Increasing the Index of Covalent Oxygen Bonding at Nitrogen Attached to Carbon

JOSEPH H. BOYER

Chemistry Department, University of Illinois, Chicago Circle Campus, Chicago, Illinois 60680, and Lawrence Livermore Laboratory, Livermore, California 94550

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Joseph Boyer completed formal education after an interruption for military duty during WWII. Research (organic chemistry of nitrogen), teaching, and consulting activities have developed continuously since 1950 except for 5 years (1961–1966) of administrative work. He has been at the Chicago address since 1966.

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I. Introduction

This review has covered chemistry associated with increases (0 to 3) for each of the parameters x and y in $CN(-)_xO_y$ systems. It is the first comprehensive treatment of the subject. Both x and y can be increased by transient and permanent covalent bonding situations from interactions between organic nitrogen and oxygen which is in the same or different organic molecule or an in inorganic compound.

Derivatives of nitrogen–oxygen bonds are characteristically unstable; nevertheless certain examples with an ordinarily slow release of energy have long been utilized in combustion explosives and fuels.[1a] A current need for molecular systems to provide continuous storage and release of energy on demand can be served by further investigations in the chemistry of nitrogen–oxygen bond derivatives.

In the absence of adequate information on the formation and function of nitrogen–oxygen bonds in naturally occurring molecules, each newly discovered example has been added to the small list with an appropriately renewed curiosity. The list now includes compounds with the following functional groups or structural units: nitro,[2a] nitroso,[3a,b] azoxy,[4a–c] nitrato,[5a,b] *N*-oxide,[2b,6a–c] hydroxamic acid,[7a–c] isoxazolidine,[8] *N*-hydroxy peptide,[9a] and hydroxyl amino acid.[9b] A NIOSH hazard review document listed 14 carcinogenic compounds, of which 11 are nitrogen derivatives: 2-(acetylamino)fluorene, 4-aminodiphenyl, benzidine, 3,3′-dichlorobenzidine, 4-(dimethylamino)azobenzene, α- and β-naphthylamines, 4-nitrobiphenyl, *N*-nitrosodimethylamine, 4,4′-methylenebis(2-chloroaniline), and ethylenimine.[10] A carcinogenicity dependent on metabolic biochemical *N*-hydroxylation has been reviewed.[6b]

Organic esters are unknown for two oxy acids of nitrogen: $HON{=}N^+(O^-)OH$ and $(HO)_2N\cdot$. The trioxodinitrate(II) ion, $N_2O_3^{2-}$, of Angeli's salt was obtained from ethyl nitrate, hydroxylamine, and sodium ethoxide (eq 1).[11a]

$$C_2H_5ONO_2 + H_2NOH \xrightarrow[C_2H_5OH]{C_2H_5O^-} {}^-ON{=}\overset{+}{N}(O^-)OH \qquad (1)$$

Sodium hydronitrite precipitated as a highly explosive yellow solid when sodium nitrite was added to a solution of sodium in ammonia (eq 2).[11a] Its weak paramagnetism suggested that

$$NaNO_2 \xrightarrow[NH_3]{Na} Na_2O_2N\cdot \rightarrow Na_4(NO_2)_2 \qquad (2)$$

it was present as a dimer. In principle, the monomer acid is tautomeric with the inorganic "parent" (eq 3) of the recently

$$(HO)_2N\cdot \rightleftharpoons H{-}N(\cdot){-}O,\ OH \qquad (3)$$

discovered alkoxy nitroxides, (R–N–(OR)O·) (section X.C.).

Stable neutral and anionic peroxyisomers, NOO, of nitrogen dioxide were suggested by ab initio SCF calculations.[11b] At about the same time nitroso oxides, $RN{=}O^+{-}O^-$, were discovered (section II.A.).

The literature was covered through the middle of 1979. A complete catalog of references is not offered, but it is hoped that the selection of citations has covered the relevant principles and has supplied a generous number of illustrations. Information was primarily retrieved from original reports for the past decade, but reliance on secondary literature sources increased with the age of the information needed.

II. Azides and Diazoalkanes

Oxygen adducts from imidogen, HN, and its sodium salt (eq 4, 5) have been known for half a century,[12,13] but adducts from

$$HN_3 \xrightarrow[-N_2]{h\nu,\ 20\ K} HN \xrightarrow{O_2} HNO_2 \qquad (4)$$

$$NaN_3 \xrightarrow[-N_2]{NaOH} NaN \xrightarrow{O_2} NaNO_2 \qquad (5)$$

nitrenes, RN, remained unknown until 1965 when a "transient which absorbs in the visible . . ." produced by a photolysis of an aryl azide in a solid matrix[14] became a likely candidate for an oxygenated derivative of an arylnitrene.

Hydroxylamine from imidogen and sulfuric acid (eq 6) was

$$HN_3 \xrightarrow[-N_2]{H_2SO_4} HN \xrightarrow{H_2O} H_2NOH \qquad (6)$$

reported in 1924.[15a] A comparable insertion of a nitrene into an OH bond, long suspected, was recently established (eq 7).[15b–d]

$$N_3CO_2C_2H_5 \xrightarrow[\substack{C_2H_5OH\\-N_2}]{heat} CH_3CH_2ONHCO_2C_2H_5 \qquad (7)$$

A new challenge to nitrene versatility appeared when a 1:1 adduct between imidogen and carbon dioxide was announced.[16]

Both the structure determination for CO_2·NH and the discovery of CO_2·NY where Y is a suitable organic group await further investigation.

Although singlet oxygen was quenched by the azide ion, the interaction did not bring about a chemical reaction.[17,18]

A. Oxygen

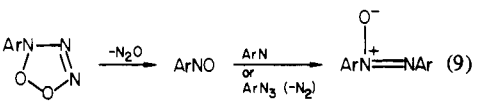
Nitrous oxide, nitrogen, an azoxyarene, an azoarene, a nitroarene, and an arylamine were produced when an azidoarene in an inert solvent fed with a stream of oxygen was irradiated by a medium-pressure mercury lamp (eq 8).[19] A

$$ArN_3 \xrightarrow[30\ °C,\ 12\ h,\ -N_2]{h\nu,\ O_2} ArN(O){=}NAr + ArNO_2 + ArN{=}NAr + ArNH_2 + N_2O \quad (8)$$

reaction assigned to triplet oxygen and a triplet organic substrate (azide or nitrene) was in agreement with sensitization and quenching results and with the formation of small amounts of an azoarene and an arylamine (typical triplet nitrene products) from phenyl azide or its *o*- or *p*-methoxy, *p*-cyano, *m*- or *p*-nitro derivatives.

Nitrous oxide, a nitrosoarene, nitrogen, and a nitroso oxide (**2**) were attributed to dissociation of a dioxatriazoline (**1**) (eq 9, 10), an oxygen–azide adduct,[19] but an alternative fate of this

$$ArN_3 \xrightarrow[30\ °C,\ 12\ h]{h\nu} ArN_3(s) \xrightarrow{ISC} ArN{-}N{=}N \longrightarrow$$



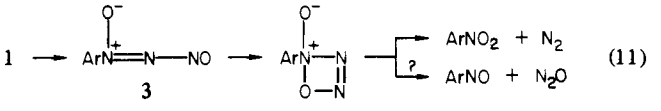
$$\xrightarrow{-N_2O} ArNO \xrightarrow[ArN_3\ (-N_2)]{ArN\ or} ArN{=}NAr \quad (9)$$

1

$$\mathbf{1} \rightarrow ArN(\cdot){-}O{-}O(\cdot) + N_2 \quad (10)$$

2

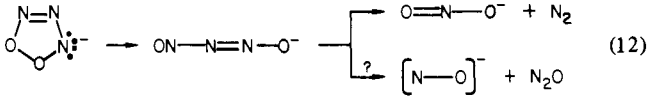
proposed adduct—ring opening into an azide *N*,*N*′-dioxide (**3**) and fragmentation—would also account for the formation of a nitroarene and nitrogen (eq 11). Sodium nitrite and nitrous acid



(11)

3

may have been generated from oxygen and an azide anion or hydrogen azide (eq 5, 12) in this manner. Azoxyarenes were



(12)

presented as nitrosonitrene adducts (eq 9),[19] but each could also have arisen from a reaction between a nitrosoarene and an azide (section II.G.3.).

A rearrangement of nitroso oxide **2** into a nitroarene (eq 13)

$$ArN_3 \rightarrow Ar\ddot{N}: \xrightarrow{ISC} Ar\dot{N}: \xrightarrow{O_2} Ar\dot{N}{-}O{-}O(\cdot) \rightarrow ArNO_2 \quad (13)$$

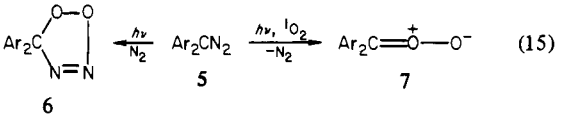
was supported by the isolation at 77 K of an aryliminodioxy diradical, presumably **2**, and a diamagnetic species thought to be a dipolar isomer, $ArN{=}O^+{-}O^-$, and the rearrangement of each into a nitroarene.[20] Photooxygenation at the terminal nitrogen of the azido group can, in principle, produce a nitro azoarene, **4**. The latter as a diazonium nitrite can fragment into nitrogen and a nitroarene (eq 14).

$$ArN_3 \xrightarrow[O_2]{h\nu} ArN{=}NNO_2 \xrightarrow{-N_2} ArNO_2 \quad (14)$$

4

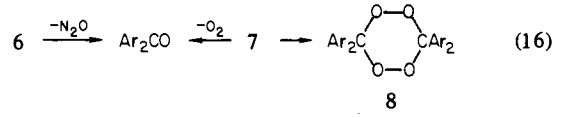
1-Nitropyrene[21] and nitroferrocene[22] have also been produced from an azide by photooxygenation.

Sensitized photooxygenation of a diazoalkane, **5** (eq 15, 16)



(15)

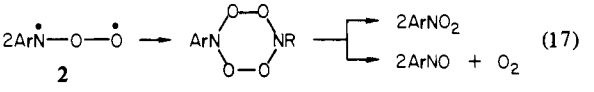
6 5 7



(16)

8

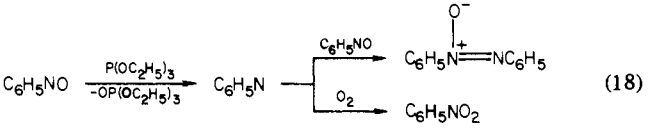
produced a carbonyl compound and a cyclic peroxide dimer.[23,24] Comparisons were seen between the probable intermediacy of **1** and **2** from an azide and a cyclic adduct **6** and a carbonyl oxide **7** from the diazo compound. A facile extrusion of nitrous oxide from each intermediate **1** and **6** could be expected. A parallel with the proposed disproportionation of a carbonyl oxide, **7**, into a carbonyl compound and a cyclic peroxide dimer, **8** (eq 16), provided another plausible route to a nitroso- and a nitroarene from a nitroso oxide **2** (eq 17).[20]



(17)

2

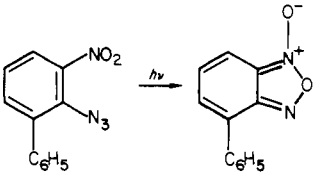
Azoxybenzene and nitrobenzene were again produced when a stream of oxygen was present as nitrosobenzene was deoxygenated by triethyl phosphite (eq 18). Since comparable



(18)

conditions without the phosphite had no effect on the nitroso compound,[19] an arylnitrene appeared to be more sensitive than the corresponding nitrosoarene toward air oxidation.

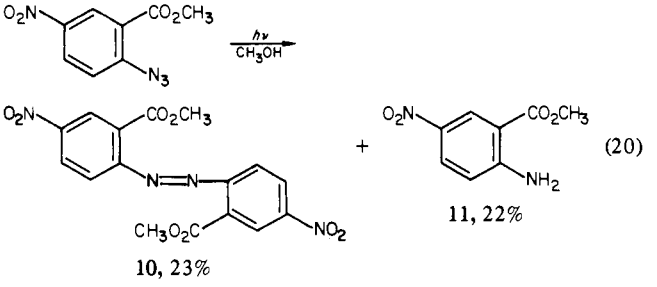
An unidentified lightly colored solid was obtained from *o*-nitrophenyl azide under photooxygenation conditions.[19] This result is puzzling in view of the ability of the nitro substituent to promote (a) intersystem crossing,[25] (b) the photolytic formation of 7-phenylbenzofuroxan (**9**) from 2-azido-3-nitrobiphenyl (eq 19,)[26] and (c) typical triplet nitrene products—an azoarene (**10**)



(19)

9, 52%

and an arylamine (**11**)—from methyl 5-nitro-2-azidoanthranilate (eq 20).[25] Other oxygen-sensitive intermediates gave seven-

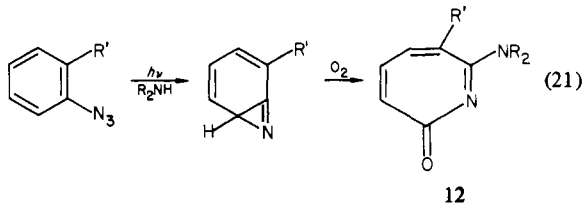


(20)

10, 23% 11, 22%

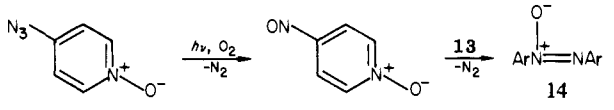
membered-ring azepinones (**12**) when derivatives (none contained a nitro group) of phenyl azide were irradiated in the presence of a nucleophile (eq 21).[27]

A few years before nitrene oxygenation was announced,[19] Japanese investigators observed that photolysis of 2- and 4-



(21)

azidopyridine (**13**) and quinoline *N*-oxides gave nitrogen and azoheteroarene oxides when oxygen was absent. In an oxygen atmosphere azoxyheteroarene oxides (**14**) were also formed (eq 22).[26,29] The results discussed above indicate that at-

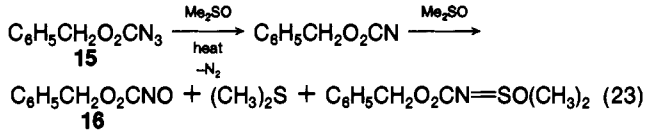


(22)

mospheric oxygen probably combined with an azide or a nitrene to produce a nitroso compound (and nitrous oxide), a precursor to an azoxyarene.

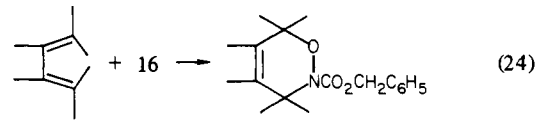
B. Dimethyl Sulfoxide

An efficient oxidation of (benzyloxycarbonyl)nitrene, from a thermolysis of benzyl azidoformate (**15**), into a carbonyl nitroso compound, **16**, by Me_2SO[30] is the first example of a promising method for bonding oxygen to nitrogen (eq 23). The unstable



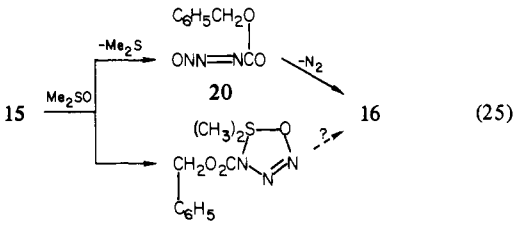
(23)

nitroso compound **16** was captured as a diene adduct, **17** (eq 24). It is not known whether the nitroso compound was cre-



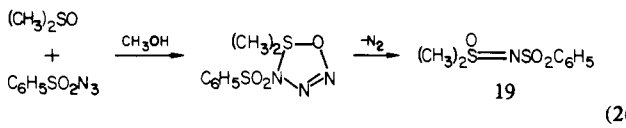
(24)

ated by a direct transfer of oxygen to an acylnitrene or by an indirect route via either a dipolar adduct (**18**) of the azide and Me_2SO or an initial oxygen transfer to the terminal azido nitrogen atom **20** (eq 25) or by some other way. Although a dipolar



(25)

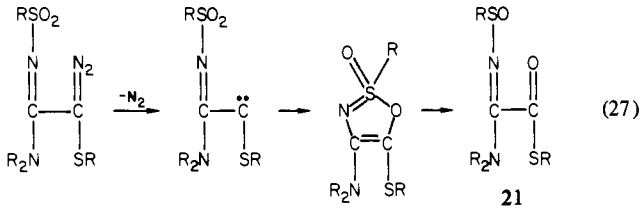
adduct accommodated the formation of *N*-(benzenesulfonyl)-dimethylsulfoximine (**19**) (eq 26) from Me_2SO and benzene-



(26)

sulfonyl azide,[31] a similarly oriented adduct (**18**) would not lead to the formation of the nitroso compound **16** by a simple fragmentation. There are precedents to support collapse of an intermediate azide *N*-oxide (**20**) into the nitroso compound **16** (section II.G.2 (eq 83) and II.I (eq 121)).

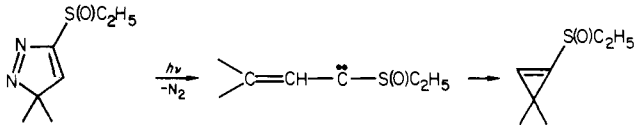
In a related reaction (eq 27) an intramolecular transfer of a



(27)

sulfonyl oxygen atom to a carbene carbon atom was proposed to account for the formation of a sulfinimide (**21**) from a sulfonimide.[32]

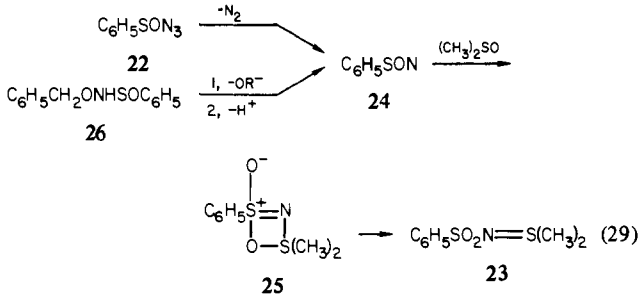
But a transfer of a sulfoxide oxygen to a proposed carbene center did not occur in the photolysis of a pyrazolenine into a sulfinylcyclopropene (eq 28). An intermediate sulfinyl carbene



(28)

was proposed.[33]

Analogous oxygenation at a nitrene nitrogen was not detected when benzenesulfinyl azide (**22**) and dimethyl sulfoxide gave a sulfimide, **23** (eq 29). An intermediate sulfinylnitrene



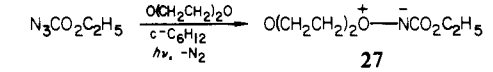
(29)

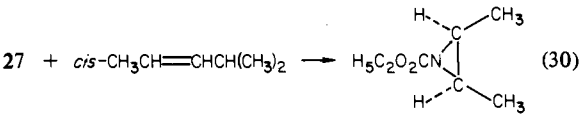
(**24**) and a four-membered ring (**25**) were postulated to account for the transfer of oxygen. The product **23** was also obtained from *N*-(benzyloxy)benzenesulfinamide (**26**).[34] There was no evidence for a transfer of an oxygen atom to nitrogen.

C. Ethers

Nitrene stabilization in the presence of tertiary amines or ethers has been associated with the adducts $R_3N^+—\bar{N}R$[35] and $R_2O^+—\bar{N}R$.[36] On the other hand, the nitrene was nucleophilic in forming the adduct $R_3B^-—^+NR$.[37]

When generated from ethyl azidoformate by photolysis in a cyclohexane solution of dioxane and *cis*-4-methyl-2-pentene, (ethoxycarbonyl)nitrene was stabilized as a singlet by an association (**27**) with the ether (eq 30). This interpretation reflected

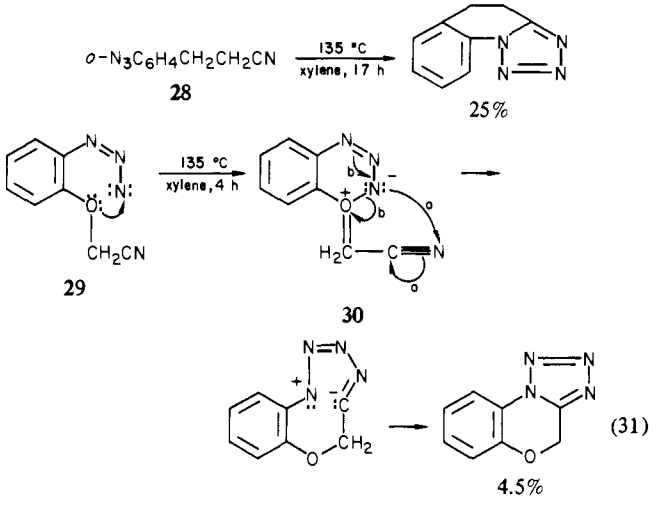




(30)

a correlation between the concentration of the ether and increased singlet nitrene activity as revealed by enhanced stereospecificity in adding to the olefin and an increase in the sum of all singlet nitrene products.[38] Compatible results were obtained from the same nitrene in a mixture of tetrahydrofuran, cyclohexane, and methylene chloride.[36]

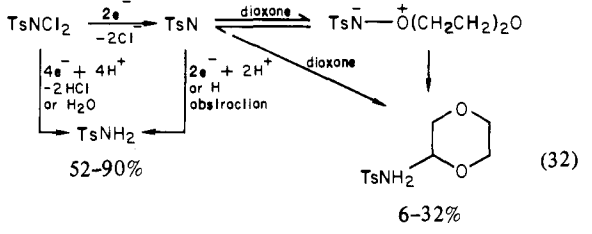
A beneficial effect from the ether oxygen was alluded to in noting a more facile intramolecular 1,3-dipolar cycloaddition from (*o*-azidophenoxy)acetonitrile (**29**) than from β-(*o*-azidophenyl)propionitrile (**28**).[39] This can be ascribed to a nucleophilic attack by the ether oxygen atom upon the latent nitrene nitrogen atom in the azido group. It is suggested that an intermediate ring structure (**30**) facilitated the transfer of nitrogen from oxygen to the cyano nitrogen atom and, in turn, a tetrazole ring closure by a transannular attraction of charges (eq 31).



(31)

More efficient reactions under milder conditions were observed for *o*-azidophenyl allyl and propargyl ethers.

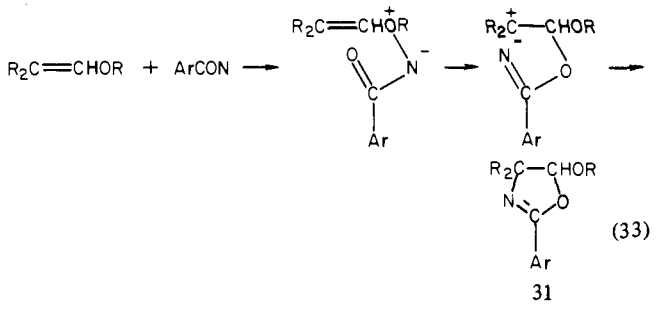
It can be assumed that a comparable dioxane–nitrene complex formed when tosylnitrene was electrochemically generated from *N,N*-dichloro-*p*-toluenesulfonamide (eq 32). Products



(32)

isolated were 2-(*p*-tolylsulfonylamino)-1,4-dioxane by nitrene insertion into one of the eight equivalent CH bonds of the ether molecule, and *p*-toluenesulfonamide, by either hydrogen abstraction or electrochemical reduction.[40]

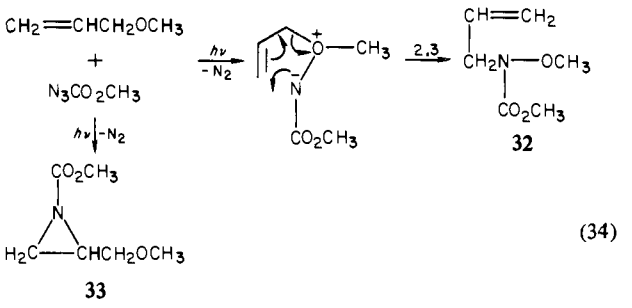
Considerable attention has been given to the formation of oxazolines **31** by the addition of acyl nitrenes (from acyl azides) to vinyl ethers.[41] Bonding between an electron deficient nitreno (eq 33) azido nitrogen and either the oxygen (eq 33) or the



(33)

β-carbon atom in the ether can initiate a sequence to product formation.

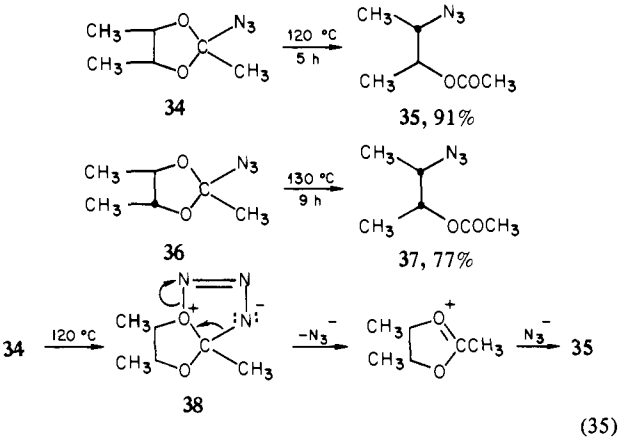
Photolysis of methyl azidoformate in allyl methyl ether gave an aziridine as the major product (26%), and an "insertion" accounted for the formation of an *N*-allyl-*N*-methoxy carbamate (**32**; 6.4%) (eq 34). It was suggested that an allylic 2,3-sigmatropic rearrangement followed an initial interaction between



(34)

the nitrene nitrogen and ether oxygen atoms to bring about the "insertion". Similar results were obtained with other allylmethyl ethers.[42] The corresponding thermal reaction gave only the aziridine **33** except when a catalytic amount of a transition-metal complex afforded an *N*-carbomethoxylmine ($RCH_2CH(R')C(OR'')=NCO_2CH_3$) as an additional product.[43]

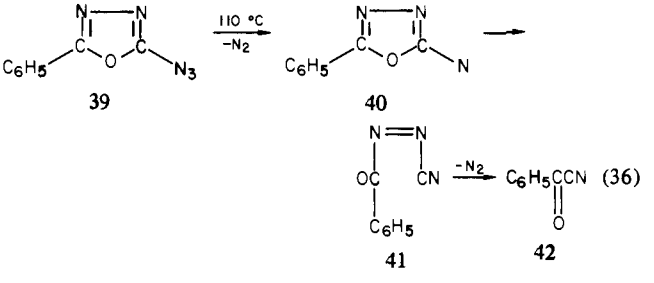
Thermal isomerization of diastereoisomers **34** and **36** of 2,4,5-trimethyl-2-azido-1,3-dioxolane gave acetates **35** and **37** of 2-azido-3-hydroxybutane by a 1,3-migration of the azido group with inversion at the terminus carbon atom (eq 35).[44] It



(35)

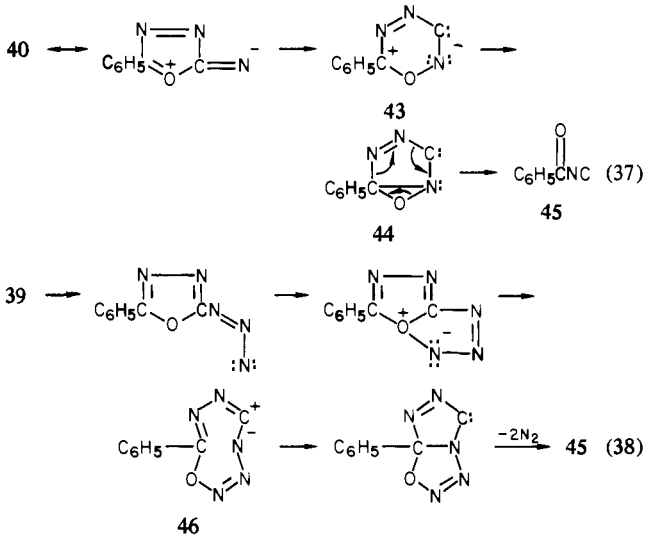
was recognized that a nucleophile could attack a dioxolan-2-ylium cation at any one of the three dioxolane carbon atoms. Assistance in dissociation of an azide anion was not described but can be seen as the result of an intramolecular charge transfer between the azido group and an ether oxygen atom with formation of an intermediate oxatriazolinium zwitterion, **38** (eq 35).

An aromatic ring oxygen atom may also attract a nitrene nitrogen atom. Benzoyl isocyanide (**45**; 2%) was a minor product from the thermolysis of 2-phenyl-5-azido-1,3,4-oxadiazole (**39**).[45,46a] The reaction was thought to proceed from a nitrene intermediate (**40**) to benzoyl cyanide (35%) by ring opening and elimination of nitrogen (eq 36). A coupling of



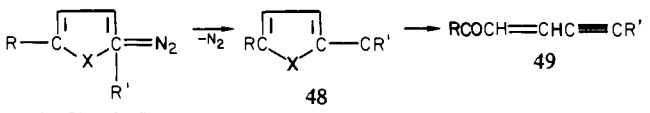
(36)

benzoyl and cyano groups (radical or ions) to produce an isocyanide is unlikely, and a rearrangement of benzoyl cyanide into an isocyanide does not occur. A sequence initiated by an electron transfer from the ring oxygen atom to either the *C*-nitrene center in intermediate **40** (eq 37) or to the *N*-nitrene center of the azido group in **39** (eq 38) followed by an elimi-



nation of nitrogen can account for the formation of benzoyl isocyanide (**45**).

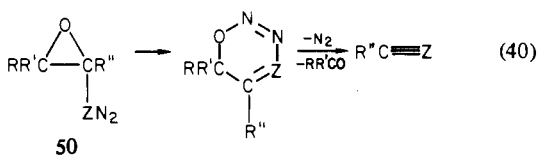
A similarity is seen between the intermediate **41** (eq 36) and the unsaturated ketones **49** obtained from diazo(2-furyl)methane (**47**, X = O) and diazo(2-thienyl)methane (47, X = S) (eq 39)



(39)

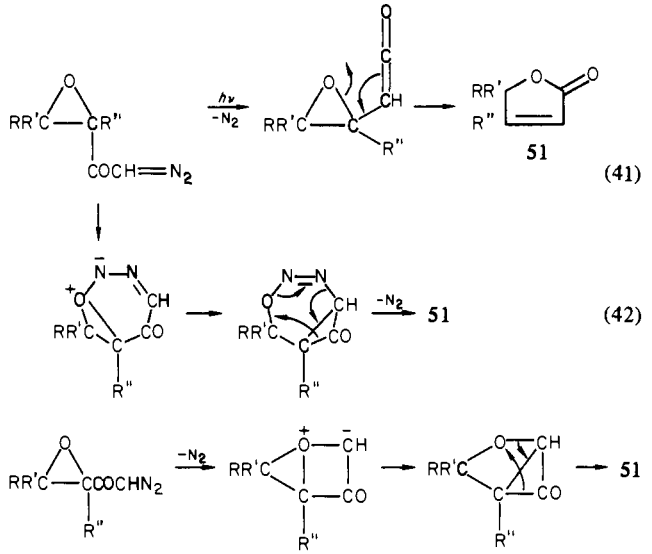
by thermolysis.[47] Proposed product formation by rearrangement with ring opening of an intermediate nitrene **40** or carbene **48** extends the similarity. The absence of a detected elimination–rearrangement product from the diazo compounds **47**, to correspond with benzoyl isocyanide **45**, suggested an absence of ring-expansion intermediates from **48** to correspond with either **43** or **46**. Independent evidence for the presence of the carbenes **48** consisted in insertion products with cyclooctane and addition products with styrene. Apparently the factors which control isomerization by ring expansion or by ring opening in these situations are not fully understood (compare section II.J).

An attraction between an ether oxygen atom and an electron-deficient nitrogen atom in a nitrene or a latent nitrene would be expected to increase as the nucleophilicity at oxygen increased. Since the oxygen atom in an oxirane has an enhanced nucleophilicty, it is probable that di- and triazapyran intermediates contribute to the Eschenmoser fragmentation[48,49] of α-diazoalkyloxiranes **50** (Z = CH) and the Kyba fragmentation[50] of azidooxiranes **50** (Z = N) (eq 40).



(40)

The phototransformation of an α,β-epoxydiazomethyl ketone into an α,β-unsaturated γ-lactone (**51**) may be a related reaction. It was described as a ring enlargement following a Wolff rearrangement (eq 41);[51] however, an initial interaction between the oxirane oxygen atom and the latent nitrene nitrogen atom in the diazomethyl group followed by collapse of a seven-membered ring and rearrangement will also account for product formation (eq 42) but is indistinguishable at this time from an interaction between the oxirane oxygen atom and the acylcarbene, concerted with or subsequent to its formation (eq 43).

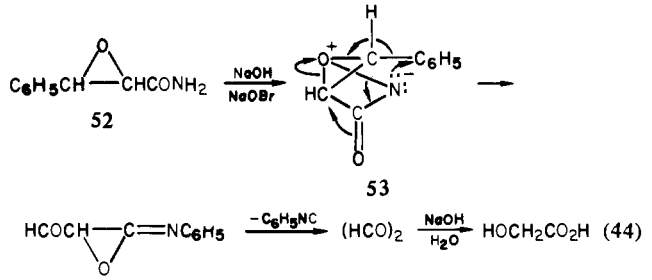


(41)

(42)

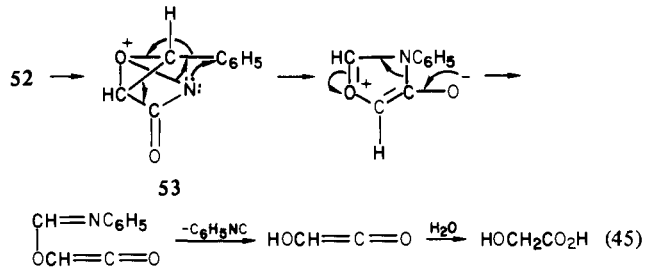
(43)

Another rearrangement further illustrated an ether–nitrene interaction. Treatment of a β-arylglycidamide (**52**) with alkaline hypobromite produced an aryl isocyanide and glycolic acid. There was no evidence for the anticipated rearrangement into an isocyanate, and the observed rearrangement was unaccounted for.[52] It is suggested that an initial association between the oxirane oxygen atom and the acylnitrene center decided the course of the reaction (eq 44). In different routes to the



(44)

product either the original acyl or benzyl carbon atom can become the isocyanide carbon atom (eq 44, 45). Confirmation

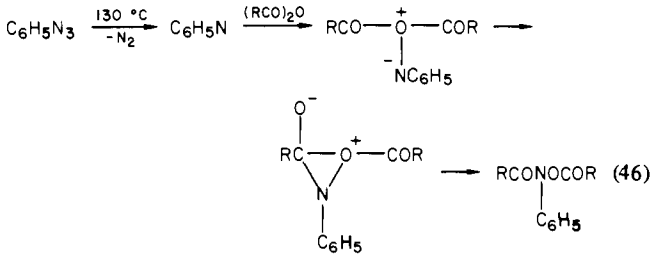


(45)

of the reaction and further investigation are needed.

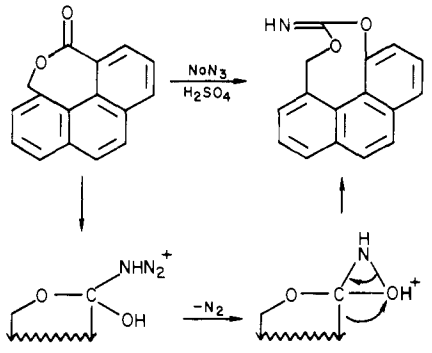
D. Carboxylic Acid Anhydrides and Lactones

An insertion of phenylnitrene into a CO single bond occurred upon heating phenyl azide in refluxing acetic or propionic anhydride.[53] Ionization of anhydride[54] and a nitrene attack upon the central anhydride oxygen followed by a rearrangement[46b] were suggested (eq 46) but judged deficient in accommodating an increased efficiency in the presence of ortho and para electron-donating groups and in reaction failure from all nitrophenyl azides.[53] The relative merits of retarded nitrogen–oxygen bond formation and enhanced nitrogen–carbon bond formation (eq 46), each conceivably a result of electron donation by an aryl substituent, have not been evaluated.



(46)

An example of a Schmidt reaction with migration to oxygen rather than nitrogen (eq 47) was accounted for by the inter-



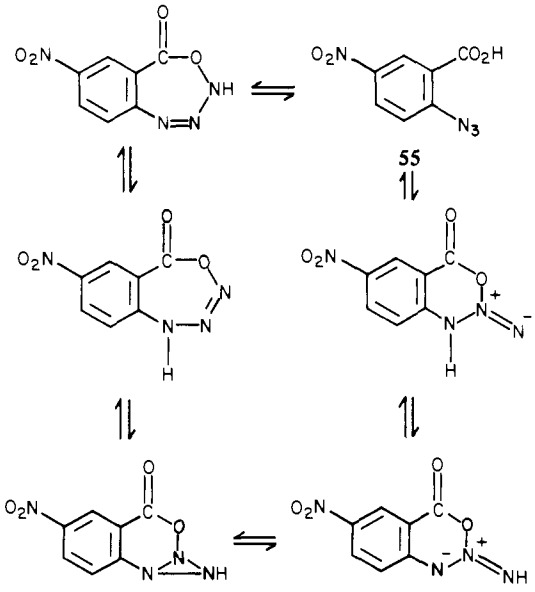
(47)

54

mediacy of a protonated oxaziridine (**54**).[55] The suggestion was consistent with a basicity at an oxaziridine oxygen atom competitive with that at nitrogen.[56] Reactions 47 and 293 (section V.D.3) are comparable.

E. Carboxylic Acids and Alcohols

A proposed intramolecular reversible cyclization for 2-azido-5-nitrobenzoic acid (**55**) in the solid state was supported by an interpretation of infrared and ultraviolet spectra. The cyclization was viewed as an attack on the middle azido nitrogen atom.[57] This cannot, however, be differentiated from a cyclization by addition to the latent nitrene nitrogen in the azido group (eq 48).



(48)

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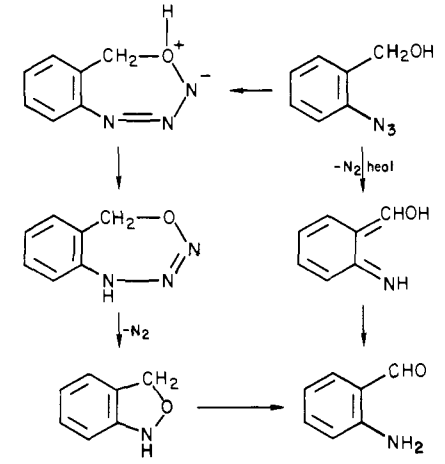
Information on a similar interaction between either an azido or a diazoalkane nitrogen with an alcohol oxygen atom is scarce. Irreversible nitrene insertion into an oxygen–hydrogen bond has been noted (eq 7), and an initial charge-transfer complex, $C_2H_5O_2C\bar{N}-O^+(H)R$, has been suggested,[15] but an earlier formation of o-aminobenzaldehyde (**56**) from o-azidobenzyl alcohol in the vapor phase at 350–360 °C was accounted for by a nitrene abstraction of hydrogen frm the nearby methylane group followed by a transfer of hydrogen from oxygen to nitrogen in a radical reaction.[58] Assistance may have been provided in a ring closure from a nucleophilic attack by the hydroxyl oxygen atom upon the terminal azido nitrogen atom. Elimination of nitrogen and rearrangement of a benzisoxazoline would lead to the amino aldehyde **56** (eq 49).



(49)

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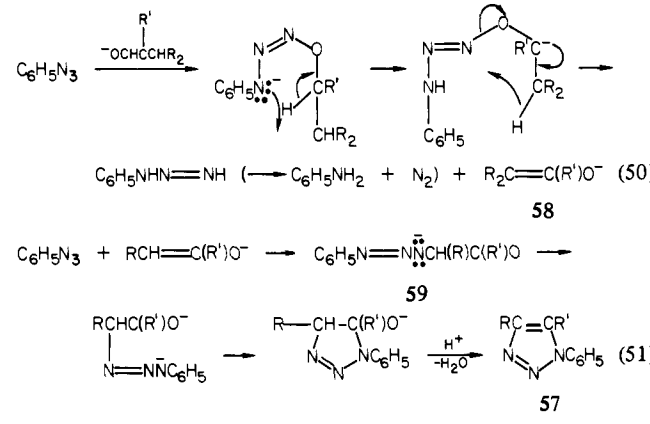
F. Alkoxides

Since 1925 a reaction between phenyl azide and sodium ethoxide has been known to produce 1-phenyl-1,2,3-triazole (**57** R = R′ = H) (eq 50, 51).[59] It was rationalized by assuming



(50)

58

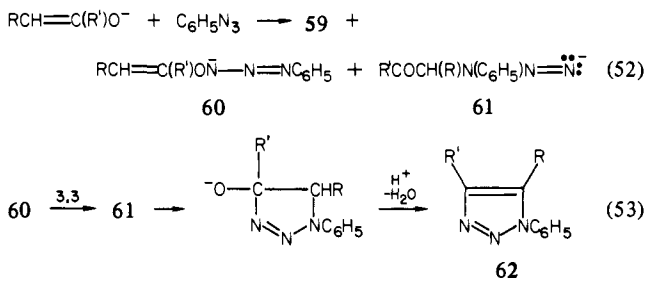
(51)

57

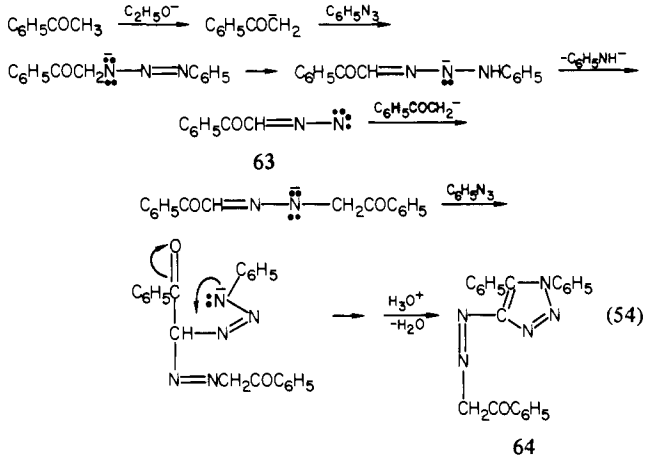
that an initial oxidation of ethoxide anion into the enolate anion **58** (R = R′ = H) of acetaldehyde with reduction of phenyl azide into aniline (eq 50) was followed by addition of the azido group to the enolate double bond and elimination of sodium hydroxide (eq 51).[60a] Higher primary alkoxides gave 4-alkyl-1-phenyltriazoles whereas the azide was reduced by a secondary alkoxide but was then unreactive toward the ketone enolate.[59] "Nucleophilic attack by an (enolate) carbanion on the terminal azide nitrogen" was suggested[60a] and is now seen as one of the several examples of anionic attacks at this latent electrophilic nitrene nitrogen atom. Reduction of an azide by alkoxide anion would, of course, provide another example (eq 50).

The necessity for new bonding between the unsubstituted terminal azido nitrogen and the enolate carbanion (rather than the oxanion) is seen from the formation of 1-phenyl-4-(alkoxycarbonyl)-5-methyltriazole (**57**, R = CO_2R, R′ = CH_3),[59,61] rather than the isomer **62** (eq 52, 53).

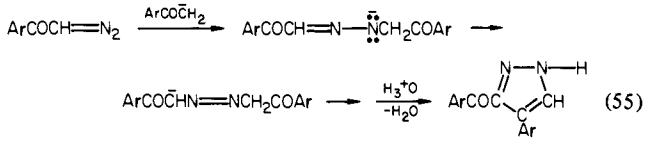
A reaction[59,62] between acetophenone and phenyl azide in the presence of sodium ethoxide is subject to a similar explanation but with an additional step in which there is a diazo transfer from nitrogen to carbon to produce diazoacetophenone



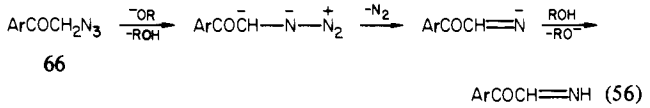
(63) (eq 54). The product triazole **64** was confirmed by an independent synthesis.



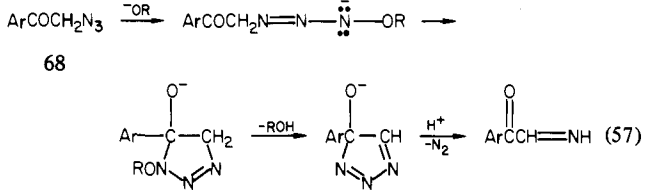
Alkyl, acyl, and sulfonyl azides have given similar transformations into triazoles.[59] The intermediate diazo transfer now offers the basis for understanding an occasional pyrazole (**65**) byproduct[59] (eq 55).



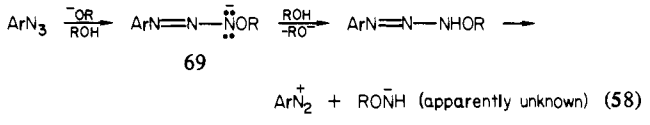
Although the base-catalyzed release of nitrogen from an α-azidocarbonyl compound **68** was proposed to proceed with an abstraction of a proton from the α-carbon atom (eq 56),[61]



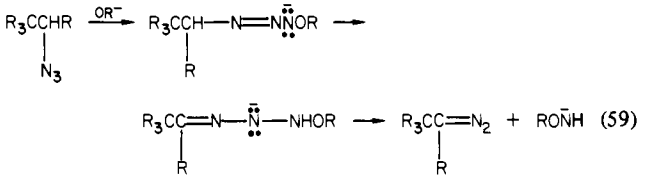
an attack by base on the terminal azido nitrogen atom may bring about the same results (eq 57).



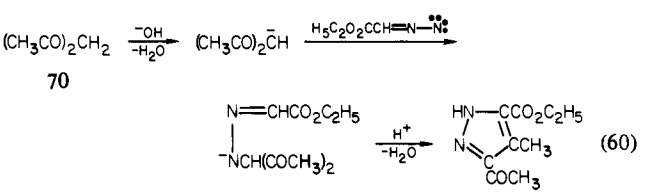
A nucleophilic attack on azido nitrogen can afford the conjugate base **69** (eq 58) of the intermediate encountered in the



formation of an aryl azide from a diazonium compound and hydroxylamine.[61] A "reverse" cleavage of a base–azide adduct into a diazo compound and a hydroxylamine anion is apparently unknown but can be anticipated (eq 59).

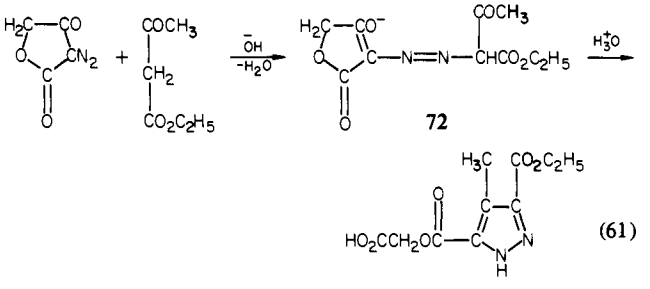


Pyrazoles were obtained from diazoacetates or diazo ketones and 1,3-dicarbonyl compounds or β-keto esters under alkaline conditions.[62] In a typical reaction, ethyl diazoacetate and acetylacetone (**70**) gave the pyrazole **71** (eq 60).[62] It is

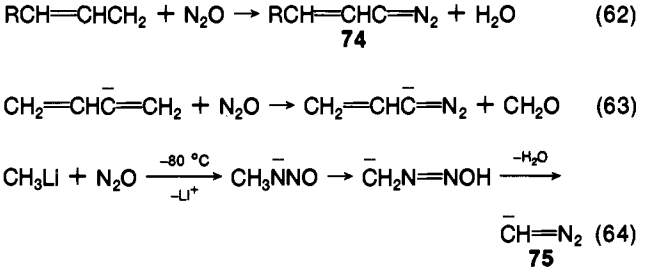


now assumed that this reaction proceeded from a nucleophilic attack at the terminal diazo nitrogen atom.

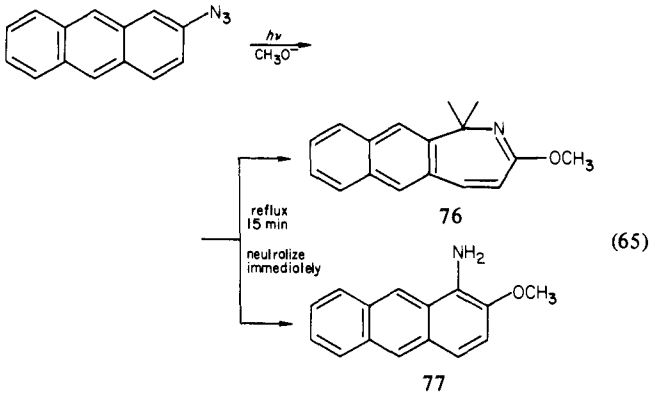
Isolation of an intermediate azo compound[62] (**72**) and its subsequent cyclization into a pyrazole (**73**) (eq 61) support this explanation.



Similar carbanionic attacks at a latent nitrene nitrogen can be seen in the recently reported transformations of dinitrogen oxide (:ÑNO) into diazo compounds **74** (eq 62, 63).[63] An older preparation of the lithium salt **75** of diazomethane from dinitrogen oxide and methyllithium has provided another example (eq 64).[64]



Polycyclic aromatic azides, in which the azido group occupies a β position, on treatment with strong alkoxide gave either ring expansion into an azepine or an α-methoxy-β-aminoarene depending upon the workup procedure (eq 65). When 2-azidoanthracene, dioxane, and potassium methoxide in methanol were irradiated (350–410 nm) for 30 min and either refluxed for 15 min or stored overnight before neutralization, a nearly quantitative yield of 3-methoxy-1*H*-naphtho[2,3-*c*]azepine (**76**) was obtained. Neutralization immediately after irradiation gave 1-amino-2-methoxyanthracene (**77**; 60%).[65] In a similar re-

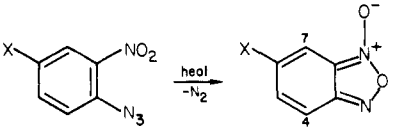


76 77 (65)

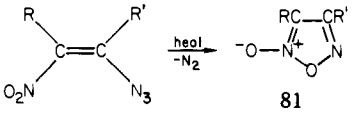
action, β-naphthyl azide and diethylamine gave 1-amino-2-(diethylamino)naphthalene.[66]

G. Nitro and Nitroso Groups

Uncatalyzed thermolysis of 2-nitroaryl azides (**78**) and (Z)-nitroazidoalkenes (**79**) have produced furoxans **80**, **81** (furazan oxides, 1,2,5-oxadiazole *N*-oxides) (eq 66, 67). A chapter on



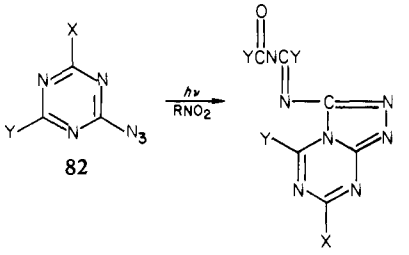
78 80 (66)



79 81 (67)

oxadiazoles covered the literature up to 1958–1959;[67a] reviews,[66,69] chapters,[70,71] and books[1,6d] have since dealt with azido, nitreno, and nitro groups and the furazan ring. Information on intra- and intermolecular interactions between the nitro or the nitroso group and either the azido or the diazoalkyl or the nitreno group to be discussed includes examples of 2-nitroaryl azides which gave azoarenes, arylamines, and nitroso compounds but not furoxans. Some of this material was omitted, and certain portions erroneously covered,[70] in a previous review.

Except for one instance, intermolecular interaction between azido and nitro groups has not been directly investigated. Triazinylnitrenes, from the azides **82**, were judged to be inert to nitro compounds (eq 68).[72]

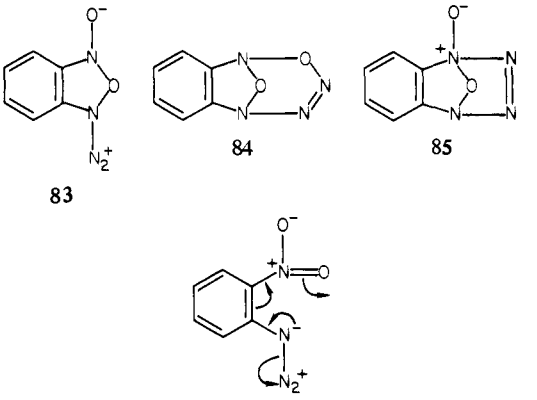


82 (68)

R = CH_3, C_2H_5, *i*-C_3H_7, C_6H_5
X = Y = OCH_3, OC_2H_5, O-*i*-C_3H_7, $N(CH_3)_2$

1. Furazans and Furoxan Formation

Two- and four-center intermediates, **83** and **84**,[73] were suggested in 1963 for the conversion of an o-nitrophenyl azide at 70–140 °C into a benzofuroxan (**80**). Other versions, **85**[74] and **86**,[75a-e] have since appeared; however, the model **85** was later withdrawn.[74] It is typically a one-product (and nitrogen)

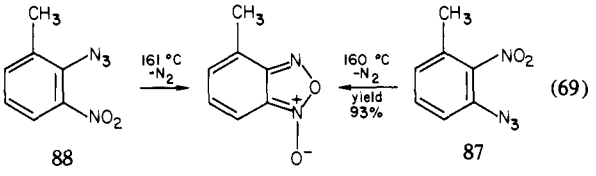


83 84 85

86

reaction—often a preparative method of choice. Above 150 °C many furoxans have decomposed.[76]

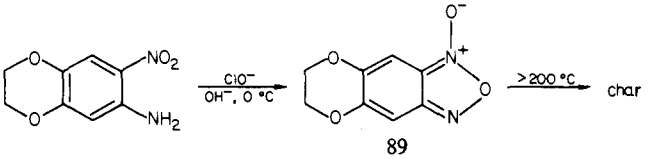
A ranking of anchimeric assistance in the release of nitrogen for ortho substituents in phenyl azide was based on kinetic measurements for thermolysis at 161 °C in decalin: H, 1; $HOCH_2$, 0.82; CH_3O_2C, 1.3; C_6H_5CO, 45.1; CH_3CO, 254; NO_2 537; $C_6H_5N{=}N$, 6680.[75] Reasons have not been forthcoming for the order or for a reversal in ranking for the phenylazo and nitro substituents at the 1-position in 2-naphthyl azides when measured in nitrobenzene.[75] A methyl substituent in 2-nitrophenyl azide decreased the rate as shown by the relative order: no CH_3, 537; 3-CH_3 ***87***, 47.6; 4-CH_3, 323; 6-CH_3 ***88***, 7.0.[75] There are conflicting data in the literature about the last compound, 2-nitro-6-methylphenyl azide (**88**). When prepared in another laboratory it "did not yield 4-methylbenzofuroxan on pyrolysis", but experimental data where not reported.[77] More reliable data are given in eq 69.[75]



88 87 (69)

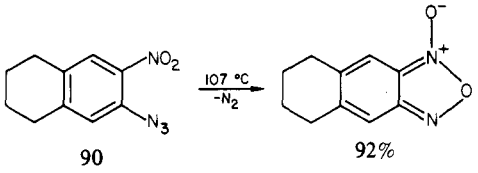
Presumably the 3- and 6-methyl substituent in **87** and **88** inhibited coplanarity for the nitro and azido groups. Spectroscopy was compatible with this interpretation in a clear differentiation of the symmetrical nitrogen–oxygen bond stretching frequency at 1366 cm^{-1} for 3-methyl-2-nitrophenyl azide (**87**) from absorption at 1345 and 1344 cm^{-1} for the 4-methyl- and 6-methyl (**88**) isomers.[75]

Assistance in the release of nitrogen has been qualitatively detected by a decrease in the temperature for gas evolution when compared with a suitable standard, e.g., phenyl azide 120 °C[7] dec[75] and o-nitrophenyl azide 65 °C dec.[78] A lack of assistance in the release of nitrogen at 210 °C for 6-azido-7-nitro-1,4-benzodioxane was unaccounted for,[79] but an inhibition to coplanarity for the nitro and azido groups, a result of normal twisting of the dioxan ring, can be suspected. Neither the expected furoxan **89**, 204 °C dec, independently prepared[79] by an oxidation of 6-amino-7-nitro-1,4-benzodioxane (eq 70), nor



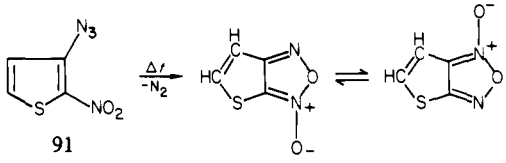
89 (70)

any other product was detected in the char mixture. For comparison, 2-azido-3-nitrotetralin (**90**), mp 85–86 °C and 107 °C dec, gave 5,6-tetramethylenebenzofuroxan, mp 106–107 °C (eq 71).[60]



(71)

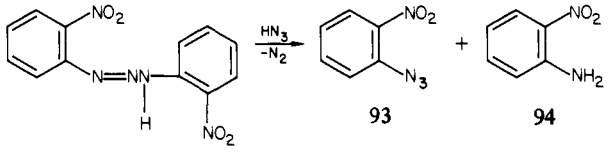
Fusion of furoxan and thiophene rings resulted from a thermolysis of 3-azido-2-nitrothiophene (**91**; eq 72).[61,62] A com-

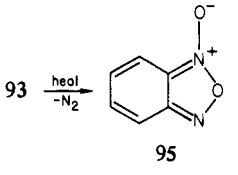


(72)

parable fusion of isoxazole and thiophene rings is found in section II.H.1 (eq 108).

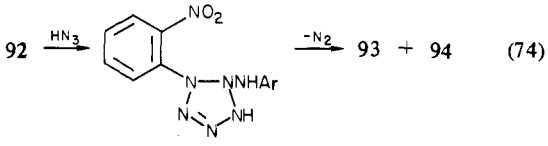
An interesting preparation of benzofuroxan was found in the treatment of 1,3-bis(*o*-nitrophenyl)triazene (**92**) with sodium azide in refluxing acetic acid (eq 73). The reaction was as-





(73)

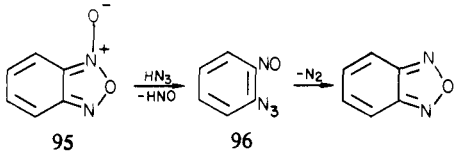
sumed to produce initially *o*-nitrophenyl azide (**93**) and *o*-nitroaniline (**94**) (73%). Benzofuroxan (**95**; 81%) was the usual thermolysis product from the azide.[83] Apparently the amine **94** in refluxing acetic acid was insufficiently nucleophilic to attack a furoxan (**95**) nitrogen atom; a stronger amine and a benzofuroxan did, however, produce a hydrazine (section IV.E). The transformation **92** → **93** + **94** (eq 73) may have proceeded by an addition–elimination sequence (eq 74), similar to a pattern



(74)

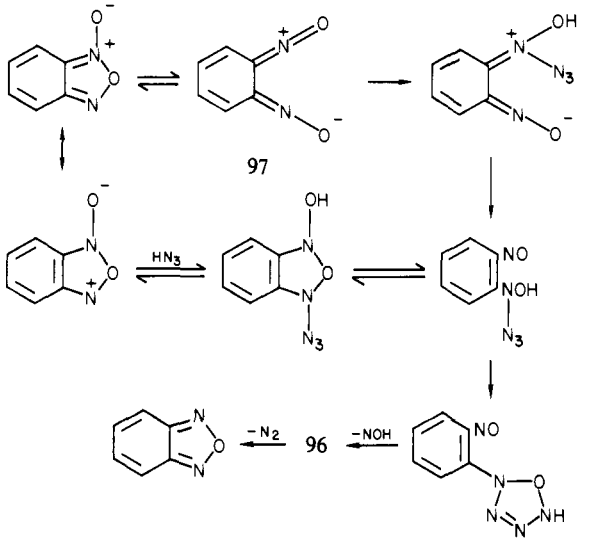
proposed for the "displacement" of a nitroso group by the azido group (see eq 76).

In a carboxylic acid at 140 °C sodium azide deoxygenated benzofuroxan (eq 75) and its 5-methyl, 5-methoxy, 5-chloro,



(75)

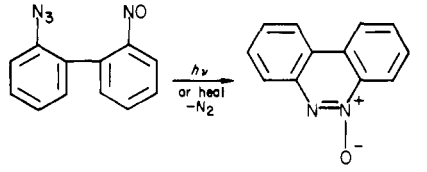
5-bromo, 5-nitro, and 4-nitro derivatives into benzofurazans.[64] Displacement of a nitroso group by an azido group (eq 75) followed by a facile thermal elimination of nitrogen was proposed. Thermolyses of other substituted 2-nitrosophenyl azides into corresponding furazans[65,66] supported the last step in eq 75, but supporting evidence for the "displacement" was not offered. An alternative formation (eq 76) of the intermediate azide **96** consists in nucleophilic attack by hydrogen azide or by the azide anion on an electron-deficient nitrogen atom in a furoxan ring or, after ring opening, in a pseudodinitroso-



(76)

benzene[67] structure (**97**). Fragmentation of the adduct would give the azide **96**. (A transformation of a benzofuroxan into a 2-nitrophenylhydrazine appears to be a related reaction (section IV.E)). The source of azide nitrogen in **96** and of nitrogen in the product benzofurazan would be revealed by tracer studies.

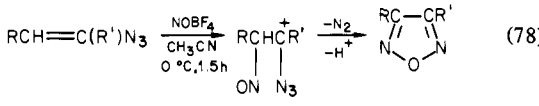
In the formation of benzocinnoline *N*-oxide from 2-nitroso-2′-azidobiphenyl (eq 77),[87] it is conceivable that a new nitrogen



(77)

to oxygen bond is present at intermediate and/or product stages.

Monocyclic furazans were obtained from alkenyl azides and nitrosyl tetrafluoroborate, presumably via the conjugate acid for a nitrosoazidoalkene (eq 78).[88]

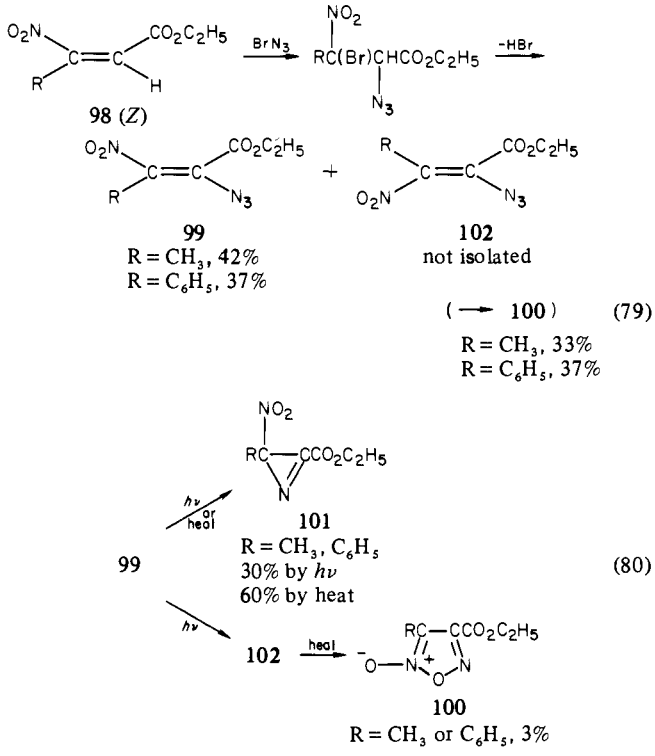


(78)

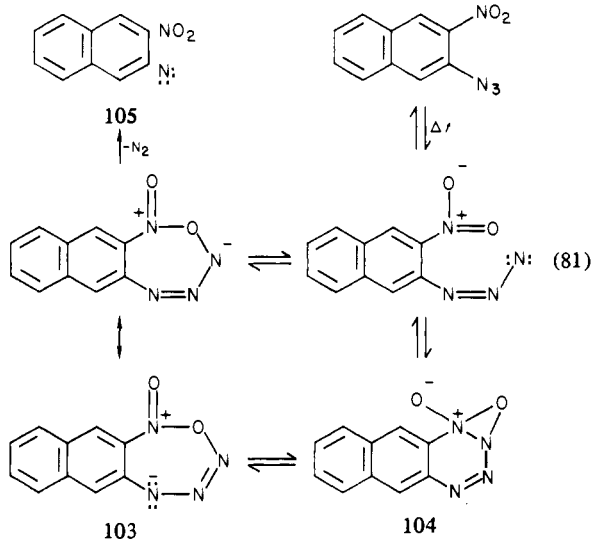
A reaction between 3-nitro-2-alkenoates (**98**) and bromine azide in equimolar amounts in *N*,*N*-dimethylformamide gave 3-nitro-2-azido-2-alkenoates **99** and 3-(ethoxycarbonyl)-4-alkylfuroxan (**100**) (eq 79, 80). In refluxing benzene the reaction produced the furoxan **100** and 2-(ethoxycarbonyl)-3-alkyl-3-nitroazirine (**101**). It was assumed that dehydrobromination of the expected adduct from bromine azide and the olefin **98** gave a mixture of (*Z*)- and (*E*)-alkenoates **102** and **99**.[89] Since previous azidonitroalkenes easily gave furoxans (sometimes on formation),[90–92] a facile thermolysis of the nitro azide **102** into the furoxan **100** would be expected. Photolysis of the olefin **99** produced the azirine **101** and the isomeric olefin **102** which easily fragmented into the furoxan **100**. It was claimed that **99** was the first example of an isolated 1,2-nitroazido olefin.[89] (See Table I.)

2. *Azoarene and Nitrosoarene Formation*

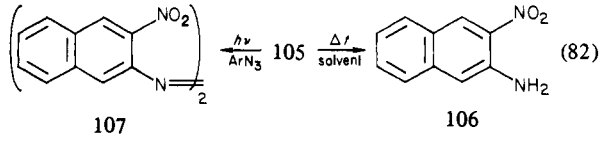
There is small group of 2-nitroaryl azides which apparently do not proceed in thermolysis from an intermediate related to **83**, **84**, and **85** or by a pericyclic process defined by **86**. Each azide in this group needs an intermediate or a process which will not only account for anchimeric assistance in the release of nitrogen but also avoid a disadvantageous *o*-quinonoid



structure. Such an intermediate is available when the azido group is bent[93-95] so that the outermost nitrogen atom, with a sextet of electrons, as an electrophile can combine with either an oxygen atom or a nitrogen–oxygen bond of the nearby nitro group to create six- and/or seven-membered-ring intermediates, e.g., **103** and **104**, presumably interconvertible (eq 81).



An erroneous description[96] of 2-azido-3-nitronaphthalene brought about its reinvestigation. Thermolysis (eq 82) gave 2-amino-3-nitronaphthalene (**106**) in low yield (the remaining



product mixture was intractable).[97] Since β-naphthyl azide released nitrogen at 120 °C,[75] anchimeric assistance was revealed for 2-azido-3-nitronaphthalene in thermolysis below 100 °C.[97] Presumably an intermediate stage, **103** ⇌ **104**, led to the formation of intermediate 2-nitreno-3-nitronaphthalene (**105**). Abstraction of hydrogen to produce the amine **106** can be seen

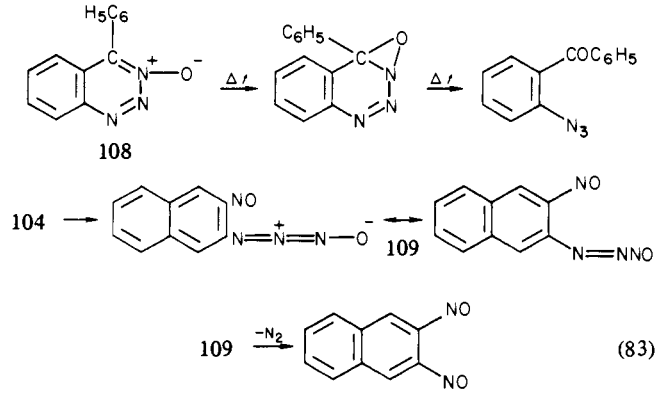
TABLE I. Furoxans ($\overline{RC{=}N(O)ON{=}CCO_2C_2H_5}$) 100 and Azirines $\overline{RC(NO_2){=}N{=}CCO_2C_2H_5}$ 101 from Nitro Olefins ($RC(NO_2){=}CHCO_2C_2H_5$) 98 and from Nitro Azides ($RC(NO_2){=}C(N_3)CO_2C_2H_5$) 99

compd	energy source	product, R = CH_3	yield, %	product, R = C_6H_5	yield, %
98	Δt	100[a]	33	100[a]	37
99	hν	100	3	100	3
		101	33	101	29
99	Δt	101	63	101	61

[a] As appropriate, the nitro azido olefins 99 (R = CH_3) in 42% and 99 (R = C_6H_5) in 37% yields were also obtained.

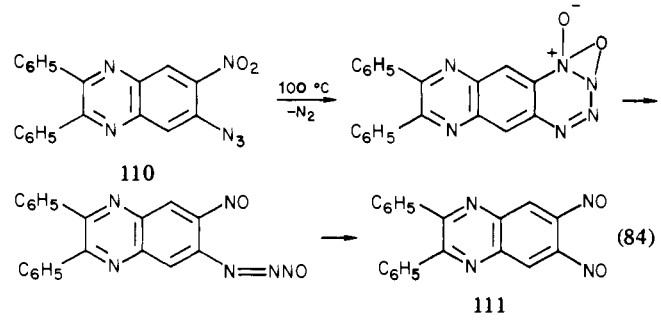
as a typical reaction of the nitrene as a triplet.[46,98] A 2,3-naphthoquinonoid furoxan or the isomeric 2,3-dinitrosonaphthalene either did not form or was destroyed by further thermolysis. Photolysis (eq 82) of the azide produced 3,3′-dinitro-2,2′-azobinaphthyl (**107**; 19%) and intractable material.[97] The best explanation for the formation of the azo compound was based on the intermediate nitrene **105**, as a triplet,[46d,e,96,99] in a coupling and elimination reaction with the azide.

A facile thermal isomerization of 4-phenylbenzotriazine 3-oxide (**108**) into *o*-azidobenzophenone[100,101] lends support to the proposed isomerisation of **104** into 2-nitrosonaphthyl azide *N*-oxide (**109**). Collapse of the *C*,*N*-dinitroso intermediate **109** into nitrogen and 2,3-dinitrososonaphthalene (eq 83) is an ex-

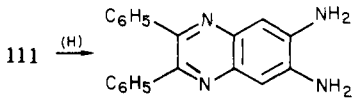


tension of a fragmentation of a nitrosoimine (>C=NNO) into nitrogen and a carbonyl derivative (sections II.C, eq 25), and II.I, eq 121). It has been substantiated in the isolation of the dinitroso compounds **111** and **112** (vide infra).

Anchimerically assisted release of nitrogen at 100 °C left a red labile solid, **111** (eq 84), with no discernible melting point,

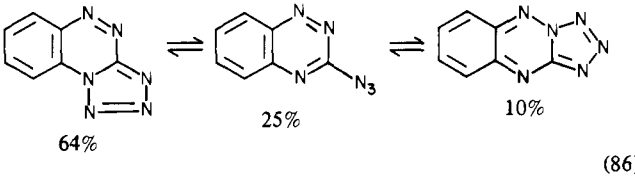


from 2,3-diphenyl-6-nitro-7-azidoquinoxaline (**110**).[102] Satisfactory elemental analyses and molecular weight required the formula $C_{20}H_{12}N_4O_2$. Further heating at 100 °C transformed the red solid product into an intractable blue-black solid with no discernible melting point and general insolubility. Both the red and blue-black forms of the product **111** were reduced to 2,3-diphenyl-6,7-diaminoquinoxaline which condensed with phenanthrenequinone (eq 85).



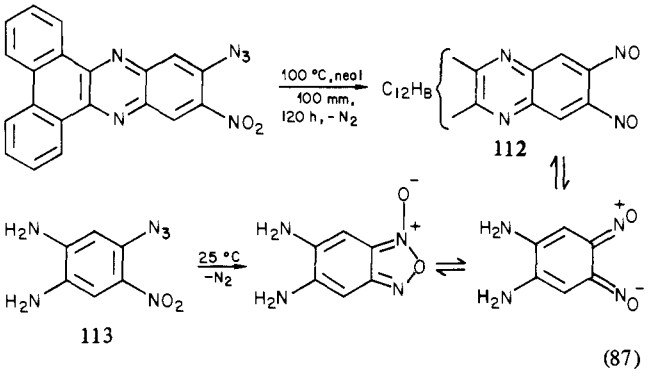
(85)

The red labile solid product was assigned the structure of 2,3-diphenyl-6,7-dinitrosoquinoxaline (**111**). A contribution to the resonance hybrid from a 2,3-quinonoid species was recognized but considered relatively unimportant to reflect an assumed lack of tolerance for the quinonoid structure.[102] It has been recently reported that simple derivatives of 2,3-naphthoquinone are known only as highly reactive transients, some of which could be trapped as Diels–Alder adducts.[103] A ternary solution equilibrium between an azide and two tetrazole isomers (eq 86) tends to support this observation.[104]



(86)

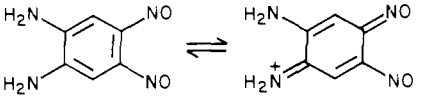
Blue-black 7,8-dinitroso-1,2,3,4-dibenzphenazine (**112**) resembled compound **111** insofar as it showed no discernible melting point and general insolubility. It gave satisfactory elemental analyses but the related molecules, 6,7-dinitrosoquinoxaline and its 2,3-dimethyl- and 2,3-di-α-pyridyl derivatives, resisted purification and were reported with a low nitrogen content.[102] *p*-Dinitrosobenzene, one of the few previously known dinitrosoarenes, resembled **111** in that a freshly prepared sample was identified as a monomolecular green solid with no discernible melting point. It rapidly changed into a yellow, presumably oligomeric, solid[105,106] (eq 87).



(87)

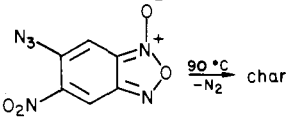
A reviewer erroneously described compounds **111**, **112**, and related molecules as furoxans.[70,98]

A low thermal stability was noted for 4-azido-5-nitro-1,2-diaminobenzene (**113**). Over several weeks at 25 °C nitrogen was lost and a blue-black solid with no melting point remained. Elemental analysis permitted $(C_6H_6N_2O_2)_x$, but a differentiation between plausible assignments as a diaminobenzofuroxan or ring-opened dinitroso isomers or tautomeric oximes (x = 1) was not made (eq 88).[107]



(88)

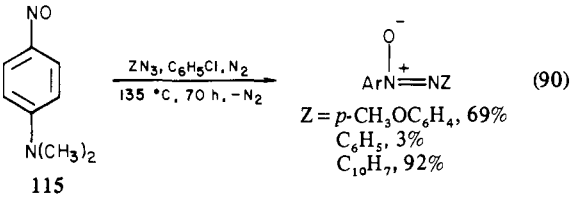
At 90 °C 5-azido-6-nitrobenzofuroxan (**114**) vigorously lost nitrogen and left an intractable residue (eq 89).[107,108]



(89)

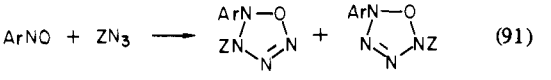
3. Azoxyarene Formation

A formal addition of a nitrene to a nitroso compound gives an azoxy compound (eq 90). In practice the nitrene would



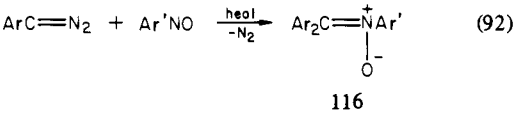
(90)

generally be derived from an azide. Preparative yields were obtained from a nitroso arene and either a naphthyl azide or a phenyl azide with an electron-donating para substituent, e.g., compound **115**.[109] An initial cycloaddition between an azide and a nitroso compound (eq 91) was considered,[110] but critical



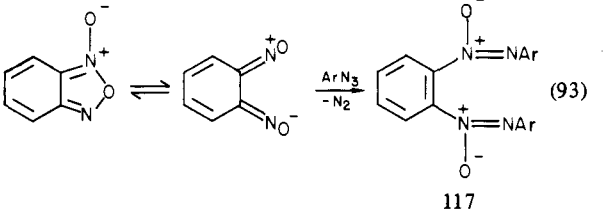
(91)

fragmentation products, e.g., nitrous oxide, ZNO, and ArN, to be expected from one or the other oxatetrazolines, were not reported. Both the azide and the nitroso compound may be nonaromatic. For example, arylazoxy cyanides were obtained from cyanogen azide and substituted derivatives of nitrosobenzene.[111] The overall reaction resembles the formation of a nitrone (**116**) from a diazoalkane and a nitroso compound (eq 92).[60e]



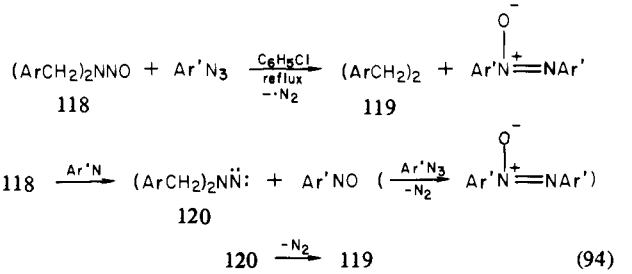
(92)

A bisazoxyarene (**117**) was obtained from benzofuroxan and an aryl azide (eq 93).[112] The probability that a ring-opened furoxan reacted with the azido group is assumed.



(93)

In a related reaction,[113] thermolysis of a mixture of 2-cyano-4-nitrophenyl azide and *N*-nitrosodibenzylamine (**118**) in chlorobenzene gave bibenzyl (**119**) (70%). Other phenyl azides afforded bibenzyls from trace amounts to low yields except for 2- and 4-cyanophenyl and 4-nitrophenyl azides which gave the expected bibenzyls in 46–48% yields. A scheme was presented which called for deoxygenation of the *N*-nitroso compound by an aryl azide (eq 94). It is unfortunate that alternative



(94)

fates of the aryl nitrene (assumed to be generated from the azide) were not pursued except possibly in one instance, when azoxybenzene, from phenyl azide, was detected by TLC. Deoxygenation of an *N*-nitroso compound by an azide (nitrene) appears to be a candidate for a third method for intermolecular

TABLE II. Anthranils 122 from Azides 121 $RC_6H_3(N_3)COR'$-1,2

121,[a] R'	122, yield, %	ref	121,[a] R'	122[b] yield, %
H	40	75b	p-$CH_3C_6H_4$	73
CH_3	100	75b	p-BrC_6H_4	70
C_6H_5	93 (39)	75b (74)	p-$CH_3OC_6H_4$	73
CH_3[c]	59	75e	p-$O_2NC_6H_4$	97
CH_3[d]	53	75e	p-ClC_6H_4	73
$C(CH_3)_3$	95	75e	p-$(CH_3)_2CHC_6H_4$	98
			p-$(CH_3)_3CC_6H_4$	85

[a] R = H. [b] Reference 72. [c] R = 3-CH_3. [d] R = 6-CH_3.

oxidation at a nitrene center (section II.A.B.).

Simultaneously with this report,[113] Russian work on dialkylaminonitrenes appeared.[114] The nitrenes were generated by a reaction between Angeli's salt and a secondary amine (eq 95). Dibenzylamine gave dibenzyl (71%), benzaldehyde ben-

$$HN_2O_3^- \rightarrow HNO + NO_2^-$$

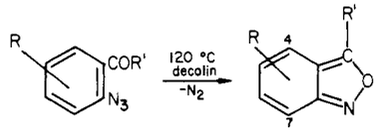
$$(ArCH_2)_2NH \xrightarrow{NOH} (ArCH_2)_2NNHOH \xrightarrow{-H_2O} \mathbf{120} \rightarrow \mathbf{119} + ArCH{=}NNHCH_2Ar + (ArCH_2)_3N + ArCH_2OH + ArCH_3 \quad (95)$$

zylhydrazone (10%), and small amounts of tribenzylamine, toluene and benzyl alcohol.

H. Carbonyl Groups

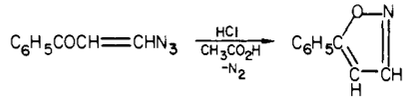
1. Anthranil and Isoxazole Formation

Thermolysis produced anthranils, e.g., **122** (2,1-benzisoxazoles), from 2-acylaryl azides, e.g., **121** (Table II), and simple isoxazoles (**123**) from (*Z*)-acylazidoalkenes (eq 96, 97).



(96)

121 122

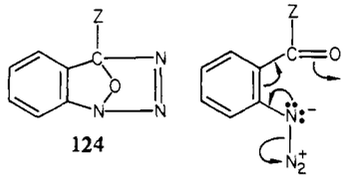


(97)

123

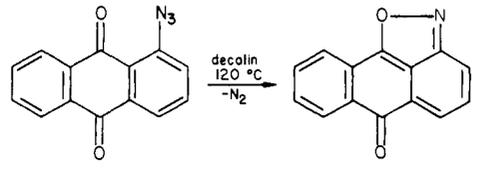
The reaction has been discussed in a review of anthranil chemistry[115a] and in other treatises on azido[71] and isoxazole derivatives.[116] A simple isoxazole (**123**) was first obtained from an acylazidoalkene in 1962.[117] In this section newer developments are described and reinterpretations of certain reports are offered.

Several features in common are found in the formation of anthranils and benzofuroxans (section II.G.1) from azides. These include the following: (1) nitrogen release was anchimerically assisted and probably concerted with product ring formation; (2) reaction efficiency correlated with coplanarity of the interacting groups; (3) preparative yields (Table II) have been typical.[75] Accordingly intermediate **124**[74] and process **125**[75] were proposed.



124 125

Anchimeric assistance in the release of nitrogen from a 2-acylaryl azide was revealed by an increase in the rate and/or a decrease in the temperature that was required for the thermolysis of phenyl azide, an arbitrary reference. A ranking order of aryl and acylaryl azides in decalin at 120 °C gave phenyl 1,α-naphthyl 4.3, β-naphthyl 2.8, 2-acetylphenyl 287, 2-acetyl-3-methylphenyl 5.1, 2-acetyl-6-methylphenyl 10.5, 2-pivaloylphenyl 61.7, and 1-azidoanthraquinone 7385; however, this order of activity remains unexplained.[75] It was claimed that intermediates related to **124** from 2-pivaloylphenyl azide and from 1-azidoanthraquinone (**126**; eq 98) were precluded by

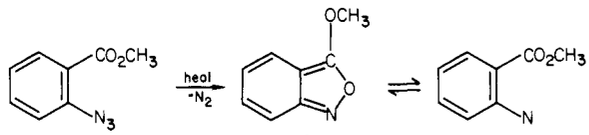


(98)

126 100%

steric inhibitions not operative in a pericyclic process defined by **125**.[75]

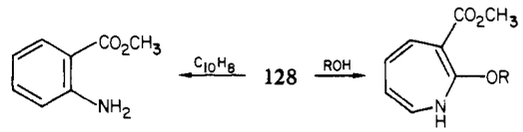
Although 3-alkoxyanthranils are unknown,[115b] it seems probable that 3-methoxyanthranil (**127**) was a precursor to the nitrene **128** (eq 99) when 2-methoxycarbonyl azide (**129**) was



(99)

129 127 128

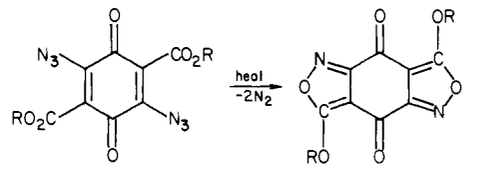
heated in either decalin or an alcohol. Hydrogen abstraction from the hydrocarbon accounted for the formation of methyl anthranilate;[75b,d] ring expansion and the addition of the alcohol accounted for the formation of an azepine (**130**; eq 100).[118]



(100)

130

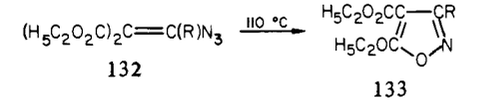
Several 2-acylphenyl azides were photolyzed into azepines.[119] An instability for 3-alkoxyanthranils hardly seems capatible with the formation of a bisisoxazole (**131**) from 2,5-diazido-3,3-bis(ethoxycarbonyl)quinone (eq 101).[120]



(101)

131

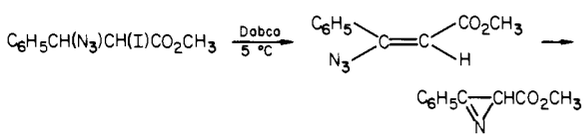
A high yield of a 3-alkyl-4-(ethoxycarbonyl)-5-ethoxyisoxazole (**133**) was obtained from an azidoalkylidenemalonic ester (**132**). Nitrogen evolution at 110 °C was considered indicative of anchimeric assistance (eq 102).[121] (E)-Methyl β-azidocinnamate



(102)

132 133

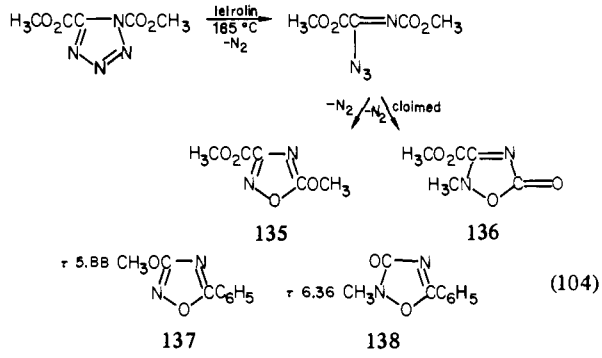
at 5 °C gave an azirine (**134**; eq 103).[122]



(103)

134

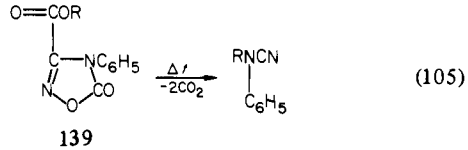
Instead of 5-methoxy-3-(methoxycarbonyl)-1,2,4-oxadiazole (**135**), thermolysis of 1,5-bis(methoxycarbonyl)tetrazole (eq 104)



(104)

137 **138**

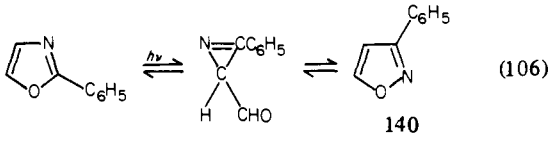
was reported to produce 2-methyl-3-(methoxycarbonyl)-Δ^3-1,2,4-oxadiazolin-5-one (**136**).[123] A unique nitrene insertion into an alkyl oxygen bond in an ester group was proposed. Product NMR values of τ 5.70 and 5.90 (reported as δ 5.70 and 5.90) are close to τ 5.88, reported for the methoxyl protons in 3-methoxy-5-phenyl-1,2,4-oxadiazole (**137**),[124] and τ 6.2 for methoxycarbonyl protons. Neither τ 5.70 nor τ 5.90 compares favorably with τ 6.36 reported for the *N*-methyl protons in 2-methyl-5-phenyl-Δ^4-1,2,4-oxadiazolin-3-one (**138**).[124] An elimination of carbon dioxide from the 3-methoxycarbonyl substituent in **135**, a preferred assignment, to account for *m/e* 114 (P – CO_2)[123] can be seen as comparable to the thermal elimination of one of the 2 mol of carbon dioxide from 3-(alkoxycarbonyl)-4-phenyl-Δ^2-1,2,4-oxadiazolin-5-one (**139**) (eq 105).[125,126]



(105)

139

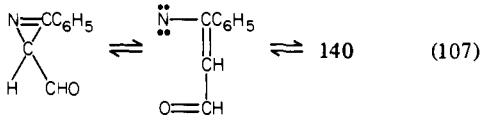
A formal relationship between the formation of an isoxazole (**123**) from an azido ketone via an intermediate acylazidoalkene (eq 97) and the photoisomerization of an oxazole (eq 106) is



(106)

140

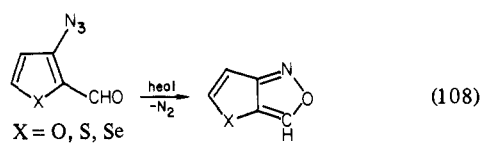
seen in the hypothetical equilibrium (eq 107) between acyl-



(107)

azirine and a nitrene. A recent review of the photochemistry of heterocycles includes the inefficient reversible photoisomerization of an oxazole into an isoxazole, presumably via an azirine.[127]

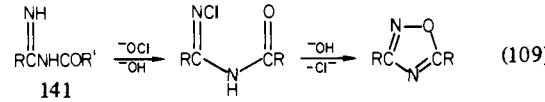
Fusion of the 2,1-isoxazole ring onto a furan, thiophene, and selenophene ring has been achieved (eq 108).[126] A compa-



(108)

rable fusion of furoxan and thiophene rings is found in section II.G.1 (eq 72).

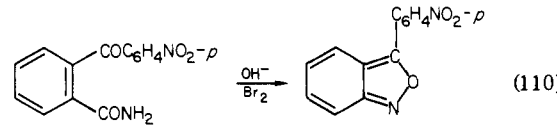
Oxidation of an acylenamine to create an isoxazole ring nitrogen–oxygen bond is apparently unknown; however, the closely related preparation of a 1,2,4-oxadiazole (eq 109) from



(109)

141

an *N*-acylamidine (**141**) and alkaline hypochlorite was recently reported.[129] A related treatment with hypbromite transformed *o*-(*p'*-nitrobenzoyl)benzamide (**142**) into 3-(*p'*-nitrophenyl)-anthranil (eq 110) without the necessity of isolating an assumed

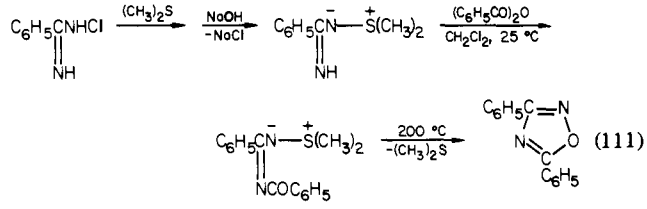


(110)

142

intermediate amino ketone.[115] A comparable reaction can be seen in section VI.C.2 (eq 350).

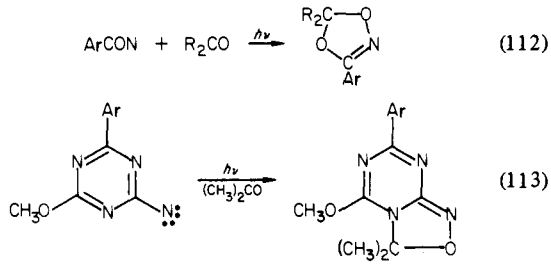
Another oxadiazole ring closure was discovered on heating neat the *N'*-benzoyl derivative **143** of *N*-benzimidoyl-*S*,*S*-dimethylsulfilimine (eq 111).[130]



(111)

143

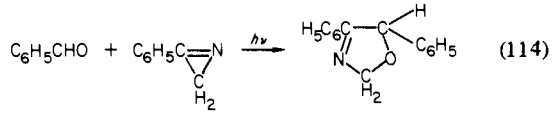
Heterocycles with nitrogen–oxygen bonding were generated from both aroyl azides and an azidotriazine by photolysis in the presence of a ketone (eq 112, 113).[131,132] Intermediate nitr-



(112)

(113)

enes were presumed, but a differentiation between product formation with or after this formation was not clear. On the other hand, irradiation of a mixture of benzaldehyde and 2-phenylazirine gave 4,5-diphenyloxazoline (eq 114).[133] Neither



(114)

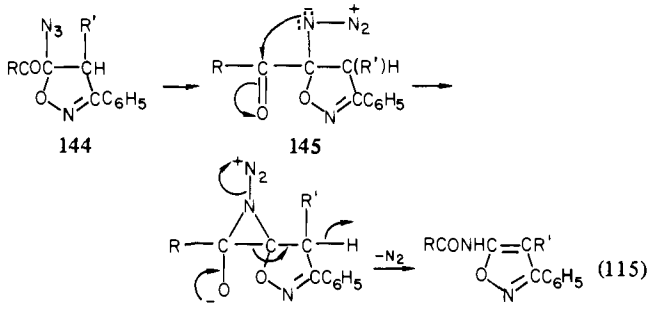
a vinylnitrene nor 3,5-diphenylisoxazoline was invoked as an intermediate.

A bonding interaction between the carbonyl oxygen and azido nitrogen atoms was recognized but not formally proposed to account for an energy transfer to the azido group by irradiation (365 nm) of ω-azido-*n*-alkanoylbenzenes, $C_6H_5CO(CH_2)_nN_3$. The transfer occurred with a decrease in the rate constant of an order of magnitude as each methylene unit between $n = 3$ and 5 was added. It was suggested that the rate decrease correlated with the size of a ring required to bring the carbonyl and azido groups close together.[134]

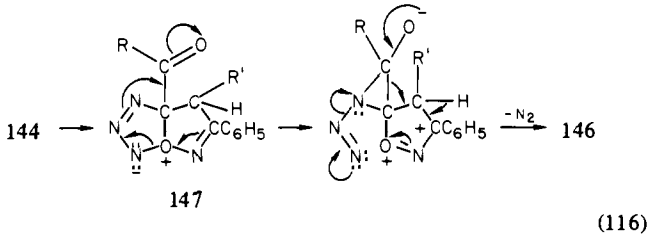
2. α-Azidocarbonyl Rearrangement

A rarely encountered migration of an acyl group from carbon to nitrogen occurred in the thermolysis at 100 °C of the azide **144** into an isoxazole, **146** (eq 115). Anchimeric assistance in the evolution of nitrogen was supported by activation pa-

rameters and was accounted for by a nucleophilic attack by nitrogen upon the nearby carbonyl carbon atom either simultaneously with or subsequent to cleavage of an azido N_1–N_2 bond (eq 115).[135] Initial nitrogen–oxygen bonding from a nucleophilic attack by the heterocyclic oxygen atom upon the latent nitrene nitrogen atom of the azido group can also account for the product **146** (eq 116).

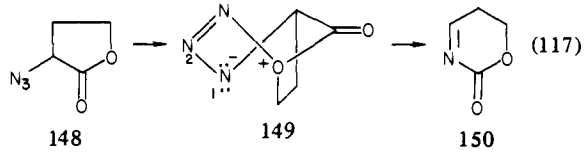


(115)



(116)

Another migration of an acyl group from carbon to nitrogen was encountered in a photolysis of the α-azido γ-lactone **148** into a ring-enlarged acylimine (**150**; eq 117).[136] An explanation

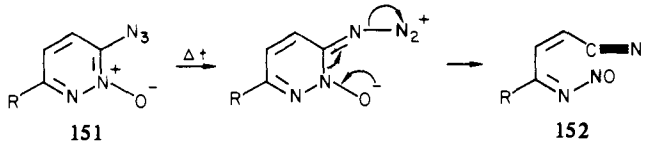


(117)

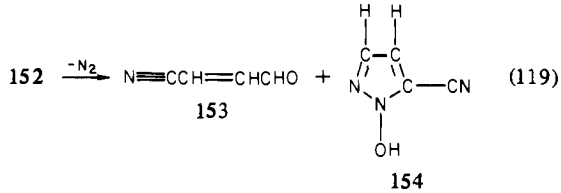
for this quantitative reaction was not offered, but enhanced acyl migration can be attributed to initial bonding between nitrogen and the lactone ring oxygen atom (eq 117). In conformations available to proposed intermediates **145**, **147**, and **149**, antiperiplanar N_1–N_2 and C–CO bonds may facilitate bonding between the electron-rich nitrogen (N_1) and the carbonyl carbon atoms. A related rationale for an acid-catalyzed decomposition of an alkyl azide has been proposed.[137]

I. Amine Oxide Groups

Thermolysis of 3-azidopyridazine 2-oxide (**151**) in refluxing toluene gave β-cyanoacrolein (**153**) and 1-hydroxy-5-cyanopyrazole (**154**; eq 118, 119).[136,139] In a similar manner azide



(118)



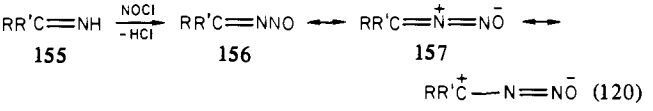
(119)

151 (R = OCH_3) gave *cis*-β-cyanoacrylate but azide **151** (R = Cl, gave maleonitrile, apparently by an elimination of nitrosyl chloride from intermediate **152** (R = Cl).[136,139]

TABLE III. Thermolysis of Azides 164 into Pyrroles 167

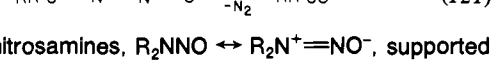
compd designator	a	b	c	d	e	f
substituent	H	CH_3	CH_3	CH_3	CH_3, CH_3	Cl
position in 164		4	5	6	4, 6	5
position in 167		3	4	5	3, 5	4
yield, %	90	44	59	74	65	82

The contraction of a nitrosimine (**152**) into a carbonyl compound (**153**) is an example of a recently developed reaction.[140] Each of nine nitroso ketimines **156**, from an imine (**155**) and nitrosyl chloride at −10 °C (eq 120) readily fragmented into a



(120)

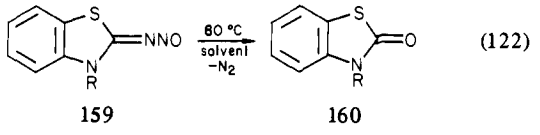
ketone and nitrogen (eq 121).[136,139] Their IR spectroscopy and



(121)

analogy with nitrosamines, $R_2NNO \leftrightarrow R_2N^+{=}NO^-$, supported contributions from 1,3- and 1,4-zwitterionic structures **157** and **158**.

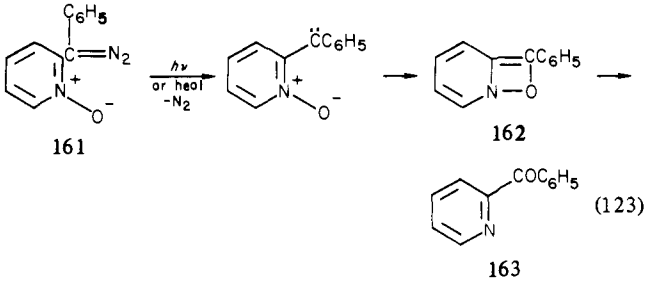
Crossover experiments with doubly labeled (^{18}O and R = CH_3) and unlabeled 2-(nitrosimino)benzothiazoline **159**, R = H, were believed to require thermolysis into a 2-benzothiazolone (**160**; eq 122) to be intermolecular.[141] The possibility of interchange



(122)

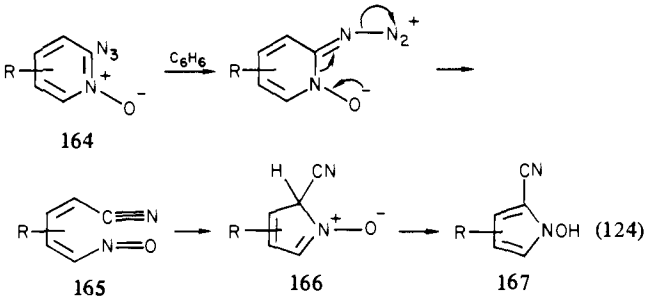
of nitroso groups prior to fragmentation was not evaluated in the brief preliminary report.

Nearly quantitative yields of 2-benzoylpyridine (**163**) were obtained from 2-(α-diazobenzyl)pyridine 1-oxide (**161**) by direct or sensitized photolysis in methanol or in benzene or by thermolysis in benzene or in decalin (eq 123). An oxazetine intermediate (**162**) was recognized[142] and proposed.[143]



(123)

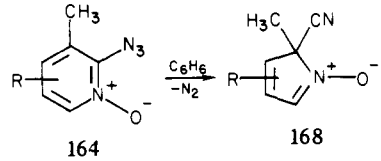
Thermolysis of 2-azidopyridine *N*-oxides (**164**) in refluxing benzene gave 2-cyano-1-hydroxypyrroles (**167**) in good yields (eq 124 and Table III), and a similar reaction gave 2-cyano-1-



(124)

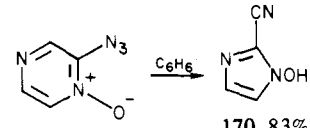
hydroxyimidazole (**170**) from 2-azidopyrazine 1-oxide (**169**; eq 126).[144] The sequence (1) thermal elimination of nitrogen from an azido group concerted with ring opening followed by (2)

ring-closure elimination of nitrogen and tautomerization into product pyrrole or imidazole was proposed to account for the reactions (eq 124). 2,2-Disubstituted pyrrole 1-oxides (**168**) were isolated when a rearrangement into a pyrrole was not available (eq 125).[144]



(125)

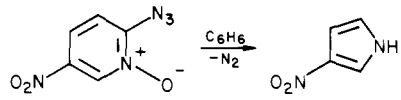
164 168



(126)

169 170, 83%

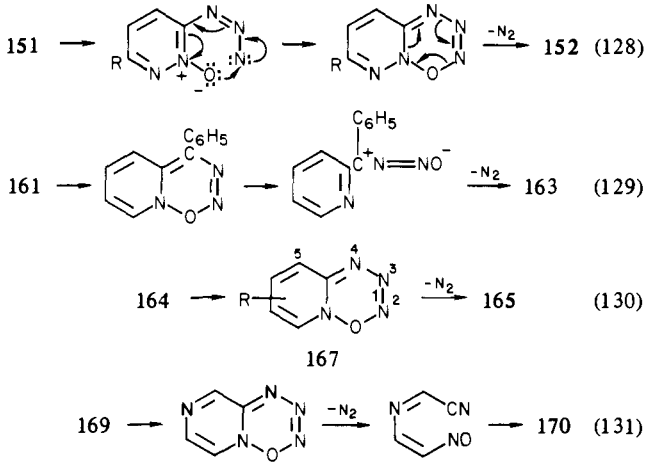
No products were identified in the tar obtained from the azides **164** (R = 3- or 4-NO_2). The formation of 3-nitropyrrole (**172**) but none of its 1-hydroxy derivative from azide **171** (eq 127) was not fully accounted for.[144]



(127)

171 172

These common features for eq 118, 123, 124, and 126 can be recognized: (1) a nucleophilic attack on the latent nitrene nitrogen of an azido or a diazoalkane group by the nearby amine oxide oxygen atom, (2) an electrocyclic opening of an intermediate tri- or tetraazapyran derivative, and (3) loss of molecular nitrogen (eq 128–131). It appears that steps 2 and



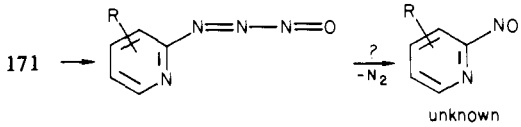
(128)

(129)

(130)

(131)

3 can be concerted with an opening of the azine ring (eq 128, 130, and 131) or that step 2 in a ring-chain tautomerization will complete a transfer of oxygen from an azine nitrogen to a diazo (eq 129) or azido nitrogen atom to be followed by a collapse of (a) the diazo oxide into a carbonyl compound (eq 129) or (b) the azido oxide into a nitroso compound (eq 132) (sections

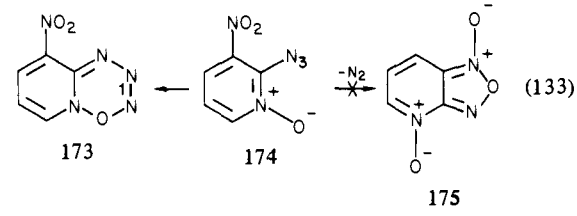


(132)

unknown

II.G.2, eq 83, and II.I, eq 121). One investigator recognized the explanation (eq 129), modified to accommodate a four-membered oxazetine ring intermediate (**162**) but judged it deficient insofar as it appeared to require (by analogy with eq 128, 130, and 131) opening of the pyridine ring, for which there was no evidence.[142]

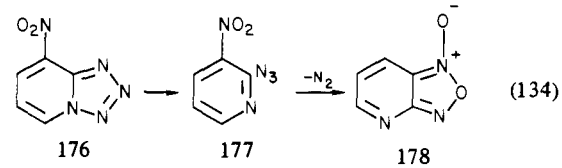
An investigation may have provided support for an intermediate tetraazapyran (**173**) in an interesting way. Thermolysis of 3-nitro-2-azidopyridine *N*-oxide (**174**) failed to poduce pyridofuroxan *N*-oxide (**175**),[144] a product expected to be stable. This is persuasive evidence that its interaction with the amine oxide oxygen discouraged an interaction between the azido group and the adjacent nitro group (eq 133). For comparison,



(133)

173 174 175

8-nitropyridotetrazole (**176**) at 170 °C presumably reacted as the azide **177** and reproducibly gave pyridofuroxan (**178**) nearly quantitatively (eq 134),[145] although there is an unsupported

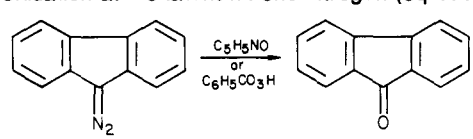


(134)

176 177 178

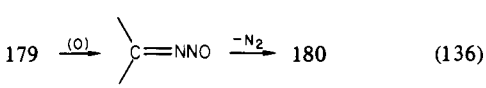
claim to a very low efficiency.[96]

Although there is no example of an intermolecular oxidation at an azido nitrogen by an amine oxide or by a peroxide, diazofluorene (**179**) has been oxidized by pyridine *N*-oxide,[146,147] perbenzoic acid,[148] and superoxide[148] into fluorenone (**180**; eq 135). Oxidation at the latent nitrene nitrogen (eq 136) as well



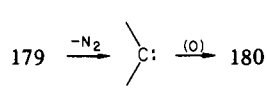
(135)

179 180



(136)

as at the hypothetical intermediate carbene center (eq 137)[147] should be considered.

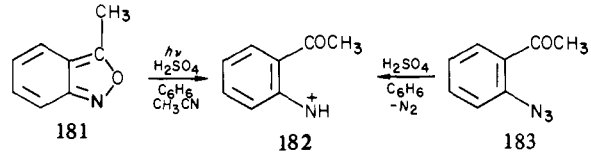


(137)

III. Positive Nitrogen Derivatives

A. Nitrenium Ions

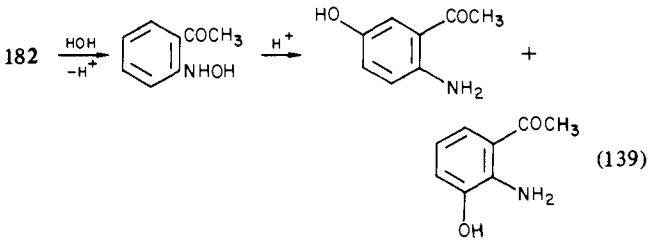
A ground-state singlet nitrenium ion (**182**) was generated by the photolysis of 2-azidoacetophenone (**183**) or 3-methylanthranil (**181**) in the presence of sulfuric acid and benzene in acetonitrile (eq 138) and was trapped directly by nucleophiles.



(138)

181 182 183

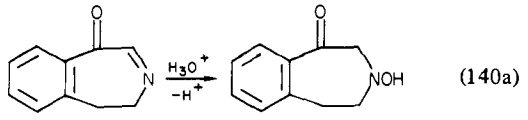
Rearrangement of an intermediate hydroxylamine accounted for the formation of mixtures of 3- and 5-hydroxy-2-aminoacetophenone (eq 139) along with anilinoacetophenone and 9-methylacridine. The hydroxylamino- and anilinoacetophenones were also obtained from the azide in benzene and ice-cooled concentrated sulfuric acid.[149]



(139)

B. Dipolar Compounds

Nucleophilic attack at nitrogen in the conjugated group, O=C—C=N— ↔ ⁻O—C=C—N⁺, was encountered in the unconfirmed hydration of compound **184** into the hydroxylamine **185**[150,151] (eq 140a). Other examples of nucleophilic attack

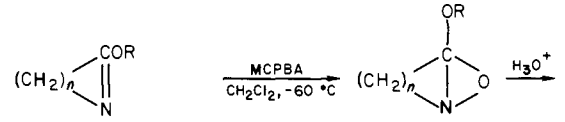


(140a)

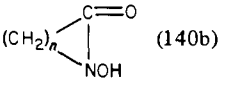
184 185

at an electron-deficient nitrogen atom in a conjugated group have been reported.[152a-k]

Hydroxylamines have also been produced in low yield from oxaziridines by peracid hydrolysis (eq 140b).[152l]



$n = 5$
R = CH_3, $CH_2CH=CHC_6H_5$

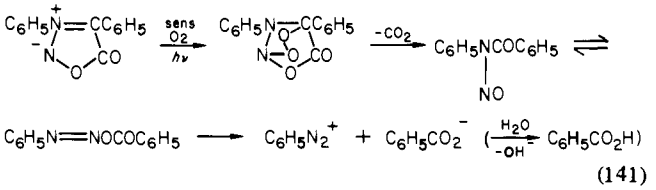


(140b)

3-13%

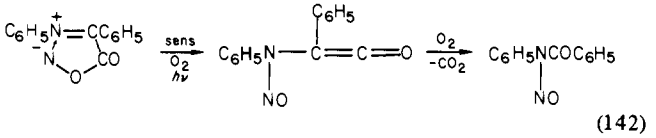
Stable adducts with increased nitrogen–oxygen bonding are unknown for 1,3-dipoles: a nitrile imine, diazoalkane, azide, nitrous oxide, azomethine imine, azimine, azoxy compound, carbonyl imine, and nitrosimine.[73,95] An inability for *N,C*-diphenylnitrilimine ($C_6H_5C^+{=}NN^-C_6H_5$) to give a sensitized reaction with singlet oxygen was recently observed.[153]

A formation of benzoic acid was accounted for by invoking a sensitized 1,3-dipolar photooxygenation of 3,4-diphenylsydnone followed by an elimination of carbon dioxide, rearrangement of *N*-nitrosobenzanilide (section IV.A) and hydrolysis of a diazotate ester (eq 141);[153] however, an alternative route



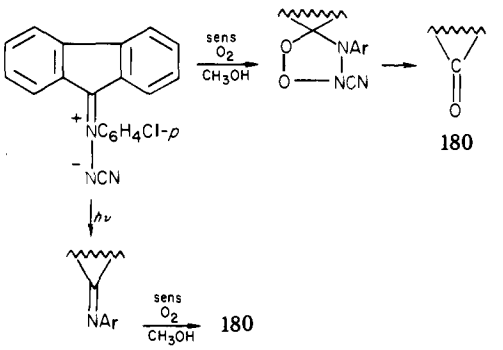
(141)

to the intermediate *N*-nitrosebenzanilide by a photooxygenation of a ketene (an open-chain isomer of the sydnone) and loss of carbon dioxide (eq 142) could also be considered.



(142)

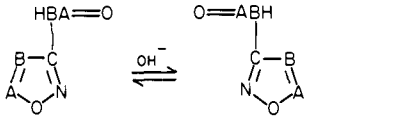
The authors reported the formation of fluorenone from the sensitized photooxygenation of *C*-biphenylene-N^{α}-(4-chlorophenyl)-N^{β}-cyanoazomethine imine (eq 143) and proposed the formation and dissociation of an intermediate 1,3-dipolar adduct



180 (143)

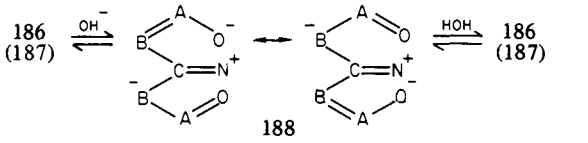
with singlet oxygen to account for it. In an alternative explanation (eq 143), the authors recognized the likely photofragmentation of an azomethine imine into an anil which, it was assumed, underwent sensitized photooxygenation into fluorenone, a reaction apparently unsupported by an established example (section VIII.E describes a related reaction of oximes). The overall reaction (eq 143) is reminiscent of the formation of fluorenone from diazofluorene and a peroxide reagent (section II.I).

Intermediate **188** accounted for the degenerate isomerization of 3-acetylamino-5-methyl-1,2,4-oxadiazole (**186**; eq 144, 145)[154a-d] and anticipated a similar characteristic for a 3-(ni-



(144)

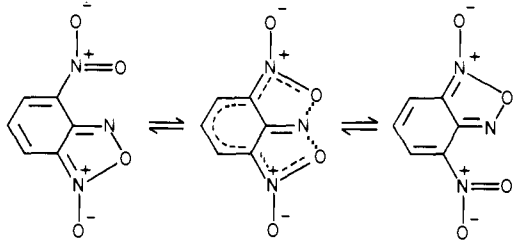
186, A = CR; B = N
187, A = N^+O^-; B = CR



(145)

188

troalkyl)-4-alkylfuroxan (**187**). Thermolysis of 4-nitrobenzofuroxan (**189**) also revealed a degenerate isomerization (eq 146)[155]



(146)

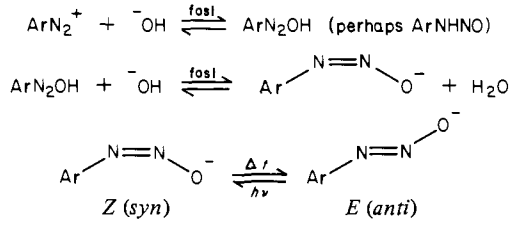
189 190 191

dependent on an intermediate **190** with an electron-deficient nitrogen atom.

Related transformations of furoxans into isoxazoles are known (section IV.G).

C. Diazonium Ions

A discussion of general properties and reactions included a description of the complex diazotate equilibria (eq 147) and related chemistry.[60c]



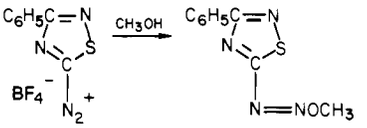
(147)

Z (*syn*) E (*anti*)

TABLE IV. Furazans 227 from Azides 224 via Phospholes 225

224, R	225 yield, %	227 R	227 yield, %
H	77	H	65
6-CH_3	81	4-CH_3	50
5-CH_3	35	5-CH_3	32
4-CH_3	42	5-CH_3	46
4-OCH_3	59	5-OCH_3	44

Coupling between an aryldiazonium cation and an oxygen-centered nucleophile has rarely produced a stable derivative of a nitrogen–oxygen covalent bond. The formation of diazo ethers **193** from thiadiazole-3- and 5-diazonium salts (**192**) remain exceptional reactions (eq 148)[158] (see Table IV).



(148)

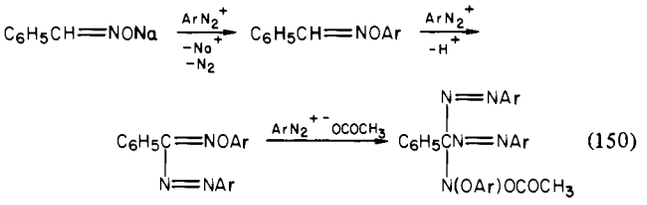
192 193

R = CH_3, 98%
R = C_2H_5, 95%
R = t-C_4H_9, 79%

An arylazo ether[157] from formaldoxime and an arenediazonium salt (eq 149) was apparently intended to be an inter-

$$CH_2{=}NOH \xrightarrow[-H^+]{ArN_2^+} CH_2{=}NON{=}NAr \xrightarrow{-N_2} CH_2{=}NOAr \quad (149)$$

mediate since other reports[158] from the senior author and from others revealed arylation at an oxime oxygen (also claimed in the patent) and azoarylation at oxime carbon (eq 150).



(150)

The nature of the interaction between a diazonium cation and an oxygen-centered nucleophile is incompletely understood. An initial charge transfer (eq 151) between a p-nitrobenzenedi-

$$p\text{-}O_2NC_6H_4N_2^+ + (CH_3)_2SO \rightleftharpoons p\text{-}O_2NC_6H_4N{=}N{-}O{-}S^+(CH_3)_2$$

$$p\text{-}O_2NC_6H_4N_2^+ + {}^-OH \xrightarrow[H_2O]{Me_2SO} ArN_2^+ \cdot {}^-OH \rightleftharpoons ArN_2OH \quad (151)$$

azonium cation and dimethyl sulfoxide (Me_2SO) was supported by absorption between 310 and 440 nm in addition to the maxima at 310 and 259 nm found for water solutions.[159] A similar interpretation was given to potentiometric redox titrations in aqueous Me_2SO for the same equilibrium mixture.[160] Typical fates of the complex included reaction with solvent, formation of a covalent bond at oxygen, and/or giving up nitrogen.[161]

A recent analysis of ^1H CIDNP for reactions between benzenediazonium tetrafluoroborates and oxygen-centered nucleophiles (eq 152) revealed polarization originating in the rad-

$$ArN_2^+ \xrightarrow{RO^-} ArN{=}NOR \xrightarrow{RO^-} \underset{\mathbf{194}}{ArN{=}NO^-}$$

$$\mathbf{194} + ArN_2^+ \rightleftharpoons \underset{\mathbf{195}}{ArN{=}NON{=}NAr} \quad (152)$$

ical pair, $ArN_2{\cdot}{\cdot}ON_2Ar$, where Ar is C_6H_5, o- and p-$O_2NC_6H_4$, and 2,4-$(O_2N)_2C_8H_3$. An absence of radical pairs, $ArN_2{\cdot}{\cdot}OR$, in reactions with sodium acetate (R = CH_3CO) and sodium phenolate (R = C_6H_5) was implied by the failure to detect CIDNP known to occur in the reaction products from acetoxy and phenoxy radicals. An analysis of g factor differences according to Kaptein's rules lent support for the precursor to the products (benzene, nitrobenzene, and m-dinitrobenzene) to be $ArN_2\cdot$ and $ArN_2O\cdot$ (eq 153) rather than the hypothetical pair Ar· and $ArN_2O\cdot$.[162]

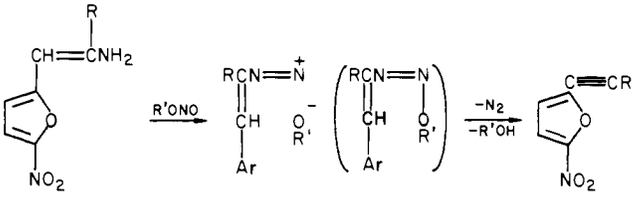
$$\mathbf{195} \rightleftharpoons ArN_2\cdot \cdot ON{=}NAr \xrightarrow[-N_2]{H\cdot} ArH + ArN_2OH \ (\xrightarrow{-H^+} \mathbf{194})$$

$$Ar = C_6H_5,\ o\text{- and } p\text{-}O_2NC_6H_4,\ 2,4\text{-}(O_2N)_2C_6H_3$$

$$RO^- = HO,\ CH_3O,\ CH_3CO,\ C_6H_5O \quad (153)$$

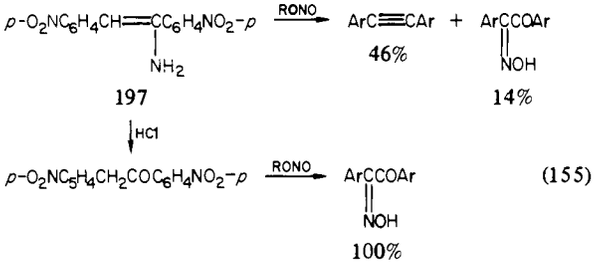
Benzenediazonium tetrafluoroborates also reacted with hydroxide anions on anionic resins. Ion exchange with the p-nitrobenzenediazonium salt brought about fixation of the diazotate anion, another species capable of accounting for diazo coupling, and presumably the diazo anhydride **195** on the resin.[163]

Other investigators have assumed the intermediacy of both a diazonium (ionic) and a diazo species (covalent) in diazonium coupling reations. The assumption was extended to a deamination of certain primary α,β-disubstituted vinylamines, e.g., the nitrofuryl- (**196**) and nitrophenylenamine (**197**), by a nitrite ester (eq 154, 155).[164]



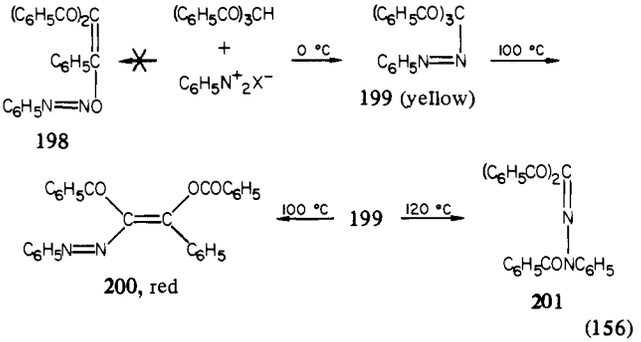
196 40–90%

(154)



(155)

A 1908 O-azo assignment (**198**) to the structure of the initial coupling product from the benzenediazonium ion and tribenzoylmethane was corrected in 1962 to a C-azo compound (**199**) (eq 156). It was advised that other O-azo compounds



(156)

in the literature be reinvestigated for the probable correction to C-azo structures.[165] Thermal isomerization into azo compound **200** and hydrazone **201** occurred (eq 156).

IV. Rearrangement and Framentations

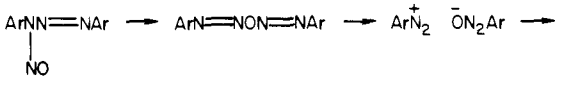
A. N-Nitroso-1,3-diaryltriazenes and N-Nitrosophenylhydrazones

An accepted sequence initiated by a rearrangement of *N*-nitrosoacetanilide into benzenediazonium acetate followed by the formation and dissociation of benzene diazo anhydride (eq 157)[166] was extended to *N*-nitroso-1,3-diaryltriazenes (**204**) (eq

$$\underset{\text{NO}}{C_6H_5NCOCH_3} \rightarrow \underset{\mathbf{202}}{C_6H_5N{=}NOCOCH_3} \rightleftharpoons \underset{\mathbf{203}}{C_6H_5N_2^+\ {}^-OCOCH_3}$$

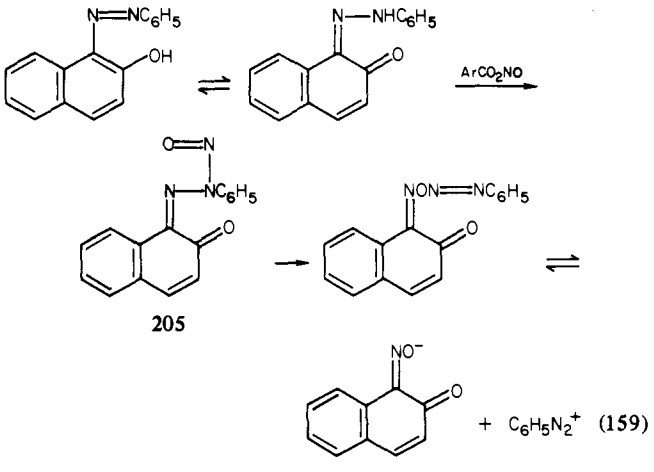
$$\mathbf{202} + \mathbf{203} \xrightarrow{-(CH_3CO)_2O} C_6H_5N_2ON_2C_6H_5 \xrightarrow{-N_2} C_6H_5N_2O\cdot + C_6H_5\cdot \quad (157)$$

158)[167] and to *N*-nitrosophenylhydrazones (**205**, eq 159).[166] By



204

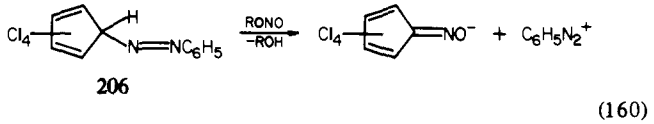
$$\text{Ar}\cdot + \text{ArN}_2\text{O}\cdot + \text{N}_2 \quad (158)$$



205

$$+ C_6H_5N_2^+ \quad (159)$$

design the latter provided an additional route to benzenediazonium ions. It may become equally important that the scheme also brought about the rarely encountered transformation of a hydrazone into an oxime by directly replacing a nitrogen atom with an oxygen atom (section IX). These changes resulted from nitrosating 1-phenylazo)-2-naphthol and related compounds, e.g., **206** (eq 160), capable of tautomeri-

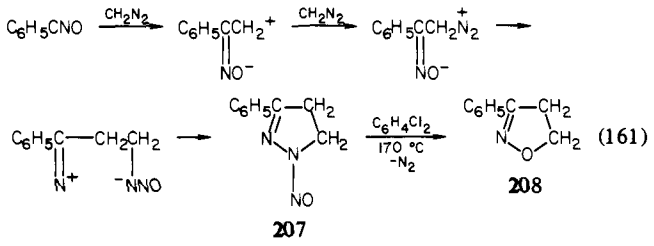


206

(160)

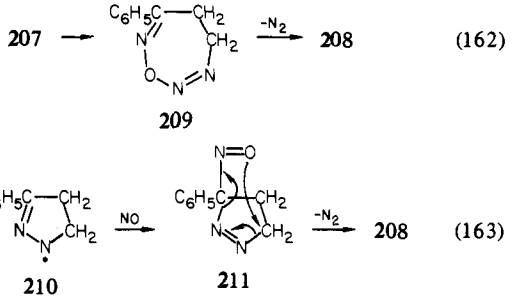
zation between azo and hydrazone forms.

A nitrogen–nitrogen bond was replaced by a nitrogen–oxygen bond in an earlier thermolysis of 1-nitroso-2-aryl-Δ^2-pyrazolines (**207**) into 3-aryl-Δ^2-isoxazolines (**208**; eq 161), presumably via



207 **208** (161)

the intermediate **209** or **210**, **211** (eq 162, 163).[169]

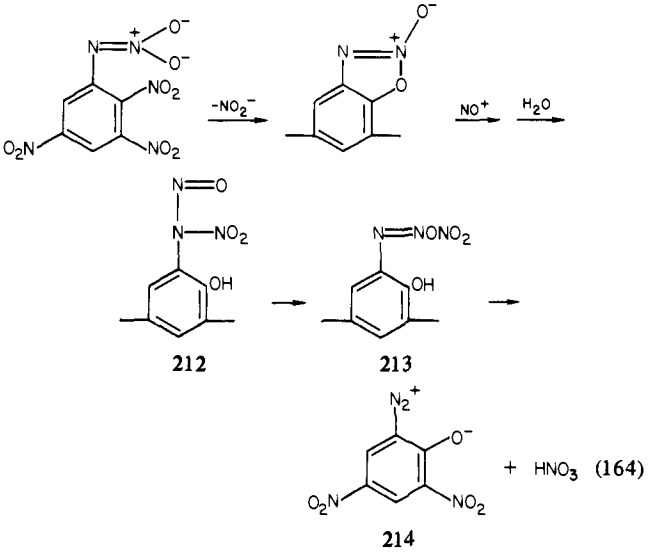


209 (162)

210 **211** (163)

B. N,o-Dinitroanilines

An examination of a series of nitroanilines led to the discovery of the formation of 4,6-dinitro-2-diazophenol (**214**; 65%) from 3,5-dinitoraniline and a mixture of 70% nitric acid and 98% sulfuric acid. A similar reaction at 0 °C produced 2,3,5-trinitrophenylnitramine, assumed to be an intermediate in the former reaction since it was transformed into the diazophenol **214** at the higher temperature (eq 164). It was ten-



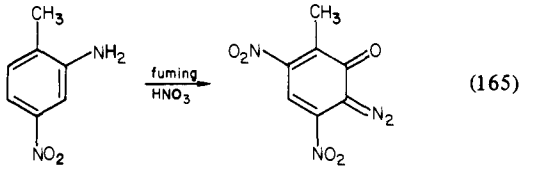
212 **213**

214

(164)

tatively suggested that the diazo function was introduced by a rearrangement of an *N*-nitroso-*N*-nitroaniline (**212**) into a diazonitrate (**213**).[170]

An earlier claim for the formation of 2-amino-4,6-dinitrotoluene from 2-methyl-5-nitroaniline and fuming nitric acid was recently shown to be incorrect. An identification of the product as 2-diazo-4,6-dinitro-3-methylphenol (eq 165) recognized the



(165)

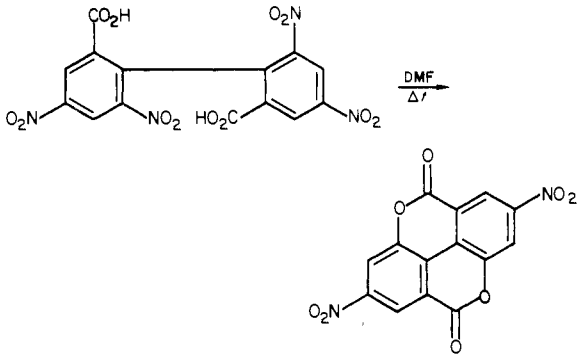
possibility that its formation involved a nitroamine intermediate with subsequent changes entirely analogous to those described in eq 164.[171]

Support for an internal nucleophilic displacement of a nitro group was found in the thermal transformation of 4,4′, 6,6′-tetranitrodiphenic acid into 2,7-dinitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-dioxapyrene (eq 166).[171]

An internal displacement of an aromatic nitro group by an oximate anion to produce a six-membered heterocycle has been postulated.[171]

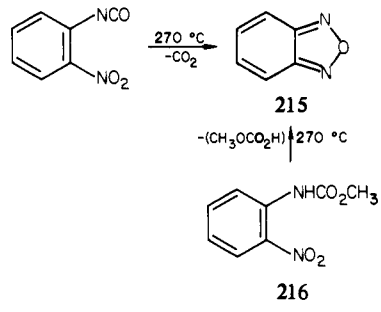
C. o-Nitro-N-acylanilines

Although o-nitrophenyl isocyanate gave benzofurazan **215** upon thermolysis, a low yield precluded its intermediacy in the



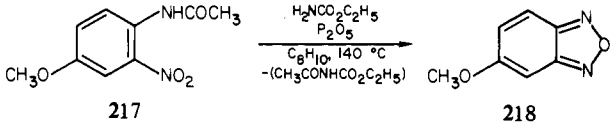
(166)

thermolysis of o-nitrophenyl carbamate **216** into the furazan (eq 167).[172] The latter, in minor modification, was a rediscovery



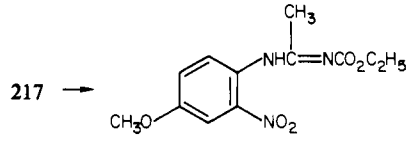
(167)

of a method first observed in the preparation of 5-methoxybenzofurazan (**218**) from 2-nitro-4-methoxyacetanilide (**217**), urethan, and phosphorus pentoxide in refixing xylene (eq 168).[173]



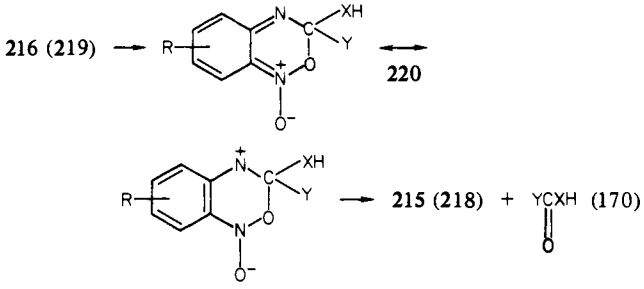
(168)

With the assumption that a condensation between the amide **217** and urethan produced the intermediate **219** (eq 169), the



(169)

transformations of **216** and **217** into furazans **215** and **218** are proposed to proceed via intermediate **220** (eq 170). There is

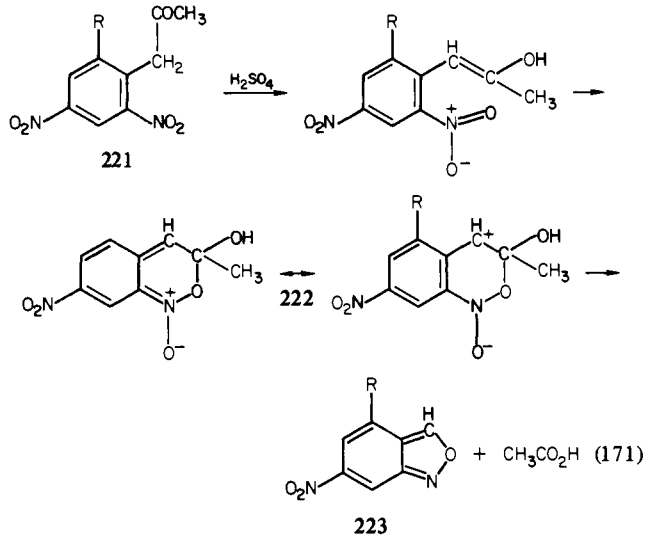


(170)

R = H; X = O; Y = OCH_3
R = 7-OCH_3; X = $NCO_2C_2H_5$; Y = CH_3

an interesting comparison between eq 170, 171 and 173 in the next section, IV.D.

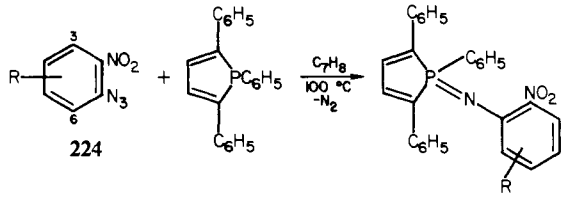
An anthranil preparation probably proceeded by a related mechanism with compound **222** as a proposed precursor to a 6-nitroanthranil (**223**) when a 2,4-dinitrophenylacetone (**221**) was heated in sulfuric acid (eq 171).[174]



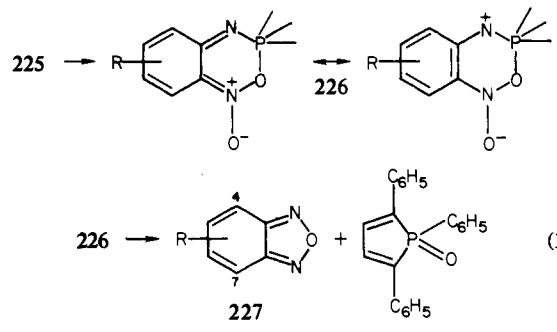
(171)

D. 1-(*o*-Nitroarylimino)-1,2,5-triphenylphospholes

Thermolysis of a 1-(o-nitroarylimino)-1,2,5-triphenylphosphole (**225**) at 150 °C in mesitylene gave the corresponding benzofurazan **227** in 32–65% yields (eq 173)[175] (see Table IV). A proposed intramolecular electrophilic attack by oxygen of the nitro group upon the nearby phosphorus atom (eq 172) was



(172)

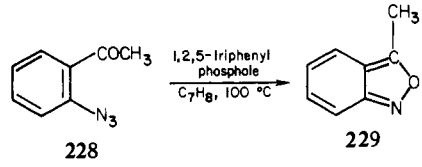


(173)

enhanced by electron release from appropriate substituents and by a relief in strain as phosphorus with a tetrahedral configuration in **225** became pentacoordinate with a trigonal-bipyramidal configuration in **226**.

The elimination (eq 172) has not differentiated between concerted and stepwise mechanisms; at this time, however, there is no evidence to support the intermediacy of an (o-nitrosoaryl)nitrene (compare eq 170).

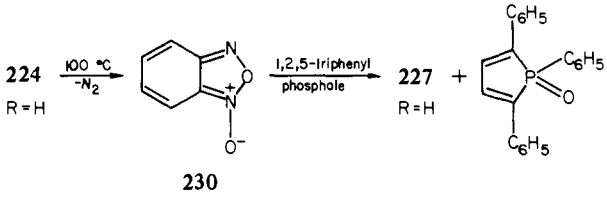
An unsuccessful attempt to obtain a phospholimine by heating o-azidoacetophenone (**228**) with 1,2,5-triphenylphosphole (eq 174) was attributed to an unfavorably competitive



(174)

thermal transformation of the azide **228** into anthranil **229**, the only product isolated; however, experimental detail was not reported. In contrast, the phosphole **225** was obtained from o-nitrophenyl azide **224** (R = H), apparently without competition from a thermal transformation into benzofuroxan **80**. The relative rates appear to fall into the descending order: eq 172 > eq 66, X = H > eq 96, R = R′ = H > phospholimine formation from **228**.

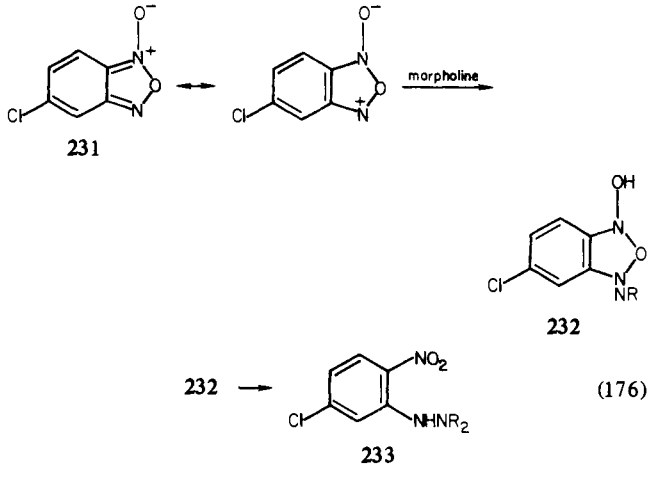
The possibility that benzofurazan **227** was produced from **224** by deoxygenation of an intermediate benzofuroxan **230** was eliminated by independent investigations (eq 175).



(175)

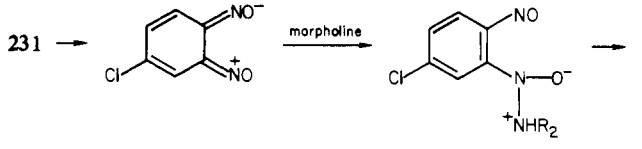
E. Nitro Compounds by Furoxan Ring Cleavage

A remarkable method for obtaining 2-nitroarylhydrazines (eq 176) was discovered in a reaction between a benzofuroxan and



(176)

a secondary aliphatic amine, e.g., a mixture of 5-chlorobenzofuroxan **231** and morpholine stored for 4 days at 0 °C gave 5-chloro-2-nitro-*N*-morpholinoaniline **233** (50%). It was suggested that the secondary amine attacked the lesser substituted furoxan nitrogen atom in an example of ring opening of a benzofuroxan to give a nitro compound.[176,177] Attack by the amine after ring opening into a pseudodinitrosobenzene structure is shown as an alternative route to the product (eq 177).

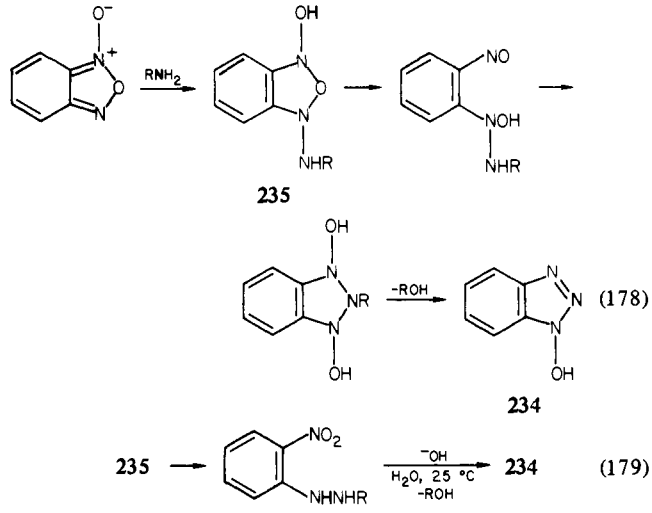


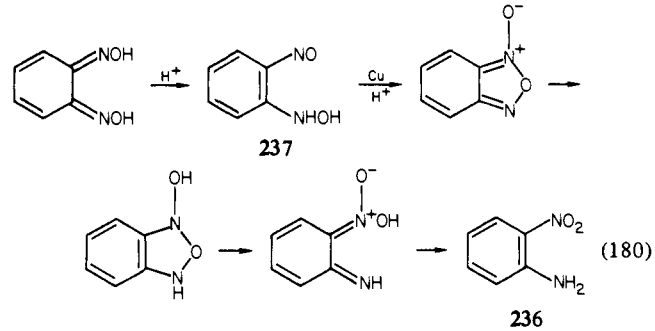
(177)

At higher temperature a 4- or 5-aminobenzofurazan was produced.[176,177]

An absence of formation of an o-nitrophenylhydrazine when ammonia or a primary amine replaced the secondary amine in eq 176 appears implied.[176,177] Since alkali easily transformed o-nitrophenylhydrazine into 1-hydroxybenzotriazole (**234**; eq 179),[178] a diversion (eq 178) and/or an extension (eq 179) of eq 176 can be expected.

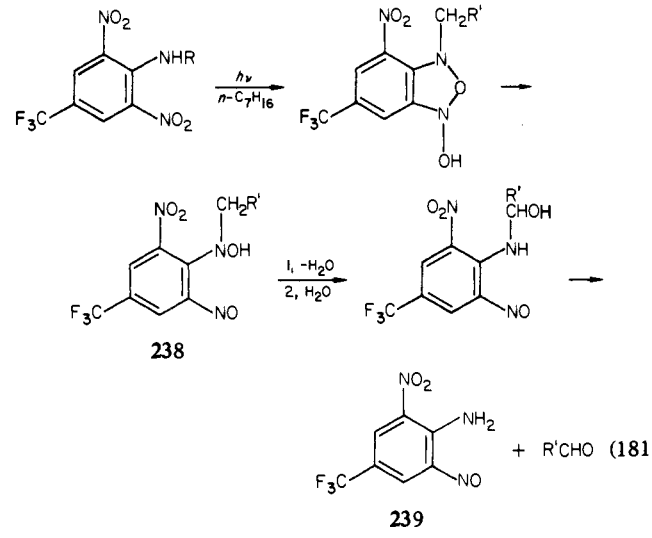
An oxygen atom transfer **231** → **232** → **233** appears related to an isomerization of the dioxime of o-benzoquinone into o-nitroaniline (**236**) and to the catalyzed transformation of benzofuroxan into the same product (**236**; eq 180).[106] An oxygen





atom transfer by ring closure of (o-nitrophenyl)hydroxylamine (**237**), ring opening, and tautomerization can be suggested for the formation of **236**.

Irradiation of *N*-alkyl-o-nitroanilines gave o-nitrosoarylamines **239** in low yield (eq 181).[179] The reaction was extended into

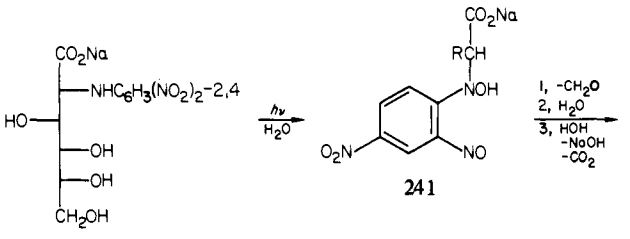


(181)

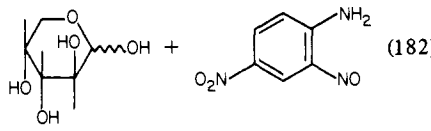
a photolytic conversion of 2-deoxy-2′-(2,4-dinitroanilino)-D-gluconate salts (**240**) in aqueous solution into 4-nitro-2-nitrosoaniline and D-arabinose (**242**; eq 182).[160] Oxidation–reduction intermediates **238** and **241** are proposed; compare eq 177 and 178.

F. Benzoisoimidazoles *N,N′*-Dioxides and Related Molecules

Benzofuroxan was converted into 2,2-dimethyl-2*H*-benzimidazole 1,3-dioxide (**243**; 86%) by treatment with 2-nitro-

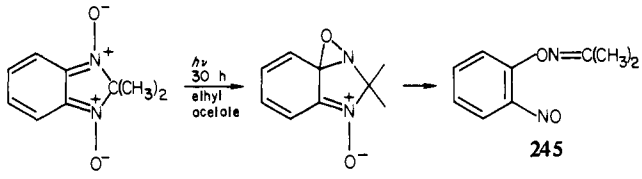


240 241



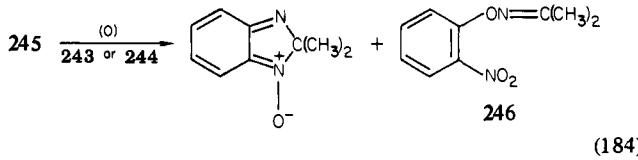
242 (182)

propane and triethylamine in chloroform. Under irradiation the dioxide **243** was changed into the *O*-(*o*-nitrophenyl)oxime **245** (21%) of acetone (eq 183). It was assumed that the *o*-



243 244 245 (183)

nitrosophenyl oxime **245** was produced by an isomerization of an intermediate oxaziridine **244** and subsequently was oxidized into the nitro compound **246** (eq 184). A small amount (10%)



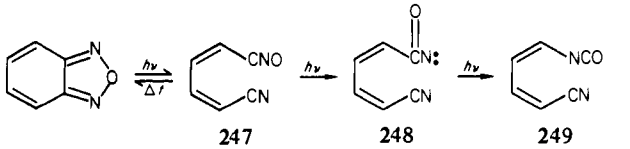
246 (184)

of 2,2-dimethyl-2*H*-benzimidazole 1-oxide was also produced.[161] This suggests that the source of oxygen for the last step could have been a dioxide **243** (or **244**) or air.

There is additional interest in the rearrangement **243** → **246** for its analogical support of a proposed isomerization of an aromatic nitro compound into nitrite ester (section IV.H).

G. Furazans and Furoxans

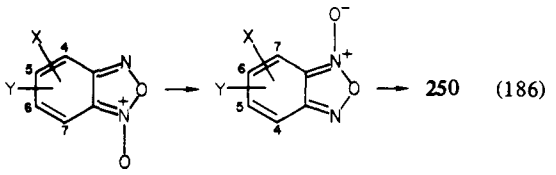
Irradiation (350 nm) reversibly isomerized benzofurazan in water into the mono-*N*-oxide **247** of muconononitrile and in hexane irreversibly into 1-isocyanato-4-cyanobutadiene (**249**) presumably via an acylnitrene (**248**; eq 185).[162] When triethyl



247 248 249 (185)

phosphite was present during irradiation, *cis*,*cis*-1,4-dicyanobutadiene was produced.[163]

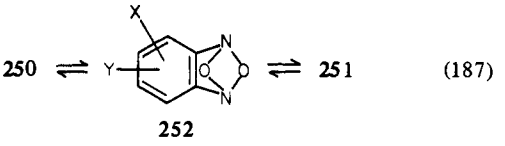
Unsymmetrically substituted benzofuroxans[70] and monocyclic furoxans[67] have each shown thermal tautomerization. Recently a photochemical interconversion of certain benzofuroxans was announced (eq 186).[184] Each of four derivatives **250a–d** gave an intermediate **251a–d** unreactive to oxygen and sufficiently stable at −150 °C for an electronic spectrum to be recorded. Each intermediate thermally reverted to itts original furoxan structure.



250a, X = 4-NO_2; Y = 7-Cl — 251a, X = 7-NO_2; Y = 4-Cl
b, X = 4-NO_2; Y = 5-Cl — b, X = 7-NO_2; Y = 6-Cl
c, X = 4-NO_2; Y = H — c, X = 7-NO_2; Y = H
d, X = 4-Br; Y = 5-OCH_3 — d, X = 7-Br; Y = 6-OCH_3

An interaction with the 4-nitro substituent was thought to provide assistance in the thermal isomerization **250** → **251**, but was not operative in the same isomerization brought about by irradiation.[164]

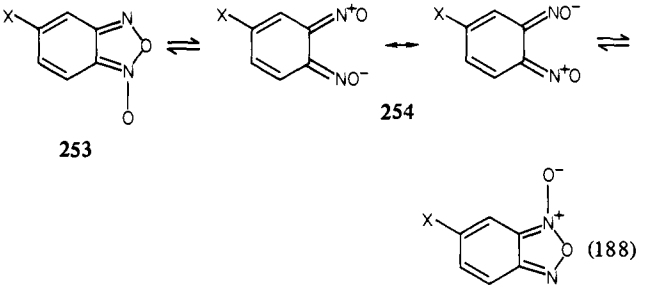
A revival of a four-membered-ring structure first proposed[185] in 1913 (eq 187) was implied for identification with an inter-



252 (187)

mediate (**252**) between benzofuroxans **250** and **251** but with the qualification that "it remains to be established whether this minimum is merely an artifact of the (CNDO/2) calculation method".[164]

A thermal tautomerization for 5-halobenzofuroxans (**253**) was more recently examined.[186] It was concluded that the reaction (eq 188) proceeded via a transition state of pseudo-*o*-di-

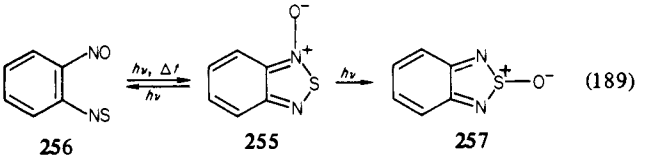


253 254 (188)

X = I, Br, Cl, F

nitrosobenzene **254**.[67] Calculations by Streitwieser's HMO method supported the intermediacy of **254** rather than a fully aromatic *o*-dinitrosobenzene which had received some attention[70] for a few years. Partially delocalized charges at appropriate positions of the carbocyclic ring provided a variation (**254**) called upon to account for reactions (not discussed here) between benzofuroxans and carbonyl compounds.[167]

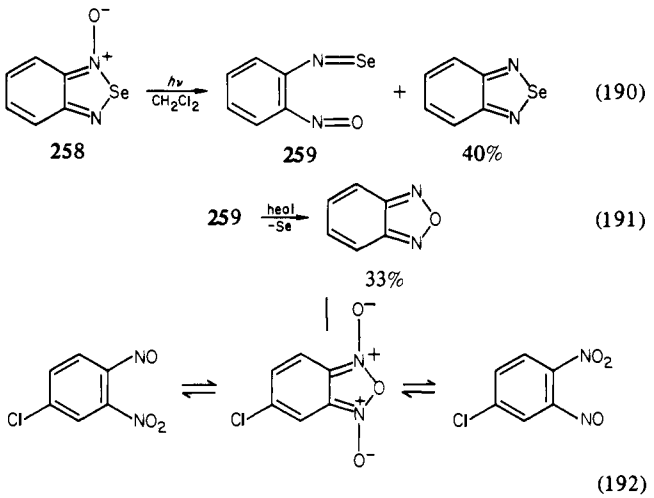
The behavior of benzo[*c*]-1,2,5-thiadiazole 2-oxide (**255**) under photolytic conditions offered reversibility (eq 189) with



256 255 257 (189)

2-thionitrosonitrosobenzene (**256**) and an irreversible isomerization (eq 189) into benzo[*c*]-2,1,3-thiadiazoline 1-oxide (**257**).[166] Photolysis of the corresponding benzo[*c*]-2,1,3-selenadiazole 2-oxide (**258**) in alcohol gave benzo furan (33%), benzo[*c*]-2,1,3-selenadiazole (40%) and selenium (eq 190, 191).[169]

A facile interconversion of 4- and 5-chloro-2-nitrosonitrobenzenes apparently depended on an interaction between adjacent nitro and nitroso groups (eq 192). An unidentified



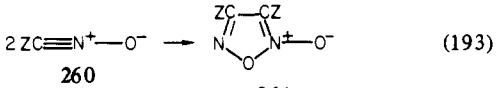
(190)

(191)

(192)

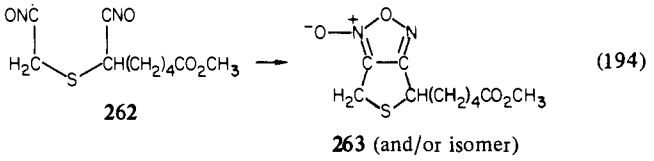
product (25%) was also formed.[190]

Nitrile oxides **260** generally dimerize into furoxans **261** (eq 193); however, the formation of 1,2,4-oxadiazole *N*-oxides and



(193)

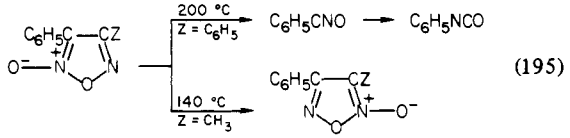
dioxadiazines can be competitive.[67c] Monomers were stabilized as steric hindrance discouraged dimerization, e.g., *tert*-butyl cyanide *N*-oxide and tetramethylterephthalo bisnitrile *N,N*-dioxide were isolated and stored for short periods.[191] The first intramolecular ring closure from a bisnitrile *N,N*-dioxide was claimed for the fusion (eq 194) of a reduced thiophene and a



(194)

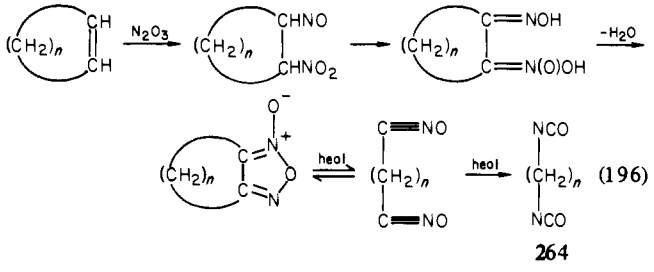
furoxan ring from the sulfide **262**.[192]

A thermal ring opening of a simple furoxan into a pair of nitrile oxides[193] can be competitive with a thermal interchange of furoxan isomers, but at higher temperatures an irreversible isomerization of a nitrile oxide afforded an isocyanate (eq 195).[67d] A patented preparation of α,ω-alkanebisisocyanates



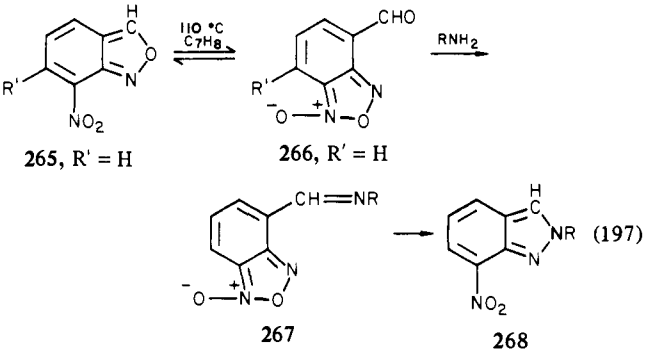
(195)

264 has utilized these properties (eq 196).[194]



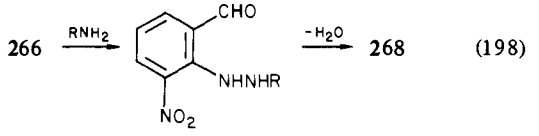
(196)

It has been claimed that a furazan(1,2,5-oxadiazole) ring is more resistant to ring opening and rearrangement than either an isoxazole (1,2-oxazole) or a 1,2,4-oxadiazole ring.[195] This generalization does not, however, apply to ring opening by reduction. An impressive heterocycle interchange occurred when heating 7-nitroanthranil (**265**) in a primary amine produced 7-nitroindazole (**268** (eq 197).[196] In the first interchange a



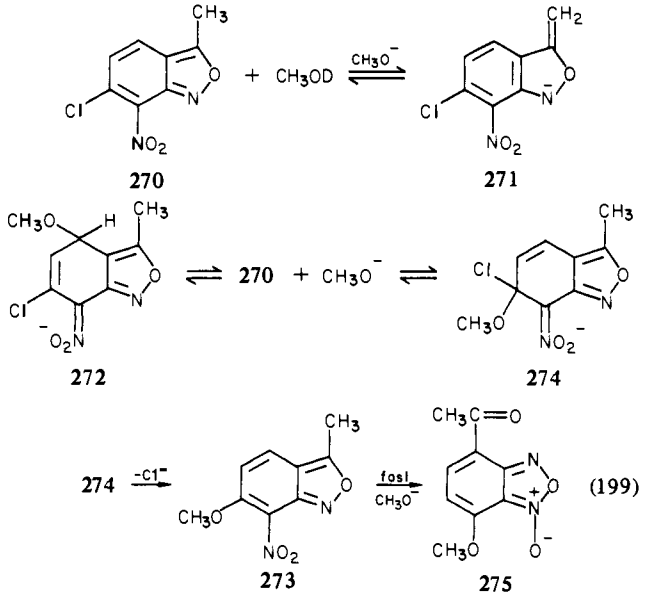
(197)

thermal equilibration between the anthranil **265** and 4-formylbenzofuroxan **266** and in the second an irreversible transformation of a 4-formimidoylbenzofuroxan (**267**), a possible (but not established) intermediate, into a 7-nitroindazole (**268**) were proposed. Competitive transformations of the furoxan **266** into intermediates **267** and **269** (compare eq 177, section IV.E) were not evaluated; however, each of the intermediates can be seen as a precursor to the indazole **268** (eq 197, 198).



(198)

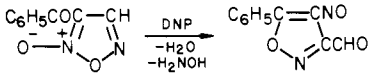
Another conversion of an anthranil into a benzofuroxan was discovered in an investigation of the kinetics of the reactivity of 3-methyl-6-chloro-7-nitroanthranil (**270**) toward methoxide anion.[197] An interpretation of the data indicated the slow step was dehalogenation of **270** by methoxide anion. Two preequilibrations were identified. One was shown by deuterium exchange to involve anion **271**, the other, an anion (**272**) of a Meisenheimer adduct to **270**. An NMR examination indicated the formation of 3-methyl-6-methoxy-7-nitroanthranil (**273**) from the anion **274** of another Meisenheimer adduct to **270**. Isomerization of the anthranil **273** into 4-acetyl-7-methoxybenzofuroxan (**275**) was reported to be fast (eq 199).[197] Thermal



(199)

equilibrations for each anthranil (**270** and **273**) with a corresponding benzofuroxan were not established, but an equilibrium between 6-chloro-7-nitroanthranil (**265**, R′ = Cl) and 4-formyl-7-chlorobenzofuroxan (**266**, R′ = Cl) was reported to lie on the side of the furoxan.[196]

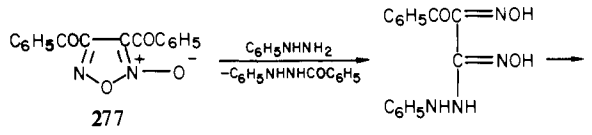
Arylhydrazines apparently attack simple acylfuroxans at carbon (compare eq 177 and 178). Benzoylfuroxan gave 3-formyl-4-nitroso-5-phenylisoxazole (**276**; eq 200)[198] and di-



(200)

276 (as DNP)

benzoylfuroxan (**277**) gave 3-(β-phenylhydrazino)-4-nitroso-5-phenylisoxazole (**278**; eq 201).[199,200]



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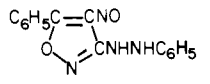
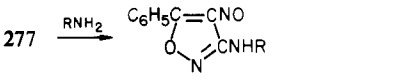


(201)

278

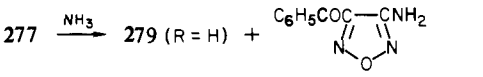
Recently Russian investigators treated the furoxan **277** with a primary amine to obtain a 3-(alkylamino)-4-nitroso-5-phenylisoxazole (**279**; eq 202). Ammonia gave the expected isoxa-



(202)

279

zole **279** (R = H) and 4-amino-5-benzoylfurazan (**280**; eq 203).[201,202]

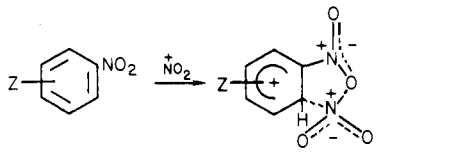


(203)

280

H. *o*-Dinitroarenes: Certain Formations and Reactions

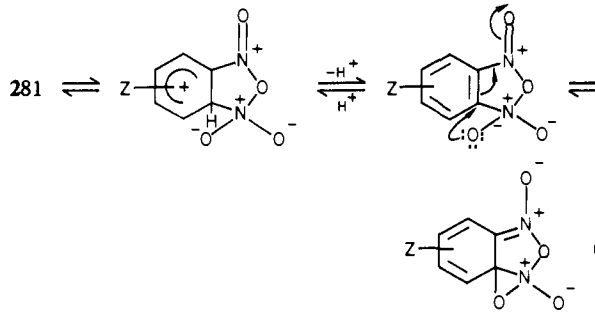
Complex **281** was proposed[203] (eq 204) to account for ortho



(204)

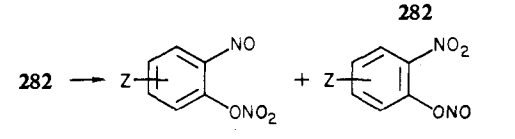
281

nitration in a nitroarene.[204] Oxidation is generally a side reaction in aromatic nitrations[1b,204] and can compete for the position ortho to a nitro substituent by initially producing an *o*-nitroaryl nitrite (eq 205, 206). The nitrite would readily afford an *o*-



(205)

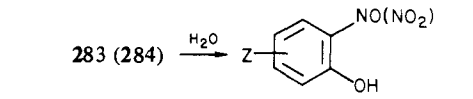
282



(206)

283 284

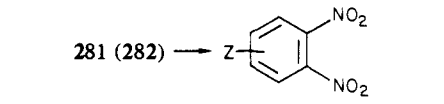
nitrophenol (eq 207) by hydrolysis and an *o*-dinitroarene (eq



(207)

285 (286)

208) by isomerization. Isomerization of aryl nitrites into nitro-



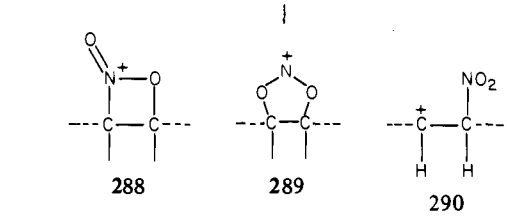
(208)

287

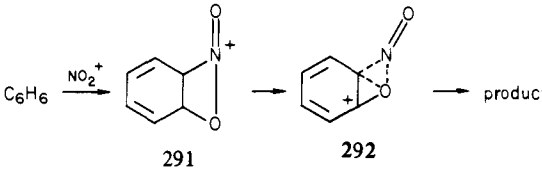
arenes[205] and of pernitrites (ROONO) into nitrates ($RONO_2$)[206,207] have been proposed. Experimental support for the latter[206] but not the former[206] is available.

Both substitutions can be accounted for by model **282**, an oxaziridine conjugate base structure for the complex **281** (eq 205). Oxaziridine ring opening can afford a mixture of nitrate (**283**) and nitrite (**284**) esters (eq 206) and an *o*-dinitroarene (**287**; eq 208).

A molecular orbital study of the nitration of ethylene by the nitronium ion revealed an asymmetric bridge (**288**) and a symmetric bridge (**289**) to have nearly equal energy and an open form (**290**) to have about 60 kcal/mol more energy.[209] Proposed intermediates **291** and **292** extended this concept to the nitration of benzene (eq 209).[209]



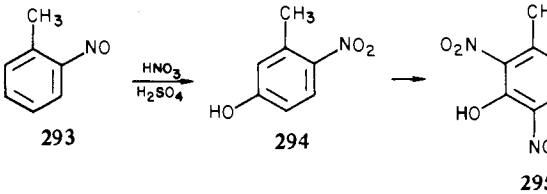
288 289 290



(209)

291 292

A thorough investigation of the oxidative nitration of toluene in the presence of mercuric salts into 2,4,6-trinitro-3-hydroxytoluene (**295**; 66%) led to the suggested "oxidation and rearrangement" of *o*-nitrosotoluene (**293**) into 2-nitro-5-hydroxytoluene (**294**) at an intermediate stage. It was implied that product formation required the occurrence of the sequence **293** → **294** → **295** (eq 210).[210] The rearrangement in **293**

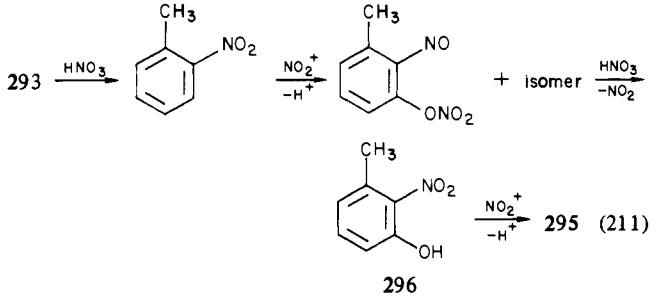


293 294 295

(210)

→ **294** was explained in terms of its relationship with a conversion of nitrosobenzene in concentrated hydrochloric acid into *p*-chloroaniline and of phenylhydroxylamine into *p*-aminophenol (section III.A).[210]

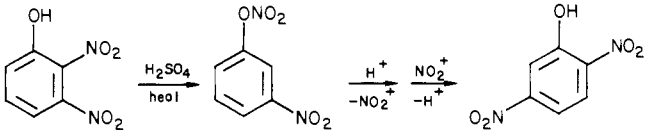
An alternative sequence (eq 211) is suggested. After oxidation of *o*-nitrosotoluene (**293**) into *o*-nitrotoluene, ortho hy-



296

droxylation (compare eq 204–207) accounted for the phenol **296** (eq 211). Straightforward nitration then produced 2,4,6-trinitro-*m*-cresol (**295**).

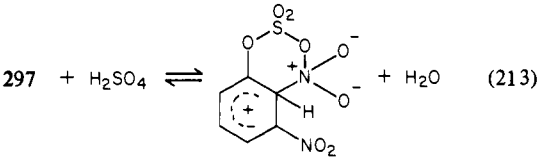
A rearrangement (eq 212) of 2,3-dinitrophenol (**297**) into 2,5-dinitrophenol (**299**) was accounted for by the proposed in-



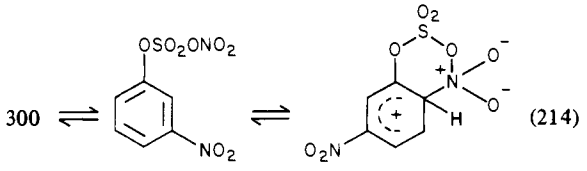
297 298 299 (212)

termediacy of a nitrate ester **298**, but without explaining its formation.[211]

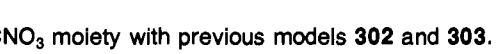
The sequence shown by eq 213–215 satisfactorily accounts for the rearrangement. The proposed intermediates **300** and



300 (213)

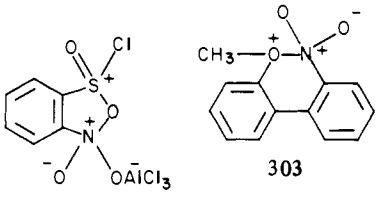


301 (214)



(215)

301 share a CNO_3 moiety with previous models **302** and **303**.

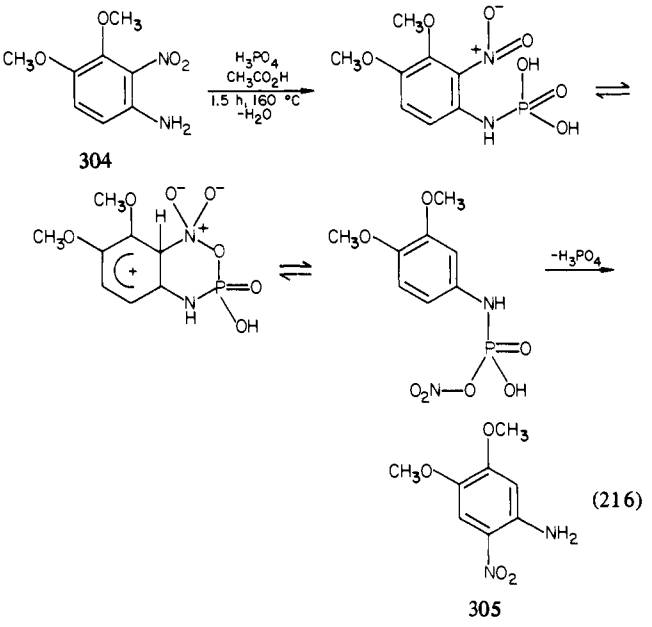


302 303

These rationalized a greater efficiency o-nitrobenzenesulfonyl chloride had over its meta and para isomers in Friedel–Crafts reactions[212] and higher melting-points for 2-methoxy-2′-nitrobiphenyls than for the 4-methoxy isomers.[213]

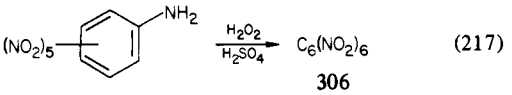
A rearrangement of 3-nitro-4-aminoveratrole (**304**) into 5-nitro-4-aminoveratrole (**305**) by heating a mixture of phosphoric and glacial acetic acids[214] can follow a similar path. The sequence of eq 216 is proposed.

A Russian report on the previously unknown hexanitrobenzene (**306**) (an earlier claim[1c] has been discredited) did not reveal the method of preparation.[215] An oxidation of pentanitroaniline by hydrogen peroxide in concentrated sulfuric acid



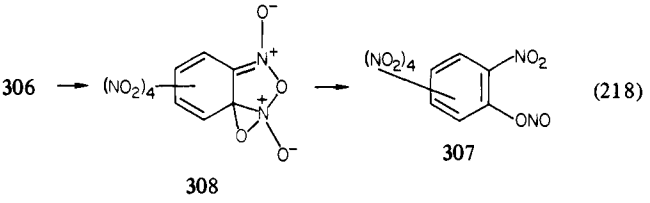
304 305 (216)

into hexanitrobenzene (**306**; eq 217) was recently described.[216]



306 (217)

An X-ray analysis showed the nitro groups lie in parallel planes at an angle of 53° with the benzene ring.[215] It was highly explosive and slowly isomerized on storage into pentanitrophenyl nitrite (**307**; eq 218) which was changed by atmospheric



308 307 (218)

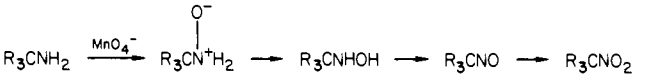
moisture into pentanitrophenol.[217] An explanation (eq 218) for the isomerization **306** → **307** is based on an intermediate **308** related to **282**. An interaction between two nitro groups in **306** is facilitated by an orientation of the nitro groups which favors a nucleophilic attack by an electron-rich oxygen atom in one nitro group upon an electron-poor nitrogen atom in an adjacent nitro group.

V. Amines

Oxidation at carbon and at nitrogen atoms in amines,[218a] amine oxidation in synthesis,[218b] aromatic amine oxidation,[218c] aminyls,[216d] aminyl oxides,[216e,219] hydroxylamines,[216f-i] and industrial peroxide oxidation of organic nitrogen compounds[216f] have been topics reviewed in the period 1968–1979.

A. Permanganate and Dichromate

In 1956 potassium permanganate in aqueous acetone treated with magnesium sulfate was introduced (eq 219) for the



(219)

oxidation of tertiary alkyl primary amines into nitro compounds in yields from 70% to 83%.[220] Ozonization also transformed *tert*-butylamine into 2-methyl-2-nitropropane (eq 220a).[221a] For

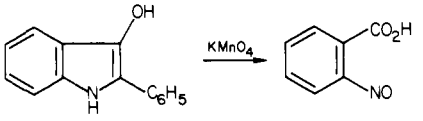
$$(CH_3)_3CNH_2 \xrightarrow[-O_2]{O_3} (CH_3)_3CNH_2^+O^- \rightarrow (CH_3)_3CNHOH \rightarrow (CH_3)_3CNO \rightarrow (CH_3)_3CNO_2 \quad (220a)$$

both reactions the intermediacy of a hydroxylamine was assumed. When extended to di-*tert*-butylamine, ozonization gave di-*tert*-butyl nitroxide as an initial product (eq 220b),[221b] but

$$((CH_3)_3C)_2NH \xrightarrow[-O_2]{O_3,\ CHCl_3} ((CH_3)_3C)_2N{-}O\cdot \rightarrow (CH_3)_3CNO_2 + ((CH_3)_3C)_2NH_2^+Cl^- + \text{other products} \quad (220b)$$

oxidation of the secondary amine by permanganate is apparently unknown. The possibility that the latter reaction will proceed from an aminyl intermediate is suggested by the formation of tetraphenylhydrazine from diphenylamine and permanganate (eq 220c)[222] (but see eq (221) for the generation of the NO bond

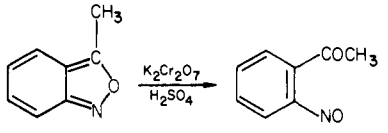
$$(C_6H_5)_2NH \xrightarrow{MnO_4^-} (C_6H_5)_2N\cdot \rightarrow ((C_6H_5)_2N)_2 \quad (220c)$$



(221)

under similar circumstances).

A report in 1896 claimed the formation of o-nitrosobenzoic acid from 2-phenyl-3-hydroxyindole by oxidation with permanganate (eq 221); another report in 1908 claimed the formation of o-nitrosoacetophenone from 3-methylanthranil by oxidation with dichromate (eq 222).[223a] These isolated exam-



(222)

ples may need confirmation.

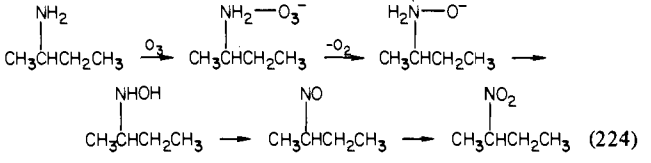
Permanganate oxidation of acetamide into acetamidyl was proposed, but the formation of acethydroxamic acid was not claimed (eq 223).[224]

$$CH_3CONH_2 \xrightarrow[OH^-]{MnO_4^-} CH_3\dot{C}ONH \xrightarrow[?]{O_2} CH_3CONHO_2\cdot \quad (223)$$

B. Ozone

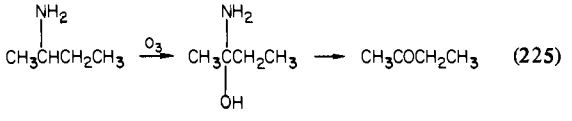
A proposed[221,225a] transfer of electrons from amine nitrogen to electrophilic ozone was substantiated by an ab initio self-consistent-field theory analysis of a charge-transfer complex between ozone and ammonia, with a predicted binding energy of 2.24 kcal/mol.[225b]

Primary aliphatic amines were oxidized into nitro compounds (eq 224) by a stream of dry ozone as it passed through a



(224)

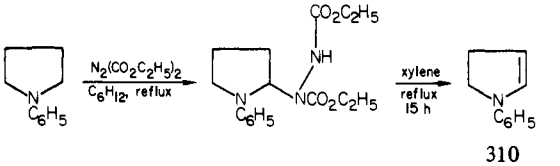
column with absorbed amine. Yields ranged from 44% for β-phenylnitroethane to 70% for 2-nitrobutane. Carboxylic acids and ketones were byproducts (2–6%) (eq 225) from oxidation

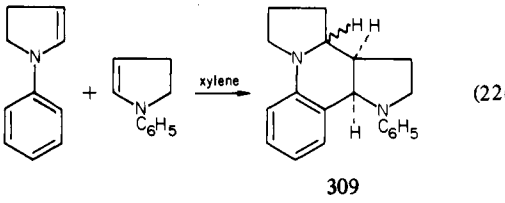


(225)

initiated at carbon. Similar reactions gave aromatic nitro compounds in low yields, from 3% for 1,3,5-trinitrobenzene to 21% for *p*-chloronitrobenzene.[225a]

A common product, **309** was obtained from *N*-phenylpyrrolidine upon dehydrogenation by either diethyl azodicarboxylate (eq 226) or ozone (eq 227) followed by a Diels–





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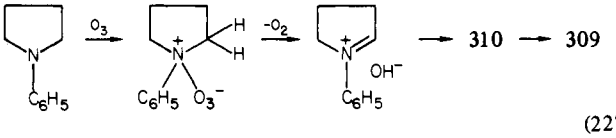
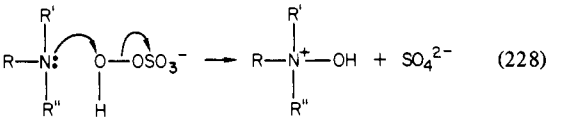


(227)

Alder dimerization of enamine **310**.[226]

C. Peroxides

Hydrogen peroxide converted amines into nitrogen–oxygen bond derivatives, generally with a low efficiency in the absence of catalyst.[216] Addition of inorganic acids or salts or carboxylic acids often improved the yield. A nucleophilic attack on oxygen was postulated for the reaction between a tertiary amine and persulfuric acid (eq 228).[227a,b]



(228)

Other reactions may, however, predominate. Peroxyacetyl nitrate acetylated primary and secondary amines nearly quantitatively, and the reaction also produced oxygen and nitrous acid (eq 229), but amine oxidation at nitrogen was not detected.

$$RNH_2 + CH_3CO_3NO_2 \xrightarrow[-O_2,\ -NOH]{CDCl_3} \underset{>90\%}{CH_3CONHR} \quad (229)$$

R = H, CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9

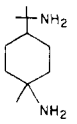
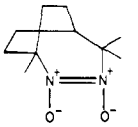
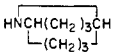
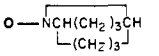
Chemiluminescence was produced from an unknown product when a tertiary amine received similar treatment.[228]

1. Pertungstates in Hydrogen Peroxide

Nitro, nitroso, azo, and azoxy compounds, hydroxylamines, amine oxides, and oximes have been obtained by dilute peroxide oxidation of amines in the presence of sodium tungstate (Na_2WO_4) (Table V).[229–233]

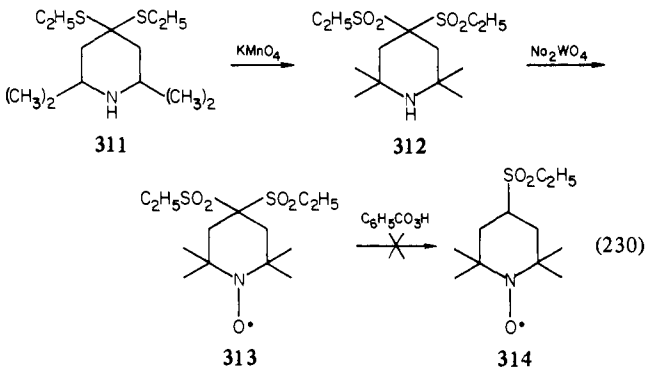
Subtle differences in oxidation requirements were encountered in an investigation on sulfur-containing nitroxyl radicals.[234] Condensation product **311** from triacetonamine and ethyl mercaptan was oxidized by potassium permanganate into a

TABLE V. Oxidation of Amines by Hydrogen Peroxide with Sodium Tungstate[a] or Phosphotungstate[b]

amine	H_2O_2, mol	solvent temp, °C	time, h	product	yield,[c] %
$(CH_3)_3CNH_2$	3	H_2O/CH_3OH (15)	24	$(CH_3)_3CNO_2$	74[d]
$(CH_3)_3CNH_2$	2	H_2O (<20)	2	$(CH_3)_3CNO$	24[e]
				$(CH_3)_3CNO$	41[e]
$(CH_3)_3CCH_2C(CH_3)_2NH_2$	2	H_2O (<20)	2	$(CH_3)_3CCH_2$ | $ONC(CH_3)_2$	36[e]
				$(CH_3)_3CCH_2$ | $O_2NC(CH_3)_2$	21[e]
n-$C_4H_9NH_2$	2	H_2O/CH_3OH (15)	24	n-$C_3H_7CH{=}NOH$	61[d]
$C_6H_5NH_2$	3	H_2O (14)	144	C_6H_5NO	20[d]
				$C_6H_5N(O){=}NC_6H_5$	50[d]
p-$O_2NC_6H_4NH_2$	2	H_2O (19)	960	p-$(O_2N)_2C_6H_4$	78[d,f]
$(n$-$C_4H_9)_2NH$	1	H_2O/CH_3OH (16)	24	$(n$-$C_4H_9)_2NOH$	25[d,g]
$(CH_3)_3N$	1	H_2O (16)	24	$(CH_3)_3NO$	100[d]
$(CH_3)_2NC_6H_5$	1	H_2O (12)	72	$(CH_3)_2N(O)C_6H_5$	d
$(H_2NC(CH_3)_2CH_2)_2$	4	H_2O (<30)	~2	$CH_2C(CH_3)_2NO$ | $CH_2C(CH_3)_2N$	73[h]
	4	H_2O (<25)	~2		8[h]
2-$CH_3C_5H_4N$[i]	1.5	H_2O (60-65)	8	α-$CH_3C_5H_4NO$	72
	2	H_2O (25)	1.5		17[b]

[a] The amount of sodium tungstate varied from 0.5 to 10 g per molar equivalent of the amine (diamine).[229-232] [b] About 1.5 g of phosphotungstic acid per molar equivalent of amine (R. M. Dupeyre and A. Rassat, *Bull. Soc. Chim. Fr.*, Part 2, 1978, 612 (1978). [c] On the basis of quantitative (>90%) consumption of amine except where noted. [d] Reference 229. [e] Reference 230. [f] 25% amine consumed. [g] 60% amine consumed. [h] Reference 231. [i] 2-Picoline. Similar oxidations were carried out on pyridine, 2-chloropyridine, 2,6-lutidine, and 3- and 4-picolines. For each mole of a pyridine about 1.5 g of a pyridinecarboxylic acid *N*-oxide was added to the reaction mixture, (I. Matsumoto and Y. Ito, Japan. Kokai 73, 81 867; *Chem. Abstr.*, 80, 120779j (1974).

sulfone **312** and further oxidized by sodium pertungstate into the nitroxide **313** (eq 230). Perbenzoic acid did not react with



311 312 313 314

(230)

313 but did oxidize **312** into the nitroxide **314** (eq 231). An

$$312 \xrightarrow{C_6H_5CO_3H} 314 \qquad (231)$$

implied inability of permanganate to attack the amine function in **311** suggests a steric inhibition.

2. Percarboxylic Acids and Anhydrides

a. Primary Amines

In a variation on the peracid oxidation of an aliphatic amine into a nitro compound, *m*-chloroperbenzoic acid in refluxing 1,2-dichloroethane transformed cyclohexylamine into nitrocyclohexane (**315**) in 86% crude yield (eq 232).[235] The high

$$c\text{-}C_6H_{11}NH_2 \xrightarrow[80\ °C,\ 30\ min]{MCPBA,\ (ClCH_2)_2} c\text{-}C_6H_{11}NO_2 \qquad (232)$$

315

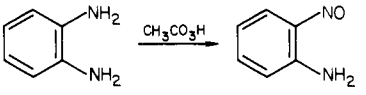
efficiency was attributed to an elimination of the acid-catalyzed isomerization of an intermediate nitroso compound into an oxime and to a more favorable equilibrium at the higher temperature (83 °C), in comparison to other peracid oxidations in methylene chloride at 23 °C or in chloroform at 61 °C, for the presence of nitroso monomer rather than its dimer; however, a characteristic blue-green color for the intermediate nitroso compound was not noted.

Permaleic acid oxidized the monoacetyl derivative of benzidine into 4-nitro-4′-aminobiphenyl (**316**; eq 233).[236] An attempt

$$p\text{-}H_2NC_6H_4C_6H_4NHCOCH_3\text{-}p' + \begin{matrix}CHCO_3H\\ \|\\ CHCO_2H\end{matrix} \longrightarrow p\text{-}O_2NC_6H_4C_6H_4NH_2\text{-}p' \qquad (233)$$

316

to reduce the latter into a hydroxylamine failed. A preparation of the hydroxylamine by an oxidation of benzidine under mild conditions was apparently not investigated. Since dropwise addition of peracetic acid oxidized *o*-phenylenediamine into *o*-nitrosoaniline[237] (**317**; eq 234), the technique should be



(234)

317

considered whenever the oxidation of one of two primary amine groups is desired.

The remarkably stable perchlorodiphenyl nitroxide (**321**) was prepared by the oxidation of *N*,*N*-diperchlorophenylhydroxylamine (**320**) with potassium ferricyanide (eq 235). An oxidation

$$\underset{\mathbf{318}}{C_6Cl_5NH_2} \xrightarrow{CF_3CO_3H} \underset{\mathbf{319}}{C_6Cl_5NO} \xrightarrow[\text{Mg, THF}\ -15\ °C\ \text{dark}]{C_6Cl_6} \underset{\mathbf{320}}{(C_6Cl_5)_2NOH} \xrightarrow{K_3Fe(CN)_6}$$

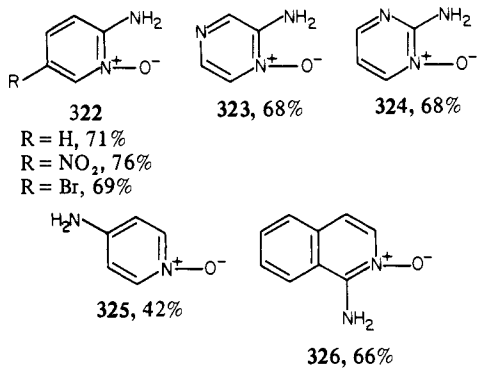
$$(C_6Cl_5)_2N{-}O\cdot \qquad (235)$$

$$\mathbf{321}$$

of pentachloroaniline (**318**) with trifluoroperacetic acid into pentachloronitrosobenzene (**319**) followed by a Grignard reaction with hexachlorobenzene provided the hydroxylamine **320**.[238]

Success in oxidation at a ring nitrogen atom of an α- or β-amino azine (**322-326**) was reported for *m*-chloroperbenzoic

acid in acetone.[239] Products and yields are shown.



322
R = H, 71%
R = NO_2, 76%
R = Br, 69%

323, 68%

324, 68%

325, 42%

326, 66%

Perbenzoic anhydride converted primary alkylamines into *O*-benzoyl-*N*-alkylhydroxyamines (eq 236).[240a] Five primary,

$$2RNH_2 \xrightarrow{(C_6H_5CO)_2O_2} RNHOCOC_6H_5 + RNH_3{}^+{}^-O_2CC_6H_5 \quad (236)$$

six secondary, and one tertiary alkyl groups were investigated. Yields ranged from 33% when the alkyl group was *n*-butyl to 91% when benzyl. The amine benzoate was also produced. Secondary amines were similarly oxidized (eq 237), but the

$$RR'NH + (R''CO)_2O_2 \rightarrow RR'NOCOR'' + R''CO_2H$$

$$R = (CH_3)_3C,\ R' = H,\ R'' = C_6H_5$$

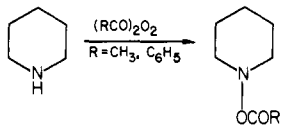
$$R = R' = CH_3,\ R'' = C_6H_5 \quad (237)$$

results were erratic.[240b]

b. Secondary Amines

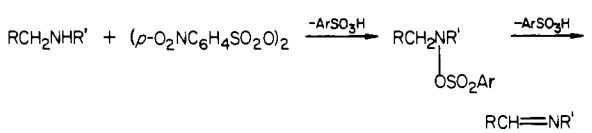
Aminyl oxides are also known as nitroxyls, nitroxides, and iminoxyls. Nitroxone was a name proposed for an aminyl oxide from an amide. Iminoxyl has also been adopted to name the radical $R_2C{=}N{-}O$. The oxidation of secondary amines and of N,N-disubstituted hydroxylamines into aminyl oxides has been reviewed.[218d,e,219] Oxidants included oxygen, hydrogen peroxide with or without cerium salts, alkaline peroxide, peroxyalkyl radicals, percarboxylic acids, benzoyl peroxide, nickel peroxide, pertungstates, silver oxide, mercuric oxide, lead dioxide, phosphotungstic acid with ammonium molybdate, potassium ferricyanide, potassium permanganate, and fluorine. Photolysis of aliphatic hydroxylamines produced short-lived aminyl oxides.

O-Acyl derivatives of hydroxylamines were obtained by treating a primary[241] or secondary[216f,242] amine with an acyl peroxide (eq 237, 238). Erratic results were partially attributed



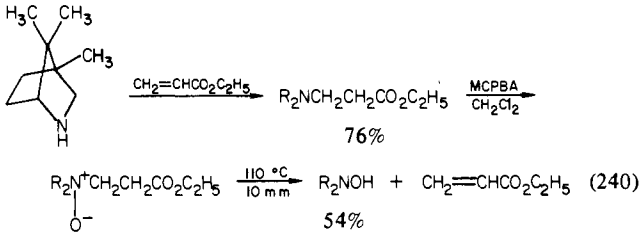
(238)

to disintegration of the initial adduct by competing free-radical pathways, to further oxidation, and to the formation of an imine by an elimination reaction (oxidative deamination). When the latter was desired, a sulfonyl peroxide was recommended (eq 239);[243] however, caution has been advised since certain hydroxylamine tosylates were explosive.[244]



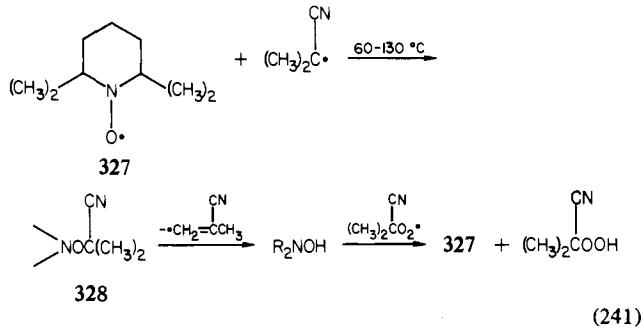
(239)

The well-known thermolysis of a tertiary amine oxide into an N,N-disubstituted hydroxylamine and an olefin has been further developed by a preparation of the tertiary amine from a secondary amine and ethyl acrylate in a Michael addition reaction. Its oxidation into the *N*-oxide derivative was achieved by treatment with MCPBA (eq 240).[244]



(240)

When the nitroxide **327** was coupled with the α-cyanoisobutyryl radical, a cycle was initiated in which a hydroxylamine (from the coupled product **328** by dissociation) was oxidized into the nitroxide **327** by a peroxyalkyl radical (eq 241).[245] To



(241)

maintain the cycle, a sufficient supply of alkyl and peroxyalkyl radicals and a nitroxide unreactive toward oxidation by the peroxyalkyl radical were needed.

An adaptation gave a scheme for amine inhibition of hydrocarbon autoxidation (eq 242). Peroxyalkyl radicals were known

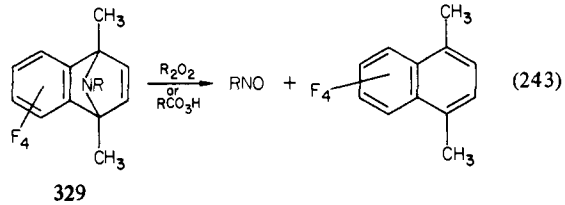
$$Ar_2NH \xrightarrow[-RO_2H]{RO_2\cdot} Ar_2N\cdot \xrightarrow[-RO\cdot]{RO_2\cdot} Ar_2NO\cdot \quad (242)$$

to oxidize diarylamines into aminyls and then into the aminyl oxides, both steps very fast.[245]

An older claim that hydroxylamines were produced when *N*-magnesium salts were treated with hydrogen peroxide has been discounted.[246]

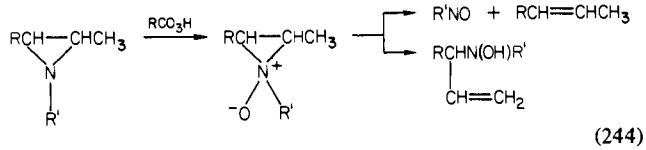
c. Tertiary Amines

An overall transformation of an *N*-alkylpyrrole into a corresponding nitrosoalkane was achieved by treating the Diels–Alder adduct **329** from the pyrrole and tetrafluorobenzyne with a peroxide (eq 243).[247]



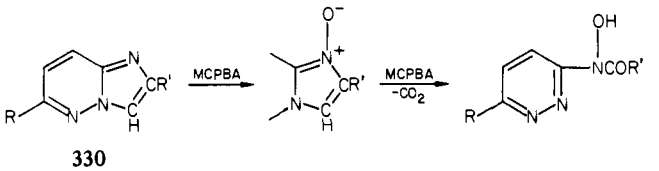
(243)

Other heterocycles are also subject to oxidative degradation into derivatives of nitrogen–oxygen bonds. *N*-Alkylaziridines were deaminated by peroxy acids into olefins and nitroso compounds (eq 244).[248] MCPBA transformed an imidazole (**330**)



(244)

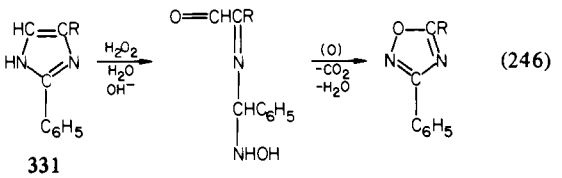
into hydroxylamine (eq 245),[249] and alkaline peroxide afforded



330

(245)

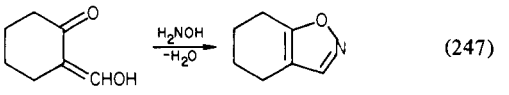
a similar reaction with the imidazole **331** (eq 246).[249]



331

(246)

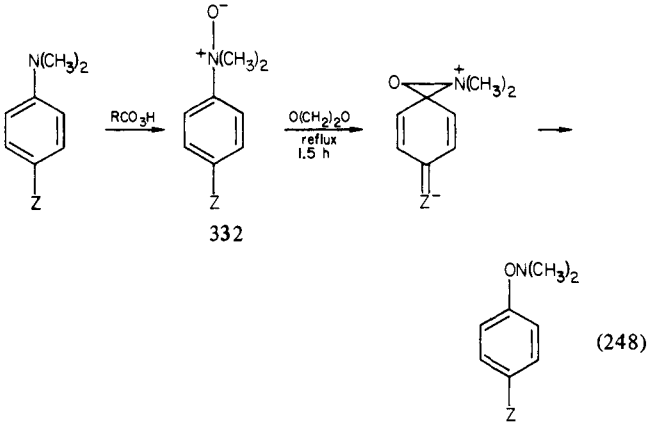
The latter reaction is reminiscent of an isoxazoline preparation from a 2-(hydroxymethylene)cyclohexanone and hydroxylamine (eq 247).[250]



(247)

Degradation of other heterocycles into derivatives of nitrogen–oxygen bonds are found in section II.I, IV.F,G, VI.B,C,F, VII.A.3, and VII.B, VIII.A,F,G,H, and IX.

A molecular rearrangement may replace or compete with fragmentation. In Meisenheimer rearrangements[251] certain tertiary amine oxides (**332**) gave N,N,O-trisubstituted hydroxylamines (**333**) when heated. Allyl,[251] benzyl,[251,252] neopentyl,[253] homoadamantyl,[253] propargyl,[254] and electron-withdrawing aryl groups[255] are known to migrate. Intermediate free radicals were implicated in the migrations of benzyl, neopentyl, and homoadamantyl groups, but aryl migration in the *N*-oxide **332** (eq 248) by an S_Ni mechanism was proposed to accommodate



332

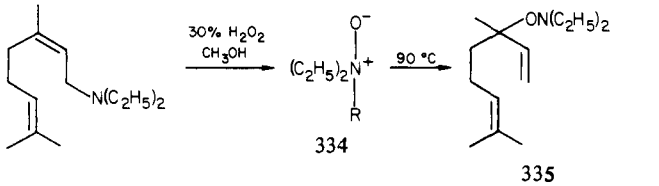
333

(248)

Z = *p*-NO_2, 96%
p-CN, 75%
o-NO_2, 55%
p-COC_6H_5, 20%
m-NO_2, 0%

a $\Delta S^{\ddagger}$ of −7.57 eu.[255]

A Meisenheimer rearrangement accounted for the transformation of *N*,*N*-diethylnerylamine oxide (**334**) into *O*-linalyl-*N*,-*N*-diethylhydroxylamine (**335**) on heating (distillation) (eq 249).[256]

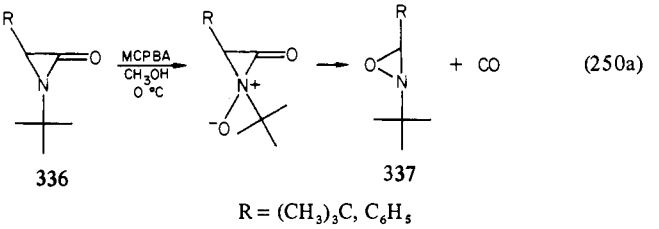


334

335

(249)

Recently *m*-chlorobenzoic acid in methanol quantitatively transformed 1,3-di-*tert*-butylaziridinone (**336**, R = $(CH_3)_3C$) into 2,3-di-*tert*-butyloxaziridine (**337**).[257] A true Meisenheimer rearrangement did not occur since the assumed intermediate aziridinone *N*-oxide did not rearrange into a four-membered ring. Instead, carbon monoxide (90%) elimination accompanied an oxaziridine ring closure (eq 250a). A similar reaction gave the



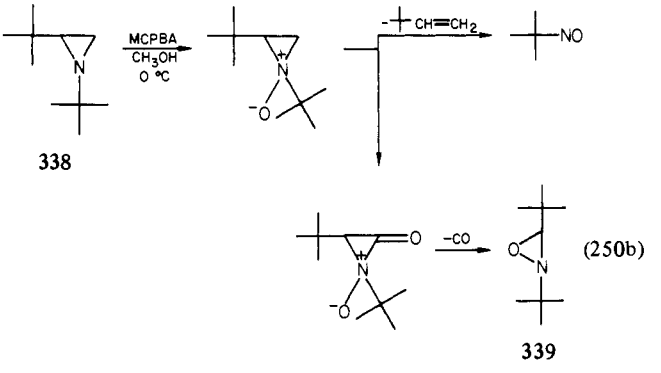
336

337

R = $(CH_3)_3C$, C_6H_5

(250a)

oxaziridine **337** (R = C_6H_5, 70%) from 1-*tert*-butyl-3-phenylaziridinone (**336**, R = C_8H_5) in the presence of lithium carbonate (to prevent an acid attack on the lactam). A related oxidation–fragmentation of 1,2-di-*tert*-butylaziridine (**338**) by MCPBA in methanol gave 2,3-di-*tert*-butyloxaziridine (**339**; 7%) and the major product, 2-methyl-2-nitrosopropane (**340**; eq 250b).[257]

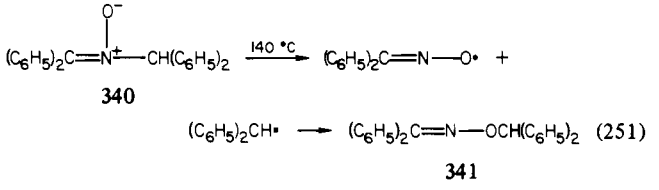


338

339

(250b)

A nitrone may give a modified Meisenheimer rearrangement. Intermediate iminoxy and benzhydryl radicals were considered for the quantitative thermal conversion of *N*-benzhydryl-α,α-diphenylnitrone (**340**) into benzophenone *O*-benzhydryloxime (**341**), $\Delta S^{\ddagger}$ = 14.5 ± 0.8 eu (eq 251).[258]

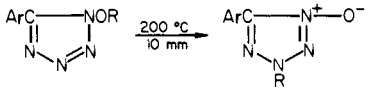


340

(251)

341

Migration of an alkyl group from oxygen to nitrogen, the reverse of the Meisenheimer rearrangement, is also known. A new preparation, of limited scope, for *N*-oxides developed from a thermal rearrangement of 1-alkoxytetrazoles into 3-alkyltetrazole 1-oxides (eq 252).[259]

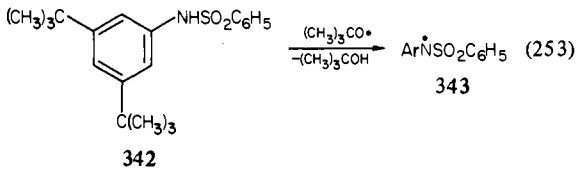


(252)

R = CH_3, 53%
R = C_2H_5, 30%

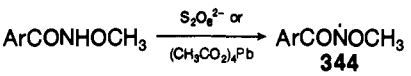
d. Amides

When an *N*-arylsulfonamide **343**, di-*tert*-butyl peroxyoxalate, and benzene are mixed in a degassed and sealed ESR tube, a facile dehydrogenation produced an *N*-aryl-*N*-sulfonylaminyl (**343**; eq 253), detected by ESR.[260] Similar reactions have produced *N*-methoxybiphenyl-2-carboxamidyls (**344**) and *N*-methoxybiphenyl-2-sulfonamidyls (**345**) from the corresponding

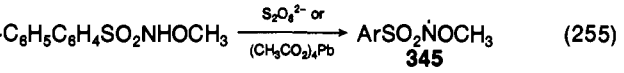


(253)

N-methoxy amides by oxidation with persulfate, lead tetraacetate, or *tert*-butoxyl radicals (eq 254, 255).[261]

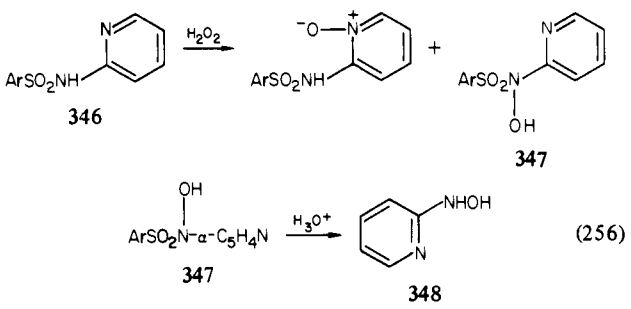


Ar = *o*-$C_6H_5C_6H_4$, *o*-(2-$O_2NC_6H_4$)C_6H_4, *o*-(4-$O_2NC_6H_4$)C_6H_4 (254)



(255)

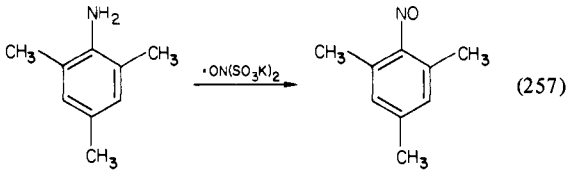
Although further oxidation of the amidyls **343**, **344**, and **345** was not reported, the radicals dimerized into hydrazine derivatives and cyclized onto the nearby aromatic ring.[261] These properties together with the ease of dehydrogenation tend to support an earlier isolated report of a peroxide oxidation of a sulfonamide (**346**) into the *N*-hydroxy sulfonamide (**347**) which upon hydrolysis gave α-(hydroxylamino)pyridine (**348**; eq 256).[262]



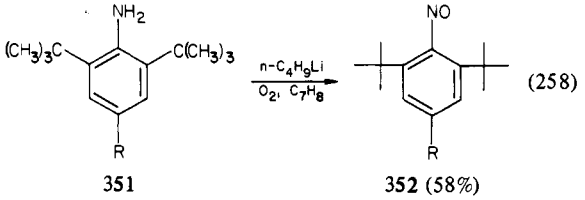
(256)

3. Fremy's Salt

Oxidation of mesidine (**349**) with Fremy's salt and base-catalyzed oxygenation (section V.D.1) of 4-substituted 2,6-di-*tert*-butylanilines (**351**) in toluene or tetrahydrofuran stopped at the nitroso stage (eq 257, 258).[264] An inhibition to further oxidation at nitrogen was attributed to steric factors.



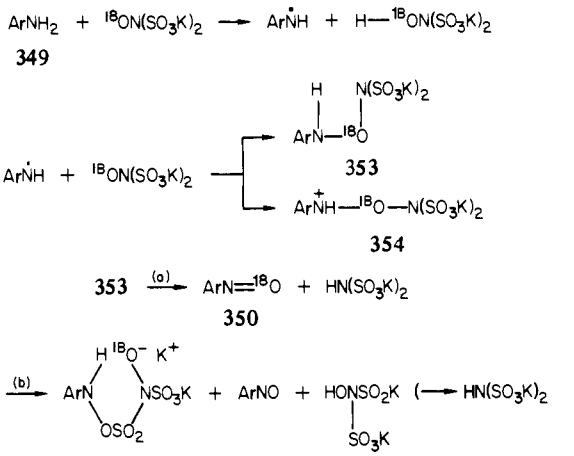
(257)



(258)

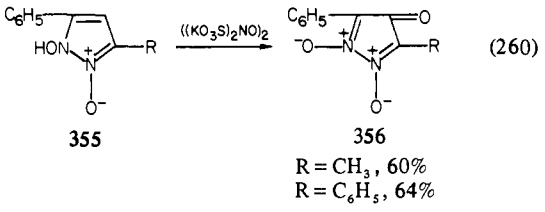
A ratio between pathways a and b of 2:1 accounted for the observed ^{18}O enrichment in the nitroso compound **350** obtained from the amine **349** and Fremy's salt labeled ^{18}ON (eq 259).[263]

Fremy's salt oxidized 3-methyl(phenyl)-5-phenyl-1-hydroxypyridazole 2-oxide (**355**) and the related hydroxylamine **357** into

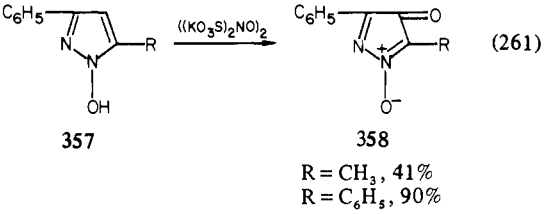


(259)

corresponding azodioxy (**356**) and azoxy compounds (**358**; eq 260, 261).[265]

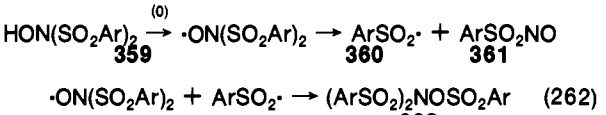


(260)



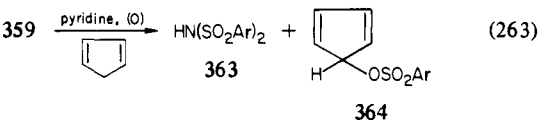
(261)

An oxidation of *N*,*N*-bis(arylsulfonyl)hydroxylamines (**359**) gave *N*,*N*,*O*-tris(arylsulfonyl)hydroxylamines (**362**; eq 262).



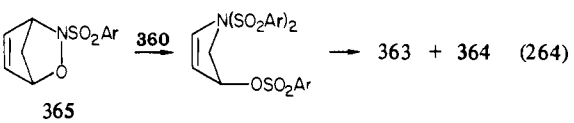
(262)

Dissociation of bis(arylsulfonyl)aminyl oxide radicals followed by radical cross-combination was assumed; however, attempts to trap the intermediate nitrosyl arylsulfinate (**361**) as an adduct with cyclopentadiene were judged unsuccessful; cyclopentadienyl arylsulfonate **364** was formed instead (eq 263).[266]



(263)

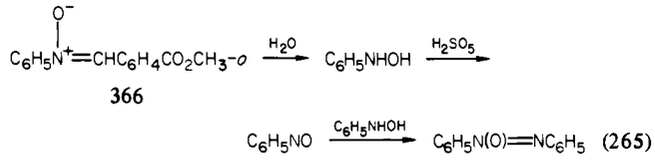
Perhaps a Diels–Alder reaction should not have been abandoned. A straightforward account of the products **363** and **364** can arise from a fragmentation of the Diels–Alder adduct **365** in the presence of arylsulfonyl radicals **360** (eq 264).



(264)

4. Persulfates and Sulfonyl Peroxides

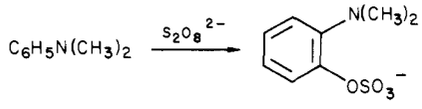
Persulfate transformed *N*-phenyl-α-(*o*-methoxycarbonylphenyl)nitrone (**366**) into azoxybenzene (eq 265). Oxidation of an intermediate phenylhydroxylamine was assumed.[267]



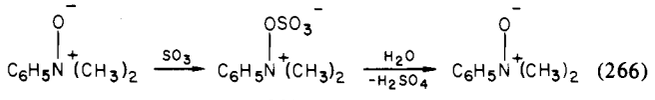
366

$$C_6H_5NO \xrightarrow{C_6H_5NHOH} C_6H_5N(O)=NC_6H_5 \quad (265)$$

An intermediate arylhydroxylamine-*O*-sulfonate was discounted as an intermediate in the peroxodisulfate oxidation (Boyland–Sims oxidation) of an aromatic tertiary amine into an *o*-aminoaryl sulfate (**367**) when it was shown that an independently prepared sample of *N,N*-dimethylphenylhydroxylammonium-*O*-sulfonate (**368**) hydrolyzed into dimethylaniline *N*-oxide sulfate but did not rearrange (eq 266). The Boyland–

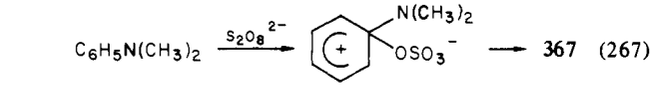


367



368

Sims reaction was then attributed to a rearrangement following an ipso attack on the aromatic ring (eq 267).[268]



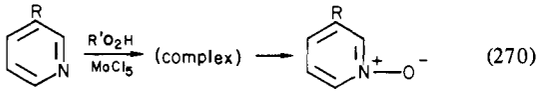
An oxidation of trityl-, benzhydryl-, and benzylamines by *p*-nitrobenzenesulfonyl peroxide (NBSP) was assumed to produce corresponding hydroxylamines, which underwent Stieglitz rearrangement (eq 268) and elimination (eq 269) reactions.[269]

$$Ar_3CNH_2 \xrightarrow{NBSP} Ar_3CNHOSO_2Ar' \rightarrow Ar_2C{=}NAr + Ar'SO_3H \quad (268)$$

$$Ar_2CHNH_2 \xrightarrow{NBSP} Ar_2CHNHOSO_2Ar' \rightarrow Ar_2C{=}NH + ArCH{=}NAr + Ar'SO_2OH \quad (269)$$

5. Molybdenum Salts with Peroxides

In an oxidation of 3-substituted pyridine derivaties (H, CH_3, CH_3CONH, CH_3OCO, Br, or CN) by *tert*-amyl hydroperoxide and catalyzed by molybdenum pentacholoride (eq 270), an oxygen



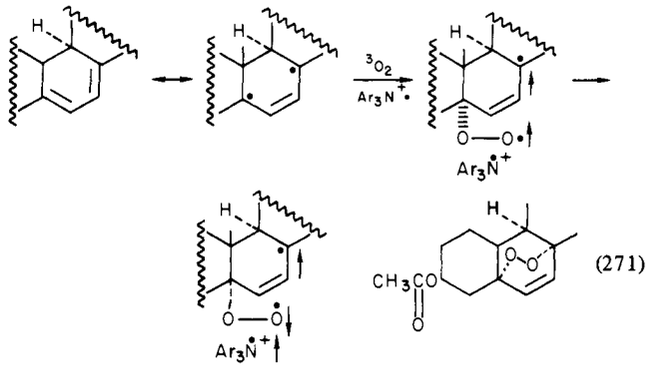
(270)

transfer to the pyridine ring nitrogen atom within a complex of a reactant and catalyst was proposed. Competitive complex formation with a cyano group could block the oxidation.[270]

D. Oxygen

Tris(*p*-bromophenyl)ammoniumyl catalyzed the thermal oxygenation of ergosteryl acetate into a peroxide. Nitrogen–oxygen attraction between an amine radical cation and triplet oxygen was assumed in a mechanism whereby a spin inversion at an oxygen atom overcame this "forbidden" addition of triplet oxygen (eq 271).[271]

An investigation of the photosensitized oxygenation of amines led to the conclusion that quenching and chemical reaction required the common intermediate zwitterion $R_3N^+-O_2^-$. Both quenching and the ionization potential of the amine increased directly with the facility of reaction of singlet oxygen and the amine. Quenching predominated when α-hydrogen was absent or there was no opportunity for the formation of an azomethine



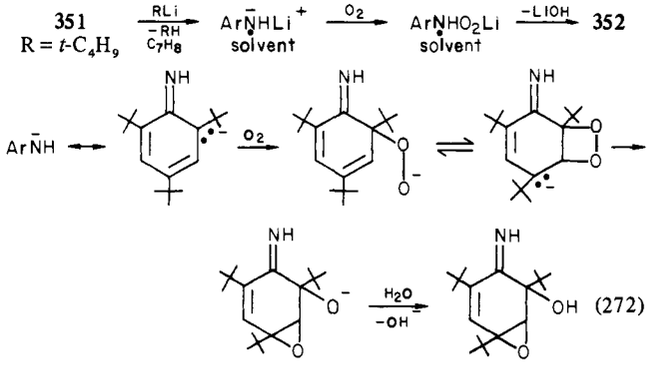
(271)

linkage by an elimination reaction.[272,273]

1. Amine Anions

Oxygenation of the hindered amine **351** (R = t-C_4H_9) in toluene was accounted for by assuming initial formation of the amine anion in the presence of a base, *n*-butyllithium or *tert*-butoxide.

In the lithium salt **351** the anionic center remained at nitrogen; however, the anionic center was effectively at an ortho position in the potassium salt (eq 272).[264]



(272)

Oxidative dimerization from the potassium salt of the amine gave the azoarene **369** (eq 273). Since a combination of

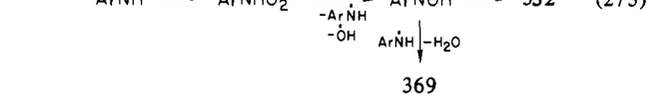
$$\underset{R = t\text{-}C_4H_9}{\mathbf{351}} \xrightarrow[O_2,\ HMPA]{t\text{-}C_4H_9OK} ArNH^-K^+ \xrightarrow[-KO_2']{O_2} ArN\dot{H} \rightleftharpoons (ArNH)_2 \xrightarrow{O_2} ArN{=}NAr \quad (273)$$

369

compounds **351** and **352** (R = t-C_4H_9) in hexamethylphosphoric triamide (HMPA) treated with potassium *tert*-butoxide did not produce *369*[264] (eq 274), a result incompatible with a previous

$$\underset{R = t\text{-}C_4H_9}{\mathbf{351}} + \mathbf{352} \xrightarrow[HMPA,\ 75\ ^\circ C]{t\text{-}C_4H_9OK} \mathbf{369} \quad (274)$$

explanation[274] for a base-catalyzed oxygenation of aniline into azobenzene (eq 275),[274–276] the formation of **369** from the



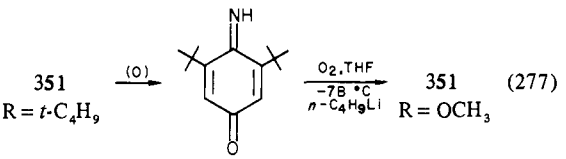
(275)

amine **351** and oxygen in HMPA/t-C_4H_9OK remained unexplained; however, an intermediate radical is a probable precursor for the nitroso compound **352**. Oxidation[277–279] of amine **351** (R = t-C_4H_9) with alkaline ferricyanide or lead dioxide produced moderate yields of the azo compound **369** via the aminyl radical (eq 276). On the other hand a base-catalyzed

$$\underset{R = t\text{-}C_4H_9}{\mathbf{351}} \xrightarrow[or\ PbO_2]{K_3[Fe(CN)_6],\ KOH} ArN\dot{H} \rightarrow \mathbf{369} \quad (276)$$

air oxidation of aniline into azobenzene was thought to proceed from an intermediate nitroso compound and/or its radical anion.[274,275]

Electrochemical oxidation[260] of the amine **351** (R = t-C_4H_9) in the presence of water gave the imine **370** (eq 277). Oxy-

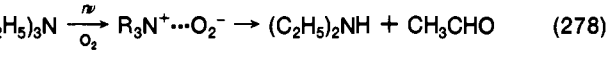


370 (277)

genation of the amine **351** (R = OCH_3) at −78 °C in THF which also contained n-butyllithium gave the quinonimine **370** (R = OCH_3).[264]

2. Amine Photooxygenation

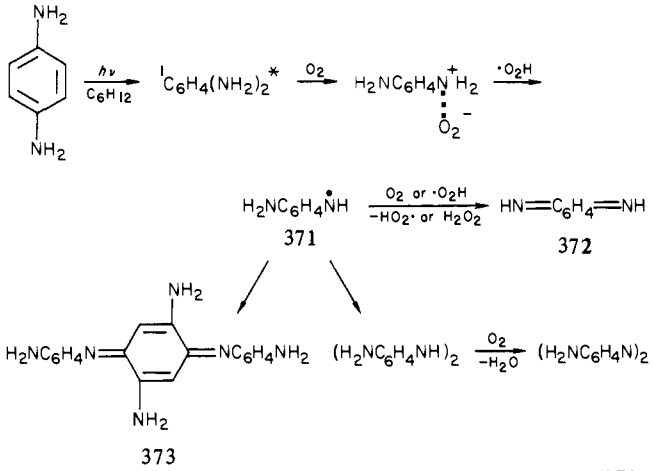
An estimated 1 mol % of diethylamine and acetaldehyde were obtained from triethylamine and oxygen by irradiation in the region of the charge-transfer band (300–400 nm) for about 1 h at 25 °C (eq 278). Intermediate radicals, detected by the



(278)

ESR method (77–300 K), were identified as methyl, ethyl, α-(diethylamino)ethyl, perhydroxyl, and diethyl nitroxide.[273,261]

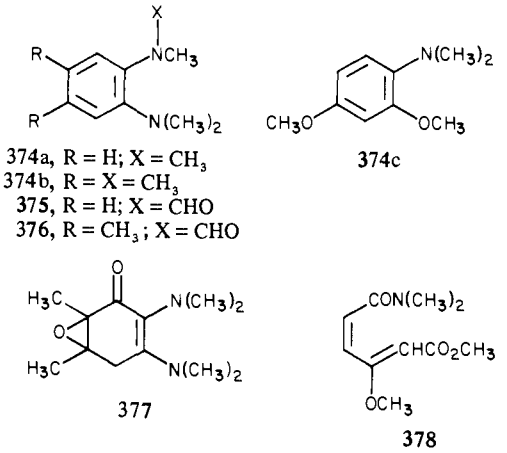
Similar photooxygenation of p-phenylenediamine in cyclohexane gave p-benzoquinone diimine (**372**), p,p'-diaminohydrazobenzene, p,p'-diaminoazobenzene, and Bandrowski's base (**373**; eq 279). ESR signals indicated high probability that



373 (279)

intermediate radicals were p-aminophenylaminyl (**371**) and hydroperoxy (or alkylperoxy).[262]

A partitioning of dye-sensitized photooxygenation of an amine into two types[263,264] was supported by kinetic investigations.[264] In type I, an interaction between an excited sensitizer and the amine gave an amine radical which reacted with oxygen; type II proceeded by a singlet oxygen mechanism. Sine they generally produced simultaneously the same products, an analytical differentiation between the two mechanisms was not entirely satisfactory. Additional complications were encountered in attempting to separate the effects of physical quenching and chemical reactions of singlet oxygen.[263] Although N,N-dimethylaniline and N,N,N',N'-tetramethyl-p-phenylenediamine were unreactive to photooxygenation in methanol containing Rose Bengal dye as a sensitizer, N,N,N',N'-tetramethyl-o-phenylenediamine (**374a**) and related amines **374b** and **374c** reacted with oxygen to produce a formamide (**375**) and tars from **372**, a formamide (**376**) and an epoxy enone (**377**; eq



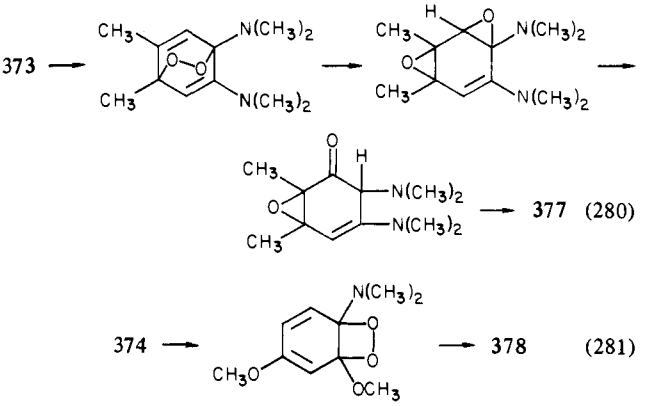
374a, R = H; X = CH_3
374b, R = X = CH_3
375, R = H; X = CHO
376, R = CH_3; X = CHO

374c

377

378

280) from amine **373**, and a cleavage product (**378**; eq 281)

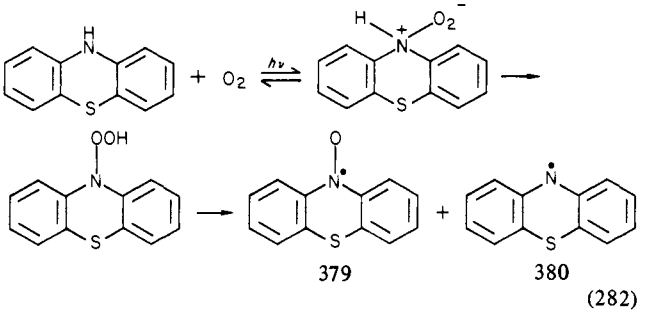


(280)

(281)

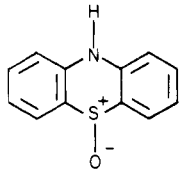
from amine **374**.[265] That a large portion of formamide **376** resulted from a type I reaction whereas singlet oxygen contributed (type II) to the formation of the epoxy enone **377** was revealed by the following: (1) an independence of sensitizer type in the formation of **377** and a decrease in the formation of **376** when Rose Bengal (E_T = 39.5 kcal) was either attached to Amberlite IRA-400 or replaced by methylene blue (E_T = 34 kcal); (2) an inhibition in the formation of formamide **376** by aprotic solvents, e.g., acetonitrile or benzene, in the heterogeneous oxidation (sensitizer attached to a resin); and (3) the addition of β-carotene (a singlet oxygen quencher) which inhibited the formation of epoxy enone **377** but had little effect on the formation of formamide **376**. It was suggested that the formation of product **377** proceeded from an intermediate 1,4-endoperoxide and that the formation of product **378** proceeded from an intermediate dioxetane (thought to be the first example of 1,2-cycloaddition of singlet oxygen to a benzene).[265]

Both phenothiazine nitroxide (**379**) and phenothiazinyl (**380**) were obtained from phenothiazine by photooxygenation in either direct light or with dye sensitization (eq 282). An earlier un-



379 **380** (282)

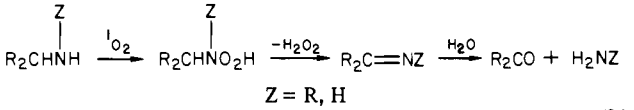
certainty about assignments for the two radicals was resolved by the ESR spectra of **379** when enriched in ^{17}O. Although phenothiazine 5-oxide (**381**) was a by product, the possibility



381

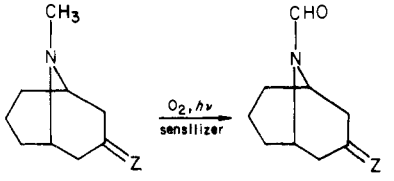
that it was the precursor to either or both radicals was rejected when similar photoxidations showed no detectable amounts of paramagnetic species derived from **381**. By separate experiments with solutions of a known nitroxide and phenothiazine, an unknown reaction between the nitroxide **379** and phenothiazine (which did not produce the radical **380**) was established. This, in turn, eliminated the nitroxide **379** as a precursor for radical **380**. The results, except for the formation of the sulfoxide **381**, were attributed to an initial attack by singlet oxygen (in direct light phenothiazine can also act as the sensitizer) upon the nitrogen lone pair of electrons followed by hydrogen migration and cleavage of either an NO or an OO bond.[266] Peracetic acid oxidized both 1,3- and 2,4-dinitro-*N*-methylphenothiazines into sulfones and left the amine nitrogen atom unchanged.[267]

A similar explanation was given to singlet oxygen reactions with other secondary and with primary amines (eq 283).[272,268]



$Z = R, H$ (283)

Singlet oxygen photooxidized *N*-methylgranatanine (**382**), sensitized by hydrocarbons (triphenylene or naphthalene), more rapidly than pseudopelletierine **383** (eq 284). Presumably there



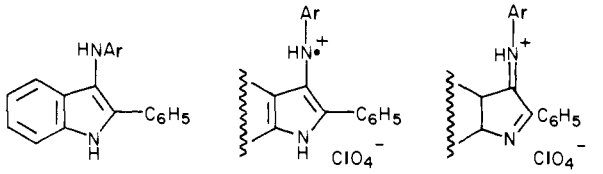
382, $Z = H_2$
383, $Z = O$ (284)

was a transannular carbonyl protection for the amine nitrogen atom in the latter (compare section XII.C).[269]

An investigation of the quenching of singlet oxygen by aliphatic amines revealed a correlation with amine ionization potentials when steric effects by α branching in the amine were absent.[290] An inverse correlation between the ionization potential of the organic solvent molecule and the wavelength of the oxygen charge-transfer complex was found.[291]

3. Enamine and Aminocyclopropane Autoxidation

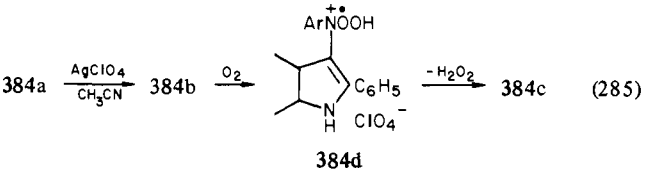
Support for an intermediate peroxide adduct from autoxidation of an amino radical cation has been claimed for a spectroscopically monitored reaction.[292] Radical cations, generated in an ESR spectrometer cavity from an amine, e.g., **384**a, and silver perchlorate, were characterized by ESR data



384a **384b** **384c**

$Ar = p\text{-}CH_3OC_6H_4$

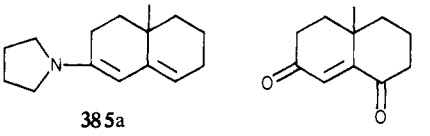
and then exposed to air. The monitored oxidation of the radical perchlorate **384b** established a correlation between decreasing absorption at 402 nm, assigned to the radical **384b**, and increasing absorption at 575 nm, assigned to the imine perchlorate **384c**. This was interpreted as support for the intermediacy of the hydroperoxide radical perchlorate **384d** (eq 285). In the absence of a direct detection of the peroxide



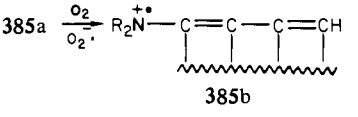
384d (285)

384d, it seems best to conclude that the data permit this specific intermediate but do not require it.

Autoxidation of an enamine **385a** derived from an α,β-unsaturated ketone produced the 1,4-dione **386** after hydrolysis.[293] It was described as a chain reaction (eq 286d) initiated by the generation of the radical cation **385b** in a charge transfer between the enamine and oxygen (eq 286a). The formation of

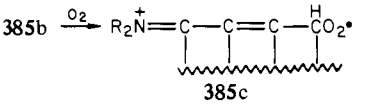


385a **386**



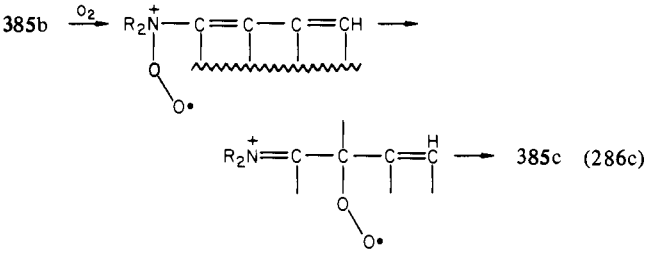
385b (286a)

an intermediate hydroperoxide radical cation **385c** by oxidation directly at carbon was proposed (eq 286b);[293] however, an initial

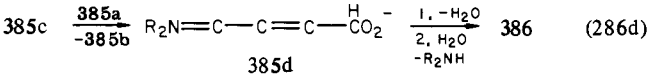


385c (286b)

oxidation at nitrogen followed by a migration of dioxygen to the carbon atom at the 4-position via transient bonding with the carbon atom at the 2-position can also be satisfactory (eq 286c).

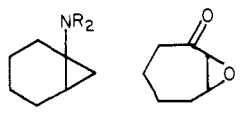


385c (286c)

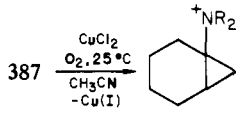


385d (286d)

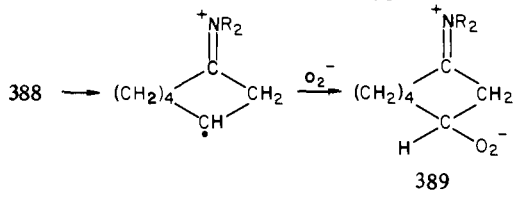
A related catalyzed autoxidation of the aminocyclopropane **387** gave an α,β-epoxy ketone **390** with the zwitterionic amino hydroperoxide **389** as a proposed intermediate produced directly by an attack from a dioxygen radical anion at carbon (eq 287a,b). The intermediate may also be formed from an initial attack by oxygen at the amine radical cation center, charge transfer and dioxygen migration to carbon (eq 288). Ring



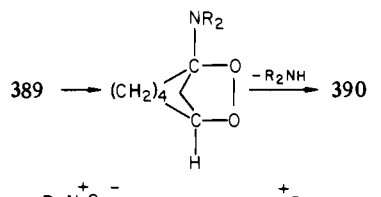
387 390



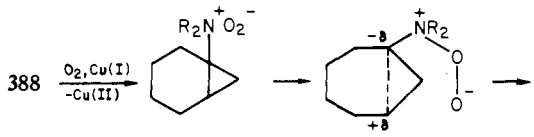
388 (287a)



389 (287b)



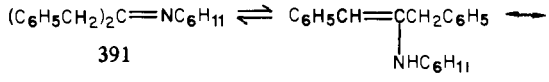
389 390 (287c)



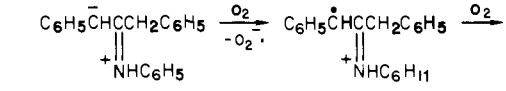
388 389 (288)

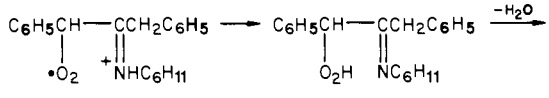
closure into a cyclic peroxide and an elimination reaction concerted with a ring contraction accounted for product formation (eq 287c).[294]

Autoxidation of the *N*-cyclohexylimine **391** of dibenzyl ketone produced cyclohexyl isocyanide, cyclohexylamine, dibenzyl ketone, benzoic acid, and presumably benzaldehyde (eq 289).[295]

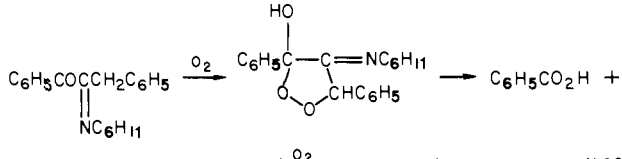


391 392



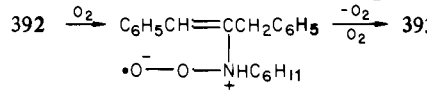


393



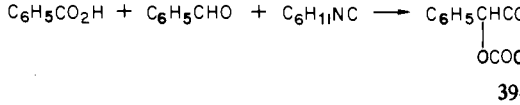
(289)

A free-radical chain reaction following an initial charge transfer accounted for the results; here also initial bonding between oxygen and the nitrogen atom of the enamine **392** can be suggested (eq 290). The amide **394**, a product of a Passerini



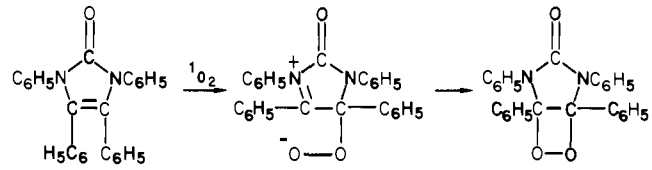
(290)

reaction (eq 291),[296] was not detected.

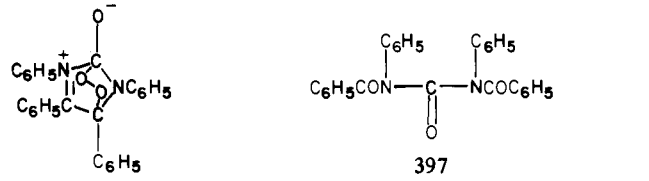


394 (291)

Dye-sensitized photooxygenation of 1,3,4,5-tetraphenylimidazolin-2-one (**395**) gave benzanilide, *N,N'*-diphenyl-*N*-benzoylbenzamidine (**396**), and *N,N'*-diphenyl-*N,N'*-dibenzoylurea (**397**) by rearrangement and fragmentation of zwitterionic peroxide **398** or a four-membered cyclic peroxide **399** (eq 292).[297] A transformation of the intermediate oxa-

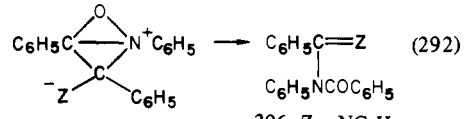


395 398 399



397

400, Z = NC_6H_5
401, Z = O



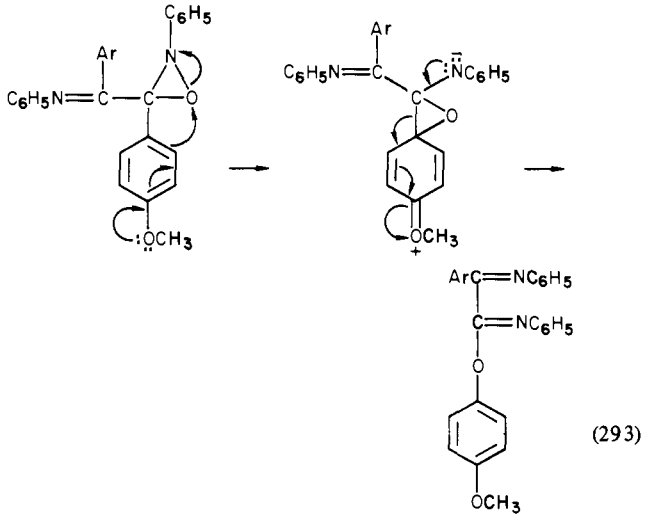
(292)

402, Z = NC_6H_5
403, Z = O

396, Z = NC_6H_5
404, Z = O

ziridine **400** into the amidine **396** was similar to a rearrangement of 2,3-diphenyl-3-benzoyloxaziridine (**401**) into dibenzoylaniline (**404**).[298]

An additional product (**405**) was obtained when the phenyl group attached to the oxaziridinyl carbon atom was replaced by *p*-methoxyphenyl. Migration of the electron-rich aryl group from a carbon to an oxygen atom was accounted for by the sequence in eq 293.[297]



(293)

405

In another situation migration from carbon to an oxaziridinyl oxygen atom brought about a variation on the Schmidt reaction

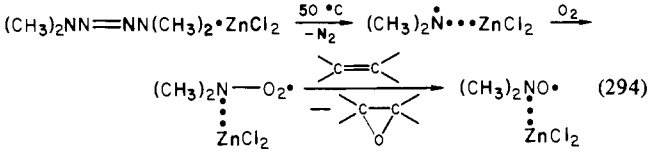
(section II.D). Essentially the same mechanistic interpretation was proposed.

4. Aminyls

Several reviews on aminyls and aminyl oxides (aminoxyls iminoxyls, nitroxyls, nitroxides) have appeared.[218e,219]

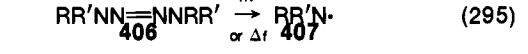
a. Alkyl- and Arylaminyls

Many nitrogen-contained radicals, e.g., dialkylaminyl,[299] diarylaminyl,[300] dialkylketiminyl,[301] and trialkylhydrazyl,[302] readily combine with oxygen and with hydroperoxides to give nitroxides. When complexed with zinc chloride, a dimethylamino radical reacted reversibly with oxygen to give an aminohydroperoxy radical. The latter was moderately efficient in epoxidizing olefins by a stereospecific donation of an oxygen atom to the alkene bond (eq 294).[303]



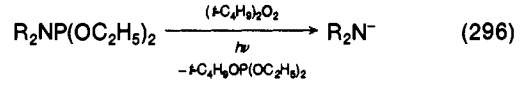
(294)

Thermolysis or photolysis of a tetrasubstituted tetrazene (**406**) has often provided an aminyl (**407**), generally not isolated (eq 295).[299a,b] More recently the photolysis of a dialkylamino-



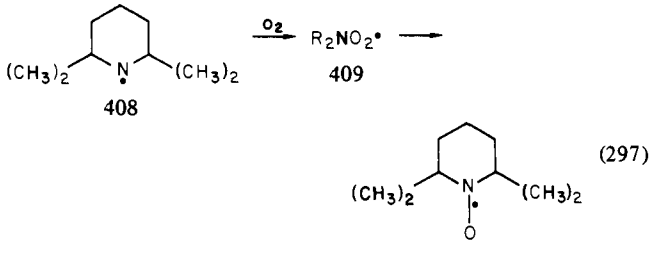
(295)

phosphine in the presence of di-*tert*-butyl peroxide has been recommended (eq 296).[304,305]



(296)

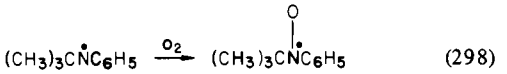
Although an active aminyl (**408**) may combine rapidly and quantitatively with molecular oxygen to form a nitroxide (**410**; eq 297), contrary claims had to be resolved.[299b,304] An initial



(297)

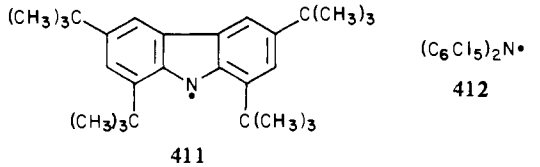
quantitative

1:1 adduct (**409**) between an aminyl and oxygen was assumed for the oxidation of a dialkyl or an alkylarylaminyl (eq 298).[299b,305]



(298)

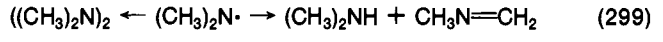
Diarylaminyls **411** and **412**, however, were found inert to oxy-



411

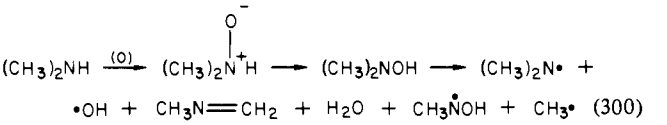
412

gen. Dimerization into a hydrazine and disproportionation into a secondary amine and an imine (eq 299) have generally been competitive with oxidation of an active aminyl.[304]



(299)

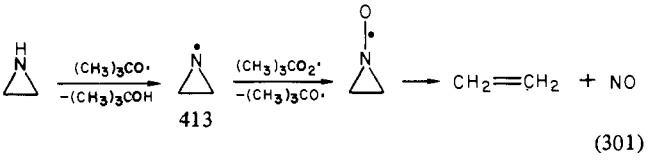
A gas-phase reaction in a cross-jet reactor produced dimethylamine oxide from oxygen atoms and dimethylamine (eq 300). The energy-rich *N*-oxide rearranged into *N*,*N*-di-



(300)

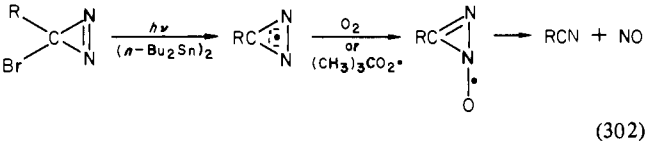
methylhydroxylamine, which fragmented.[306] Although detection of the dimethylamine radical was claimed, its reaction with oxygen was not.

Diazirinyl, aziridinyl, diaziridinyl, and oxaziridinyl radicals (section VI.D.2) do not form stable nitroxides. Aziridinyl **413** reacted readily with peroxy radicals, but the presumed nitroxide decomposed rapidly into ethylene, the only organic product, and nitric oxide (not detected) (eq 301).[307] An analogous reaction



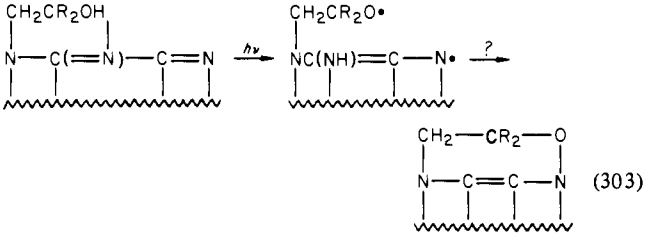
(301)

between diazirinyl radicals and oxygen or peroxy radicals was suggested as a possible method for the formation of a nitrile (eq 302).



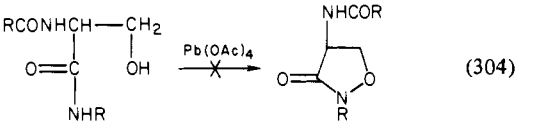
(302)

On the other hand, coupling an alkoxyl radical with an aminyl to form a hydroxylamine is virtually unknown. Intramolecular coupling to produce a proposed seven-membered cyclic hydroxylamine, a desired intermediate, was unsupported (eq 303).[308] Later an attempted oxidative cyclization from a β-



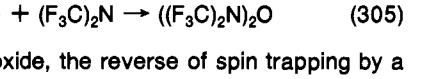
(303)

hydroxy amide by treatment with lead tetracetate was unsuccessful (eq 304).[309] Somewhat related is the isolated example



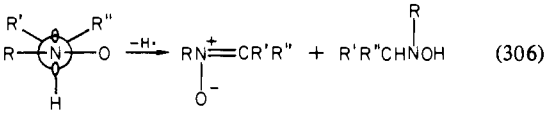
(304)

of the formation of a bisdialkylaminooxide by coupling bis(trifluoromethyl) nitroxide—which is incapable of a disproportionation by β-scission—with its aminyl precursor (eq 305).[310]



(305)

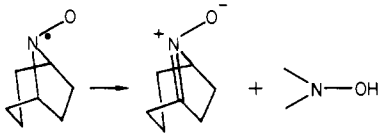
β-Scission of a nitroxide, the reverse of spin trapping by a nitrone, affords a disproportionation into a nitrone and a hydroxylamine (eq 306). It has been correlated with a confor-



(306)

mation in which the β-CH bond and the orbital of the unpaired electron are coplanar. Certain nitroxides are stable because

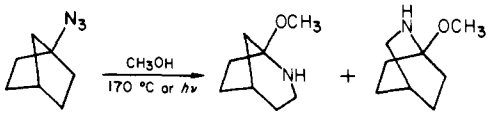
this conformation is forbidden. This stability can be enhanced when nitrone formation at a bridgehead position would violate Bredt's rule. Thus nitrone **414** formed very slowly from nortropane-*N*-oxy and was found to be very reactive (eq 307).[311]



(307)

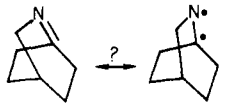
414

There is an extraordinary interest in bridgehead nitrones, e.g., **414**. It was previously concluded that high-energy bridgehead imine intermediates were avoided in the decomposition of 1-azidonorbornane by a rearrangement concerted with an addition of solvent (eq 308).[312] A search for evidence of a reaction



(308)

between the hypothetical diradical **415** and oxygen was unsuccessful. Resonance may, of course, account for the greater stability of a bridgehead nitrone relative to the corresponding imine (eq 309).[311]

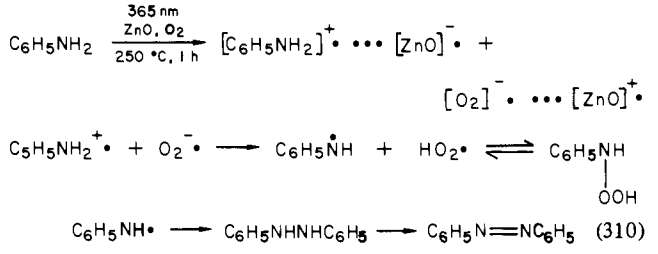


415

(309)

b. Aniline and Oxygen

A photooxidation of aniline catalyzed by zinc oxide was reported to give azobenzene (eq 310) with about 40% efficiency

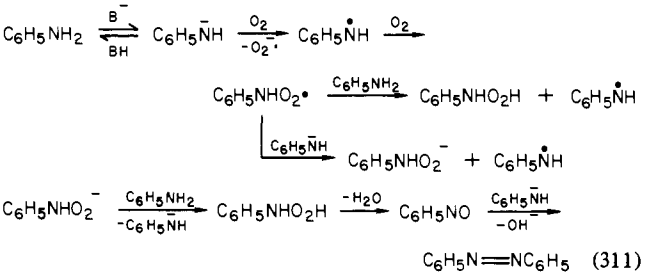


(310)

(no other product was described).[313] It was claimed that a superoxide anion was generated by a transfer of an electron from zinc oxide to an oxygen molecule. Interaction of aniline with the superoxide anion was considered to produce anilino radicals, perhaps via an anilino hydroperoxide. Azobenzene then was presumably produced from coupling of the anilino radicals and dehydrogenation of hydrazobenzene.[313]

Aniline, in dimethyl sulfoxide with an excess of potassium *tert*-butoxide, absorbed an equimolar amount of oxygen and was converted into azobenzene via a condensation with nitrosobenzene, an undetected intermediate.[274,275] Azobenzene-^{14}C was obtained when nitrosobenzene-^{14}C was added to the oxidizing solution. When the normal and radioactive products were obtained with the same efficiency, the intermediacy of nitrosobenzene was confirmed. A scheme which bypassed the intermediacy of phenylhydroxylamine was proposed (eq 311).[274,275]

The known oxidation of hydrazobenzene into azobenzene was not involved in the oxidation of aniline, for two reasons. First its intermediacy was not compatible with the ^{14}C work described above. Also it was shown that 2 mol of oxygen/mol of hydrazobenzene was required for its conversion into azobenzene whereas 1.25 mol of oxygen would account for the conversion of aniline into azobenzene via hydrazobenzene (eq 312, 313).[275]



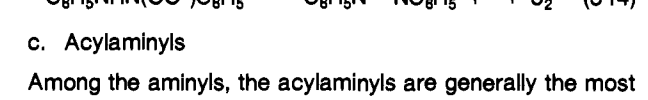
(311)

$$2C_6H_5NH_2 + 0.5\ O_2 \xrightarrow{B^-} 2C_6H_5\dot{N}H + H_2O$$

$$2C_6H_5\dot{N}H \rightarrow C_6H_5NHNHC_6H_5 \quad (312)$$

$$C_6H_5NHNHC_6H_5 + 2O_2 \xrightarrow{B^-} C_6H_5N{=}NC_6H_5 + 2O_2^- \quad (313)$$

A base-catalyzed oxidation of hydrazobenzene was shown to produce superoxide anion (eq 314).[275]

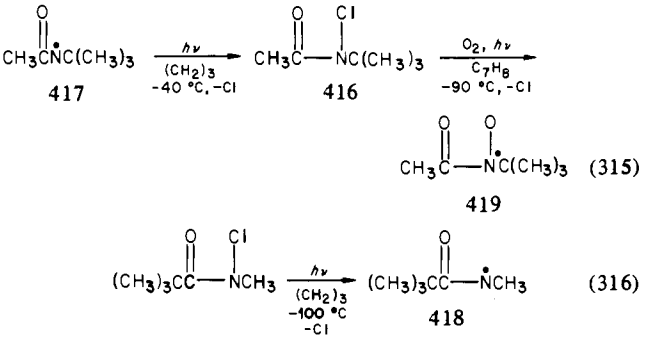


(314)

c. Acylaminyls

Among the aminyls, the acylaminyls are generally the most unstable. Diacylaminyls were so extremely short-lived that they were detected only indirectly as their adducts with 2-methyl-2-nitrosopropane.[314] An acylaminyl was easily oxidized into an acylaminyl oxide, also known as an acyl nitroxide or a nitroxone.[315]

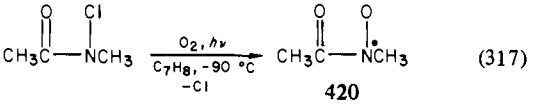
Differentiation between an acylaminyl and its *N*-oxide was uncertain before the definitive work of Danen and Gellert[315] in 1972 confirmed certain of the earlier reports on acyl nitroxides.[316,317] These investigators generated (1) two amido radicals (acylaminyls) (**417** and **418**) from *N*-chloro amides, e.g., **416** by photolysis in cyclopropane in the cavity of an ESR spectrometer (eq 315, 316), and (2) two nitroxones (**419** and



(315)

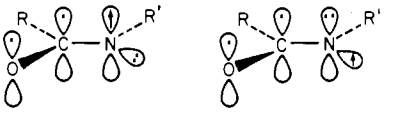
(316)

420) by similar treatment of air-saturated toluene solutions of corresponding *N*-chloro amides (eq 315, 317). ESR hyperfine



(317)

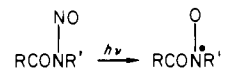
splitting structure constants and g values clearly supported the assigned structures **417**–**420** with a π-**421** rather than a σ-**422**



421 422

electronic ground state for an acylaminyl.[315] Nitroxone conformations were also determined from ESR values.[314]

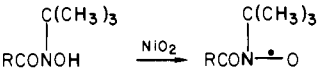
Nitroxones, generally obtained from either oxidation of hydroxamic acids[318] (VI.A,C,D,E) or by spin trapping,[317] have recently been produced from *N*-nitroso secondary amides by photolysis at −90 to −20 °C in toluene (eq 318). An analogous



(318)

formation of an alkoxy radical from a *C*-nitroso compound was noted.[319a] Neither the source of oxygen in the radical nor the generality of the reaction has been established; an alkoxy radical was not reported for the photolysis of 2-methyl-2-nitrosopropane.[319b]

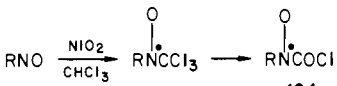
Nitroxones **423** and **424** were obtained from *N*-*tert*-butylhydroxamic acids (eq 319) and from a mixture of chloroform



(319)

423

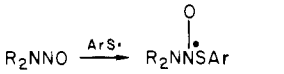
and 2-methyl-2-nitrosopropane (eq 320) by treatment with nickel



(320)

424

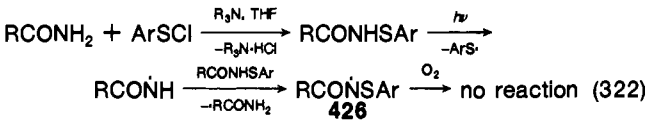
peroxides.[320] From another investigation a nitroxide radical derivative (**425**) of a nitrosamine was reported (eq 321).[321]



(321)

425

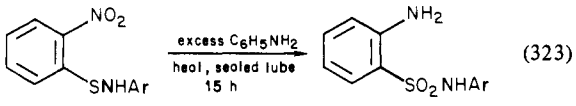
N-Acyl-*N*-arylthioaminyls (**426**) were generated from a sulfenamide by hydrogen abstraction in both photolytic and thermal processes (eq 322). These radicals and *N*-aryl-*N*-arylthio-



(322)

426

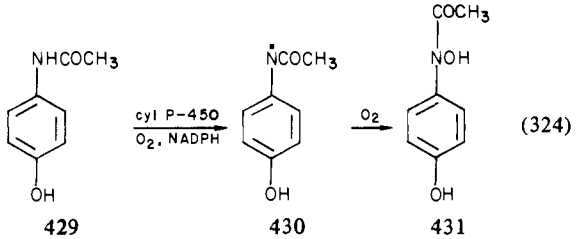
aminyls (ArṄSAr′) were not sensitive to or reacted slowly with oxygen.[322-324] This is reminiscent of a thermal rearrangement of 2-nitrobenzenesulfenanilide (**427**) into 2-aminobenzenesulfonanilide (**428**), a product of intramolecular transfer of oxygen from the nitro group to the sulfur atom.[325] The reaction proceeded equally well in the presence or absence of oxygen (eq 323).



(323)

427 428

N-Acetyl-*N*-hydroxy-*p*-aminophenyl (*N*-hydroxyacetaminophen, **431**), a postulated toxic metabolite of acetaminophen (**429**), has been considered to be an oxidation of the latter (eq 324).[326] There seems to be a good possibility that the oxidation



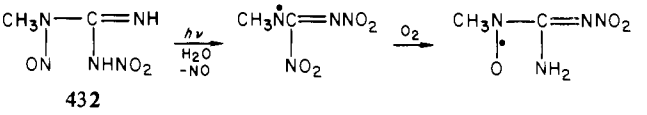
(324)

429 430 431

proceeds from an amidyl (**430**).

d. Imidyl Aminyls

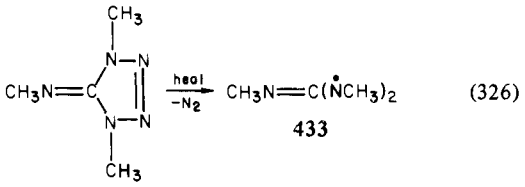
^{15}N was introduced into two positions of *N*-methyl-*N*′-nitro-*N*-nitrosoguanidine (**432**) to investigate photolysis and photooxygenation reactions (eq 325). An ESR analysis of the rad-



(325)

432

icals was consistent with the interpretation shown.[327] Tris(imino)methane (**433**) was recently prepared, but a reactivity of this remarkable diradical toward oxygen was not noted[328] (eq 326).

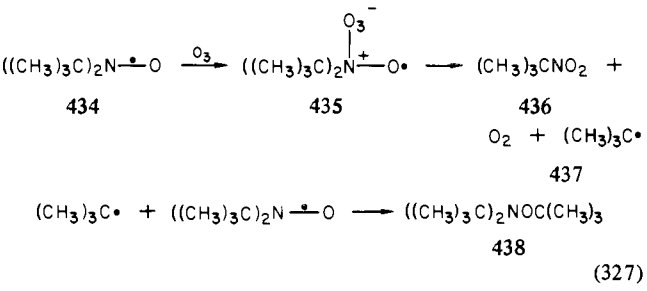


(326)

433

e. Aminyl Oxides

Oxidation of nitroxides has received little attention. In one report ozonization of di-*tert*-butyl nitroxide gave 2-methyl-2-nitropropane and tri-*tert*-butylhydroxylamine (eq 327). The initial adduct **435** was assumed.[329]



(327)

434 435 436 437 438

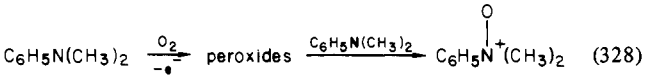
VI. Hydroxylamines, Linear and Cyclic

N-Mono- and N,N-disubstituted hydroxylamines are easily oxidized into nitroso compounds and nitroxides. A weak oxygen–hydrogen bond has been cited as a contributing factor to this exceptional reactivity. At the assignment of 70 kcal/mol, it is weaker by 10–15 kcal than the corresponding bond in an oxime.[219]

Mild conditions for these oxidations have been sufficient for a wide variety of reagents: air, Fehling's solution, Tollens' reagent, ferric chloride, permanganate, chromic acid, periodate, bromine, iodine, ferricyanide salts, and peroxybenzoic acid were cited in a general text on nitrogen compounds.[60d] Manganese dioxide,[330a,b] periodates,[331a,b] lead tetraacetate,[332] *m*-chloroperbenzoic acid,[333] nitrosodisulfonates (Fremy's salt),[334a] oxides of lead, mercury, and silver, hydrogen peroxide, and *tert*-butyl hydroperoxide in the presence of a catalytic amount of cobalt stearate,[334b] fluorine, nickel peroxide,[334c] and nitrosobenzene[334b] were also successful.

A. Electrochemical Oxidation

Although *N*,*N*-dimethylaniline was electrochemically indirectly oxidized in part into its *N*-oxide derivative (eq 328),[335] this



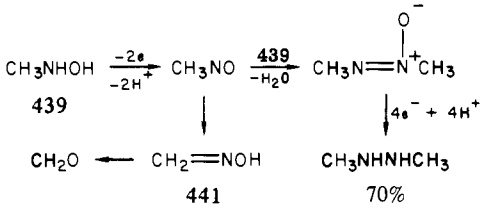
(328)

technique has not been successful in covalently bonding oxygen to nitrogen attached to carbon; however, electrochemical dehydrogenation of hydroxylamine derivatives is well-known. Electrochemical formation of other bonds has been more successful. A nitration[1b] of naphthalene by the action of nitrogen

dioxide on the electrochemically generated naphthalene radical cation (eq 329) was claimed[336a] and disputed.[336b]

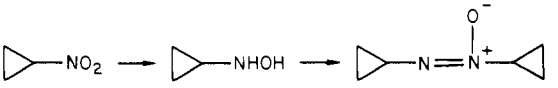
$$C_{10}H_8 \xrightarrow{-e^-} (C_{10}H_8)^{+\cdot} \xrightarrow[+e^-]{NO_2} C_{10}H_7NO_2 \qquad (329)$$

Anodic waves for *N*-alkylhydroxylamines in aqueous alkaline solutions containing sulfite ions provided a quantitative method of analysis before the electrolytic reactions were known. After investigations on *N*-methylhydroxylamine (**439**), as a model, established nitrosomethane as the primary product, azoxymethane as a condensation product, and 1,2-dimethylhydrazine as a cathodic reduction product (eq 330), the method was



(330)

extended to a preparation of azoxycyclopropane (**440**; eq 331).[337]



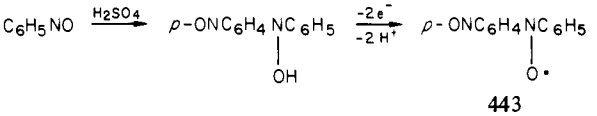
(331)

Isomerization of nitrosomethane into formaldoxime (**441**) was decreased by maintaining lower temperatures (ice cooling) and higher concentrations of the hydroxylamine **439**.[337] A similar anodic oxidation of *N*-benzylhydroxylamine **442** and its α-methyl and α-phenyl derivatives gave the oximes of benzaldehyde, acetophenone, and benzophenone in excellent yields (eq 332).[336]

$$\underset{\mathbf{442},\ R = H}{C_6H_5CH(R)NHOH} \xrightarrow[-2H^+]{-2e^-} C_6H_5C(R)=NOH \qquad (332)$$

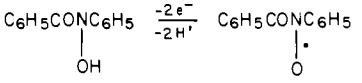
R = H, 95%
R = CH_3, 100%
R = C_6H_5, 100%

Anodic oxidation generated *p*-nitrosodiphenyl (**443**; eq 333)



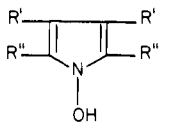
(333)

and other diaryl nitroxides from *N*,*N*-diarylhydroxylamines. A similar oxidation gave *N*-phenyl-*N*-benzoyl nitroxide (eq 334).[339,340]



(334)

Pyrrole nitroxides were also obtained by electrolytic oxidation of *N*-hydroxypyrroles (**444**).[341]



444

R′ = C_6H_5; R″ = C_6H_5
R′ = $CO_2C_2H_5$; R″ = *t*-$(CH_3)_3C$
R′ = $CO_2C_2H_5$; R″ = CO_2CH_3
R′ = CH_3; R″ = *p*-CH_3O-C_6H_4

O-Methyl and *O*-*tert*-butylhydroxylamines, benzohydroxamic acid, its *p*-cyano derivative, phthalhydroxamic acid, and isonicotinohydroxamic acid gave no anodic waves, but ethyl and benzyl N-hydroxycarbamates (**445**) in the presence of an amine gave *N*,*O*-(alkoxycarbonyl)- and *O*-alkoxycarbonyl *N*-hydroxycarbamates alcohols, and *N*-alkylacetamides by anodic oxidation in acetonitrile (eq 335).[342,343]

$$\underset{\mathbf{445}}{HONHCO_2CH_2R} \xrightarrow{(O)} (RCH_2OCO)_2NOCO_2CH_2R +$$
R = CH_3, C_6H_5
$$RCH_2OCO_2NHCO_2CH_2R + RCH_2OH + CH_3CONHR \qquad (335)$$

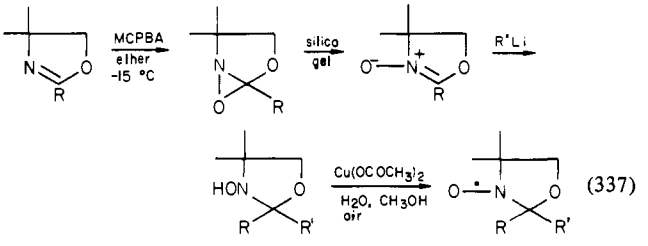
B. Oxygen and Peroxides

Diethylhydroxylamine (DEHA), because of its rapid reaction with alkyl, alkoxy, or peroxy radicals or with air to produce diethyl nitroxide (**446**), captured interest for its potential as a combatant of photochemical smog brought about by oxidation of nitrogen oxides in the presence of hydrocarbons (eq 336).[344,345]

$$\underset{DEHA}{(C_2H_5)_2NOH} + Z\cdot \rightarrow ZH + \underset{\mathbf{446}}{(C_2H_5)_2N{-}O\cdot}$$

$$DEHA + O_2 \xrightarrow[\text{or RH (gas phase)}]{0\text{–}60\ ^\circ C,\ C_6H_5Cl} \mathbf{446} + HO_2\cdot \qquad (336)$$
Z = R or RO_2

Apparently all hydroxylamines with a free hydroxyl group at nitrogen attached to one or two hydrocarbon groups is subject to air oxidation. Nitroxide formation generally required the absence of hydrogen attached to either nitrogen or the α-carbon atom.[334b] Such a hindered hydroxylamine (**447**) is the precursor to 4,4-dimethyloxazolidine-*N*-oxy (doxyl) (**448**) in a new preparation of the latter in four steps from 4,4-dimethyloxazoline (eq 337). The last step is an efficient catalyzed air oxidation.

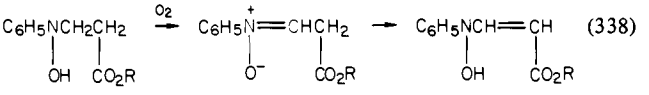


(337)

447 448

Doxyl derivatives have been highly successful as spin labels.[346]

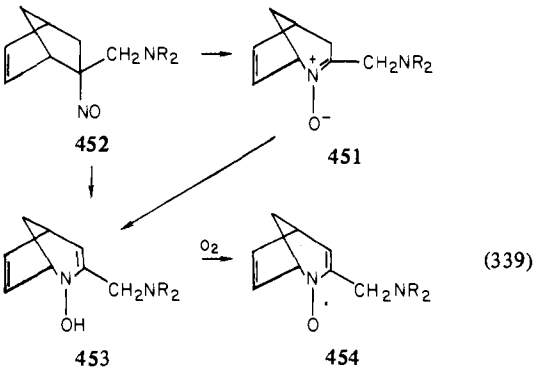
Air oxidized a β-(*N*-phenylhydroxylamino)acrylate (a Michael adduct from an acrylic ester and phenylhydroxylamine) into a nitrone (**449**) which tautomerized into an *N*-phenyl-*N*-alkenylhydroxylamine (**450**; eq 338).[347]



(338)

449 450

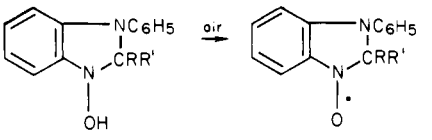
Isomerization of a nitrone into an ene hydroxylamine, e.g., **499** → **450**, is rarely encountered, but the nitrone **451** was considered to be a possible intermediate in the facile rearrangement of the nitroso compound **452** into the ene hydroxylamine **453** as well as in the subsequent air oxidation of **453** into the nitroxide **454** (eq 339).[348]



(339)

452 451 453 454

A facile autoxidation of the hydroxylamines **455** precluded their isolation (eq 340).[349]

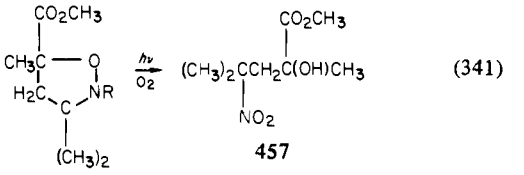


(340)

455

R = CH_3; R' = C_6H_5; R = R' = H

Oxidation of an N,O-disubstituted hydroxylamine is unusual; nevertheless the isoxazolidines **456** were photooxidized into nitro compounds **457** (eq 341).[350]



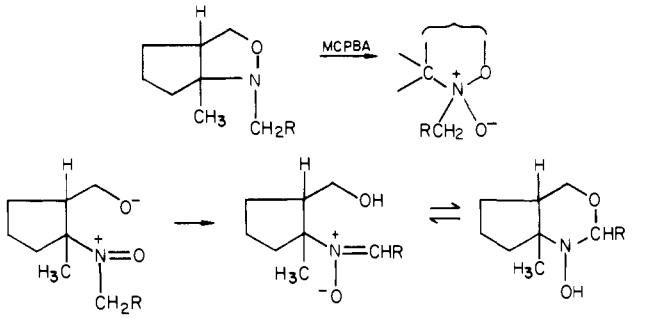
(341)

456

457

R = H, 60%
R = CH_3, C_2H_5, $(CH_3)_2CH$, 6-9%

On the other hand a peroxycarboxylic acid oxidized *N*-methylisoxazolidines into *N*-hydroxy-1,3-tetrahydrooxazines with *N*-(γ-hydroxypropyl)methylenenitrones (**458**) as proposed intermediates (eq 342).[351]

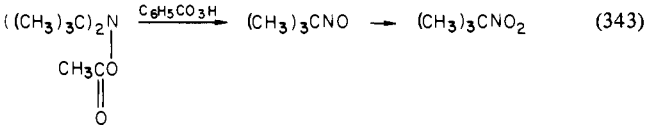


458

R = H, C_6H_5

(342)

Perbenzoic acid and *N,N*-di-*tert*-butylhydroxylamine or its *O*-acyl derivatives gave 2-nitroso-2-methylpropane and *tert*-butyl benzoate (eq 343). Removal of a *tert*-butyl group by



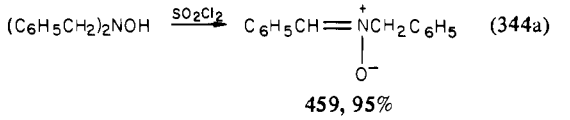
(343)

α-cleavage at nitrogen is related to the ring opening of a nitrosonium salt (section XII.G) into a nitroso olefin.[352a]

C. Halogens and Derivatives

1. Sulfuryl Chloride

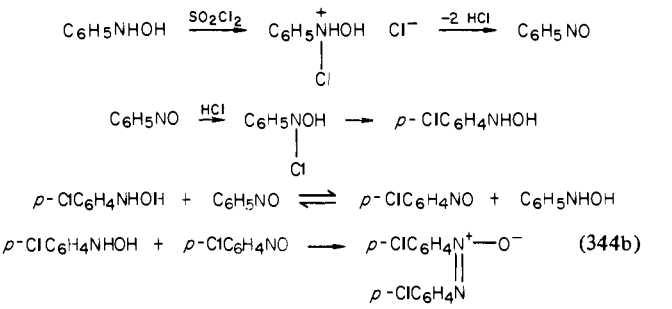
Sulfuryl chloride converted *N,N*-dibenzylhydroxylamine into the *N*-benzylnitrone **459** of benzaldehyde (eq 344a). Phe-



(344a)

459, 95%

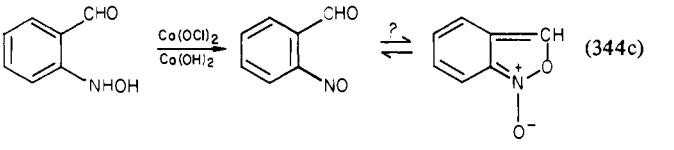
nylhydroxylamine gave a more complicated reaction (eq 344b).[353]



(344b)

2. Hyphalites and Halogens

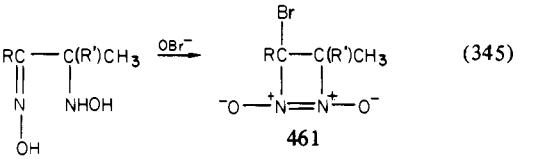
Neither IR nor NMR spectroscopy detected anthranil *N*-oxide (**460**), a suggested[70] tautomer of *o*-nitrosobenzaldehyde, when the latter was produced from o-(hydroxyamino)benzaldehyde by oxidation with calcium hypochlorite[354] (eq 344c).



(344c)

460

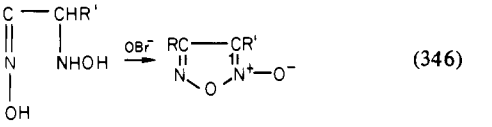
Oxime derivatives of α-acyl-α,α-dialkylhydroxylamines gave 1,2-diazetine 1,2-dioxides (**461**) when treated with sodium hypobromite (eq 345). Furoxans were produced when α-hydro-



(345)

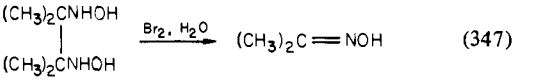
461

gen was present (eq 346).[355-357] Aqueous bromine degraded



(346)

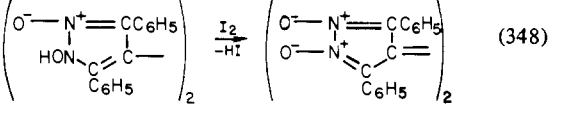
2,3-bis(hydroxyamino)-2,3-dimethylbutane (**462**) into acetone oxime (eq 347).[358]



(347)

462

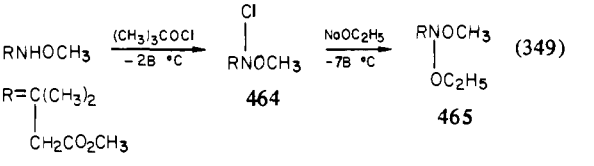
Iodine oxidized a 3,3'-bi(*N*-hydroxypyrazole) into a nonplanar molecule (**463**; eq 348), a biradical detected by ESR.[359,360]



(348)

463

Chiral stabilization was sought at nitrogen directly attached to more than one oxygen atom (section VII.A,I) and was extended to an open-chain system.[361,362] Sodium ethoxide and the *N*-chlorohydroxylamine **464** gave the *N*-alkoxyhydroxylamine **465** (eq 349). An abstract of this work did not state that



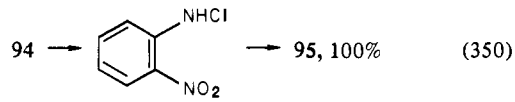
(349)

464

465

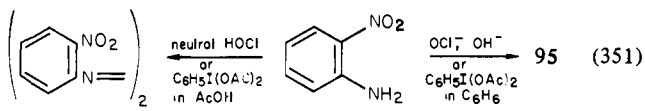
compound **435** displayed chiral stability.[382]

Presumably alkali brought about α elimination at nitrogen when it transformed *N*-chloro-*o*-nitroaniline (**466**) into benzofuroxan (**95**; eq 350).[383] Unfortunately a simple thermolysis



466 (350)

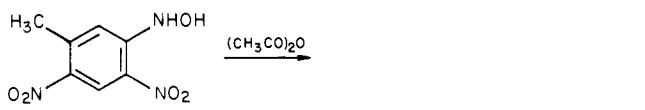
was not reported. The furoxan **95** was also obtained from *o*-nitroaniline (**94**) by treatment with phenyl iodosoacetate in benzene or with alkaline hypochlorite (eq 351); in acetic acid



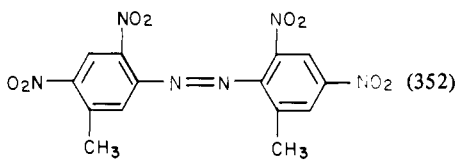
467 94 (351)

the former, and in neutral hypochlorite solution the latter, gave the azo compound **467** (eq 351).[67d,363]

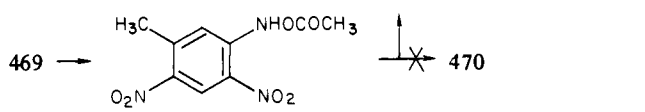
An *O*-acetyl intermediate (**468**), comparable to the chloro compound **466**, can be assumed in the transformation of the *o*-nitrophenylhydroxylamine (**469**), when heated in acetic anhydride, into an azo compound (eq 352).[364] Apparently there



469

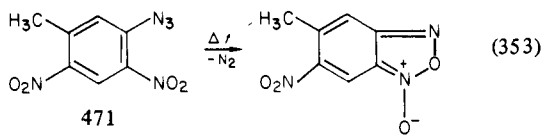


(352)



468

was no formation of the furoxan **470** independently obtained from the azide **471** (eq 353).[364b] The question of assistance



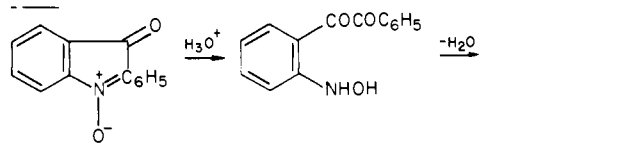
471 470 (353)

from the nearby nitro group in the ejection of chlorine from compound **466** or acetate from compound **468** has not been resolved.

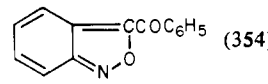
Although earlier claims for the formation of benzofuroxans from *o*-nitroarylhydroxylamines were discredited,[1c] perhaps the general question of interaction between an arylhydroxylamino group (or its derivatives, e.g., **466** and **468**) and ortho substituents, e.g., nitro and acyl, should be reinvestigated. An intermediate hydroxylamine was assumed in the transformation of the nitrone **472** upon treatment with acid into the anthranil **473** (eq 354).[365]

3. Periodates

Even without enhancement by an attached electron-withdrawing acyl or cyano group, nitroso derivatives of varied structures have been dienophilic, but nitrosocyanide and the nitrosoacyls showed a very high order of reactivity (eq



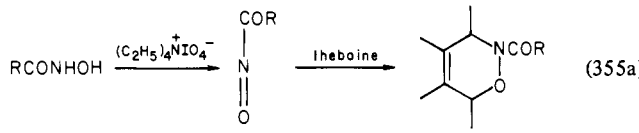
472



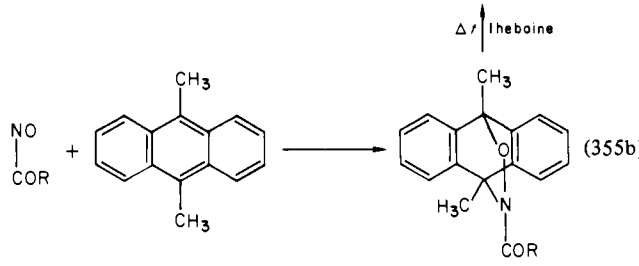
(354)

473

355a).[366a] The unstable nitrosoacyls cannot be isolated and



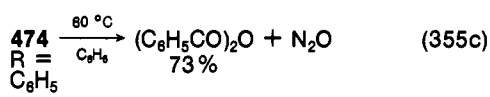
(355a)



474

(355b)

stored, but they have been liberated in situ by an easy thermolysis of their stable adducts (eq 355b) with 9,10-dimethylanthracene.[366a,b] Tetraethylammonium periodate has been recommended for the oxidation of benzo- or acetohydroxamic acid in the presence of a diene (eq 355a).[366a] Thermolysis of the adduct **474** (R = C_6H_5) in benzene gave benzoic anhydride and nitrous oxide (eq 355c).[366a] Dimethyl sulfoxide oxidized an



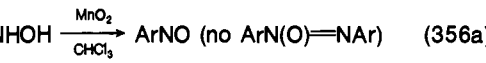
(355c)

acyl nitrene (section II.B).

D. Metal Oxides and Salts

1. Manganese Dioxide

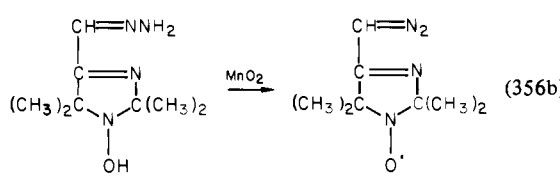
Solvent selection boosted the reaction efficiency from under 40% to over 90% in producing nitrosoarenes from *N*-arylhydroxylamines by oxidation with activated manganese dioxide in chloroform (eq 356a) rather than water, the more often used solvent.[367a]



(356a)

Ar = α-$C_{10}H_7$, β-$C_{10}H_7$, *p*-$ONC_6H_4C_6H_4$, C_6H_5

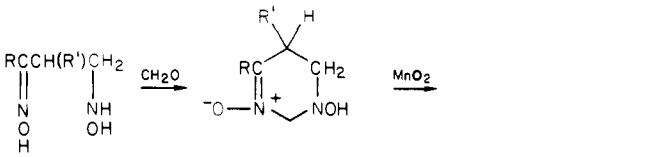
Dehydrogenation by manganese dioxide transformed the hydrazone function into a diazo group and the hydroxylamine portion of the imidazolidine **475** into a nitroxide (eq 356b).[367a]



475 (356b)

Pyrimidine *N,N'*-dioxides were obtained in poor to good yields from 1-hydroxy-1,2,5,6-tetrahydropyrimidine 3-oxides by oxida-

tion with activated manganese dioxide (eq 356c).[367c]

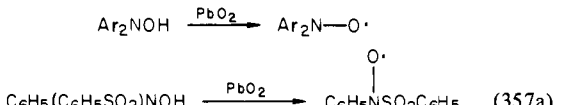


(356c)

$R = C_6H_5$, $R' = CH_3$, H; R = R' = H

2. Lead Dioxide and Tetraacetate

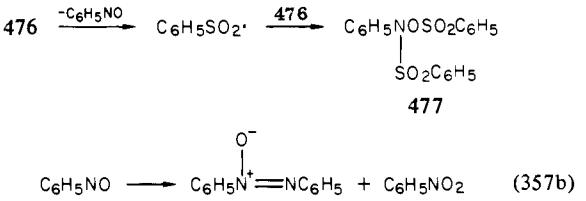
Although *N,N*-diarylaminyl oxides were generally produced from a hydroxylamine and lead dioxide (eq 357a), a replace-



(357a)

476

ment of one or both aryl groups with (an) arenesulfonyl group(s) led to an unstable aminyl oxide. Fragmentation and recombination accounted for the formation of trisubstituted hydroxylamines **477** (eq 357b). A mixture of nitrobenzene and az-

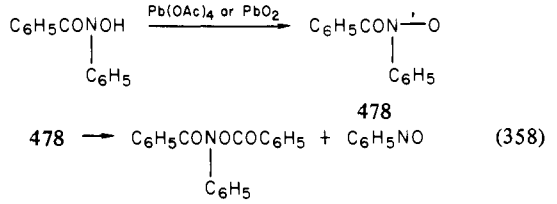


477

(357b)

oxybenzene was also produced. Lead tetraacetate produced the aminyl oxide **476**, but silver oxide, manganese dioxide, and nitric acid in acetic acid each gave no reaction.[368a,b]

Fragmentation was a common property for radical **476** and its benzoyl analogue **478** (eq 358).[368a,b] Other examples of α

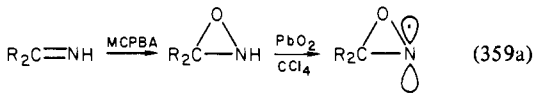


478

(358)

cleavage of aminyl oxides can be found in section V.D.4.e.

Lead dioxide oxidized 3,3-diphenyl- and 3,3-di-*tert*-butyloxaziridine into oxaziridinyls **479** (eq 359a). The possibility of



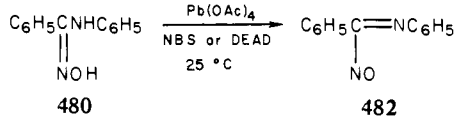
(359a)

479

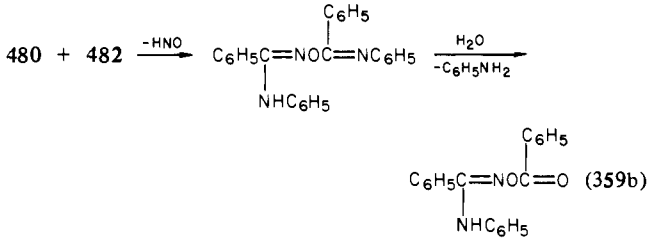
$R = C_6H_5$, $(CH_3)_3C$

an oxaziridinyl oxide (a nitroxide) structure rather than that of **479** was not permitted by ESR parameters. An assignment of the unpaired electron to an orbital at nitrogen with largely 2p character was indicated. The radical **479** (R = C_6H_5) decayed after 1 h at 50 °C into the corresponding oximino radical, but the radical **479** (R = $(CH_3)_3C$) gave an ESR signal with constant intensity for 24 h.[369] The sensitivity of these radicals to oxygen was not noted.

Either lead tetraacetate, *N*-bromosuccinimide, or diethyl azodicarboxylate (DEAD) oxidized the amidoxime **480** (tautomeric with an imidoylhydroxylamine) into the *O*-benzoyl derivative **481** of the oxime of benzanilide (eq 359b). An intermediate



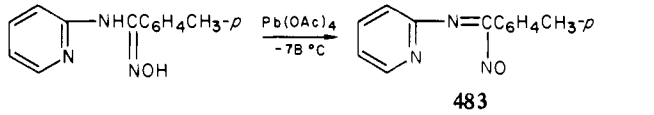
480 482



(359b)

481

condensation of *N*-phenyl-*C*-nitrosobenzaldimine (**482**) with the oxime **480** was assumed.[370] When similarly prepared at −78 °C, *N*-(α-pyridyl)-*C*-nitroso-*p*-methylbenzaldimine (**483**; eq 360)

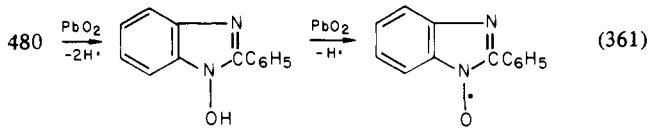


483

(360)

was isolated as its adduct with thebaine[371] (see eq 355b).

Oxidation of the amidoxime **480** with lead dioxide gave 2-phenylbenzimidazoyl *N*-oxide (**484**; eq 361). An initial ring

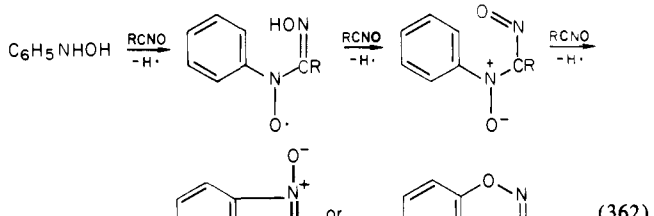


(361)

484

closure from the amidoxime into an *N*-hydroxyimidazole followed by oxidation of the hydroxylamine was proposed.[371,372] At the present time, ring closure from **482** cannot be ruled out (eq 361).

The initial radical from phenylhydroxylamine and a nitrile oxide was further oxidized into a cyclic radical (**485a** or **485b**) (eq 362). It was claimed that the size of the substituent deter-

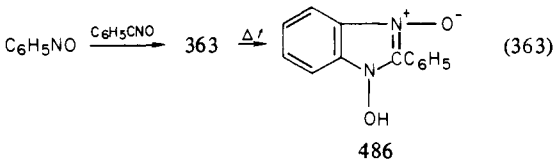


(362)

485a 485b

$R = CH_3$, C_6H_5 $R = (CH_3)_2CH$, $(CH_3)_3C$

mined the selection of product.[371,372] Intermediate **485a** (R = C_6H_5) was presumably a precursor to 2-phenyl-1-hydroxybenzimidazole *N*-oxide (**486**) in an earlier reaction (eq 363)

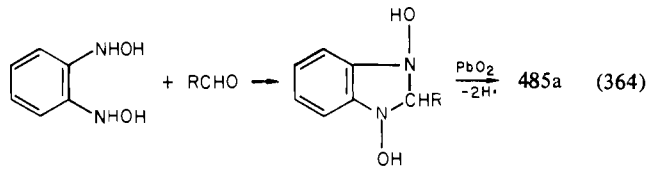


(363)

486

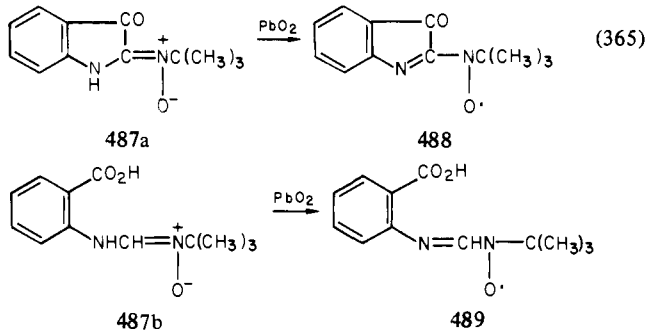
between nitrosobenzene and benzonitrile oxide.[373] A third reaction, more recently reported, between *o*-phenylenedi-

hydroxylamine and an aliphatic aldehyde in the presence of lead dioxide also produced radical **485a** (eq 364).[374]



(364)

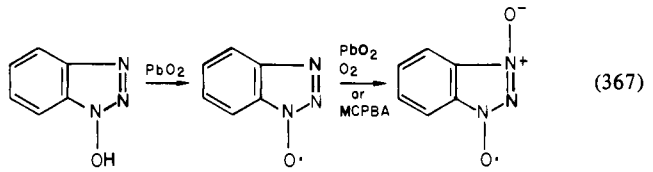
Other amidine *N*-oxides (**487a** and **487b**) were oxidized by lead dioxide into nitroxides **488** and **489** (eq 365, 366).[375,376]



(365)

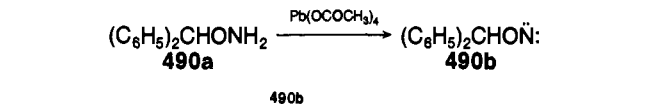
(366)

Benzotriazol-1-oxy 3-oxide was obtained from 1-hydroxybenzotriazole and either MCPBA or lead dioxide in the presence of air (eq 367).[376b]



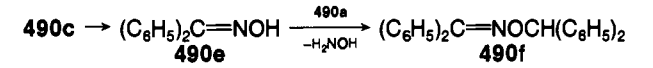
(367)

Lead tetraacetate and *O*-(diphenylmethyl)hydroxylamine (**490a**) in methylene chloride apparently produced diphenylmethoxynitrene (**490b**) and its rearrangement product, nitrosodiphenylmethane, since an adduct of these isomers was isolated. It was given the structure of an alkoxyazoxyalkane (**490d**; eq 368a).[377] The intermediate nitroso compound **490c**



(368a)

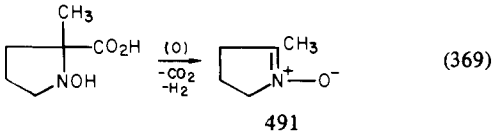
also rearranged into an oxime (**490e**) which gave an oxime ether (**490f**) by transoximation with the hydroxylamine **490a** (eq 368b).[376]



(368b)

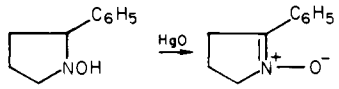
3. Mercuric Oxide

An interesting oxidative decarboxylation of 1-hydroxy-2-methylpyrrolidine-2-carboxylic acid gave the nitrone **491**[379] (eq 369). A structurally related nitrone (**492**) was obtained from



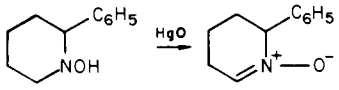
(369)

1-hydroxy-2-phenylpyrrolidine and mercuric oxide[380] (eq 370), but a similar reaction upon the homologous hydroxylamine gave



(370)

a nitroxide (**493**; eq 371a) in which the azomethine double bond

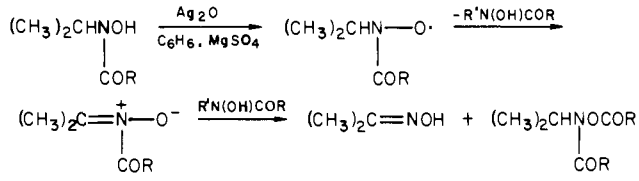


(371a)

was not in conjugation with the phenyl substituent.[381] An explanation[380] based on steric factors is unconvincing and might be resolved by spectroscopic analysis (see section VIII.F).

4. Silver Oxide

Oxidation of *N*-isopropylbenzohydroxamic acid by silver oxide produced benzoyl isopropylnitroxide (a_N = 2.28 and a_N = 2.55 G, R = C_6H_5, eq 371b). Oxidation proceeded to the final



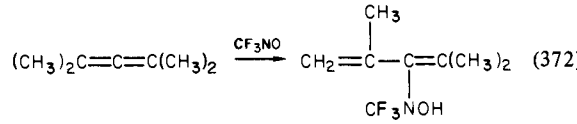
(371b)

products, acetoxime and *N,O*-dibenzoylisopropylhydroxylamine, via a postulated nitrone intermediate.[382]

E. Oxidative Elimination

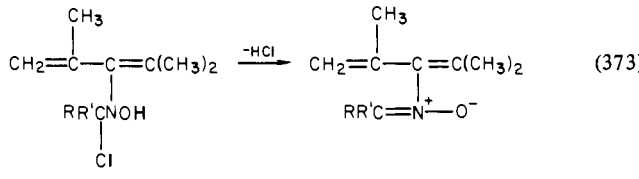
1. Dehydrohalogenation

An ene reaction between nitroso compounds and allenes gave unsaturated hydroxylamines. With tetramethylallene and trifluoronitrosomethane, the reaction stopped at the hydroxylamine stage (eq 372), but dehydrochlorination of the hydrox-



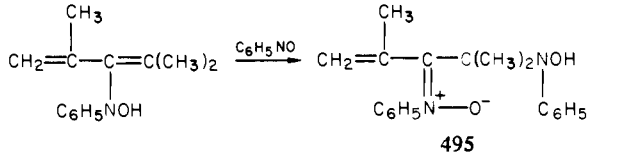
(372)

ylamines **494** from α-chloronitrosoalkanes produced unsaturated nitrones (eq 373). Two moles of nitrosobenzene com-



(373)

bined with tetramethylallene to give a nitrone hydroxylamine (**495**; eq 374).[383,384]

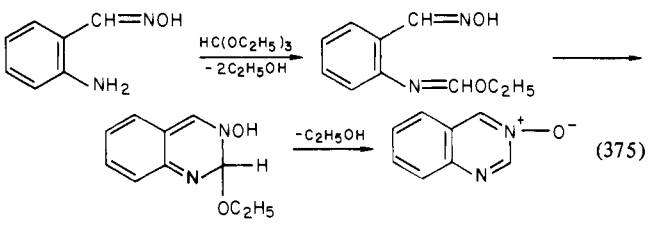


(374)

2. Elimination of an Alcohol, Ammonia, and/or Water

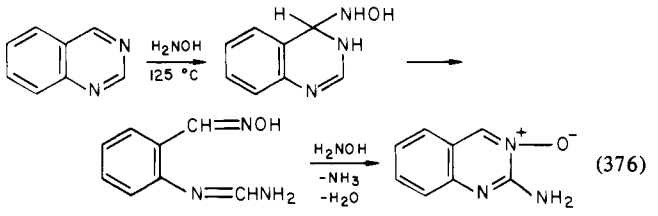
Often used to prepare an imidate ester or an isocyanide, the condensation between an orthoester and a primary amine can be diverted by a ring closure when appropriate functional groups

are nearby. The condensation with o-aminobenzaldoxime gave quinazoline 3-oxide (eq 375).[365]



(375)

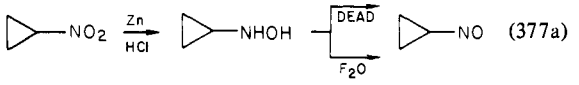
A preparation of 2-aminoquinazoline 3-oxide appears to be related (eq 376).[365,366]



(376)

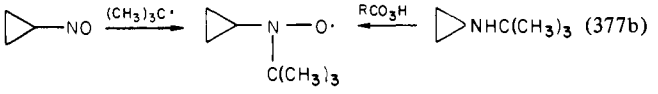
3. Dehydrogenation

Diethyl azodicarboxylate (DEAD) has dehydrogenated hydroxylamines into nitroso compounds.[377,367] It gave a more attractive route to nitrosocyclopropane (eq 377a)[368] than an



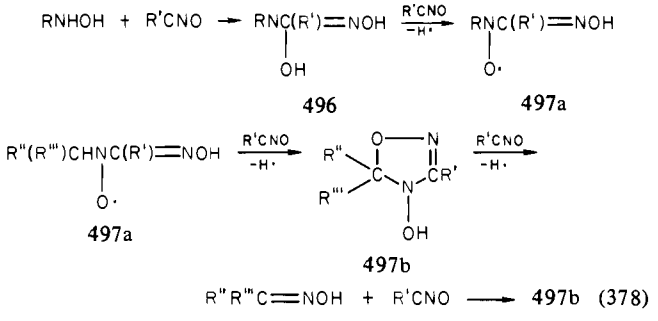
(377a)

earlier oxidation with oxygen difluoride.[369] In accordance with stabilization of a developing radical position adjacent to a cyclopropyl ring,[390] the cyclopropyl nitroxides were relatively long-lived (eq 377b).[368]



(377b)

Dehydrogenation of hydroxylamines was easily brought about by mild treatment with a nitrile oxide.[391] It has provided an attractive preparation of an *N,N'*-dihydroxyamidine (**496**) by the addition of a nitrile oxide to a simple hydroxylamine followed by dehydrogenation (eq 378). The initial nitroxide **497a** was sensitive to oxidative ring closure into an oxadiazolinyl oxide (**497b**). The latter was also obtained directly from a ketoxime and a nitrile oxide (eq 378). In contrast, amidoximes have not been

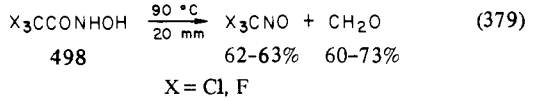


(378)

affected by this reagent.[372] (See section VI.D.2 for dehydrogenation of an amidoxime by DEAD.)

4. Dissociation of Trihaloacethydroxamic Acids

The formation of a trihalonitrosomethane and formaldehyde from a trihaloacethydroxamic acid (**498**) by thermolysis (eq 379)

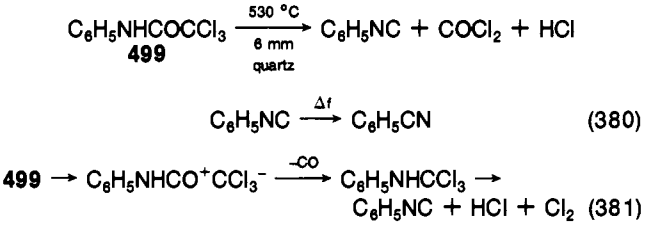


(379)

X = Cl, F

has not been satisfactorily accounted for. The nitrosomethane was liberated as a blue gas, trapped as a blue liquid, and identified by distillation, density, and molecular weight and halogen analysis. Paraformaldehyde was collected as a colorless sublimate in the condenser, was soluble in water, and gave an iodine equivalent analysis.[391] An isocyanate was not produced.[392]

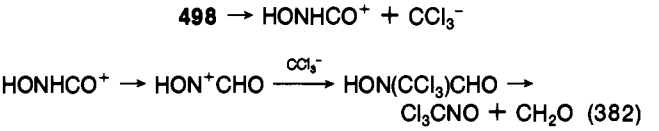
Thermolysis of trichloroacetanilide (**499**) gave phosgene and benzonitrile (presumably by rearrangement of phenyl isocyanide) (eq 380).[393] An explanation (eq 381) based on an ion-pair



(380)

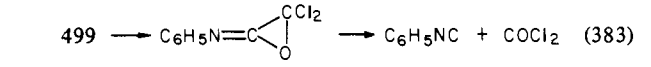
(381)

intermediate[394] lends itself to the thermolysis of **498** (eq 382).



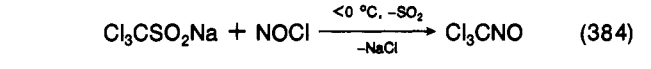
(382)

It should be noted that an alternative explanation for eq 380 based on internal displacement followed by fragmentation of an α-lactam was proposed (eq 383).[394]



(383)

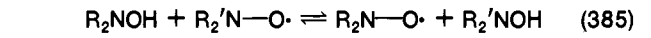
Trichloronitrosomethane has been obtained from sodium trichloromethylsulfinate and nitrosyl chloride (eq 384).[395]



(384)

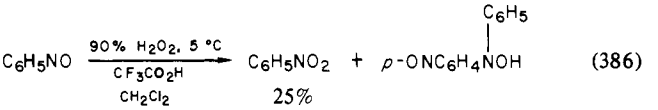
F. Redox

An exchange of hydrogen atoms between hydroxylamines and nitroxides was recently described (eq 385).[396]



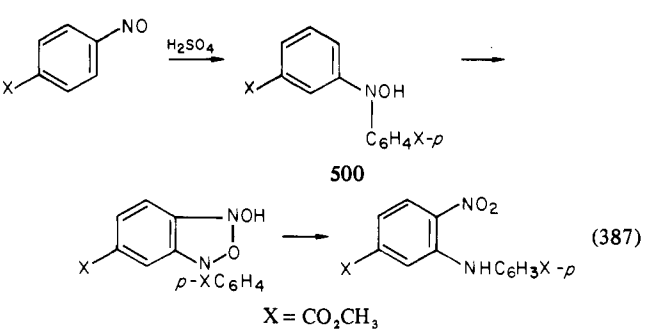
(385)

An acid-catalyzed dimerization of nitrosobenzene into *p*-nitrosodiphenylhydroxylamine (eq 386)[397] served as a precedent



(386)

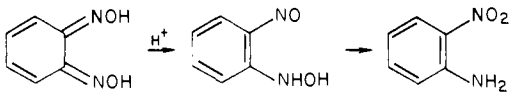
for the suggested intermediacy of the hydroxylamine **500** in the dimerization of methyl 4-nitrosobenzoate in concentrated sulfuric acid. A further intramolecular interaction of ortho substituents gave dimethyl 2-nitrodiphenylamine-4',5-dicarboxylate (eq 387).[398]



(387)

X = CO_2CH_3

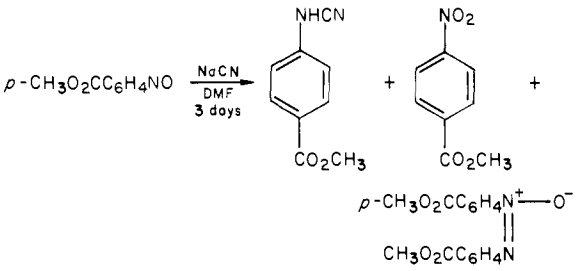
A disproportionation of o-nitrosophenylhydroxylamine had been suggested as an intermediate stage in the acid-catalyzed isomerization of the dioxime of o-benzoquinone into o-nitroaniline (eq 388).[108] The proposed isomerization described in



(388)

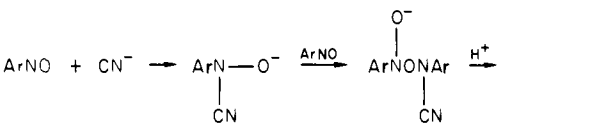
eq 387 is closely related.

For investigation of a hydroxylamine anion in the presence of a nitroso compound, the latter was treated with a half-molar quantity of sodium cyanide in dimethylformamide and the mixture stored. After 30 min the major product was an azoxy compound with minor amounts of a cyanamide and a nitro compound (eq 389). After 3 days the product mixture con-

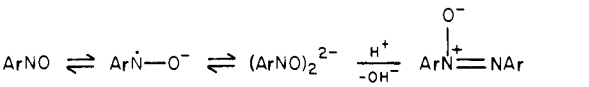


(389)

tained the latter two, each in 30% yield, and the azoxy compound in 20% yield. A preliminary explanation was offered and is shown in eq 390 and 391.[399]

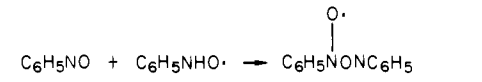


(390)



(391)

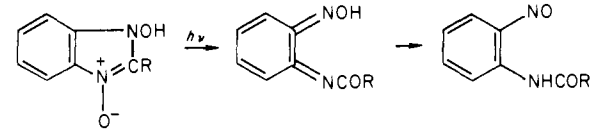
In the addition of nitrosobenzene and phenyl nitroxide in Me_2SO (eq 392), another adduct with the NON atom sequence



(392)

(eq 390) has been tentatively claimed.[275]

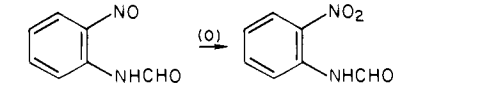
Irradiation from sunlight for 1 day transformed 1-hydroxybenzimidazole 3-oxide into o-nitroformanilide and 1-hydroxy-2-methylbenzimidazole 3-oxide into o-nitrosoacetanilide (eq 393).



(393)

R = H, CH_3

A better yield was produced when irradiation came from a high-pressure mercury lamp for 2 h.[398] An oxidant needed for the formation of the nitro compound was not identified (eq 394).[400]

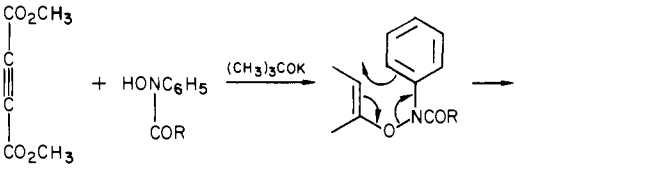


(394)

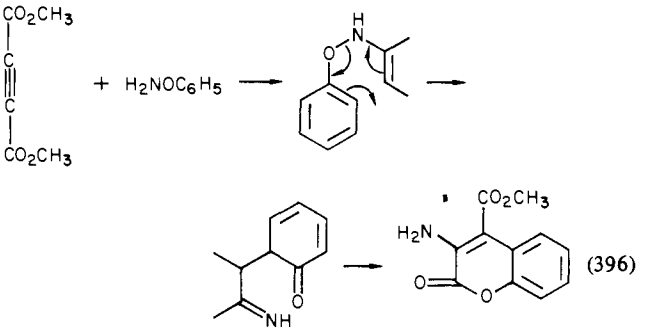
2%

G. Isomerization

Spontaneous irreversible rearrangements of certain unsaturated hydroxylamines were thought to proceed by [3,3]-sigmatropic shifts (eq 395, 396).[401]



(395)



(396)

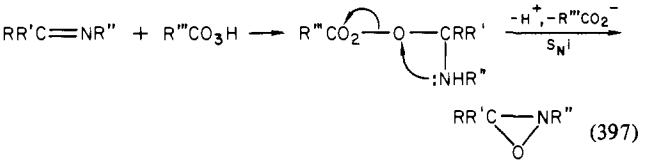
VII. Imines

Oxidation of imines has been described in general reviews.[60e,223a,402]

A. Peroxides and Ozone

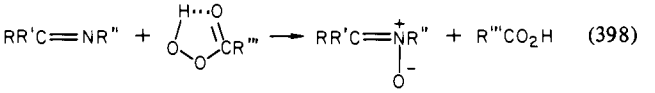
1. Ketimines, Ketazines, and Aldimines

An examination of a two-step process (eq 397) for the



(397)

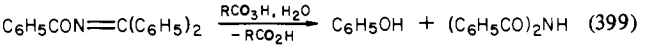
peracid oxidation of an imine into an oxaziridine by standard ab initio LCAO-SCF molecular orbital theory and calculation of molecular geometries, molecular energies, and charge distribution[403] was not in disagreement with a previous assignment of a two-step process based on kinetic studies.[404] A facile thermolysis of an adduct from an aliphatic imine and hydrogen peroxide into an oxaziridine,[405] investigations on stereochemistry,[406,407] and magnetic effects[406,409] provided additional support. Nitrone formation as a competing one-step process (eq 398) was explained by a nucleophilic attack of the lone pair of



(398)

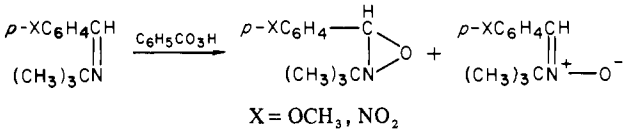
electrons at the imine nitrogen on the peroxy acid.[403-407]

An analogy with the Baeyer-Villiger reaction was seen in an earlier peracid oxidation of an *N*-benzoylimine into a phenol (eq 399).[298]



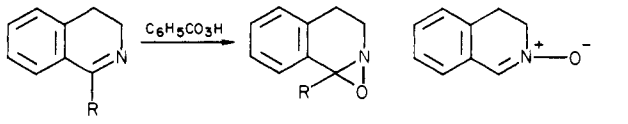
(399)

Kinetics for the reaction between perbenzoic acid and benzylidene-*tert*-butylamines (eq 400) to give oxaziridines were complicated from acceleration by carboxylic acids and protic solvents and deceleration by basic solvents, e.g., ethers and



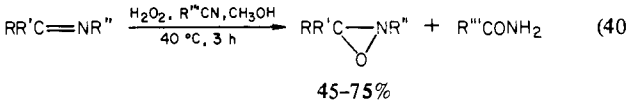
$X = OCH_3, NO_2$ (400)

alcohols.[404] Negative ρ values in benzene, dioxane, and *tert*-butyl alcohol[410] became nearly zero in ethanol. Nitrone formation (eq 400) was affected by para substitution and solvent: $OCH_3 \gg H > Cl \gg NO_2$ and dioxane > benzene $\gg$ *tert*-butyl alcohol > ethanol.[403] Although an oxidation of 3,4-dihydroisoquinoline and 3,4-dihydro-1-methylisoquinoline with perbenzoic acid (eq 401) afforded similar results,[411] addition to the imine double bound in the former and an S_Ni reaction of the adduct in the latter oxidation were rate determining for the formation of an oxaziridine (eq 401).



$R = H, CH_3$ (401)

Equimolar quantities of hydrogen peroxide, an alkyl or aryl cyanide, and an aldimine or ketimine in methanol gave good yields of oxaziridines, apparently without accompanying nitrone formation (eq 402). The method was claimed to be superior

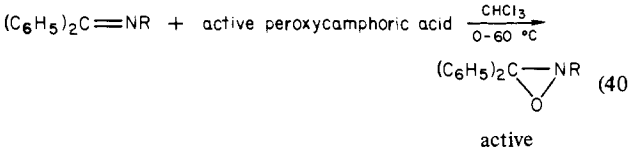


45–75% (402)

$R = (CH_3)_2CH$, $R' = H$, $R'' = sec\text{-}C_4H_9, i\text{-}C_3H_7, c\text{-}C_6H_{11}$
$RR' = (CH_2)_5$, $R'' = c\text{-}C_6H_{11}$; $R''' = C_6H_5, CH_3$

to others utilizing peracids, hydroperoxides in the presence of molybdenum salts, or hydrogen peroxide in ether.[412] An intermediate imino percarboxylic acid, R''''C(=NH)OOH, may have been the effective oxidizing agent.

Asymmetric oxidation of ketimines, achieved by treatment with optically active percarboxylic acids (eq 403), gave oxa-

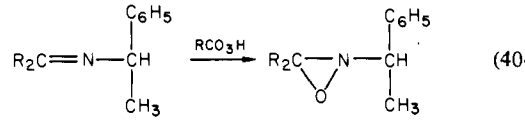


active (403)

$R = CH_3, C_2H_5, (CH_3)_2CH, (CH_3)_3C$

ziridines, claimed to be the first examples of optically active compounds in which a rigid tercovalent nonbridgehead nitrogen atom was solely responsible for molecular asymmetry.[413,414]

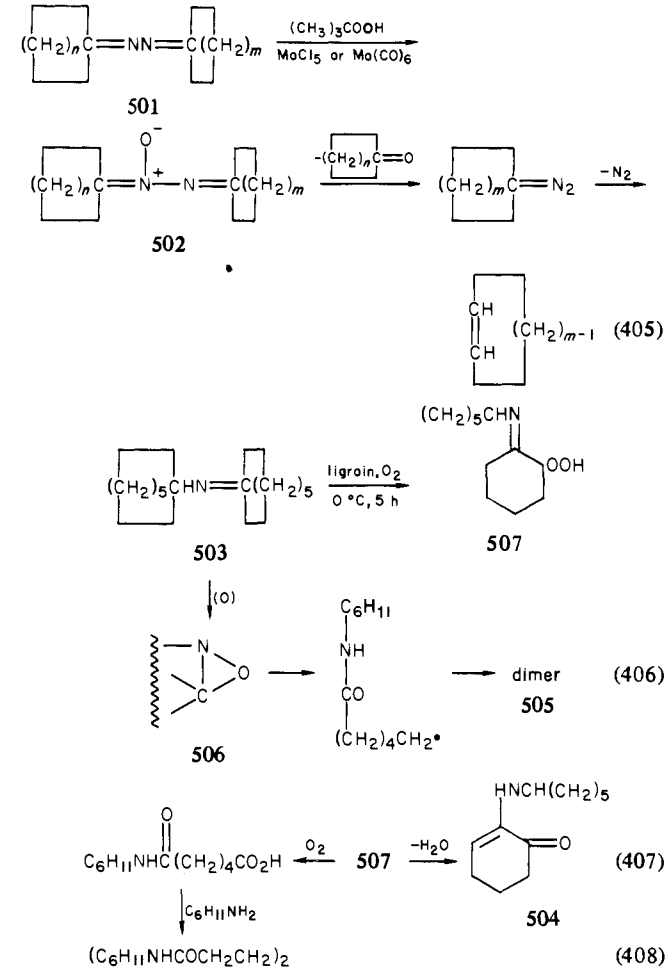
Asymmetric induction from chiral substitutents on an imine nitrogen atom also afforded a high degree of stereospecificity in peroxyacid oxidation of the imine into an oxaziridine (eq 404).[415]



(404)

A catalyzed peroxidation of the ketazine **501** gave cycloalkenes and cycloalkanones via cleavage of an assumed azine oxide (**502**; eq 405).[416]

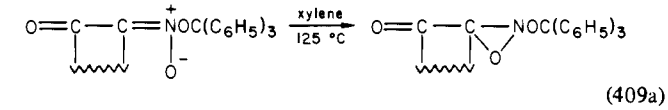
Autoxidation of *N*-cyclohexylidenecyclohexylamine (**503**) gave the aminocyclohexanone **504**, *N,N'*-dicylohexyladipamide, and the *N,N'*-dicyclohexyldiamide **505** of 1,12-dodecanedioic acid (eq 406, 407, 408). An explanation for the formation of the



(405) (406) (407) (408)

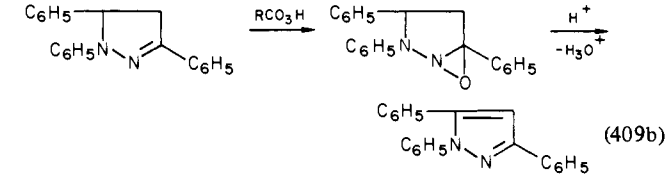
latter diamide was based on the intermediacy of the spiro-oxaziridine **506**, detected chromatographically. The oxidant responsible for the formation of the oxaziridine was not identified but was assumed to be a peroxide, e.g., **507**, formed in the mixture.[417]

There continues to be a particular interest in an oxaziridine with a substituent atom other than carbon attached to nitrogen. An *N*-alkoxyoxazirdine (eq 409a),[418] indirect evidence for an



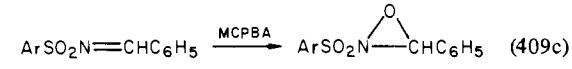
(409a)

unstable bicyclic *N*-aminooxadiridine (eq 409b),[419] and an *N*-



(409b)

sulfonyloxazirdine (eq 409c), claimed in error to be the first

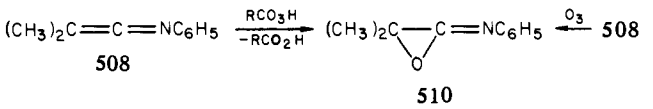


(409c)

oxaziridine with an exocyclic atom other than carbon attached to nitrogen,[420] are known.

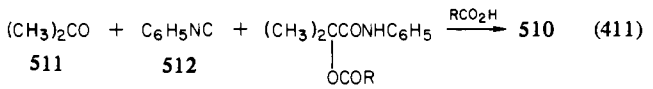
2. Ketenimines

Oxidation at the olefinic linkage in the ketanimine **508** gave an α-acyloxyamide (**509**) on treatment with a peracid (eq 410, 411). Presumably an α-lactam (**510**) intermediate was produced by either peracid or by ozone and fragmented into a

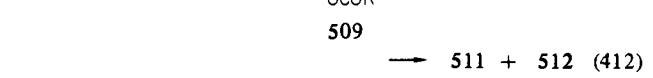


(410)

ketone (**511**) and an isocyanide **512** (eq 411, 412).[421] It should



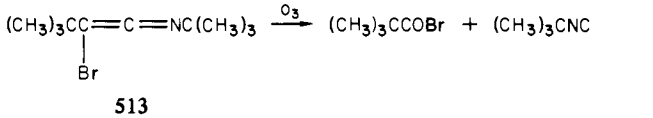
(411)



(412)

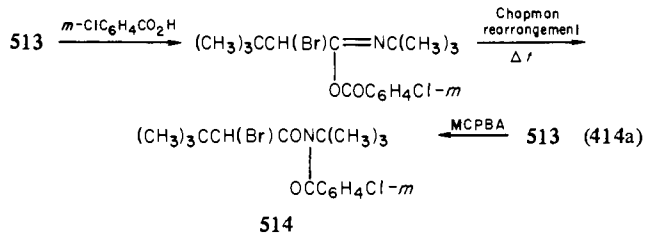
be noted that the peracid oxidation mixture consisted in a set of starting materials, **511**, **512**, and RCO_3H, and product **509** of a Passerini reaction (section V.D.3).

Ozone and the ketenimine **513** gave *tert*-butyl isocyanide and pivaloyl bromide, as expected (eq 413). It was unexpected



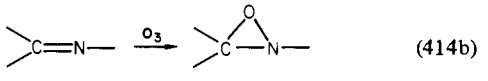
(413)

to obtain the imide **514** from the ketenimine **513** and either MCPBA or *m*-chlorobenzoic acid. This result left doubt about the role of the peracid (eq 414a).[421]



(414a)

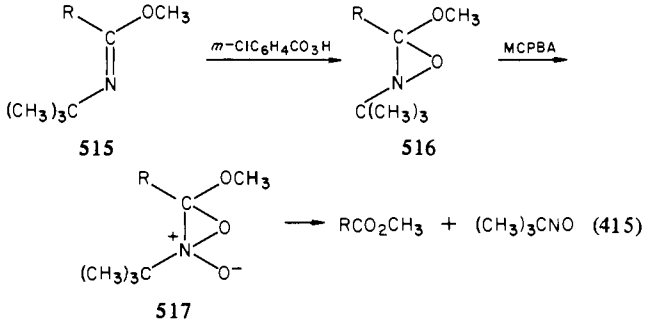
Simpler imines combined with ozone to give oxazirans (eq 414b).[422]



(414b)

3. Imidate Ester

Acyclic imidates **515** were oxidized by *m*-chloroperbenzoic acid into oxaziridines **516** (eq 415) in good yields, apparently

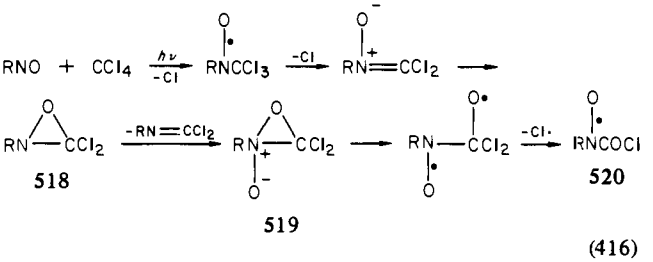


(415)

R = H, $C(CH_3)_3$, CH_3

without formation of the isomeric nitrones.[423] Imine protonation, facilitated by electron donation from the alkoxy substituent, inhibited a nucleophilic attack by the lone pair of electrons at imine nitrogen on a peracid oxygen atom, assumed to be necessary for nitrone formation. When 2 equiv of peracid was present, oxidation gave an ester and a nitroso compound. An oxaziridine *N*-oxide (**517**) intermediate was proposed (eq 415).

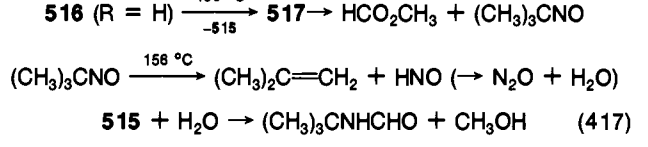
A photolytic disproportionation of an oxaziridine (**518**) on another occasion was assumed to proceed by homolytic cleavage of the ring NO bond in the cyclic *N*-oxide **519**. Expulsion of halogen left an alkyl acyl nitroxide (**520**; eq 416).[318]



(416)

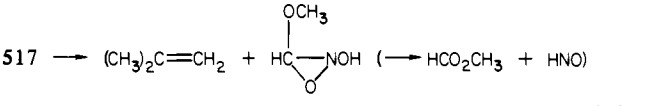
Apparently, fragmentation of **519** into phosgene and a nitrosoalkane did not occur.[316]

An initial thermal disproportionation of oxaziridine **516** (R = H) into the *N*-oxide **517** and imidate **515** accounted for the formation of isobutene (10%), methyl formate (11%), *N*-*tert*-butylformamide (7%), the ester **515** (6%), and methanol (18%) (eq 417).[423]



(417)

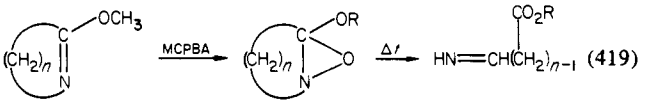
Thermolysis of 2-nitroso-2-methylpropane at 158 °C was considered to be the source of isobutylene. An alternative source of the olefin would be thermolysis of the *N*-oxide **517** (eq 418).



(418)

Oxidation of oxime methyl ethers ($R_2C{=}NOCH_3$) with di-*tert*-butyl peroxide did not produce oxaziridines: the only product reported was an iminoxylakyl radical ($R_2C{=}NOCH_2\cdot$).[424]

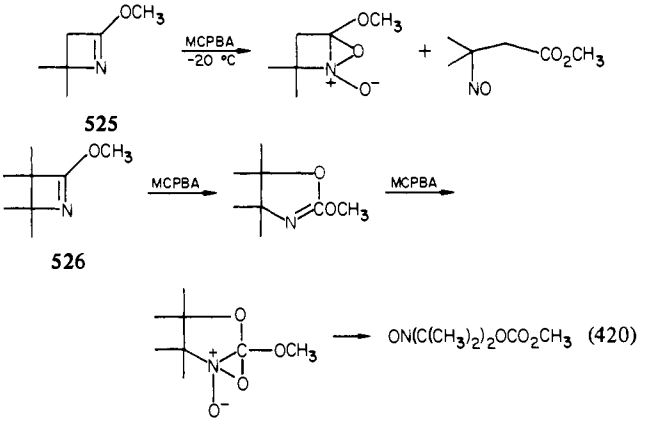
On the other hand, oxidation of cyclic imidates **521** and **522** gave thermally unstable bicyclic oxaziridines **523** and **524** (eq 419). Each decomposed violently on concentration.[423]



(419)

521, $n = 3$ **523**, $n = 3$
522, $n = 5$ **524**, $n = 5$

Baeyer–Villiger products resulted from the peracid oxidation of 2-alkoxyazetines **525** and **526** in which abstractable hydrogen was not present at the position next to nitrogen (eq 420).

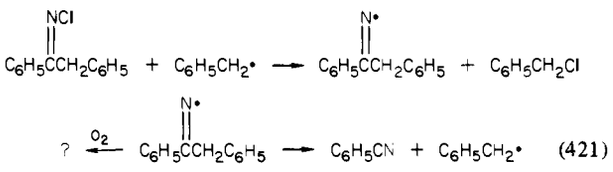


(420)

Unstable 1-aza-5-oxabicyclo[2.1.0]pentanes were probable intermediates.[423]

4. Iminyls

Very little is known about the ability of a ketimino radical to combine with an oxygen molecule. A thermolysis of phenyl benzyl *N*-chloroketimine into benzonitrile and benzyl chloride was accounted for by assuming the intermediacy of the ketimino free radical in a chain reaction (eq 421). The presence

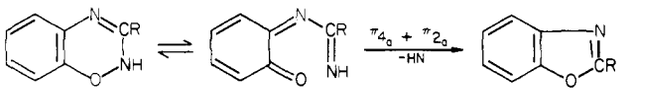


(421)

of oxygen, which inhibited the reaction and decreased the formation of benzyl chloride relative to benzonitrile, seemed to provide a better trap for benzyl than for the ketimino radical.[425] An aldimino radical intermediate has been suggested[426] for the poorly understood conversion of an aldehyde into a nitrile by treatment with ammonia, base, oxygen, and copper salt.

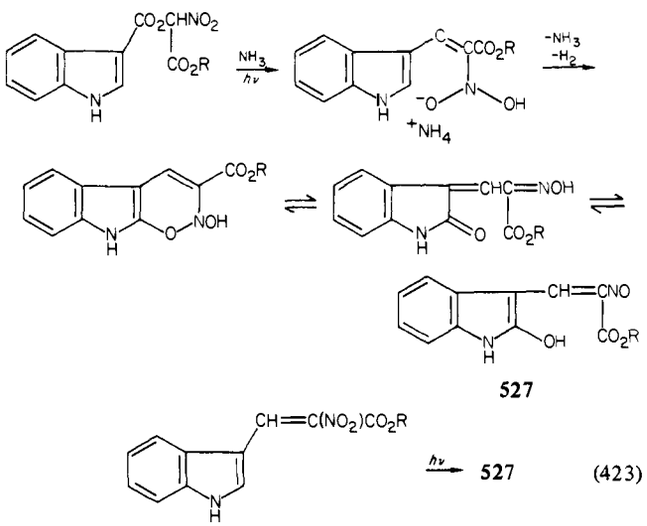
B. Electrocyclization

An assumed equilibrium between an oxadiazine and a quinone imine[427] (eq 422) depended on a reversible electro-



(422)

cyclization in which a nitrogen–oxygen bond is formed and cleaved.[427] An alternative electrocyclization gave a benzoxazole (eq 422).[427] A similar opening of a proposed oxadiazine intermediate accounted for phototransformations of α-nitro-β-(3-indoyl)propionic and acrylic esters into oxindoles **527** (eq 423).[426]

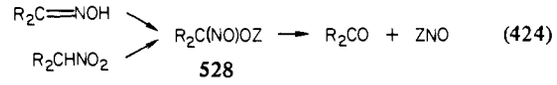


(423)

VIII. Oximes[60f]

A. Deoximation

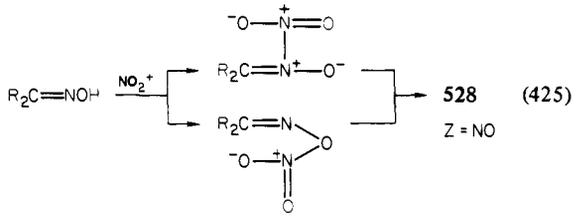
Carbonyl compounds have been recovered from their oxime derivatives by hydrolytic, reductive, and oxidative deoximations.[429-436] An intermediate *gem*-nitrosoalkanol (**528**, Z = H) or ester (Z = COR) appears to be a common feature for the oxidation methods (eq 424). It has been isolated in certain



(424)

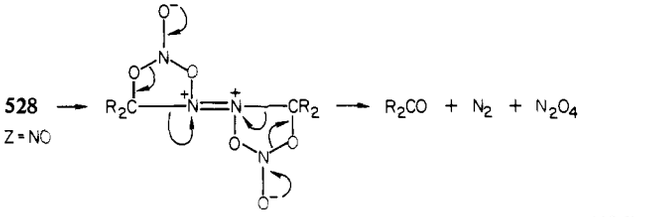
instances and sometimes detected by its transient blue-green color. The same intermediate was proposed for the Nef reaction whereby nitroalkanes have been hydrolyzed by acids into carbonyl compounds.[60g]

Nitrosonium[430,431] and nitronium[431] salts converted oximes into corresponding aldehydes and ketones with comparable efficiencies (53% to 84% yields) (eq 424, 425). Product forma-



(425)

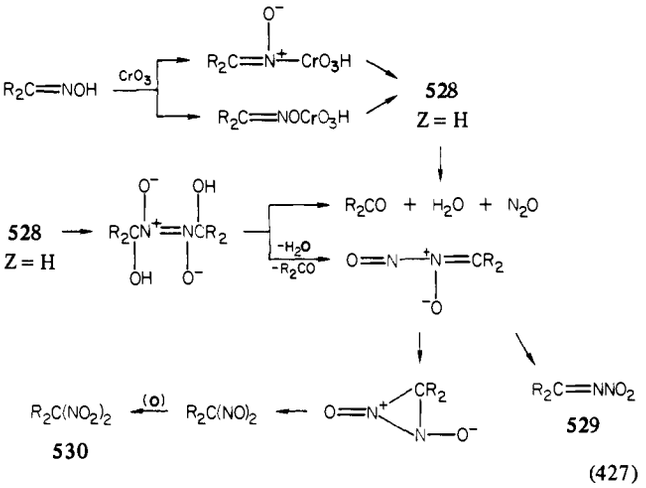
tion was assigned to a fragmentation of the dimeric form of **528** (Z = NO) (eq 426). Nitration (nitrosation) probably occurred



(426)

at the oxime nitrogen atom[361,430,436] rather than at the oxygen atom as was assumed.[431] Both routes to the intermediate are shown.

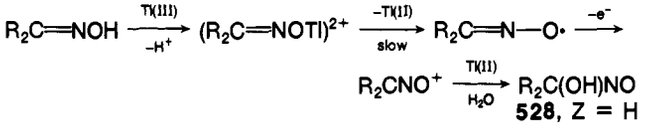
Recently the Jones reagent, a chromium trioxide–pyridine complex, and periodic acid were reported as deoximating reagents for ketoximes with most yields in the range 80–95% (eq 427).[432,433] An oxime of camphor gave 2-nitroimino-



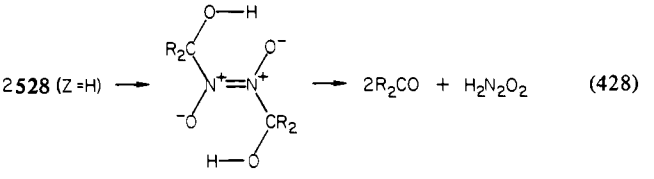
(427)

bornane (**529**). Without differentiating betweem initial attacks at oxime nitrogen or oxygen atoms, the intermediate **528** (Z = H) and its dimer were proposed. The suggested routes[432,433] to products of deoximation, conversion to nitrimines, and oxidation into nitro compounds (**530**) are shown. The latter two reactions were previously restricted to nitrosating agents.[361]

Thallium(III), lead(IV), cerium(IV), dichromate, and permanganate salts also transformed ketoximes into ketones.[435,437,438] A second-order reaction between thallium(III) acetate and an aliphatic ketoxime was presented as a one-electron oxidation into an iminoxy radical followed by a slow one-electron oxidation into intermediates **528** (Z = H). Frag-

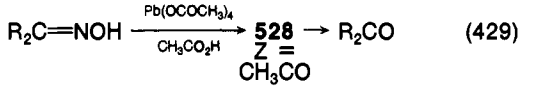


mentation of the dimeric form of the latter was proposed to account for the formation of the ketone (eq 428). Presumably

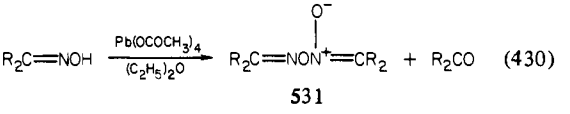


hyponitrous acid was formed simultaneously.[437]

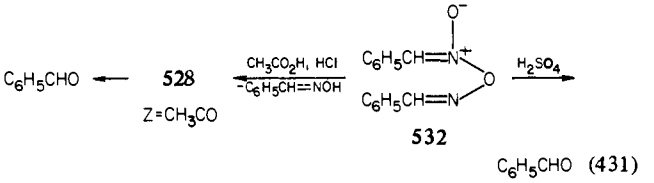
Oxidative deoximation by lead tetraacetate gave excellent yields of seven aliphatic and seven aromatic aldehydes and ten aliphatic and alicyclic and six aromatic ketones.[436] The intermediate **528** (Z = CH_3CO) has appeared in most of the ionic, radical, radical ion, and concerted mechanistic pathways which have been proposed,[361,429] but the reaction remains incompletely understood (eq 429).



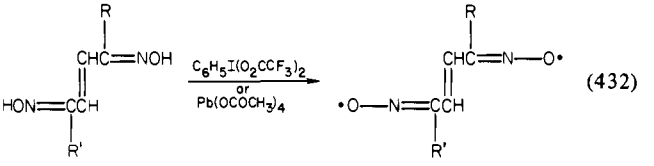
When the solvent was changed from acetic acid to an ether, benzene, or methylene chloride, oxime anhydride *N*-oxides (**531**) as well as the carbonyl compounds were obtained (eq 430).[439-442] The anhydride structure was previously preferred



for similar products obtained from oximes and dinitrogen tetroxide.[443] Recent NMR spectroscopic analyses[440] supported the unsymmetrical anhydride structure **531** rather than a symmetrical azine *N,N'*-dioxide structure, $R_2C{=}N(O)N(O){=}CR_2$,[444a] but there are contrary claims.[444b] A disproportionation of benzaldehyde *N*-oxide (**532**) in a mixture of hydrochloric and glacial acetic acids gave the nitroso compound **528** and benzaldoxime (eq 431).[440]

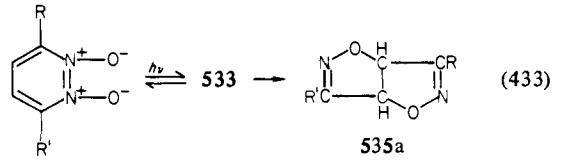


Oxidation of unsaturated dioximes of α,β-diketones by lead tetraacetate or phenyliodoso bis(trifluoroacetate) gave mixtures of the isomers 3,6-disubstituted pyridazine 1,2-dioxides (**534**) and 3,6-disubstituted 3a,6a-dihydroisoxazolo[5,4-*d*]isoxazoles (**535**) (eq 433).[445,446] The intermediacy of a bisiminoxyl (**533**)



(432)

533



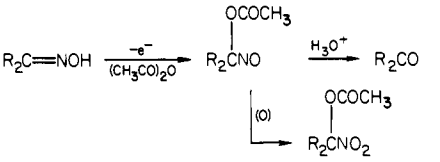
(433)

534

$R = R' = CH_3$; $R = CH_3$, $R' = C_6H_5$; $R = R' = C_6H_5$

also accounted for the photoisomerization **534** → **535**.[446]

A brief preliminary announcement described an electrochemical oxidation for the recovery of carbonyl compounds from their oxime derivatives (eq 434).[447] Isolation of a deep-

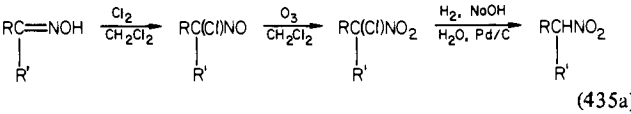


(434)

blue intermediate oil, presumed to be a *C*-nitroso compound, was made possible by careful control of solvent nucleophilicity and current density. Conversion of the oil into a ketone on treatment with aqueous acid paralleled the chemistry brought about by the conversion of an oxime into a carbonyl compound on treatment with lead tetraacetate (eq 429, 430). The intermediate nitroso compound was chemically oxidized (eq 434) into a nitro compound.[447]

B. Halogens and Hypohalites

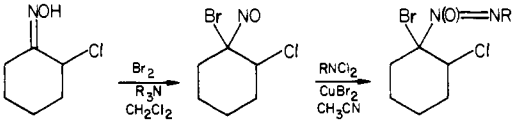
Ketoximes have been conventiently converted into nitro compounds in three steps: chlorination of the oxime in methylene chloride, ozonization of the nitroso compound in the same solvent, and catalytic hydrogenolysis in the presence of sodium hydroxide (eq 435a). The two-pot operation was carried out



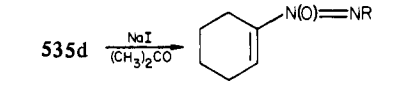
(435a)

without purification of the chloronitroso and chloronitro compounds and was found to be generally superior to (1) direct oxidation of the ketoxime by trifluoroperacetic acid, (2) oxidation of the nitroso intermediate by nitric acid with or without the presence of hydrogen peroxide or by oxygen under irradiation, and (3) nitrite displacement of a secondary halide. On the other hand, certain ketoximes did not react with chlorine, and there would be functional groups that could not survive the reaction conditions.[448]

α-β-Unsaturated nitroso compounds, e.g., **535b**, are scarcely known. Their preparation by dehalogenation of 1,2-dihalonitrosoalkanes appears promising since α,β-unsaturated azoxy compounds are now available in nearly quantitative yields by a similar route (eq 435b).[449] The neutral medium should retard

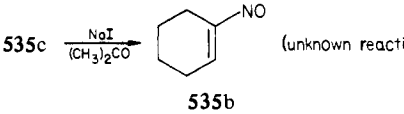


535c 535d



(435b)

96%

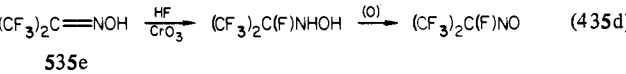


(435c)

535b

isomerization into an α,β-unsaturated oxime (see eq 456).

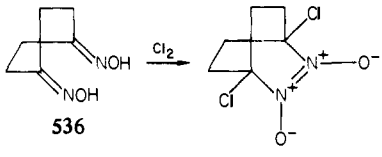
A nitroso compound was also obtained when the oxime **535e** was treated with the combination of hydrogen fluoride and chromium trioxide. Presumably an intermediate hydroxylamine was involved (eq 435d).[450]



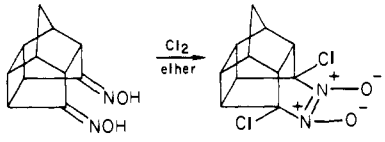
(435d)

535e

Intramolecular coupling of nitroso groups produced in a reaction between chlorine and the dioximes **536** and **537** accounted for the formation of the azodioxides **538** and **539** (eq 436, 437).[232,233]



536 538 (436)



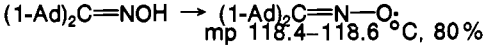
537 539 (437)

Aldoximes and sodium hypohalite have produced nitrile oxides (eq 438).[191]

(438)

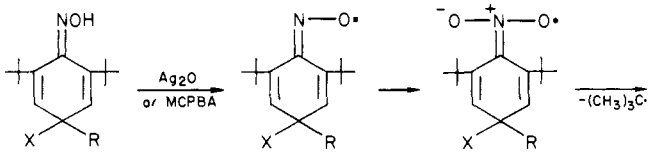
C. Metal Oxides

A remarkable, stable sky-blue 1,1′-biadamantylmethyleneiminoxyl was prepared from the oxime and lead dioxide (eq 439).[451]

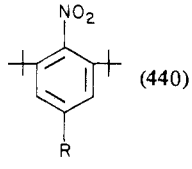


(439)

Another search for stable iminoxyls gave a preparative method for 4-alkyl-2,6-di-*tert*-butylnitrobenzene (**541**) from an oxidation of 4-alkyl-1-(hydroxyimino)-2,4,6-tri-tert-butyl-2,5-cyclohexadienes (**540**) with silver oxide, MCPBA, or nickel peroxide in benzene at room temperature (eq 440). An intermediate



540 542



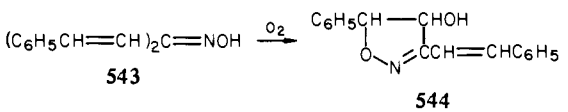
541 (440)

iminoxyl radical (**542**) was detected by ESR. Variations in the 4-alkyl substituent included ethyl, isopropyl, benzyl, and 1-adamantyl and yields ranged from 37% to 96%.[452]

Silver carbonate oxidized aromatic aldoximes into nitrile oxides and hydroxylamines into nitrones.[453]

D. Cyclizations

The cations Cu(II), Co(II), or Mn(II) promoted the autoxidation of α,β-unsaturated ketoximes, e.g., **543**, into dihydroisoxazoles **544** (eq 441) and byproducts such as benzaldehyde and cinnamonitrile.[454]



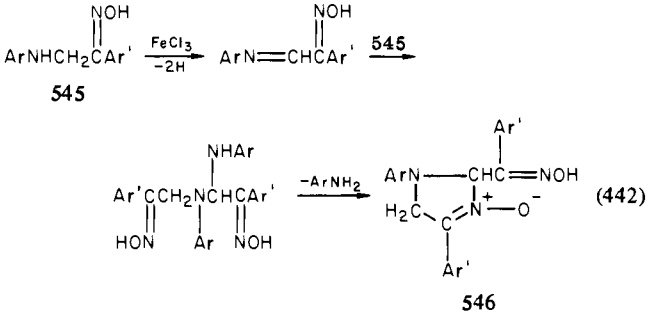
543 544 (441)

TABLE VI. *p*-Nitrosoanilines 548 from Enamines $R^1R^2NC(CH_2R)$=CHR and Oximes $R^3COC(=NOH)COR^4$ (eq 445)

enamine[a] R^1NR^2	oxime R^3	oxime R^4	days[b]	yield, %
$HNCH_2CH_2OH$	CH_3	CH_3	0.5	2
$N(CH_2CH_2OH)_2$	CH_3	CH_3	4	71
$N(CH_2)_5$[c]	CH_3	CH_3	3	81
$HNCH_2CH_2OH$	C_6H_5	CH_3	2	12
$N(CH_2CH_2OH)_2$	C_6H_5	CH_3	8	70
$N(CH_2CH_2OH)_2$	*p*-ClC_6H_4	CH_3	8	78
$N(CH_2CH_2OH)_2$	C_6H_5	C_6H_5	4	25
$N(CH_2)_5$	C_6H_5	C_6H_5	47	15
HNC_6H_{11}	C_6H_5	C_6H_5	22	62
$N(CH_2CH_2OH)_2$	γ-C_5H_4N[d]	CH_3	76	67
$N(CH_2CH_2OH)_2$	γ-C_5H_4N	*p*-ClC_6H_4	7	68
$N(CH_2CH_2OH)_2$	γ-C_5H_4N	α-C_4H_3S[e]	30	22
$N(CH_2CH_2OH)_2$	α-C_4H_3O[f]	CH_3	4	43
HNC_6H_{11}	α-C_4H_3O	*p*-ClC_6H_4	5	50
HNC_6H_{11}	α-C_4H_3S	CH_3	3	57

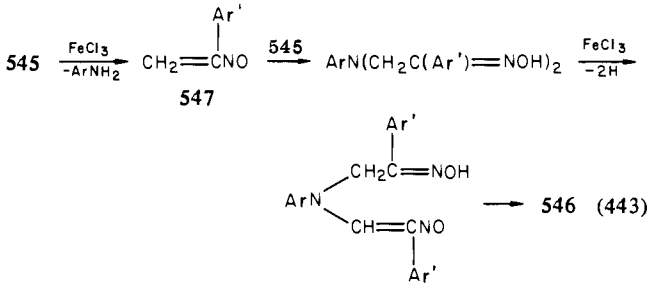
[a] R = H except where noted. [b] 25 °C. [c] R = $CO_2C_2H_5$. [d] γ-Pyridyl. [e] α-Thienyl. [f] α-Furyl.

A similar oxidative cyclization followed a self-condensation when an α-arylaminoacetophenone oxime (**545**) was treated with ferric chloride. The author suggested initial dehydrogenation of the amine function into an imine followed by condensation with the starting material (eq 442).[455] In an alternative



545 546 (442)

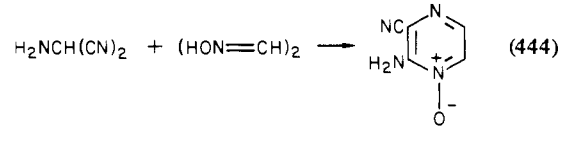
explanation (eq 443), an elimination of aniline would afford an



547 546 (443)

intermediate vinyl nitroso compound (**547**). Addition to the starting material, ring closure, and dehydrogenation would then give the product **546**.

A related ring closure was recently disclosed in a preparation of 2-amino-3-cyanopyrazine *N*-oxide from aminomalononitrile tosylate and glyoxime (eq 444).[456]



(444)

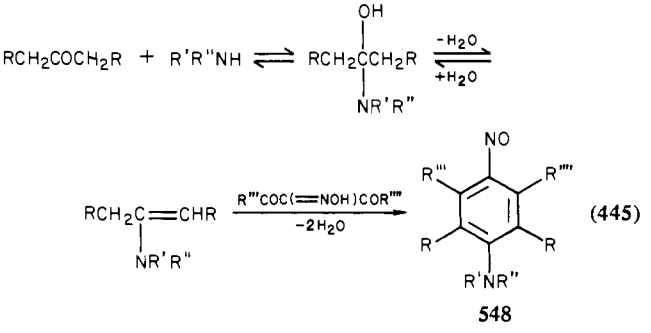
p-Nitrosoanilines **548** (Table VI) were produced from β,β'-

TABLE VII. Nitrosophenols 549 and 550 from Oximes $RCOC(=NOH)COCH_3$ and Ketones $R'CH_2COCH_3$ (eq 446 and 447)

oxime R	ketone R′	hours[a]	product[b] yield, %
CH_3	H	3	73[c]
CH_3	CH_3	5	36[c]
CH_2CH_3	H	3	67[c]
C_6H_5	H	11	100
p-ClC_6H_4	H	15	83
p-$CH_3C_6H_4$	H	15	57
p-$CH_3OC_6H_4$	H	15	21
α-C_4H_3S	H	15	54
C_6H_5	CH_3	15	44
p-ClC_6H_4	CH_3	15	62
p-CH_3C_6H	CH_3	15	54
p-$CH_3OC_6H_4$	CH_3	15	45
H	*d*	0.3	64
C_6H_5	*d*	48	25
p-ClC_6H_5	*d*	24	37
p-$CH_3C_6H_5$	*d*	100	19

[a] 25 °C. [b] *p*-Nitrosophenol **550** except where noted. [c] *o*-Nitrosophenol 549. [d] Ketone is diethyl acetonedicarboxylate.

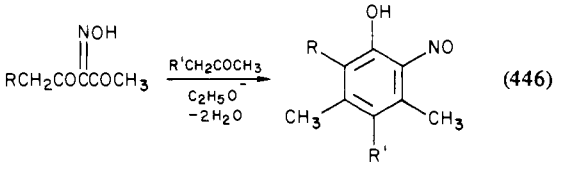
dioxooximes and enamines in base-catalyzed condensations (eq 445).[457] Nitrosophenols **549** and **550** were obtained from



(445)

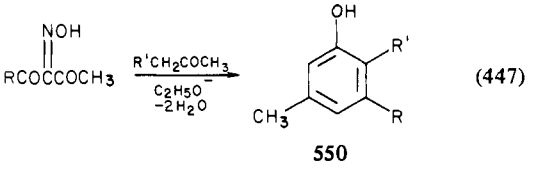
548

similar reactions (eq 446, 447) (Table VII).[458]



(446)

549



(447)

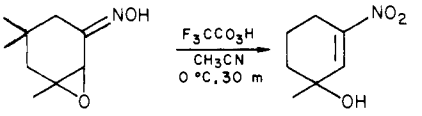
550

Primary and secondary aliphatic amines were successful in eq 445, but aromatic amines failed to give nitrosoaryl products. Preparative yields of *p*-nitrosoanilines **578** were obtained from acetone and from diethyl acetonedicarboxylate, but other aliphatic ketones produced only detectable amounts of products **548** which could not be isolated.

A four to five molar excess of sodium ethoxide relative to the hydroxyimino-β-dicarbonyl compound was found to be optimal for eq 446 and 447. It was noted that *o*-nitrosophenols were formed exclusively when R and R′ were hydrogen or methyl (Table VII) and that *p*-nitrosophenols were exclusively formed when one of the groups R and R′ was aromatic. There was a tendency for eq 447 to be slower with R an aryl group. Methyl ethyl ketone gave lower yields than acetone, and no product formation was detected from either dipropyl or dibutyl ketones. Activation of α-methylene units of ketones was beneficial and permitted the catalyst to be an alcohol solution of alkali. The factors which brought about the formation of *p*-nitrosophenols, but not *o*-nitrosophenols, from diethyl acetonedicarboxylate were not apparent (Table 6).

E. Peroxide, Ozone, and Oxygen

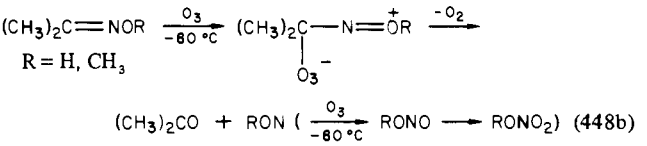
Trifluoroperoxyacetic acid was introduced in 1955 as a reagent for preparing nitro compounds from oximes.[60f] It has been successfully applied to oximes of carbohydrates[459] and to α,β-epoxy oximes. The latter gave γ-hydroxy-α-nitro olefins (eq 448a).[460]



(448a)

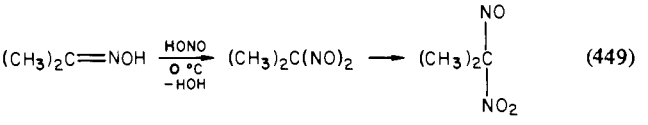
86%

Ozone produced ketones in good to excellent yields from corresponding oximes in methylene chloride at −80 °C.[461] Similar treatment gave the ketone and methyl nitrite from the *O*-methyloxime of acetone (eq 448b). The mechanism in eq



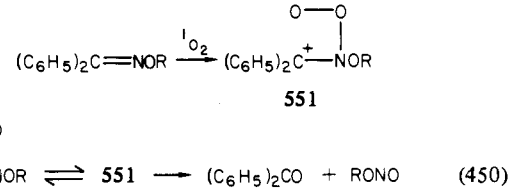
(448b)

448b was suggested:[461] however, ozonization of an *O*-nitrene has not been established. The explanation was supported by the byproduct formation of 2-nitroso-2-nitropropane (eq 449).[461]



(449)

An oxidation of a benzophenone *O*-alkyloxime ether produced the ketone and an alkyl nitrite in a reaction (eq 450)



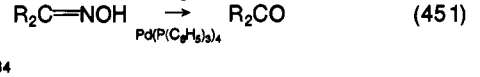
551

552

(450)

claimed to offer the first example of singlet oxygen attack at an unsaturated bond between atoms other than carbon.[462] A dependence on the presence of oxygen, the dye sensitizer and light was shown by quenching with 1,4-diazabicyclo[2.2.2]octane, a known singlet oxygen quencher, and by 2-methyl-2-butene, a singlet oxygen acceptor. Relative reaction rates for 2-methyl-2-butene, benzophenone oxime, its *O*-methyl ether, its oximate anion, and acetone oxime were approximately 130, 7.7, 20, 34, and 1. The order was compatible with an increase in electron donation to the π bond and electrophilic attack by singlet oxygen. An expectation for the formation of an ionic adduct (**551**) with the olefin[463] can be extended to the oxime, its *O*-alkyl ether, or its oximate anion. Product formation can apparently proceed from either the zwitterion[463] or the isomeric azadioxetane **552**.

A palladium–phosphine complex catalyzed the autoxidation of a ketoxime into the corresponding ketone in good yield (eq 451) but without describing the oxidation fate of the oxime



(451)

nitrogen atom.[464]

F. Tautomerization

An equilibrium between a nitrosoalkane and a simple oxime continues to be assumed,[465a] although it does not have factual support (eq 452). Isomerization of nitrosoalkanes, nitrosolic

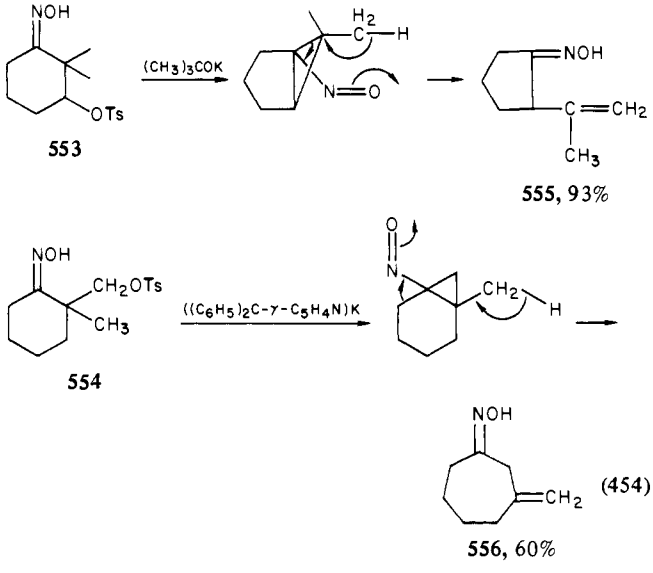
$$R_2CHNO \rightleftharpoons R_2C{=}NOH \qquad (452)$$

acids (RC(NO)=NOH), nitrosoindoles, nitrosopyrroles, and nitrosophenols has been discussed.[80h,223b,465b]

Alkylation at the oxime carbon atom has been rarely encountered. An exceptional iminoxyl coupling gave an *O*-nitrosoalkyloxime (eq 453).[466]

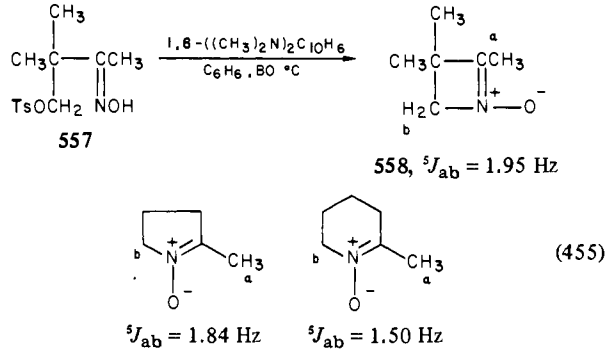
$$((CH_3)_3C)_2C{=}N{-}\dot{O} \xrightarrow[-20\ °C]{\text{slow}} ((CH_3)_3C)_2C{=}N{-}O{-}C(CNO)((CH_3)_3C)_2 \qquad (453)$$

Intramolecular alkylation at carbon has recently been proposed as an intermediate event. Nitrosocyclopropanes were stereospecifically generated and rearranged in a base-catalyzed reaction of cyclanone oximes **553** and **554**. A transient blue color, indicative of a *C*-nitroso compound, was noted. Ring-contracted (**555**) and ring-expanded (**556**) products were isolated (eq 454). Contracted rings, via nitrosocyclobutane in-



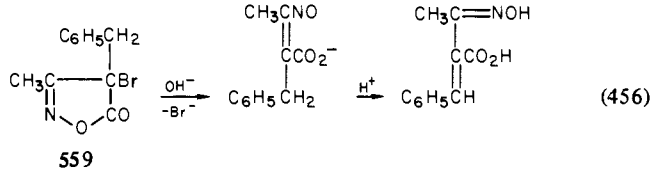
termediates, were produced when the leaving groups were in γ positions.[467]

Intramolecular alkylation at nitrogen afforded cyclic nitrones from linear bifunctional tosylate oximes (eq 455). The first four-membered cyclic nitrone (**558**) was prepared from the γ-tosyloxy ketoxime **557** in cyclization catalyzed by 1,8-bis(dimethylamino)naphthalene (eq 455). It was stable for a few

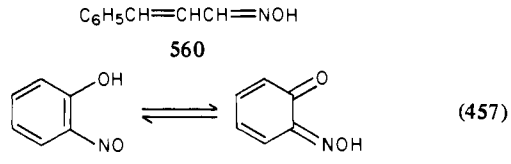


days at room temperature. A homoallylic transoid coupling across the nitrone system compaed favorably with a similar coupling for five- and six-membered cyclic nitrones.[466]

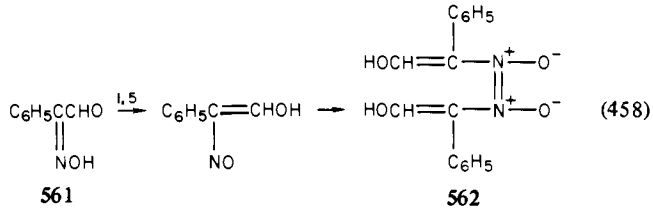
Aqueous sodium hydroxide transformed 4-bromo-3-methyl-4-benzyl-2-isoxazolin-5-one (**559**) into the oxime of α-acetylcinnamic acid (eq 456).[469a] Presumably a nitroso olefin was an intermediate.



Tautomerization of an α,β-unsaturated oxime, e.g., cinnamaldoxime, **560**, is generally unknown except for quinone monoximes; e.g., see eq 457.[223c,466] When nitrogen or oxygen

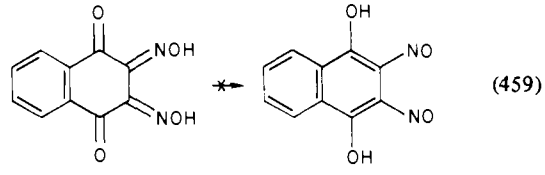


atoms occupy the β position, isomerization into the nitroso form has been reported; e.g., a monoxime **561** of phenylglyoxal gave the dimer **562** of its nitroso isomer (eq 458)[469b] but a similar



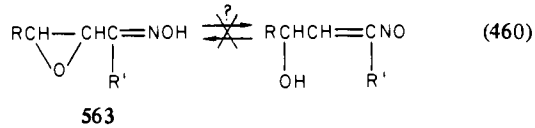
isomerization of a glyoxal dioxime is not known (compare the suggested isomerization of o-quinone dioxime into o-nitrosophenylhydroxylamine **237**, (section IV.E).

Apparently a 2,3-dioxime of 1,2,3,4-tetraoxotetralin **562** did not isomerize into 1,4-dihydroxy-2,3-dinitrosonaphthalene (eq 459).[67e] Reexamination of the molecule with modern tools

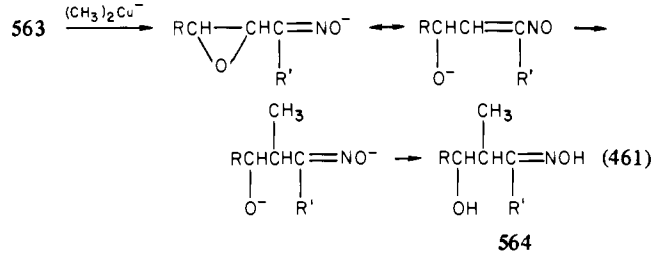


should be carried out.

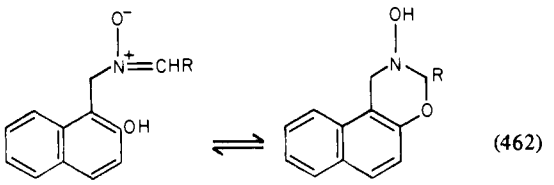
Although tautomerism between an α,β-expoxy oxime **563** and an α-nitroso-γ-alkenol (eq 460) is unknown, alkylation of



the anion, delocalized over a six-atom system, gave an α-alkyl-β-hydroxy oxime (**564**; eq 461).[470]

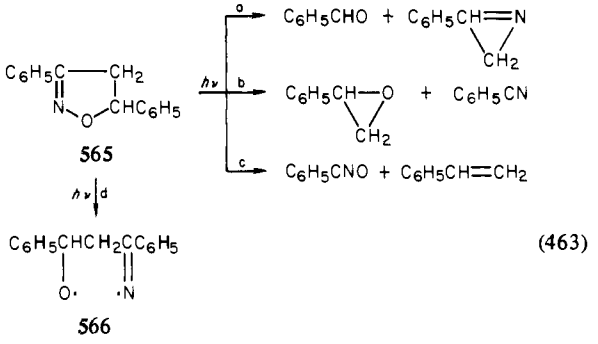


An example of tautomerism between a hydroxylamine and a hydroxynitrone has been reported (eq 462).[471]



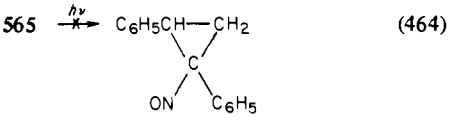
(462)

Initial cleavage of a CO bond was mildly competitive with cleavage of an NO bond in the photolysis of 3,5-diphenyl-2-isoxazoline (**565**; eq 463). There was no evidence for the



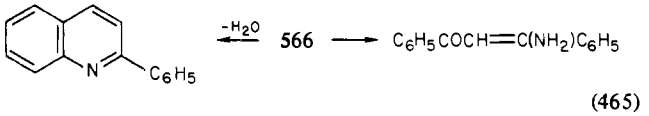
(463)

intermediacy of a nitrosocyclopropane (eq 464).



(464)

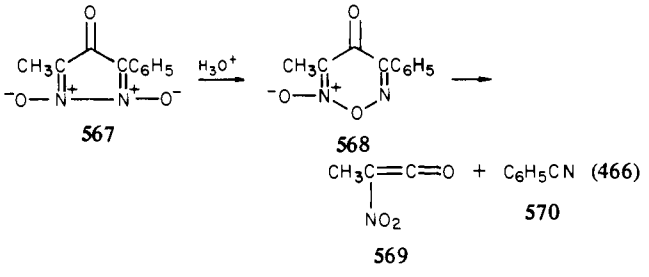
Isolated products included benzaldehyde, benzonitrile, styrene, 4,5-diphenyl-3-oxazoline (from recombination of intermediates in path a), 2-phenylquinoline, and β-aminochalcone. The latter two were thought to be formed from the diradical **566** by isomerization and dehydration as required (eq 465).[472]



(465)

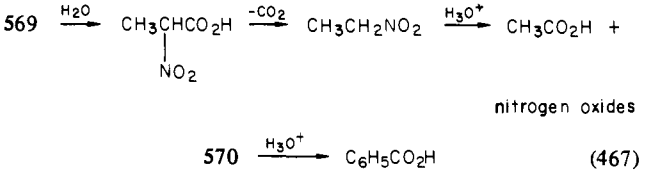
G. Oxidative Elimination

A fragmentation of 3-methyl-5-phenyl-4-oxo-4*H*-pyrazole 1,2-dioxides (**567**) in dilute sulfuric acid gave benzoic acid, acetic acid, carbon dioxide, and nitrogen oxides (eq 466).[473]



(466)

The results were accounted for by proposing an initial acid-catalyzed ring enlargement into a 2,6-diaza-γ-pyrone (**568**) followed by dissociation into benzonitrile and methylnitroketene. Hydrolysis and decarboxylation then produced benzoic and acetic acids, carbon dioxide, and nitrogen oxides (eq 467).

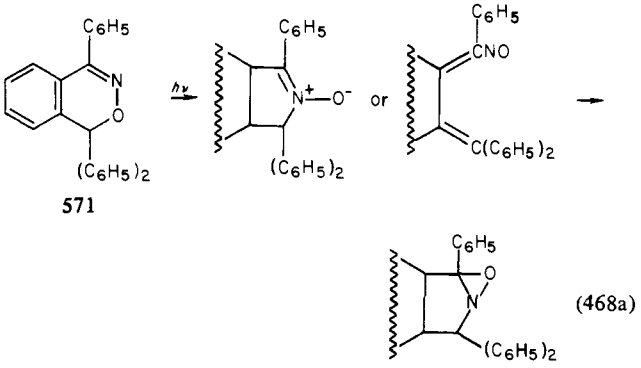


(467)

An earlier rejection of a 2,6-diaza-γ-pyrone structure in favor of a pyrazole 1,2-dioxide structure for the oxidation product from methylene ketones and nitrous acid was based on ^{13}C NMR spectroscopy.[473,474] The suggestion that a 2,6-diaza-γ-pyrone structure, e.g., **568**, may occur as an intermediate needs additional support. Although the products of acid hydrolysis of the heterocycle may be accounted for by the intermediacy of **568**, their formation may not require it.

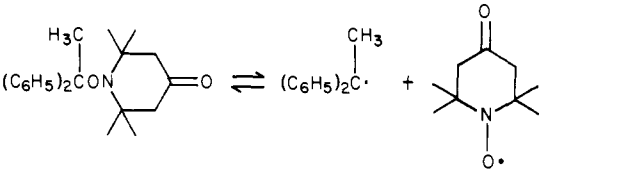
H. Isomerization

Photoisomerization of the 6*H*-oxazine **571** involved cleavage of the trityl carbon–oxygen bond rather than the oxime nitrogen–oxygen bond. For the quantitative conversion into an oxaziridine both a direct route and the possible intermediacy of a nitrone or a nitroso compound were recognized (eq 468a).[475a]



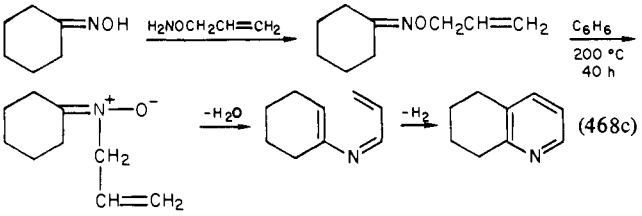
(468a)

Another weak carbon–oxygen bond (~ 21.4 kcal/mol) was reported for 2,2,6,6-tetramethyl-4-oxo-1-(1,1-diphenylethoxy)-piperidine (eq 468b).[475b]



-21.4 kcal/mol (468b)

O-Allyloxime ethers gave 2,3-sigmatropic rearrangements. Further thermolysis of the nitrone from the allyl ether of cyclohexanone gave 5,6,7,8-tetrahydroquinoline in 43% yield (eq 468c).[475c] Formation of the intermediate nitrone was based

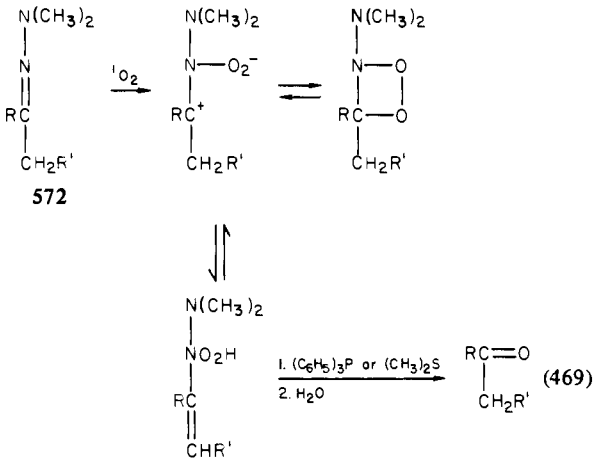


(468c)

on an ESR spectrometric investigation.

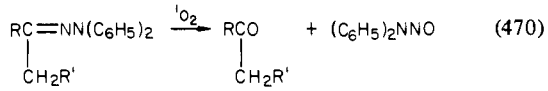
IX. Hydrazones[601]

A mild cleavage of *N,N*-dimethylhydrazones **572** by singlet oxygen led to the formation of carbonyl compounds by reduction of hydroperoxides (eq 469).[476] The dye-sensitized photooxygenation in methanol, tetrahydrofuran, or methylene chloride at −78 °C to 20 °C was followed by treatment with triphenylphosphine or dimethyl sulfide and hydrolysis and gave the expected ketone in fair to good yields (48–88%). An ene-type reaction was proposed and was supported by a lack of reactivity from adamantone *N,N*-dimethylhydrazone. An initial ionic adduct was presumably a precursor to either a hydroperoxide or an azadioxetan.[463] Support for the latter came with



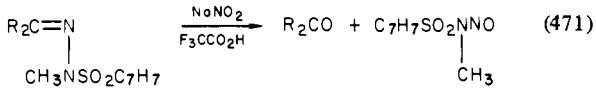
572

the isolation of *N*-nitrosodimethylamine and a ketone in comparable yields (eq 470).[477] A related formation of an *N*-



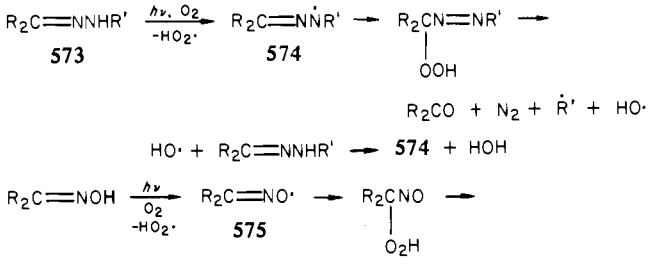
(470)

nitrososulfonamide was recently established for a reaction between an *N*-methylsulfonylhydrazone and nitrous acid (eq 471).[476]



(471)

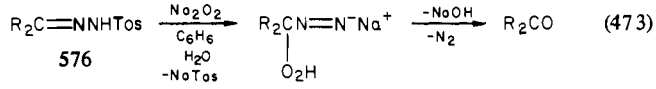
At about the same time Tezuka and Narita reported on the formation of ketones from hydrazone **573** and oxime derivatives under photolysis (high-pressure mercury lamp, Pyrex filter) in the presence of ground-state triplet oxygen (eq 472). Benzo-



(472)

phenone was obtained quantitatively from its phenylhydrazone and oxime derivatives in benzene. In contrast, irradiation (low-pressure mercury lamp) of methanol solutions of the phenylhydrazone or oxime derivative of cyclohexanone in the presence of oxygen gave very poor yields of the ketone (eq 472). The results were attributed to the stability of intermediate radicals **574** and **575**.[479]

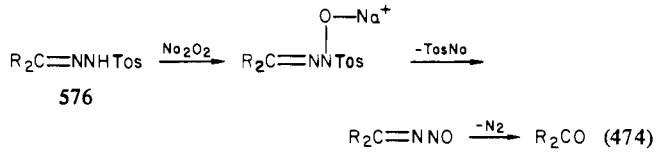
In another procedure a ketone was generated from its tosylhydrazone **576** on treatment with sodium peroxide in a two-phase system, benzene/water,[480] or with a methanol or dioxane solution of hydrogen peroxide and potassium carbonate (eq 473).[481] An S_N2' attack by the hydroperoxide anion



(473)

(analogous to a reaction on a tosylhydrazone by alkaline hypochlorite) followed by fragmentation was proposed.[460]

Initial hydroxylation at the amide nitrogen (eq 474) offers an alternative account of the reaction. A similar hydroxylation of a sulfonamide is described in section V.C.3 (eq 256). After a base-catalyzed elimination of a sulfinate, collapse of a nitros-

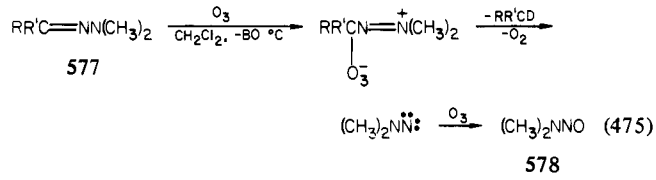


576

(474)

imine (section II.I) would produce a carbonyl compound.

Ketones, in good to excellent yields, and *N*-nitrosodimethylamine were obtained from *N,N*-dimethylhydrazones **577** and ozone. An explanation based on an unestablished oxidation of an *N*-nitrene by ozone was offered (eq 475).[481]



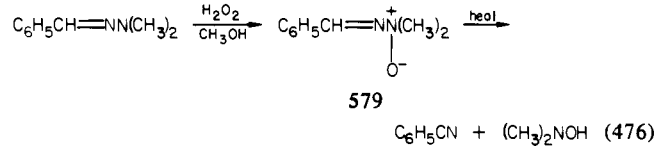
577

(475)

578

R = CH_3, R′ = C_6H_5; RR′CO, 97%
R = CH_3, R′ = *p*-BrC_6H_4; RR′CO, 98-100%
R = R′ = CH_3; RR′CO, 96%
RR′ = $(CH_2)_4$; RR′CO, 65%
RR′ = $(CH_2)_5$; RR′CO, 90%

In its fragmentation into a nitrile[482] (eq 476) the proposed

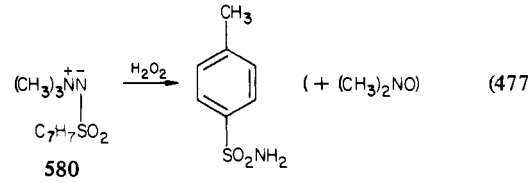


579

(476)

intermediate hydrazone *N*-oxide **579** resembled a tertiary amine oxide in a Cope elimination to produce an olefin and a hydroxylamine. It is unfortunate that the fate of the dimethylamino moiety was not determined; however the formation of *N,N*-dimethylhydroxylamine appears likely. The reaction may have provided an example of the rarely encountered direct transformation of an NN bond in an organic compound into an NO bond (section IV.A).

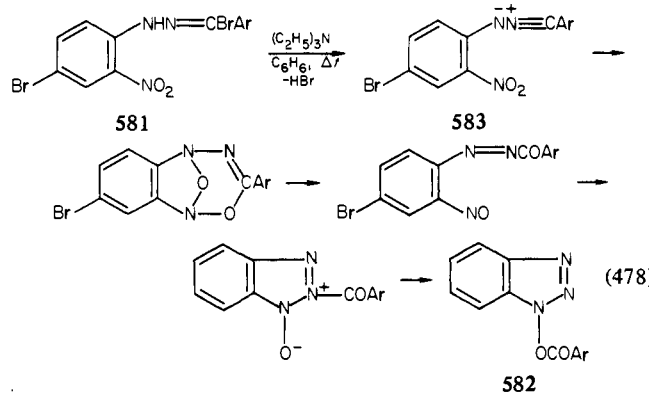
Peroxide attack on an aminimide has received very little attention. In an isolated report trimethylamine *p*-toluenesulfonylimide (**580**) and hydrogen peroxide (30%) gave *p*-toluenesulfonamide, but trimethylamine oxide was not found (eq 477).[483]



580

(477)

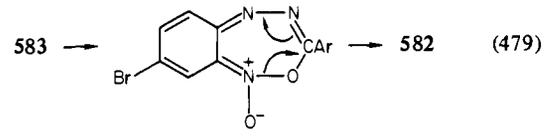
Thermolysis of the hydrazonoyl bromide **581** in a solution of benzene and triethylamine gave an aroyl derivative of a 1-hydroxybenzotriazole (eq 478). An intermediate dipolar addition



581 583 582

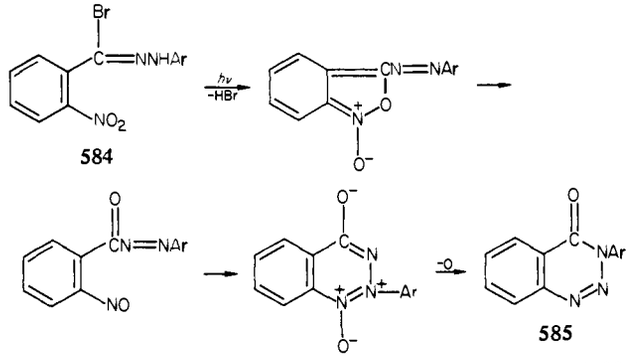
(478)

of a nitro group to a nitrilimide group, cleavage of certain nitrogen–oxygen bonds, cyclization, and migration of an aroyl group from a nitrogen to an oxygen atom were proposed to account for the formation of the product **582**.[484] An alternative explanation proceeds from the nitrilimide **583** by a ring-closure isomerization in which a nucleophilic oxygen atom of the nitro group attacked the electron-poor carbene atom (compare eq 81). Collapse of the seven-membered ring would bring about an isomerization into the triazole **582** (eq 479).



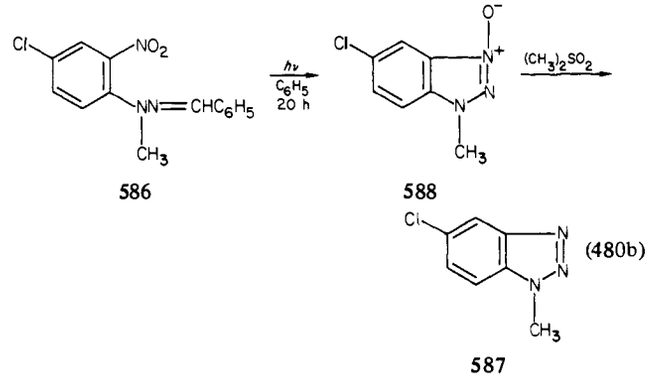
(479)

A similar interaction between a nitro group and a putative carbene center followed by ring opening, a new ring closure, and cleavage of a nitrogen–oxygen bond in an *N*-oxide group accounted for the photolysis of the hydrazonoyl bromide **584** into a triazinone **585** (eq 480a).[485]



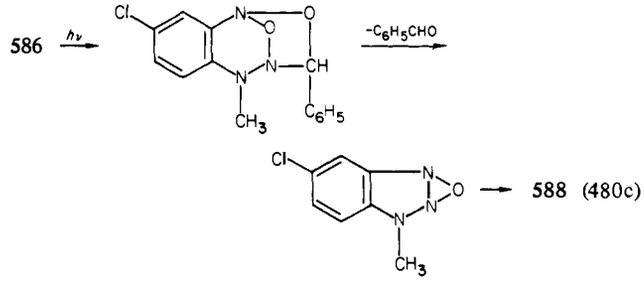
(480a)

Irradiation of hydrazone **586** gave benzaldehyde and 1-methyl-6-chlorobenzotriazole (**587**), and its 3-oxide **588** (eq 480b).[485] An internal dipolar addition, fragmentation, and



(480b)

isomerization were proposed (eq 480c). An independent



(480c)

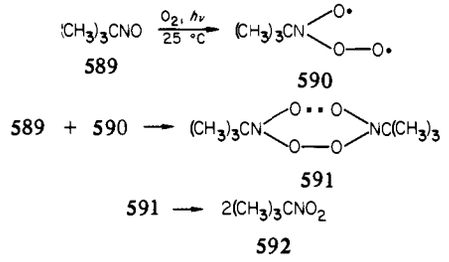
preparation (eq 480b) confirmed product identification. An isomeric benzotriazole 2-oxide was not detected (compare eq 517). Other interactions between nitro and azomethine groups are described in section IV.C.

X. Nitroso Compounds

A general survey of nitroso compounds briefly covered oxidation by nitric acid, hydrogen peroxide, permanganate, chromic oxide, persulfuric acid, ammonium persulfate, hypochlorite, peroxyacetic acid, peroxytrifluoracetic acid, and ozone.[223] See section VIII.B for an ozonization reaction.

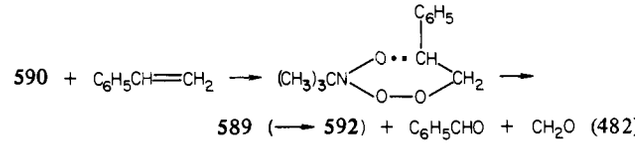
A. Oxygen

An inability of ground-state molecular oxygen in the dark to react with 2-nitroso-2-methylpropane[486] gave a warning that nitroso compounds are unreliable in spin-trapping oxygen-centered radicals.[487] Under red-light irradiation the nitroso compound **589** and oxygen in great excess gave the nitro compound **592** in yields of better than 90% (eq 481). It was



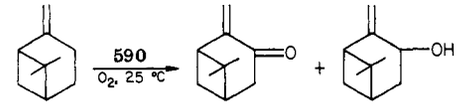
(481)

concluded that singlet oxygen was not involved when β-pinene was present since a double-bond shift in the latter did not occur (eq 483). An adduct (**590**) of oxygen and the nitroso compound was proposed to account for addition to styrene (eq 482) and



(482)

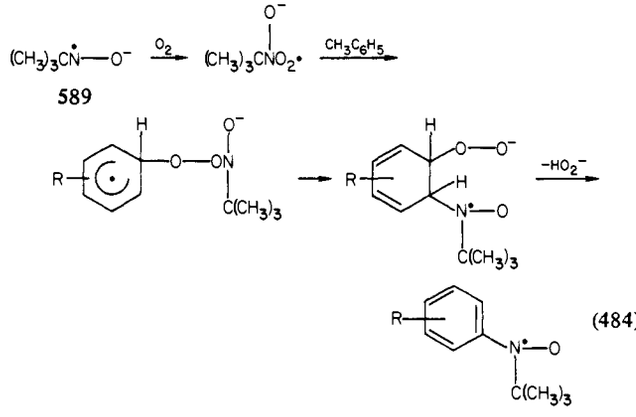
abstraction of allylic hydrogen (eq 483) and for the formation



(483)

of the nitro compound **592** by a dissociation of a second adduct **591**.[486]

A corresponding radical-anion adduct from the radical anion of 2-nitroso-2-methylpropane (**589**) and oxygen was also proposed (eq 484). In the presence of an arene, a nitroxide and



(484)

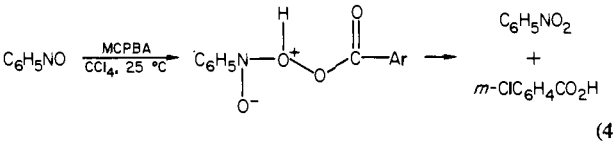
peroxide were produced.[486]

trans-1,4-Dichloro-1,4-dinitrosocyclohexane and 2-nitroso-2-2-methylpropane (**589**) quenched singlet oxygen with efficiencies that made them comparable to β-carotene. Less than 3% of the quenching resulted from a chemical reaction between singlet oxygen and the nitroso compound. Excitation to a low-

lying n,π^* nitroso triplet state for quenching by a physical process was suggested.[469]

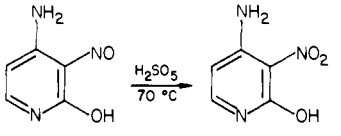
B. Peroxides

A one-step nucleophilic displacement mechanism was recognized for general applicability in peroxy acid oxidations of organic derivatives at electron-releasing atoms or groups, e.g. amines (section V.C), sulfides, olefins, or acetylenes. Exceptions have been found in imines (section VII.A.), carbonyl compounds (Baeyer–Villiger oxidation), and sulfoxides which oxidize by a two-step mechanism. A direct nucleophilic displacement mechanism for the oxidation of nitrosobenzene into nitrobenzene by peroxyacetic acid was confirmed in an investigation with *m*-chloroperbenzoic acid (MCPBA) in various solvents (eq 485).[490]



(485)

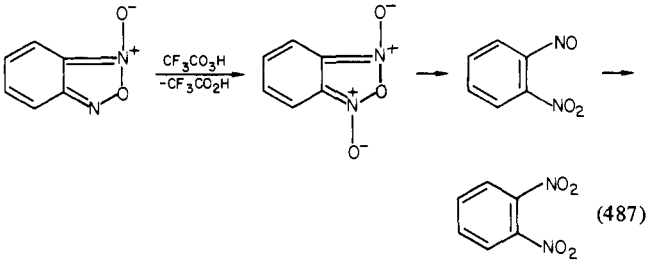
A subtle sensitivity to requirements for oxidation can be seen in the oxidation of 2-hydroxy-3-nitroso-4-aminopyridine into a nitro compound (**593**) by hydrogen peroxide in sulfuric acid (eq 486).[223]



(486)

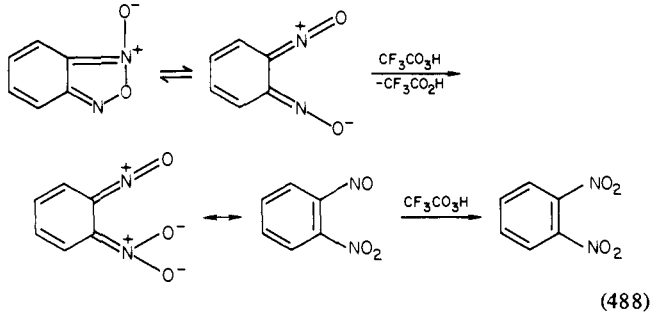
593

The initial success in oxidizing benzofuroxan into o-dinitrobenzene[397] (eq 487) was extended to a quantitative oxidation

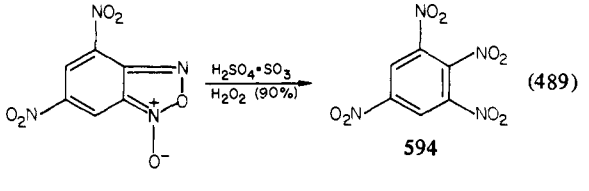


(487)

of 3,5-dinitrobenzofuroxan into 1,2,3,5-tetranitrobenzene (**594**) by replacing trifluoroperoxyacetic acid with 90% hydrogen peroxide in oleum (eq 489).[491] A nucleophilic attack on the peroxidic oxygen atom by a nitrogen atom in the furoxan ring or in a pseudodinitrosoarene after ring opening was recognized (eq 488).



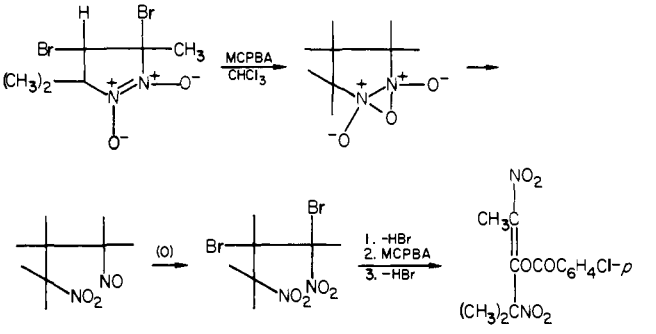
(488)



(489)

594

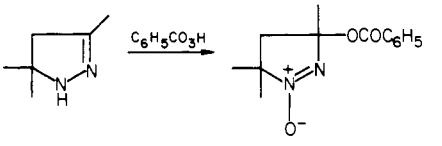
In a related reaction *m*-chloroperbenzoic acid oxidized *cis*-3,4-dibromo-3,5,5-trimethylpyrazoline 1,2-dioxide (recognized as an intramolecular nitroso "dimer") into an open-chain 1,3-dinitro compound (**595**) in 48% yield.[492] Support for the claim (eq 490) that this oxidation proceeded directly from the "dimer"



595

(490)

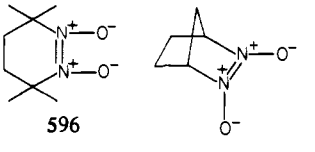
was offered in citing earlier oxidation of 3,5,5-trimethylpyrazoline by perbenzoic acid into 3-(benzoyloxy)-3,5,5-trimethyl-Δ^1-pyrazoline 1-oxide without cleaving the ring (eq 491).[493]



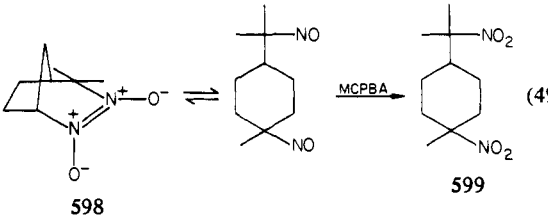
(491)

Compare eq 409b.

Investigations gave no evidence of a thermal ring opening of azo dioxides **596** and **597** into dinitroso isomers;[229-233] other bicyclic and polycyclic azodioxides were stable at 250 °C.[230] These azo dioxides were also unreactive toward further oxidation; e.g., there was no reaction from compound **596** in refluxing aqueous permanganate for 12 h.[231] In contrast, azo dioxide **598** isomerized into a dinitroso compound which gave a blue solution in benzene. It was efficiently oxidized by MCPBA into the corresponding dinitroalkane (**599**; eq 492).[229] Presumably



596 597



(492)

598 599

oxidation proceeded from the dinitroso isomer.

A reaction from mixing a primary (RCH_2CO_3H) or secondary (R_2CHCO_3H) peroxy acid with a nitrosating agent in a solvent gave a blue-green color indicative of the presence of a *C*-nitroso compound.[494] A nitroso dimer, a nitro compound, and a nitrite were isolated. Peroxyphenylacetic acid and nitrosyl chloride in petroleum ether at 0 °C gave bis-α-nitrosotoluene, benzyl nitrite, and α-nitrotoluene (eq 493). Dinitrogen tetroxide

$$C_6H_5CH_2CO_3H \xrightarrow{NOCl} \underset{7\%}{(C_6H_5CH_2NO)_2} + \underset{40\%}{C_6H_5CH_2NO_2} + \underset{50\%}{C_6H_5CH_2ONO} \quad (493)$$

reacted with an unspecified peroxy acid to give a nitro compound as the predominant product. Tertiary peroxycarboxylic

acids (R_3CCO_3H) failed to react with a nitrosating agent.[494] The results have not been confirmed.

tert-Butylnitrosoacetylene was oxidized by hydrogen peroxide in ether into *tert*-butylnitroacetylene (eq 494).[495]

$$(CH_3)_3CC{\equiv}CNO \xrightarrow[\text{ether}\ -60\ ^\circ C]{H_2O_2} (CH_3)_3CC{\equiv}CNO_2 \quad 40\% \qquad (494)$$

C. Oxygen-Centered Radicals

Spin trapping by a *C*-nitroso compound failed to discriminate between peroxy and alkoxy radicals; both gave alkoxy radical adducts **600** and nitrate esters. This interesting result was explained by a sequence in which a peroxylalkyl nitroxide and a peroxy nitrite (**600**) were proposed intermediates (eq 495).[496]

$$R'O_2\cdot + RNO \rightleftharpoons R'O_2\overset{O}{\overset{|}{N}}\cdot R \xrightarrow{-RNO_2} R'O\cdot \xrightarrow{RNO} R'O\overset{O}{\overset{|}{N}}\cdot R \quad \mathbf{600}$$

$$R'O_2\overset{O}{\overset{|}{N}}\cdot R \xrightarrow{-R\cdot} R'O_2NO \longrightarrow R'O\cdot + NO_2 \longrightarrow RONO_2 \qquad (495)$$

R' = $(CH_3)_3C$, R = $(CH_3)_3C$, $(CH_3)_2CCl$
R' = $(CH_3)_2CCN$, R = $(CH_3)_2CCN$, $(CH_3)_2CCl$, C_6H_5

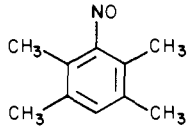
A similar result was noted when alkyl radicals, in the presence of oxygen and a nitroso compound, were photolytically generated from a nitrosoalkane or an azoalkane (eq 496, 497).[496]

$$R'N{=}NR' \xrightarrow[O_2,\,RNO]{365\ nm} R'O\overset{O}{\overset{|}{N}}\cdot R \qquad (496)$$

R = alkyl or aryl; R' = alkyl

$$RNO \xrightarrow[O_2]{>540\ nm} RO\overset{O}{\overset{|}{N}}\cdot R \qquad (497)$$

Dissociation of an alkoxynitroxide from nitrosodurene (**601**) and di-*tert*-butyl peroxide under irradiation accounted for the formation of the *tert*-butyl radical detected by ESR, and the implied formation of a nitrodurene (**602**; eq 498).[497]



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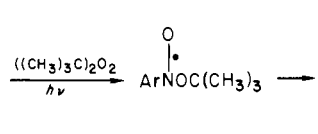
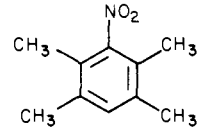




602

+ $(CH_3)_3C\cdot$ (498)

A nitroxide (**603**) from 2 mol of nitrosotrifluoromethane and an alkoxy radical dissociated into nitrotrifluoromethane and an alkoxyaminyl. The latter dimerized into a hydrazine compound (**604**; eq 499).[498] A related sequence of reactions can account for the dimer[499] of nitrosotrifluoromethane (eq 500).

$$RO\cdot \xrightarrow{CF_3NO} CF_3NOR \xrightarrow{CF_3NO} CF_3N(OR)\text{-}\overset{\cdot}{N}\text{-}O \xrightarrow{-CF_3NO_2}$$

603

$$CF_3NOR \longrightarrow \left(CF_3N(RO)\text{-}\right)_2 \qquad (499)$$

604

$$CF_3NO \xrightarrow{-NO\cdot} CF_3\cdot \xrightarrow{CF_3NO} (CF_3)_2N\text{-}\overset{\cdot}{O} \xrightarrow{NO} (CF_3)_2NONO \qquad (500)$$

An anionic adduct **605** from 2-nitroso-2-methylpropane and *tert*-butoxide accounted for the formation of 2-nitro-2-methylpropane and isobutylene by dissociation (eq 501).[486]

$$(CH_3)_3CNO \xrightarrow{(CH_3)_3CO^-} (CH_3)_3CN(O^-)OC(CH_3)_3$$

605

$$605 \xrightarrow{-(CH_3)_3C^+} (CH_3)_3CNO_2^{2-} \xrightarrow{2(CH_3)_3CNO}$$

$$(CH_3)_3CNO_2 + 2(CH_3)_3CN\text{-}\overset{\cdot}{O}^- \qquad (501)$$

In an explanation for the addition of a formaldimine to a nitroso compound, an initial abstraction of hydrogen by the nitroso group was proposed. Product **607** formation required coupling of the formaldimino and the nitrogen-centered radical tautomer **606** of a monosubstituted nitroxide (eq 502).[500]

$$RN{=}CH_2 \xrightarrow[-RN{=}\dot{C}H]{R'NO} R'\dot{N}OH \rightleftharpoons R'NHO\cdot \xrightarrow{RN{=}\dot{C}H}$$

606

$$RN{=}CHNOH \longrightarrow RNHCH{=}\overset{+}{N}(\overset{-}{O})R' \qquad (502)$$

607

D. Carbodiimide *N*-Oxides

A carbodiimide-*N*-oxide (**608**) was an assumed intermediate in the combination of isopropyl isocyanide and 2-nitroso-2-methylpropane and apparently was responsible for oxidation of the latter into 2-nitro-2-methylpropane (**609**; eq 503). Other

$$(CH_3)_3CNO + (CH_3)_2CHNC \longrightarrow (CH_3)_3C\overset{+}{N}(O^-){=}C{=}NCH(CH_3)_2$$

608

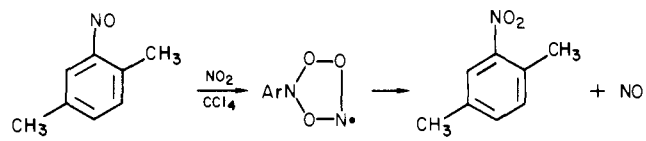
$$(CH_3)_3CNO \xrightarrow{608} (CH_3)_3CNO_2 + (CH_3)_3CN{=}C{=}NCH(CH_3)_2 \qquad (503)$$

609

products include 1-*tert*-butyl-2-isopropyldiaziridinone and *N*,*N*'-diisopropylcarbodiimide.[501]

E. Nitrogen Dioxide

Second-order kinetics, dependent on the concentration of each reactant, was found for the oxidation of 2,5-dimethylnitrosobenzene by dinitrogen tetroxide into 2,5-dimethylnitrobenzene (eq 504). The result was accounted for by a proposed 1,3-cycloaddition mechanism and supported earlier observations that nitrations of *N*-methyl-*N*-nitrosoaniline and of *p*-dimethoxybenzene in carbon tetrachloride proceeded by nitrosation followed by an oxidation with dinitrogen tetroxide (eq 505).[502]



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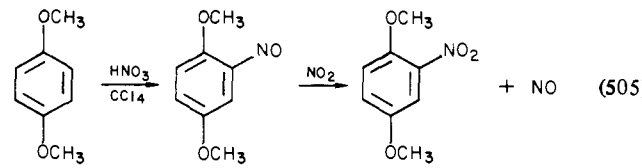


(505)

F. Disproportionation

At 80 °C for 24 h *n*-perfluoronitrosopropane (**610**) disproportionated into the corresponding nitro compound **611**, tri(perfluoro-*n*-propyl)hydroxylamine (**612**), and a perfluoro-*n*-propylimine (**613**) of perfluoroacetaldehyde (eq 506). Photolysis

$$\underset{\mathbf{610}}{n\text{-}C_3F_7NO} \xrightarrow[24h]{80\ ^\circ C} \underset{\mathbf{611},\ 11\%}{n\text{-}C_3F_7NO_2} + \underset{\mathbf{612},\ 8\%}{(n\text{-}C_3F_7)_2NOC_3F_7\text{-}n} + \underset{\mathbf{613},\ 72\%}{n\text{-}C_3F_7N{=}CFC_2F_5} \quad (506)$$

of the nitroso compound **610** gave two dimers, **614** and **615**, triperfluoro-*n*-propylamine, tetraperfluoro-*n*-propylhydrazine, and the hydroxylamine **612** (eq 507).[503]

$$\mathbf{610} \xrightarrow[16\ h]{h\nu} \mathbf{612} + \underset{\mathbf{614}}{(n\text{-}C_3F_7)_2NONO} + \underset{\mathbf{615}}{(n\text{-}C_3F_7)_2NNO_2} + (n\text{-}C_3F_7)_3N + ((n\text{-}C_3F_7)_2N)_2 \quad (507)$$

XI. Azo and Azoxy Compounds[60c]

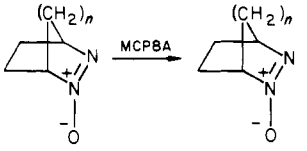
Peracid oxidation of azo compounds into azoxy compounds (eq 508) and the condensation of hydroxylamines and nitroso

$$CH_3NHOH + C_6H_5NO \longrightarrow CH_3N{=}\overset{+}{N}(O^-){-}C_6H_5 \xrightarrow{C_6H_5CO_3H} CH_3N{=}NC_6H_5 \quad (508)$$

compounds into azoxy compounds (eq 508) have been covered in reviews on the general and spectroscopic properties[504] of these functional groups.

A. Peroxides

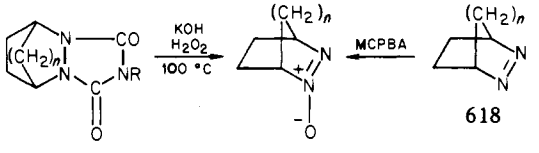
Azoxy compounds have been oxidized by peroxides into azodioxy compounds (eq 509), otherwise recognized as inter-



(509)

or intramolecular nitroso dimers (section X.B).[232] Structure assignments have been confirmed by NMR spectroscopy.

Alkaline peroxide at 80–100 °C transformed the cyclic hydrazides **616** into the azoxy compounds **617** (eq 510). Since



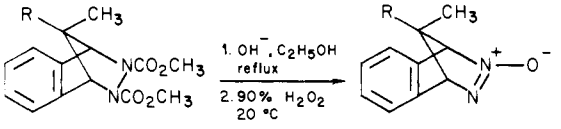
(510)

616 617 618

$n = 1\text{-}4$, R = C_6H_5, CH_3

their anticipated thermal instability tended to preclude the intermediacy of azo compounds **618**, percarbamates may be the suspected precursors to the compounds **617**. It was noted, however, that MCPBA had been successful in oxidizing these and other cyclic azo compounds into the more stable azoxy compounds.[505]

When alkaline peroxide oxidation of cyclic hydrazides was extended to the preparation of benzobicyclic azoxy compounds **619** (eq 511), a vibromixer was reported to be "absolutely



(511)

619

essential".[506]

B. Rearrangements

1. Isonitramines

Alkylation of nitrosohydroxylamines produced *N*-nitroso-*N'*-alkoxyamines (**620**) and an isomer thought to be either an *N*-alkoxydiazene *N'*-oxide (**621**) or *N*-alkyl-*N'*-diazene dioxide (**622**) (eq 512).[504]

$$\underset{\text{cupferron}}{C_6H_5N(NO)-O^-} \xrightarrow{CH_3I} \underset{\mathbf{620}}{C_6H_5N(NO)-OCH_3} + \underset{\mathbf{621}}{C_6H_5\overset{+}{N}(O^-){=}NOCH_3} \text{ or } \underset{\mathbf{622}}{C_6H_5\overset{+}{N}(O^-){=}\overset{+}{N}(O^-)CH_3} \quad (512)$$

A preference for structures corresponding to **621** rather than **622** was based on two NMR methylene signals for the product from benzylation of *N*-nitrosobenzylhydroxylamine (eq 513) and

$$C_6H_5CH_2N(NO)-O^- \xrightarrow{C_6H_5CH_2I} C_6H_5CH_2\overset{+}{N}(O^-){=}NOCH_2C_6H_5 \quad (513)$$

one methylene signal for the previously known dimer of α-nitrosotoluene (eq 514).[504]

$$C_6H_5CH_2NO \longrightarrow C_6H_5CH_2\overset{+}{N}(O^-){=}\overset{+}{N}(O^-)CH_2C_6H_5 \quad (514)$$

Isonitramines have recently been shown by X-ray analysis to be hydroxydiazenium oxides **623** corresponding to **621** rather

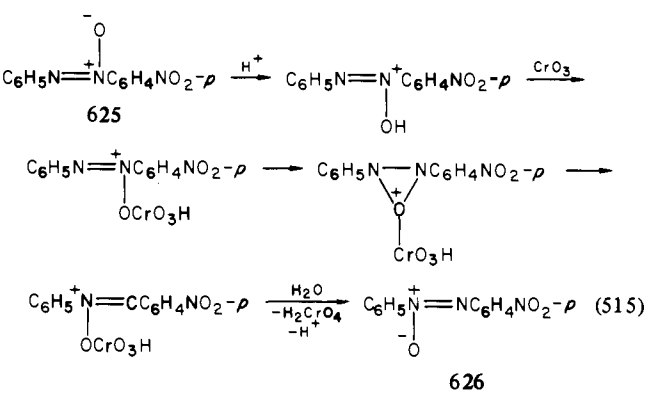
$$\underset{\mathbf{623}}{RN^+(O^-){=}NOH} \qquad \underset{\mathbf{624}}{RNNO(OH)}$$

R = C_6H_5, c-C_6H_{11}, *cis*-4-methyl, c-C_6H_{10}

than nitrosohydroxylamines **624**, the previously accepted assignment.[507]

2. Azoxy Compounds

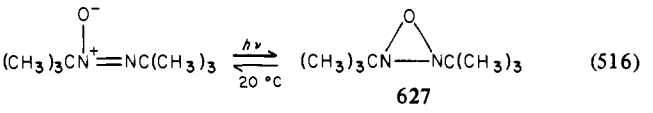
A rearrangement of β-*p'*-nitroazoxybenzene (**625**) into α-*p'*-nitroazoxybenzene (**626**) was catalyzed by chromium trioxide in acetic acid,[508] sulfuric acid,[508] or an arylsulfonyl anhydride.[504] An investigation with isotopes (^{15}N, ^{18}O) established that the rearrangement proceeded from an intramolecular migration of oxygen and the intermediacy of an oxadiaziridine ring (eq 515).[508]



(515)

626

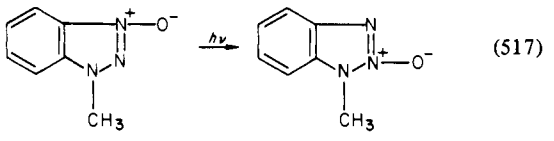
Irradiation of azoxy-2-methyl-2-propane in pentane at 10 °C gave di-*tert*-butyloxadiaziridine (**627**; eq 516) as the first es-



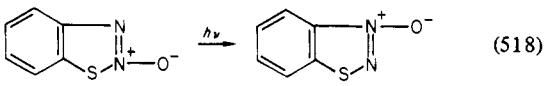
(516)

627

tablished example of this ring system although it had been postulated previously on several occasions.[509] The ring has since been implicated in the transfer of oxygen from one nitrogen to an adjacent one in a preparation of 1-methyl-1,2,3-benzotriazole 2-oxide[510] and of benzothiadiazole 3-oxide (eq 517, 518).[511] It should be noted that photo-Wallach rear-

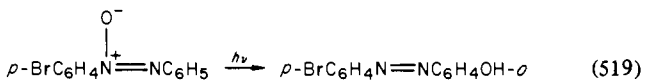


(517)



(518)

rangement has been observed for azoxyarenes (eq 519).[512,513]

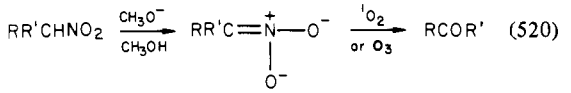


(519)

XII. Miscellaneous Items

A. Nitro Compounds

Singlet oxygen,[514] ozone,[515] and hydroperoxides[515] have transformed nitronate salts into carbonyl compounds (eq 520).

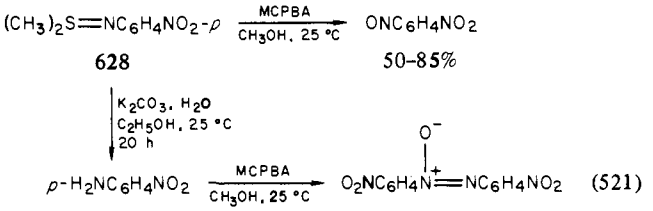


(520)

Presumably the azomethine linkage is attacked by an electron-deficient oxygen atom; however, mechanistic detail is unavailable, and the fate of nitrogen is unknown.

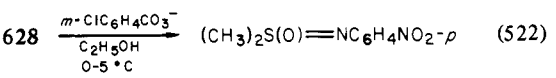
B. Sulfilimines

MCPBA converted *S,S*-dimethyl-*N*-(*p*-nitrophenyl)sulfilimine (**628**) into *p*-nitronitrosobenzene in high yield (eq 521). This



(521)

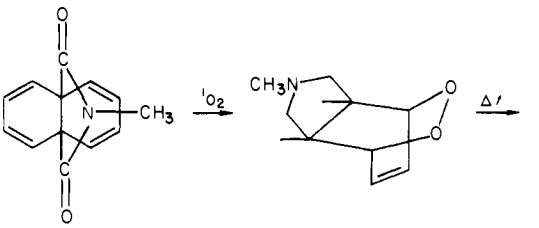
unexpected result did not occur when the sulfilimine was treated with completely formed MCPBA anion. Instead the anticipated sulfoximine was obtained almost quantitatively (eq 522).[516]



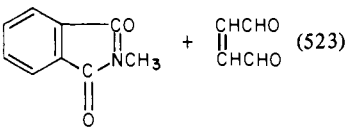
(522)

C. Nonbonding Control of Oxygenation

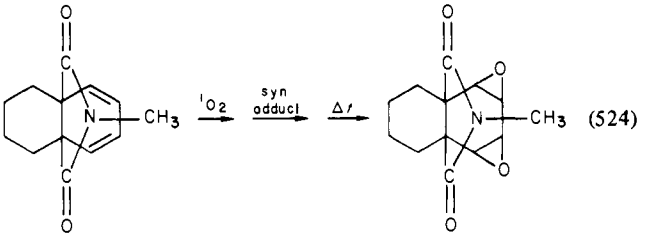
Singlet oxygen reacted with the tetraene **629** and with the diene **630** by a highly selective syn attack to give a peroxide endo to the heterocyclic ring (eq 523, 524). For comparison, singlet oxygen gave an anti peroxide when it reacted with the



629



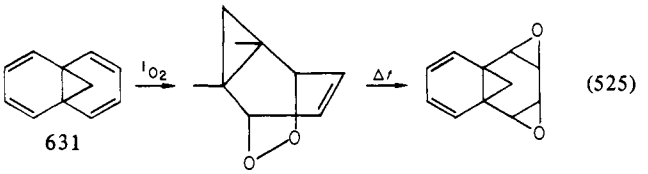
(523)



630

(524)

tetraene **631** (eq 525). The controlling factor for syn-peroxide



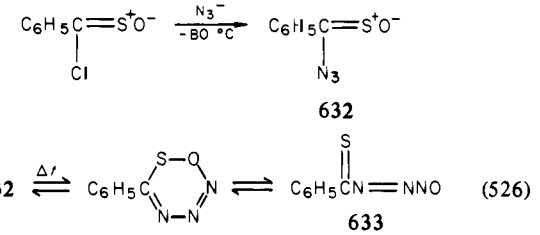
631

(525)

formation was thought to be a secondary orbital interaction between singlet oxygen and the π^* orbitals of the amide function in the heterocyclic bridge.[517]

D. Thiocarbonyl Azide *S*-Oxides

Thiobenzoyl azide *S*-oxide (**632**) did not show a structure change on warming until thermolysis at −40 °C gave benzonitrile, nitrogen, sulfur, and sulfur dioxide.[518] In contrast, a thioacyl azide is stable and exists predominantly as the tautomeric thiatriazole.[518] An assistance in the thermolysis of the azide **632** through an internal nitrogen–oxygen interaction is assumed and can be directly accounted for by a reversible cyclization (eq 526).

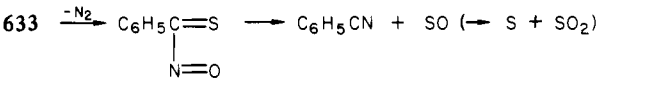


632

633

(526)

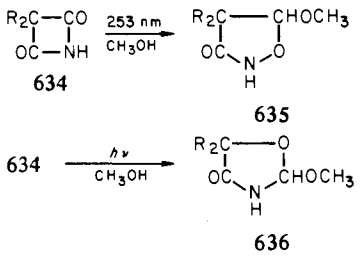
A fragmentation of **633** via a thiobenzoyl nitroso compound would be expected (section II.I) (eq 527).



(527)

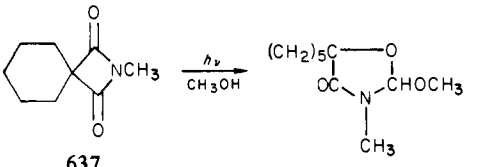
E. Azetidine-2,4-dione Rearrangement

A ring-expansion product from 3,3-diisopropylazetidine-2,4-dione (**634**) under irradiation was identified as "5-methoxy-4,4′-diisopropylisoxazolid-3-one" (**635**) in 1972 (eq 528).[519] The



634 635 636 (528)

photo ring expansion product was later identified as 2-methoxy-5,5-diisopropyloxazolid-4-one (**636**) in 1975[520] and as "5-methoxy-4,4′-diisopropylisoxazolid-3-one" (**635**) in 1976 but with a structural formula for 2-methoxy-5,5-diisopropyloxazolid-4-one (**636**).[521] Japanese investigators in 1979 obtained a 2-methoxyoxazolid-4-one (**638**) from the azetidine-2,4-dione **637** with no claim for the formation of an isomeric 5-methoxyisoxazolid-3-one (eq 529).[522] At this time there appears to be no

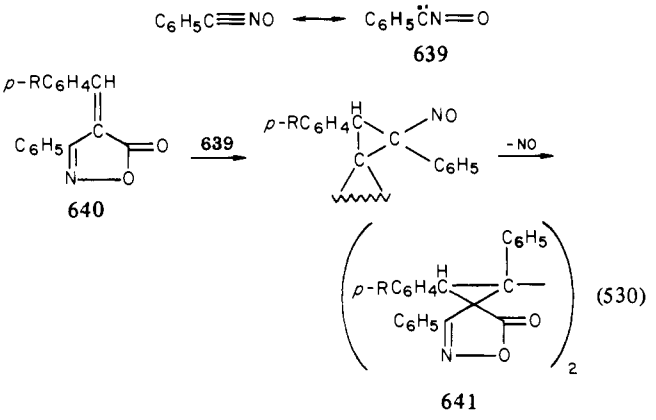


637 638 (529)

reason to believe the ring expansion gave an isoxazolidone; it would have required an unprecedented migration of a nitrogen atom from carbon to oxygen.

F. Phenylnitrosocarbene

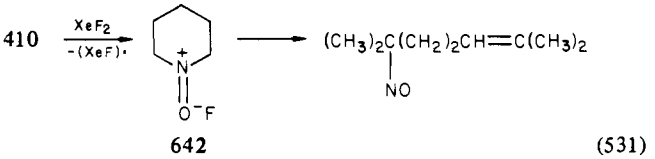
Benzonitrile oxide was considred to be phenylnitrosocarbene (**639**) in its reaction with isoxazolones **640** to produce a cyclopropyl dimer (**641**; eq 530) along with other products.[523]



639 640 641 (530)

G. α-Fragmentation of Nitrosonium salts and Nitroxides

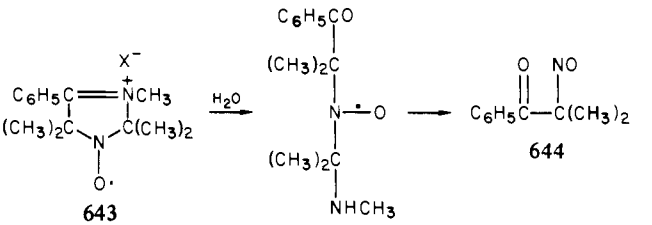
Both xenon difluoride[524] and tungsten hexachloride[525] oxidized the nitroxide **410** into a nitrosonium salt, e.g., **642**. Thermolysis then produced a nitroso olefin (eq 531).[524]



642 (531)

A similar α-fragmentation of an assumed intermediate linear nitroxide was proposed for the hydrolytic transformation of an imidazolinium nitroxide (**643**) into 2-nitroso-2-benzoylpropane (**644**), isolated as a dimer (eq 532).[526]

Extensive absorption from 310 to 370 nm correlated with a charge-transfer interaction between di-*tert*-butyl nitroxide and



643 644

X = $MeOSO_2O^-$, ClO_4^- (532)

carbon tetrachloride. Irradiation at 313 or 366 nm produced 2-methyl-2-nitrosopropane, isobutylene, *tert*-butyl chloride, O-(trichoromethyl)-*N*,*N*-di-*tert*-butylhydroxylamine, and di-*tert*-butylhydroxylammonium chloride. The intermediacy of the trichloromethyl radical and di-*tert*-butyloxoammonium chloride was assumed (eq 533).[527]

$$((CH_3)_3C)_2N{-}O\cdot \xrightarrow[h\nu]{CCl_4} ((CH_3)_3C)_2N^+{=}O\ Cl^- + \cdot CCl_3 \rightarrow (CH_3)_3CNO + (CH_3)_3CCl + CH_2{=}C(CH_3)_2 + ((CH_3)_3C)_2NOCCl_3 + ((CH_3)_3C)_2NHOH^+\ Cl^- \quad (533)$$

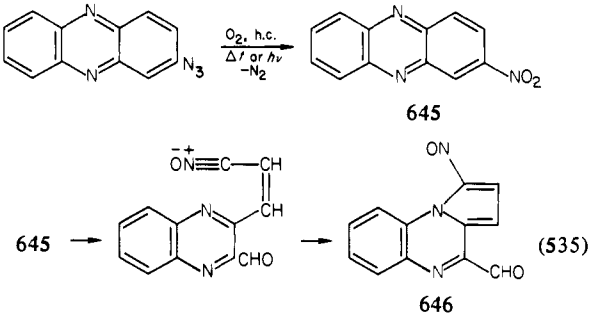
H. Oxidation of *N*-Nitroso-*N*-arylhydrazines

An oxidation of an *N*-nitroso-*N*-arylhydrazine has not been investigated since 1910 when treatment with cupric acetate followed by acetic acid or aqueous ammonia produced an *N*-nitrosohydroxylamine, isolated as a copper salt (eq 534).[528]

$$ArN(NO)NH_2 \xrightarrow{Cu(OCOCH_3)_2} \xrightarrow[\text{or } NH_4OH]{CH_3CO_2H} Cu(O{-}N(NO)Ar)_2 \quad (534)$$

XIII. Addendum

Methyl aroylhydroxamates ($ArCONHOCH_3$), amides, and isocyanates were photolytically obtained from aroyl azides in methanol.[529] Photooxygenation of azides (RN_3) in polymer matrices presumably produced nitrene adduct diradicals (R$\dot{N}$–O–O·) and subsequently aminyl peroxides (RNHCO·) by hydrogen abstraction. The latter accounted for the formation of amines by further abstraction of hydrogen (product derivatives of NO bond systems were not reported).[530] On the other hand, photooxygenation of 2-azidophenazine in different hydrocarbons gave, in addition to 2-nitrophenazine (**645**), a nitrosopyrrole (**646**) accounted for by an isomerization (eq 535) of compound **645**.[531]

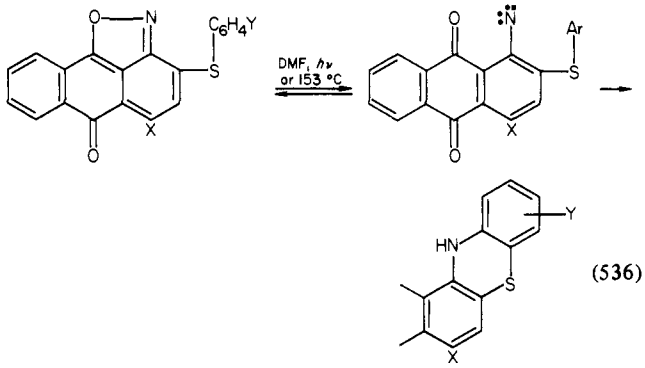


645 646 (535)

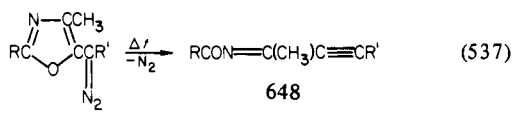
Thermolyses of phenyl azides in decalin showed rate enhancement for ortho substituents: formyl (22.8), benzoyl (70), annd azoaryl (21, 780).[532]

Competitive ring closures gave isoxazoles (reversibly) and thiazines from an intermediate nitrene obtained either photolytically or thermally from 1-azido-2-arylthioanthraquinones (eq 536).[533]

Thermolysis gave an *N*-acetylimine (**648**) of a butyn-3-one from a 5α-(diazoalkyl)oxazole (**647**) and a nitrile and a propyn-3-al or -3-one from a 5α-(diazoalkyl)isoxazole (**649**) (eq 537, 538).

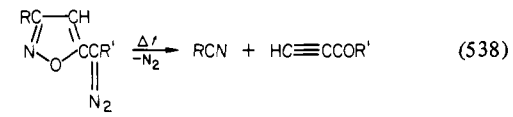


(536)



(537)

647 648

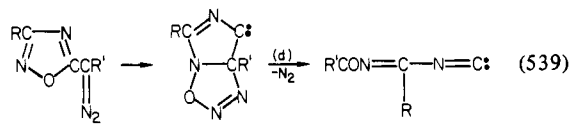


(538)

649

These were seen as results dependent on an initial development of a carbene center at the diazocarbon atom (cf. eq 39). A general scheme for eq 38, 39, 537, and 538 is now offered (see eq 38 for details) (Scheme I, paths a–c).

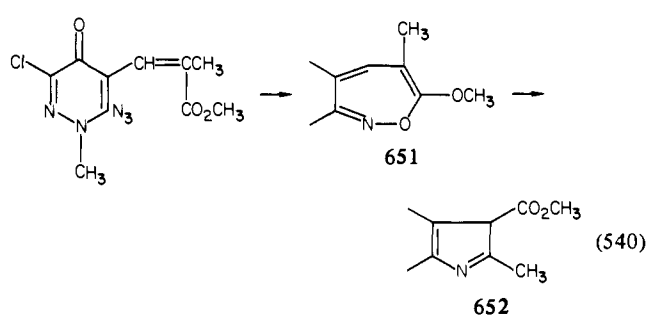
For product formation: (a) a carbonyl group was preferred to a nitroso group,[534] (b) covalent bonds were preferred to charge separation, and (c) an isocyanide was produced by an appropriate fragmentation, but a similar formation of an intermediate alkylidenecarbene (>C═C:) was not encountered. An *N*-acyl derivative of an imidoisocyanide can be expected from a 5α-(diazoalkyl)-1,2,4-oxadiazole (**650**), by path d (unknown at the present time) (eq 539).



(539)

650

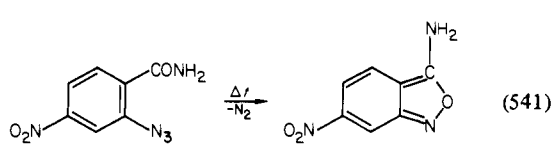
The formation of an isopyrrole (**652**) from a δ-azidopentadienoic acid ester by thermolysis was attributable to the intermediacy of a seven-membered ring vinylogue (**651**) of an isoxazole.[535]



(540)

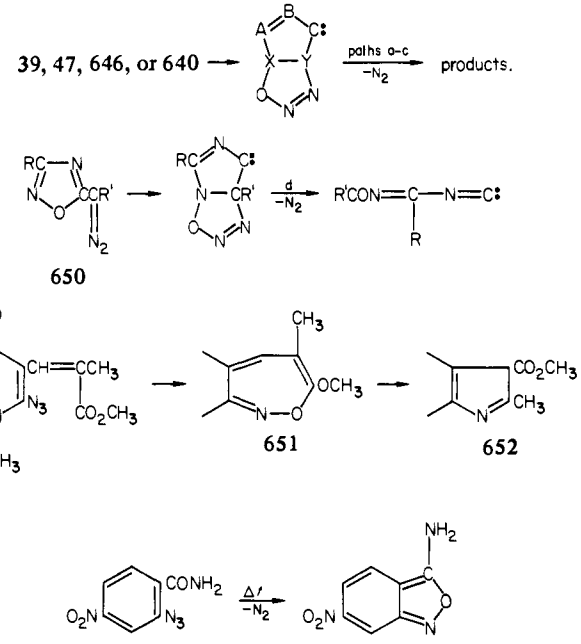
651 652

Apparently 2-aminoanthranil is more stable than 2-hydroxyanthranil (Section II.H.1); thermolysis of 2-azido-4-nitrobenzamide gave a derivative of the amine (eq 541).[536]



(541)

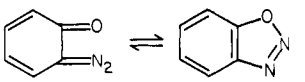
Scheme I



path	products	eq	products
a	O=X–A=B–C≡Y	38	$C_6H_5CON{=}NCN$ (major)
		39	RCOCH=CHC≡CR′
		537	RCON=C(CH$_3$)C≡CR′ (products at 200 °C)
b	O=Y–C$^-$=B–A$^+$–X → O=YC≡B + A≡X	538	R′COC≡CH + RCN
		537	R′COC≡CH + RCN (products at 300 °C)
c	O=X–C$^+$–B=A$^-$ → O=X–Y=C: + B≡A	38	C_6H_5CONC (minor) + N_2
d	O=Y–X=A–B=C:		

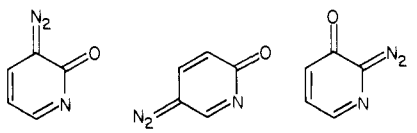
X = C_6H_5C, Y = A = B = N, from **39** in eq 38
X = RC, Y = R′C, A = B = CH, from **47** in eq 39
X = RC, Y = R′C, A = N, B = CCH_3, from **647** in eq 537
X = N, Y = R′C, A = RC, B = CH, from **649** in eq 538

Ultraviolet photoelectron spectroscopy established an equilibrium between α-diazocyclohexadienone and 1,2,3-benzoxadiazole in the gas phase (eq 542). A structure determi-



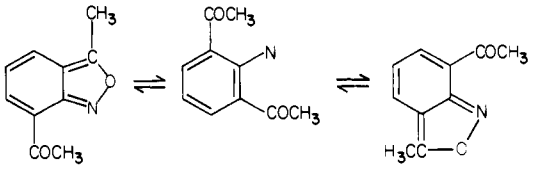
(542)

nation for the three isomeric diazopyridones came from an investigation of their ionization potentials. The data supported the quinonoid structures **653a–c** for each in the gas phase.[536]



653a 653b 653c

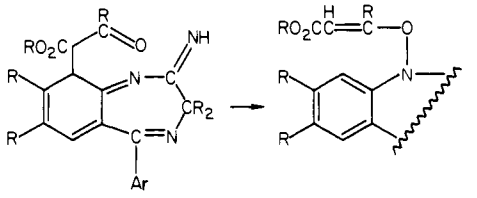
The thermally degenerate reversibility for 7-acetyl-3-methyl-2,1-benzisoxazole (**654**) was seen as a [1.9] sigmatropic shift (eq 543)[539] but may have occurred via delocalized 1,6-diacetylphenylnitrene (cf. eq 144–146).



(543)

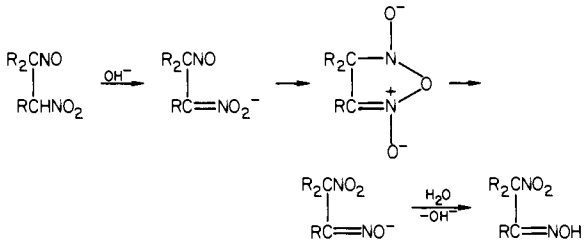
654

The formation of an NO bond in an unusual Cope rearrangement gave a hydroxylamine (eq 544).[540]



(544)

A base-catalyzed intramolecular transfer of oxygen from a nitro to a nitroso group occurred when the nitro group was attached to a secondary carbon atom and the nitroso group was attached to a tertiary carbon atom (eq 545).[541] An apparent absence of the reverse reaction is reminiscent of nitrolic acids ($RC(=NOH)NO_2$) for which the *gem*-nitroso-*aci*-nitroalkane tautomers ($RC(=NO_2H)NO$) are unknown.[601]



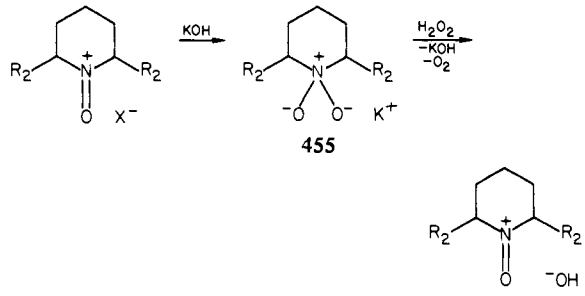
(545)

Both superoxide anion radical and molecular oxygen oxidized *o*-phenylenediamine into *o*-nitroso- and *o*-nitroanilines (cf. eq 234) and *o*,*o*′-diaminoazobenzene.[542] Percarboxylic acids reacted with di- and triphenylguanidine in methanol and tetrahydrofuran to form nitroxyl radicals.[543] A transfer of the oxaziridine oxygen atom to brucine has been refuted.[544]

Oximes were efficiently produced from mixtures of air, ammonia, and a ketone on a silica catalyst at about 200 °C.[545] In another situation, acetone reacted with ammonia and monopersulfuric acid at 30 °C to give the azine (90%) of acetone.[546]

A recent report described a complex mixture of products from benzofuroxan and diethylamine[547] (cf. Section III.E). It contained quinoxaline 1,4-dioxide (15%), *o*-benzoquinone dioxime (5%), benzofurazan (10%), 1-hydroxy-2-methylbenzimidazole 3-oxide (3%), *o*-nitrosoaniline (5%), *o*-nitroaniline (<3%), 3-methylbenzotriazine (5%), 3-methylbenzotriazine 4-oxide (10%), and *o*-nitro-*N*,*N*-diethylhydrazinobenzene (10%).

Quaternary ammonium salts with two NO covalent bonds at the tetrahedral nitrogen atom are not often encountered. The salt **655** was found to be an oxidizing agent (eq 546).[548]

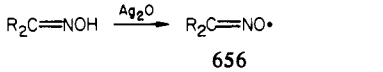


455

(546)

Acetylenes have dehydrogenated hydroxylamines into nitrones (cf. Section VI.E.3).[549]

Bis(1-adamantyl) ketoxime gave the sterically hindered iminoxy radical **656** upon oxidation by silver oxide.[550]

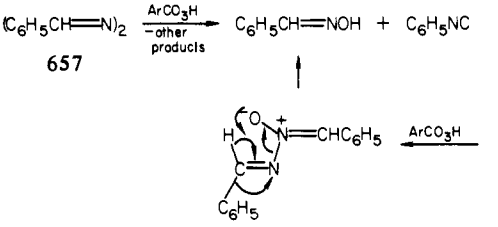


(547)

656

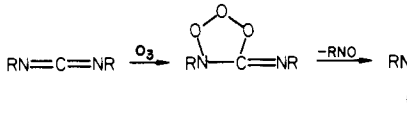
R = 1-adamantyl

An unaccounted for formation of benzaldoxime and phenyl isocyanide from the treatment of benzaldazine **657** with *p*-carbomethoxyperbenzoic acid[551] can be seen as an extension of the Beckmann rearrangement of an oxime (eq 548).



(548)

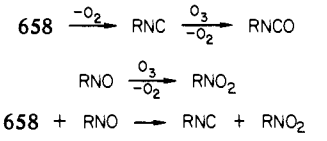
Nitrocyclohexane, cyclohexyl isocyanate, and several other compounds were produced from dicyclohexylcarbodiimide and ozone.[552] These compounds in the complex mixture were attributable to an initial electrophilic attack by ozone on a carbodiimide nitrogen atom (eq 549). Ozone was the reagent



(549)

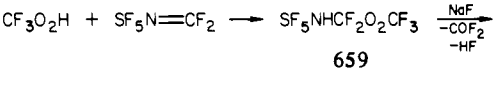
658

recognized for oxidation of undetected intermediate nitroso and isocyano compounds,[552] but the isocyanate oxide **658**, a proposed intermediate, is also a peroxide and can combine with nitrosocyclohexane to produce directly the isocyanide and nitro compounds (eq 550).



(550)

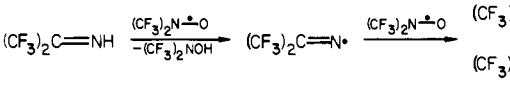
Treatment with sodium fluoride transformed pentafluorothioaminopentafluorodimethyl peroxide (**659**) into 2-(pentafluorothio)-3,3-difluorooxaziridine (eq 551).[553]



659

(551)

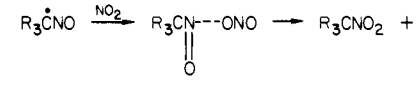
A perfluoro-*o*-(dimethylamino)acetoxime (**660**) was obtained along with other products from the combination of perfluoroacetonimine and perfluorodimethylaminoxyl (eq 552).[554]



660

(552)

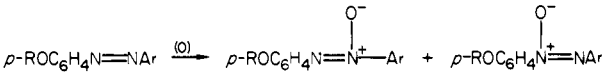
Isotopic labeling established an oxygen atom transfer rather than a displacement reaction on a carbon atom in the oxidation of a tertiary alkyl nitroso compound into a nitroalkane by treatment with nitrogen dioxide (eq 553).[555]



(553)

Azobenzoate esters were more efficiently oxidized by the ethyl ester of perterphthalic acid (40%) than by hydrogen peroxide (30%) into azoxy compounds (eq 554). Nearly equal amounts (ranging from 38:62 to 48:52 for A:B) of azoxy esters were obtained and identified by NMR analysis.[556]

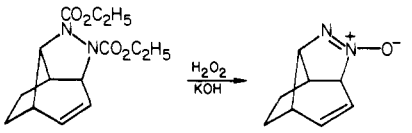
The location of the NO bond in the azoxy compound **661**, obtained from the corresponding hydrazide and alkaline hydrogen peroxide (30%), was established by an X-ray analysis after NMR spectroscopy did not lead to an assignment (eq 555).[557]



A B

(554)

$R = C_5H_{11}, C_{10}H_{21}$; $Ar = p'\text{-}C_6H_3(O'\text{-}X)CO_2R$; $X = H, Cl$; $R = C_5H_{11}, CH_3C_4H_8$



661

84% (555)

Benzeneseleninic anhydride $((C_6H_5SeO)_2O)$ in anhydrous tetrahydrofuran at 25 °C dehydrogenated phenylhydroxylamine into nitrosobenzene (89%) and *tert*-butylhydroxylamine into 2-nitroso-2-methylpropane (96%).[556]

XIV. References

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