The infrared spectrum of the sulfone (0.54% in KBr wafer) showed the following principal frequencies: 3424, 2958, 2932, 2857, 1492, 1464, 1449, 1400, 1314, 1293, 1258, 1204, 1166, 1153, 1117, 1095, 1074, 1031, 1002, 928, 901, 887, 787, 741, 728, and 700 cm.$^{-1}$.

Benzyl 2-methylbutyl sulfone from IX. The hydrogenation procedure was repated using IX, and the product after recrystallization from ethanol melted 82.5–83.0°. A mixed melting point with an authentic sample of benzyl 2-methylbutyl sulfone showed no depression.

Benzyl pentyl sulfone. A Grignard reagent was prepared from 30.2 g. (0.200 mole) of 1-bromopentane and 4.9 g. (0.20 g.-atom) of magnesium in 200 ml. of ether. The solution was maintained at $-15 \pm 5°$ while anhydrous sulfur dioxide was introduced slowly for approximately 1 hr. The resulting slurry was allowed to warm to room temperature and was separated by filtration. The solid material was washed with ether and dried in *vacuo*. There was a quantitative yield of the sulfinic salt which was dissolved in 200 ml. of commercial absolute ethanol. To this solution was added 25.3 g. (0.200 mole) of benzyl chloride and the reaction mixture was heated to reflux for 10 hr. The hot solution was diluted with 500 ml. of water and 31.2 g. (69%) of white solid precipitated. The product was recrystallized twice from methanol and melted 101.0–101.5°.

Benzyl isopentyl sulfone. The procedure for the preparation of benzyl pentyl sulfone was employed using 1-bromo-3-methylbutane. The reflux time was shortened to only 3 hr. Yield of product: 13%, m.p. 103.5–104.0° (lit.,[18] 103–104°).

The infrared spectrum of the sulfone (0.38% in KBr wafer) showed the following principal frequencies: 3496, 3030, 2923, 1503, 1477, 1459, 1414, 1319, 1282, 1265, 1209, 1170, 1160, 1123, 1035, 930, 892, 832, 790, 743, and 701 cm.$^{-1}$.

Benzyl butyl sulfone. The procedure for the preparation of benzyl pentyl sulfone was employed, using 1-bromobutane. The yield of product was 53%, m.p. 96.0–96.5°.

Benzyl 2-methylbutyl sulfone. The procedure for the preparation of benzyl pentyl sulfone was employed using 1-bromo-2-methylbutane. The sulfone was isolated in 66% yield, m.p. 83.5–84.0°.

Anal. Calcd. for $C_{12}H_{18}O_2S$: C, 63.68; H, 8.02; S, 14.17. Found: C, 63.90; H, 8.16; S, 14.32.

The infrared spectrum of the sulfone (0.31% in KBr wafer) showed the following principal frequencies: 3508, 3039, 2985, 2941, 1506, 1464, 1412, 1315, 1267, 1210, 1173, 1160, 1123, 1076, 1038, 931, 894, 788, and 701 cm.$^{-1}$.

BLACKSBURG, VA.

[CONTRIBUTION FROM ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

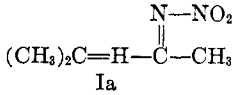
The Structure and Reactions of Pernitrosomesityl Oxide[1]

JEREMIAH P. FREEMAN

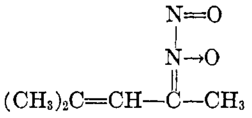
Received September 1, 1961

Evidence is presented to establish that the structure of pernitrosomesityl oxide is that of 3,5,5-trimethylisopyrazole 1,2-dioxide. Its reduction products were also examined and structures assigned, and correlations with acid-catalyzed addition products were made. The first pair of isomeric α,β-unsaturated aliphatic azoxy compounds was synthesized.

When mesityl oxide oxime is treated with a nitrite ester in acetic acid, a white solid, $C_6H_{10}N_2O_2$, called pernitrosomesityl oxide (I) is produced in good yield.[2] The nitrimine structure Ia was suggested[2] for this material based upon the investigations of Scholl[3] on pernitroso compounds of the terpene series. This formulation was rejected by Fusco[4] in favor of structure Ib which contains the unique *N*-nitrosonitrone function. Later investigators could not confirm or deny either structure but believed that pernitrosomesityl oxide had a different structure than did pernitrosocamphor.[5] Since the arguments[4] for structure Ib were based on the unsupported assignment of structures to products obtained by acid treatment of pernitrosomesityl oxide, an investigation of these products as well as of the pernitroso compound was indicated.

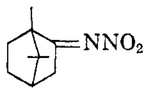

$(CH_3)_2C{=}H{-}\overset{\overset{N-NO_2}{\|}}{C}{-}CH_3$

Ia


$(CH_3)_2C{=}CH{-}\overset{\overset{\overset{N=O}{|}}{\overset{N\rightarrow O}{\|}}}{C}{-}CH_3$

Ib

Since pernitrosocamphor possesses the nitrimine structure II,[6] it was originally supposed that pernitrosomesityl oxide possessed a similar structure. However, comparison of some physical and chemical properties of the two compounds suggested that they contained different arrangements of the pernitroso function. The first striking difference between pernitrosomesityl oxide and other aliphatic pernitroso compounds is its comparatively



II

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[1] This research was carried out under Army Ordnance Contract DA-01-021-ORD-11878.

[2] C. Harries and R. Gley, *Ber.*, **32**, 1330 (1899).

[3] R. Scholl, *Ann.*, **345**, 363 (1906).

[4] R. Fusco and G. Trisoglio, *Atti accad. Italia, Rend. classe sci. fis. mat. nat.*, [7] **2**, 618, 751 (1941).

[5] J. W. Suggitt, G. S. Myers, and G. F. Wright, *J. Org. Chem.*, **12**, 373 (1947).

[6] J. P. Freeman, *Chem. & Ind.* (*London*), 1624 (1960); *J. Org. Chem.*, **26**, 4190 (1961).

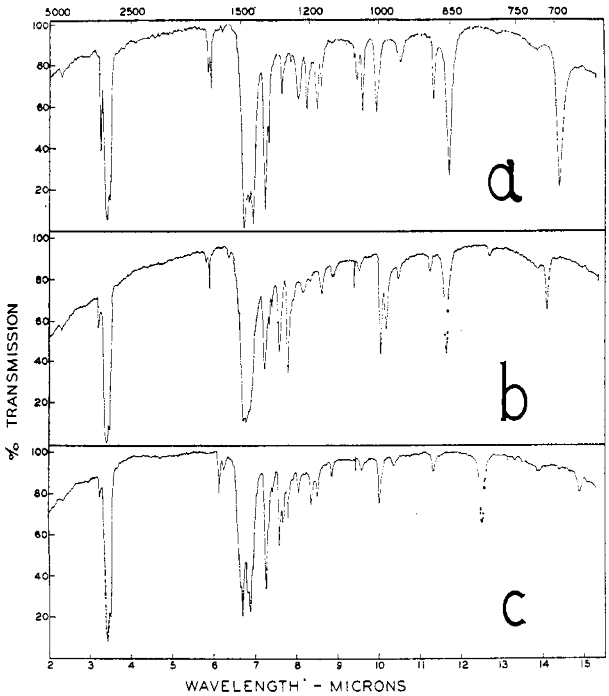


Fig. 1. Infrared spectra (Nujol mulls) of: a. pernitrosomesityl oxide (Ic); b. 3,5,5-trimethylisopyrazole 2-oxide (IV); c. 3,5,5-trimethylisopyrazole 1-oxide (VI)

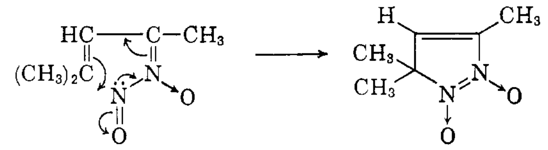
high melting point (138°),[7] and low solubility in organic solvents which indicate a more polar functional group. Secondly, while pernitrosocamphor dissolves in aqueous base to form a stable anion from which the starting material can be regenerated by acidification, pernitrosomesityl oxide dissolves in alkali only when heated and then it is converted to the parent oxime and nitrite ion[9]; it is difficult to rationalize the formation of an oxime from a nitrimine.[10] Finally the spectral properties of I also set it apart from other pernitroso compounds.

Spectral data. The infrared spectrum of I (Fig. Ia) shows no absorption due to an *N*-nitro group[11] in the region of 1500–1600 cm.$^{-1}$ (asymmetric stretching) or 1250–1300 cm.$^{-1}$ (symmetric stretching). The strong band at 1485 cm.$^{-1}$ is, however, most probably associated with a double bonded nitrogen-oxygen function. For instance, aliphatic azoxy compounds[12] absorb in the range of 1485–1540 cm.$^{-1}$, C-nitroso compounds[13] in the range of 1498–1620 cm.$^{-1}$, and *N*-nitroso compounds[11] at 1430–1500 cm.$^{-1}$.

The ultraviolet spectrum of I (λ_{max} 310, ϵ_{max} 4500; λ_{max} 216, ϵ_{max} 9740) also indicates that a nitrimine function[6] is not present and suggests a highly conjugated system.

The proton magnetic resonance spectrum of I (in $DCCl_3$) furnishes critical evidence concerning its structure (Table I). The spectrum was quite different from that of mesityl oxide[14] which has bands at 4.03 τ (broad, HC═C), 7.95 τ (singlet, CH_3CO, CH_3C═C), and 8.14 τ (doublet, CH_3C═C), and which should be an excellent model for structures Ia and Ib. The spectrum of I indicates the presence of a vinyl proton, a methyl group attached to unsaturated carbon, and two methyl groups attached to a saturated carbon atom. The splitting of the band due to the single methyl group is of such an order as to suggest its coupling to the vinylic proton through a double bond.[15]

It is possible to arrive at a structure for I which accommodates these structural features by a redistribution of the electrons in structure Ib:



Ib Ic

Structure Ic, 3,5,5-trimethylisopyrazole 1,2-dioxide, satisfies the infrared and ultraviolet spectral data also; further discussion of these spectra will be taken up in connection with the spectra of some of the reaction products of I.

The mode of formation of Ic is consistent with the highly electrophilic nature of the nitroso group. In the case of aliphatic nitroso compounds this property is reflected in the tendency to dimerize. In nitrosoamines and nitrite esters there is considerable double bond character to the N—N and N—O bonds due to the interaction of the unshared electrons of the nitrogen and oxygen

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[7] The melting point of I was originally reported[2] as 156° but that melting point has not been confirmed. If I is heated in ethanol, the recrystallization solvent, for too long a time, it is partially converted to an isomer, m.p. 156°, whose structure (IX) is discussed below. Recent reports,[5,8] of the synthesis of I list m.p. 140° and 138°.

[8] S. G. Brooks, R. M. Evans, G. F. H. Green, J. S. Hunt, A. G. Long, B. Mooney, and L. J. Wyman, *J. Chem. Soc.*, 4614 (1958). These authors suggested an oxime nitrite structure for I.

[9] (a) C. Harries, *Ann.*, **319**, 230 (1901); (b) However, I forms an organometallic derivative under treatment with Grignard reagents from which it is regenerated upon hydrolysis; R. Fusco and F. D'Alo, *Atti accad. Italia, Rend. classe sci. fis. mat. nat.*, [7] **3**, 113 (1942).

[10] Compounds of the pernitrosocamphor type can be hydrolyzed by hot alkali but the parent ketones or imines are obtained.

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, 1958, p. 302.

[12] B. W. Langley, B. Lythgoe, and L. S. Rayner, *J. Chem. Soc.*, 4191 (1952).

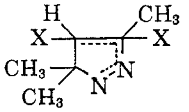
[13] B. G. Gowenlock and W. Lüttke, *Quart. Revs.*, **12**, 321 (1958).

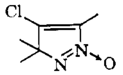
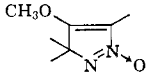
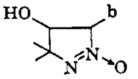
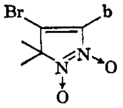
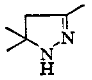
[14] L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London, 1959, p. 83.

[15] Coupling constants through four bonds, one of which is olefinic, vary from 0.4–2 c.p.s.; R. R. Fraser, *Can. J. Chem.*, **38**, 549 (1960); *cf.* L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958); J. H. Richards and W. F. Beach, *J. Org. Chem.*, **26**, 623 (1961); ref. 14, p. 85.

TABLE I

Proton Frequencies[a] of Pyrazoline Derivatives



Compound	$(CH_3)_2C$	CH_3C	HC	Others
Ic[b]	8.38	7.75 (d, J = 2)[c]	3.65	
IV	8.62	7.92 (d, J = 1.5)	2.90	
VI	8.60	7.88 (d, J = 1.5)	4.10	
III	8.55, 8.42	8.00	5.33	
V[b]	8.35, 8.28	7.70	5.55	
	8.59	7.92		
	8.70	7.78		5.88
VIII	8.38, 8.30	7.95	7.60, 7.28 7.00, 6.65	
	8.68, 8.60	8.40 (d, J = 6)		5.63[d]
	8.42	7.78		
	8.82	8.18	7.72	5.02

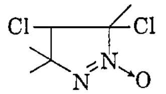
[a] The NMR spectra were measured with a Varian Associates high resolution spectrometer, V-4300-B, using a 40 Mc. probe. The spectra were measured in dilute carbon tetrachloride solution unless otherwise stated with tetramethylsilane as internal reference, and are calculated in terms of τ values. [b] Measured in deuterochloroform. [c] Notation in brackets: d = doublet. Coupling constant is given in cycles per second. [d] Center of complex band.

atoms with the nitroso group.[16] In the case of unsaturated pernitroso compounds,[6] the driving force for the rearrangement of the N-nitroso oxime intermediate to the nitrimine is probably the electron deficiency of the nitroso group, which cannot be satisfied by the adjacent quaternary nitrogen. In the case of pernitrosomesityl oxide, the metastable intermediate Ib can obtain electrons from the double bond; olefins are known to react with C-nitroso compounds.[13] Ring formation would be expected to be more facile than oxygen migration when it is possible.

Since the spectral properties of pernitrosomesityl oxide suggested structure Ic, attention was turned to the reactions of the compound to see if they also were consistent with that structure.

Addition reactions. Treatment of I with concentrated hydrochloric acid[2] produced the white solid, $C_6H_{10}Cl_2N_2O$, which had been assigned the structure of 3,5,5-trimethyl-3,4-dichloropyrazoline 2-oxide (III).[4] Its infrared spectrum confirmed the presence of an azoxy function[12] (strong band at 1515 cm.$^{-1}$), but gave no information about the position of the oxygen atom.[17] The NMR spectrum of II

I + HCl →



III

(Table I) is consistent with this structure. When III was treated with zinc dust in ethanol, a white solid, $C_6H_{10}N_2O$, was obtained, whose infrared spectrum (Fig. Ib), which was very similar to that of I, indicated that it was an α,β-unsaturated azoxy com-

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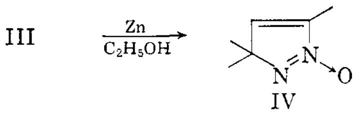
(16) W. D. Phillips, C. E. Looney, and C. P. Spaeth, *J. Molecular Spectroscopy*, 1, 35 (1957); C. E. Looney, W. D. Phillips, and E. L. Reilly, *J. Am. Chem. Soc.*, 79, 6136 (1957).

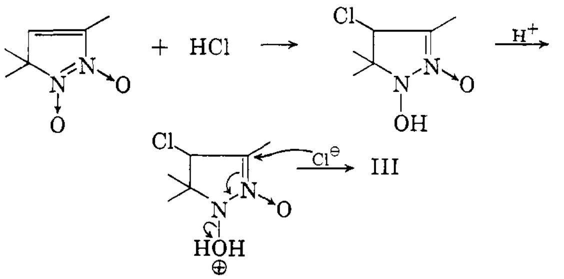
(17) Fusco[4] assigned structure III without any proof and while admitting the possibility of the other isomer.

pound. Its NMR spectrum (Table I) was very similar to that of I, showing the coupling of a vinyl proton and methyl group through a double bond. Its ultraviolet spectrum (λ_{max} 241, ϵ_{max} 6300) strongly suggested structure IV, 3,5,5-trimethylisopyrazole 2-oxide, rather than the 1-oxide. The position of the maximum corresponds well with that suggested by Stevens and his co-workers[18] for unsaturated azoxy

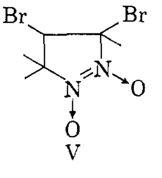


compounds of this configuration.[19] The 4-chloro- and 4-methoxy-3,5,5-trimethylisopyrazole 2-oxideas described previously[4] also show maxima in this region (λ_{max} 248, ϵ_{max} 7920 and λ_{max} 246, ϵ_{max}7730, respectively).

These data support Fusco's structure III for the product of the reaction of I with hydrochloric acid. Its formation from Ic is pictured readily and also explains the preferential removal of oxygen from the nitrogen next to the *gem*-dimethyl group. Routes to III from Ib are torturous and do not readily explain the production of only one of the isomeric azoxy compounds.



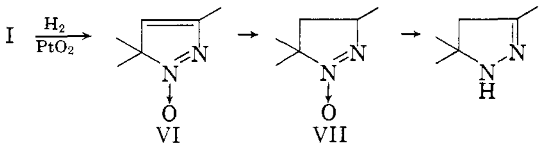
Pernitrosomesityl oxide reacts with bromine to form a dibromide[9b] which may be formulated as 3,4-dibromo-3,5,5-trimethyl-Δ^1-pyrazoline 1,2-dioxide (V). In agreement with this structural assignment,



its NMR spectrum (Table I) is similar to that of III. The ultraviolet spectrum of V shows maxima as might be expected of a *cis*-nitroso dimer.[13]

Upon treatment with base V is transformed to 4-bromo-3,5,5-trimethylisopyrazole 1,2-dioxide whose ultraviolet spectrum is similar to that of Ic (see Experimental).

Reduction. Further support for structure Ic was derived from a study of the reduction of pernitrosomesityl oxide. The only reported reduction product of I is 3,5,5-trimethylpyrazoline.[9] Catalytic reduction proceeded stepwise and could be controlled. The first reduction product was a white solid, $C_6H_{10}N_2O$, isomeric with compound IV and also an α,β-unsaturated azoxy compound. Its infrared spectrum (Fig. Ic) showed vinyl hydrogen (3080 cm.$^{-1}$), olefinic (1632 cm.$^{-1}$), and azoxy group absorption (1495 cm.$^{-1}$). This reduction product is assigned the structure of 3,5,5-trimethylisopyrazole 1-oxide (VI). This structure is supported by its ultraviolet spectrum which has two maxima: λ_{max} 305, ϵ_{max} 3800, λ_{max} 226, ϵ_{max} 2100. The higher maximum is considerably higher than that predicted,[13] but, by comparison with that of compound IV, it is apparent that VI is the more conjugated isomer.



The infrared spectra of VI and I are strikingly similar suggesting that the band at 1485 cm.$^{-1}$ in the latter is due to the grouping $C{=}C{-}N{=}N^{\oplus}{-}O^{\ominus}$; the strain of the five-membered ring accounts for the relatively high olefinic band frequencies. The ultraviolet spectrum of I and VI are also so similar as to suggest that the same chromophoric system is present in both. Finally, the NMR spectrum[20] of VI (Table I) is very similar to that of I. These data support structure Ic for pernitrosomesityl oxide. Compound VI may arise easily from Ic by a thermodynamically controlled removal of an oxygen atom.

If the catalytic reduction was interrupted after approximately two-thirds of the hydrogen uptake had occurred, it was occasionally possible to isolate a white solid, $C_6H_{12}N_2O$, believed to be 3,5,5-trimethyl-Δ^1-pyrazoline 1-oxide (VII). Apparently the production of this compound is dependent upon the activity of the catalyst but no detailed study was made. The structure of VII was based on the structure of VI, its elementary analysis, and its infrared spectrum ($\gamma_{N=N\rightarrow O}$ 1510 cm.$^{-1}$, no vinyl

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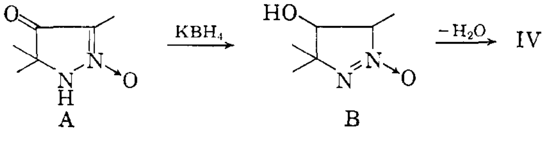
[18] C. L. Stevens, B. T. Gillis, J. C. French, and T. H. Haskell, *J. Am. Chem. Soc.*, **80**, 6088 (1958).

[19] Compound IV was also obtained by reduction of ketone A with potassium borohydride; J. P. Freeman, to be published.

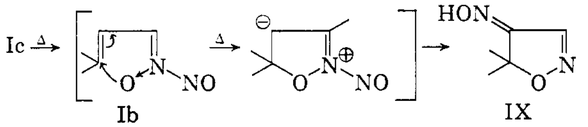


[20] It is interesting that in the spectra of Ic and VI the vinyl proton resonance occurs at higher field than in that of compound IV. This indicates that it is more shielded in these compounds whereas it might have been expected that the more extended conjugation in Ic and VI would have made the β-carbon less electron rich and the proton less shielded in these compounds. For instance, in α,β-unsaturated ketones the β-proton appears at considerably lower field than does the α-proton.

H).[21] Complete reduction of I yielded 3,5,5-trimethylpyrazoline.[9a]

It was possible to reduce I to VI by using potassium borohydride in boiling ethanol, but the procedure was complicated by side reactions. Lithium aluminum hydride caused complete reduction to the trimethylpyrazoline. Since both these reagents reduce pernitrosocamphor to the corresponding nitramine,[6] it is apparent that both the site and mode of reduction are different for pernitrosomesityl oxide. This in turn argues for a different mode of arrangement of the pernitroso function in the two compounds.

Hydrolysis and thermal rearrangement. It remains to explain two reactions of I: its thermal conversion to 3,5,5-trimethyl-4-isoxazolone oxime (IX),[9a] and its hydrolysis to mesityl oxide oxime and nitrite ion.[9a] Since both reactions are readily explained on the basis of structure Ib, the first step of both is probably the thermal conversion of Ic to Ib. That the cleavage occurs at a carbon-nitrogen bond rather than at the nitrogen-nitrogen bond as in nitroso dimers may be explained by the highly conjugated system that is generated (Ib). Fusco's suggestions[4] concerning the mode of rearrangement of Ib to IX seem reasonable and represent an early recognition that nitrones can add to olefins, a reaction which is only now finding general applicability.[23] This rearrangement proceeds readily in boiling acetonitrile. The hydrolysis is simply explained by attack of the base on the electron-deficient nitroso group of intermediate Ib with expulsion of the oxime anion.



Ib

IX

Summary. The physical and spectral properties of pernitrosomesityl oxide combined with a knowledge of the structures of its addition, reduction, and degradation products show that its structure is that of 3,5,5-trimethylisopyrazole 1,2-dioxide (Ic).

EXPERIMENTAL[24]

Catalytic reduction of pernitrosomesityl oxide. A solution of 14 g. (0.1 mole) of pernitrosomesityl oxide[2] in 150 ml. of absolute ethanol was shaken in a Parr hydrogenator under 40 lb. of hydrogen in the presence of 0.5 g. of platinum oxide until 20 lb. of hydrogen was absorbed. During the hydrogenation a solid, which proved to be starting material, separated. This solid and the catalyst were removed by filtration and the filtrate concentrated. The resulting solid was triturated with boiling hexane; the insoluble material proved to be starting material. Upon cooling the hexane solution precipitated white crystals, m.p. 75–77°; yield 2.6 g. (20%). Recrystallization from hexane yielded a pure sample of *3,5,5-trimethylisopyrazole 1-oxide* (VI), m.p. 77–78°.

Anal. Calcd. for $C_6H_{10}N_2O$: C, 57.12; H, 8.00; N, 22.21. Found: C, 57.40; H, 8.34; N, 22.30.

If the reduction was allowed to proceed until no more hydrogen uptake occurred, *3,5,5-trimethylpyrazoline,* b.p. 60° (22 mm.), was obtained; yield 5.7 g. (50%). Its infrared spectrum was identical to that of an authentic sample[25] and it formed a *phenylthiourea,* m.p. 100–101°.

Anal. Calcd. for $C_{13}H_{17}N_3S$: C, 63.12; H, 6.93; N, 16.99. Found: C, 63.37; H, 7.25; N, 16.69.

When the reduction was interrupted after 30 lb. of hydrogen had been absorbed, trimethylpyrazoline was the main product but occasionally small amounts of *3,5,5-trimethyl-Δ^1-pyrazoline 1-oxide,* m.p. 53–54° (from hexane), were obtained.

Anal. Calcd. for $C_6H_{12}N_2O$: C, 56.21; H, 9.44; N, 21.86. Found: C, 56.46; H, 9.62; N, 21.75.

Reduction of pernitrosomesityl oxide with potassium borohydride. To a solution of 7.1 g. (0.13 mole) of potassium borohydride in 50 ml. of ethanol was added a solution of 7.1 g. (0.05 mole) of pernitrosomesityl oxide in 50 ml. of ethanol. The mixture was heated under reflux for 2 hr. It was then poured into water and the organic products were extracted with methylene chloride. Upon concentration of these extracts a semisolid residue was obtained. Trituration with pentane removed an oil and left a solid residue which, upon crystallization from pentane–chloroform, had m.p. 156–158°. This material proved to be *3,5,5-trimethyl-4-isoxazolone oxime* (IX) by comparison with an authentic sample.[2,4]

The pentane-soluble oil was distilled to give a small amount of mesityl oxide oxime and 2.4 g. (38%) of *3,5,5-trimethylisopyrazole 1-oxide,* m.p. 77–78°.

Preparation of 3,5,5-trimethylisopyrazole 2-oxide. A mixture of 8.0 g. (0.4 mole) of 3,4-dichloro-3,5,5-trimethylpyrazoline 2-oxide,[2,4] 10 g. of zinc dust, and 75 ml. of ethanol was heated under reflux for 3 hr. It was then cooled, filtered, and concentrated to yield a solid residue which was recrystallized from hexane, m.p. 79–80°; yield 1.8 g. (35%).

Anal. Calcd. for $C_6H_{10}N_2O$: C, 57.12; H, 8.00; N, 22.21. Found: C, 57.11; H, 8.13; N, 22.02.

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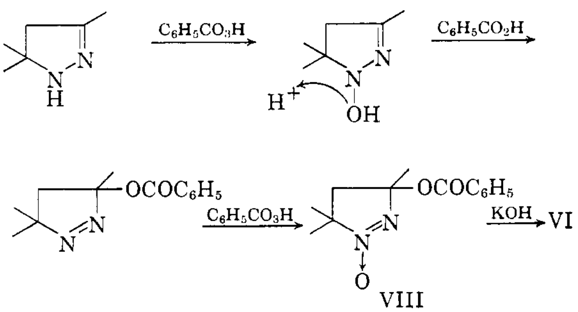
(21) In an attempt to prepare an authentic sample of VII, 3,5,5-trimethylpyrazoline was oxidized with perbenzoic acid by the method described for the conversion of a phenylhydrazone to an azoxybenzene derivative.[22] The desired compound was not obtained, but instead, 3-benzoyloxy-3,5,5-trimethyl-Δ^1-pyrazoline 1-oxide (VIII) was obtained. Details of the structure proof may be found in the Experimental section. Further work on this system is in progress. A possible scheme for its formation is:



VIII

(22) J. N. Brough, B. Lythgoe, and P. Waterhouse, *J. Chem. Soc.,* 4069 (1954).

(23) N. A. LeBel and J. J. Whang, *J. Am. Chem. Soc.,* **81,** 6334 (1959); C. W. Brown, K. Marsden, M. A. T. Rogers, G. M. B. Tylor, and R. Wright, *Proc. Chem. Soc.,* 254 (1960); G. R. Delpiene and M. Lamchen, *Proc. Chem. Soc.,* 386 (1960); R. Grashey, R. Huisgen, and H. Leitermann, *Tetrahedron Letters,* **12,** 9 (1960).

(24) We are indebted to Mrs. Carolyn Haney for the NMR data.

(25) J. Curtius and B. Wissing, *J. prakt. Chem.,* [2] **50,** 548 (1894).

Reaction of 3,5,5-trimethylpyrazoline with perbenzoic acid. To a solution of 75 ml. of 1.05*M* perbenzoic acid[26] in methylene chloride was added 5.6 g. (0.05 mole) of 3,5,5-trimethylpyrazoline[25] in 50 ml. of methylene chloride at −5–0° during a 45-min. period. The mixture was stirred at 5–15° overnight, made basic by the addition of solid sodium carbonate, and diluted with water. The organic layer was separated, combined with methylene chloride extracts of the aqueous layer, dried, and concentrated. A yellow oil that crystallized upon standing was obtained; yield 1.8 g. (14%). Recrystallization from hexane yielded white platelets, m.p. 88–89°.

Anal. Calcd. for $C_{13}H_{16}N_2O_3$: C, 62.88; H, 6.50; N, 11.28. Found: C, 63.05; H, 6.70; N, 10.88.

Its infrared spectrum showed bands attributable to an aromatic ester (1725 cm.$^{-1}$) and an azoxy group (1520 cm.$^{-1}$). Its NMR spectrum (Table I) indicated the presence of three methyl groups; quartet at 7.60, 7.28, 7.00, and 6.65 τ is due to two slightly nonequivalent protons.[27] Treatment of this material with potassium hydroxide in ethanol at 20° for 15 min. converted it to 3,5,5-trimethylisopyrazole 1-oxide. All these features are nicely accommodated by structure VIII.

Dibromopernitrosomesityl oxide (V). This material was prepared by the published method.[9b] Its ultraviolet spectrum in ethanol showed a maximum at 290 mμ, ϵ_{max} 7000 and a broader band centering at λ_{max} 233, ϵ_{max} 2500. The longer wave length band is consistent with the structure V as nitroso dimers absorb in this region.[13]

4-Bromo-3,5,5-trimethylisopyrazole 1,2-dioxide.[9b] The ultraviolet spectrum of this material showed maxima at λ_{max} 327, ϵ_{max} 3700, λ_{max} 220, ϵ_{max} 8300. Its infrared spectrum was also similar in the 6–7 μ region to that of Ic.

Preparation of 3,5,5-trimethyl-4-isoxazolone oxime. A solution of 7.1 g. (0.05 mole) of pernitrosomesityl oxide in 25 ml. of acetonitrile was heated under reflux for 5 hr. Nitrogen oxides were evolved. Upon removal of the solvent a solid residue was obtained which was recrystallized from hexane–chloroform, m.p. 156–157° (lit.[2,4] m.p. 156°). Its infrared spectrum showed hydroxyl absorption at 3 μ and $C{=}N$ absorption at 1655 cm.$^{-1}$. Its NMR spectrum (measured in CH_2Cl_2) showed singlets at 8.05 τ [$(CH_3)_2C$], 7.65 τ ($CH_3C{=}N$), and 0.88 τ ($=N{-}OH$).

HUNTSVILLE, ALA.

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[26] L. S. Silbert, E. Siegel, and D. Swern, Abstracts, 139th Meeting of the American Chemical Society, St. Louis, Mo., April 1961, p. 15–O.

[27] Ref. 14, p. 85.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Heterocyclic Compounds. X. Hydrogenated Derivatives of Isoindole and 2-Azaazulene from Reductive Cyclization of γ-Nitro Ketones[1]

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Nitromethane, nitroethane, and 2-nitropropane condensed with α,β-unsaturated cycloalkenyl ketones to yield a series of γ-nitro ketones (see Table I).

Hydrogenation of representative nitro ketones over Raney nickel yielded Δ^1-pyrrolines (XIII and XIX). Hydrogenation of the nitro ketones over platinum yielded mixtures of the corresponding pyrrolidines (XVa and XVIIa) and cyclic hydroxylamines (XVI and XVIII).

When pyrrolines XIII and XIX were hydrogenated over platinum, pyrrolidines XVb and XVIIb, isomeric with XVa and XVIIa, were obtained. Evidently pyrrolines are not the precursors of pyrrolidines in reductive cyclization of these γ-nitro ketones. Hydroxylamine XVI is not the intermediate in reductive cyclization of nitro ketone VII to pyrrolidine XVa over platinum, nor does this reaction proceed by initial reduction of the keto group.

Earlier papers in this series, and others cited therein, suggest that reductive cyclization of γ-nitro ketones is a potentially versatile method for synthesis of hydrogenated and partially hydrogenated nitrogen heterocycles. Our investigations now have been extended to a series of γ-nitro ketones containing a five-, six-, or seven-membered ring, reduction of which might be expected to yield fused ring systems.

Representative γ-nitro ketones were prepared by Michael type condensations of nitro alkanes with α,β-unsaturated cycloalkenyl ketones (see Table I). Nitromethane, nitroethane, and 2-nitropropane reacted with 1-acetylcyclopentene to give comparable yields of the respective γ-nitro ketones. With 1-acetylcyclohexene and 1-acetylcycloheptene, yields of nitro ketones varied considerably, evidently because of steric factors dependent upon size of ring and complexity of nitro alkane. In the presence of sodium ethoxide, 2-nitropropane gave no adduct with 1-acetylcyclohexene, even after two days in boiling ethanol.

Low pressure hydrogenation of 1-acetyl-2-nitromethylcyclohexane (VII) and 1-acetyl-2-nitromethylcycloheptane (X) over Raney nickel yielded pyrroline derivatives XIII and XIX, respectively. These pyrrolines exhibit the spectral and chemical properties characteristic of other Δ^1-pyrrolines.[2-5] They show strong imine absorption in the 6.1-μ

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[1] Abstracted from a portion of the Ph.D. dissertation of Satinder Kessar.

[2] M. C. Kloetzel, J. L. Pinkus, and R. M. Washburn, *J. Am. Chem. Soc.*, **79**, 4222 (1957).

[3] M. C. Kloetzel and J. L. Pinkus, *J. Am. Chem. Soc.*, **80**, 2332 (1958).

[4] M. C. Kloetzel, F. L. Chubb, and J. L. Pinkus, *J. Am. Chem. Soc.*, **80**, 5773 (1958).

[5] M. C. Kloetzel, F. L. Chubb, R. Gobran, and J. L. Pinkus, *J. Am. Chem. Soc.*, **83**, 1128 (1961).