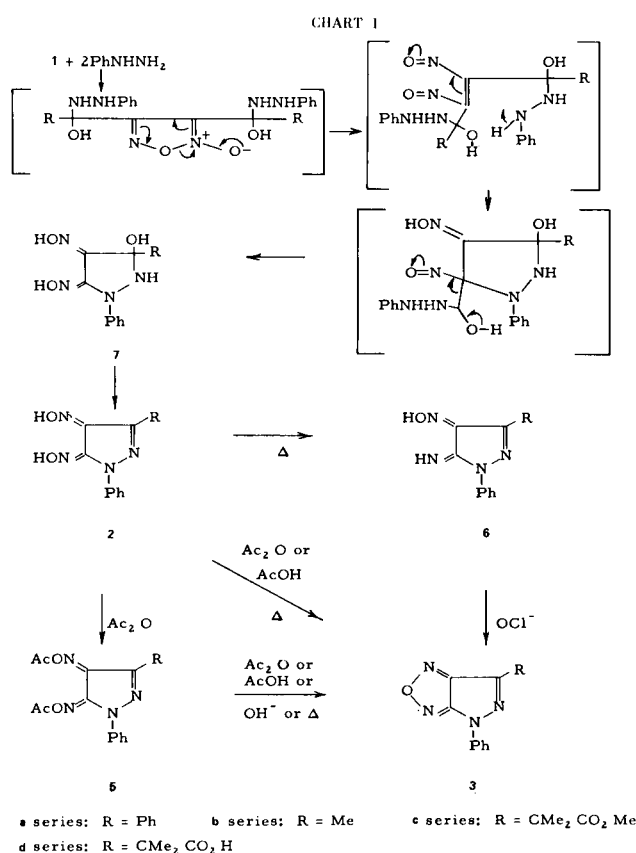
Compound **2a** (assumed to have formula A) reportedly gave 1,3-diphenyl-5-imino-4-oximino-2-pyrazoline (**6a**) of unequivocal structure, and also carbon monoxide, merely upon being refluxed in benzene solution (8). Neither the source of the carbon monoxide nor the skeletal rearrangement and loss of only an oxygen atom required by this formulation were discussed. The experimental method of identifying the carbon monoxide also was not given.

We have confirmed that **2a** does indeed give **6a** when refluxed in benzene, toluene, or xylene, but we were unable to detect carbon monoxide as a reaction product. Authentic **6a** was oxidized with aqueous hypochlorite solution to afford **3a**. The corresponding oxidation of **6b** to **3b** has been reported (20).

The reactions described above are formulated in Chart 1. In contrast to the previous formulation, both molecules of phenylhydrazine have added to the carbonyl

groups of **1** in the initial steps.

The experiments were carried out with three different diacetylfuroxans **1a-c**. The UV-vis absorption spectra of the corresponding compounds in each series were quite similar, and nearly identical in the **b** and **c** series. This correspondence was also found in the IR spectra; except for the easily recognizable CMe_2 and CO_2Me bands, the spectrum of each of the **c** series of compounds was very similar to the spectrum of the corresponding compound in the **b** series. Similarly, the **a** series spectra matched well the **b** series spectra except for the increased intensities of various bands assignable to the phenyl group. These spectral similarities confirm that analogous structures are being studied in the three series, and that Perkin's glyoxime peroxide is also a furoxan.



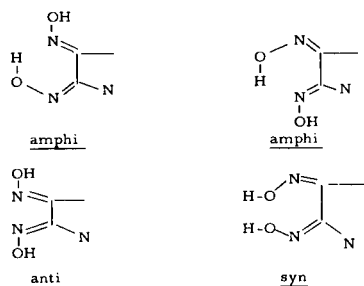
In the experiments with diacetylfuroxan we were unable to obtain any material having the reported (4) melting points, and none of the substances we did obtain was either the mono- or diphenylhydrazone of **1b**. The first product from **1b** and phenylhydrazine, which crystallized directly from the reaction mixture, had m.p. 156° and the empirical formula $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_3$. Structure **7b** seems likely for this material on the basis of the following evidence. Its IR spectrum shows no C=O stretching absorption. Short heating in xylene converted it to **2b**.

Chromatography over silica converted it to the unstable isomer of **2b** (see below). The NMR spectrum of a freshly prepared sample in DMSO-*d*₆ shows the C-Me proton shifts at 1.42 ppm and in subsequent scans the spectrum gradually reverted to that of **2b** (C-Me protons at 2.12 ppm), with the concomitant appearance of a broad peak attributable to water.

During the preparation of **2a** and **2c** the analogous compounds **7a** and **7c** were not obtained. Possibly they lose water more readily than **7b**.

The next product which separated from the reaction mixture after removal of **7b** had m.p. 143-161°, little changed by recrystallization. Its IR spectrum suggested that it was merely a mixture of **2b** (m.p. 121°) and *N*'-acetyl-*N*-phenylhydrazine (m.p. 129°), and chromatography separated it into these components. Experimentally, various mixtures of these pure solids did indeed exhibit melting points higher than those of either component. A mixed melting point elevation is an uncommon occurrence among organic materials.

The dioxime **2b** after purification by recrystallization showed m.p. 121°. Chromatography over silica, however, converted it to an isomer of m.p. 137°. The IR spectra of these isomers were significantly different, but the absence of absorption near 1550 cm⁻¹ indicated that the oximino → nitroso tautomerism was not involved. Their UV-vis absorption spectra were very similar. The higher melting isomer rapidly reverted to **2b** in solution, and also even in the potassium bromide pellet used for the IR determination. Thus, the freshly prepared pellet gave the spectrum of the isomer, but when reused about 15 minutes later gave the spectrum of **2b**. We have not investigated which of the four possible geometrical forms of the dioxime represent **2b** and its isomer, but the ready conversion of **2b** to **3b** suggests that **2b** is one of the *amphi* forms. The rapid reversion of the isomer weakly suggests that only one, rather than both oxime groups, are involved in the isomerization, and the *anti* rather than the *syn* isomer seems more likely on steric grounds. Further, among the isomers of phenylglyoxime (21), phenylmethylglyoxime (22), and benzil dioxime (23) the *anti* forms melt higher than the *amphi* forms.



Similar isomerizations of **2a** and **2c** during chromatography were not observed.

In summary, a 3,4-diacylfuroxan (**1**) appears generally to react with phenylhydrazine to give a 3-substituted-4,5-dioximino-1-phenyl-2-pyrazoline (**2**), which can be readily converted to a 6-substituted-4-phenyl-4*H*-pyrazolo[3,4-*c*]furazan (**3**) or to a 3-substituted-5-imino-4-oximino-1-phenyl-2-pyrazoline (**6**).

The thermal reaction that converts **2** to **6** probably is a bimolecular oxidation-reduction reaction. We have not been able to isolate any identifiable oxidation product of **2**, however. A reasonable mechanism can be written which would give the furoxan corresponding to **3** as the oxidized product, but such a compound, with a furoxan ring fused to a five-membered ring, is expected to be unstable (24). A study of this deoxygenation reaction and its possible extension to other cyclic and open-chain dioximes is in progress.

In the concurrent reinvestigation of the reactions of **1a-c** with aniline (Chart 2) we confirmed that **1a** initially gives the unstable oximinoamidoxime **8a** (C=O absorption at 1660 cm⁻¹ and strong, broad absorptions near 960 cm⁻¹) which readily loses water to give a dark red material (**9a**) (11). The IR spectrum of **9a** shows no strong absorption attributable to carbonyl stretching, but does show a very strong band at 1560 cm⁻¹ attributable to N=O stretching. Therefore **9a** is 3-anilino-4-nitroso-5-phenylisoxazole, as Wieland suggested (1). This material rearranges easily to the colorless isomer **10a**, both in solution and in the solid state. The conversion occurs slowly upon storing the solid, and rapidly upon warming **9a** in ethanol or acetic acid, or during the m.p. determination at the usual heating rates, or upon heating a potassium bromide pellet; the pellet decolorizes and gives the IR spectrum of **10a**. The IR spectrum of **10a** shows no N=O band at 1550 cm⁻¹, strong C=O bands at 1660 and 1645 cm⁻¹, and bands at 1580 and 890 cm⁻¹ attributable to the furazan nucleus (18,25). Boeseken (6) early assigned structure D to this material; Wieland (11) and Boeseken (12) later preferred the 1,2,4-oxadiazole structure C for this compound, chiefly because upon alkaline hydrolysis it gave 1-cyano-3-phenylurea (12). Boeseken suggested that the initial dioxime intermediate **8a** underwent a Beckman rearrangement before cyclization, and Wieland suggested that **10a** was formed but readily rearranged. Such Beckman rearrangements under these mild, non-acidic conditions seem unlikely. We suggest that the rearrangement occurs in the proof of structure of the putative 1,2,4-oxadiazole, in that hydrolysis of **10a** with strong base could give the cyanoamidoxime **11**, which then could undergo the Tiemann-Pinnow rearrangement (26) to **12**. This rearrangement is known to occur under basic conditions.

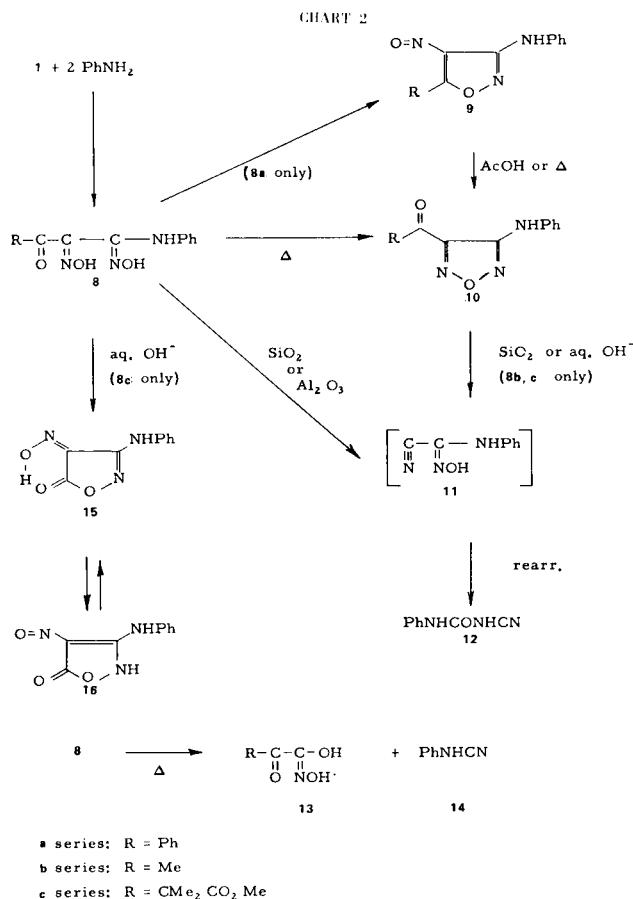
In contrast to **1a**, compounds **1b** and **1c** react with aniline to give **8b** (strong absorptions at 986 and 965 cm^{-1}) and **8c** (985, 965 cm^{-1}) as stable products. These materials can be recrystallized from benzene without suffering dehydration. Refluxing in acetic acid, acetic anhydride, or toluene, or keeping the solid just below its melting points, converted these dioximes to the corresponding furazans **10**, as evidenced by the disappearance of the oxime bands and the concomitant appearance of furazan bands at 1580 and 890 cm^{-1} . These furazans were obtained only as thick oils which resisted all attempts at purification by distillation or by crystallization, even after repeated chromatography.

During these experiments we observed that passage of **10b-c**, or better **8a-c**, over silica or acidic alumina afforded in each case a small fraction of strongly adsorbed material whose IR spectrum showed cyano group absorption at 2230 cm^{-1} . Similarly, heating **8a-c** *in vacuo* gave a "sublimate" also having cyano groups. These materials were expected to be **11**, formed by the "second-order" or "abnormal" Beckmann rearrangement of **8**. However, the volatile product obtained thermally from **8a** was identified by its simple IR spectrum as phenylcyanamide (**14**). The IR spectra of the volatile thermal products from **8b** and **8c** were more complex, but after subtracting the bands due to **14**, the remaining peaks could clearly be assigned to the acylhydroxamic acids **13b** and **13c**, respectively; these apparently distilled with the **14**, whereas **13a** did not.

The cyano-containing materials formed during chromatography, however, did *not* contain **14**, as indicated by their IR spectra, and therefore probably do contain **11**. Pure **11** free from carbonyl-containing impurities could not be isolated by further chromatography.

Thus the dioximes **8** apparently undergo purely thermal cleavage in a manner different from the acid-catalyzed cleavage.

The dioxime **8c** is cleaved by aqueous base to isobutyric acid and an acidic material which Perkin formulated as 5-carboxy-2-phenyl-1,2,3,6-oxatriazine (*cf.* formula D), but which we find by direct comparison to be the known (27) 3-anilino-4-oximino-5-isoxazolone (**15**). The NMR spectrum of **15** in DMSO- d_6 shows the oxime proton as a singlet at 8.52 ppm whose integral is almost exactly one-fifth that of the total phenyl protons, suggesting that the structure in this solvent is **15** exclusively. However, the IR spectrum (in potassium bromide) shows not only moderately strong absorptions at 1775 cm^{-1} (attributable to β,γ -unsaturated γ -lactone carbonyl lowered by hydrogen bonding) and 1645 cm^{-1} (oximino C=N), but also moderate absorptions near 1750 cm^{-1} and 1550 cm^{-1} , which may respectively be assigned to the C=O and N=O groups of formula **16**.



EXPERIMENTAL

The melting points (Thomas-Hoover apparatus) and boiling points are uncorrected. IR spectra were taken on Perkin-Elmer Models 137 and 621 in potassium bromide pellets unless stated otherwise; the absorption bands given are all strong and sharp except where indicated. UV-vis spectra were determined in ethanol on a Beckmann DK-1. NMR spectra were taken by Simon Research Labs, Elgin, Illinois. Mass spectra were run by Morgan-Schaffer Corporation, Montreal, Quebec. Analyses were by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Materials.

Methyl dimethylacetoacetate was obtained from Shawnee Chemicals, Springfield, Ohio. Its IR spectrum showed the absence of the monomethyl derivative (**28**), and it contained no material extractable with 25% aqueous potassium hydroxide (**29**), so the ester was used as received for the preparation of **1c**. Prepared according to the literature were the following substances: **1a**, m.p. 83-85°, lit. (30) 87°; **1b**, b.p. 84-86°/0.6 mm. (31), lit. (32) 65°/0.1 mm.; **1c**, m.p. 64-65°, lit. (1) 65°; **2a**, m.ps. 73°, 112°, 116° (33); lit. 65° (6), 75° (6), 87° (8), 106° (5); **2c**, m.ps. 149° dec., 157° dec., and 139° dec. after recrystallization from ethanol (IR and UV-vis spectra identical before and after recrystallization), lit. (1) 154° dec. and 139° dec. (ethanol); **3c**, m.p. 83-85°, lit. (1) 88-89°; **3d**, m.p. 161-163°, lit. (1) 163-164°; **6a**, m.p. 205°, lit. (34) 207°; **6b**, m.p. 197-198.5°, lit. (20) 199-200°; **8c**, m.p. 132-135°, lit. (1) 137°; **14**, m.p. 40-50°, lit. (35) 44-46°; **15**,

156° explodes, lit. (1) 155° explodes; 5-amino-1,3-diphenylpyrazole, m.p. 129-131°, lit. 129-131° (36); 5-amino-3-methyl-1-phenylpyrazole, m.p. 109-110°, lit. (37) 110-111.5°.

4,5-Bis(acetoxyimino)-1,3-diphenyl-2-pyrazoline (**5a**).

A mixture of 1.30 g. of **2a** in 25 ml. of acetic anhydride was kept at 75-80° for 15 minutes, and the deep red solution was then slowly concentrated at room temperature in a stream of dry air. The precipitate was removed and washed successively with small amounts of acetic anhydride and acetone to afford 1.22 g. of bright red needles, m.p. 151-152° dec. Longer reaction times, higher reaction temperatures, and attempts at recrystallization all led to the formation of **3a** or mixtures of **5a** and **3a**. When **5a** was melted in a sublimation apparatus, the condensed liquid was identified by IR as acetic anhydride (38). IR (chloroform, Perkin-Elmer 621, high-resolution conditions): ν (C=O) 1793, 1777 cm^{-1} . UV λ max ϵ , 226 (12,800), 267 (18,500), 279sh (13,200), 387 $\text{m}\mu$ (5,500); λ min ϵ 220 (12,300), 237 (9,900), 319 $\text{m}\mu$ (1,200).

Anal. Calcd. for $\text{C}_{19}\text{H}_{16}\text{N}_4\text{O}_4$: C, 62.63; H, 4.43; N, 15.38. Found: C, 62.69; H, 4.34; N, 15.37.

4,5-Bis(acetoxyimino)-3-methyl-1-phenyl-2-pyrazoline (**5b**).

Similarly, **2b** gave **5b**, m.p. 143-144° (ethanol).

Anal. Calcd. for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_4$: C, 55.63; H, 4.67; N, 18.53. Found: C, 55.53; H, 4.48; N, 18.46.

Compound **2c** gave **5c** as indicated by absorption at 1790 cm^{-1} in its IR spectrum, but all attempts to purify the crude material converted it to **3c**.

4,6-Diphenyl-4*H*-pyrazolo[3,4-*c*]frazan (**3a**).

A solution of 0.32 g. of **2a** in 10 ml. of acetic anhydride was refluxed 1 hour and worked up as above to give 0.21 g. of yellow needles, m.p. 173-173.5° (ethanol), lit. (5) 172°. This material was similarly obtained starting from **5a**, and also by refluxing either **2a** or **5a** in acetic acid, pyridine, or ethanol containing triethylamine. IR, 1600, 1540, 1505, 1475, 1440, 1350, 1285, 1125, 1105, 1075, 1000, 842, 778, 750, 719, and 689 cm^{-1} ; UV, λ max ϵ , 227 (16,500), 268 (26,700), 383 $\text{m}\mu$ (8,700); λ min ϵ , 219 (14,800), 238 (11,300), 305 $\text{m}\mu$ (600).

Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{N}_4\text{O}$: C, 68.69; H, 3.84; N, 21.36; mol. wt., 262. Found: C, 68.56; H, 3.70; N, 21.38; mol. wt. (osmometric), 266.

4,5-Dioximino-3-hydroxy-3-methyl-1-phenylpyrazolidine (**7b**).

To a solution of 0.40 g. of **1b** in 50 ml. of ethyl ether was added a solution of 0.50 g. of phenylhydrazine in 15 ml. of ethyl ether. Within 1 minute a yellow solid had precipitated, which was immediately removed by filtration and washed with ethyl ether and pentane to give 0.25 g. (45%) of **7b**, m.p. 156° dec. UV, λ max ϵ , 239 (16,400), ca. 309 $\text{m}\mu$ sh (3,200).

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_3$: C, 50.84; H, 5.12; N, 23.72. Found: C, 51.40; H, 4.87; N, 23.84.

4,5-Dioximino-3-methyl-1-phenyl-2-pyrazoline (**2b**) (stable isomer).

After removal of the **7b** in the above procedure, the filtrate was evaporated to leave a yellow-orange solid suspended in an orange gum. Trituration with benzene at room temperature removed the latter, leaving 10% yield of **2b**, m.p. 121-122° (benzene). IR, 1640, 1555w, 1205w, 1180m, 1115, 1055m, 1025, 982, 915m, 845m, 797m, 769m, 731, and 690 cm^{-1} ; UV, λ max ϵ , 258 (14,900), 398 $\text{m}\mu$ (3,280); λ min ϵ , 229 (6,960), 330 $\text{m}\mu$ (960).

Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2$: C, 55.04; H, 4.62; N, 25.67. Found: C, 55.00; H, 4.52; N, 25.65.

The above was repeated, but the filtrate was concentrated and chilled and the precipitate removed. This material had m.p. 143-161°; its IR spectrum appeared to be a superposition of the spectra of **2b** and *N'*-acetyl-*N*-phenylhydrazine. Chromatography of this material over silica using benzene:ethyl ether (1:1) eluent removed **2b**. Elution with acetone was required to remove the *N'*-acetyl-*N*-phenylhydrazine, identified by its m.p. (127-128°) and by mixture m.p. and IR spectra comparisons with an authentic sample.

The original filtrate after removal of the mixture precipitated additional *N'*-acetyl-*N*-phenylhydrazine upon dilution with pentane. Unstable isomer **2b**.

When either the above isomer or **7b** was placed on a silica column (benzene solution) and eluted with benzene:ethyl ether (1:1), evaporation of the eluate gave material having m.p. 137°. IR: 1650m, 1620m, 1605, 1400m, 1190m, 1105, 1060m, 1035, 973, 908m, 789m, 762, and 701 cm^{-1} ; UV, λ max ϵ , 220 (7,240), 257 (13,600), 397 $\text{m}\mu$ (3,480); λ min ϵ , 211 (7,000), 228 (6,990), 331 $\text{m}\mu$ (1,360).

Recrystallization of this material from ethanol or benzene gave the stable isomer, as indicated by m.p., mixture m.p., and IR spectral comparisons. The bulk solid had reverted to the stable form during several weeks' storage. The reversion in the potassium bromide pellet has already been mentioned.

1,3-Diphenyl-5-imino-4-oximino-2-pyrazoline (**6a**).

A solution of 1.00 g. of **2a** in 50 ml. of xylene was refluxed 1 hour (the solution suddenly turned dark after about 5 minutes), cooled, and filtered to remove 0.25 g. (26%) of **6a**, m.p. 207° (toluene) (lit. (8) 207-208°), identical by mixture m.p. and IR spectral comparisons with authentic **6a** prepared by nitrosation of 5-amino-1,3-diphenylpyrazole (34). IR 1635, 1515m, 1250, 1160, 965, 853m, 793m, 781m, 770m, and 700 cm^{-1} ; UV, λ max ϵ , 246 (18,900), 322 (13,900), 367 $\text{m}\mu$ sh (3,810); λ min ϵ , 289 $\text{m}\mu$ (5,400).

The filtrate after removal of the **6a** was evaporated and the residual dark gum was taken up in chloroform and chromatographed over silica. Elution with 2 x 100 ml. pentane: benzene (1:1) gave 0.18 g. of **3a** (identified by m.p. and IR spectrum); 3 x 100 ml. benzene next eluted ca. 0.01 g. of red tar whose IR spectrum was uninformative; 100 ml. benzene: ethyl ether (1:1) and 3 x 100 ml. ethyl ether gave 0.08 g. of **6a**; 2 x 100 ml. acetone and finally 100 ml. methanol each removed less than 0.01 g. of red tars, whose IR spectra were different from that of the benzene eluate but were equally uninformative.

Test for carbon monoxide during the formation of **6a**.

In a 3-necked flask, equipped with a gas inlet tube and an exit through a column of moist potassium hydroxide pellets and then a 0.1% solution of palladium chloride in an acetone:water (1:1) (v/v) mixture, were placed 30 ml. of xylene and 1.2 g. of **2a**. While being swept with a stream of nitrogen the solution was refluxed for 30 minutes. The palladium chloride solution was then acidified with three drops of concentrated hydrochloric acid and filtered through a fluted filter paper. The paper did not show any dark stain of metallic palladium. This is a simple but sensitive qualitative test for carbon monoxide (39).

The reaction mixture was worked up as before, and substantially the same proportions of products were found.

5-Imino-3-methyl-4-oximino-1-phenyl-2-pyrazoline (**6b**).

Similarly, 0.3 g. of **2b** when refluxed in xylene gave 0.06 g. (22%) of **6b**, m.p. 195-197°, identical with authentic **6b** prepared by the nitrosation of 5-amino-3-methyl-1-phenylpyrazole (**20**). IR: 1650, 1550m, 1500m, 1240, 1080m, 1065, 1022m, 983, 871m, 793m, 765m, and 693 cm⁻¹; UV, λ max ϵ , 225 (12,100), 307 (14,600), ca. 350 m μ sh (4,300); λ min ϵ , 266 m μ (3,480). Methyl 2-(5-imino-4-oximino-1-phenyl-2-pyrazolinyl)isobutyrate (**6c**).

A solution of 0.50 g. of **2c** in 20 ml. of xylene gave no precipitate after 2 hours refluxing, so it was concentrated *in vacuo* and diluted with pentane to give a dark red powder having m.p. 170-172°, which gave red needles of **6c**, m.p. 175-176° after three recrystallizations from ethanol-water. IR: 1725, 1640, 1550w, 1525m, 1240, 1100m, 1035m, 1017m, 985, 905m, 870m, 842m, 792m, 769m, and 698 cm⁻¹; UV, λ max ϵ , 225 (7,500); 310 (7,100), ca. 350 m μ sh (ca. 2,800); λ min ϵ , 266 m μ (1,930).

Anal. Calcd. for C₁₄H₁₆N₄O₃: C, 58.33; H, 5.59; N, 19.43. Found: C, 58.08; H, 5.58; N, 19.14.

Oxidations of **6** to **3**.

The reported (**20**) preparation of **3b** from **6b** was repeated except that a large excess of "Clorox" was used (100 ml. for 0.8 g. of **6b**) to give **3b**, m.p. 89-90°; lit. (**20**) 94-95°. Similarly, **6a** and **6c** gave **3a** and **3c**, respectively. The compounds obtained by this oxidation were identical by mixture m.p. and IR spectral comparisons with those produced by the direct dehydration of the corresponding **2**.

Acetylanilinoxyglyoxime (**8b**).

To a solution of 1.80 g. of **1b** in 50 ml. of ethyl ether was added dropwise 1.95 g. of aniline. After standing at room temperature for 1 hour, the mixture was treated with 10 ml. of pentane and the resulting precipitate (0.40 g.) was removed. The IR spectrum of this precipitate indicated that it was acetanilide contaminated with a small amount of **8b**. The filtrate was diluted with 50 ml. pentane to precipitate 0.42 g. (19%) of cream-colored **8b**, m.p. 116-117°, lowered to 110-111° after recrystallization from benzene. The initial and recrystallized products had identical IR spectra and both gave acceptable analyses. IR: 1650m, 1605, 1550, 1145, 986, 965, 947m, 871, 822, 759, 735m, 722m, and 695 cm⁻¹.

Anal. Calcd. for C₁₀H₁₁N₃O₃: C, 54.30; H, 5.01; N, 18.99. Found: (110-111°): C, 54.39; H, 5.12; N, 18.95.

3-Anilino-4-nitroso-5-phenylisoxazole (**9a**).

To a solution of 10.0 g. of **1a** in 150 ml. of ethyl ether was added dropwise 7.05 g. of aniline and the mixture was allowed to stand two days. Filtration removed 3.80 g. of benzanilide, identified by m.p. and IR spectra. The filtrate was evaporated *in vacuo* to leave a brown residue whose IR spectrum shows C=O at 1700, C=N at 1655, and strong oxime N-O near 960 cm⁻¹. Thus this material presumably contains **8a**.

Trituration of the crude **8a** with ethanol at room temperature left 6.7 g. (68%) of a dark red solid, which could be recrystallized unchanged from ethanol only when operating with the utmost speed. The m.p. could not be taken in the usual manner, for the material thermally isomerized to **10a**, as indicated by its decoloration and final m.p. near 200°. When placed in the heating bath at various temperatures an apparent melting, rapid decoloration, and resolidification occurred near 130°. After being heated at 100° for 3 minutes, the potassium bromide pellet gave the IR spectrum of **10a**. A sample of **9a** that had been stored at room temperature for

26 days had decolorized and was found by IR to have been almost entirely converted to **10a**. IR: 1560 v.s. (N=O), 1300 (N=O dimer?), 1280, 1225, 1155, 895, 820, 783, and 728 cm⁻¹; UV, λ max E_{1cm}^{1%}: 242 (2,900), 268 sh (1,600), 338 (1,300), 424 m μ (360); λ min E_{1cm}^{1%}, 221 (1,900), 306 (820), 388 m μ (310). The E_{1cm}^{1%} is given because the sample probably was contaminated with **10a** owing to isomerization.

Anal. Calcd. for C₁₅H₁₁N₃O₂: C, 67.92; H, 4.18; N, 15.84. Found: C, 67.52; H, 4.19; N, 15.74.

3-Anilino-4-benzoylfurazan (**10a**).

The reaction of **1a** with aniline described above was repeated and the crude **8a** was refluxed in ethanol for 1 hour. Cooling deposited 8.42 g. (80%) of **10a**, m.p. 204-205° (ethanol) (lit. (**10**) 205°). Similarly, **9a** was readily converted to **10a** upon heating a few minutes in ethanol or acetic acid. IR: 1660 (C=O), 1645 (C=O...HN), 1580 (furazan), 1505, 1210, 1180, 1060m, 1030m, 940, 890m (furazan), 758, 719, and 683 cm⁻¹; UV, λ max ϵ , 254 m μ (30,400); λ min ϵ , 220 m μ (5,580).

Attempted preparations of **9b**, **9c**, **10b** and **10c**.

Conversions of **8b** and **8c** to the corresponding **9** and **10** were attempted by the following methods: heating the bulk solid just below its m.p.; refluxing in toluene, ethanol, acetic acid, and acetic anhydride; and passage of a benzene solution through a column of silica or alumina. In every case the product was a yellow-orange glass that could not be induced to crystallize from any of various solvents. The IR spectra of these glasses, however, showed a diminution of the oximino C=N band near 1645 cm⁻¹ and the concomitant appearance of bands near 1580 and 890 cm⁻¹. At no stage in these experiments was there any evidence of a red material showing strong N=O absorption near 1550 cm⁻¹.

Attempts to prepare the diacetate derivatives by treatment of **8b** and **8c** with acetic anhydride led to amorphous material whose IR spectra showed absorptions near 1800 cm⁻¹.

Thermal cleavage of **8a-c**.

Attempts to distil the crude furazans **10b** and **10c** in a sublimation apparatus at ca. 150° and 0.1 mm. pressure gave small amounts of materials condensable at -78°, whose IR spectra showed CN absorption at 2230 cm⁻¹.

A similar experiment using 90 mg. of **8a** gave 35 mg. of colorless sublimate whose IR spectrum was identical with that of an authentic sample of phenylcyanamide (**14**) (**35**). IR: 2230, 1600, 1500, 1430m, 1305m, 1245, 1180m, 895m, 831w, 750, and 690 cm⁻¹.

When **8b** was similarly sublimed, the volatile product was a red substance which melted below room temperature. Its IR spectrum (liquid film) showed all the bands of **14** plus the following: 1710 (C=O); 1640 (C=N); 1550m (N=O tautomer); 1450 (C-Me); 1370 (C-Me); and 968m cm⁻¹ (OH). From the probable assignments given, it appears that the sublimate also contained the expected **13b**.

Similarly, the IR spectrum (liquid film) of the product from **8c** showed all the bands of **14** plus 1730 (ester C=O), 1705 (C=N), 1635 (C=N), 1550m (N=O), 1470 (C-Me), 1450 (C-Me), 1385 and 1365 (CMe₂), 1280 (CO-OMe), 1195 (C-CMe₂-C), 1155 (CO-OMe), and 965m cm⁻¹ (OH), all attributable to **13c**.

After potassium bromide pellets of **8a-c** had been kept at 150° for 1-2 minutes, they gave IR spectra showing the CN absorption and the other changes indicated.

Acid cleavage of **8a-c**.

Chromatography of the crude **10b** and **10c** gave about 10% of a red oil which required acetone or methanol for its elution. Its complex IR spectrum showed absorption at 2230 cm^{-1} and several bands in the $1750\text{-}1500\text{ cm}^{-1}$ region. Similar materials were obtained in 20-50% yield when **8a-c** were chromatographed over silica or acidic alumina. Attempts to purify these materials further by chromatography or distillation *in vacuo* were unsuccessful; only unstable red oils were formed whose IR spectra indicated various carbonyl bands. However, the bands at 1430 , 1245 , 750 , and 690 cm^{-1} associated with **14** were definitely absent in these spectra. Thus these materials contain a different nitrile, which may be **11**.

3-Anilino-4-oximino-5-isoxazolone (**15**).

Phenyl isothiocyanate was added to ethyl sodioacetoacetate (prepared in benzene using sodium hydroxide (**40**)) to give 39% of ethyl acetylmalonate monothioanilide, m.p. $75\text{-}78^\circ$ (lit. (**41**) $82\text{-}83^\circ$). This was converted in 60% yield to 3-anilino-5-isoxazolone, m.p. 182° dec. (lit. (**27**) 185° dec.), which was nitrosated to afford 80% of **15**, m.p. 156° explodes (lit. (**27**) 149° explodes). This material was identical by mixture m.p. and IR spectral comparisons with that obtained from **8c** by treatment with aqueous base (1). IR: 1775 , 1750 , 1645 , 1605 , 1580 , 1550 , 1300 , 1210 , 1035 , 970 , 903 , 840 , 812 , 761 , 748 , and 690 cm^{-1} ; UV, λ_{max} ϵ , 238 ($24,400$), 314 ($10,800$), $375\text{ m}\mu$ ($5,050$); λ_{min} ϵ , 262 ($6,480$), ca. $350\text{ m}\mu$ (ca. $4,400$).

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