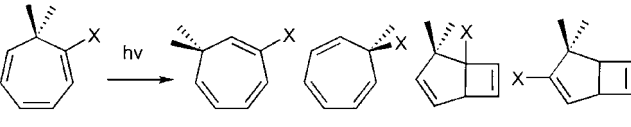


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Table 1. 1-Substituted cycloheptatrienes: substituent dependence of product formation (%)^a


Me ₂ N	—	—	97	3
MeO	—	35	65	—
MeS	—	65	35	—
Me	2	98	—	—
H	99.8	—	0.2	—
CN	100	—	—	—

^a After TerBorg *et al.*¹¹

the acceptor and towards the donor substituent. This nicely explains the observed selectivity of the reaction, which corresponds to 100:0 in the case of 1-CN-CHT and 2:98 in the case of 1-CH₃-CHT for products of a sigmatropic shift away from and towards the substituent (Table 1).¹¹

Mechanism (c) is responsible for the photochemistry of 2,3-di-*tert*-butylbutadiene. The steric effect of the *tert*-butyl groups prevents the existence of the *s*-cisoid and the central butadiene CI,¹² and only one critical point exists in the intersection space.¹³ It corresponds to the *s*-transoid minimum in the intersection space of butadiene and is characterized by a particularly small 1,3-distance. It is therefore not surprising that in the presence of 2,3-di-*tert*-butyl substituents the corresponding bicyclo[1.1.0]butane, which is usually a minor side product of the butadiene photocyclization, becomes the major photoproduct.¹⁴

Mechanism (d), finally, is assumed to play a role in the photochemistry of 1-substituted CHT, where donor substituents are shown to favor the electrocyclic formation of substituted bicyclo[3.2.0]heptadienes (Table 1).¹¹ It is most likely that the electrocyclization occurs through a CI different from that of the sigmatropic shift, and that the excited-state barrier on the way to this CI is higher or lower than that on the sigmatropic-shift reaction path if the CHT ring is substituted in 1-position by donor and acceptor substituents, respectively.

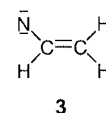
RING-OPENING REACTIONS OF 2H-AZIRINES

In recent papers, the role of conical intersections in the photochemistry¹⁵ of 2H-azirines (1) was described and their thermal ring-opening reactions (C. Bornemann and M. Klessinger, in preparation) were discussed. The results for the unsubstituted and alkyl-substituted 2H-azirines, which according to our calculations should exhibit very much the same reactivity, can be briefly summarized as follows:

1. Cleavage of the CC bond of the azirine ring yields the

corresponding nitrile ylides **2**. The thermal ring opening is a one-step reaction, which, however, requires an activation energy of 55 kcal mol⁻¹ (1 kcal = 4.184 kJ). From the charge distribution at the transition state it may be concluded that this reaction is possible only with electron donors on C1 and at high temperatures,¹⁵ in agreement with experimental observation.¹⁶

2. The photochemical CC ring opening is the principal photoreaction of the 2H-azirine system, and is characteristic for the $n\pi^*$ excited state. Relaxation from the Franck–Condon (FC) geometry leads to an S_1/S_0 conical intersection, from which the corresponding nitrile ylides **2** are reached without activation energy. Triplet intermediates are apparently not involved. This mechanism fully explains the experimental observations.¹⁵
3. Cleavage of the CN double bond is the S_2 photoreaction of aliphatic 2H-azirines and is initiated by $\pi\pi^*$ excitation of the C=N chromophore. Deactivation of the S_2 occurs via an S_2/S_1 conical intersection and leads to vinyl nitrene **3** in its first excited singlet state, which may deactivate by fluorescence to yield vinyl nitrene in the singlet ground state. This, however, is a reactive intermediate, which may undergo either a barrierless back-reaction to form the corresponding 2H-azirine¹⁴ or else ISC to form a stable triplet nitrene.¹⁵



4. Finally, cleavage of the CN single bond occurs thermally and yields the most stable C₂H₃N isomers acetonitrile and ketene imine (C. Bornemann and M. Klessinger, in preparation).¹⁶

EFFECT OF PHENYL SUBSTITUENTS ON THE PHOTOCHEMISTRY OF 2H-AZIRINES

The effect of the phenyl substituent on the photochemistry of 3-phenyl-2H-azirine (**4a**) cannot be explained by the mechanisms discussed above. In this case, it is rather the excitation step (1) which is affected by the substituent. The calculated absorption spectrum of **4a**, which is dominated by $\pi \rightarrow \pi^*$ transitions localized in the phenyl group, agrees well with the experimental spectrum, which resembles a perturbed benzene spectrum such as that of styrene [CASSCF calculations were performed using Gaussian 98;¹⁷ if, for instance, the active space (AS) is chosen to contain the nitrogen lone-pair orbital in addition to the four bonding and four antibonding π MOs, i.e. ten electrons in nine orbitals, this is denoted in terms of symmetry labels a' and a'' as AS 5.4' (occ. 26,9; closed

25,1) in the case of **4a** with a total of 31 doubly occupied MOs in the ground configuration]. The low-intensity $n \rightarrow \pi^*$ transition is apparently hidden by the aromatic bands. Therefore, for excitation with a laser pulse of 308 nm, as described by Albrecht *et al.* (E. Albrecht, C. Bornemann, M. Klessinger, J. Mattay, C. Siegner and S. Steenken, in preparation), similar photochemical reactivity is to be expected as for benzene in its lowest singlet-excited state, and the triplet intermediate observed by Albrecht *et al.* is most likely the stable triplet state of 3-phenyl-2H-azirine. This was verified by calculating the triplet absorption spectrum, which shows only one band near 455 nm, in good agreement with the band at 465 nm observed in the time-resolved spectrum of Albrecht *et al.* (E. Albrecht, C. Bornemann, M. Klessinger, J. Mattay, C. Siegner and S. Steenken, in preparation).

As a possible mechanism for the formation of the triplet species, ISC from the S_1 minimum geometry $^1\mathbf{4a}^*$ to the close-lying $T_2(1^3A'')$ is assumed. In this state, a barrierless path leads from the $^1\mathbf{4a}^*$ geometry to a T_2/T_1 conical intersection $^3\mathbf{CI}$, from which two equivalent T_1 minima of 3-phenyl-2H-azirine are reached. The results are summarized in Fig. 1, where relative CASPT2 energies are shown [CASPT2 calculations based on state-average CASSCF reference functions were performed at the CASSCF stationary points using MOLPRO96¹⁸ and MOLCAS¹⁹; for additional results including optimized geometric parameters, see Albrecht *et al.* (E. Albrecht, C. Bornemann, M. Klessinger, J. Mattay, C. Siegner and S. Steenken, in preparation)]. After vertical excitation into the $S_1(2^1A')$ state, relaxation occurs to the S_1 minimum ca 4.4 kcal mol⁻¹ lower in energy than the FC geometry. In the vicinity of this minimum ISC to the close-lying $T_2(1^3A'')$ state is most

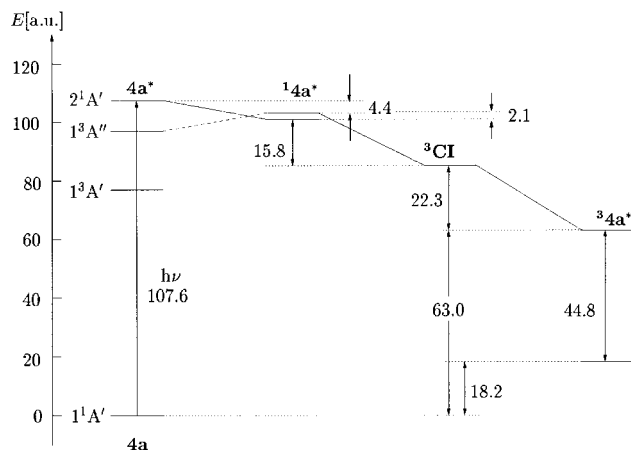


Figure 1. Reaction path for the S_1 photoreaction of 3-phenyl-2H-azirine (**4a**) and formation of its triplet state $^3\mathbf{4a}^*$. CASPT2 energies E_{rel} in kcal mol⁻¹ are plotted relative to the ground-state minimum **4a**. [CASPT2, AS: 5,4' (occ. 26,9; closed 25,1)/ANO[3s2p1d]/[2s,1p]/CASSCF, AS: 4,3' (occ. 26,8; closed 25,2)/6-31G]

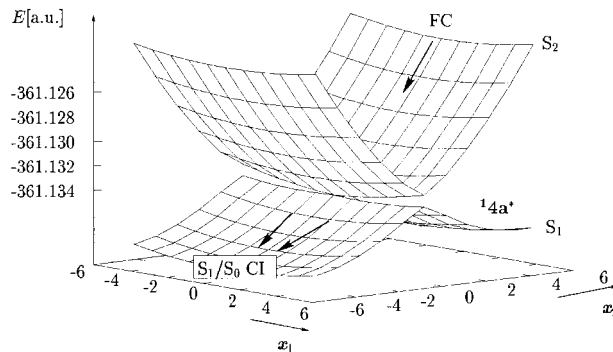


Figure 2. CASSCF potential energy surfaces for the S_2 and S_1 states of 3-phenyl-2H-azirine (**4a**) at the S_2/S_1 conical intersection, as function of x_1 and x_2 in units of 10^{-2} (amu)^{1/2} bohr. The arrows on the S_1 surface point toward a reaction valley leading to the S_1/S_0 conical intersection. [AS: 5, 4' (occ. 26, 9; closed 25, 1)/6-31G*]

likely, and by way of the T_2/T_1 conical intersection the minimum of the $T_1(1^3A')$ state is reached. The total reaction path is barrierless and the energy gain is 38.1 kcal mol⁻¹.

The $S_2(1^1A'')$ state of 3-phenyl-2H-azirine is an $n\pi^*$ -excited state, and the S_2 photochemistry resembles the S_1 photochemistry of the aliphatic 2H-azirines, and since according to the experimental results the 3-phenylnitrile ylide is formed in an fast reaction during the laser pulse used for excitation, it is likely that two conical intersections between S_2 and S_1 and between S_1 and S_0 are involved. An S_2/S_1 conical intersection could indeed be found in the vicinity of the FC geometry; as the S_2 surface exhibits a very steep descent from the FC geometry toward the S_2/S_1 conical intersection (Fig. 2), an exclusive deactivation of the S_2 state through this conical intersection followed by a passage through the S_1/S_0 conical intersection is most likely. Barrierless reaction paths from this conical intersection lead to two equivalent vinyl nitriles, which differ only by a rotation of the CH_2 group through 180°. Alternatively, if direct excitation at the chosen wavelength $\lambda = 248$ nm does not occur under the conditions of the experiment, the photochemical process could start in a hot S_1 state with vibrational excitation permitting the molecule to overcome a barrier in the S_1 state that results from an avoided touching with S_2 , in competition with vibrational cooling. This type of 'hot excited state' photochemistry is common in benzene derivatives, as is known particularly from the work of Becker *et al.*²⁰



As *ab initio* calculations for 2,3-diphenyl-2H-azirine

(4b) at the same level of accuracy as those presented so far are too demanding, we used the semiempirical MNDOC-CI method^{13,21} to investigate the photochemistry of this compound. As the optimized geometry for the S_1/S_0 conical intersection already resembles that of the nitrile ylide, it can be concluded that 2,3-diphenyl-2H-azirine undergoes the same photoreactions as the aliphatic 2H-azirines, i.e. a barrierless reaction path leads from the FC geometry via a conical intersection to the nitrile ylide.

The difference between the monophenyl derivative 3-phenyl-2H-azirine (4a) and the 2,3-diphenyl-2H-azirine (4b) lies in the different symmetries of these two molecules: whereas the monophenyl compound with phenyl and azirine rings coplanar belongs to point group C_s , the diphenyl compound belongs to C_1 . Owing to the lack of symmetry, the $\pi\pi^*$ and $n\pi^*$ configurations, which in the planar compound have different symmetries and dominate the S_1 and S_2 state, respectively, can mix, and the $n\pi^*$ contribution to the S_1 wavefunction is apparently sufficient to determine the reactivity of this state.

It remains to be shown why the photochemistry of the monophenyl compound 4a is wavelength dependent whereas that of the diphenyl derivative 4b is not, that is, why 3-phenyl-2H-azirine (4a) appears to violate Kasha's rule.²² For both compounds, the S_1 state can be reached by rapid IC from higher excited states via conical intersections close to the FC geometry, as is to be expected for those cases where Kasha's rule is valid. The important point is that at the FC geometry, owing to symmetry, the S_1 state of 4a is a pure $\pi\pi^*$ -excited benzene state, which undergoes ISC to the triplet state, while after excitation at short wavelengths a point of lower symmetry is reached, where the $\pi\pi^*$ and $n\pi^*$ configurations can mix to such an extent that the S_1 reactivity is determined by the $n\pi^*$ contribution to the wavefunction, similarly as in the case of the diphenyl compound. This is independent of the detailed mechanism and occurs either after passage through the S_2/S_1 -conical intersection, which would correspond to a violation of Kasha's rule, or else after crossing the S_1 barrier in a 'hot excited-state' reaction.

CONCLUSIONS

The main difference between alkyl- and aryl-substituted 2H-azirines can be seen in the fact that benzene absorptions occur at longer wavelengths than the azirine $n\pi^*$ excitation which is responsible for the nitrile ylide formation. Hence the influence of phenyl substitution on the photochemistry of the azirine system can be traced back to two different effects:

1. the energetic order of the excited states, with the aromatic $\pi\pi^*$ absorption at longer wavelengths than the azirine $n\pi^*$ band; and
2. the symmetry of the system: if a plane of symmetry exists (point group C_s), the $\pi\pi^*$ and $n\pi^*$ excitations belong to different irreducible representations and do not mix so S_1 corresponds to a pure benzene state, but if the system has no symmetry (point group C_1), even the lowest excited state has sufficient $n\pi^*$ character to produce the nitrile ylide. Hence we would predict that for 2,2-diphenyl- and 2,2,3-triphenyl-2H-azirine excitation of the S_1 produces the benzene photochemistry, whereas systems such as 2-phenyl-2H-azirine without a symmetry plane should yield only nitrile ylides.

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