185-nm Photochemistry of Olefins, Strained Hydrocarbons, and Azoalkanes in Solution

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185-nm Photochemistry of Olefins, Strained Hydrocarbons, and Azoalkanes in Solution

By Waldemar Adam* and Thomas Oppenländer

Dedicated to Professor Dietrich Schulte-Frohlinde on the occasion of his 60th birthday

The possibility to excite *directly* at 185 nm chromophores that absorb in the vacuum-UV has stimulated increased activity during the last decade in this field of photochemistry. Whereas photochemical reactions at $\lambda < 200$ nm have been thoroughly investigated in the gas phase, only recently have intensive studies on the 185-nm photochemistry of organic compounds in *solution* provided new insights. Despite the high excitation energies, *selective* photoreactions are promoted in the short-lived singlet excited states (Rydberg photochemistry). In contrast to conventional photochemistry ($\lambda > 220$ nm), 185-nm irradiation preferentially results in *intramolecular* rearrangement, fragmentation, and isomerization reactions. Intermolecular radical couplings and abstractions as well as dimerizations (π,π^*-excitation) compete minimally. Besides the straightforward denitrogenation of photoresistant ("reluctant") azoalkanes, important applications of the short-wavelength photolysis are also found in technology (photolithography) and medicine (193-nm laser). Broadening the scope of the synthetic potential of the 185-nm photochemistry, which so far has been limited to direct *cis/trans* isomerizations, presents a challenge for the chemist.

1. Why 185-nm Photochemistry?

The photon as a "reagent" plays an important role in synthetic organic chemistry. During the last 15 years this has been particularly exemplified in the elegant syntheses of ring systems, especially four-membered rings and natural products.[1] The development of new photochemical equipment makes it possible to perform photoreactions over a wide range of wavelengths. For example, the continuous output of a synchrotron extends from the near infrared to X-ray radiation.[2]

For the organic chemist, however, it is essential to perform photochemistry as economically as possible. In 185-nm photochemistry this is accomplished by using Suprasil equipment and low-pressure mercury lamps. Such apparatus is comparably cheap and allows vacuum-UV photochemistry to be performed in solution[3] with *n*-pentane or other UV-transparent hydrocarbons as solvents. Despite the high excitation energy of 6.7 eV (647.8 kJ/mol), 185-nm photolysis of suitable substrates leads to defined products. Their formation can be rationalized according to defined mechanistic concepts. Besides the few preparative applications using 185-nm radiation, e.g., the syntheses of (*E*)-cyclooctene[4] and (*Z*)-2,2,5,5-tetramethyl-3-hexene ("di-*tert*-butylethylene"),[5] the main focus of research in

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this stimulating field of organic photochemistry is on mechanistic studies. One of the principle goals of these studies is to describe the nature of the electronic states that are reached by high-energy excitation with 185-nm photons.

Recently, *Srinivasan* et al.[6] investigated whether UV radiation ($\lambda < 200$ nm) could be used for practical purposes. For example, laser photolysis (193 nm) might prove useful for photolithographic processes or in medicine. Since the excess energy can be converted into the translational energy of small molecular fragments, a process called ablation, the surrounding material is not burned. In medical applications, this should be of considerable advantage over the usual laser techniques.

2. Mechanistic Concepts in 185-nm Photochemistry

Organic photochemistry with vacuum-UV radiation is not limited to the well-examined alkenes[3a, 7] and cyclopropanes.[8] Endoperoxides,[9] azoalkanes,[10] unsaturated ketones,[11] acetylenes,[12] alcohols, amines, ethers,[13] and trihalomethanes,[13f] and other bichromophoric systems such as oxacycloalkenes[14] and tetrahydropyridines[15] have been investigated in detail. Especially the degradation of halocarbons on 185-nm irradiation of aqueous solutions[13f] should acquire substantial significance in the treatment of waste water. The 185-nm photolysis of hexamethyldisiloxane[16] yields a multitude of photoproducts, the formation of which can be explained by means of radical intermediates. The gas-phase photolysis ($\lambda < 200$ nm) of olefins is described elsewhere.[17] However, there are significant differences[3c] between 185-nm photolyses in the gas phase and in solution.

The photoreversible $(Z)/(E)$ isomerization of cyclooctene,[18] which can be monitored by quantitative capillary gas chromatography, is the most commonly used chemical actinometer for the calibration of low-pressure mercury lamps. It is thereby possible to determine the absolute light output (I_0^{185}) of the UV lamp employed.[19] This method enables reproducible quantum yields Φ to be obtained for the diverse compounds employed in 185-nm photolyses.

In this article we present the mechanistic knowledge acquired during the last decade on 185-nm photochemistry in liquid media. Because mainly photoinduced isomerizations, rearrangements, and fragmentations have been investigated, we will limit the discussion to the intensively investigated olefins, cyclopropanes, and azoalkanes.

2.1. Olefins

Since the early studies by *Kropp* et al.[3d, 20] the formation of rearrangement products on 185-nm photolysis of olefins has been interpreted in terms of carbene intermediates. These are formed via a 1,2-carbon shift from the excited (π,3s) Rydberg state of the olefin (Scheme 1). Experimental evidence for the involvement of Rydberg states in vacuum-UV excitation of olefins is provided by nucleophilic trapping reactions[20, 21] with alcohols, leading to ethers (Scheme 1), and by the remarkable pressure dependence of the vacuum-UV spectra of alkenes.[22] Furthermore, on excitation with 185-nm photons, olefins exhibit a weak, but

measurable fluorescence[23] with quantum yields of about 10^{-4} to 10^{-6}. This fluorescence results presumably from the (π,3s) Rydberg state.
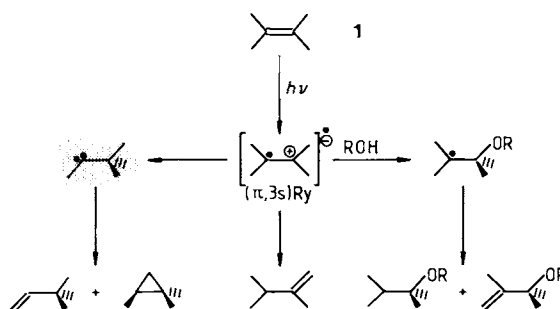
Scheme 1. Rearrangements and subsequent reactions of olefins such as 2,3-dimethyl-2-butene 1 on irradiation. Ry = Rydberg.

In contrast to the simple triplet-state photochemistry of olefins,[21] their photoreactivity on direct 185-nm excitation is often more complex. This is due to strong coupling of different excited states (Fig. 1). In spite of the similar energies of the π,π^*, (π,3s) Rydberg, and π,σ^*_{CH} singlet states of olefins (Fig. 1), distinct photoreactivity of each excited
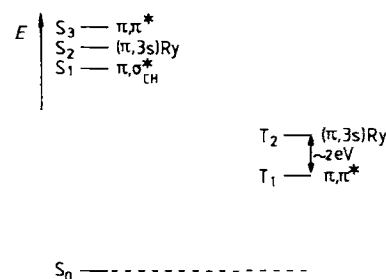

Fig. 1. Electronic states of olefins [21].

state can be observed. For example, the product distribution in the UV photolysis of 2,3-dimethyl-2-butene 1 is strongly dependent on the excitation wavelength.[24] Furthermore, there exists a direct connection between the wavelength dependence and the quantum yield of fluorescence[23] of the alkene. With increasing wavelength of excitation the chemical yield of the carbene products (Scheme 1) and the fluorescence quantum yield increase. This is a direct indication for the involvement of a Rydberg state as precursor to the intermediary carbene. The π,π^* excited state leads to $(Z)/(E)$ isomerizations and hydrogen abstractions.[24]

In general, the 185-nm photoreactivity of cyclic and bicyclic olefins can be summarized according to Scheme 2. Many examples that fit this scheme have been extensively investigated by *Inoue* et al.[3c, 25] and by *Srinivasan* et al.[3a] In monocyclic olefins a 1,2-alkyl versus a 1,2-hydrogen shift is clearly favored (93%).[3a] A typical, recently studied[26] example is cyclopentene, which reacts with the formation of bicyclo[2.1.0]pentane and methylenecyclobutane.
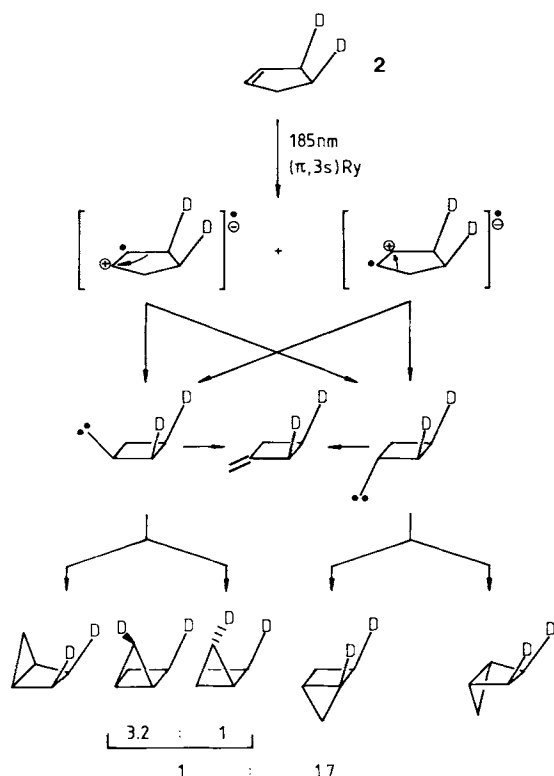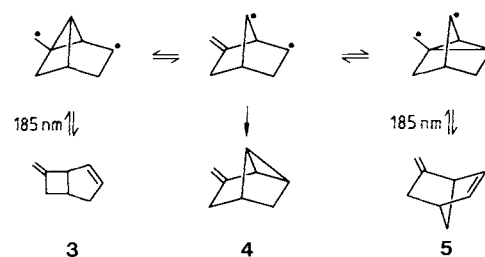
A carbene intermediate is in accord with the recent results of the 185-nm photolysis of *cis*-3,4-dideuteriocyclo-
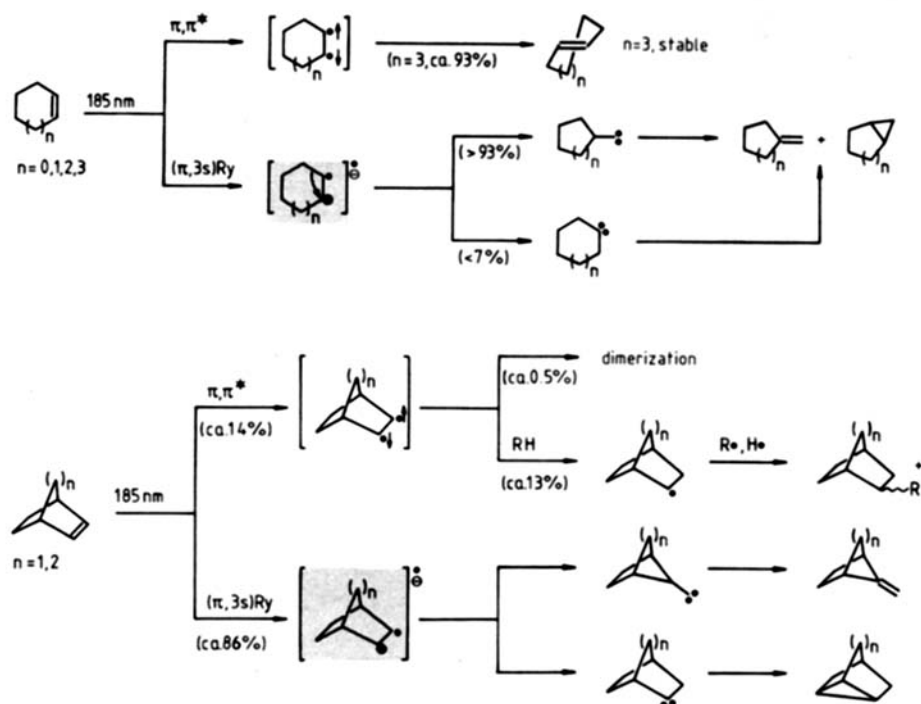
Scheme 2. 185-nm Photochemistry of mono- and bicyclic olefins [3a, 25].

pentene **2** (Scheme 3).[26e] In bridged bicyclic olefins (Scheme 2), however, both processes compete.[7,25] The bichromophoric diolefins **3** and **5** represent exceptions, because they rearrange efficiently into one another on 185-nm irradiation and transform irreversibly to the tricyclic compound **4**.[27] This photoreactivity does not correspond to that of Scheme 2, but rather involves di-π-methane rear-

rangements.[28] Carbene reactivity seems to be of no importance for such dienes.

The 185-nm photochemistry of annelated cyclobutenes **6**[29] can again be described according to the general mechanism of Scheme 2. The π,π* excited state of cyclobutene **6** undergoes Woodward–Hoffmann allowed electrocyclic ring opening[30] to give the 1,3-diene **7**. On the other hand, the (π,3s) Rydberg state rearranges to the carbene **8**, which subsequently fragments into acetylene and the cycloalkene **9**.[31]

Scheme 3. 185-nm Photochemistry of cis-3,4-dideuteriocyclopentene **2**.

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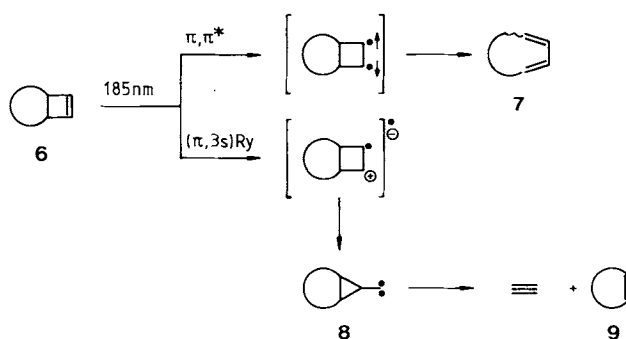
The 185-nm photolysis of cyclobutene[26a, d] provides important mechanistic insights into this process. The corresponding photoproducts can be rationalized in terms of the intermediacy of cyclopropylmethylene 10 and cyclobutylidene 11.[31] Additional evidence for these carbenes comes from comparison of the behavior of the thermally generated carbenes with those resulting from the 185-nm irradiation of olefins (Table 1). The similar product ratios of methylenecycloalkane to bicycloalkane in the 185-nm photolysis of the homologous alkenes and the thermolysis of the corresponding tosylhydrazones proves convincingly this conjecture.
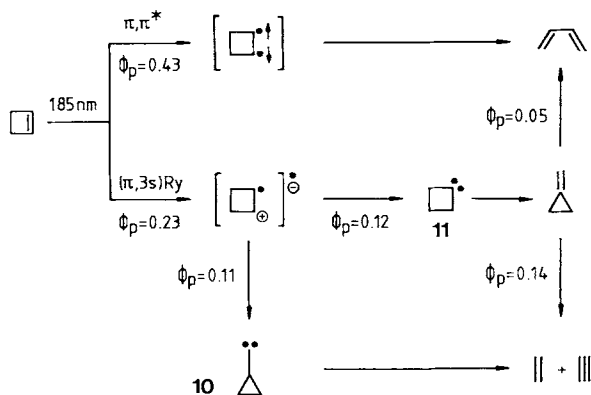
Table 1. 185-nm-Photochemistry of the homologous cycloalkenes A; formation of the bicyclic compounds C and the methylenecycloalkanes D from the cycloalkylmethylenes B.

n	Quantum yields			Product ratios	
	Φ_S [a]	Φ_P [b] C	Φ_P [b] D	$\Sigma \Phi_P$	D/C 185 nm	D/C therm. [c]
5	—	0.008	0.007	0.015	0.9	—
4	—	0.02	0.10	0.12	5.0	11.5
3	—	0.07	0.05	0.12	0.7	0.4
2	0.15	0.03	0.04	0.07	1.3	1.4
1	0.71	[d]	0.12	0.12	—	—

[a] Φ_S = quantum yield of substrate consumption. [b] Φ_P = quantum yield of product formation. [c] The cycloalkylmethylenes (carbenes) B were generated via basic decomposition of the corresponding tosylhydrazones [31]. The basic decomposition of cyclopropylcarbaldehyde tosylhydrazone did not lead to bicyclo[1.1.0]butane C, n = 1 [31]. [d] Not formed.

The essential step in the transformation of cyclopropenes such as 12[32] and allenes such as 14[33] on 185-nm irradiation corresponds to a cyclopropene–vinylcarbene
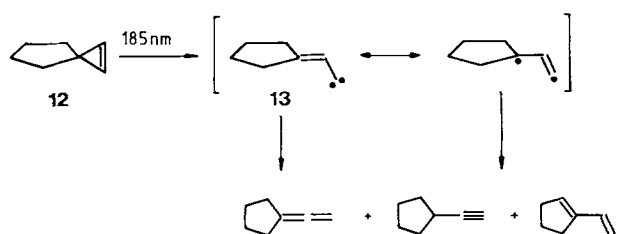
rearrangement.[34] The UV photolysis of spiro[2.4]hept-1-ene 12[32] yields as primary product the vinylcarbene 13, which rearranges to the observed photoproducts. Similar intermediates have been proposed in the 185-nm photolysis of vinylidenecyclobutane 14.[33] Besides the rearranged products that are formed from the two possible vinylcarbenes 15 and 16, butatriene and ethene are produced via a [2 + 2] cycloreversion.
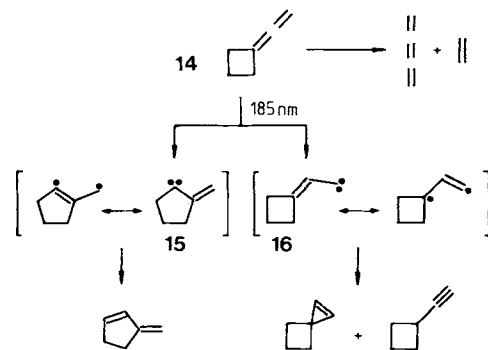
Intramolecular interactions between nonconjugated chromophores seem not to exist on 185-nm activation, but selective reactivity of the isolated chromophores can be observed. The 185-nm photolysis of 4-vinylcyclohexene 17[35] leads to products that are formed by selective excitation of the endocyclic double bond. The photoproducts
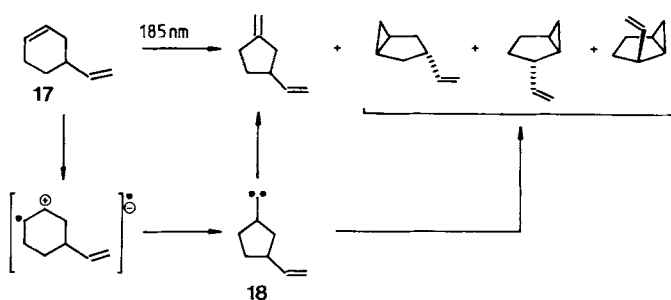
can be explained in terms of carbene 18. This carbene is formed from the (π,3s) Rydberg state of the cyclohexene double bond[35] since the photoproducts still contain the vinyl group intact. One would have expected a more complex product mixture had interaction between the chromophores in the excited vinylcyclohexene taken place.

Analogous selectivity can be observed in the 185-nm photolysis of γ,δ-unsaturated enones such as 19.[11] Instead
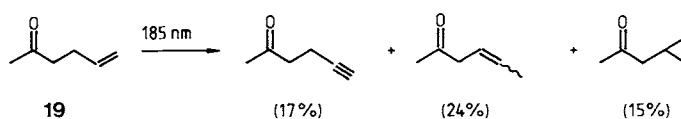
of the usual carbonyl photochemistry, such as intermolecular formation of oxetanes, the products are mainly derived from excitation of the C=C bond with preservation of the carbonyl functionality. Therefore, intramolecular energy transfer from the C=C bond to the carbonyl group is unlikely.[11]

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2.2. Cyclopropanes

Identification of the electronic state that is formed on 185-nm excitation of cyclopropanes is not easy. Besides very weak Rydberg transitions, cyclopropanes exhibit measurable σ,σ^* transitions in the vacuum-UV region.[36] The gas-phase photolysis (147 nm and 163 nm) of cyclopropane[37] itself yields ethene and methylene (69%) via cleavage of two C–C bonds. This type of fragmentation is favored as the main reaction path in the direct 185-nm photolysis of substituted cyclopropanes in solution[8] (Scheme 4).

The photoreactivity of alkylcyclopropanes is a function of the substitution pattern. 1,1-Disubstituted[8] as well as 1,2-disubstituted[38] mono- or bicyclic alkylcyclopropanes react mainly via breakage of two bonds of the cyclopropane chromophore. Spirocyclopropanes[8] and 1,1-disubstituted cyclopropane derivatives cleave principally to form methylene (path a, d; 23–52%), whereas the related process in 1,2-disubstituted cyclopropanes[38] (path e, f; ≦11%) competes very little with fragmentation into the corresponding substituted carbenes (path g, h; 57–85%). The theoretical calculations of *Rossi*[39] show that the cleavage of two C–C bonds is not concerted, but follows a stepwise

Scheme 5. 185-nm Photochemistry of 2,3-dideuteriobicyclo[2.1.0]pentane 20.

Scheme 4. 185-nm Photochemistry of 1,1- and 1,2-disubstituted alkylcyclopropanes [8, 38]. For (a)–(j) see text.

mechanism (paths a, c and a, d or paths e, f and g, h). Normally, the most substituted cyclopropane ring bond cleaves first. The stereoisomerization of *cis*-1,2-diethylcyclopropane[40] (path g, j; $R^1 = R^2 = Me$) takes place to about 10%, but it is of subordinate importance compared with the fragmentation process. Generally, the isomerization products, which are formed via cleavage of one C–C

bond of the cyclopropane chromophore (paths a, b and g, i), are clearly disfavored compared with the corresponding fragmentation products.

Bicyclo[2.1.0]pentane (cf. 20) behaves differently, because mostly (about 89%) homolysis of the bridge bond of the cyclopropane chromophore takes place (Scheme 5).[26a] This behavior was attributed to a Woodward-Hoffmann

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allowed [2 + 2] cycloreversion. Such a process is not possible in the higher homologous bicyclo[n.1.0]alkanes.

The efficient fragmentation of cyclobutanes on 185-nm excitation could be demonstrated for bicyclo[4.2.0]octane **21**.[26a, h] Possibly a radical cation mechanism can account for these fragmentations, because on 185-nm irradiation Rydberg transitions are possible. In contrast to bicyclo[2.1.0]pentane (cf. **20**), the homologous bicyclo[1.1.0]butane **22**[26a] fragments via one-bond and two-bond cleavages to the same extent.
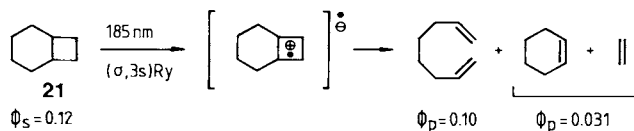
Srinivasan et al.,[26c] on the other hand, found by means of deuterium-labeling experiments a 10:1 ratio of butadiene and cyclobutene. Possibly, no corrections were made for the appreciable photolability of cyclobutene. However, the observed deuterium distribution in the photoproducts is in agreement with the results of *Adam* et al.[26d] and supports the mechanism shown in Scheme 6.
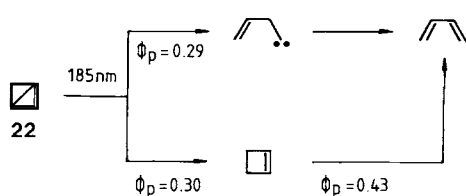
Scheme 6. 185-nm Photochemistry of bicyclo[1.1.0]butane **22**.

Comparison of the 185-nm photoreactivity of the homologous bicyclo[n.1.0]alkanes (Table 2) convincingly shows that bicyclo[2.1.0]pentane (n = 2) is a special case. The *exo/ endo* isomerization (Scheme 7)[26a] supports this fact. The isomerization is, however, quite inefficient ($\Phi_{iso} = 0.03$) compared with the fragmentation into 1,4-pentadiene ($\Phi_p = 0.16$) and with the formation of cyclopentene ($\Phi_p = 0.12$). Already these few examples show that the con-

Table 2. 185-nm Photochemistry of the homologous bicyclo[n.1.0]alkanes **A** to the cycloalkenes **B** and the 1,n + 2-alkadienes **C**.

n	Quantum yields			Product ratio	Homolysis [a] [%]	
	Φ_S	Φ_P B	Φ_P C	C/B	one-bond	two-bond
6	—	—	—	—	≈ 17	≈ 83
5	0.54	0.06	0.48	8.0	12	88
4	0.21	[b]	0.14	—	—	[c]
3	0.51	0.22	0.29	1.3	43	57
2	0.25	0.12	0.16	1.3	89	11
1	0.65	0.30	0.29	1.0	51	49

[a] One-bond and two-bond cleavages of the C—C bonds of the cyclopropane chromophore. [b] Not formed. [c] The fragmentation of two bonds of the cyclopropane chromophore seems to be the main reaction path [38].
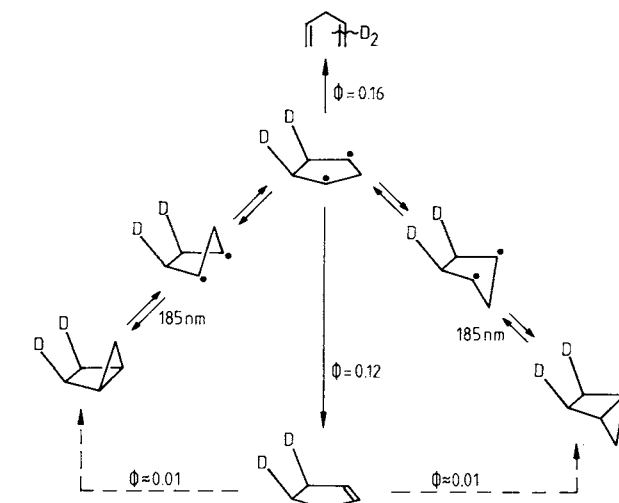
Scheme 7. Photochemical isomerization of *cis*-2,3-dideuteriobicyclo[2.1.0]pentane (cf. Scheme 3 and Scheme 5).

version of bicyclo[n.1.0]alkanes into the corresponding cycloalkenes on 185-nm irradiation seems to be a general reaction.

n = 1,2,3,4,5,6
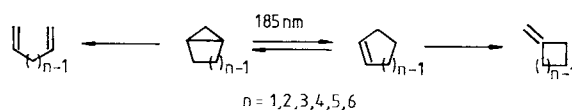
Surprisingly, the carbene elimination in quadricyclane **23**[41] plays an insignificant role, although **23** contains two cyclopropane chromophores. The formation of carbene **24** on 185-nm irradiation of quadricyclane could be reversi-

ble, so that re-addition to the double bond could regenerate the starting material and thereby account for the inefficiency ($\Phi = 0.02$) of this process.[41] The side products, 6-methylfulvene and 1,3,5-cycloheptatriene, are also formed in traces in the direct 254-nm (< 5%) and triplet-sensitized (< 0.5%) photolyses of quadricyclane. Therefore, the use of the quadricyclane–norbornadiene system as an efficient solar energy storage system[42] has been questioned.[41]
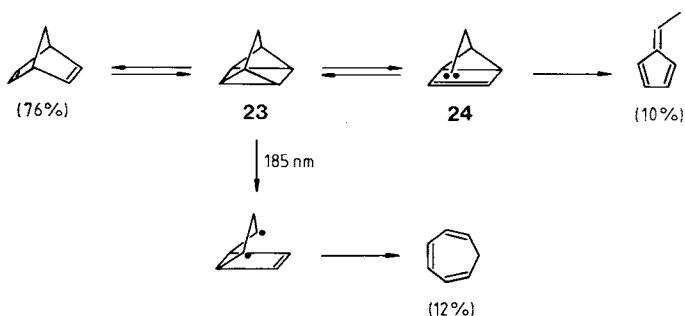
The 185-nm photolysis of compounds containing two different chromophores, e.g., cyclopropanes and olefins, provides evidence for intramolecular interactions between the excited chromophores and thus distinctive photochemical behavior of the excited states. The wavelength dependence of the UV photolysis of bicyclo[4.1.0]hept-3-ene **25**[43]

once again indicates that two or more different excited singlet states participate in one and the same molecule. Decreasing the photon energy (λ = 185, 193, and 214 nm) results in an increase of those products that are formed by selective excitation of the C=C bond of **25** and a corresponding decrease in the photoproducts derived from excitation of the cyclopropane chromophore. This observation becomes understandable when it is recognized that the first excited singlet state (S$_1$) of cyclopropanes lies higher in energy than the first singlet (π,3s) Rydberg state of olefins.[36]

185 nm

25

(16%)

(72%)

26
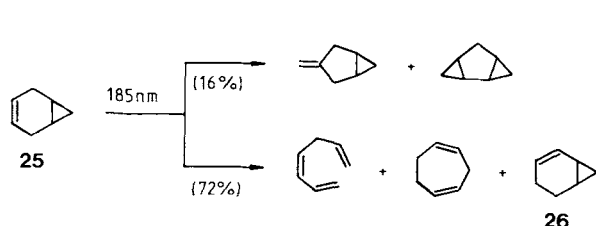
The formation of product **26** during photolysis of the bichromophoric compound **25** can possibly be rationalized in terms of an intermediary electronically excited 1,4-diene (cf. **27**).[44] The excited intermediate **27** undergoes subsequent di-π-methane rearrangement to the isomer [D$_2$]-**26**. Indeed, these interesting speculations about the reaction mechanism of the 185-nm photolysis of **25** were verified through deuterium-labeling experiments.[44] Besides the formation of vibrationally excited or "hot" photoproducts,[40,45] an adiabatic reaction path is also possible.[46]

D$_2$

185 nm

[D$_2$]-25

di-π-methane rearrangement

[D$_2$]-26

electronically excited

27

deactivation
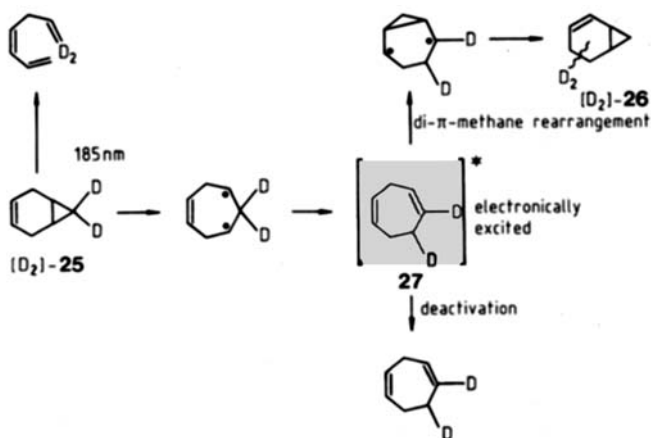
In contrast to these results, the product distribution in the 185-nm photolysis of bicyclo[4.1.0]hept-2-ene **26**[47] is independent of the excitation wavelength. In compound **26** the double bond is in conjugation with the cyclopro-

185 nm

26

(38%)

(7%)

(8%)

(9%)

(3%)

(7%)

28 (1-2%)

29 (12%)
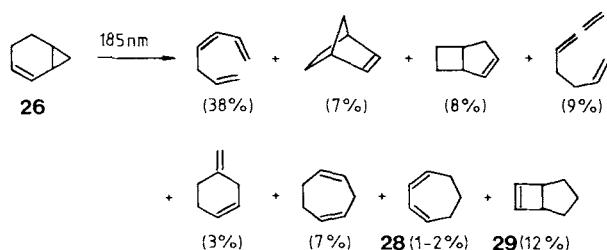
pane ring. Therefore, no differentiation between the olefin and cyclopropane reactivity should be expected. Consequently, the 185-nm photochemistry of **26** is more complex than that of its isomer **25**.

Analogous behavior is observed for 1,3-cycloheptadiene **28**,[47b] which, independent of the excitation wavelength (λ = 185, 229, or 254 nm), reacts mainly (88–99%) to give bicyclo[3.2.0]hept-6-ene **29**. However, substitution at C-7 in **26** with a methyl group (**30**) leads to exo/endo isomerization[48] as a side reaction.

CH$_3$

185 nm

CH$_3$

H$_3$C

30-exo

185 nm

30-endo
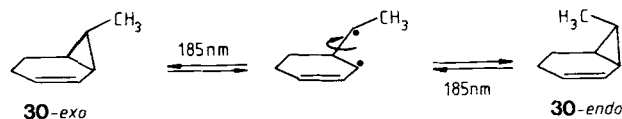
2.3. Azoalkanes

The thermal and photochemical reactivity of azoalkanes strongly depends on their structure.[49] Thus, to the group of photoresistant azoalkanes belong the structures **31** to **35**.[10,50] Their quantum yields of denitrogenation at the usual wavelengths (λ > 300 nm) are generally lower than

31

32

33

34

35
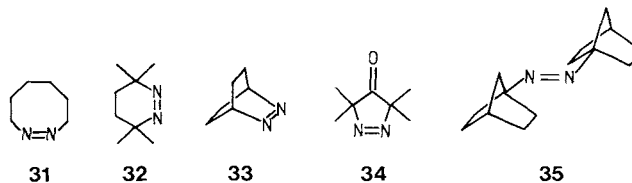
0.05.[51] In the case of six-membered azoalkanes, the quantum yield appears to be independent of whether the azo chromophore is part of a mono-, bi-, or polycyclic structure. The most important deactivation processes responsible for the photostability of these azoalkanes are fluorescence, radiationless deactivation, (Z)/(E) isomerization, intramolecular cyclizations, and phototautomerism.[52]

Photostable azoalkanes are of no synthetic value, because the crucial nitrogen elimination step cannot be realized to form the desired new C–C bond. A classical example for this is the attempt to synthesize cubane[53] by photolysis of diazabasketene **36**, which failed to undergo nitrogen elimination. As was shown in 1980,[51] the 185-nm photolysis of diazabasketene leads to efficient denitrogenation. However, instead of cubane,[54] cyclooctatetraene and benzene were formed. Moreover, the quantum yield of nitrogen elimination was about 1000 times higher at λ = 185 nm than at λ > 300 nm. 1,2-Diaza-1-cyclooctene **31**[26a,g] was recently shown to be effectively denitrogen-

185 nm

−N$_2$

Δ

36

+ HCN

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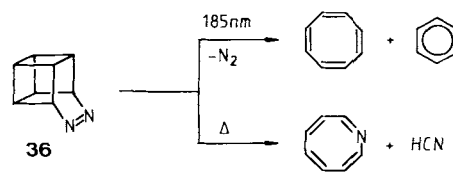
ated on 185-nm excitation. Again, the efficiency of the de-nitrogenation was increased by about 26- to 42-fold, depending on the configuration about the N=N bond.
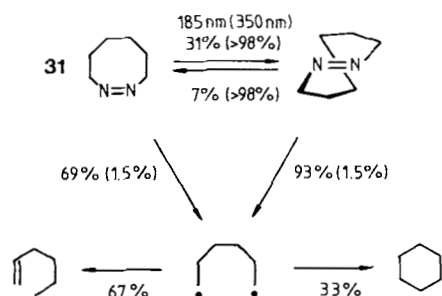
An interesting bichromophoric substrate is 3,3,5,5-tetra-methyl-3,5-dihydropyrazol-4-one **34**.[55] The 185-nm irradiation of **34** leads to denitrogenation and decarbonylation.[55] In this case the nitrogen elimination is six times more efficient than the CO elimination. The intermediary tetramethylcyclopropanone rearranges via ring opening to the enone or eliminates carbon monoxide to form dimethyl-2-butene.
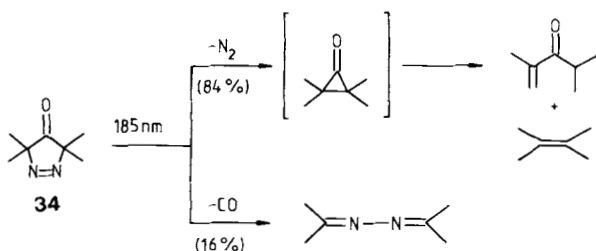
A definitive assignment of the excited states that are involved in 185-nm excitation of azoalkanes is difficult.[36,51] These may be π,π^*, n_+,π^*, n_+,σ^*, or diverse Rydberg transitions[56] (Fig. 2). Nevertheless, 185-nm photolysis of simple azoalkanes might enable predictions to be made about the excited states that are involved in such photochemistry. In this connection it is of interest that the 185-nm excitation of 2,3-diazabicyclo[2.2.1]hept-2-ene **37**[19a,26b] is quite

different from the 350-nm photolysis. In the latter case only traces (<1%) of cyclopentene could be identified, whereas bicyclo[2.1.0]pentane was formed in >99% yield. As shown in Figure 3, on 185-nm photolysis, denitrogenation affords considerable quantities of cyclopentene, presumably via zwitterionic species. Such intermediates should have a considerable influence on the product distribution.

From this perspective, the photochemistry of the bicyclic azoalkanes 2,3-diazabicyclo[2.2.1]hept-2-ene **38a**[57] and spiro[cyclopropane-1′,7-2,3-diazabicyclo[2.2.1]hept-2-ene] **38b**[58] and of their exo-dideutero derivatives was exam-

ined in detail. Depending on the reaction conditions of the denitrogenation, the azoalkanes **38** preferred to undergo double inversion to give the bicyclo[2.1.0]pentanes **39**.[57]
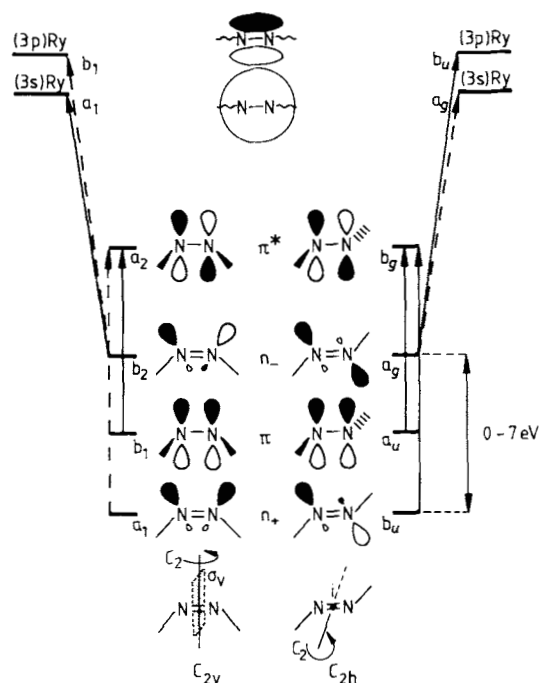
Fig. 2. High-energy electron transitions in (Z)- and (E)-azoalkanes. ⟶, symmetry-allowed transition; – – →, symmetry-forbidden transition.
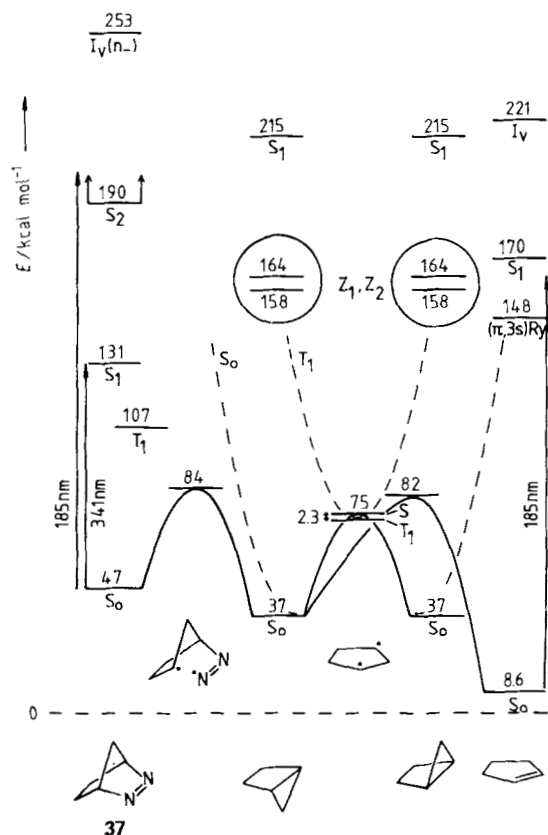
Fig. 3. Relative energies of 2,3-diazabicyclo[2.2.1]hept-2-ene, 37, bicyclo[2.1.0]pentane, and cyclopentene.

37, R=H
38, R+R=-CH₂-CH₂-

Δ/hν
-N₂

39-exo + **39**-endo + **40**

a, R=H ; b, R+R = -CH₂-CH₂-
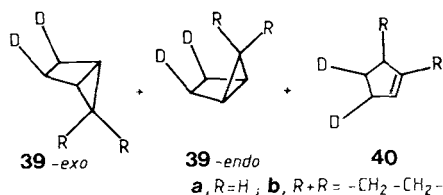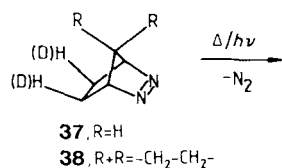
The rearrangement to the olefins **40** depends on the spin state and energy of the intermediary 1,3-cyclopentadiyl. In addition, the reaction path involving the zwitterionic species **41**, formed on 185-nm irradiation via concerted nitrogen elimination, might be possible.[26a]

41
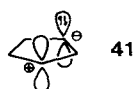
In the long-wavelength ($\lambda > 300$ nm) photolysis of **38**, one-bond cleavage was postulated,[26f] the initially formed diazenyl diradical subsequently loses nitrogen, giving 1,3-cyclopentanediyl. Presumably, in the long-wavelength ($\lambda > 300$ nm) photolysis of azomethane,[26j] the primary step also involves one-bond cleavage to the corresponding diazenyl radical. Thus, the 185-nm photochemistry allows valuable mechanistic insights to be obtained into the denitrogenation of azoalkanes.

Attractive substrates for the examination of intramolecular interactions of distinct chromophores are the tricyclic azoalkanes **42**.[59] Their 185-nm photolysis results in deni-

42

185 nm

43

1,2-shift | cyclization | fragmentation
<10% | >70% | <10%

44

185nm

a, R=R'=H ; b, R+R = -CH₂-CH₂-, R'=H ; c, R+R = R'+R' = -CH₂-CH₂-

trogenation and mainly formation of the tricyclic product **44**. In addition, the 1,3-diradical **43** undergoes a 1,2-carbon shift ($< 10\%$) and fragmentation ($< 10\%$), so that numerous photoproducts are formed.[59]

3. Prospects

On the basis of this brief review it is apparent that 185-nm photolysis *in solution*, still a rather young branch of organic photochemistry, offers a broad spectrum of challenging mechanistic problems. At first sight one gathers the impression that the complex product mixtures reflect a multitude of mechanistic processes. This is surely the case when hydrogen abstraction occurs and entry into the usual chemistry of free radicals ensues. However, the thorough mechanistic investigations of the last decade have shown that a definite regularity obtains in the behavior of the higher excited states that are reached on irradiation with 185-nm photons. The photochemistry of alkenes (Scheme 2), cyclopropanes (Scheme 4), and azoalkanes clearly supports this observation. However, when one considers what is still unknown about such complex photochemical processes, the gratifying progress appears quite modest. In order to motivate the interest of the novice as well as the expert, Table 3 summarizes those substances that have been investigated so far. Only a few purely radical processes have been included, because the main emphasis of this review concerns unimolecular transformations, such as isomerizations, rearrangements, and fragmentations, induced by means of 185-nm excitation.

Intensive efforts are required on all fronts before short-wavelength ($\lambda < 250$ nm) photochemistry achieves the status presently enjoyed by long-wavelength photochemistry ($\lambda > 250$ nm). Innovation is highly desirable, especially from the point of view of apparatus design. The present light sources (low-pressure mercury lamps) radiate mainly 254-nm light, so that many interesting problems, e.g., the behavior of substrates with coupled chromophores, can hardly be investigated. It is essential that convenient and efficient filters or monochromatic light sources with *sufficient* intensity be developed for such studies. Laser technology should provide important contributions. An ideal situation would obtain if a broad range of intense laser lines at regular intervals would become available in the 180- to 250-nm region, so that the wavelength dependence of the product formation could be assessed. Studies of this type are essential for recognizing the nature of the higher excited states, such as Rydberg, π-π*, and σ-σ* transitions.

This brings us to another problem, namely, the spectroscopy of the higher excited states. Despite some efforts,[36] our knowledge and understanding is rather modest in this area. Coupled with theoretical calculations, spectroscopic investigations (such as absorption, fluorescence, and photoelectron spectroscopy) on model substrates should be helpful.

Whether the 185-nm photochemistry will prove itself in preparative work is undoubtedly of interest to the organic chemist. Until now the utility has been modest, but 185-nm photochemistry represents presently the most direct and convenient entry into strained *trans*-cycloalkenes, e.g.,

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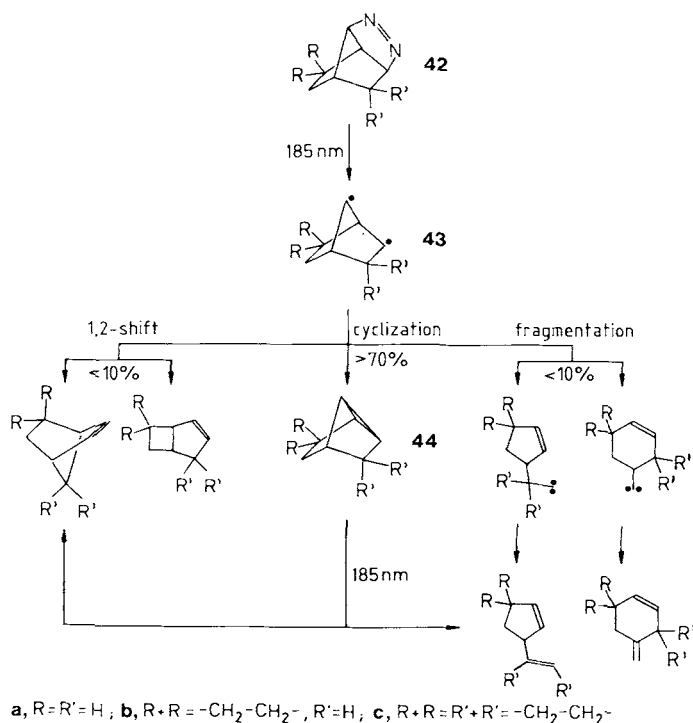
Table 3. 185-nm Photoreactions in *n*-pentane as solvent. The quantum yield Φ_P or the product yield is given for each product.

Substrate	Empirical formula	Photoproducts				Ref.
CH_3OD	CDH_3O	CH_4 0.05	CH_3CH_3 0.007	CH_2O 0.31	CH_3CH_2OH 0.025	[13d]
$CHCl_3/H_2O/O_2$	CCl_3H	CO_2 [a]	HCl [a]			[13f]
$CHBr_nCl_{3-n}/H_2O$ n=1,2,3		CO [a]	HBr [a]	HCl [a]		[13f]
	C_4H_6	0.43	0.12	$H_2C=CH_2$ 0.07	$HC\equiv CH$ 0.04	[26a]
	C_4H_6	0.05	<0.01	$H_2C=CH_2$ 0.08	$HC\equiv CH$ 0.06	[26a]
	C_4H_6	0.29	0.02	$H_2C=CH_2$ 0.03	$HC\equiv CH$ 0.02 □ 0.30	[26a]
	C_5H_8	0.04	0.03	0.01	C_5H_{11} 0.001 C_5H_{11} 0.006 $C_{10}H_{22}$ 0.005	[7,19a]
	C_5H_8	32%	7.5%	2%		[26b]
	C_5H_8	0.12	0.16	0.01		[19a,26]
	C_6H_8	30.2%	39.6%	30%		[45b]
	C_4H_6	0.054	0.044	0.078	$=== H_2C=CH_2$ 0.12 $\quad$ 0.14 $\quad$ 6%	[33]
	C_6H_{10}	0.05	0.07			[3a,c]
	C_6H_{10}	0.22	0.29			[8,26a]
$/O_2$	C_6H_{12}	OOH 70%	OH 18.3%	O 11.7%		[60]
	C_6H_{12}	2.6%	3.9%	38%	[a]	[24]
	C_6H_{12}	19%	4%	$C_{10}H_{22}$ 8%	$Me-\equiv-C_3H_7$ 5%	[3e]
	C_6H_{12}	$H_2C=CH_2$ 29%	29%	32%		[40]
	C_7H_8	76%	12%	10%		[41]
	C_7H_{10}	0.07	0.07	0.005	C_5H_{11} 0.24%	[0.06%]₂	[7]
		<<0.01%	0.01%	$C_{10}H_{22}$ 0.003		
	C_7H_{10}	$HC\equiv CH$ 0.054	0.16			[29]
	C_7H_{10}	38%	7%	8%	9% 3%	[47]
		7%	1-2%	12%		
	C_7H_{10}	11.6%	3.9%	16.7%	37.5% 17.4%	[43,44]
	C_7H_{10}	0.11	0.093	0.029		[32]
	C_7H_{10}	8.4%	42%			[59]
	C_7H_{10}	0.18	0.05	0.01		[26a]
	C_7H_{10}	88-99%				[47b]
	C_7H_{12}	0.10	0.02			[3a,c,25]
	C_7H_{12}	0.13				[8,38a]

Table 3. (Continued)

Substrate	Empirical formula	Photoproducts						Ref.
	C_7H_{14}	26%	24%	23%	27%			[40]
	C_7H_{14}	44%	44%	1%	2%	4%	6%	[40]
	C_7H_{14}	42%	46%	2%	[b]	10%	?	[40]
	C_8H_{10}	[a]	[a]					[46]
	C_8H_{10}	[a]	[a]	[a]				[46]
	C_8H_{10}	87%	13%					[27]
	C_8H_{10}	50%	50%					[27]
	C_8H_{12}	$HC\equiv CH$ [a]	0.15	0.053	0.018			[29]
	C_8H_{12}	27.6%	11.6%	37.8%	23%			[35]
	C_8H_{12}	12%	18%	3%	9%	33%		[48]
		5%	5%					
	C_8H_{12}	27%	16%	6%	6%	6% 14% 16%		[48]
	C_8H_{12}	0.20	0.01					[3a]
	C_8H_{12}	0.09	0.02					[3a]
	C_8H_{12}	0.74	0.35					[38a]
	C_8H_{12}	64-99%	3-10%	2-4%	0.5-1%			[47b]
	C_8H_{14}	0.03	[c]	$H_2C=CH_2$	0.10			[26a]
	C_8H_{14}	0.03	0.008	0.007	0.004	0.003 0.001 0.0001		[3c,4,18,19b]
	C_8H_{14}	84%	2.1%	3.6%				[3c]
	C_8H_{14}	52%	7%	14%	13%			[8]
	C_8H_{14}	0.06	0.48					[8,38a]
	C_8H_{16}	C_8H_{16} isomers 54%	18%					[11]
	C_8H_{16}	C_5H_{11} 15%	$C_5H_{11}\equiv-C_6H_{13}$ 18% 27%	$C_{10}H_{22}$ [a]				[3e]
	C_9H_{12}	[a]	[a]					[46]
	C_9H_{12}	[a]						[46]

Table 3. (Continued)

Table 3. (Continued)

Substrate	Empirical formula	Photoproducts				Ref.
	C_9H_{12}	12%	44%	12%		[59]
	C_9H_{12}	30%	5%	5% / 10% / 7%		[8]
	C_9H_{14}	0.16	0.25	$C_{10}H_{22}$ 0.034		[12]
	C_9H_{16}	≈ 83%	≈ 17%			[38b]
	C_9H_{18}	36%	5%	9%	C_9H_{18} 22%	[8]
$\triangleright$–C_6H_{13}	C_9H_{18}	13%	17%	7%		[8]
		4%	C_8H_{16} 17%	C_9H_{18} 9%		
n-C_8H_{17}–C≡CH	$C_{10}H_{18}$	n-C_8H_{17}–CH=CH$_2$ 0.14	$C_{10}H_{22}$ 0.034			[12]
n-C_4H_9–C≡C–n-C_4H_9	$C_{10}H_{18}$	0.10	0.16	$C_{10}H_{22}$ 0.068		[12]
	$C_{10}H_{20}$	40% (isolated)				[5]
	$C_{11}H_{14}$	21%	40%	1%		[59]
	$C_6H_{11}N$	74%	Me–N–Me / Me 22%			[15]
	$C_8H_{13}N$	[a]	Me–N–Me / Me [a]			[15]
	$C_8H_{13}N$	Me–N 〜〜 >90%				[15]
	$C_5H_8N_2$	0.26	0.23	0.03	<0.01	[19a,26]
	$C_6H_{10}N_2$	18%	9%			[51]
	$C_6H_{12}N_2$	N=N 0.14	0.20	0.11		[26a]
	$C_6H_{12}N_2$	N=N 0.03	0.25	0.13		[26a]
	$C_7H_8N_2$	44%	56%			[26a]
	$C_7H_8N_2$	34%	66%			[26a]
	$C_7H_{10}N_2$	0.22	0.11	<5%		[26a]
	$C_7H_{10}N_2$	8.1%	73%	4.9%	4.4%	[59]
	$C_8H_8N_2$	27%	4%			[51]
	$C_8H_{16}N_2$	22%	12%			[51]

Substrate	Empirical formula	Photoproducts				Ref.
	$C_9H_{12}N_2$	7.3%	77%	4.1%	3.9%	[59]
	$C_{11}H_{14}N_2$	5.4%	88%	2.5%	1.7%	[59]
	$C_{14}H_{22}N_2$	3%	4%	C_5H_{11} [c]		[10]
	$C_{16}H_{26}N_2$	5%	37%	0.3% C_5H_{11}		[10]
	$C_{18}H_{30}N_2$	3%	44%	0.2% C_5H_{11}		[10]
Ad–N=N–Ad [d]	$C_{20}H_{18}N_2$	Ad–Ad 12%	Ad–H 35%	Ad–C_5H_{11} 4%		[10]
	$C_7H_{12}N_2O$	N–N 15%	48%	29%		[55]
CH_3CH_2OH	C_2H_6O	H$_2$ [a]	CH_3CHO [a]	CH_3–CH–CH–CH$_3$ OH OH [a]		[13a]
	C_4H_6O	CHO [a]	$CH_3CH=CHCHO$ [a]			[14]
Me_3C–OH [e]	$C_4H_{10}O$	0.306	0.256	Me_3C–O– 0.059 / =O 0.031	OH 0.0044 / Me 0.001	[13a]
	C_5H_8O	CHO [a]	CHO [a]	[a]		[14]
	$C_6H_{10}O$	17%	25%	15%		[11]
	$C_7H_{10}O$	CHO [a]	CHO [a]			[13b]
	$C_7H_{12}O$	62%	4%	6%	2% / 2%	[11]
	$C_8H_{12}O$	CHO	CHO			[13b]
Me_3C–O–CMe_3	$C_8H_{18}O$	0.87	OH 0.84	+ 18 products		[13c]
	$C_{10}H_{18}O_2$	[a]	[a]	[a]	[a]	[9]

[a] Quantum yield or product yield unknown. [b] Traces detectable. [c] The product was not determined quantitatively. [d] Ad=1-Adamantyl. [e] In cyclohexane as solvent.

trans-cyclooctene, or sterically congested *cis*-alkenes, e.g., *cis*-2,2,5,5-tetramethyl-3-hexene ("*cis*-di-*tert*-butylethene").

For such synthetic problems, which until now could only be realized by means of long-wavelength photochemistry in an indirect manner, short-wavelength photochemistry offers attractive possibilities. We regard the future of 185-nm photochemistry optimistically. Undoubtedly, the main sphere of action will lie in mechanistic studies.

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