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THE REACTION OF 4-PYRONES WITH HYDROXYLAMINE

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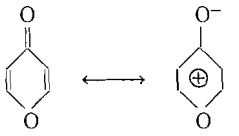
ABSTRACT

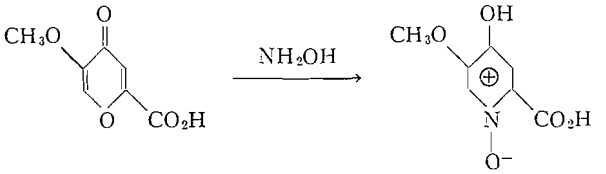
Treatment of 2,6-dimethyl-4-pyrone with hydroxylamine gives 4-hydroxyamino-2,6-lutidine 1-oxide. Under the influence of light or in weakly basic media this is converted in the presence of air to 4,4′-azoxydi-2,6-lutidine 1,1′-dioxide. In a strongly basic medium it is converted to 4,4′-azodi-2,6-lutidine 1,1′-dioxide. Similar results are obtained in the case of 2,6-diethyl-4-pyrone.

On treatment with hydroxylamine, 4-pyrones usually fail to give oximes (1). In some cases, no reaction occurs; this lack of reactivity can be attributed to the quasi-aromatic nature of the 4-pyrone ring system (I) (1, 2). In other cases, reaction proceeds via opening



I

of the pyrone ring; for example, the methyl ether of comenic acid (II) forms the 4-hydroxypyridine-1-oxide derivative III (or its tautomer) (3). The reaction of 2,6-dimethyl-3,5-



II III

dicarboethoxy-4-pyrone (IV) with hydroxylamine also must involve initial ring opening, but the intermediate in this case recloses to give an isoxazole derivative (V) (4). The following route seems probable:

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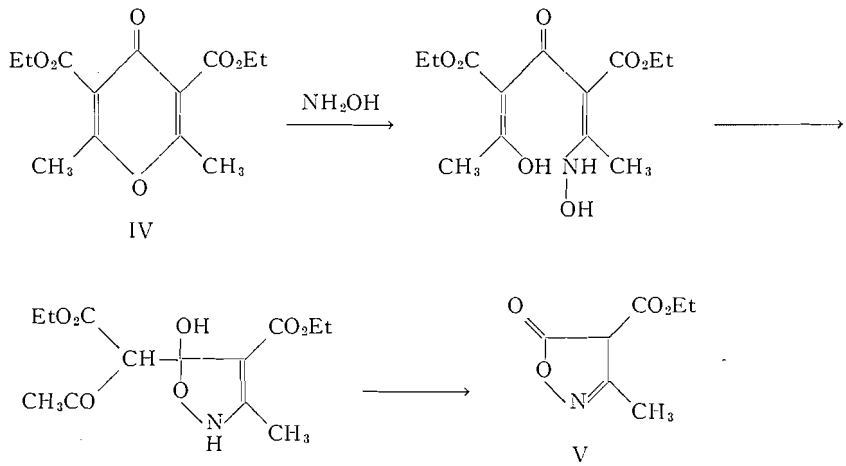
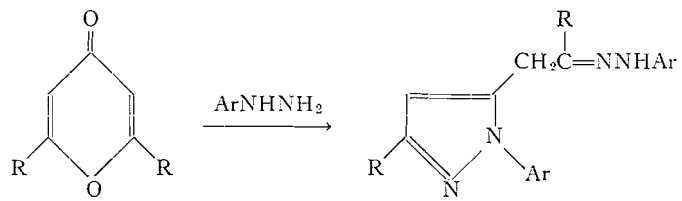


IV V

Related complexities often attend the reactions of 4-pyrones with other amines; thus, Ainsworth and Jones (5) have observed that 2,6-dialkyl-4-pyrones (VI) give pyrazole derivatives (VII) with phenylhydrazine and its derivatives.



VI VII

In connection with studies on the oximes of the photodimers of 4-pyrones (6) we have had occasion to examine the reactions of hydroxylamine with 2,6-dimethyl- and 2,6-diethyl-4-pyrone and have found that here too simple derivative formation does not occur.

Treatment of 2,6-dimethyl-4-pyrone with an excess of hydroxylamine hydrochloride and pyridine in boiling ethanol gives two crystalline products. When pure these are colorless, but in the presence of traces of bases or of light they rapidly assume a yellow or pink color. Their elemental composition corresponds to the empirical formulae $C_7H_{10}N_2O_2$ and $C_7H_{10}N_2O_2.HCl$. The latter compound was demonstrated to be the hydrochloride of the former by the interconversion of the two products under mild conditions.

The ultraviolet spectrum (λ_{max}^{EtOH} 280 mμ (log ϵ 4.31), 215 mμ (shoulder, log ϵ 4.27)) of the free base, $C_7H_{10}N_2O_2$, closely resembles that of 4-amino-2,6-lutidine 1-oxide (VIII*a*)[3] (λ_{max}^{EtOH} 275 mμ (log ϵ 4.23), 210 mμ (apparent, log ϵ 4.21)). Its infrared spectrum (Nujol) shows strong bands at 3.10, 6.10, and 8.37 μ. This product is therefore assigned structure IX*a*, whose formation involves, in undetermined order, ring opening, reclosure, and oxime formation by the pyrone. This formulation is preferred to the tautomeric structure X on the basis of the presence of a very strong band at 8.37 μ in the infrared spectrum of the compound, which may be assigned to the N^+—O^- group (9), and of analogy to the case of 4-aminopyridine-1-oxide (VIII*b*) (10).

[3]*Prepared by hydrogenation of 4-nitro-2,6-lutidine 1-oxide (7); this compound has been prepared independently in similar fashion by other workers (8).*

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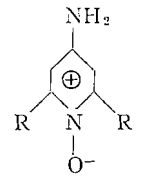
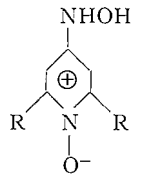
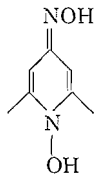


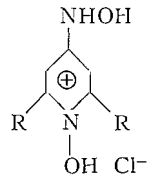
VIII*a*, R = CH_3
VIII*b*, R = H



IX*a*, R = CH_3
IX*b*, R = C_2H_5



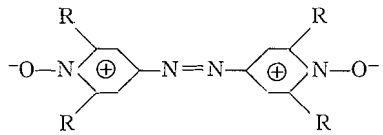
X



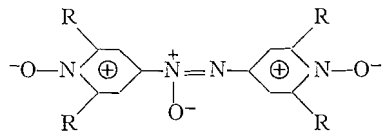
XI*a*, R = CH_3
XI*b*, R = C_2H_5

The ultraviolet spectrum of the hydrochloride, $C_7H_{10}N_2O_2.HCl$, is very similar to that of the parent base, and its infrared spectrum (λ_{max}^{Nujol} 3.20, 3.65 (sh), 3.80 (sh), 6.10 μ) shows only medium intensity absorption in the 7.5- to 8.5-μ region. This product is therefore considered to have structure XI*a*, rather than that derived by protonation of the nitrogen atom of the hydroxyamino group in IX*a*. The observed position of protonation is in accord with expectation based on theoretical considerations and on analogy with the case of VIII*b* (10, 11).

When either IX*a* or XI*a* is treated with aqueous 10% sodium hydroxide, a deep red coloration immediately occurs and an orange-red crystalline product, $C_{14}H_{16}N_4O_2$, is formed. The source and color of this compound suggested that it is the azo compound XII*a*. This view is supported by the close correspondence of its ultraviolet spectrum



XII*a*, R = CH_3
XII*b*, R = H
XII*c*, R = C_2H_5



XIII*a*, R = CH_3
XIII*b*, R = H
XIII*c*, R = C_2H_5

to that of 4,4′-azodipyridine 1,1′-dioxide (XII*b*) (Table I). An independent synthesis of XII*a* was therefore carried out by the reduction of 4-nitro-2,6-lutidine 1-oxide with sodium nitrite and base (12):[4] the product was shown to be identical with that obtained from IX*a* or XI*a*.

TABLE I

Ultraviolet spectra

	λ_{max}^{EtOH} (mμ)	log ϵ
4,4′-Azodipyridine 1,1′-dioxide (XII*b*)*	405	4.5
	255	4.05
4,4′-Azodi-2,6-lutidine 1,1′-dioxide (XII*a*)	401	4.53
	258	4.12
4,4′-Azodi-2,6-diethylpyridine 1,1′-dioxide (XII*c*)	408	4.59
	260	4.16
4,4′-Azoxydipyridine 1,1′-dioxide (XIII*b*)*	395	4.4
	250	4.1
4,4′-Azoxydi-2,6-lutidine 1,1′-dioxide (XIII*a*)	393	4.39
	249	4.05
4,4′-Azoxydi-2,6-diethylpyridine 1,1′-dioxide (XIII*c*)	399	4.40
	252	4.04

*H. J. den Hertog, C. H. Henkens, and J. H. van Roon. Rec. Trav. Chim. **71**, 1145 (1952).

[4]*After this phase of our investigation had been completed, a report (8) became available to us which describes the preparation of XII*a *and XIII*a *from 4-nitro-2,6-lutidine 1-oxide by methods similar to those described here.*

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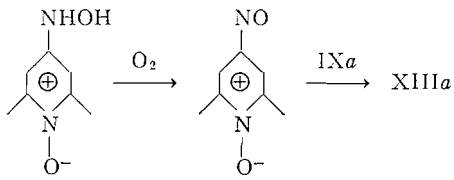
Exposure of aqueous solutions of IX*a* or XI*a* to light leads to the formation of a yellow crystalline product, $C_{14}H_{16}N_4O_3$. The same product is obtained much more rapidly when these compounds are treated with dilute aqueous ammonia or with aqueous sodium bicarbonate. Its ultraviolet spectrum (Table I) and infrared spectrum are similar to those of XII*a*. It was established to be the azoxy compound XIII*a* by its independent synthesis by the reduction of 4-nitro-2,6-lutidine 1-oxide with zinc (12).[4]

The formation of the azoxy compound XIII*a* from the hydroxylamine derivative IX*a* is analogous to the formation of azoxybenzene from *N*-phenylhydroxylamine. One route for the latter reaction has been found to involve oxidation of the hydroxylamine with atmospheric oxygen (13). This has been shown also to be the case for the present reaction, since it was found that XI*a* is not converted to the azoxy compound by the action of light nor by aqueous sodium bicarbonate when air is rigidly excluded from the reaction system. The formation of the azoxy compound can then be suggested to occur by the following route, analogous to that proposed for the formation of azoxybenzene (13(*a*), 14):



IX*a* XIV

The photochemically induced oxidation of the hydroxyamino compound IX*a* to the nitroso compound XIV may be analogous to other autoxidation reactions, which are accelerated by light (15). The formation of XIII*a* in the presence of either aqueous ammonia or sodium bicarbonate (pH 7–9) proceeds in the absence of light. The pH of the reaction solution plays a critical role in the dark reaction, for at pH 5–6 no azoxy compound is formed, while at pH 12–13 (aqueous sodium hydroxide) only the azo compound XII*a* is formed; however, the data available at present do not permit the designation of the function of the basic reagents in the formation of the azoxy compound.[5]

The formation of the azo compound at pH 12–13 was found to proceed in the absence of both air and light.[6] It is possible that this reaction involves proton abstraction from IX*a* by hydroxide ion to form XV. Formation of the azo compound XII*a* could then occur either by α-elimination to give XVI followed by reaction of this with unchanged hydroxyamino compound IX*a* (route A) or by hydride transfer to IX*a* to give the disproportionation products XIV and VIII*a* followed by condensation of these (route B). The fact that no azoxy compound is formed under the strongly basic conditions militates against, but does not exclude, the intermediacy of the nitroso compound XIV in this case; route A is therefore preferred.

The reaction of 2,6-diethyl-4-pyrone with hydroxylamine hydrochloride and pyridine follows a similar course to that of the 2,6-dimethyl compound, giving the hydroxyamino compound IX*b*. Treatment of this product with aqueous 10% sodium hydroxide yields the azo compound XII*c*. In the case of IX*b*, unlike that of IX*a*, treatment with concentrated aqueous ammonia in the presence of air yields a mixture of azoxy compound

[5]*Bases have also been found to accelerate the oxidation of N-phenylhydroxylamine by air (13). The influence of pH on the autoxidation of amines is known to be complex (16).*

[6]*In the absence of air, N-phenylhydroxylamine gives azoxybenzene and aniline when treated with aqueous sodium hydroxide, while on treatment with ethanolic hydroxide it gives azobenzene as the sole product (13(b)).*

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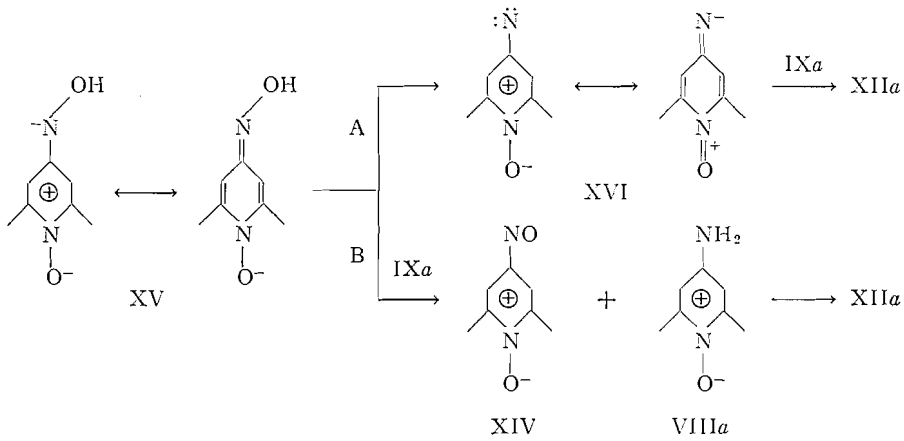

(XIII*c*) and azo compound (XII*c*) in comparable quantities. However, the azoxy compound is the sole product when an aqueous solution of IX*b* is irradiated. The structures XII*c* and XIII*c* are assigned to these products on the basis of their origin and elemental analyses and the correspondence of their infrared and ultraviolet spectra (Table I) to those of the azo and azoxy compounds obtained in the 2,6-dimethyl series.[7]

EXPERIMENTAL[8]

Reaction of 2,6-Dimethyl-4-pyrone with Hydroxylamine. Formation of IXa and XIa[9]

A mixture of 2,6-dimethyl-4-pyrone (20.0 g, 0.16 mole), hydroxylamine hydrochloride (20.0 g, 0.28 mole), dry pyridine (120 ml), and ethanol (120 ml) was boiled under reflux for 6 hours. The ethanol was then removed at room temperature under reduced pressure and the remaining solution was treated with water (50 ml) and cooled at 0° for 72 hours. The yellow solid (14.0 g) which separated was crystallized from a mixture of aqueous ethanol and chloroform to give IX*a* as pale yellow plates (2.7 g, 11%). This was recrystallized five times from methanol/acetone, giving colorless plates. The product did not melt sharply: when heated above 100° it turned yellow and a slow transition to a red-colored product occurred between 100° and 200°, followed by melting at ca. 200°.

Anal. Calc. for $C_7H_{10}N_2O_2$: C, 54.53; H, 6.54; N, 18.17. Found: C, 54.54; H, 6.66; N, 18.40.

λ_{max}^{Nujol} 2.85 (w), 3.10 (sh), 6.10 (vs), 8.37 (vs) μ; λ_{max}^{EtOH} 215 mμ (sh, log ϵ 4.27), 280 mμ (log ϵ 4.31).

Ethanol and chloroform were removed at room temperature under reduced pressure from the mother liquor from the first crystallization of IX*a*. The remaining yellow aqueous solution was treated with acetone and cooled at 0° for several days to give XI*a* as pale yellow plates (2.2 g, 9%). This was recrystallized seven times from aqueous acetone, giving colorless plates whose behavior on heating was similar to that of IX*a*.

Anal. Calc. for $C_7H_{11}ClN_2O_2$: C, 44.09; H, 5.82; Cl, 18.63; N, 14.70. Found: C, 44.04; H, 6.15; Cl, 18.35; N, 14.65.

λ_{max}^{Nujol} 3.20 (vs), 3.65 (sh), 3.80 (sh), 6.10 (vs), 8.30 (m), 8.45 (m); λ_{max}^{EtOH} 218 mμ (log ϵ 4.13), 280 mμ (log ϵ 4.27).

Reaction of XIa with Pyridine. Formation of IXa

A mixture of XI*a* (0.15 g) and dry pyridine (2 ml) was stirred until solution was complete (4–5 minutes). Most of the pyridine was removed under reduced pressure and the residue was dissolved in water (10 ml). The solution was treated with chloroform (70 ml) and the mixture was cooled at 0° for several hours, when a solid (0.072 g) separated. This was shown to be identical with IX*a* by infrared spectral comparison.

Reaction of IXa with Hydrochloric Acid. Formation of XIa

A solution of IX*a* (0.10 g) in dilute hydrochloric acid (1:10; 10 ml) was treated with acetone (70 ml). The solution was cooled at 0° for several days, when a solid (0.044 g) separated, which was shown to be identical with XI*a* by infrared spectral comparison.[10]

[7]*After this manuscript had been completed, Dr. A. R. Katritzky, Cambridge University, kindly drew our attention to the fact that related results have recently been reported for the case of 4-pyrone (17).*

[8]*Melting points are uncorrected.*

[9]*These products were found to be very sensitive to light and bases (vide infra); their preparation and purification were carried out in acid-washed glassware in the dark or in subdued light.*

[10]*For storage, it was found advantageous to convert IXa to the hydrochloride.*

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4-Amino-2,6-lutidine 1-Oxide (VIIIa)

A solution of 4-nitro-2,6-lutidine 1-oxide (7) (0.51 g) in ethanol (75 ml) was hydrogenated over 5% palladium–charcoal (0.053 g). After 1 hour 3 molar equiv. of hydrogen had been absorbed. The solution was then filtered and the ethanol was removed under reduced pressure. The residue was recrystallized from ethanol/benzene to give VIII*a* as white needles, m.p. 265° decomp. (lit. (8) m.p. 264–266°); λ_{max}^{Nujol} 2.80, 3.00, 5.90 (sh), 6.05, 8.35, 8.45 μ; λ_{max}^{EtOH} 275 mμ (log ϵ 4.23), 210 mμ (apparent, log ϵ 4.21).

Reaction of XIa with Aqueous Bases[11]

(i) pH 12–13. Formation of XIIa

A solution of XI*a* (0.30 g) in water (20 ml) was brought to pH 12–13 with aqueous 10% sodium hydroxide. The resulting dark red solution immediately deposited a fluffy, orange-red solid (0.20 g, 90%). Crystallization from aqueous ethanol afforded XII*a* as orange-red needles, m.p. 257–259° decomp.

Anal. Calc. for $C_{14}H_{16}N_4O_2$: C, 61.75; H, 5.92; N, 20.58. Found: C, 61.50; H, 5.91; N, 20.31.

$\lambda_{max}^{CHCl_3}$ 3.0 (w), 4.1 (w), 6.18, 6.40, 6.86, 7.28, 8.82 μ.

When this experiment was performed with the rigid exclusion of oxygen, XII*a* was again obtained in 80% yield. The same product was also obtained when the reaction was carried out in the dark.

The azoxy compound XIII*a* was recovered unchanged after treatment with aqueous 10% sodium hydroxide.

(ii) pH 7–9. Formation of XIIIa

A solution of XI*a* (0.055 g) in water (10 ml) was brought to pH 7–8 with aqueous 10% sodium bicarbonate. During 30 minutes a yellow solid (0.037 g, 85%) was deposited. Crystallization from aqueous ethanol gave XIII*a* as yellow needles, m.p. 248–250° decomp.

Anal. Calc. for $C_{14}H_{16}N_4O_3$: C, 58.32; H, 5.59; N, 19.44. Found: C, 58.22; H, 5.56; N, 19.31.

$\lambda_{max}^{CHCl_3}$ 3.0 (w), 4.1 (w), 6.19, 6.45, 6.71, 7.26, 8.75, 9.12 μ.

The azo compound XII*a* was recovered unchanged after subjection to the conditions of this experiment.

When XI*a* was treated with aqueous 10% sodium bicarbonate with the exclusion of oxygen, no reaction occurred.

Treatment of an aqueous solution of XI*a* with dilute aqueous ammonia at pH 8–9 in the presence of air also gave XIII*a* (70%); the reaction proceeded in both the presence and absence of light. Concentration of the aqueous mother liquor in this case gave further XIII*a* and a trace of the azo compound XII*a*, identified by infrared spectral comparison and mixture melting point.

Effect of Light on XIa.[11] *Formation of XIIIa*

When an aqueous solution of XI*a* (pH 5–6) was exposed to daylight it turned yellow and slowly deposited yellow needles of XIII*a*, identified by infrared spectral comparison and melting point. When oxygen was rigidly excluded from the solution, no reaction occurred.

4,4′-Azodi-2,6-lutidine 1,1′-Dioxide (XIIa)

An authentic sample of this compound was prepared by the reduction of 4-nitro-2,6-lutidine 1-oxide (7) with aqueous sodium nitrite and sodium hydroxide according to the method used by Ochiai (12) for the preparation of 4,4′-azodipyridine 1,1′-dioxide from 4-nitropyridine 1-oxide. The product crystallized from ethanol as orange-red needles, m.p. 257–259° decomp. (lit. (8) m.p. 248° decomp.).[12] This was shown by infrared spectral comparison and a mixture melting point determination to be identical with the product, m.p. 257–259° decomp., obtained from XI*a*.

4,4′-Azoxydi-2,6-lutidine 1,1′-Dioxide (XIIIa)

An authentic sample of this compound was prepared by the reduction of 4-nitro-2,6-lutidine 1-oxide (7) in aqueous solution with zinc according to the method used by Ochiai (12) for the preparation of 4,4′-azoxydipyridine 1,1′-dioxide from 4-nitropyridine 1-oxide. The product crystallized from ethanol as yellow needles, m.p. 248–250° decomp. (lit. (8) m.p. 233° decomp.).[12] This was shown by infrared spectral comparison and a mixture melting point determination to be identical with the product, m.p. 248–250° decomp., obtained from XI*a*.

Reaction of 2,6-Diethyl-4-pyrone with Hydroxylamine. Formation of IXb

A solution of 2,6-diethyl-4-pyrone (5 g, 0.033 mole) and hydroxylamine hydrochloride (5 g, 0.072 mole) in ethanol (30 ml) and pyridine (30 ml) was boiled under reflux for 6 hours. The reaction mixture was freed from solvent under reduced pressure. The brown oily residue was dissolved in water (20 ml) and cooled at 0° for 72 hours, when a viscous oil separated. The aqueous solution was decanted and cooled at 0° for a further 48 hours, giving a yellow solid deposit (1.2 g, 20%). Several crystallizations from ethanol/acetone gave IX*b* as colorless flakes. This product did not melt sharply; when heated at 135° it turned yellow and melted with decomposition at ca. 170°.

[11]*Similar results were obtained with the parent compound, IXa.*

[12]*The melting points of the azo and azoxy compounds are very sensitive to the rate of heating; we have also obtained melting points similar to those reported earlier (8).*

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Anal. Calc. for $C_9H_{14}N_2O_2$: C, 59.32; H, 7.74; N, 15.38. Found: C, 59.06; H, 7.79; N, 15.41.
λ_{max}^{Nujol} 3.2 (sh), 3.75 (sh), 6.12 (s), 8.45 (m), 8.56 (m) μ.

Reaction of IXb with Aqueous Bases

(i) pH 12–13. Formation of XIIc

A solution of IX*b* (0.10 g) in water (4 ml) was brought to pH 12–13 with aqueous 10% sodium hydroxide. The azo compound XII*c* (0.060 g, 65%) precipitated rapidly and after crystallization from aqueous ethanol was obtained as red needles, m.p. 176–177°.

Anal. Calc. for $C_{18}H_{24}N_4O_2$: C, 65.83; H, 7.37; N, 17.07. Found: C, 65.54; H, 7.46; N, 16.97.
$\lambda_{max}^{CHCl_3}$ 2.95 (w), 4.1 (w), 6.20, 6.41, 6.83, 8.82 μ.

(ii) pH 7–9. Formation of XIIc and XIIIc

When aqueous solutions of IX*b* were brought to pH 7–9 with either aqueous 10% sodium bicarbonate or dilute aqueous ammonia, an orange-colored product was deposited which was shown to be a mixture of the azo compound XII*c* and the azoxy compound XIII*c* by infrared spectral comparison.

Irradiation of IXb. Formation of XIIIc

A solution of IX*b* (0.10 g) in water (10 ml) was irradiated with a fluorescent lamp for 60 hours. A red crystalline solid (0.055 g) separated. The aqueous mother liquor was extracted with ethyl acetate and the extract was dried and freed of solvent under reduced pressure, giving an orange solid (0.021 g). The combined solid material (80%) was crystallized three times from aqueous ethanol and once from petroleum ether (b.p. 60–70°) to give XIII*c* as orange needles, m.p. 127–128°.

Anal. Calc. for $C_{18}H_{24}N_4O_3$: C, 62.77; H, 7.02; N, 16.27. Found: C, 62.61; H, 7.09; N, 16.11.
$\lambda_{max}^{CHCl_3}$ 2.95 (w), 4.1 (w), 6.18, 6.46, 6.75, 8.76, 9.05 μ.

ACKNOWLEDGMENTS

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