RING CONTRACTION OF CYCLIC OLEFINS: CHEMICAL PROCESSES SPECIFIC TO ELECTRONICALLY EXCITED STATES?

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Summary

The photochemical ring cleavage and ring contraction reactions of cyclic olefins are reviewed. The retro Diels—Alder processes cannot be unambiguously linked to a particular electronic state. Although there seem to be some differences between the bicycloalkane products observed in the photosensitization (triplet) and the direct photolysis (singlet) of cyclo-olefins, these differences do not warrant assignment of the formation of a given bicycloalkane to a particular electronic state. Ring contraction to the corresponding vinylcycloalkane can occur from either the triplet or the "hot" ground state. The formation of methylenecycloalkanes appears to be a reaction specific to a Rydberg singlet state of the cycloalkenes.

1. Introduction

The first physical process which occurs in an olefin under far UV irradiation is the promotion of an electron from a higher occupied molecular orbital to an unoccupied external orbital: the photoexcited molecule becomes electronically excited. The electronically excited state may be either a singlet state, as is generally the case in direct photolysis, or a triplet excited state, as for example when mercury atoms, $Hg(^3P_1)$, are used in photosensitization experiments. Both electronic states have many available channels for the dissipation of energy. However, depending on the nature of the photoexcited molecule, only a few are open. Obviously, the main question is the following: are these channels typical of each state? In the case where these channels give rise to the formation of products, can these products be linked unambiguously to the original state?

The aim of this article is to re-examine the photochemistry of cyclic olefins to try to discover such links between electronically excited states and

some of the observed products. Indeed, the recent finding that a vinylcycloalkane is formed in appreciable quantities in the direct photolysis of the corresponding cyclic olefin in the vapour phase (see Fig. 1 [1]) justifies this review of the available data. The formation of vinylcycloalkanes in the mercury photosensitization of cyclo-olefins is generally believed to proceed via the triplet electronic state of the olefins (see below).
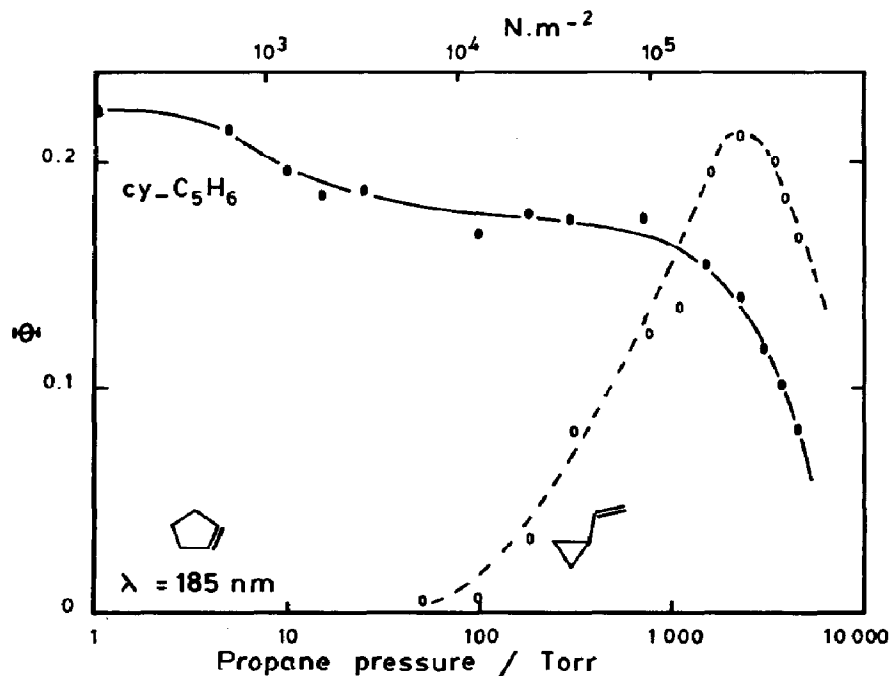

Fig. 1. 184.9 nm photolysis of cyclopentene: vinylcyclopropane (○) and cyclopentadiene (●) quantum yields vs. the pressure of added propane (experimental details published in ref. 1).

2. Review of the literature results

The first studies of the mercury photosensitization of cyclic olefins were undertaken early in the 1960s [2 - 5]. However, the numerous improvements in analytical procedures as well as the better general knowledge of olefinic photochemistry gave rise to various re-investigations and to studies of suitably substituted cyclic olefins in the 1970s. We will place particular emphasis on the more recent work for the purpose of this article, and encourage readers to refer to the earlier papers for more information or details.

The main results obtained in gaseous $Hg(^3P_1)$ photosensitization of cyclic olefins are given in Table 1. Although the retro Diels–Alder reaction was observed in cyclohexenes [4, 5, 7, 8], ring contraction to the corresponding vinylcyclopropane is the most important process observed for

TABLE 1

Comparison of the quantum yields[a] of the retro Diels–Alder (A) and the ring contraction processes to a vinylcycloalkane (B) or a bicyclo[n.1.0]alkane (C)[b] in the Hg($^3P_1$) photosensitization of cyclic olefins

Olefin	A	B	C	Pressure (Torr)	Reference
Cyclopentene	—	0.35	—	a	2, 3
1-Methylcyclopentene	—	0.3	—	a	6
Cyclohexene	0.2	0.06	—	a	4, 5
3-Methylcyclohexene	0.04	0.003	—	a	7
cis-4,5-Dimethylcyclohexene	0.006[c]	0.005	—	a	8
trans-4,5-Dimethylcyclohexene	0.01[c]	0.006	—	a	8
Cycloheptene	—	0.054	0.088	d	9
cis-Cyclo-octene	—	e	0.049	4.5	11, 12
cis-Cyclononene	—	f	1.18[g]	1	13

[a]Except for cycloheptene and cyclo-octene, the quantum yields were obtained by extrapolation of the "high pressure" data to zero pressure (see ref. 6). For the ring contraction to vinylcycloalkane this procedure is delicate: the yields go through a maximum value at low to intermediate pressures.
[b]The original number of carbon atoms in the ring is equal to n + 3.
[c]The original cis or trans geometry of the ring methyl groups is not conserved in the 2-butene products.
[d]The experimental pressure was not specified. These yields are much higher than those obtained by De Maré [5] for the Hg($^3P_1$) photosensitization of cycloheptene at 21 Torr.
[e]Not detected. This surprising result is corroborated by the finding that ϕ(vinylcyclohexane) < 0.001 [10].
[f]Not detected (yield, less than 0.01 μmol).
[g]Yield in micromoles.

cyclopentenes [2, 3, 6]. However, the quantum yield of this process decreases very quickly with an increase in the number of carbon atoms (degrees of freedom) present in the cyclo-olefin. (In this context the extrapolated quantum yield of vinylcyclopropane from cyclopentene appears to be underestimated whereas the quantum yield reported for vinylcyclopentane from cycloheptene [9] seems abnormally high.) The formation of a methylenecycloalkane in the photosensitizations of the cyclic olefins has never been reported. Conversely, the formation of bicyclo[n.1.0]alkanes (where n + 3 is equal to the number of carbon atoms in the original ring) has only been observed in the photosensitization of the higher homologues, cycloheptene [4, 5, 9], cyclo-octene [11, 12] and cyclononene [13]. The Hg($^3P_1$) photosensitizations of cyclo-octene and cyclononene also afford appreciable quantities of other bicyclic compounds [11 - 13].

In the case of the direct photolysis of cyclic olefins in the vapour phase at 184.9 nm (Table 2), the retro Diels–Alder process is prominent for cyclohexene [14 - 16]. For the 4,5-dimethylcyclohexenes, however, the quantum yield of the retro Diels–Alder process is more than a factor of 10 lower than for cyclohexene [8]. As far as ring contraction processes are concerned,

TABLE 2

Comparison of the yields (in micromoles) of the retro Diels–Alder (A) and ring contraction processes to vinylcycloalkanes (B), methylenecycloalkane (C) or bicyclo[n.1.0]-alkane (D) in the direct 184.9 nm photolysis of cyclic olefins at low pressure

Olefin	A	B	C	D	Pressure (Torr)	Reference
Cyclohexene	0.9[a]	0.00	0.02	0.002	[b]	15, 16
cis-4,5-Dimethylcyclohexene	0.06[c]	[d]	0.005[e]	—	5	8
trans-4,5-Dimethylcyclohexene	0.06[c]	[d]	0.006[f]	—	5	8
Cycloheptene	—	0.181	0.038	0.008	3	15, 16
cis-Cyclo-octene	—	0.373	0.017	0.017	3	15, 16
trans-Cyclo-octene	—	0.428	0.022	0.029	3	15, 16
cis-Cyclononene	—	0.13	—	[g]	1	13

[a]Extrapolation of the data of Collin and Deslauriers [14] to zero pressure yields ϕ(retro Diels–Alder) ≈ 0.82.
[b]Extrapolated to zero pressure.
[c]In contrast to the photosensitization results (Table 1), the original cis and trans geometry of the ring methyl groups is conserved in the 2-butene products.
[d]Not detected in significant yields [8].
[e]cis-3,4-Dimethyl-1-methylenecyclopentane. The yield is pressure independent.
[f]trans-3,4-Dimethyl-1-methylenecyclopentane. The yield is pressure independent.
[g]Not detected (yield less than 0.01 μmol).

vinylcycloalkane formation appears only in the photolysis of cycloheptene or higher members of the series [13, 15, 16]. The formation of methylenecycloalkane and that of bicyclo[n.1.0]alkanes occurs generally.

The results for the direct photolysis of cyclo-olefins in solution at 184.9 nm appear to be more straightforward (see Table 3). Formation of vinylcycloalkane isomers is not observed. In contrast, methylenecycloalkane and bicyclo[n.1.0]alkanes are observed in all cases, albeit in low quantum yields, except for cyclobutene where bicyclo[1.1.0]butane is not formed [17].

3. Discussion of the various processes

The main primary processes observed in cycloalkene photochemistry can be roughly divided into fragmentation (concerted or not concerted) and ring contraction to a vinylcycloalkane, a bicycloalkane or a methylenecycloalkane.

3.1. Concerted fragmentation processes

Gibbons et al. [2, 3] reported that the Hg($^3P_1$) photosensitization of cyclopentene results in the formation of no cyclopentadiene and in only small amounts of hydrogen, in sharp contrast with the thermal decomposition where hydrogen and cyclopentadiene are the major products [24].

TABLE 3

Comparison of the quantum yields for the formation of methylenecycloalkanes (A) and bicyclo[n.1.0]alkanes (B) in the direct 184.9 nm photolysis of cyclic olefins in solution

Olefin	A	B	B/A	Solution	Reference
Cyclobutene	0.12	[a]	0.00	n-Heptane	17
Cyclopentene	0.031	0.032	1.03	n-Pentane	18
	(27)[b]	(28)[b]	—	n-Pentane	18
	0.04	0.03	0.7_5	n-Heptane	19
Cyclohexene	0.05	0.07	1.4	c	20
	(22)[b]	(43)[b]	1.9_5	n-Pentane	15
4-Vinylcyclohexene	0.02^d	0.04_5 [d]	2.3	n-Pentane	21
Cycloheptene	0.10	0.02	0.2	c	20
	(34)[b]	(27)[b]	0.79	n-Pentane	15
cis-Cyclo-octene	0.007	0.008	1.1^e	n-Pentane	23
	(2.1)[b]	(2.8)[b]	1.3_3	n-Pentane	15
trans-Cyclo-octene	(2.1)[b]	(3.6)[b]	1.7_1	n-Pentane	15
	0.007 ± 0.002	0.008 ± 0.002	1.14	n-Pentane	23
2-Norbornene	0.07	0.07	1.0	c	20
	f	0.019	—	n-Pentane	18
	f	(9.8)[b]	—	n-Pentane	18
Bicyclo[2.2.2]oct-2-ene	0.00	0.019	∞	n-Pentane	18
	0.20	0.01	0.05	c	20
Bicyclo[3.3.0]oct-2-ene	0.09	0.02	0.2_2	c	20

[a]No bicyclo[1.1.0]butane is formed [17].
[b]The numbers within brackets are in product per cent, based on the cycloalkene consumed [15].
[c]The solvent used was not specified.
[d]Relative quantum yield calculated using the quantum yields for product formation given in ref. 20 and the product yield reported in ref. 21.
[e]Note that Kropp et al. [22] found a B/A product ratio of 2 when they irradiated cis-cyclo-octene in n-pentane solution with a Hanovia 450 W medium pressure arc. Under the same conditions, cyclodecene and cyclododecene photolysis afforded no methylenecycloalkane or bicyclo[n.1.0]alkane.
[f]Not determined owing to incomplete vapour phase chromatography separation [18]. Note that the quantum yield of nortricyclene (0.019) is very close to that (0.023, [18]) obtained by changing the yield reported by Srinivasan and Brown [20] in the same ratio as for those of the products of cis-cyclo-octene photolysis (see refs. 18 and 20).

Hydrogen formation in the mercury photosensitization most probably proceeds stepwise via hydrogen-atom abstraction by hydrogen atoms produced in β(C—H) bond cleavage in the triplet cyclopentene molecule. In the direct photolysis of cyclopentene, the fragmentation of the photoexcited molecule can give cyclopentadiene and molecular hydrogen directly in a concerted process

$$\text{⬠} + h\nu \longrightarrow \text{⬠} + H_2 \tag{1}$$
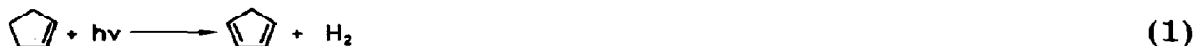
in agreement with the Woodward—Hoffmann rules [1, 25]. It has been proposed [1] that cyclopentadiene formation in the 100 - 1000 Torr pressure range ($\phi \approx 0.18$; see Fig. 1) occurs via this process.

The retro Diels–Alder process, fragmentation of a cyclohexene to a 1,3-diene and an olefin

$$\text{⬡} + h\nu \longrightarrow C_2H_4 + 1.3 - C_4H_6 \tag{2}$$

is often presumed to be a concerted reaction occurring from the ground electronic state [26 - 28] in agreement with the Woodward–Hoffmann rules [25]. The retro Diels–Alder reaction has been observed in the $Hg(^3P_1)$ photosensitization of cyclohexene [4, 5] of 3- and 4-methylcyclohexene [4, 5, 7] and of cis- and trans-4,5-dimethylcyclohexenes [8]. The trans to cis 1,3-pentadiene isomer ratio from 3-methylcyclohexene [7] and the loss of the original cis or trans geometry in the 2-butenes formed from cis- or trans-4,5-dimethylcyclohexene [8] indicate that the retro Diels–Alder process in the $Hg(^3P_1)$ photosensitization of cyclohexenes is a two-step process: (i) cleavage of a $\beta(C—C)$ bond in the vibrationally excited triplet state molecule to give an allyl–alkyl radical with a finite lifetime followed by (ii) cleavage of the second ring $\beta(C—C)$ bond to yield an olefin and a 1,3-diene (which could be formed in its triplet state [4, 5, 7]).
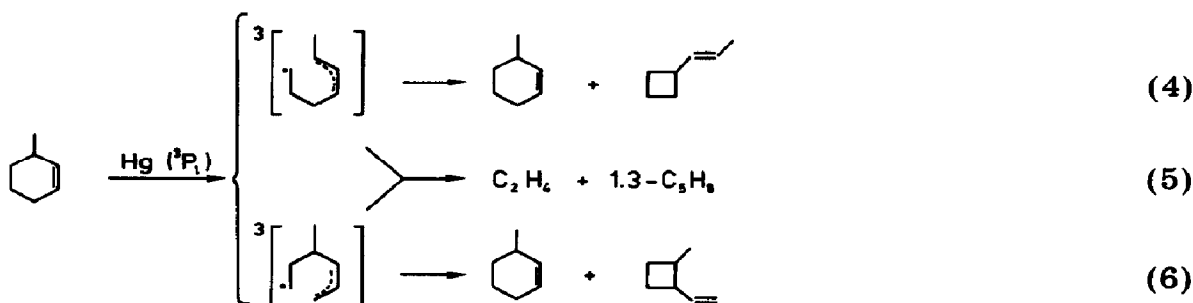
The retro Diels–Alder reaction occurs with a high quantum yield in the direct photolysis of cyclohexene vapour at 184.9 nm [14]. The photolysis of the cis- and trans-4,5-dimethylcyclohexenes in the vapour phase yields 2-butenes in which the original cis and trans geometry is conserved; this is consistent with a concerted process but not with a biradical process. The fact that the retro Diels–Alder reaction is not observed for cyclo-olefins in solution probably indicates that the precursor is sufficiently long lived to be completely stabilized in solution. This suggests the involvement of the ground electronic state in agreement with the symmetry conservation rules.

From the above considerations it is clear that the retro Diels–Alder process cannot be unambiguously linked to a particular electronic state.

3.2. Ring contraction to a vinylcycloalkane

$$\text{⬡}_m \xrightarrow{\quad Hg\ (^3P_1)\quad} \text{⬡}'_m \qquad m = 0-2 \tag{3}$$
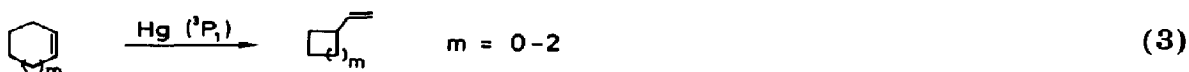
Whereas vinylcyclopropane and vinylcyclobutane are major products in the mercury photosensitization of cyclopentene [2, 3] and cyclohexene [4, 5] respectively, their formation has not been reported in the direct photolysis of cyclopentene in solution [18, 19] or cyclohexene [14 - 16] at low pressures. Thus it was very tempting to link such a formation to the triplet electronic state where the mechanism involves a primary $\beta(C—C)$ bond rupture [4, 5, 7]. The allyl–alkyl radical formed may then decompose further (see above) or may undergo cyclization to form either the starting cyclo-olefin or the corresponding vinylcycloalkane(s) [4, 5, 7]:

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$$\text{(4)}$$

$$\xrightarrow{\text{Hg }(^3P_1)} \left\{ \begin{array}{l} \end{array} \right.$$

$$\longrightarrow \quad C_2H_4 \ + \ 1.3\text{-}C_5H_8 \qquad \text{(5)}$$

$$\text{(6)}$$

The formation of vinylcycloalkanes in low yields has been observed in the direct photolysis of gaseous cycloheptene and higher members of the series at low pressures (Table 2). In contrast, no vinylcycloalkanes have been reported in the photolyses of cyclo-olefins in solution [15 - 23]. Since inter-system crossing from a singlet excited state to a triplet one is not assumed to be an efficient process in olefins, it may be proposed that the molecule in the first singlet electronic state S_1 undergoes internal conversion to the ground state S_0, *i.e.* the original electronic energy is transferred into the vibrational framework of the molecule. The molecule in the hot S_0 state (highly vibrationally excited) may then be deactivated collisionally or, in the cases of cyclopentene and cyclohexene, undergo fragmentation in a concert-ed process (reactions (1) and (2) respectively).

The difference between the photoreactivities of the small and medium-size cyclic olefins towards the formation of vinylcycloalkanes in solution may be reconciled if one considers their thermal reactions: for instance vinylcyclopropane isomerizes to cyclopentene [24] whereas cyclononene yields vinylcycloheptane [13, 29].

Very recently, the formation of vinylcyclopropane was observed in the high pressure photolysis of cyclopentene at 184.9 nm (Fig. 1 [1]) in one of our laboratories. The mechanism proposed for the vinylcyclopropane forma-tion involves the vibrationally hot ground state, S_0. A lifetime of about 5×10^{-10} s was measured for the hot excited precursor. This is a much longer lifetime than that obtained for the methylenecyclobutane precursor, which was estimated to be 10^{-11} s [1].

The formation of vinylcycloalkanes from cyclo-olefins is thus apparent-ly more dependent on the photolysis or photosensitization conditions than on the multiplicity of the initially formed excited state. Their presence or absence amongst the reaction products therefore cannot be used to imply the participation or non-participation of a specific electronic state in the reaction.

3.3. *Ring contraction to bicycloalkanes*

In the mercury photosensitization of cyclic olefins in the vapour phase, ring contraction to bicyclo[*n*.1.0]alkanes

$$\xrightarrow{\text{Hg}(^3P_1)} \qquad m = 3\text{--}5 \qquad \text{(7)}$$

has only been observed for the higher members of the series (see Table 1). Norcarane formation from cycloheptene-1,2-d_2 has been shown by Inoue *et al.* [9] to proceed in a stepwise process in which a 1,2-hydrogen shift is followed by closure of the resulting 1,3-biradical. Bicyclo[n.1.0]alkane formation in the mercury photosensitization of cyclo-octene and cyclononene presumably occurs via a similar two-step mechanism. Note that other bicycloalkanes (*i.e.* bicyclo[$(n-1)$.2.0]alkanes and bicyclo[$(n-2)$.3.0]-alkanes [11 - 13] are also formed in the mercury photosensitization of the large cyclo-olefins. The formation of these other bicycloalkanes is also proposed to proceed via a stepwise process: transannular hydrogen abstraction to yield a biradical which then undergoes ring closure [11 - 13].

Ring contraction to bicyclo[n.1.0]alkane isomers is also observed in the direct photolysis of cyclo-olefins both in the vapour phase and in solution. The major (and apparently only) exception appears to be cyclobutene. Indeed, Adam *et al.* [17] state "Still more surprising at first sight is the fact that bicyclo[1.1.0]butane is not formed in the 185 nm photolysis of cyclobutene". The major product from the cyclobutene photolysis is 1,3-butadiene which can be formed by electrocyclic ring-opening of π,π^* excited cyclobutene [17]. Bicyclo[n.1.0]alkane formation in the direct photolysis of cyclo-olefins is generally accepted to proceed via carbenes formed by a 1,2 C—C bond shift occurring in their π,R(3s) singlet Rydberg electronic state [18, 19, 30]. This mechanism was first formulated for 1,2-dimethylcyclohexene


(8)
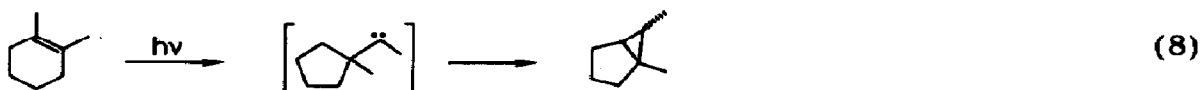
by Fields and Kropp [30]. In contrast to the mercury photosensitization, the participation of a cyclic 1,3-diradical in the formation of the bicyclo-[n.1.0]alkanes in the direct photolysis of cycloalkenes does not seem to be important. Indeed Srinivasan and Brown [20] argued against such a mechanism in the direct photolysis of cyclohexene-3,3,6,6-d_4 on the basis of the stereoselectivity observed for the deuterium distribution in the bicyclo-[3.1.0]hexane product.

As mentioned above, other bicycloalkanes are observed under various experimental conditions. In the mercury photosensitization they are presumed to arise through transannular hydrogen-atom abstraction. In the direct photolysis the proposed mechanism involves 1,2-hydrogen-atom migration to yield a carbene, followed by selective carbene insertion [22].

At the present time, although there seem to be some differences between the bicycloalkane products observed in the photosensitization (triplet) and direct photolysis (singlet) of cyclo-olefins, these differences do not warrant assignment of the formation of a given bicycloalkane to a particular electronic state.

3.4. Ring contraction to a methylenecycloalkane

Here the situation is different. Methylenecycloalkane formation has never been reported in the $Hg(^3P_1)$ photosensitization of cyclic olefins. Conversely, it has been observed in the direct photolysis of many cyclic olefins in solution and in the vapour phase (see Tables 2 and 3 and the references cited therein). Inoue et al. [15, 16] found that the photolysis of cycloheptene-1,2-d_2 yielded methylenecyclohexane with the deuterium atoms situated only on the exo-methylene carbon and proposed the following mechanism for its formation:

(9)
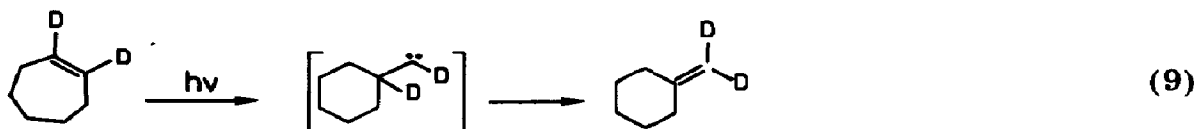
The intermediate is thus of the same type as that proposed by Fields and Kropp [30] for bicyclo[n.1.0]alkane formation (reaction (8)) from cyclo-olefins. However, Srinivasan and Brown [20] found that the deuterium distribution in the methylenecyclopentane product from the photolysis of cyclohexene-3,3,6,6-d_4 indicates the existence of a second channel for its formation:

(10)

The carbene intermediate is formed by a 1,2-hydrogen-atom shift and, presumably, also occurs in the $\pi,R(3s)$ state of the excited cyclo-olefin [20]. The ratio of the methylenecyclopentane arising from the carbenes formed by the 1,2 C—C bond and 1,2-hydrogen-atom shifts was found to be 5:1 respectively [20].

It thus appears that although there may be two different types of intermediates leading to methylenecycloalkene formation from cyclic olefins, both arise from the $\pi,R(3s)$ Rydberg singlet state of the cyclo-olefin. On the basis of the above, it therefore seems that the formation of methylenecycloalkanes from cyclic olefins in photochemical systems can be linked unambiguously to the olefinic $\pi,R(3s)$ electronic state.

4. Conclusions

The retro Diels—Alder reaction of cyclohexenes can occur either from the triplet state via an open chain allyl—alkyl radical or from the ground electronic state in a concerted process. Similarly, for the ring contraction of a cycloalkene to the corresponding vinylcycloalkane, two distinct reaction pathways are available: (i) in the $Hg(^3P_1)$ photosensitization of the cyclo-olefin, the reaction apparently proceeds via a "long-lived" triplet open-chain

biradical and (ii) in the direct photolysis the intermediate is probably a short-lived (about 10^{-10} s for cyclopentene $\rightarrow$ vinylcyclopropane) species in the "hot" ground state. Formation of bicyclo[n.1.0]alkanes is also observed in both the triplet photosensitization and the direct photolysis of cyclo-olefins. Again the mechanisms are different, involving 1,3-diradical and carbene intermediates respectively. Only the formation of methylenecyclo-alkanes from cycloalkenes appears to be a photoreaction specific to a partic-ular electronic state of the cyclo-olefin, $i.e.$ specific to the $\pi,R(3s)$ Rydberg singlet state.

Acknowledgments

References

1 W. Makulski and G. J. Collin, *J. Phys. Chem.*, *91* (1987) 708.
2 W. A. Gibbons, W. F. Allen and H. E. Gunning, *Can. J. Chem.*, *40* (1962) 568.
3 W. A. Gibbons, *M.Sc. Thesis*, University of Alberta, Edmonton, 1961.
4 G. R. De Maré, O. P. Strausz and H. E. Gunning, *Can. J. Chem.*, *43* (1965) 1329.
5 G. R. De Maré, *Ph.D. Thesis*, University of Alberta, Edmonton, 1965.
6 G. R. De Maré, N. Antheunis, J. Olbregts and M. Termonia, *J. Photochem.*, *4* (1975) 299.
7 G. R. De Maré, *Bull. Soc. Chim. Belges, 81* (1972) 459.
8 Y. Inoue, S. Takamuku and H. Sakurai, *Bull. Chem. Soc. Jpn.*, *48* (1975) 3101.
9 Y. Inoue, M. Kadohira, S. Takamuku and H. Sakurai, *Tetrahedron Lett.*, *5* (1974) 459.
10 N. Antheunis and G. R. De Maré, unpublished results, 1974.
11 Y. Inoue, K. Moritsugu, S. Takamuku and H. Sakurai, *J. Chem. Soc., Perkin Trans. II*, (1976) 569.
12 S. Takamuku, K. Moritsugu and H. Sakurai, *Bull. Chem. Soc. Jpn.*, *44* (1971) 2562.
13 Y. Inoue, S. Takamuku and H. Sakurai, *Bull. Chem. Soc. Jpn.*, *49* (1976) 1147.
14 G. J. Collin and H. Deslauriers, *Can. J. Chem.*, *61* (1983) 1970.
15 Y. Inoue, S. Takamuku and H. Sakurai, *J. Chem. Soc., Perkin Trans. II*, (1977) 1635.
16 Y. Inoue, S. Takamuku and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, (1975) 577.
17 W. Adam, T. Oppenländer and G. Zang, *J. Am. Chem. Soc.*, *107* (1985) 3921.
18 Y. Inoue, T. Mukai and T. Hakushi, *Chem. Lett.*, (1982) 1045.
19 W. Adam and T. Oppenländer, *J. Am. Chem. Soc.*, *107* (1985) 3924.
20 R. Srinivasan and K. H. Brown, *J. Am. Chem. Soc.*, *100* (1978) 4602.
21 R. Srinivasan and K. H. Brown, *Tetrahedron Lett.*, *39* (1978) 3645.
22 P. J. Kropp, J. D. Mason and G. F. H. Smith, *Can. J. Chem.*, *63* (1985) 1845.
23 H.-P. Schuchmann, C. Von Sonntag and R. Srinivasan, *J. Photochem.*, *15* (1981) 159.
24 M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, (1961) 3547.
25 R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, 1970.
26 D. C. Tardy, R. Ireton and A. S. Gordon, *J. Am. Chem. Soc.*, *101* (1979) 1508.

27 S. W. Benson, *Thermochemical Kinetics*, Wiley, New York, 1976, 2nd edn., pp. 108 - 114, 140.
28 R. E. Townshend, G. Ramunni, G. Segal, W. J. Hehre and L. Salem, *J. Am. Chem. Soc.*, *98* (1976) 2190.
29 J. K. Crandall and R. J. Watkins, *J. Org. Chem.*, *36* (1971) 913.
30 T. R. Fields and P. J. Kropp, *J. Am. Chem. Soc.*, *96* (1974) 7559.