INDO Molecular Orbital Study of α-Heteroatom Nitrenes

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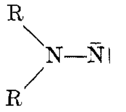
The results of INDO valence-shell electron molecular orbital calculations are reported for a number of heteroatom (O, N, S) substituted nitrenes to provide a framework in which to evaluate the experimental observations on these intermediates. Geometry searches have been performed for the simplest species, HON, and H_2NN, indicating that both molecules are bound in preferred singlet ground states. Computed atomic charges and binding energies are shown to be consistent with the observed relative reactivities of the various nitrenes toward electrophilic olefins.

The chemistry of diazenes[1b,2] (*i.e.*, the 1,1-disubstituted species, **1**) and oxynitrenes,[3] **2**, have been of

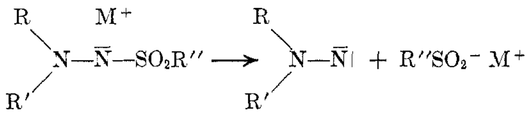


1

$R{-}O{-}\bar{N}|$

2

considerable recent interest. Diazenes have been generated by thermal decomposition of 1,1-disubstituted 2-sulfoxyhydrazine salts (eq 1) and by oxidation



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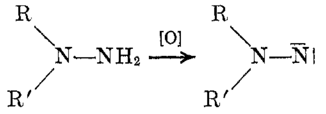
of a variety of *N*-amino compounds (eq 2).



(2)

McBride[4] has elegantly shown that the oxidation of 1,1-dialkylhydrazines, **3**, in acidic solution proceeds *via* a diazene (Scheme I).

SCHEME I

$$\underset{\mathbf{3}}{R_2NNH_2} \overset{H^+}{\rightleftharpoons} R_2NNH_3^+$$

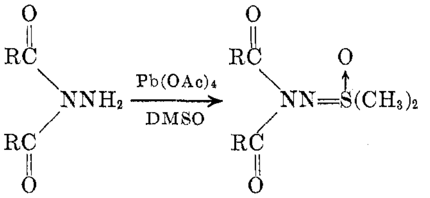
$$R_2NNH_3^+ \overset{[O]}{\rightleftharpoons} R_2\overset{+}{N}{=}NH + 2H^+ + 2e^-$$

$$R_2\overset{+}{N}{=}NH + OH^- \rightleftharpoons R_2\overset{+}{N}{=}\overset{-}{N} + H_2O$$

$$R_2\overset{+}{N}{=}\overset{-}{N} + R_2\overset{+}{N}NH \longrightarrow R_2\underset{+}{\overset{H}{N}}N{=}NNR_2$$

$$R_2\underset{+}{\overset{H}{N}}N{=}NR_2 \xrightarrow{-H^+} R_2NN{=}NNR_2$$

Diazenes generated by oxidation reactions have been trapped in several cases.[5-8] When acyl-substituted hydrazines were oxidized with lead tetraacetate in dimethyl sulfoxide, the diazene was trapped by dimethyl sulfoxide to give dimethylsulfoximine derivatives[6] (eq 3). The diazene has been regenerated by

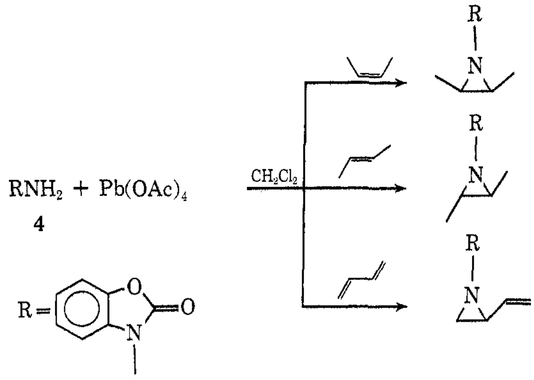


(3)

thermolysis and photolysis of the sulfoximines to give identical products as are obtained from oxidation of the corresponding hydrazine in the absence of dimethyl sulfoxide.

Lead tetraacetate oxidation of 3-aminobenzoxazolineone (**4**) in the presence of olefins and dienes yielded the corresponding aziridine[7] (Scheme II). The stereospecific additions to cis and trans olefins and the 1,2 addition to 1,3-butadiene all indicate a singlet diazene intermediate. This is further substantiated by stereospecific addition, even at low olefin concentration.

SCHEME II



Recently, Rees and coworkers[8] have found that electrophilic olefins, those substituted with inductively or conjugatively electron-withdrawing groups, were effective "traps," and in some cases gave a higher yield of the aziridine. This fact, along with the singlet character of the nitrene, was explained by delocaliza-

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[1] (a) Correspondence to this author should be mailed to Air Products and Chemicals, Inc., P. O. Box 538, Allentown, Pa. 18105. (b) For a review see W. I. Lwowski, Ed., "Nitrenes," Interscience, New York, N. Y., 1970, Chapter 10.

[2] (a) C. G. Overberger, M. Valentine, and J. P. Anselme, *J. Amer. Chem. Soc.*, **91**, 687 (1969), and references cited therein; (b) D. M. Lemal, T. W. Rave, and S. D. McGregor, *ibid.*, **85**, 1944 (1963).

[3] J. H. Boyer and J. D. Woodyard, *J. Org. Chem.*, **33**, 3329 (1968); A. Hassner, R. Wiederkehr, and A. J. Kascheres, *ibid.*, **35**, 1962 (1970).

[4] (a) W. R. McBride and H. W. Kruse, *J. Amer. Chem. Soc.*, **79**, 572 (1957); (b) W. H. Urry, H. W. Kruse, and W. R. McBride, *ibid.*, **79**, 6568 (1957); (c) W. R. McBride and E. M. Bens, *ibid.*, **81**, 5546 (1959).

[5] Reference 1, p 361.

[6] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *Chem. Commun.*, 146 (1969); C. W. Rees and M. Yelland, *ibid.*, 377 (1969).

[7] R. S. Atkinson and C. W. Rees, *ibid.*, 1230 (1967); R. S. Atkinson and C. W. Rees, *J. Chem. Soc. C*, 772 (1969).

[8] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *ibid.*, 576 (1970).

tion of the lone pair of the tervalent nitrogen into the vacant p orbital of the univalent nitrogen. This could

$$R_2NN \longrightarrow R_2\overset{+}{N}{=}\overset{-}{N}$$

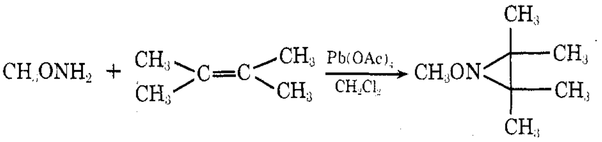
cause the singlet to be the ground state and would also increase the nucleophilic character of the intermediate.

Lemal[9,10] has shown that diazenes are generated by α elimination of 1,1-dialkyl-2-arenesulfonylhydrazines on treatment with base to yield tetrazenes. However, there have been no reports of addition of the dialkyl-

$$R_2NNHSO_2Ph \xrightarrow{\text{base}} R_2NN{=}NNR_2$$

diazene generated by base treatment to olefins or dialkyldiazene insertion into C–H bonds.

An oxynitrene has been postulated as an intermediate in the lead tetraacetate oxidation of methoxyamine in the presence of tetramethylethylene[11] (eq 4).



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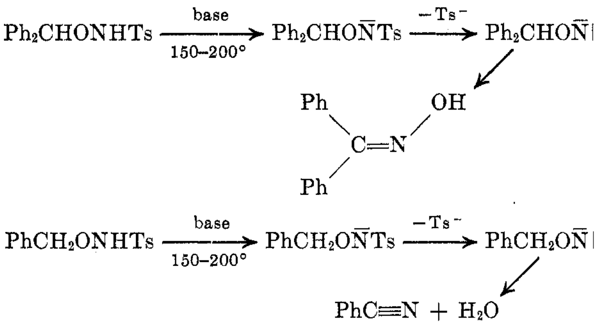
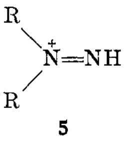
When *O*-benzhydryl-*N*-*p*-toluenesulfonylhydroxylamine or *O*-benzyl-*N*-*p*-toluenesulfonylhydroxylamine were treated with base (sodium hydride or butyllithium) in triglyme and heated at 150–200°, O to N migration occurred.[12] An oxynitrene intermediate could explain the results (Scheme III).

SCHEME III



Lemal and coworkers[10] have shown that diazenium ions, **5**, can be generated at room temperature. However, we have found that oxynitrenium cations, **6**, were



5

$RO\overset{+}{N}H$

6

not formed even with prolonged heating at 56° under the same reaction conditions.[13]

Since heteroatoms adjacent to a nitrene are believed to stabilize the nitrene, a comparison of the stabilizing effects of some heteroatoms was done. Reported here are the results of LCAO–MO–SCF calculations on a number of heteroatom (O, N, S) substituted nitrenes which provide a more systematic framework on which to base conclusions from experimental observations.

Method.—Approximate LCAO–MO calculations for those systems containing only first-row atoms were performed using the INDO (intermediate neglect of differential overlap) method.[14,15] This semiempirical model employs a minimum basis set of valence shell atomic orbitals (AO's) and neglects differential overlap in all two-electron integrals except one-center exchange types. For HSN, the CNDO (complete neglect of differential overlap) method, as modified for second-row elements, was employed.[16,17] Both the INDO and CNDO methods are documented to be quite successful in reproducing various molecular properties: experimental bond angles are predicted with good accuracy; calculated bond distances are less satisfactory, but still exhibit good correlation with observed values; dipole moments normally agree remarkably with the experimental quantities; and calculated binding energies are typically high in magnitude. Computations were carried out with the standard CNINDO program[18] on a Burroughs B5500 computer.

To obtain a qualitative estimate of bonding from our calculations, we computed a bond index,[19–21] W_{ab}, which is simply the square of the bond order, where

$$W_{ab} = (P_{ab})^2 = \sum_{i}^{\text{occ}} \sum_{j}^{\text{MO's}} c_{ia}c_{ib}c_{ja}c_{jb} \tag{5}$$

i and j label the doubly occupied MO's and a and b label AO's in the LCAO expansion. The total bond index between two atoms, W_{AB}, is then obtained by summing W_{ab} over all AO's on atoms A and B.

$$W_{AB} = \sum_{a}^{\text{on A}} \sum_{b}^{\text{on B}} W_{ab} \tag{6}$$

Molecular geometries for HON, H_2NN, and HSN were obtained by minimizing the total energy of each system with respect to all bond angles (except for the out-of-plane angle for H_2NN) and bond distances. Bond lengths for LiON were taken from Andrews' infrared study[22] followed by minimization of the total energy with respect to the LiON bond angle. CH_3ON was constructed by replacing the hydrogen in HON with a methyl group at the computed equilibrium configuration. Finally, the geometry of succinimidonitrene was based on the X-ray structure of succinimide.[23]

The relative stabilities of nitrenes is a question of considerable interest, and cannot be answered simply by quoting the total binding energies estimated in the available INDO programs. Total binding energies would lead one to the conclusion that large systems are

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[9] D. M. Lemal, F. Menger, and E. Coats, *J. Amer. Chem. Soc.*, **86**, 2395 (1964).

[10] D. M. Lemal, C. D. Underbrink, and T. W. Rave, *Tetrahedron Lett.*, 1955 (1964).

[11] S. J. Brois, *J. Amer. Chem. Soc.*, **92**, 1079 (1970).

[12] F. A. Carey and L. J. Hayes, *J. Amer. Chem. Soc.*, **92**, 7613 (1970).

[13] F. A. Carey and L. J. Hayes, 1971, unpublished data.

[14] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

[15] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, Chapters 3 and 4 and references to other works cited therein.

[16] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

[17] D. P. Santry, *J. Amer. Chem. Soc.*, **90**, 3309 (1968).

[18] P. A. Dobosh, Program No. 141 of the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

[19] K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

[20] C. Trindle and O. Sinsnoglu, *J. Amer. Chem. Soc.*, **91**, 853 (1969).

[21] C. Trindle, *ibid.*, **91**, 219 (1969).

[22] L. Andrews, 1971, personal communication.

[23] R. Mason, *Acta Crystallogr.*, **9**, 405 (1956).

inevitably more stable than small systems; however, this implication is a direct consequence of the obvious fact that larger molecules have more bonds and hence more binding energy than small molecules.

Hess and Schaad[24] show us how to deal properly with binding energies, by analogy with their treatment of Hückel delocalization energies. Recognizing that acyclic polyenes have little π delocalization, Hess and Schaad represented the π energy of these systems as a superposition of "bond" contributions. The resonance stabilization for cyclic systems is the residual π energy after bond contributions are set aside. This approach clarified a number of paradoxes associated with the customary predictions of stability based on Hückel energies.

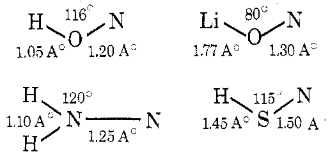
We collected INDO binding energies for 18 molecules containing the kinds of bonds typically encountered in organic systems of H, C, N, and O. This number is smaller than we had wished, because we limited our attention to molecules for which energy-optimized geometries had been determined.[25] Experience shows that optimized geometries are essential to meaningful estimates of features of potential surfaces.[26] All these molecules can be represented by a single dominant valence bond structure, and should, therefore, have highly localizable charge distributions. Multiple regression analysis[27] enabled us to generate a number of binding energy predictor equations, of linear form in the number of bonds of distinct types.

The best *single* predictor of binding energy is the total number of bonds, irrespective of type. This reflects the fact that binding energy must increase with the number of bonds, as anticipated. Almost 88% of the variance in binding energy is accounted for by the number of bonds. Total valence electrons is a less suitable measure, since lone pairs make little contributions to the binding energy. One may generate predictor formulas by considering only molecules without α-nitrene fragments, or by including such molecules in the sample. The proper choice is not clear; so we made both in turn.

Results

Geometry searches were carried out for HON, LiON, H_2NN, and HSN. All four molecules were found to be bound, and in Chart I, the equilibrium geometries at the potential minima are presented. LiON has been isolated by Andrews in an argon matrix, and our calculated bond angle of 80° agrees well with the experimentally estimated value (77.7°).[22] To our knowledge, HON, H_2NN, and HSN have not yet been isolated; however, HON and H_2NN are the simplest homologs of the intermediates which have been postulated in certain reactions.

CHART I
COMPUTED EQUILIBRIUM GEOMETRIES



Listed in Table I are the computed total energies and binding energies for all of the nitrenes considered in this work. For HON, CH_3ON, and H_2NN we computed both the singlet and triplet (using optimum singlet geometries) species. In all three cases, the singlet species is predicted to be more stable than the triplet, generally by more than 1 au.

TABLE I
COMPUTED TOTAL AND BINDING ENERGIES

Registry no.	Molecule	Multiplicity	Total energy, au	Binding energy, au
35337-59-8	HON	Singlet	−29.2925	−0.6885
	HON	Triplet	−28.0893	0.5147
35337-60-1	CH_3ON	Singlet	−37.6439	−1.8276
	CH_3ON	Triplet	−36.0014	−0.1850
36529-65-4	LiON	Singlet	−28.7600	−0.5625
35337-54-3	H_2NN	Singlet	−23.6459	−1.0221
	H_2NN	Triplet	−22.5992	0.0246
36529-67-6	HSN[a]	Singlet	−22.6646	−0.1832
	HSN[b]	Singlet	−22.8056	−0.3241
36529-68-7	Succinimidonitrene	Singlet	−87.6437	−5.4184

[a] CNDO without d orbitals on sulfur. [b] CNDO with d orbitals on sulfur.

The relative stabilities of these nitrenes can be predicted by using linear predictor formulas. It was found that, if nitrenes are excluded, linear predictor formulas contain a root-mean-square error of *ca.* 0.1 au, or 4–10%. Departures of computed INDO binding energies from binding energies estimated from the predictor formulas must exceed 0.2 au if we are to attach any significance to the disparity. Of the α-heteronitrenes LiON falls below the predicted binding energy, CH_3ON, H_2NN, and HON are accurately predicted, while succinimidonitrene is exceedingly stabilized relative to the estimate of the predictor. The order of stability of α-heteroatom nitrenes is indicated to be succinimidonitrene $\gg$ CH_3ON > H_2NN > LiON $\sim$ HON.

If one includes nitrenes in the sample of data from which the predictor equation is constructed, the quality of the linear predictions diminishes; there is more scatter in the data, due in part to the fact that nitrenes are not so highly localized as more common bonds. The best predictor equation makes reference to total bonds, CO double bonds, and CC double bonds. It accounts for 98% of variance in our data, with a residual error (root mean square) of 0.13 au. Inspection of predicted binding energies and INDO computed values shows that succinimidonitrene's stability is high, LiON's is low, and the other stabilities are unsurprising. This trend agrees in large part with the trends observed above, *even though the nitrene binding energies are now influencing the predictor equation.*

The calculated net atomic charges are displayed in Chart II. It is significant to note the existence of a substantial charge separation within each molecule and a relatively large negative charge on each of the

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[24] B. A. Hees, Jr., and L. J. Schaad, *J. Amer. Chem. Soc.*, **93**, 305 (1971); see also M. J. S. Dewar and C. de Llano, *ibid.*, **91**, 789 (1969).

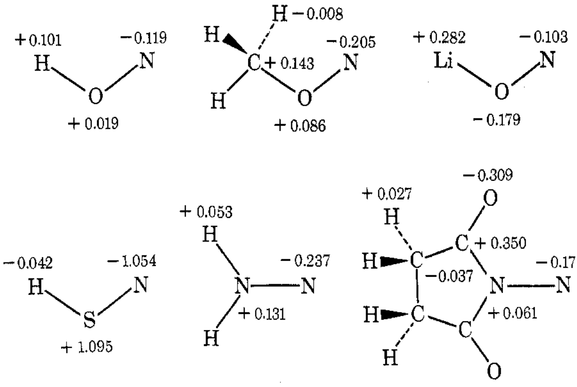
[25] M. S. Gordon and J. A. Pople, *J. Chem. Phys.*, **49**, 4643 (1968); see also ref 14; J. A. Pople, D. L. Beveridge, and N. S. Ostlund, *Int. J. Quantum Chem.*, **1**, 293 (1967).

[26] M. S. Gordan, *J. Amer. Chem. Soc.*, **91**, 3122 (1969).

[27] A particularly convenient vehicle for this analysis is the SPSS (Statistical Package for the Social Sciences) program described in N. Nie, D. H. Bent, and C. H. Hull, "SPSS," McGraw-Hill, New York, N. Y., 1970.

Chart II

Computed Net Atomic Charges



nitrene nitrogens. The variation of this negative charge among the molecules correlates well with the expected nature of the nitrene substituents. On passing from HON to CH_3ON, the negative charge increases from −0.119 to −0.237, consistent with the electron-donating character of the methyl group. In comparing H_2NN and succinimidonitrene, one would expect a substantial lowering of the negative charge in the latter due to the electron-withdrawing capabilities of the adjacent carbonyl groups. This hypothesis is borne out by the INDO calculations, but not to the extent that has been previously postulated for this molecule. For HSN, the CNDO calculation including d orbitals yields a net charge of −1.054 on the nitrene nitrogen. This figure is nearly five times greater than that for any of the other molecules. In comparing HON with H_2NN, we note that the oxygen in HON transfers less charge to the nitrene nitrogen than the corresponding nitrogen in H_2NN.

The computed dipole moments are tabulated in Table II, and are entirely consistent with the predicted large separation of charge in these molecules evidenced in Chart II. In view of the previous success of the INDO and CNDO methods in reproducing known molecular dipole moments, it is not unreasonable to postulate that the computed figures lie within one Debye of the true values.

Table II

Computed Dipole Moments

Molecule	Dipole moment, D
HON	2.18
CH_3ON	2.86
LiON	4.88
H_2NN	3.19
HSN[a]	9.09
Succinimidonitrene	5.25

[a] CNDO with d orbital on sulfur.

Finally, in Table III, we present the total indices, W_{AB}, for the nitrene bond in each of the substituents. The electron-donating character of the methyl group has increased the ON bond index in CH_3ON relative to HON, and the electron-withdrawing nature of the carbonyl groups in succinimidonitrene have decreased the NN bond index relative to H_2NN. All of the nitrene bond indices, except that for HSN, lie between one and two, implying partial double bond character for these bonds.

Table III

Computed Bond Indices

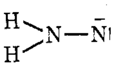
Molecule	Bond index (W_{XN})
HON	1.69
CH_3ON	1.74
LiON	1.69
H_2NN	1.87
HSN[a]	2.54
Succinimidonitrene	1.44

[a] CNDO with d orbitals on sulfur.

Discussion

The INDO calculations for the diazenes and oxynitrenes have given us a better understanding of the chemistry of these intermediates. In the geometry searches (by varying one parameter and keeping the remaining constant until a minimum was obtained), potential minima were found for both HON and H_2NN, indicating that both molecules should be bound. Replacement of the hydrogen in HON with a methyl group caused an increase in stability of the nitrene, which suggests that the alkylated nitrenes should be more stable than the unsubstituted compounds.

Diazenes are known to add to olefins stereospecifically,[7,8] which is in agreement with the calculated ground state singlet for isodiimide (**7**) and the predicted high stability of the singlet succinimidonitrene (**8**).



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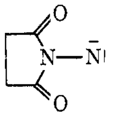

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The nucleophilic character of diazenes toward electrophilic olefins[8,28] can be explained on the basis of the predicted negative charge localized on the nitrene nitrogen of these intermediates. The addition of the methyl group to HON caused a substantial increase in the negative charge on the nitrene nitrogen, which can qualitatively be interpreted to signify an increase in importance of the dipolar resonance structure of CH_3ON relative to HON. By analogy, we would expect alkylated diazenes to possess a greater negative charge on the nitrene nitrogen than in H_2NN, with a corresponding increase in importance in the dipolar resonance structure. Hence, dialkyldiazenes should be more selective toward electrophilic olefins than diacyldiazenes, whose electron-withdrawing substituents would be expected to decrease the charge on the nitrene nitrogen and the importance of the dipolar resonance structure.[29] Our calculations support this argument in that the charge on the nitrogen in succinimidonitrene has been reduced from −0.24 to −0.17 and the bond index has been reduced from 1.87 to 1.44 relative to isodiimide.

Subsequent to this work, Peslak[30] reported *ab initio* molecular orbital studies of HON. He found that HON's bond angle was 112° compared to our 116° and the bond lengths were R (N–O) = 1.32 and R (H–O) = 0.99 Å as compared to our bond lengths of R (N–O) = 1.20 and R (H–O) = 1.05 Å. More signifi-

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(28) M. Bandru and A. Foucaud, *C. R. Acad. Sci., Ser. C*, **270**, 104 (1970).

(29) Reference 1, p 363.

(30) J. Peslak, Jr., D. S. Klett, and C. W. David, *J. Amer. Chem. Soc.*, **93**, 5001 (1971).

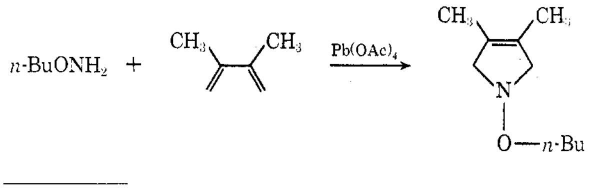
cantly, Peslak predicts the gross atomic charges as *H* = 0.39, *O* = −0.50, and *N* = 0.10. We have found that the nitrene nitrogen has the negative charge (Chart II).

The fact that only diazenes with electron-withdrawing groups add to olefins has been suggested to result from the negative substituent's effect of increasing the energy content and reactivity of the diazene without depriving it completely of its nucleophilic character.[29] Our calculations support the decrease in nucleophilic character, but, in view of the predictor equations, the stability of the diacyldiazene is not decreased; rather, it is increased. Thus we are led to postulate that the difference in reactivity between dialkyldiazenes and diacyldiazenes may result from the increased stability of the latter, allowing them to exist for sufficient time to react intermolecularly with the olefins.

In comparing HON and H_2NN, we note that the INDO calculations predict the diazene to be more stable than oxynitrene, implying that the former should be easier to generate. This is experimentally supported by the following data. *O*-benzyl-*N*-methanesulfonylhydroxylamine was stable in base at 100° for 18 hr,[13] whereas 1,1-dialkyl-2-benzenesulfonylhydrazines are decomposed in base at 110° within 15 min, yielding tetrazine, which can be reasonably postulated to arise through diazene intermediates.[9] The nitrene nitrogen of H_2NN is significantly more negative than the nitrene nitrogen of HON, and we would expect this trend to be maintained in the alkylated species. Hence, it is reasonable to anticipate alkyloxynitrenes to be less selective toward electrophilic olefins than dialkyldiazenes.

For oxynitrene, the singlet species was found to be the ground state, and therefore it should add to olefins stereospecifically. However, there has been only one report in which an oxynitrene has been postulated as an intermediate in an intermolecular trapping experiment.[11] Stereochemistry could not be deduced from this reaction (eq 4). Due to the lack of experimental evidence for the existence of free oxynitrene intermediates, it is somewhat difficult to draw any sound conclusions as to the electronic structure and properties of these compounds. Our INDO calculations simply predict these species to be bound in a singlet ground state, and less stable than the corresponding diazenes. This computed singlet character of oxynitrenes is entirely consistent with the postulated rearrangements shown in Scheme III.

Recent results[31] indicate that an oxynitrene is not the intermediate in the lead tetraacetate oxidation of O-substituted hydroxylamines. When *O*-*n*-butylhydroxylamine was oxidized by lead tetraacetate in the presence of 2,3-dimethyl-1,3-butadiene at −73°, the product was 1-*n*-butoxy-3,4-dimethyl-3-pyrroline (eq 7). It was found that nonstereospecific addition occurred in the presence of *cis*- and *trans*-2-butene.



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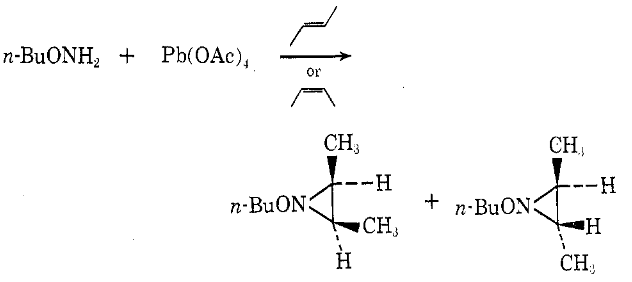
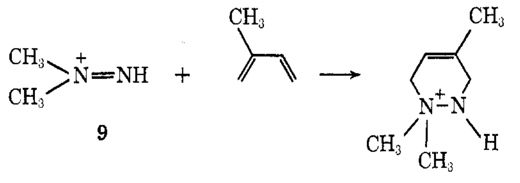


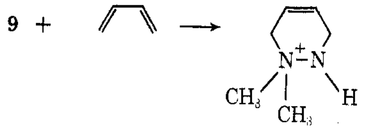
If the ground state of oxynitrene is indeed a singlet, as predicted by the INDO calculations, these reactions could not proceed *via* a free nitrene.

It is known that dialkyldiazenium ions add to olefins.[4b,32] When 1,1-dimethyldiazenium salt (**9**) was treated with isoprene or 1,3-butadiene at 0°, 1,4 addition occurred (eq 8 and eq 9, respectively). By analogy, it seems reasonable that the reactions of O-substituted hydroxylamines with lead tetraacetate in the presence of olefins could proceed through an oxynitrenium cation, **6** (eq 10), rather than the free nitrene, **2**.

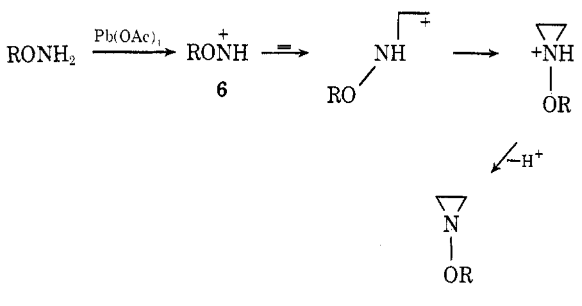


9

(8)



(9)



(10)

To complete our study of the nitrenes, we carried out calculations on HSN and LiON. Geometry searches were carried out for HSN varying both the bond angle and bond distances and for LiON using Andrews' bond distances and varying the bond angle. Potential minima were found for both molecules. The binding energies and total energies are given in Table I. The atomic charge on the nitrogen of HSN is considerably larger relative to the other nitrenes studied.

The atomic charges found for LiON are in agreement with Peslak's results.[30] Both the oxygen and nitrogen have a negative charge and lithium has a positive charge. The theoretical bond angles (80 and

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[31] This work is the subject of a paper in preparation: F. A. Carey and L. J. Hayes.

[32] W. H. Urry, P. Szecoi, C. Ikoku, and D. W. Moore, *J. Amer. Chem. Soc.*, **86**, 2224(1964).

81°[30]) are in close agreement with the experimentally determined value (77.7°).

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Base-Induced Decomposition of β-Nitroalkyl Nitrates

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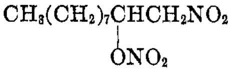
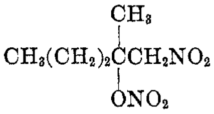
The elimination of nitric acid from β-nitroalkyl nitrates proceeds *via* an E1cb type of mechanism when the nitro and nitrate groups are attached to primary and secondary carbon atoms, respectively. Where the nitrate function is on a tertiary carbon, it has not been unequivocally shown that an E2 mechanism is operative, although the evidence points in that direction. Previous interpretation of the relative rate differences ascribed to 1,2-dinitrooctadecane, 1-nitro-2-octadecyl nitrate, and 1-nitro-2-octadecyl nitrite as differences in leaving group abilities may require reconsideration. Most likely these eliminations depend both on the leaving group abilities and on the acidity of the nitromethylene protons.

The elimination of the elements of nitric acid by a base from β-nitroalkyl nitrates has been known for many years. Usually, the β-nitroalkyl nitrate was studied as a component of a mixture formed from the addition of nitrogen dioxide to an olefinic linkage.[1] This mixture, consisting of β-nitroalkyl nitrate, β-nitro alcohol,[2] and 1,2-dinitroalkanes, yielded the corresponding nitro olefin. Siefert,[3] working with pure materials, found the following order of reactivity with pyridine: 1,2-dinitrooctadecane > 1-nitro-2-octadecyl nitrite > 1-nitro-2-octadecyl nitrate. These results were interpreted in terms of leaving group effects. With such structures the activating effect of the nitro group on proton release might figure importantly, along with leaving group effects, in the elimination process. This communication reports some preliminary results of a study of the pyridine-induced decomposition of β-nitroalkyl nitrates to nitro olefins and sheds some further light on the mechanism of the reaction. 1-Nitro-2-decyl nitrate (**1**), 1-nitro-2-methyl-2-pentyl nitrate (**2**), and 1-nitro-2-methyl-2-propyl nitrate (**3**) were chosen as model compounds.



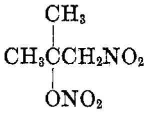
$$CH_3(CH_2)_7\underset{ONO_2}{\underset{|}{C}}HCH_2NO_2$$

1



$$CH_3(CH_2)_2\underset{ONO_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2NO_2$$

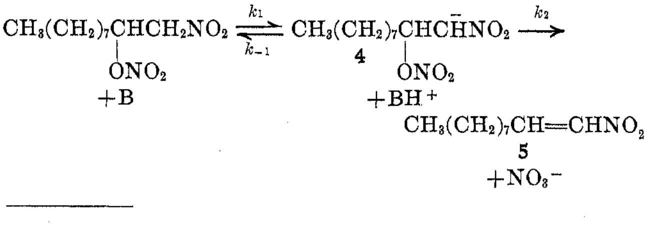
2



$$CH_3\underset{ONO_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2NO_2$$

3

One possible reaction path would involve proton abstraction in an equilibrium step, followed by elimination of nitrate ion from the intermediate carbanion (E1cb type), *e.g.*, from 1.

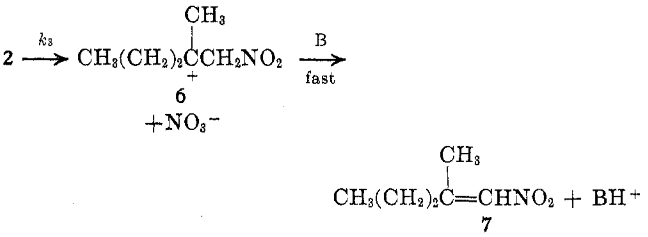


$$CH_3(CH_2)_7\underset{ONO_2}{\underset{|}{C}}HCH_2NO_2 + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{4}{CH_3(CH_2)_7\underset{ONO_2}{\underset{|}{C}}H\bar{C}HNO_2} + BH^+ \xrightarrow{k_2} \underset{5}{CH_3(CH_2)_7CH{=}CHNO_2} + NO_3^-$$

The steady-state approximation for such a process yields the rate expression of eq 1.

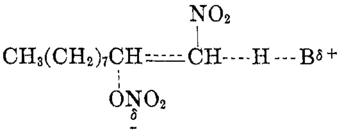
$$-\frac{d[1]}{dt} = \frac{k_1k_2[1][B]}{k_{-1}[BH^+] + k_2} \tag{1}$$

On the other hand, the nitro nitrate could lose nitrate ion in an unimolecular rate-determining step, forming a carbonium ion[4] which could eject a proton to form the nitro olefin (*e.g.*, from **2**).



$$2 \xrightarrow{k_3} \underset{6}{CH_3(CH_2)_2\underset{+}{\overset{CH_3}{\overset{|}{C}}}CH_2NO_2} + NO_3^- \xrightarrow[\text{fast}]{B} \underset{7}{CH_3(CH_2)_2\overset{CH_3}{\overset{|}{C}}{=}CHNO_2} + BH^+$$

Between these two extremes, there can exist intermediate situations in which bond-breaking at the nitro methylene carbon acts in concert with double bond formation and bond-breaking of the leaving group, leading to an E2 type mechanism (*e.g.*, for **1**).



$$CH_3(CH_2)_7\underset{\underset{\delta-}{ONO_2}}{\underset{\vdots}{C}}H \,{=}{=}{=}\, \overset{NO_2}{\overset{|}{C}}H\cdots H\cdots B^{\delta+}$$

8

Table I gives the kinetic and product data for the decomposition of **1** and **2** in benzene and/or *m*-xylene in the presence of equimolar amounts of pyridine. For **1**, the product obtained in near quantitative yield is 1-nitro-1-decene (**5**), identified by infrared [strong absorption at 6.55 and 7.3 μ (vinyl NO_2 asymmetric and symmetric stretch, respectively)] and by nuclear magnetic resonance [a two-proton multiplet at δ 2.25 (CH_2-$CH{=}CHNO_2$), a one-proton multiplet at 6.9 (CH_2-$CH{=}CHNO_2$), and a one-proton multiplet at 8.25 ($CH_2CH{=}CHNO_2$)]. The reaction is second order, first order in both **1** and pyridine, through two half-lives. Pyridinium nitrate precipitates from solution

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[1] V. V. Perekalin, "Unsaturated Nitro Compounds," Daniel Davy, New York, N. Y., 1964.

[2] Before treatment with base, the reaction mixture was hydrolyzed, converting the potentially explosive β-nitroalkyl nitrite to the β-nitro alcohol.

[3] W. K. Seifert, *J. Org. Chem.*, **28**, 125 (1963).

[4] For a discussion of a tertiary nitrate which reacts *via* an E1 process, see D. N. Kevill and R. F. Sutthoff, *J. Chem. Soc. B*, 3366 (1969).