

Theoretical Study of the Reactions of Ethene with Diimide Species¹

Daniel J. Pasto* and Daniel M. Chipman*

Contribution from the Department of Chemistry and Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, and the Institut de Chimie, Université Louis Pasteur de Strasbourg, Strasbourg, France. Received October 23, 1978

Abstract: Ab initio SCF calculations have been carried out on the minimum energy pathways for reduction of ethane by *cis*-, *trans*-, and 1,1-diimide. *cis*- and 1,1-diimide each undergo synchronous transfer of hydrogen to ethene (diimide reduction) with 4-31G energy barriers of 26.7 and 45.8 kcal/mol, respectively. The present result with *cis*-diimide is in distinct contrast with the results of a previous calculation which gave an energy barrier of ~60 kcal/mol. *trans*-Diimide reacts with ethene by either of two equally favorable pathways: (1) an indirect process corresponding to prior isomerization to *cis*-diimide with a 4-31G energy barrier of 46.0 kcal/mol; (2) a direct 1,3-addition to ethene to produce ethylaminonitrene with a 4-31G energy barrier of 45.3 kcal/mol. Various modes of decomposition of alkylamino- and dialkylaminonitrenes have been explored, the most favorable pathway apparently being a two-step, homolytic dissociation in which cleavage of the first C-N bond is the slow step. Concerted rearrangement of aminonitrene to *trans*-diimide is a "forbidden" process possessing a 4-31G energy barrier of 81.5 kcal/mol. The results of this theoretical study are discussed in terms of the known experimental facts on the diimide reduction reaction and decomposition of dialkylaminonitrenes.

Introduction

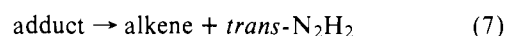
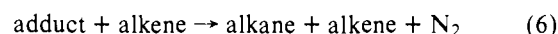
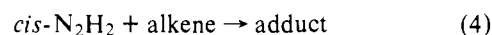
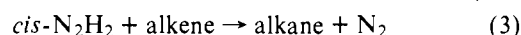
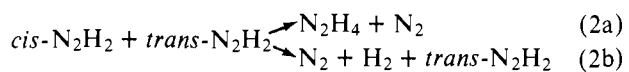
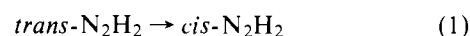
The reduction of alkenes to alkanes by diimide has not only become a useful synthetic reaction, but has also gained considerable attention from the mechanistic and theoretical viewpoint. Although the reduction of alkenes in the presence of hydrazine had been reported as early as 1905,² it was not until 1961 that results from several laboratories implicated diimide as the active reducing agent.³⁻⁵ The observation that the reduction of alkenes and alkynes occurred in a highly stereoselective syn manner resulted in the suggestion that *cis*-diimide was the active reducing agent, the hydrogens being transferred to the double bond in a concerted manner via a six-centered transition state.⁶

This proposed mechanism gained acceptance without serious consideration of the kinetics and thermodynamics of the diimide system, and the probable stereochemistry of the molecules produced in the various modes of formation of diimide which include (1) the oxidation of hydrazine,^{3,4} (2) thermal cycloreversion of the diimide-anthracene adduct,⁷ (3) hydrolysis of azodicarboxylic acid,³⁻⁵ (4) pyrolysis of *p*-toluenesulfonylhydrazine,^{5b} and (5) the microwave discharge decomposition of hydrazine.⁸ Of these procedures, (2) and (4) undoubtedly directly produce *cis*-diimide. Infrared spectral evidence also indicates that *cis*-diimide is formed, at least in part, in procedure (5).⁹ The stereochemistry of the diimides formed in procedures (1) and (3) has not been determined, although mechanistic and thermodynamic considerations suggest that *trans*-diimide should be the dominant isomer formed.

In order for reduction to occur with only *cis*-diimide, a rapid *cis*-*trans* interconversion is necessary in procedures (1) and (3). But the results of theoretical calculations on the N₂H₂ system are not consistent with any mechanism incorporating a rapid *cis*-*trans* interconversion. Calculations using a variety of methods and basis sets indicate that *trans*-diimide is more stable than the *cis* isomer by 5.8-10.1 kcal/mol,^{10,17} with an energy barrier for conversion of *trans* to *cis* of 46.3-60.0 kcal/mol.^{10,12-15,17} Obviously, any mechanism requiring this interconversion is untenable considering the rapid rates of reduction normally observed.

The results of a gas-phase kinetic study of the reaction of diimide (generated by the microwave discharge decomposition of hydrazine) with alkenes has been interpreted in terms of a complex reaction scheme (eq 1-7) in which the rate-controlling

step is the conversion of *trans*- to *cis*-diimide (eq 1), with only *cis*-diimide acting as the reducing agent.¹⁸



The results of an ab initio theoretical study¹⁹ on the reaction of *cis*-diimide with ethane, however, gave a calculated energy barrier of ~60 kcal/mol, resulting in the suggestion that, in fact, the rate of reaction between ethene and diimide is not controlled by the rate of isomerization of *trans*- to *cis*-diimide.¹⁹

From a practical viewpoint, if all the conclusions drawn from the calculations were correct, the reduction of alkenes by diimide would not be a kinetically feasible reaction! In the calculations on the reaction of *cis*-diimide with ethene¹⁹ a stable complex was found with a

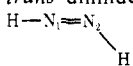
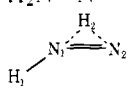
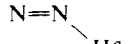


distance of 3.6 Å, this separation distance being maintained during the transfer of the hydrogens from *cis*-diimide to ethene.¹⁵ As this restriction on the structure of the interacting reactants during the course of the reaction did not intuitively seem reasonable, more detailed calculations were undertaken on the reactions of *cis*- and *trans*-diimide and 1,1-diimide (aminonitrene) with ethene.

Results and Discussion

Molecular orbital calculations using the GAUSSIAN 70 program²⁰ were made on reactants, structures along minimum-energy pathways, transition states, intermediates, and products at the STO-3G level using RHF for closed shells and UHF for open shells, with complete geometry optimization

Table I. STO-3G and 4-31G Energies and Structures of Various N₂H₂ and N₂H Species

species		structural parameters ^c	E, au (STO-3G)	E, au (4-31G)
<i>cis</i> -diimide (1)		N=N, 1.254; NH, 1.060; <NNH, 111.5	-108.545 06	-109.793 70
<i>trans</i> -diimide (2)		N=N, 1.250; NH, 1.059; <NNH, 103.4	-108.555 73	-109.804 83
	(4)	N=N, 1.246; N ₁ H, 1.052; N ₂ H, <1.083; N ₁ N ₂ H, 108.3	-108.451 11	-109.731 47
H ₂ N=N (3)	(3)	N=N, 1.289; NH, 1.033; <NNH, 123.4	-108.533 44	-109.795 01
	(5)	N=N, 1.308; N ₁ H ₁ , 1.050; N ₁ H ₂ , 1.119; N ₂ H ₂ , 1.300; <N ₂ N ₁ H ₁ , 121.3; N ₂ N ₁ H ₂ , 64.2	-108.384 69	-109.665 14
	(6)	N=N, 1.233; NH, 1.063; <NNH, 110.4	-107.989 46	-109.231 21
N=N-H ^a (7)	(7)	N=N, 1.205; NH, 1.012	-107.931 87	-109.205 32
N≡N		N≡N, 1.133	-107.500 65	-108.747 10

^a Pure doublet state calculated by the MOLE program. ^b Calculated by the GAUSSIAN 70 program. ^c Bond lengths in Ångstroms; angles in degrees.

(except as noted). A few RHF calculations on open-shell systems were carried out with the MOLE²¹ program to ensure proper spin states for the wave functions. Energies of reactants, transition states, intermediates, and products have also been calculated at the 4-31G level on the STO-3G optimized structures. Although a few of the species discussed in this paper have been previously studied theoretically using other basis sets, these have been recalculated at the fully optimized STO-3G and 4-31G levels for internal consistency.

N₂H₂ and N₂H Systems. The total energies and geometry-optimized structures of various N₂H₂ and N₂H species are presented in Table I. The present calculations indicate that *trans*-diimide (2) is more stable than the *cis* isomer (1) by 6.7 (STO-3G) and 7.0 (4-31G) kcal/mol.²² The energy barriers to conversion of *trans*- to *cis*-diimide via the bent-linear transition state 4 are 65.6 (STO-3G) and 46.0 (4-31G) kcal/mol. The 4-31G barrier is in close agreement with values obtained from calculations using larger basis sets (46.9 using double ζ¹³ and 46.3 kcal/mol using 4-31G + p¹⁷) and is in reasonable agreement with a large basis CI¹⁵ value of 55 kcal/mol. Previous calculations^{13,15,17} have all indicated that internal rotation is much less favorable than planar inversion for this isomerization.

An alternative pathway for isomerization of 1 or 2 involves homolytic dissociation to produce a hydrogen atom and the N₂H species 6 followed by recombination to give 2. Geometry optimization calculations on 6 using the GAUSSIAN 70 program resulted in a structure having a very impure spin state. As the N=N in 6 is lengthened from 1.235 to 1.326 Å (the latter being the energy optimized value) the energy decreased while ⟨S²⟩ increased from 1.150 to 1.372, compared to 0.7500 for a pure doublet. For this reason, geometry-optimized RHF STO-3G calculations were performed on the pure doublet state of 6 using the MOLE program,²¹ resulting in the structure and energies given in Table I. The pure doublet of 6 thus calculated lies 11.2 and 17.3 kcal/mol above the UHF GAUSSIAN 70 structures at N=N lengths of 1.235 and 1.326 Å, respectively. The dissociation-recombination pathway for conversion of 2 to 1 is thus calculated to have energy barriers of 62.6 (STO-3G) and 46.2 (4-31G) kcal/mol. Since a chemical bond is being broken, corrections for electron correlation and zero-point energies would tend to increase these numbers somewhat, perhaps by 20–30 kcal/mol or even more. Hence, homolytic dissociation followed by recombination is not likely to compete with internal inversion for isomerization of 1 to 2.

STO-3G calculations on the linear form of N₂H (7) using

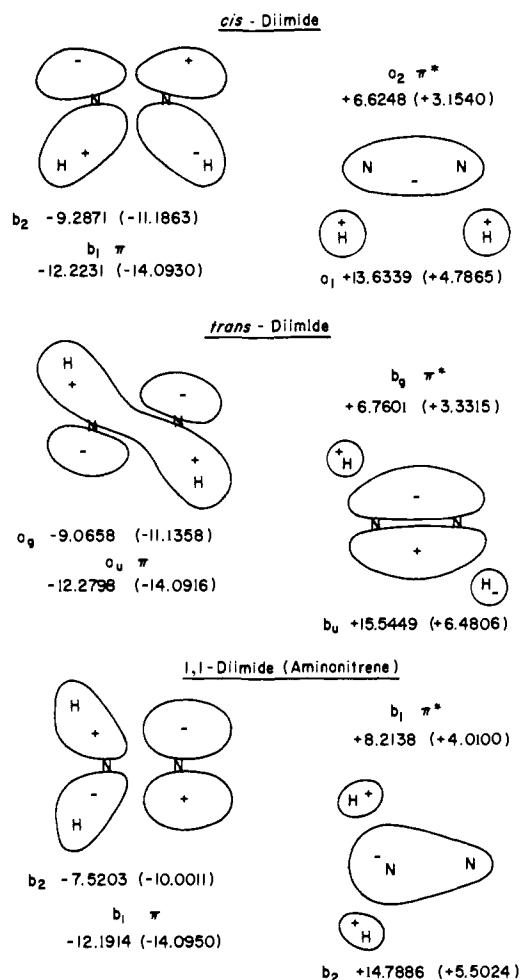
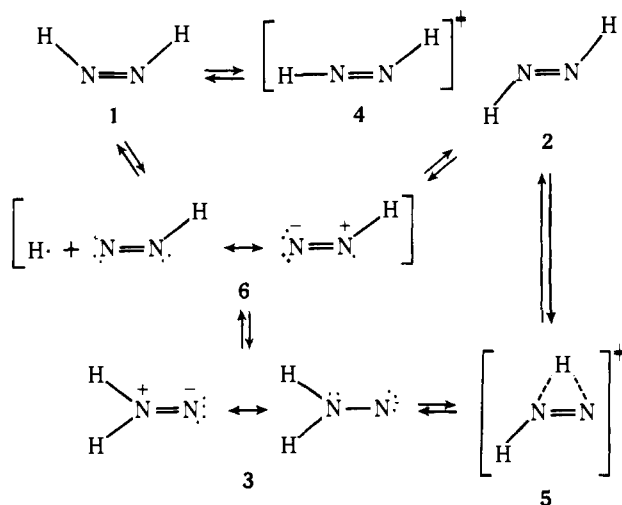


Figure 1. Wave functions and STO-3G (4-31G) energies (eV) of the two highest occupied and two lowest unoccupied MOs of 1, 2, and 3.

the GAUSSIAN 70 programs resulted in a reasonably pure doublet spin state (⟨S²⟩ = 0.7814). These calculations indicate that the linear form lies considerably above the bent form [36.1 (STO-3G) and 16.2 (4-31G)²³ kcal/mol]. Moreover, improving the calculations to also give a pure spin state for the linear form would further increase these numbers. Thus, the linear form will not be considered further in this article.

The present calculations indicate that 2 is more stable than 1,1-diimide (aminonitrene, 3)²³ by 14.0 (STO-3G) and 6.2 (4-31G) kcal/mol. Previous calculations gave energy differences of 14.6–17.4¹¹ and 26¹⁵ kcal/mol.²⁴ The minimum-



energy pathway for concerted rearrangement of **3** to **2**, a formally "forbidden" four-electron, suprafacial [1.2] sigmatropic rearrangement²⁶ via the planar transition state **5**, was explored. Rearrangement via this pathway is calculated to have energy barriers of 93.3 (STO-3G) and 81.5 (4-31G) kcal/mol. Alternatively, a dissociation-recombination pathway via **6** has calculated energy barriers of 48.6 (STO-3G) and 40.0 (4-31G) kcal/mol (cf. the "experimental" value²⁷ of 59.8 ± 2 kcal/mol). In this case, it is clear that homolytic dissociation-recombination is the preferred pathway.

The STO-3G and 4-31G energies and the STO-3G wave functions of the two highest occupied and two lowest unoccupied MOs of **1**, **2**, and **3** are presented in Figure 1.

Reaction of cis-Diimide (1) with Ethene. Concerted reaction theory suggests that the transfer of the hydrogens of **1** to a C=C should be a facile process, the transition state being a six-electron, aromatic transition state.²⁸ From a frontier molecular orbital (FMO) viewpoint,²⁹ the HOMO of **1** is of appropriate symmetry for interaction with the π^* LUMO of ethene, while the second UMO of **1** has the appropriate symmetry for interaction with the HOMO of ethene (see Figure 1).

The reaction of **1** with ethene has been investigated by first maintaining full C_{2v} symmetry and freezing the ground-state geometry of both reactants. An energy minimum was found at a C=C to N=N separation distance of 3.49 Å, similar to the value of 3.6 Å reported previously.¹⁹ The complex **8** (see Figure 3) lies 1.4 (STO-3G) and 3.7 (4-31G) kcal/mol below the total energy of the reactants. Potential energy surface scan calculations out to a separation distance of 7 Å indicate that there is no energy barrier involved in the formation of **8**.

Energies along the reaction coordinate from **8** to nitrogen and eclipsed ethane were calculated at various C---H-N distances and all other parameters were optimized. (Relaxation of the enforced C_{2v} symmetry did not alter the structures along the reaction coordinate.) The total energies were plotted vs. C---H distance (see Figure 2) and the position of maximum energy was taken as the transition state. The structure **9** at the transition state was fully optimized and the 4-31G energy calculated on the STO-3G optimized structure (see Figure 3). The energy barriers thus obtained are 36.5 (STO-3G) and 26.7 (4-31G) kcal/mol.

The various structural parameter values along the reaction coordinate are plotted in Figure 2 as a function of the C---H-N distance. It is important to note that as the C---H-N distance decreases the C=C to N=N distance also decreases, but to a lesser extent. It is not until well after the transition state that the nitrogen molecule rapidly exits after approaching to within ~ 2.43 Å of the C=C. The unreasonable

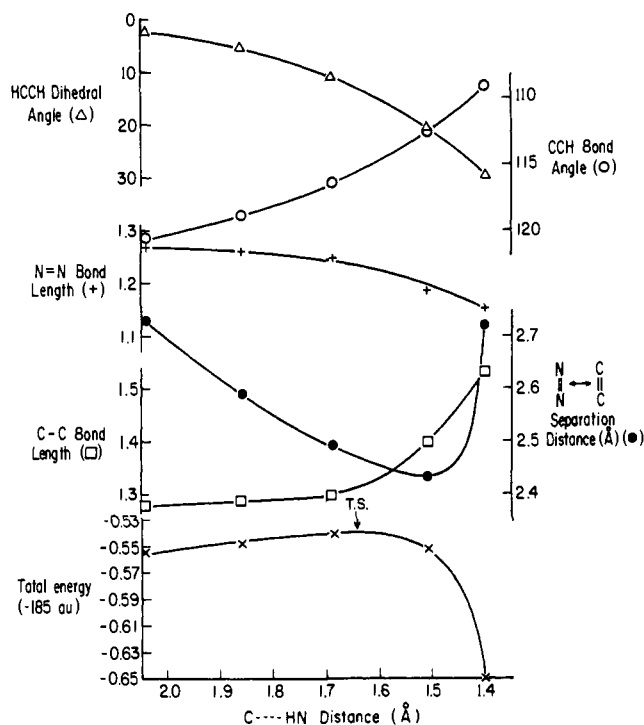


Figure 2. Plots of changes in geometrical parameters and total energy along the reaction coordinate for the reaction of *cis*-diimide with ethene.

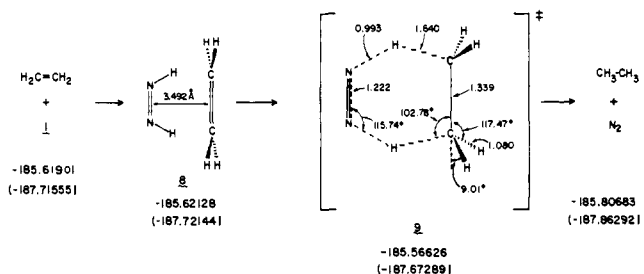
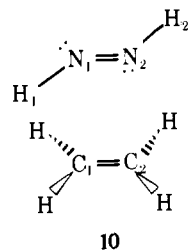


Figure 3. Structures and energies of reactants, complex (**8**), transition state (**9**), and products in the reaction of **1** with ethene. The geometries of **1** and ethene in **8** are those of the ground-state reactants. Nonparenthesized energies are from the STO-3G calculations, and parenthesized from 4-31G calculations. The STO-3G and 4-31G energies of staggered ethane are taken from ref 35.

assumption that this C=C to N=N distance remains constant at that in the complex during transfer of the hydrogens from **1** to the C=C is the reason for the high energy barrier reported previously.¹⁹ The presently calculated energy barrier is consistent with the known facile nature of the diimide reduction reaction.

trans-Diimide (2) with Ethene. 1,3-Addition. Although the present calculations on the reaction of *cis*-diimide with ethene indicate that the reaction is facile, the problem of the *trans* to *cis* isomerization of diimide still remains. Can **2** react directly with ethene without prior isomerization?

Analysis of the Mulliken populations from a preliminary calculation on structure **10**, in which **1** is replaced by **2** in



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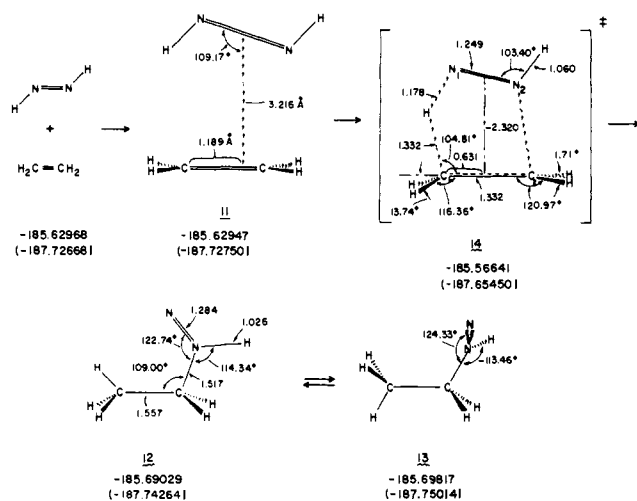
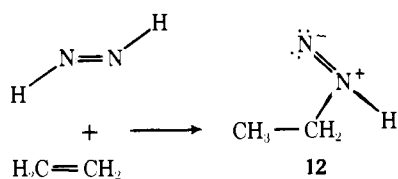


Figure 4. Geometries and energies (nonparenthesized, STO-3G; parenthesized, 4-31G) of the complex, transition state, and product in the reaction of *trans*-diimide with ethene.

complex **8**, shows that attractive interactions exist between H_1 of **2** and C_1 of ethene, and between the nonbonded pair of electrons on N_2 of **2** and C_2 of ethene! (Note that the HOMO of **2**, Figure 1, has the appropriate symmetry for a 1,3 interaction of **2** with the LUMO of ethene.) Geometry optimization calculations, in which the vertical and horizontal displacement distances and the tilt angle of the axis of the $\text{N}=\text{N}$ relative to the $\text{C}=\text{C}$, using the ground-state structures of **2** and ethene, indicate the existence of a slight energy minimum representing complex **11** (Figure 4) which lies 0.1 (STO-3G) and 0.5 (4-31G) kcal/mol below the reactants. While these numbers are too small to state with assurance that the interaction is attractive, it is at least clear that there is no substantial barrier to the formation of **11** from **2** and ethene.

The interactions between **2** and ethene in **11** suggest that reaction of **2** with ethene could result in the formation of an adduct having structure **12**, and calculations were undertaken



on that structure. In **12**, all C-H bond lengths and C-C-H bond angles were arbitrarily assigned values of 1.090 Å and 109.5°, respectively. All other structural parameters in the syn eclipsed conformation of **12** were optimized (see values in Figure 4). Structure **12** represents a stable intermediate which lies 38.0 (STO-3G) and 10.0 (4-31G) kcal/mol below the reactants. Calculations were also carried out on other conformations of **12**, the perpendicular staggered conformation, **13**, being of lowest energy [42.9 (STO-3G) and 14.8 (4-31G) kcal/mol below the reactants; see Table II].

It is interesting to note that Hinsberg and Dervan³⁰ recently reported the formation and characterization of the 1,1-dialkyldiazene **15** at -78 °C. The infrared spectrum of **15** shows an intense band at 1595 cm^{-1} ($\nu_{\text{N}=\text{N}}$) which is remarkably

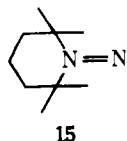


Table II. Energies of Conformers of **12**^a

Conformations of 12	energy, STO-3G (4-31G), au
syn eclipsed (12)	-185.690 29 (-187.742 64)
syn staggered	-185.697 56
anti eclipsed	-185.689 07
anti staggered	-185.696 92
perpendicular eclipsed	-185.692 73
perpendicular staggered (13)	-185.698 17 (-187.750 14)

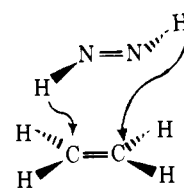
^a The geometry of the syn eclipsed structure **12** was optimized as described in the text. With the exception of **13** all other conformers were obtained by rotation of the C-C and C-N bonds without relaxation of any other geometrical parameters. See Figure 4 for the optimum geometry of **12** and **13**.

similar to the $\nu_{\text{N}=\text{N}}$ in *trans* azo compounds (1576 cm^{-1}). The calculated $\text{N}=\text{N}$ bond length in **12** of 1.284 Å is similar to that in **1** (1.254 Å) and **2** (1.250 Å) and is consistent with the infrared data of **15**.

The reaction coordinate for conversion of complex **11** to **12** was calculated in the following manner. Minimum energy structures were calculated as a function of the $\text{C}_1\text{---H---N}$ distance between that in the complex to that in **12** and all structural parameters were optimized except the C-H bond lengths, which were kept at 1.082 Å. At long $\text{C}_1\text{---H---N}$ distances the N_2H portion of **2** moved toward the center over the $\text{C}=\text{C}$. As the $\text{C}_1\text{---H---N}$ distance approached that in **12** difficulty was encountered in the optimization of the position of the N_2H fragment. Potential energy surface scan calculations were then carried out at selected $\text{C}_1\text{---N---H}$ distances in which the N_2H fragment was forced to move toward its final position in **12**. It was immediately apparent that both the $\text{C}_1\text{---N---H}$ distance and the movement of the N_2H were intimately linked along the reaction coordinate. A partial energy surface was constructed, the position of the transition state was then approximated, and final geometry optimization was carried out giving the transition-state structure **14** (Figure 4). The energy barriers for the formation of **12** from reactants via **14** are 39.7 (STO-3G) and 45.3 (4-31G)²³ kcal/mol, making this reaction pathway potentially accessible.

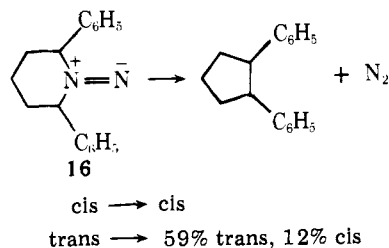
The process depicted in Figure 4 can be described as involving an electrophilic transfer of hydrogen to C_1 with nucleophilic attack by nitrogen on C_2 . This is nicely reflected by the STO-3G transition state charge densities. The hydrogen being transferred from **2** to C_1 bears a charge of +0.19 (compared to ~+0.07 for the other hydrogens attached to C_1 and C_2 and +0.17 for hydrogen attached to N_2). The charge on C_1 is -0.23 while that on C_2 is -0.04. These results would lead one to anticipate that alkenes bearing electron-donating groups, particularly at C_1 , should be less reactive, while those bearing an electron-withdrawing group capable of stabilizing partial negative charge formation at C_1 should be more reactive.

The direct transfer of the hydrogens from **2** to ethene as illustrated in the following manner was not investigated because of the lack of appropriate symmetry relationships between the interacting HOMOs and LUMOs of the reactants.



Conversion of **12** (or a Conformer) to Nitrogen and Ethane. Several 1,1-dialkyldiazenes have been generated as transient intermediates and certain of the features of their decomposition

have been studied. Decomposition of optically active 1,1-bis(α -methylbenzyl)diazine produces 2,3-diphenylbutane in which only $\sim 35\%$ of the optical activity has been retained,³¹ while decomposition of **16** gives the results shown.³² Decomposition of unsymmetrically substituted 1,1-dibenzyl diazenes



produces no crossover products.³³ In systems where elimination occurs as well as coupling, the effect of substituents suggests that a radical, and not ionic, pathway is operative, at least in part.³⁴ The results described can be rationalized as either arising from two competitive pathways, one being a radical pathway which results in complete racemization but with no escape from the solvent cage along with a concerted pathway which retains stereochemistry, or a single radical pathway in which partial stereochemistry is retained. Should such an intermediate as **12** be formed in the reaction of **2** with ethene stereospecific collapse would be required suggesting that a concerted pathway would be operative. We have explored possible modes of concerted and radical decompositions of 1-ethyl-1,1-diazene (**12**), and, although specific details of the processes have not been successfully delineated, some general conclusions can be reached.

It is, first of all, instructive to consider the bonding interactions in **12** or its conformers. Regardless of the conformation, the Mulliken population analysis indicates that the long-range interaction between the hydrogen on nitrogen and the methylene carbon is of an antibonding nature, this interaction being least in the perpendicular staggered conformation **13**.

Several homolytic and concerted pathways were considered and energy profiles calculated. Geometry optimization calculations indicated that the lowest energy pathway for breaking the C–N bond in the syn, anti, or perpendicular conformations of the reduction intermediate was directly along the axis of the C–N bond. Interestingly, as the C–N distance was increased, the C₂–H–N distance increased proportionately more rapidly owing to increasing antibonding interactions between the hydrogen 1s AO and the AOs on carbon. At C–N distances of $\sim 1.86 \text{ \AA}$ the energies were already higher than that of the ethyl radical³⁵ plus bent $\cdot\text{N}_2\text{H}$. (During the stretching of the C–N bond, the C₂H₅ fragment approached the geometry of the ethyl radical³⁵ consistent with partial homolytic dissociation and not an ionic, or heterolytic, cleavage.) Intuitively, one would have anticipated that homolytic cleavage of the C–N to form the ethyl radical and $\cdot\text{N}_2\text{H}$ would be associated with an energy barrier only slightly greater than the difference in energies of starting and final states [28.7 (STO-3G) and 21.2 (4-31G) kcal/mol, both of which probably underestimate the true value]. However, UHF STO-3G calculations, both working out from the adduct and working in from the fragments, suggest that an appreciable energy barrier exists for the combination process, it being calculated to be as high as 50 kcal/mol (STO-3G). Use of a more realistic basis set and inclusion of correlation effects would be expected to substantially lower this barrier, and indeed might even make it disappear.

An alternative dissociation process involves homolytic cleavage of the N–H bond. The relative energetics of N–C vs. N–H bond cleavage was evaluated with methylaminonitrene (**17**), the results of which are shown in Figure 5. Of the two

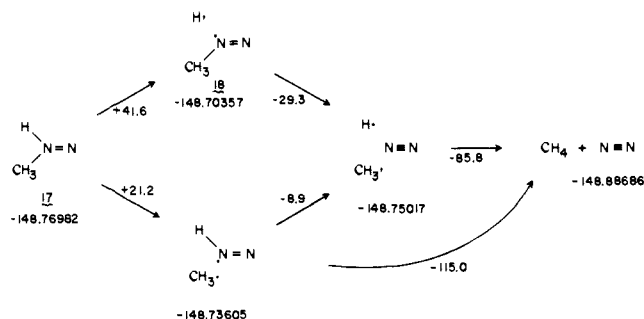
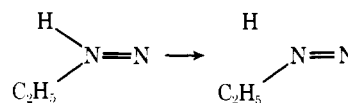


Figure 5. Relative energetics of homolytic dissociation processes in the conversion of **17** to methane and nitrogen (4-31G energies). The energies of the methyl radical and methane are taken from ref 35. The bond lengths used in the calculation of **17** are the same as those derived from the geometry optimization calculations on **12**. The geometry in radical **18** was assumed to have the bond lengths and angles of **6** and **12** and was calculated using the MOLE program. The energies by the arrows are in kcal/mol.



processes the homolytic dissociation process involving initial cleavage of the C–N bond is favored if one assumes that the energy barriers will be proportional to the energy differences. In this process the slow step is the dissociation of the C–N bond, the subsequent dissociation of **6** and combination of the methyl radical and hydrogen atom being indicated to be rapid processes. A more probable route, however, would be a rapid abstraction of the hydrogen of **6** by the methyl radical to directly form the products. Should this process be extremely rapid, relative to reorganization within the solvent cage, retention of stereochemistry might well prevail. Thus, the overall reduction of the C=C via an alkylaminonitrene could result in the syn addition of the hydrogens of **2** to the C=C.

In view of the foregoing, calculations on the energetics of the homolytic breakdown of a dialkylaminonitrene were carried out with **19** at the STO-3G level, the results of which are given in Figure 6. While corrections due to electron correlation and to zero-point averaging are undoubtedly important here, our calculations are probably sufficiently accurate to draw the qualitative conclusions that cleavage of the first C–N bond is rate limiting, with the cleavage of the second C–N bond and combination of the methyl radicals being very rapid processes. These predictions are in accord with the stereochemical details of such decomposition processes. (No concerted decomposition of **19** was investigated.)

Several concerted modes of decomposition of **12**, or any of its conformers, to ethane and nitrogen were briefly investigated. Attempts at twisting or rolling the H–N=N fragment of **12** while stretching the C–N bond in order to force formation of the C–H bond resulted in unreasonably high energies. This again is due to the antibonding interactions that exist between the H 1s AO and the AOs on C. Attempts at inserting the nitrogen molecule into a C–H bond of ethane similarly resulted in unreasonably high energies.

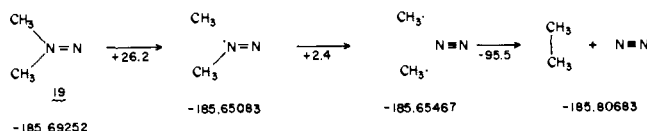
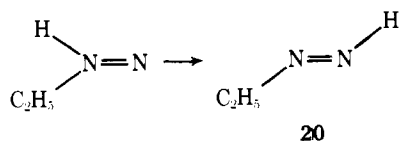


Figure 6. Energetics (STO-3G) of homolytic decomposition of dimethylaminonitrene (**19**). The bond lengths and angles in **19** were taken to be the same as in **17** (see caption to Figure 5).

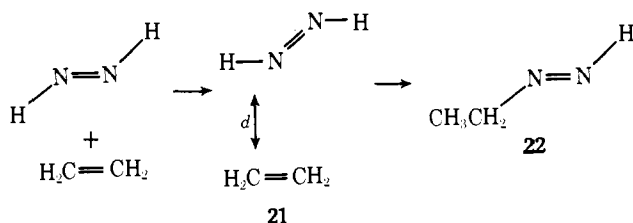
The possibility of a concerted rearrangement of the reduction intermediate to an alkyldiimide (**20**), which could de-



compose to ethane and nitrogen, is also not a reasonable process. The energy barrier for such a process must be similar in magnitude to that for the concerted rearrangement of **3** to **2** [93.3 (STO-3G) and 81.5 (4-31G) kcal/mol].

In view of prior calculations on aminonitrene and substituted aminonitrenes³⁶ which have suggested that the triplet state is lower in energy than the singlet state, and owing to our difficulty in connecting the reduction intermediate to either ethyl radical plus $\cdot\text{N}_2\text{H}$ or ethane plus nitrogen, the energy of the triplet state of the reduction intermediate was calculated. Using the STO-3G optimized singlet geometry, the triplet is calculated to be ~ 15 kcal/mol more stable than the singlet, raising the possibility that the triplet state is involved in the mechanism. Although diacylamino nitrenes add stereospecifically to alkenes, suggesting a singlet ground state,³⁷ extrapolation to the present systems is dangerous owing to the significant differences in the nature of the groups attached to the aminonitrene. The recent³⁷ generation and characterization of a dialkylaminonitrene should allow for an experimental resolution to this problem.

1,2-Addition of 2 to Ethene. A second possible mode of reaction of **2** with ethene is via a 1,2-addition of the N—H across the C=C. Although in a formal sense this represents a forbidden [$\sigma_2s + \pi_2s$] process, it is conceivable that such an addition occurs but not in the manner implied. Inspection of the HOMO of **2** (Figure 1) shows that it has the appropriate symmetry for transfer of the H to one carbon with concomitant attack by the nonbonded pair of electrons of the nitrogen on the other carbon of the C=C to form an alkyldiimide (**22**). Calculations were carried out on structure **21** in which the



N—H was symmetrically placed with its bond axis parallel to that of the C=C. The STO-3G energies of the nonoptimized structures with separation distances d of 2.0 and 1.8 Å were respectively 48 and 86 kcal/mol above the combined energies of the reactants. Since in our experience optimization of the other geometrical parameters might be expected to reduce the energy by only 20–30% and since we were undoubtedly far from the transition state, it was concluded that this mode of reaction is not energetically feasible and no further calculations along this line were attempted.

Reaction of Aminonitrene (3) with Ethene. Although the HOMO of **3** is comprised mostly of a contribution of the in-plane p AO on the terminal nitrogen of **3**, an appreciable contribution from the antisymmetric combination of the N—H σ bonds is apparent (Figure 1). This similarity in the nature of the HOMOs of **1**, **2**, and **3** suggested that **3** might be capable of transferring its hydrogens to ethene in an energetically feasible process. Accordingly, calculations were undertaken on this reaction pathway.

As in the case of the reactions of **1** and **2** with ethene, calculations indicate the existence of a stable complex (**23** in

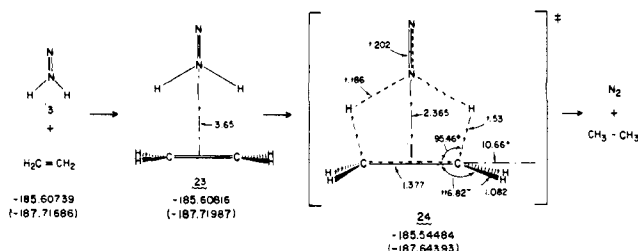


Figure 7. Structures and energies of the reactants, complex, and transition state in the reaction of aminonitrene (**3**) with ethene.

Table III. Energy Barriers (in kcal/mol) for the Direct Reactions of **1**, **2**, and **3** with Ethene

diimide	ΔE (STO-3G)	ΔE (4-31G)	C---H-N, Å
1	36.5	26.7	1.64
2	39.7	45.3	1.33
3	39.2	45.8	1.53

Figure 7). Energies of fully geometry optimized structures at various C---H-N distances along the reaction coordinate were calculated maintaining full C_{2v} symmetry. The transition state was taken as the maximum in the energy vs. C---H-N plot. All other geometrical parameters were then fully optimized giving the transition-state structure **24** and energy shown in Figure 7. The energy of the complex lies 0.5 (STO-3G) and 1.9 (4-31G) kcal/mol below that of the reactants, while the transition state lies 39.2 (STO-3G) and 45.8 (4-31G) kcal/mol above the reactants.

Summary

Several noteworthy conclusions can be drawn from this study.

1. In the two-step reaction of **2** with ethene involving (a) initial trans to cis isomerization of diimide, followed by (b) hydrogen transfer from *cis*-diimide to ethene, the rate-limiting step is (a) (4-31G energy barrier ~ 45 kcal/mol) rather than step (b) (4-31G energy barrier ~ 27 kcal/mol). This contrasts with an earlier, less complete, theoretical study¹⁹ which implies that step (b) is rate limiting.

2. An alternative direct pathway for the reduction, corresponding to stepwise transfer of the two hydrogens from *trans*-diimide to ethene, appears to be just as favorable (4-31G energy barrier ~ 45 kcal/mol; see Table III). Transfer of hydrogen from 1,1-diimide to ethene also has a barrier of ~ 46 kcal/mol, but isomerization of *trans*- to 1,1-diimide is unfavorable (4-31G energy barrier ~ 82 kcal/mol). Reactions with substituted ethenes should have lower energy barriers owing to the raising of the HOMO and/or lowering of the LUMO of the C=C.

3. Although **1**, **2**, and **3** form stable complexes with ethene, their low binding energies would suggest that they are not kinetically active species as previously suggested¹⁸ (eq 4-7).

4. The results of calculations on the possible modes of decomposition of alkylamino- and dialkylaminonitrenes suggest that a stepwise, homolytic dissociation pathway is probably favored in which cleavage of the first C-N bond is the slow step, which is consistent with the stereochemical evidence.

Finally, we should note that, while several important new insights have been gained as a result of this study, the calculated energy barriers are still somewhat too high to satisfactorily explain the kinetics of ethene reduction by diimide. It is possible that more refined calculations would lower the barriers somewhat. Also, it should be recognized that in reality the reaction of diimide with an alkene is more complex in that disproportionation of diimide to produce hydrazine and nitrogen also occurs. The disproportionation reactions between

the various diimide species are currently under study in our laboratories and will be reported on at a later time.

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- (22) Geometry-optimized STO-3G calculations on **1**, **2**, and **4** have been reported previously (see ref 13).
- (23) Although the 4-31G calculations on the STO-3G optimized structures of **1** and **2** readily converged from the EH initial guess, such was not the case with **3** and **5**. Convergence was achieved by initiating the 4-31G calculations from a density matrix composed of the STO-3G density matrix for the inner orbital components and an all zero density matrix for the outer orbital components. This procedure was also required for other aminonitrene species.
- (24) Although at this point only the singlet electronic state of **3** is considered, it should be pointed out that it is not clear whether the singlet or triplet state of **3** is lowest in energy. Double ζ plus polarization basis set calculations with extensive CI suggest that the triplet is slightly lower in energy (ref 15) while GVB-CI calculations suggest that the singlet lies ~ 15 kcal below the triplet (ref 25).
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