Synthesis, Carbon-13 Nuclear Magnetic Resonance, and Mass Spectral Studies of 3-Aroyloxy-3,5,5-trimethyl-1-pyrazoline N-Oxides

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A new oxidative method for the synthesis of 1-pyrazolines (**2**) from 2-pyrazolines (**1**) utilizing benzoyl peroxides was discovered. Oxidation of **2** with *m*-chloroperbenzoic acid resulted in the formation of the corresponding 1- and 2-oxides (**3** and **4**). Chemical degradation of **4** and ^{13}C NMR and mass spectral fragmentation studies of **2, 3,** and **4** led to unequivocal assignment of the position of the N-oxide function.

The recent interest in the chemistry of the azoxy function is partly related to its occurrence in natural products with potent physiological activity. Cyasin[2] a potent carcinogen[3] and elaiomycin[4] a tuberculostatic agent[5] serve as examples. Furthermore, azoxides are believed to be hydrolytic metabolic intermediates responsible for the biological activity of the clinically useful nitrosoureas.[6] Our interest in 3-aroyloxy-1-pyrazoline *N*-oxides as potential anticancer agents is based on the rationale that related azoxides could be generated upon the in vivo hydrolysis of these compounds.

Unlike previous reports on the preparation of cis[7] and trans[7a,8] azoxyalkanes, synthetic methods for 3-oxysubstituted azoxides are rather limited. Methoxide fragmentation of a nitrosourethanocyclopropane furnished a 3-methoxy-1-pyrazoline 1-oxide.[9] Silver ion assisted displacement of bromide in phenylbromomethyldiazene 1-oxide by oxygen nucleophiles afforded the corresponding substituted compounds.[8] Peracid oxidation of 3-acetoxy- and 3-benzoyloxy-3,5,5-trimethyl-1-pyrazolines (**2a** and **2b**) furnished, depending on the peracid used, the corresponding 1- and 2-oxides.[10] It is this latter method that was used in the present work to prepare the title compounds.

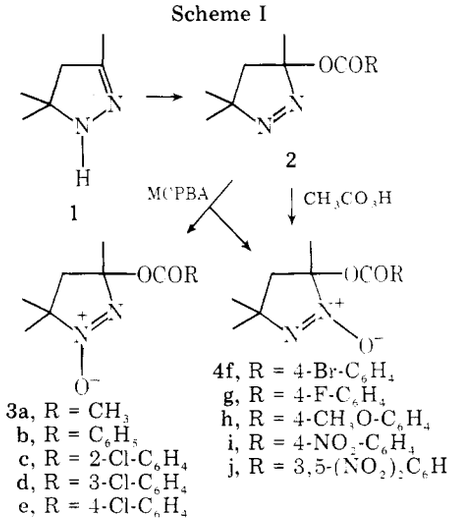
Freeman synthesized **2a** and **2b** by oxidation of the 2-pyrazoline (**1**) with lead tetraacetate and lead tetrabenzoate, respectively.[10] The instability of lead salts of substituted benzoic acids[11] did not allow the use of this method for the preparation of a variety of aromatic esters whose rates of hydrolysis could have interesting biological implications. However, a new method for oxidation of such 2-pyrazolines was discovered when it was noted that treatment of **1** with an equimolar quantity of benzoyl peroxide, with the aid of illumination, yielded the known **2b.**[10] This same method permitted the synthesis of the substituted 3-benzoyloxy-1-pyrazolines (**2c–i**) as shown in Scheme I. The benzoyl peroxides were prepared by treatment of the corresponding acid chloride with sodium or hydrogen peroxide.[12]

The reactions were carried out in chloroform or benzene at room temperature and gave 40–60% yields of the product. It is believed that this oxidation takes place via radical intermediates as depicted in Scheme II.

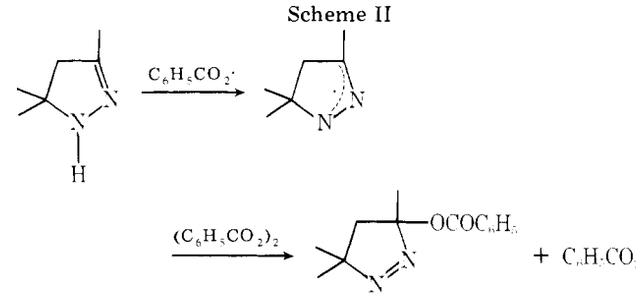
Similar oxidations have been reported. α-Benzoyloxy ketones have been prepared by treatment of their enamines with benzoyl peroxide followed by hydrolysis.[13] Pyrimidines have also been oxidized to their 5-benzoyloxy derivatives.[14]

Peracid oxidation of **2** followed already reported procedures.[10] While peracetic acid gave only the 2-oxide (**4**), *m*-chloroperbenzoic acid (MCPBA) gave a mixture of the 1- and 2-oxides (**3** and **4**). The need for both isomers prompted us to use the latter method where separation of the *N*-oxide mixture was accomplished by column chromatography on silica gel. This method of separation, although it furnished pure isomers, resulted in extensive decomposition of what is believed to be the 1-oxide isomer (**3**) (vide infra). This is evidenced by gas

Scheme I



Scheme II



generation and the isolation of the corresponding benzoic acid.

Oxidation of the 4-nitrophenyl compound (**2i**) produced unexpected results. In addition to the 1- and 2-oxides, a minor product was isolated whose mass spectrum suggested the presence of chlorine in the molecule evidenced by pairs of peaks at *m/e* 300, 298; 158, 156; 111, 139; and 113, 111, with intensity ratios of 1:3. The last six fragments are characteristic of chlorobenzoic acids as has been observed in the mass spectra of **3c–3e** and **4c–4e.** That the chlorine is in the meta position is shown by the identity of the aromatic regions in the ^{13}C- and ^{1}H-NMR spectra to those of **3d** and by the absence of the AA'BB' pattern expected for *p*-nitro benzoic acid. The presence of chlorine was further confirmed by elemental analysis which gave the compound an empirical formula of $C_{13}H_{15}N_2O_4Cl$. Based on the above data the structure of the compound could be either **5** or **6.**[15]

Although ultraviolet data could be used to distinguish between cyclic azoalkane *N*-oxides and *N,N'*-dioxides,[16] this method could not be applied here, since the ultraviolet spectra of **2d, 3d, 4d** and the unknown were almost identical.[19] However, the carbonyl absorption of **5** (**6**) was distinctly different

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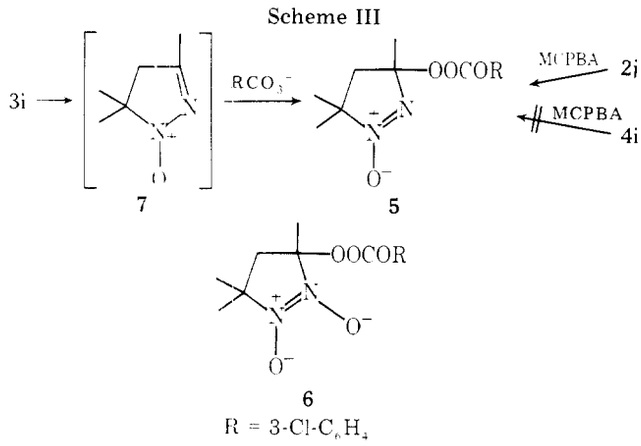
Scheme III



from (1786 cm^{-1}) and was shifted to higher frequency than those for **2d, 3d,** and **4d** (1748 cm^{-1}). Since analogous frequency differences have been observed between esters and peresters,[20] the compound is assigned structure **5.**

The formation of the perester **5** is visualized to arise from protonated **3i** (Scheme III). Elimination of 4-nitrobenzoic acid furnished the intermediate **7** which is trapped with the more nucleophilic *m*-chloroperbenzoate ion to give the product **5.** Support for this mechanism was obtained when **3i** and **4i** were subjected to oxidation with MCPBA. The perester **5** was obtained from the former only thus ruling out the intermediacy of the latter. The oxidation of the 3,5-dinitrophenyl compound **2j** with MCPBA gave increased **5** and the 2-oxide **4j,** while the 1-oxide **4i** was not obtained. This demonstrates further that the stronger the electronegativity of the substituents on the phenyl ring the easier the solvolysis of the 1-oxide.

Determination of the *N*-oxide position was derived from chemical and spectral methods. Freeman reported[10] the base decomposition of **4b** and the isolation of mesityl oxide from the reaction mixture. This result could be duplicated for our compounds resulting in the isolation of the α,β-unsaturated ketone.

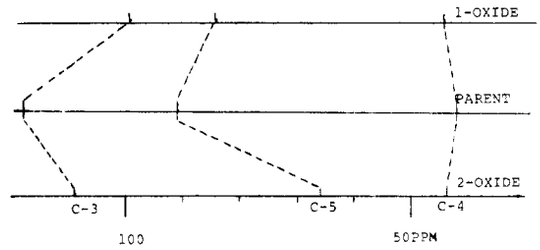


Figure 1.

In addition to the above chemical approach, two spectral methods have been developed for determining the position of the *N*-oxide, namely, ^{13}C-NMR and mass spectral fragmentation studies. The chemical shifts of the carbonyl carbons as well as those of C-3, C-4, and C-5 in compounds **2, 3,** and **4** are listed in Tables I, II, and III, respectively.

It is noted that *N*-oxidation exerts very little influence on the chemical shifts of >C=O and C-4 while it has a shielding effect on both C-3 and C-5. The shileding magnitude however is not the same for both carbons and is reversed as one goes from a 1-oxide to the isomeric 2-oxide. For example, C-5 is less shielded in **3b** than in **4b** (−6.29 vs. −24.74 ppm) while the reverse is true for C-3 which is more shielded in **3b** than in **4b** (−17.79 vs. −8.86 ppm). A schematic representation of the average of shileding effects on carbons 3, 4, and 5 is shown in Figure 1.

A suggestion for the greater shielding of C-3 in the 1-oxides is offered in Scheme IV. Resonance effects of the *N*-oxide increase electron density at the neighboring nitrogen in **9** and **11,** which results in the observed shielding of the adjacent carbon. Analogous shielding effects have been observed for pyridine oxide[21] and 1,2,4-triazine 1- and 2-oxides.[22]

The observed smaller shielding of C-5 and C-3 in the 1- and 2-oxides, respectively, appears, at first glance, to be an anomaly since one expects the positive charge at the oxygen-bearing nitrogen in **9** and **11** to deshield the adjacent C-3 and C-5, respectively. A reasonable explanation is derived from

Table I. Physical Data and Yields of 1-Pyrazolines (2)

2	Registry no.	^{13}C chemical shift, ppm C_4	C_5	C_3	>C=O	Mp, °C	Yield, %
b	65441-76-1	42.2	90.8	118.1	164.5	68–70 (lit. 70–71)[10]	59
c	65441-77-2	41.8	90.5	118.5	163.4	Oil	20
d	65453-03-4	41.7	90.3	118.1	163.0	37–8	75
e	65441-78-3	42.0	90.6	118.3	163.6	75–6	42
f	65441-79-4	42.0	90.5	118.2	163.7	94–6	55
g	65441-80-7	42.2	90.4	117.9	163.4	70–4	50
h	65441-81-8	41.8	90.5	118.2	163.3	64–7	46
i	65441-82-9	42.1	91.4	119.7	163.4	113–5	42
j	34277-62-8	41.9	91.1	119.4	160.5	159–61	35

[a] Satisfactory analytical data (±0.4 for C, H, and N) were reported for all compounds.

Table II. Physical Data and Yields of 1-Pyrazoline 1-Oxides (3)[a]

3	Registry no.	^{13}C chemical shifts, ppm C_4	C_5	C_3	>C=O	Mp, °C	Yield, %
b	65441-83-0	45.5	84.6	100.3	164.9		*b*
c	65441-84-1	45.1	84.6	100.9	163.7	Oil	27
d	65441-85-2	45.4	84.6	100.6	163.6	52–64	28
e	65441-86-3	45.5	84.8	100.6	164.1	117–19	26
f	65441-87-4	45.6	84.6	100.5	164.1	110–12	37
g	65441-88-5	45.4	84.5	99.9	163.9	110–14	32
h	75441-89-6	45.3	84.7	100.4	163.8	112–14	28
i	65441-90-9	45.5	85.6	101.9	163.8	123	18

[a] Satisfactory analytical data (±0.4 for C, H, and N) were reported for all compounds. [b] Prepared by the method reported in ref 10.

Table III. Physical Data and Yields of 1-Pyrazoline 2-Oxides (4)[a]

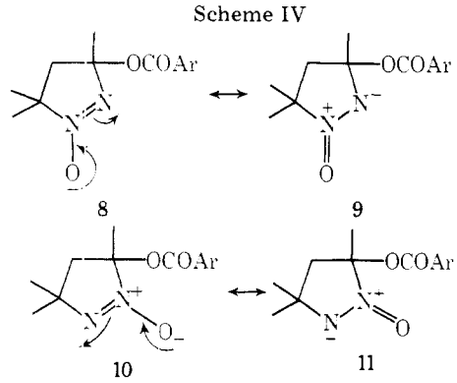
4	Registry no.	^{13}C chemical shifts, ppm C_4	C_5	C_3	>C=O	Mp, °C	Yield, %
b	65441-91-0	43.8	66.1	109.2	163.7		*b*
c	65441-92-1	44.1	66.3	109.6	162.6	92–5	23
d	65441-93-2	43.8	66.2	109.4	162.5	125–7	29
e	65441-94-3	44.1	66.4	109.6	163.1	136–7	21
f	65441-95-4	44.0	66.2	109.4	163.0	137–40	14
g	65441-96-5	44.2	66.1	109.2	163.5	138–40	16
h	65441-97-6	44.1	66.2	109.4	162.8	120–4	18
i	65441-98-7	43.7	66.7	110.7	163.1	187–8	23
j	65441-99-8	43.8	66.5	110.1	160.0	183–5	21

[a] Satisfactory analytical data (± 0.4 for C, H, and N) were reported for all new compounds. [b] Prepared by the method reported in ref 10.

the ^{1}H-NMR data of pyridine and the pyridinium ion.[23] In pyridine, H-2 experiences most the anisotropic effect of the lone electron pair of nitrogen and thus is most deshielded. However, upon protonation, H-3 and H-4 experience a deshielding effect with little change in the chemical shift of H-2. The deshielding effect of the positive charge on nitrogen is largely canceled by the reduction in the anisotropy of the nitrogen atom. Using this argument one can explain the observed shielding of the carbons adjacent to the positive nitrogen in **9** and **11** as a result of incomplete cancellation of two opposite effects. ^{1}H-NMR studies on cis azoxyalkanes have been reported to cause shielding of α protons;[7] however, the authors indicated that similar effects on α carbons were not observed.

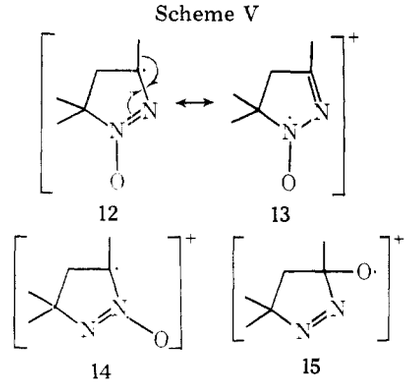
Mass spectral data of compounds **2, 3,** and **4** provided an additional method for the location of the N-oxide function. A mass unit *m/e* 127 appeared in the fragmentation pattern of only the 1-oxides, Scheme V. This fragment corresponds to the relatively stable radical cation **12** which can be resonance stabilized by the *N*-oxide function as shown in **13.** This explains the absence of the corresponding species **14** of the 2-oxide which lacks similar resonance stabilization. That the *m/e* 127 peak is not due to species **15** is provided by the absence of this unit in the spectra of the parent pyrazolines (**2**).

Scheme IV



8 9 10 11

Scheme V



12 13 14 15

Experimental Section

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{13}C-NMR spectra were recorded on Varian CFT-20 and ^{1}H-NMR data on Varian A-60 or Jeolco C-60HL NMR spectrometers. All NMR spectra were determined in $CDCl_3$, except for the 4-nitro and 3,5-dinitrophenyl derivatives (**i** and **j**) which were obtained in deuterioacetone and are expressed as δ in ppm units downfield from Me_4Si. Mass spectra were obtained on a DuPont 490 mass spectrometer. Elemental analyses were performed by Microanalysis, Inc., Wilmington, Del. Melting points and yields, which were not optimized, for the 1-pyrazolines (**2**) and their 1- and 2-oxides (**3** and **4**) are listed in Tables I, II, and III, respectively.

3-(4-Chlorobenzoyloxy)-3,5,5-trimetyl-1-pyrazoline (2e). The following procedure is representative for all other substituted 3-benzoyloxy-3,5,5-trimethyl-1-pyrazolines.

A mixture of 14.5 g (0.14 mol) of **1,** 46.7 g (0.15 mol) of 4-chlorobenzoyl peroxide, and 550 mL of benzene or chloroform was stirred at room temperature, under nitrogen and illumination by incandescent light, for 12 h. The mixture was filtered and then washed with saturated aqueous sodium bicarbonate solution. The benzene or chloroform layer was dried and filtered through a short column of silica gel. Evaporation of the filtrate and recrystallization of the residue twice from aqueous ethanol or ether–hexane gave **2e.** When crystallization was not possible, column chromatography on silica gel eluting with an ether–hexane mixture was used to purify the products.

3-(4-Chlorobenzoyloxy)-3,5,5-trimethyl-1-pyrazoline 1- and 2-Oxides (3e and 4e). The following procedure is also representative for all other substituted 3-benzoyloxy-3,5,5-trimethyl-1-pyrazoline 1- and 2-oxides.

To a solution of the pyrazoline (**2e,** 3.9 g, 0.015 mol) in 10 mL of chloroform was added a solution of 3-chloroperbenzoic acid (6.1 g, 0.03 mol calcd at 85% purity) in 180 mL of chloroform, and the reaction mixture was stirred at room temperature for 18 h, washed with three 50-mL portions of saturated aqueous sodium bicarbonate solution, dried, and evaporated to give 4.5 g of the crude product which showed two spots on thin layer chromatography (TLC). Column chromatography of the mixture over 120 g of silica gel after elution with benzene–acetone (99:1) gave first 1.45 g of the 1-oxide (**3e**) then 0.7 g of the 2-oxide (**4e**) for a total yield of 51%. After recrystallization from chloroform–hexane, the analytical samples were obtained.

3-(3-Chlorobenzoylperoxy)-3,5,5-trimethyl-1-pyrazoline 1-Oxide (5). To a solution of the pyrazoline (**2i,** 7.5 g, 0.027 mol) in 40 mL of chloroform was added a solution of 3-chloroperbenzoic acid (7.5 g, 0.037 mol calcd at 85% purity) in 220 mL of chloroform and the reaction mixture was stirred at room temperature for 20 h and then another portion of 3-chloroperbenzoic acid (5g, 0.025 mol) in 100 mL of chloroform was added. The reaction mixture was stirred at room temperature for another 20 h, washed with three 100-mL portions of saturated aqueous sodium bicarbonate solution, dried, and evaporated to give 7.9 g of the crude product which showed two spots upon TLC, with the same R_f value as **3i** and **4i.** A first attempt to separate the mixture resulted in the loss of half the amount due to decomposition. The recovered mixture (3.5 g) was washed with aqueous sodium bicarbonate and was rechromatographed on silica gel (100 g), eluting with benzene–acetone (99:1), giving first 0.60 g of a mixture of **3i** and **5,** with **5** as a major component. Further elution yielded the 2-oxide

(4i) for a total yield of 23%. After recrystallization twice from chloroform–hexane, there was obtained pure **5**: mp 91–2 °C; ^{1}H NMR δ 1.58 (s, 3 H), 1.67 (s, 3 H), 1.85 (s, 3 H), 2.39 and 2.61 (AB q, 2 H, J = 14 Hz), 7.23–7.92 (m, 4 H); ^{13}C NMR δ 23.07, 26.52, 27.06 (3 CH_3), 43.70 (C-4), 83.92 (C-5), 103.66 (C-3), 134.41, 133.33, 130.30, 129.55, 128.84, 126.92 (aromatic carbons), 162.11 (C=O); mass spectrum (70 eV) m/e (relative intensity) 300 (M^+), 158 (3-chlorobenzoic acid) (14), 156 (42), 141 (11), 139 (33), 128 (24), 127 (100), 126 (8), 56 (11), 55 (7), 43 (40), 42 (5), 41 (10).

Anal. Calcd for $C_{13}H_{15}N_2O_4Cl$: C, 52.27; H, 5.06; N, 9.38; Cl, 11.87. Found: C, 52.54; H, 4.95; N, 9.48; Cl, 11.85

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Registry No.—**1**, 3975-85-7; **5**, 65442-00-4; 4-chlorobenzoyl peroxide, 94-17-7; benzoyl peroxide, 94-36-0; 2-chlorobenzoyl peroxide, 3033-73-6; 3-chlorobenzoyl peroxide, 845-30-7; 4-bromobenzoyl peroxide, 1712-82-9; 4-fluorobenzoyl peroxide, 582-92-3; 4-methoxybenzoyl peroxide, 849-83-2; 4-nitrobenzoyl peroxide, 1712-84-1; 3,5-dinitrobenzoyl peroxide, 15866-24-7.

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Synthesis of 3-Substituted 2-Isoxazolines and 5,6-Dihydro-1,2,4*H*-oxazines

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3-Nitro-2-isoxazoline (**1a**) can be prepared by nitrosation of 1-chloro-3-nitropropane followed by in situ tautomerization and cyclization. Similarly, 3-nitro-5,6-dihydro-1,2,4*H*-oxazine (**1b**) can be prepared from 1-chloro-4-nitrobutane. The nitro group of compounds **1a** and **1b** is readily substituted by a wide variety of nucleophiles. The resulting 3-substituted 2-isoxazolines and 5,6-dihydro-1,2,4*H*-oxazines are normally obtained in fair to excellent yield.

Studies directed at the application of 2-oxazolines[1] and 5,6-dihydro-1,3,4*H*-oxazines[2] to organic synthesis have been extensive and have certainly reaped substantial reward. On the other hand, 2-isoxazolines have received relatively little attention toward their utilization in synthetic problems.[3] In furthering the study of 2-isoxazolines, we wish to report a convenient synthetic approach which allows for their preparation with a hefty array of 3 substituents.[4] This approach also provides easy access to the corresponding six-membered heterocycles (5,6-dihydro-1,2,4*H*-oxazines) which have hitherto received scant attention.[5]

Key intermediates in our approach are 3-nitro-2-isoxazoline (**1a**) and the corresponding six-membered heterocycle **1b**. These can be prepared in yields of 79 and 48%, respectively, by treating 1-chloro-3-nitropropane and 1-chloro-4-nitrobutane with a combination of *n*-propyl nitrite and sodium nitrite in Me_2SO. A convenient alternative preparation[6,7] of **1a** involves treatment of 1-bromo-3-chloropropane with sodium nitrite in DMF; however, the yield of this reaction is only about 50%.[6]

It is proposed that compounds **1a** and **1b** are formed from the nitro compounds[8] by the mechanism of Scheme I. Support for this mechanism rests in the previously reported ability of the combination of *n*-propyl nitrite and sodium nitrite to nitrosate a primary or secondary nitro compound at the α position.[9] For a primary nitro compound, this nitroso derivative would be expected to tautomerize to a nitrolic acid (α-nitrooxime). Normally the nitrolic acid would then be converted to a carboxylic acid.[9b] Here, however, the nitrolic acid preferentially cyclizes via intramolecular substitution (Scheme I). In the preparation of **1b**, a 15% yield of γ-butyrolactone (**2**) is also obtained. This is consistent with the formation and lactonization of 4-chlorobutyric acid as shown in Scheme I. Apparently conversion of the nitrolic acid to carboxylic acid competes with cyclization in this case.

Nucleophilic attack of the carbon–nitrogen double bond of compounds **1a** and **1b** could conceivably occur at either carbon (typical of imines) or at nitrogen (β to the nitro group; compare the reactions of nitroolefins). In fact, we have observed only attack at carbon, the nitro group being expelled in the process. Thus, nitro compounds **1a** and **1b** undergo substitution similar to imidoyl chlorides.[10] Tables I and II

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