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A PM3 STUDY OF THE REACTIONS OF PROPENE WITH SINGLET OXYGEN AND OTHER ENOPHILES

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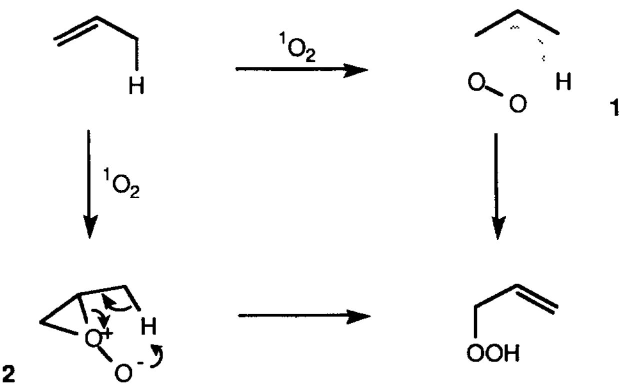
Abstract Two alternative reaction pathways, one involving a 6-membered ring transition state, the other, a strained 3-membered intermediate, have been located on the PM3 semi-empirical potential energy surfaces for the reactions of singlet oxygen, nitrosyl hydride, nitrosoformaldehyde, diazene, 1,2,4-triazoline-3,5-dione and methyleneamine with propene Except for nitrosyl hydride, the calculations suggest that both pathways have similar energy requirements in each case

Introduction

In recent years much attention has focused on the mechanistic details of the "ene reaction" of singlet ($^1\Delta_g$) oxygen with alkenes bearing allylic hydrogens[1] Some workers have postulated that the reaction is concerted[2], with a transition state (**1**) similar to that involved in the hydrocarbon ene reaction[3] of ethylene with an appropriate olefin Other workers have suggested that experimental evidence supports the formation of a "perepoxide" intermediate (**2**) which subsequently rearranges by abstraction of an allylic proton to give the product hydroperoxide[4] (Scheme 1)

Scheme 1



Apart from Loncharich's incomplete *ab initio* study[5] of the reaction of singlet oxygen (**3a**) with propene, no reports of any theoretical studies involving a concerted mechanism have appeared Other calculations have investigated the "perepoxide" pathway[6] and the feasibility of a biradical mechanism[7], although high-level calculations have largely discounted the latter, putting it some 5 kcal mol^{-1} above that for the perepoxide[8]

The formal similarity of the ene reactions with enophiles such as singlet oxygen, alkenes, alkynes, triazolinediones, nitroso compounds and formaldehyde has frequently been discussed[9] Apart from Houk's recent report[10] of an *ab initio* study of the reactions of ethylene (**3b**) and formaldehyde (**3c**) with propene, very little work concerning the theoretical aspects of the concerted ene reaction has appeared in the literature

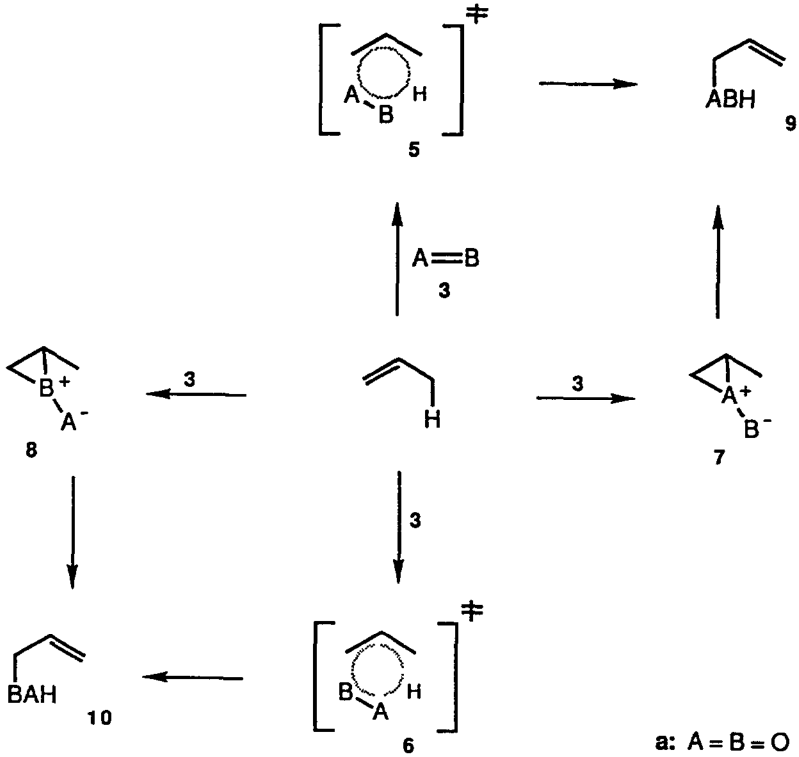
As part of our continued interest in the chemistry of hydroperoxides, it was felt that a theoretical treatment of the reaction of propene with singlet oxygen[11], as well as other π-isoelectronic systems, would provide valuable insight into the similarities and differences that might be expected in these reactions

To that end, the PM3[12] semi-empirical potential energy surfaces for the reactions of singlet oxygen (**3a**), nitrosyl hydride (**3d**), nitrosoformaldehyde (**3d**), 1,2,4-triazoline-3,5-dione (**4a**), (an analogue of **4b**), diazene (**3f**), methyleneamine (**3g**), N-methylmethyleneamine (**3h**) as well as formaldehyde (**3c**) and ethylene (**3b**) with propene were investigated with the specific intention of locating the concerted transition state for the ene reaction in each case, as well as any likely "perepoxide-type" intermediates New insight into the steric and electronic demands of both reaction mechanisms is provided

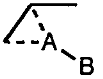
Methods

All molecular orbital calculations were performed at the Restricted Hartree-Fock (RHF) level using the PM3[12] Hamiltonian in MOPAC version 5 0[13] Structures were optimized to minima using the BFGS[14] method or to transition states as described by Dewar and co-workers[15] on either a VAX 6310, SUN 4/260 or Solbourne 5/602 computer All structures were proven as corresponding to the appropriate stationary point by evaluation of the complete set of harmonic force constants in each case Molecular mechanics[16] calculations were performed using the MM2 program[17] on a Solbourne 5/602 computer

Scheme 2



a: A = B = O
b: A = B = CH_2
c: A = CH_2, B = O
d: A = NH; B = O
e: A = NCHO, B = O
f: A = B = NH
g: A = NH, B = CH_2
h: A = NCH_3, B = CH_2



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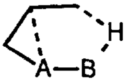

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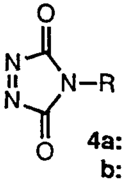
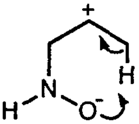


4a: R = H
b: R = CH_3



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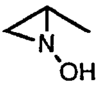

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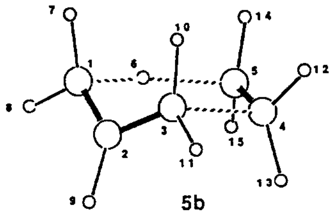
Results and Discussion

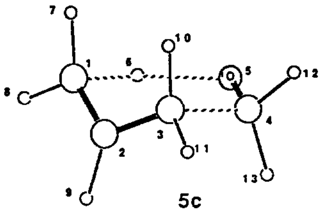
With the recent suggestions[12,18] that PM3 outperforms both AM1 and MNDO, we felt that, although relatively untested, this was the semi-empirical method of choice in this study In fact, preliminary work[11] using MNDO and AM1 proved unsatisfactory, with AM1 predicting an exclusively concerted mechanism for the reaction between singlet oxygen and propene, and MNDO, a mechanism involving a number of (asynchronous) steps The AM1 and MNDO results were not unexpected, as MNDO is known to favour asynchronous pathways[19], while AM1 tends to prefer synchronicity[20]

In order to test the reliability of the PM3 method when applied to the ene reaction, transition structures were evaluated for the reaction of the ethylene (**3b**), formaldehyde (**3c**) and singlet oxygen (**3a**) with propene These results are compared with the *ab initio* data of Loncharich and Houk[5,10]

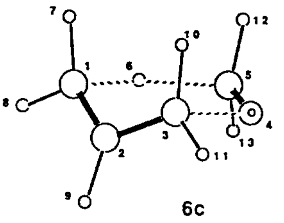
Clearly, only one orientation of ethylene and propene is possible, leading to transition structure **5b** and ultimately 1-pentene (**9b**) (Scheme 2) Formaldehyde (**3c**), on the other hand, can orientate itself in two ways, giving rise to two transition structures (**5c, 6c**) which ultimately yield but-3-en-1-ol (**9c**) and allyl methyl ether (**10c**) respectively



5b



5c



6c

Inspection of structures **5b** and **5c** reveals a close similarity to those reported in the *ab initio* study[10] Relative energies for these structures are given in Table 1, while the geometries are detailed in Table 2

The PM3-calculated transition state distances, r(3,4) = 1 968Å, r(1,6) = 1 285Å and r(5,6) = 1 512Å for **5b** compare favourably to the values of 2 110Å, 1 218Å and 1 524Å respectively, calculated at the 3-21G level of *ab initio* theory[10] The predicted activation energy of 33 8 kcal mol^{-1} is in good agreement with the value of 31 2 kcal mol^{-1} calculated at the correlated MP2/6-31G*//3-21G level of theory[10] and supports previous suggestions that PM3 data reflect those of correlated (MP2/3-21G) methods[18a]

Table 1 Summarizing the PM3-calculated Energy[a] Profiles for the Various Reaction Pathways in this Study

Substrate	**Intermediate or Transition State**				
	5	**6**	**7**	**11**	**12**
3a	28 3	-	29 4	29 7	29 9
3b	33 8	-	-	-	-
3c	43 3	50 3	-	-	-
3d	35 7	49 3	5 0	27 7	29 6
3e	35 1	45 0	14 4	34 5	33 6
3f	40 8	-	28 4	41 2	40 8
3g	34 4	38 3	33 5	-	-
3h	45 5	45 1	-	-	-
4a	31 4 (**4c**)	-	10 1 (**4d**)	32 4(**4e**)	29 9 (**4f**)

[a] Energies in kcal mol^{-1} (relative to **3** + propene)

The geometry of the transition structure (**5c**) in the reaction of formaldehyde (**3c**) with propene compares favourably with the 3-21G data[10] While the transition state distance for r(3,4) of 1 732Å, is somewhat shorter than the 3-21G value of 2 016Å, the overall shape of the structure remains the same The r(1,6) and r(5,6) distances of 1 293Å and 1 542Å respectively are similar to the 3-21G values of 1 311Å and 1 406Å The PM3 data suggest that the transition state (**5c**) is slightly later than that predicted at the 3-21G level of theory, with the qualitative features of the reaction being similar The activation energy of 43 3 kcal mol^{-1} as calculated in this study is significantly higher than the MP2/6-31G*//3-21G value[10] of 27 5 kcal mol^{-1}, however, it compares favourably with the 3-21G value[9] of 38 2 kcal mol^{-1} and the STO-3G value[10] of 43 4 kcal mol^{-1}

The transition structure (**6c**) leading to allyl methyl ether is also consistent with expectation The activation energy of 50 3 kcal mol^{-1} as calculated by PM3 is some 7 kcal mol^{-1} less favourable than that for the alternative orientation (**5c**) of formaldehyde and reflects the poorer orbital overlap in **6c** as compared to that in **5c** This is as expected on the basis of Frontier Orbital Theory (see later)

Singlet oxygen with propene

A comprehensive study of the PM3 potential energy surface for the reaction of singlet oxygen with propene has revealed two feasible pathways leading to the same hydroperoxide product The pathway of lower energy is that which proceeds via the "concerted" ene transition state (**5a**) Inspection of structure **5a** reveals distinct similarities to structures **5b, 5c** and **6c** previously determined for the reactions of ethylene and formaldehyde with propene The transition states all resemble "flattened" cyclohexane chair conformations

Of some 1 4 kcal mol^{-1} higher in energy is the transition state (**11a**) leading to the perepoxide intermediate (**7a**) This intermediate (**7a**) is predicted to lie in a shallow well, being only 0 3 kcal mol^{-1} lower than **11a** and only 0 5 kcal mol^{-1} below the transition state (**12a**) for rearrangement to the hydroperoxide (**9a**) Structural details are given in Table 3, while the energy profiles are summarized in Table 1

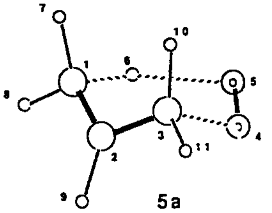
Inspection of Table 3 clearly reveals that **5a** is an "early" transition state, with relatively long forming bonds [r(3,4) = 1 635Å, r(5,6) = 1 695Å] and short breaking bonds [r(1,6) = 1 189Å] and is in agreement with the suggestions by Nickon[2] of an "early" transition state to accommodate their experimental findings

Comparing these data with those of Loncharich[5], in which r(3,4) = 1 898Å, r(5,6) = 1 819Å and r(1,6) = 1 117Å, it is apparent that PM3, once again, predicts the concerted transition state (**5a**) to be later than that predicted at the 3-21G level of theory The PM3-calculated energy barrier of 28 3 kcal mol^{-1} compares very favourably with the 3-21G value[5] of 29 3 kcal mol^{-1}, however it is about 12 kcal mol^{-1} higher in energy than the single point MP2/6-31G*//3-21G value[5] of 16 1 kcal mol^{-1} This result suggests that electron correlation may play an important role in the correct description of these structures The inclusion of correlation in the PM3 method proved unsuccessful Thus, neither **5a, 7a** nor **11a** could be located as corresponding to the appropriate stationary points using PM3-CI (3x3) The validity of PM3-CI is unclear since, like other semi-empirical methods, the parameterization should, to some degree, take electron correlation into account[21] Our data tend to suggest that while PM3 appears to behave like a correlated *ab initio* method in the case of ethylene and propene, when oxygen is incorporated, the PM3 data appear more like those available from single-determinant *ab initio* techniques

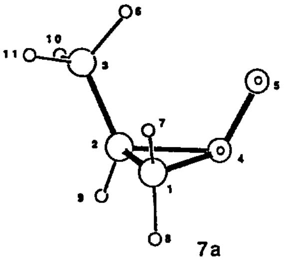
Loncharich was unable to locate the transition state (**11a**) for formation of the perepoxide (**7a**) on the 3-21G potential energy surface, however, he was able to locate the structure of alternative trans geometry[22] His 3-21G data suggest that **11a** might be expected to lie about 35 kcal mol^{-1} above the energy of the reactants This is to be compared with the value of 29 4 kcal mol^{-1} in this study Again, 3-21G suggests that **11a** is an earlier transition state than that calculated by PM3, with r(1,4) = 1 980Å and r(2,4) = 1 992Å

It is interesting to note that while PM3 predicts **7a** to lie in a shallow well, the 3-21G data imply that the well is significant with **7a** being some 40 kcal mol^{-1} below the transition state (**11a**) and about 18 kcal mol^{-1} below the rearrangement transition state (**12a**) Thus, the 3-21G data suggest that it should be possible to isolate **7a**, while PM3 indicates that this would be unlikely To the best of our knowledge, no perepoxide intermediates have been isolated from any singlet oxygen "ene" reaction

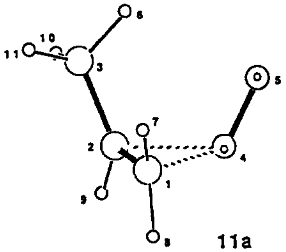
It is useful to compare our data with those of Tonachini and co-workers[23] who report a MC-SCF study of the reaction of singlet oxygen with ethylene The PM3-calculated bond lengths of 1 559Å for r(1,4) and 1 664Å for r(2,4) in **7a** are in good agreement with the value of 1 559Å for the C-O distance in the perepoxide derived from ethylene as calculated at the MC-SCF/4-31G level of theory It is curious to note that Tonachini et al. were unable to locate a transition structure for the direct formation of that perepoxide while CASSCF *ab initio* calculations performed by Hotokka et al. provided this structure[8,24] Indeed the CASSCF value of 1 76Å for the C-O distance in that transition structure is in good agreement with the values of 1 642Å and 1 809Å for r(1,4) and r(2,4) respectively as calculated in this study



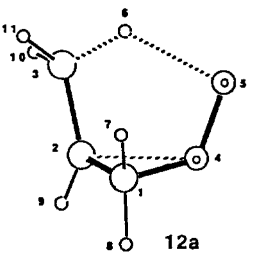
5a



7a



11a



12a

The prediction by PM3 that the perepoxide (**7a**) is loosely-bond is in agreement with the conclusions of a number of workers[4] and is clearly evident from the low barriers to rearrangement and relatively long bonds The final transition state (**12a**) is once again "early" and easily achieved due to the cis orientation[22] of groups in **7a**

The calculated activation energies of 28 3 kcal mol^{-1} for the concerted reaction and 29 7 kcal mol^{-1} for the perepoxide pathway are lower than the prediction of 33 8 kcal mol^{-1} for the ene reaction involving ethylene and suggests that singlet oxygen reactions should be more easily realized than those involving ethylene The reaction is also predicted to be exothermic, with the product hydroperoxide being some 40 7 kcal mol^{-1} lower in energy than the starting materials

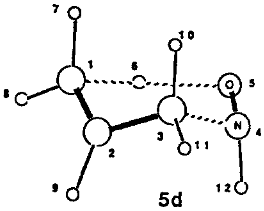
No experimental data exist for the parent reaction of singlet oxygen with propene Z-2-Butene is reported[25] to react with singlet oxygen yielding ene-products with an experimentally determined barrier of 10±1 kcal mol^{-1} Work in our laboratories has shown[26] that more substituted olefins react more readily with singlet oxygen than those with fewer substituents Thus, one might expect the energy barrier for the reaction of propene with singlet oxygen to be somewhat higher than the value of ~10 kcal mol^{-1} quoted for butene

Substantial evidence has been accumulated to support the involvement of an intermediate in these ene reactions[27]. For example, the isotope effects observed by Stephenson and co-workers[27a] for the reaction of singlet oxygen with tetramethylethylene seems unambiguously to require an intermediate in the reaction

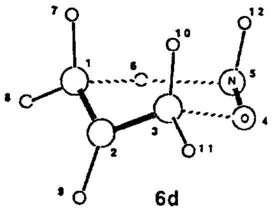
Qualitatively, this study predicts that both reaction pathways, that via the concerted transition state (**5a**) and that via the perepoxide (**7a**), are viable alternatives While that proceeding via **5a** is favoured slightly, one cannot ignore either mechanism Solvent may play an important role, with polar solvents favouring the perepoxide pathway, as has been suggested by Jefford and co-workers[28], who propose a solvent-dependent change of mechanism to explain their results

Nitrosyl Hydride and Nitrosoformaldehyde with Propene

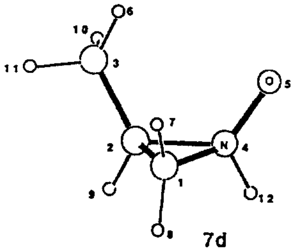
As was the case for the reaction of singlet oxygen with propene, the PM3 potential energy surface for the reaction of nitrosyl hydride (**3d**) with propene also reveals concerted and stepwise pathways to give "ene" products In a similar fashion to formaldehyde, **3d** is also able to align itself in two different ways, leading to two different possible products Two transition states (**5d, 6d**) as well as two different strained intermediates (**7d, 8d**) can be envisaged Extensive work, however, failed to located **8d** at a stationary point on the PM3 energy surface Transition states (**5d, 6d**), the aziridine N-oxide (**7d**) and the transition states **11d** and **12d**, for the formation and subsequent rearrangement of **7d** to the hydroxylamine (**9d**), were located and are summarized in Table 4 while the relevant energies are summarized in Table 1



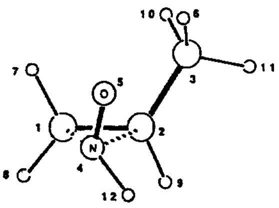
5d



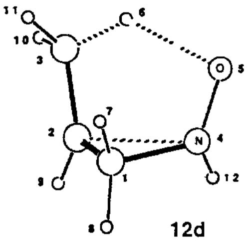
6d



7d



11d



12d

It is interesting to note, however, unlike singlet oxygen (**3a**), nitrosyl hydride (**3d**), is predicted to react via the aziridine N-oxide (**7d**), the cyclic transition state of lower energy (**5d**) being some 8 kcal mol^{-1} higher in energy than the transition state (**11d**) for the formation of **7d** The barrier for formation of **7d** is calculated to be 27 7 kcal mol^{-1}, a value similar to that for the reaction of singlet oxygen with propene, whereas the concerted transition states (**5d, 6d**) are calculated to be 35 7 kcal mol^{-1} and 49 3 kcal mol^{-1} respectively above the energy of the reactants This is not unexpected and reflects the stability of amine N-oxides as compared to perepoxides

Inspection of Table 4 reveals some interesting features of the geometries of the various structures involved in this reaction Firstly, the separation of C(3) and C(4) in the transition state (**5d**) is calculated to be extremely short at 1 552Å, while the distances associated with hydrogen transfer (1 512Å and 1 365Å) are similar to other values in this study

It was initially felt that **5d** did not correspond to the concerted transition state, but rather to that for proton transfer in the zwitterion (**13**) Extensive searching, however, failed to located **13** as corresponding to a minimum on the PM3 energy surface This together with the normal-coordinates produced in the force constant calculation provided strong evidence that **5d** did indeed belong to the expected transition state The calculations therefore suggest that while the reaction via **5d** is concerted, it is highly asynchronous with the carbon-nitrogen bond almost fully formed during hydrogen transfer

Secondly, the transition state (**11d**) for the formation of **7d** appears at first glance to contain some unusual features The close C(1)-N(4) separation of 1 662Å, while maintaining a longer C(2)-N(4) distance of 2 139Å indicates that this reaction also proceeds via a highly asynchronous transition state Closer inspection of the data reveals that this "unusual" geometry is a result of rigid orbital requirements in the transition state (**11d**) For this reaction to proceed, both non-bonding (lone-pair) and π orbitals on nitrogen must interact with the olefin These orbitals are orthogonal and therefore naturally lead to structure **11d**

Once formed, the aziridine N-oxide (**7d**) can either rearrange to the product (**9d**) or to the cyclic hydroxylamine (**14**) The former process is calculated to have an energy barrier of 24 6 kcal mol^{-1}, while the latter, a barrier of 55 1 kcal mol^{-1} The high activation energy associated with the transformation of **7d** to **14** is in accordance with expectation, as 1,2-shifts of this type are disallowed thermally[29]

The calculations also suggest that this overall transformation (propene + **3d** → **9d**) is exothermic, with the product (**9d**) lying some 15 8 kcal mol^{-1} lower in energy than the reactants The PM3 prediction, therefore, is that "ene" products arising from the reaction of nitrosyl hydride (**3d**) with propene have come **via** the "perepoxide"-type mechanism Indeed, Baldwin and co-workers[30] have shown that aziridine-N-oxides prepared by the ozonation of aziridines readily rearrange to the corresponding hydroxylamines. This result indicates that N-oxides like **7d** do rearrange as predicted by PM3.

The regiochemistry of the concerted reaction is also in keeping with expectation. In the frontier-orbital description of the ene-reaction[31], the LUMO of the π-bond of the enophile (in our case, **3d**) interacts with the HOMO of the π-bond of the olefin (propene) and the LUMO of the allylic C-H bond. When the enophile is nitrosyl hydride (**3d**), the smaller coefficient of the LUMO resides on oxygen, as depicted in Figure 1. The best orbital overlap is achieved with the alignment of reactants as indicated. Similar orbital considerations adequately describe the PM3-predicted regiochemistry of the ene reaction of formaldehyde (**3c**) with propene.

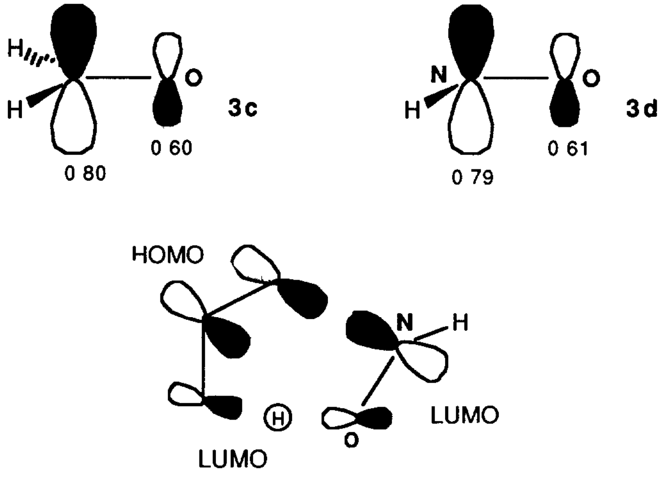


Figure 1 Depicting the lowest unoccupied molecular orbitals of formaldehyde (**3c**) and nitrosyl hydride (**3d**) as calculated by PM3 as well as the frontier orbital description of the ene reaction.

When nitrosoformaldehyde (**3e**) is reacted with propene instead of **3d**, PM3 calculations suggest that both concerted and stepwise processes are energetically similar (Table 1). The predicted energy barrier for the rate determining step in each pathway is 35.1 kcal mol^{-1} via **5e**, 45.0 kcal mol^{-1} via **6e** and 34.5 kcal mol^{-1} for the formation of the aziridine N-oxide (**7e**). It is clear, that when compared with the reaction of nitrosyl hydride (**3d**) with propene, in which **7d** is calculated to be only 5 kcal mol^{-1} higher in energy than the reactants, the similarity in energies for the two pathways in the reaction of **3e** with propene is mainly due to destabilization of the aziridine N-oxide (**7e**), which is predicted to be 14.4 kcal mol^{-1} less stable than the reactants. This is consistent with the fact that **7e** contains an electron-withdrawing group on a positively charged nitrogen.

The PM3 calculations therefore suggest that the reaction between nitrosoformaldehyde (**3e**) and propene resembles that of a "sluggish" singlet oxygen reaction, with factors such as solvent perhaps playing an important role

Diazene and 1,2,4-Triazoline-3,5-dione with Propene

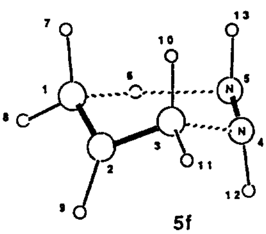
The principle features of the potential energy surface, as calculated by PM3, for the reaction of diazene (**3f**) with propene are similar to those for the reaction of singlet oxygen (**3a**) with propene Once again, PM3 predicts both concerted and stepwise pathways leading to the product diamine (**9f**)

Unlike the reaction involving **3d**, the activation energy associated with the concerted transition state (**5f**), at 40 8 kcal mol^{-1}, is slightly lower than the energy barrier to the formation of the "perepoxide"-type intermediate (**7f**), at 41 2 kcal mol^{-1} The intermediate, **7f**, is predicted to lie some 28 4 kcal mol^{-1} above the energy of the reactants, with barriers to "reverse" reaction and rearrangement to **9f** of 12 8 kcal mol^{-1} and 12 4 kcal mol^{-1} respectively Clearly, **7f** is relatively less stable than the similar intermediate (**7d**) in the reaction of nitrosyl hydride (**3d**) with propene This again probably reflects the stability of amine oxides

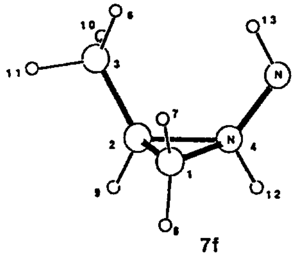
Both pathways in the reaction of diazene are predicted to be substantially less favourable than the similar reactions involving singlet oxygen (**3a**) or nitrosyl hydride (**3d**) The geometric features of the concerted transition state (**5f**), the intermediate (**7f**) as well as the transition states (**11f, 12f**) for the formation and subsequent rearrangement of **7f** are listed in Table 5, while the relative energies are to be found in Table 1

Inspection of Table 5 clearly indicates the similarities between the structures involved in the reaction of diazene with propene and those associated with the reaction of nitrosyl hydride Once again, the concerted transition state (**5f**) is predicted to by ansynchronous, as is the transition state (**11f**) for the formation of **7f** Clearly, similar orbital constraints are at work in the transition state (**11f**) as were observed for **11d**

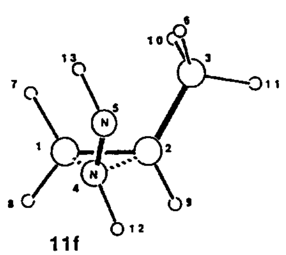
With the high barriers associated with the reaction of diazene with propene, it was surprising to find a substantial lowering of the energy barriers in the reaction of 1,2,4-triazoline-3,5-dione (**4a**), with propene PM3 calculations suggest that the transition state (**4c**) for the concerted reaction of **4a** with propene is some 31 4 kcal mol^{-1} higher in energy than the starting materials The pathway leading to the "perepoxide"-type intermediate (**4d**) is slightly less favoured than the concerted pathway The transition state (**4e**) for the formation of **4d** is calculated to be 32 4 kcal mol^{-1} above the energy of the of the reactants In turn, **4d** is 10 1 kcal mol^{-1} higher in energy than the reactants, with a barrier to rearrangement (via **4f**) (to the product) of 19 8 kcal mol^{-1}



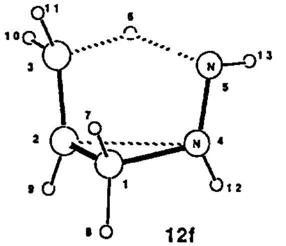
5f



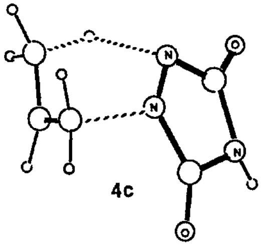
7f



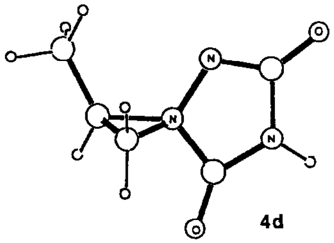
11f



12f



4c



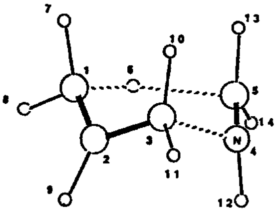
4d

It is clear, therefore, that PM3 calculations suggest that the mechanistic details of the reaction of singlet oxygen with propene should be very similar to that for the reaction of **4a** (or indeed **4b**) with propene It is not surprising therefore that ene-products are observed[9b] in reactions involving **4b**

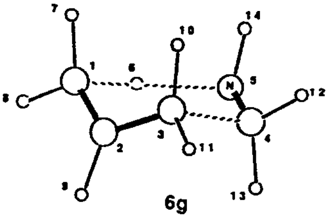
Methyleneamine and N-Methylmethyleneamine with Propene

A PM3 study of the reaction of methyleneamine (**3g**) with propene was able to locate two concerted transition structures (**5g, 6g**) leading to the expected ene products While it was possible to locate the "perepoxide"-type intermediate (**7g**) as a minimum on the potential energy surface, PM3 failed to converge to a transition state (**11g**) for the formation of **7g** Extensive computer time was spent attempting to minimize the gradients associated with the transition structure, without success

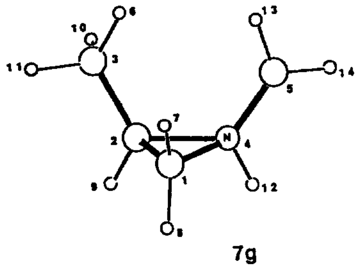
The PM3 data have indicated that the transition state (**5g**), at 34 4 kcal mol^{-1} above the energy of the reactants is favoured over the alternative orientation (**6g**) by 3 9 kcal mol^{-1} The strained intermediate (**7g**) was found to lie some 33 6 kcal mol^{-1} above the energy of the starting materials Even without a transition state energy, it would appear that **7g** is predicted, at best, to lie in a shallow well with both concerted and stepwise processes being of similar energy, and at worst, to be on a pathway significantly less favoured than that via **5g** Details of structures **5g, 6g** and **7g** are displayed in Table 6, while the energy profiles are summarized in Table 1



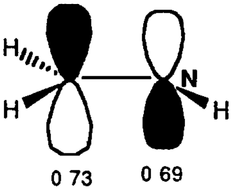
5g



6g



7g



3g

It is interesting to note that the calculations suggest that this ene reaction proceeds via a transition state of **reverse** regiochemistry to the other asymmetrical systems in this study It is the carbon that the hydrogen is predicted to be transferred to, not the nitrogen as might be expected by analogy with formaldehyde Inspection of the PM3-generated LUMO for the imine (**3g**) indicates a possible reason for this The calculations suggest that the coefficients on carbon and nitrogen in **3g** are very similar, at 0 73 and -0 69 respectively This, in turn suggests that orbital constraints in the concerted transition states (**5g, 6g**) might, in turn, be less significant than steric factors Indeed, when N-methylmethyleneamine (**3h**) was used instead of **3g**, the concerted transition states (**5g, 6g**) are calculated to be far more equal, with energies of 45 5 and 45 1 kcal mol^{-1} respectively above the reactants This suggests that the introduction of a methyl substituent on the nitrogen in **6g** is less sterically demanding than the similar introduction in **5g**

To further highlight this point, MM2-strain energies were determined for the PM3-optimized transition structures (**5c, 6c**) in the ene reaction of formaldehyde and propene When the strain associated with bond formation and bond disruption is subtracted from the total strain energy (this is compensated for by orbital interactions), the MM2 calculations indicate that transition structure **5c** is more strained than **6c** by about 5 kcal mol^{-1}, yet PM3 suggests that **5c** is favoured over **6c** by some 7 kcal mol^{-1} Clearly, orbital considerations are the dominating factor in this reaction, leading to the regiochemistry via the more strained transition state (**5c**)

In cases where orbital constraints are not as important, as one might expect in the reaction of methyleneamine (**3g**) with propene, steric factors might be responsible for the observed regiochemistry By analogy with the reaction involving formaldehyde, **5g** would be expected to be

Table 2 Geometric Features[a], Heats of Formation[b] of Transition Structures **5b, 5c** and **6c** as calculated by PM3

Variable	Structure		
	5b	5c	6c
r(1,2)	1 412	1 394	1 404
r(1,6)	1 285	1 293	1 333
r(1,7)	1 093	1 094	1 093
r(1,8)	1 089	1 089	1 088
r(2,3)	1 388	1 422	1 402
r(2,9)	1 095	1 097	1 094
r(3,4)	1 968	1 732	1 742
r(3,10)	1 094	1 101	1 097
r(3,11)	1 091	1 098	1 094
r(4,5)	1 398	1 307	1 289
r(4,12)	1 093	1 101	-
r(4,13)	1 122	1 102	-
r(5,6)	1 512	1 542	1 480
r(5,12)	-	-	1 087
r(5,13)	-	-	1 089
r(5,14)	1 087	-	-
r(5,15)	1 087	-	-
θ(1,2,3)	118 7	119 7	117 6
θ(1,2,9)	119 6	120 0	120 2
θ(1,6,5)	147 5	143 6	138 6
θ(2,1,6)	99 3	94 5	101 0
θ(2,1,7)	118 8	119 8	119 1
θ(2,1,8)	117 9	119 2	118 6
θ(2,3,4)	101 8	103 8	103 3
θ(2,3,10)	118 9	115 2	119 2
θ(2,3,11)	119 8	115 8	118 5
θ(3,4,5)	110 6	113 6	116 0
θ(4,5,6)	107 6	108 5	110 5
θ(4,5,12)	-	-	116 6
θ(4,5,13)	-	-	115 4
θ(4,5,14)	119 8	-	-
θ(4,5,15)	120 2	-	-
θ(5,4,12)	118 3	111 8	-
θ(5,4,13)	116 4	112 9	-
ω(1,2,3,4)	-68 0	-70 6	-66 3
ω(1,2,3,10)	-37 8	-43 2	-41 2
ω(1,2,3,11)	179 5	172 4	176 8
ω(2,1,6,5)	-25 6	-33 5	-28 3
ω(2,3,4,5)	39 6	41 5	40 6
ω(2,3,4,12)	-162 3	-161 6	-
ω(2,3,4,13)	84 2	82 3	-
ω(3,2,1,6)	59 8	60 8	58 5
ω(3,2,1,7)	45 4	39 2	44 4
ω(3,2,1,8)	-175 8	-176 1	-173 4
ω(3,4,5,6)	-12 6	-16 5	-14 9
ω(3,4,5,12)	-	-	-95 4
ω(3,4,5,13)	-	-	119 6
ω(3,4,5,14)	-97 2	-	-
ω(3,4,5,15)	113 3	-	-
ΔH_f	56 9	15 6	22 6

a Distances (r) in Å, bond angles (θ) and dihedral angles (ω) in degrees b ΔH_f in kcal mol^{-1}

Table 3 Geometric Features[a] and Heats of Formation[b] of Structures **5a**, **7a**, **11a** and **12a** as calculated by PM3

Variable	Structure			
	5a	**7a**	**11a**	**12a**
r(1,2)	1 424	1 457	1 427	1 422
r(1,4)	-	1 558	1 642	1 561
r(1,6)	1 188	-	-	-
r(1,7)	1 097	1 098	1 096	1 100
r(1,8)	1 091	1 096	1 096	1 097
r(2,3)	1 414	1 482	1 477	1 456
r(2,4)	-	1 666	1 809	1 876
r(2,9)	1 096	1 104	1 101	1 097
r(3,4)	1 634	-	-	-
r(3,6)	-	1 103	1 104	1 146
r(3,10)	1 101	1 098	1 098	1 096
r(3,11)	1 097	1 097	1 096	1 093
r(4,5)	1 261	1 271	1 241	1 269
r(5,6)	1 694	-	-	1 831
θ(1,2,3)	118 3	121 6	121 4	118 3
θ(1,2,4)	-	59 4	59 6	54 2
θ(1,2,9)	120 2	119 7	120 2	121 2
θ(2,1,4)	-	67 0	71 8	77 2
θ(1,6,5)	133 8	-	-	-
θ(2,1,6)	100 9	-	-	-
θ(2,1,7)	116 5	120 9	121 2	120 5
θ(2,1,8)	116 6	121 3	121 1	120 0
θ(2,3,4)	96 3	-	-	-
θ(2,3,6)	-	111 7	111 3	104 8
θ(2,3,10)	118 5	110 6	111 3	113 8
θ(2,3,11)	118 2	111 6	111 8	113 9
θ(2,4,5)	-	118 4	117 5	108 9
θ(3,4,5)	115 3	-	-	-
θ(3,6,5)	-	-	-	125 6
θ(4,5,6)	105 1	-	-	96 2
ω(1,2,3,4)	-76 1	-	-	-
ω(1,2,3,6)	-	-59 6	-60 8	-57 6
ω(1,2,3,10)	-36 8	60 0	58 3	58 0
ω(1,2,3,11)	175 6	180 0	180 0	-175 8
ω(1,2,4,5)	-	104 0	102 9	107 6
ω(2,1,6,5)	-26 1	-	-	-
ω(2,3,4,5)	64 2	-	-	-
ω(2,4,5,6)	-	-	-	7 2
ω(3,2,1,4)	-	106 0	101 4	89 3
ω(3,2,1,6)	59 5	-	-	-
ω(3,2,1,7)	49 7	-2 8	-5 9	-21 0
ω(3,2,1,8)	-176 7	-152 5	-156 6	-165 6
ω(3,4,5,6)	-38 1	-	-	-
ω(4,1,2,9)	-	-96 3	-93 8	-94 7
ω(4,3,2,9)	-91 7	-	-	-
ΔH_f	53 1	54 2	54 5	54 7

[a] Distances (r) in Å, bond angles (θ) and dihedral angles (ω) in degrees [b] ΔH_f in kcal mol^{-1}

Table 4 Geometric Features[a] and Heats of Formation[b] of Structures **5d, 6d, 7d, 11d, 12d** as calculated by PM3

Variable	Structure				
	5d	**6d**	**7d**	**11d**	**12d**
r(1,2)	1 386	1 399	1 500	1 411	1 424
r(1,4)	-	-	1 529	1 622	1 588
r(1,6)	1 365	1 336	-	-	-
r(1,7)	1 095	1 093	1 100	1 099	1 104
r(1,8)	1 089	1 089	1 098	1 097	1 102
r(2,3)	1 455	1 416	1 495	1 471	1 458
r(2,4)	-	-	1 547	2 139	2 098
r(2,9)	1 095	1 095	1 109	1 095	1 093
r(3,4)	1 552	1 688	-	-	-
r(3,6)	-	-	1 099	1 102	1 134
r(3,10)	1 107	1 094	1 097	1 103	1 097
r(3,11)	1 104	1 096	1 097	1 101	1 093
r(4,5)	1 298	1 271	1 258	1 214	1 233
r(4,12)	0 998	-	0 994	0 999	0 997
r(5,6)	1 512	1 526	-	-	1 904
r(5,12)	-	0 994	-	-	-
θ(1,2,3)	118 5	118 5	120 0	121 4	119 6
θ(1,2,4)	-	-	60 2	49 3	49 3
θ(1,2,9)	120 9	120 2	118 3	120 7	121 5
θ(1,6,5)	135 9	137 0	-	-	-
θ(2,1,4)	-	-	61 4	89 4	88 1
θ(2,1,6)	97 3	98 9	-	-	-
θ(2,1,7)	120 1	119 5	119 6	118 8	118 7
θ(2,1,8)	119 3	118 9	120 6	118 5	118 1
θ(2,3,4)	102 6	101 7	-	-	-
θ(2,3,6)	-	-	112 7	111 7	106 1
θ(2,3,10)	114 6	118 2	110 2	111 4	113 6
θ(2,3,11)	114 6	117 7	110 7	111 6	113 4
θ(2,4,5)	-	-	124 3	114 9	103 8
θ(2,4,12)	-	-	112 9	85 2	91 5
θ(3,4,5)	115 5	115 7	-	-	-
θ(3,4,12)	108 9	-	-	-	-
θ(3,6,5)	-	-	-	-	125 4
θ(4,5,6)	106 9	108 6	-	-	-
θ(4,5,12)	-	111 4	-	-	-
ω(1,2,3,4)	-70 6	-69 9	-	-	-
ω(1,2,3,6)	-	-	-35 9	-49 9	-59 6
ω(1,2,3,10)	-45 9	-42 2	84 4	69 6	56 3
ω(1,2,3,11)	171 1	180 0	-156 3	-170 2	178 9
ω(1,2,4,5)	-	-	111 0	108 6	118 4
ω(1,2,4,12)	-	-	-104 4	-134 6	-124 5
ω(2,1,6,5)	-35 9	-33 5	-	-	-
ω(2,3,4,5)	57 1	50 9	-	-	-
ω(2,3,4,12)	68 8	-	-	-	-
ω(2,4,5,6)	-	-	-	-	4 7
ω(3,2,1,4)	-	-	111 0	108 6	118 4
ω(3,2,1,6)	56 1	59 1	-	-	-
ω(3,2,1,7)	40 7	42 9	-1 2	-16 9	-30 2
ω(3,2,1,8)	-172 6	-173 9	-139 4	-154 2	-165 9
ω(3,4,5,6)	-37 1	-28 2	-	-	-
ω(3,4,5,12)	-	-81 2	-	-	-
ω(4,1,2,9)	-	-	-107 7	-96 9	-100 9
ω(4,3,2,9)	-96 4	-95 4	-	-	-
ΔH_f	55 9	69 5	25 2	47 9	49 8

a Distances (r) in Å, bond angles (θ) and dihedral angles (ω) in degrees b ΔH_f in kcal mol^{-1}

Table 5 Geometric Features[a] and Heats of Formation[b], of Structures **5f**, **7f**, **11f** and **12f** as calculated by PM3

	Structure			
Variable	**5f**	**7f**	**11f**	**12f**
$r(1,2)$	1 403	1 498	1 442	1 437
$r(1,4)$	-	1 533	1 527	1 606
$r(1,6)$	1 285	-	-	-
$r(1,7)$	1 096	1 100	1 105	1 105
$r(1,8)$	1 089	1 098	1 104	1 102
$r(2,3)$	1 436	1 495	1 472	1 403
$r(2,4)$	-	1 551	1 972	2 348
$r(2,9)$	1 095	1 109	1 095	1 095
$r(3,4)$	1 608	-	-	-
$r(3,6)$	-	1 098	1 101	1 285
$r(3,10)$	1 106	1 099	1 100	1 095
$r(3,11)$	1 102	1 098	1 097	1 089
$r(4,5)$	1 322	1 317	1 273	1 323
$r(4,12)$	1 000	0 996	0 995	1 000
$r(5,6)$	1 605	-	-	-
$r(5,13)$	0 994	0 997	0 996	0 994
$\theta(1,2,3)$	118 4	120 3	120 8	118 4
$\theta(1,2,4)$	-	60 3	50 2	41 3
$\theta(1,2,9)$	120 5	118 3	119 1	119 7
$\theta(1,6,5)$	134 5	-	-	-
$\theta(2,1,4)$	-	61 6	83 2	103 8
$\theta(2,1,6)$	100 6	-	-	-
$\theta(2,1,7)$	118 5	120 9	118 6	115 7
$\theta(2,1,8)$	118 3	120 5	118 7	115 3
$\theta(2,3,4)$	102 9	-	-	-
$\theta(2,3,6)$	-	113 3	112 2	100 7
$\theta(2,3,10)$	115 8	110 9	111 8	118 4
$\theta(2,3,11)$	115 3	110 7	111 0	117 8
$\theta(2,4,5)$	-	127 5	118 5	92 7
$\theta(2,4,12)$	-	113 6	95 9	92 5
$\theta(3,4,5)$	115 8	-	-	-
$\theta(3,4,12)$	108 4	-	-	-
$\theta(3,6,5)$	-	-	-	134 6
$\theta(4,5,6)$	106 3	-	-	-
$\theta(4,5,13)$	110 1	112 8	114 2	110 4
$\omega(1,2,3,4)$	110 1	112 8	114 2	110 4
$\omega(1,2,3,6)$	-	-30 9	-50 2	-56 8
$\omega(1,2,3,10)$	-436 2	89 4	69 9	47 5
$\omega(1,2,3,11)$	173 7	-151 9	-170 2	-173 3
$\omega(1,2,4,5)$	-	113 7	115 8	132 7
$\omega(1,2,4,12)$	-	-105 3	-122 8	-118 6
$\omega(2,1,6,5)$	-34 2	-	-	-
$\omega(2,3,4,5)$	-69 2	-	-	-
$\omega(2,3,4,12)$	76 2	-	-	-
$\omega(2,4,5,6)$	-	-	-	4 3
$\omega(2,4,5,13)$	-	-36 5	-70 8	-97 3
$\omega(3,2,1,4)$	-	110 5	102 4	69 4
$\omega(3,2,1,6)$	57 1	-	-	-
$\omega(3,2,1,7)$	46 9	1 4	-10 7	-46 3
$\omega(3,2,1,8)$	-173 7	-139 7	-145 8	-173 7
$\omega(3,4,5,6)$	-33 3	-	-	-
$\omega(3,4,5,13)$	-68 4	-	-	-
$\omega(4,1,2,9)$	-	-107 9	-100 4	-97 6
$\omega(4,3,2,9)$	-97 6	-	-	-
ΔH_f	85 0	72 6	85 4	85 0

a Distances (r) in Å, bond angles (θ) and dihedral angles (ω) in degrees b ΔH_f in kcal mol^{-1}

Table 6 Geometric Features[a] and Heats of formation[b] of structures **5g**, **6g** and **7g** as calculated by PM3

	Structure		
Variable	**5g**	**6g**	**7g**
r(1,2)	1 406	1 433	1 497
r(1,4)	-	-	1 523
r(1,6)	1 276	1 185	-
r(1,7)	1 094	1 097	1 100
r(1,8)	1 089	1 092	1 098
r(2,3)	1 406	1 412	1 570
r(2,4)	-	-	1 570
r(2,9)	1 096	1 091	1 107
r(3,4)	1 837	1 660	-
r(3,6)	-	-	1 098
r(3,10)	1 097	1 104	1 099
r(3,11)	1 094	1 100	1 097
r(4,5)	1 370	1 346	1 344
r(4,12)	1 099	0 995	0 991
r(4,13)	1 097	-	-
r(5,6)	1 573	1 719	-
r(5,13)	-	1 089	1 082
r(5,14)	0 991	1 089	1 081
θ(1,2,3)	119 4	117 7	120 3
θ(1,2,4)	-	-	59 5
θ(1,2,9)	119 6	120 5	117 9
θ(1,6,5)	142 8	134 3	-
θ(2,1,4)	-	-	62 6
θ(2,1,6)	97 8	104 7	-
θ(2,1,7)	118 6	115 4	119 6
θ(2,1,8)	118 7	115 4	120 5
θ(2,3,4)	101 9	101 7	-
θ(2,3,6)	-	-	110 5
θ(2,3,10)	117 4	117 4	112 7
θ(2,3,11)	117 3	116 7	110 7
θ(2,4,5)	-	-	124 9
θ(2,4,12)	-	-	111 8
θ(3,4,5)	111 5	114 7	-
θ(3,4,12)	99 5	110 3	-
θ(3,4,13)	102 2	-	-
θ(4,5,6)	107 2	103 8	-
θ(4,5,13)	-	117 2	122 3
θ(4,5,14)	112 5	121 7	122 0
ω(1,2,3,4)	-70 6	-69 8	-
ω(1,2,3,6)	-	-	-38 2
ω(1,2,3,10)	-40 1	-41 7	82 9
ω(1,2,3,11)	175 6	174 7	-158 5
ω(1,2,4,5)	-	-	109 8
ω(1,2,4,12)	-	-	-106 1
ω(2,1,6,5)	-34 4	-29 2	-
ω(2,3,4,5)	47 3	60 3	-
ω(2,3,4,12)	-172 6	68 4	-
ω(2,3,4,13)	72 3	-	-
ω(2,4,5,13)	-	-	-41 5
ω(2,4,5,14)	-	-	135 8
ω(3,2,1,4)	-	-	109 8
ω(3,2,1,6)	60 7	55 6	-
ω(3,2,1,7)	44 1	55 9	2 0
ω(3,2,1,8)	-176 3	-174 4	-138 9
ω(3,4,5,6)	-23 4	-35 6	-
ω(3,4,5,13)	-	-61 5	-
ω(3,4,5,14)	-87 3	141 9	-
ω(4,1,2,9)	-	-	-107 8
ω(4,3,2,9)	-96 0	-99 7	-
ΔH_f	65 8	61 9	6 10

a Distances (r) in Å, bond angles (θ) and dihedral angles (ω) in degrees b ΔH_f in kcal mol^{-1}

the less strained transition state in the reaction of **3g** and hence the transition state of lower overall energy

Conclusions

These calculations have shown that both concerted and stepwise pathways, the former involving 6-membered transition states, the latter strained "perepoxide" type intermediates, exist on the PM3 potential energy surfaces for the reactions of a number of π-isoelectronic enophiles with propene

Except for nitrosyl hydride (**3d**) which is predicted to react exclusively via the aziridine N-oxide (**7d**), both concerted and stepwise pathways are calculated to be of similar energy, in each case In particular instances, namely reactions involving singlet oxygen (**3a**), nitrosyl hydride (**3d**) and 1,2,4-triazoline-3,5-dione (**4a**), the reactions are all predicted by PM3 to have similar energy requirements It is not surprising, therefore, that ene products have been isolated in reactions involving **3a, 3d** and **4b** with appropriately substituted olefins

Finally, a balance of steric and electronic factors are found to operate in the concerted transition states (**5, 6**), controlling the regiochemistry in these reactions

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