Registry No.—**8**, 17953-12-7; **11a**, 17953-13-8; **11b**, 17953-14-9; **12a**, 17953-15-0; diphenyl triketone, 643-75-4; 1-acetyl-3,5-diphenyl-4-acetoxypyrazole, 17953-16-1; 3,3-dinitro-1-phenyl-1-butene, 17953-17-2; 2,3,3-trinitro-1-phenyl-1-butene, 17953-18-3; 3,5-diphenyl-4-nitrato-2-isoxazoline, 17953-19-4.

The Nitrosation of α,β-Unsaturated Oximes. V. The Synthesis and Chemistry of 1-Hydroxypyrazole 2-Oxides[1]

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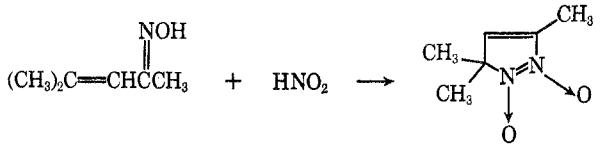
Nitrosation of α-substituted α,β-unsaturated oximes with sodium nitrite in acetic acid produces 1-hydroxypyrazole 2-oxides (**3**). These compounds are relatively strong organic acids and form chelates with a variety of transition metals. Reduction yields the corresponding N-hydroxypyrazoles or the parent pyrazoles. Acylation leads to a molecular rearrangement and production of 3-acyloxypyrazolenine 1-oxides (**10**). Nitrosation converts the 4-alkyl derivatives into 4-nitro-1,2-diazacyclopentadiene 1,2-dioxides (**16**).

Previous investigations of the action of nitrosating agents on α,β-unsaturated oximes involved oximes unsubstituted in the α position. Mesityl oxide oxime, a β-substituted derivative, was converted into 3,5,5-trimethylpyrazolenine 1,2-dioxide (**1**)[3] while a variety of other oximes were converted into 3,4-diazacyclopentadienone 3,4-dioxides (**2**).[4]



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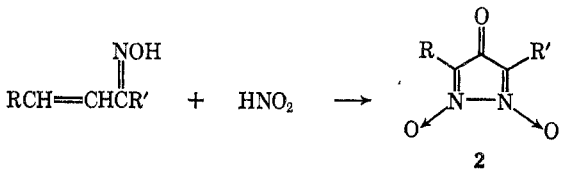

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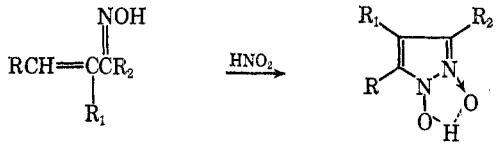
In 1904, Harries and Tietz[5] reported the nitrosation of 3-methyl-4-phenyl-3-buten-2-one oxime to a high-melting white solid of composition $C_{11}H_{12}N_2O_2$, to which they assigned a nitrimine[6] structure.

In a previous communication[7] we proposed that the structure of this product is analogous to that of compound **2** and actually is 1-hydroxy-3-phenyl-4,5-dimethylpyrazole 2-oxide (**3**, R = C_6H_5, R_1 = R_2 = CH_3). This reaction is rather general and a series of these compounds has been made (Table I).



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(1) We are grateful to the donors of the Petroleum Research Fund of the American Chemical Society and to the National Cancer Institute of the National Institutes of Health (Grant No. 1 RO1-CA10742-01) for support of this research.

(2) Alfred P. Sloan Fellow, 1966–1968.

(3) J. P. Freeman, *J. Org. Chem.*, **27**, 1309 (1962).

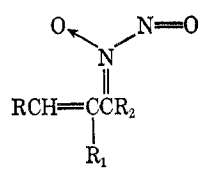
(4) J. P. Freeman and D. L. Surbey, *Tetrahedron Lett.*, 4917 (1967); J. P. Freeman, J. J. Gannon, and D. L. Surbey, *J. Org. Chem.*, **34**, 187 (1969).

(5) C. Harries and H. Tietz, *Ann.*, **330**, 237 (1904).

(6) J. P. Freeman, *J. Org. Chem.*, **26**, 4190 (1961).

(7) J. P. Freeman and J. J. Gannon, *J. Heterocycl. Chem.*, **3**, 544 (1966).

Structure.—The assignment of the hydroxypyrazole oxide structure to these compounds is based upon their elemental analyses, analogy to the structure of pernitrosomesityl oxide[3] from which these structures are derived by a prototropic shift, their acidity, spectral properties, and chemical reactions. While taken individually, none of these unequivocally proves the assigned structure; collectively they rule out alternative structures such as **4**, **5**, or **6**.



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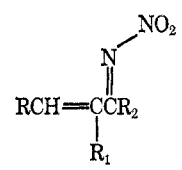

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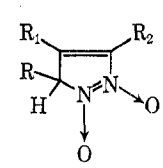

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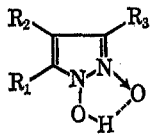
Physical Properties.—All of these compounds are characterized by high melting points and limited solubility in most solvents. However, all are soluble in dilute sodium hydroxide from which they can be recovered by acidification. Their sodium salts can be isolated and are stable, crystalline materials. The acidity of one of these compounds, 1-hydroxy-3-phenyl-4,5-dimethylpyrazole 2-oxide (**8**), was measured by the method of Calvin[8a] and Bjerrum[8b] and its pK_a was 6.3.

The infrared spectra of these compounds showed no distinctive band associated with O–H stretching but were characterized by broad diffuse absorption between 4 and 6 μ. At longer wavelengths the bands were sharp and distinguishable. The hydroxyl proton was not observed in the nmr spectrum of the 1-hydroxypyrazole 2-oxide previously reported,[7] but it has been found at low fields in the other examples listed in Table I. Both the nmr chemical shift of this proton and the infrared data are suggestive of a highly chelated proton (*cf.* OH chemical shift of enolic β diketones and their infrared spectra). The ultraviolet spectra of these compounds and their sodium salts are rather similar suggesting a highly polar O–H bond.

The nmr spectrum of 1-hydroxy-3,4,5-trimethylpyrazole 2-oxide (**7**) consists of two sharp singlets at δ 1.95 (3 H) and 2.20 (6 H) in addition to a singlet at

(8) (a) M. Calvin and M. K. Wilson, *J. Amer. Chem. Soc.*, **67**, 2003 (1945); (b) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase & Sons, Copenhagen, 1941, p 121.

TABLE I
1-HYDROXYPYRAZOLE 2-OXIDES



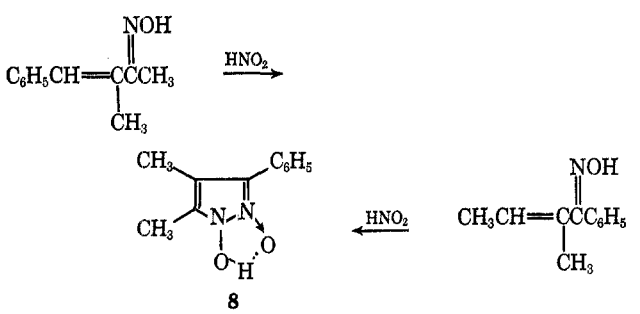
Compound			Registry		Yield,		Ultraviolet spectra (C_2H_5OH)		Calcd, %			Found, %		
R_1	R_2	R_3	no.	Mp, °C	%	Nmr, δ[a]	λ_{max}, mμ	Log ϵ_{max}	C	H	N	C	H	N
C_6H_5	C_6H_5	C_6H_5	17953-29-6	230–232	95		260	4.4	76.81	4.91	8.53	76.12	5.07	8.46
CH_3	CH_3	CH_3	17953-31-0	169–170	83	1.95 (s, 3)	250	3.8	50.69	7.09	19.71	50.58	7.22	19.31
						2.20 (s, 6)								
						15.80 (s, 1)								
CH_3	CH_3	C_6H_5	15674-34-7	200	96	2.08 (s, 3)	230	4.1	64.70	5.88	13.72	64.49	6.12	14.05
						2.29 (s, 3)	288	4.0						
C_6H_5	CH_3	C_6H_5	17953-33-2	213–214	87	2.15 (s, 3)	262	4.4	72.17	5.30	10.52	71.85	5.57	10.02
						9.00 (s, 1)	285	4.3						

[a] Measured in dimethyl sulfoxide-d_6; TMS standard.

δ 15.8 (1 H). The magnetic equivalence of two of the methyl groups constitutes additional evidence for the chelate structure **7** in which rapid tautomerism causes the 3 and 5 methyl groups to be equivalent. Even at −60° the spectrum does not change.

7

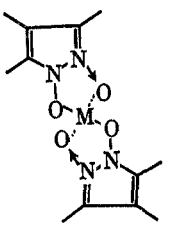
A symmetrical structure is also indicated by the fact that the same 1-hydroxypyrazole 2-oxide (**8**) was obtained from the nitrosation of either 3-methyl-4-phenyl-3-buten-2-one oxime or 1-phenyl-2-methyl-2-buten-1-one oxime.



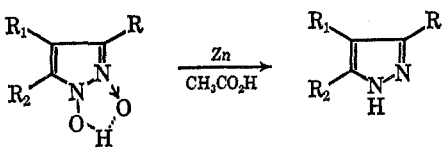
8

Chemical Properties. Chelate Formation.—Addition of an aqueous solution of the sodium salt of **8** to aqueous solutions of a variety of metal ions [Cu(II), Co(II), Ni(II), Cd(II)] resulted in the precipitation of highly colored, flocculent precipitates, which were highly insoluble in all solvents. Elemental analyses indicated 2:1 complexes.

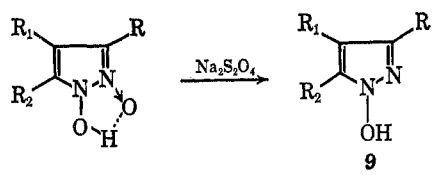
The chelate character of these new materials is inferred from their colors and the appearance of metal–ligand stretching frequencies in the far-infrared region at 500–550 cm^{-1}, a typical region for metal–oxygen bonds.[9] The structure of these chelates presumably resembles those of β diketones



Reduction.—The hydroxypyrazole oxides were easily reduced by zinc in acetic acid to the parent pyrazoles.



Under milder conditions the same reagents yielded first the corresponding N-hydroxypyrazoles **9**, the first reported members of this class of compounds. In



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practice sodium dithionite proved to be a more useful reagent for effecting this selective reduction (Table II).

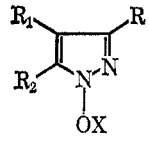
Two isomeric N-hydroxypyrazoles should be possible when R and R_2 are different but only one isomer, whose structure is somewhat uncertain, has been isolated from these reductions. Some inferences about their structure have been made on the basis of further reactions. These will be discussed in a later section.

The isolation of N-hydroxypyrazoles from the reduction of the nitrosation products is highly suggestive of the presence of a pyrazole nucleus in those compounds. While it is always possible that reduction has been accompanied by ring closure, the mildness of the dithionite reduction is not consistent with that possibility.

Acylation.—Treatment of the hydroxpyrazole oxides with either acetic anhydride–sodium acetate or *p*-nitrobenzoyl chloride in pyridine produced acyl derivatives but of rearranged structure. For example, treatment

(9) M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, p 242.

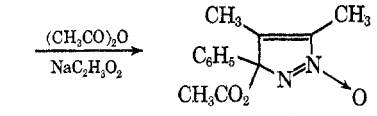
TABLE II
N-HYDROXYPYRAZOLES AND DERIVATIVES



Compound			Registry		Bp (mm) or	Calcd, %			Found, %		
R	R_1	R_2	no.	X	Mp, °C	C	H	N	C	H	N
CH_3	CH_3	CH_3	17953-34-3	H	183–184	57.12	7.99	22.20	57.24	8.15	22.14
C_6H_5	CH_3	C_6H_5	17953-35-4	H	204–206	76.78	5.64	11.19	76.78	5.78	11.02
C_6H_5	CH_3	CH_3	14397-26-3	H	167–168	70.19	6.43		70.15	6.60	
CH_3	CH_3	CH_3	17953-36-5	p-$NO_2C_6H_4CO$	137–139	57.73	4.76	15.27	57.17	5.15	15.30
C_6H_5	CH_3	CH_3	17953-37-6	p-$NO_2C_6H_4CO$	152–154	64.09	4.48	12.46	64.00	4.76	12.40
C_6H_5	CH_3	CH_3	14490-99-4	CH_3	115 (0.3)[a]	71.26	6.98	13.85	71.72	7.76	13.97
C_6H_5	CH_3	CH_3	17953-71-8	p-$CH_3C_6H_4SO_2$	105	63.14	5.30	8.18	63.36	5.36	8.19

[a] Liquid.

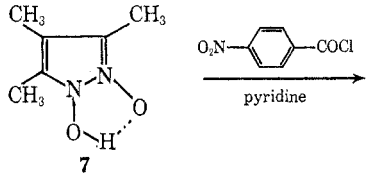
of compound **8** with acetic anhydride yielded 3-acetoxy-3-phenyl-4,5-dimethylpyrazolenine 1-oxide (**10**).



10

The structure of **10** rests on its elemental analysis, its infrared spectrum[10] ($\nu_{N=N\rightarrow O}$ 1500 cm^{-1}, $\nu_{C=O}$ 1760 cm^{-1}), its ultraviolet spectrum[11] (λ_{max} 247, ϵ_{max} 7000) and its nmr spectrum, which shows that the two methyl groups (δ 1.93 and 2.12) are homoallylically coupled[12] (J = 1.3 cps), which is consistent with their *cis* attachment to a rigid double bond which is no longer part of an aromatic system.

Additional evidence for this structure was obtained from p-nitrobenzoylation of hydroxypyrazole oxide **7** and also of the hydroxypyrazole **12**. The former reaction yielded a p-nitrobenzoate, **11**, whose infrared



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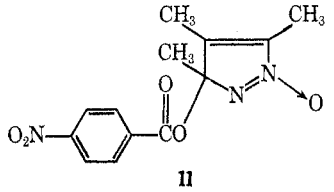

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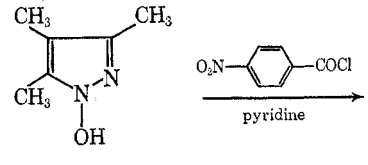

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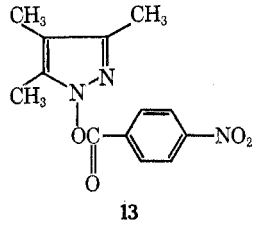
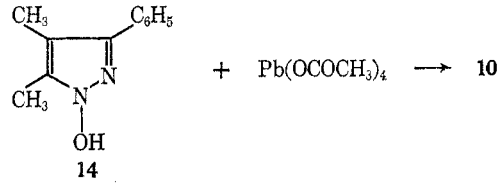


13

spectrum contained a band at 1735 cm^{-1} attributable to the ester carbonyl band and whose nmr spectrum showed the homoallylically coupled methyl groups at δ 1.98 and 2.15. (The uncoupled methyl group signal was at δ 1.77.) Similar reaction of **12** produced a p-nitrobenzoate, whose infrared spectrum showed carbonyl absorption at 1790 cm^{-1} and whose nmr spectrum showed sharp singlets for the methyl groups at δ 1.98, 2.14, and 2.21. The high ester carbonyl frequency in the latter compound is that expected of an N-acyloxy group[13] and accordingly the structure of this compound is assigned as **13**.

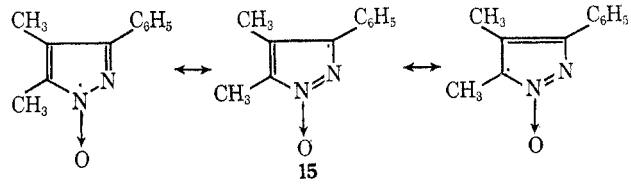
The relative positions of the ester and N-oxide functions is assigned somewhat arbitrarily based upon the ultraviolet spectra of the acetates which show no absorption beyond 250 mμ consistent[14] with an α,β-unsaturated azoxy compound with a partial structure —C=C—N(→O)=N— rather than —C=C–N=N-(→O)–.

Acetate **10** could be synthesized independently from the hydroxypyrazole **14** by treatment of it with



14

lead tetraacetate.[7] Unfortunately, neither the structure of **14** nor the structure of product **10** can be inferred directly from this reaction since details about the mechanism are lacking. However, if the first step is oxidation of the hydroxypyrazole to the nitroxide[15] **15**, then coupling of the nitroxide with an acetoxy



15

group might be expected at either position 3 or 5. Coupling does occur preferentially, however, at the carbon bearing the phenyl group since the methyl groups are homoallylically coupled in the product.

(10) In the infrared spectra of two other pyrazolenine oxides,[3] the stretching frequency of the azoxy function was at 1485 cm^{-1}.

(11) The ultraviolet spectra of pyrazoles is characterized by strong absorption in the 250–260-mμ region.

(12) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

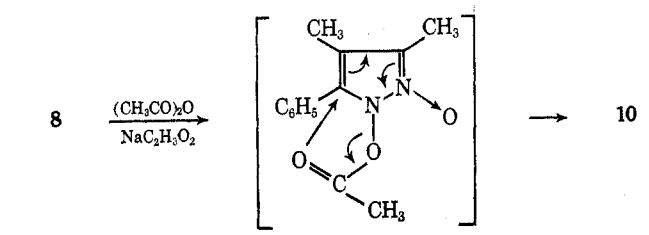
(13) J. P. Freeman, *J. Amer. Chem. Soc.*, **80**, 5954 (1958).

(14) C. L. Stevens, B. T. Gillis, J. C. French, and T. H. Haskell, *ibid.*, **80**, 6088 (1958).

(15) For similar oxidations of saturated hydroxylamine derivatives, see, for example, G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 444 (1965).

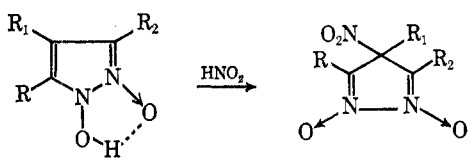
If the ultraviolet evidence can be trusted, then the phenyl group in hydroxypyrazole **14** must be in position 3.

The details of the conversion of **8** to **10** or **7** to **11** during acylation are unknown but an intramolecular migration similar to a Claisen rearrangement may be envisioned. On the other hand, the reaction bears



similarities to the Wallach rearrangement and other aromatic nucleophilic rearrangements.[16] Attack of acetate ion on the ring followed by loss of acetate from nitrogen may be involved. Recently a similar analogy and scheme were proposed for some aromatic substitutions of N-fluoro compounds.[16] Tracer experiments will be examined to determine the details of the process.

Nitrosation. Hydroxypyrazole oxides bearing alkyl groups in position 4 undergo nitrosation followed by oxidation at that position to yield the corresponding 4-nitropyrazolenine 1,2-dioxides, **16**.[4] This reaction



3 **16**

may be viewed most simply as an electrophilic substitution reaction to produce a nitroso compound which is oxidized rapidly by excess nitrous acid. Details of the synthesis of these compounds and their subsequent thermal decomposition may be found in paper IV of this series.[4]

Experimental Section[17]

Preparation of 1-Hydroxypyrazole 2-Oxides.—The oximes were prepared by literature methods: 3-methyl-4-phenyl-3-buten-2-one oxime, mp 112.5° (lit.[18] mp 103–104°); 1,3-diphenyl-2-methylpropenone oxime, mp 144–148° (lit.[19] mp 145–161°); 3-methyl-3-penten-2-one oxime, mp 76–78° (lit.[20] mp 76.5°); 1,2,3-triphenylpropenone oxime, mp 207° (lit.[21] mp 208–209°).

1-Phenyl-2-methyl-2-buten-1-one Oxime.—The ketone was prepared by the method of Abell,[19] bp 118–122 (10 mm) [lit.[22] bp 117 (10 mm)]. A mixture of 20 g (0.125 mol) of ketone, 9 g of $NH_2OH \cdot HCl$ and 6 g of sodium acetate was heated under reflux in a mixture of 100 ml of ethanol and 50 ml of water for 3 hr. The oxime crystallized when the solution was cooled: mp 105–107°; yield 12.3 g (56%).

Anal. Calcd for $C_{11}H_{14}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.27; H, 7.66; N, 7.79.

The following method was found to be generally applicable for the compounds in Table I.

1-Hydroxy-3(5)-phenyl-4,5(3)-dimethylpyrazole 2-Oxide (8).—To 15.0 g (0.086 mol) of 3-methyl-4-phenyl-3-buten-2-one oxime dissolved in 50 ml of CH_3CO_2H and cooled with stirring in an ice bath was added very slowly a solution of 6.0 g (0.087 mol) of $NaNO_2$ dissolved in 5 ml of water. At or immediately preceding the addition of the final drops of this solution, a white precipitate formed in the reaction mixture. The final drops were added and the slurry was vigorously stirred for 5 min, filtered immediately, washed quickly with two 20-ml portions of cold (−20°) 95% ethanol, and quickly transferred to a vacuum desiccator for drying. It is important to keep the product away from the light as much as possible. The product was dried for several hours: yield 16.7 g (96%); mp 200° dec.

Sodium Salt of 8.—A 2.0-g (0.0098 mol) sample of **8** was dissolved in 20 ml of 10% sodium ethoxide solution. Upon dilution with a large excess of dry ether a flocculent precipitate appeared, and, after the solution was cooled to 0°, the precipitate was collected and dried: mp 270°; 2.2 g (99% yield); nmr (D_2O) δ 1.92, (s, 3), 2.16 (s, 3), 7.40 (m, 5).

Anal. Calcd for $C_{11}H_{11}N_2O_2Na$: C, 58.40; H, 4.90; N, 12.39. Found: C, 58.29; H, 5.00; N, 12.19.

Chelates of 8. Copper.—To a solution of 0.50 g (0.0022 mol) of the sodium salt of **8** in 5 ml of water was added an aqueous cupric acetate solution. The heavy greenish brown precipitate was collected and air dried, mp 245° dec. An almost quantitative yield was obtained.

In addition to the above procedure in which the ligand (sodium salt) was present in excess, the reaction was run under conditions where the cupric acetate was present in excess. The same greenish brown chelate was formed. The same result was obtained in ethanolic solution. The product was washed four times with water, methanol and acetone, centrifuged, and dried.

Anal. Calcd for $C_{22}H_{22}N_4O_4Cu$: C, 56.22; H, 4.72; N, 11.92. Found: C, 56.49; H, 4.89; N, 11.70.

Cobalt.—A 0.50-g sample of the sodium salt of **8** was mixed with 0.81 g (0.0022 mol of cobalt(II) nitrate according to the previous procedure. A dark violet precipitate was formed, collected, and dried, mp 230–60° dec. Again the same violet product formed when the metallic ion was present in excess. The product was washed four times with water, methanol, and acetone, dried, and analyzed.

Anal. Calcd for $C_{22}H_{22}N_4O_4Co \cdot 2H_2O$: C, 52.70; H, 5.23; N, 11.18. Found: C, 53.55; H, 4.86; N, 11.25.

Reduction of 1-Hydroxypyrazole 2-Oxides. 3-Phenyl-4,5-dimethylpyrazole.—A 1-g sample of **8** was refluxed with 4 g of zinc powder in 25 ml of CH_3CO_2H for 4 hr. The mixture was filtered and the filtrate was diluted with water. The white precipitate was filtered and recrystallized from hexane, mp 108–109°.

Anal. Calcd for $C_{11}H_{12}N_2$: C, 76.74; H, 6.97; N, 16.27. Found: C, 76.90; H, 7.10; N, 16.19.

An authentic sample was prepared by heating a mixture of 8.8 g of 3-methyl-4-phenylbutane-1,3-dione[23] and 5 ml of 90% hydrazine in 20 ml of ethanol for 1 hr. The material isolated upon dilution with water was identical in all respects with that obtained by reduction.

3,5-Diphenyl-4-methylpyrazole.—A slurry of 2 g of **3** (R = R_2 = C_6H_5; R_1 = CH_3) and 6 g of zinc powder in 50 ml of CH_3CO_2H was stirred vigorously for 1 hr at room temperature. The mixture was filtered to remove the zinc and then concentrated. Ice was added to the residue and the solid that crystallized was recrystallized from 95% ethanol: mp 227–228°; yield 1.5 g (85%); nmr ($CDCl_3$) δ 2.30 (s, 3), 7.55 (m, 5), 13.10 (s, 1).

Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 82.88; H, 6.16; N, 11.84.

Preparation of 1-Hydroxypyrazoles and Derivatives (Table II).—The following procedure was generally applicable to the preparations, X = H, listed in Table II.

1-Hydroxy-3,5-diphenyl-4-methylpyrazole.—To 4.0 g (0.015 mol) of **3** (R = R_2 = C_6H_5; R_1 = CH_3) was added a solution of 12.0 g (0.069 mol) of $Na_2S_2O_4$ (Baker Chemical) in 350 ml of water. The mixture was refluxed for 12 hr and cooled. The solid residue was filtered and recrystallized from 95% ethanol, yielding 2.5 g (67%) of white solid, mp 204–206°. Treatment of this compound with zinc in CH_3CO_2H as above produced 3,5-diphenyl-4-methylpyrazole identical with that above.

1-*p*-Nitrobenzoxy-3,4,5-trimethylpyrazole (13).—To a 1.5-g

(16) T. E. Stevens, *Chem. Commun.*, 1181 (1967); *J. Org. Chem.*, **33**, 2664 (1968).

(17) The nmr spectra were measured with an Varian Associates A-60A nmr spectrometer. This instrument was acquired under National Science Foundation equipment grant GP-6875. Except for the spectra of compounds listed in Table I, all spectra were measured in $CDCl_3$ (TMS standard).

(18) C. Harries and G. Mueller, *Ber.*, **35**, 966 (1902).

(19) R. Abell, *J. Chem. Soc.*, 2834 (1953).

(20) L. K. Evans and A. E. Gillam, *ibid.*, 565 (1943).

(21) E. Knoevenagel and R. Weissgerber, *Ber.*, **26**, 443 (1893).

(22) E. E. Blaise and I. Herman, *Ann. Chim.*, [8] **23**, 529 (1911).

(23) C. Weygand and H. Forkel, *Ber.*, **61**, 687 (1928).

(0.012 mol) sample of 1-hydroxy-3,4,5-trimethylpyrazole (**12**) slurried in 6 ml of pyridine was added (at 0°) 0.75 g (0.0041 mol) of *p*-nitrobenzoyl chloride. The mixture was stirred for 5 min at 0° and then warmed on a steam bath for 3 min. It then was poured into 15 ml of water and stirred vigorously. The light precipitate which formed was isolated by decantations, washed with 5 ml of 10% Na_2CO_3 solution, dried, and recrystallized from 95% ethanol giving 1.0 g (31% yield) of **13**.

1-Methoxy-3-phenyl-4,5-dimethylpyrazole.—To a solution of 0.5 g of sodium in 50 ml of absolute ethanol was added 4 g (0.02 mol) of **14**. To this solution was added 3 g (0.02 mol) of CH_3I in 25 ml of ethanol. The resulting mixture was heated under reflux overnight during which time a brown color had developed. The solvent was evaporated and the residue extracted with ether several times. The combined ether extracts were dried and concentrated to an orange oil. The oil was chromatographed on silica gel yielding the main product, now a pale yellow oil: bp 115° (0.3 mm); $n^{20}D$ 1.5710 (ir KBr disk, 985 cm^{-1} (OCH_3); nmr ($CDCl_3$) δ 2.07 (s, 3), 2.13 (s, 3), 3.97 (s, 3), 7.47(m, 5); uv max (EtOH) 253 mμ (log ϵ 3.9).

1-Toluenesulfonoxy-3-phenyl-4,5-dimethylpyrazole.—To 2.0 g (0.01 mol) of **14** dissolved in 40 ml of pyridine at 10° was added 2.2 g (0.012 mol) of *p*-toluenesulfonyl chloride slowly with stirring. Stirring was continued for 3 hr at 10°. After warming to 25°, the mixture was heated on a steam bath for 15 min and poured into a mixture of 60 ml of concentrated hydrochloric acid and 800 ml of ice–water. The mixture was stirred vigorously and the crude whitish product that formed was collected, dried, and then recrystallized from $CHCl_3$–*n*-C_6H_{14}, yield 2.6 g (68%).

3,5-Diphenyl-3-acetoxy-4-methylpyrazolenine 1-Oxide. Method A.—A 2.0-g (0.0075 mol) sample of 1-hydroxy-3,5-diphenyl-4-methylpyrazole 2-oxide was mixed with a slurry of 15 ml of acetic anhydride and 5 g of sodium acetate. After standing for 1 hr, the solution was gently warmed on the steam bath for 10 min and then poured into 100 ml of cold 10% hydrochloric acid. After stirring for 30 min, the solution was extracted with 50 ml of $CHCl_3$ and washed with two 20-ml portions of saturated Na_2CO_3 solution. The combined organic fractions were washed with 15 ml of saturated NaCl solution, and dried ($MgSO_4$). Concentration of filtered solution yielded an oily solid which very slowly crystallized from $CHCl_3$ at −20°. After recrystallization from $CHCl_3$–*n*-C_6H_{14}, 1.3 g (56% yield), mp 111–112°, was obtained: ir (KBr disk) 1760 (ester C=O), 1500 cm^{-1} (—N=N-(→O)—); nmr ($CDCl_3$) δ 1.91 (s, 3), 2.18 (s, 3).

Anal. Calcd for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.09. Found: C, 70.17; H, 5.45; N, 9.29.

Method B.—A 2.0-g (0.0080 mol) sample of 1-hydroxy-3,5-diphenyl-4-methylpyrazole was slurried in 10 ml of dry benzene. The mixture was cooled in an ice bath and 2.0 g (0.0045 mol) of lead tetraacetate (G. Frederick Smith Chemical Co.) was added to the stirred mixture. The resulting suspension was stirred for 5 hr as the mixture was permitted to warm to 25°. The slurry was filtered to remove the lead salt and the filtrate was concentrated. A pinkish solid (apparently a mixture of lead acetate and unreacted starting material) precipitated and was filtered. Further concentration of the filtrate eventually yielded 0.6 g (24%) of solid which was recrystallized from 95% ethanol, mp 108–110°. The product was shown to be identical with the material prepared by method A by mixture melting point and identity of infrared spectra.

3-Phenyl-3-acetoxy-4,5-dimethylpyrazolenine 1-Oxide (10). Method A.—A 2.0-g (0.0098 mol) sample of **8** was stirred in a slurry of 15 ml of acetic anhydride and 5 g of sodium acetate. After stirring for 15 min the solution was warmed on a steam bath for 5 min and poured into ice–water (100 ml) and stirred again for 1 hr. The oily product was extracted into 50 ml of ether, washed with 20 ml of 10% Na_2CO_3 solution, then with 50 ml of saturated NaCl solution, and dried ($MgSO_4$). Evaporation of the ether gave a yellow oil which crystallized from a minimal amount of 95% ethanol at −20°, yielding white crystalline **10**, mp 98–103°. It was recrystallized from 95% ethanol yielding 0.5 g (21%), mp 110°.

Anal. Calcd for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.27; H, 5.97; N, 11.10.

Method B.—To 1.0 g (0.005 mol) of **14** in an ice-cooled dry benzene solution (30 ml) was added an equivalent amount of lead tetraacetate and the solution was stirred for 1 hr. After warming to 25°, the solution was filtered and the filtrate concentrated. The oily residue was crystallized and recrystallized from absolute ethanol yielding approximately 1.0 g of product, mp 109–110° (85%). The infrared spectrum and mixture melting point confirmed its identity with the compound prepared by method A.

3,5-Diphenyl-3-*p*-nitrobenzoxy-4-methylpyrazolenine 1-Oxide.—To 2.0 g (0.0075 mol) of 1-hydroxy-3,5-diphenyl-4-methylpyrazole 2-oxide slurried in 8 ml of pyridine was added 2.0 (0.011 mol) of *p*-nitrobenzoyl chloride with vigorous stirring. The mixture was warmed on a steam bath for 15 min and poured into 100 ml of cold water and stirred vigorously. The yellow product crystallized, was washed with 15 ml of 10% Na_2CO_3 solution, filtered, and recrystallized from ethanol and then $CHCl_3$–*n*-C_6H_{14}: mp 192–194°; 2.5 g (81%); ir (Nujol) 1735 (ester C=O), 1500 (—N=N(→)O—), 1520, 1340 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 2.08 (s, 3).

Anal. Calcd for $C_{23}H_{17}N_3O_5$: C, 66.50; H, 4.12; N, 10.12. Found: C, 66.23; H, 4.23; N, 9.91.

3,4,5-Trimethyl-3-*p*-nitrobenzoxypyrazolenine 1-Oxide.—By the same procedure hydroxypyrazole oxide **7** was converted in 68% yield into white crystals of **11**, mp 172–174° (hexane–$CHCl_3$).

Anal. Calcd for $C_{13}H_{13}N_3O_5$: C, 53.61; H, 4.50; N, 14.43. Found: C, 53.41; H, 4.85; N, 14.44.

3,4,5-Triphenyl-3-*p*-nitrobenzoxypyrazolenine 1-Oxide.—By the same procedure hydroxypyrazole oxide **3** (R = R_1 = R_2 = C_6H_5) was converted into the yellow title compound: mp 223–225°, (hexane–$CHCl_3$) in 80% yield; ir (Nujol) 1730 (ester C=O) 1530 (—N=N(→O)—), 1550, 1375 cm^{-1} (NO_2).

Anal. Calcd for $C_{28}H_{19}N_3O_5$: C, 70.43; H, 4.01; N, 8.80. Found: C, 70.36; H, 4.10; N, 8.79.

Registry No.—**8** Na salt, 17953-72-9; **8** Cu chelate, 17949-26-7; **8** Co chelate, 17949-27-8; **10**, 14490-98-3; **11**, 17953-43-4; **13**, 17953-36-5; 1-phenyl-2-methyl-2-buten-1-one oxime, 18052-14-7; 3-phenyl-4,5-dimethylpyrazole, 13618-35-4; 3,5-diphenyl-4-methylpyrazole, 17953-46-7; 3,5-diphenyl-3-acetoxy-4-methylpyrazolenine 1-oxide, 17953-47-8; 3,5-diphenyl-3-*p*-nitrobenzoxy-4-methylpyrazolenine 1-oxide, 17953-48-9; 3,4,5-triphenyl-3-*p*-nitrobenzoxypyrazolenine 1-oxide, 17953-49-0.