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Characterization of Methylenepropenylidenecyclohexadiene Derivatives and Their Competing 1,6-Electrocyclic Reaction and 1,7-Hydrogen Shift at Room Temperature

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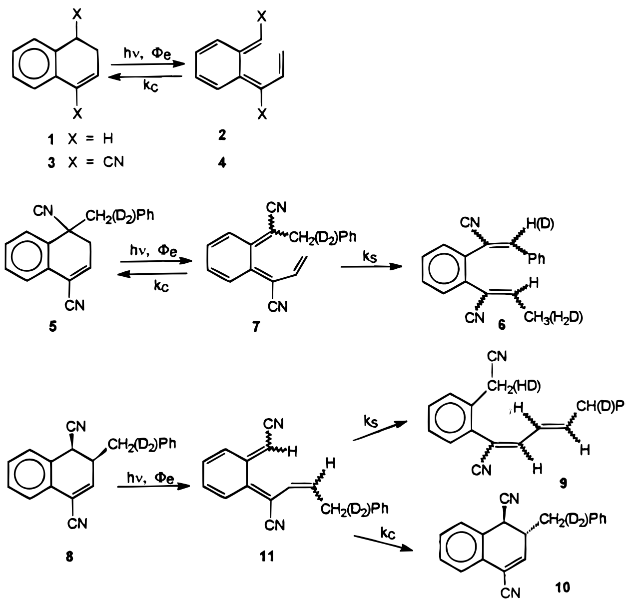
The interconversion between 1,3,5-hexatriene and 1,3-cyclohexadiene and related electrocyclic reactions have been the subject of many experimental and theoretical investigations.[1] Thermal processes have been thermodynamically and kinetically characterized and occur at relatively high temperatures.[1b,c] It is interesting to characterize a system where the process occurs at room temperature or below. Pentaene **2**, expected to be generated by photolysis of 1,2-dihydronaphthalene (**1**, Scheme 1), is an appropriate model, since there is a strong thermodynamic drive toward rearomatization. The photochemistry of compound **1**[2] and of several of its derivatives[3−8] has been thoughroughly investigated, and the many products reported have all been rationalized as arising from (thermal and photochemical) ring closure, cycloaddition, and (whith alkyl-substituted derivatives) sigmatropic rearrangements of *o*-xylylenes of type **2**.[2−8] However, the generation of polyenes of this type by the ring opening of fused cyclohexadienes has been directly documented only in the particular case of triphenyl-9,9a-dihydroanthracene.[9] It occurred to us that incorporation of conjugated substituents would allow direct observation of this compound and a better discrimination between the following reactions. We now report that polyenes of type **2** can be spectroscopically and chemimically characterized starting from some cyano derivatives of **1**.

The dinitrile **3**[10] underwent no irreversible reaction by irradiation in both polar and apolar solvents (λ 254 nm, $\Phi_{-\mathbf{3}} \leq 3 \times 10^{-3}$). However, flash photolyzing (λ 254 nm)[11] an acetonitrile solution of **3** resulted in a conspicuous end of pulse absorption between 370 and 500 nm (maximum at 450 nm, see Figure 1a). This was red-shifted by 60 nm with respect to parent *o*-xylylene[12] and closely correponded to that reported for its 1,8-diphenyl derivative.[9] Therefore, it was assigned to the 5-methylene-6-(2-propenylidene)-1,3-cyclohexadiene **4** (see Scheme 1). Assuming that the absorbtivity of this compound is close to that of *o*-xylylene[12] allowed a rough evaluation of the quantum yield for ring opening (Φ_e ca 0.1); this rearrangement is expected to occur in the picosecond range.[1e] The transient absorption showed a first-order decay, with $k = 4.2$ s^{-1} at 25 °C. Since no irreversible reaction occurs under this condition, this can be safely attributed to the thermally allowed cyclization ($k = k_c$, Scheme 1).

Scheme 1



Irradiation of the 1-benzyl derivative **5** caused an efficient reaction leading to the alkenes **6** as a mixture of the four (two main) stereoisomers (Scheme 1). No attempt to draw any conclusion for the isomeric distribution was made due to the easy *E*/*Z* isomerization of the alkene in steady state irradiations. When the α,α-D$_2$ derivative was used,[10] selective deuterium incorporation at the methyl group was observed (see Scheme 1). The quantum yield of reaction (see Table 1) was affected little by deuteration. Flash photolysis evidenced a transient with shape and intensity similar to the previous case (Figure 1b) but much shorter-lived and with a marked deuterium effect [k(H) $= 440$ s^{-1}, k(D) $= 80$ s^{-1}, D effect of 5.5]. These data show that the polyene **7** is formed and is the intermediate for the end products, which arise through a [1,7]-sigmatropic hydrogen shift. The efficiency of the photochemical ring opening is not greatly changed with respect to the conversion of compound **3** into **4** (Φ_e ca 0.1 in both cases). With **5**, this is near to the quantum yield for the irreversible reaction. Since there is no reason to expect that electrocyclic ring closure is significantly accelerated in this case, the fast decay observed for **7** is attributed to sigmatropic shift ($k = k_c + k_s \approx k_s$) in Scheme 1) with little contribution from the electrocyclic reaction. In accord with this mechanism, the deuterium effect shows up only on the decay rate of the intermediate, not on the steady state quantum yield of the final products [$\Phi = \Phi_e k_s/(k_c + k_s)$, where $k_s \gg k_c$] and is

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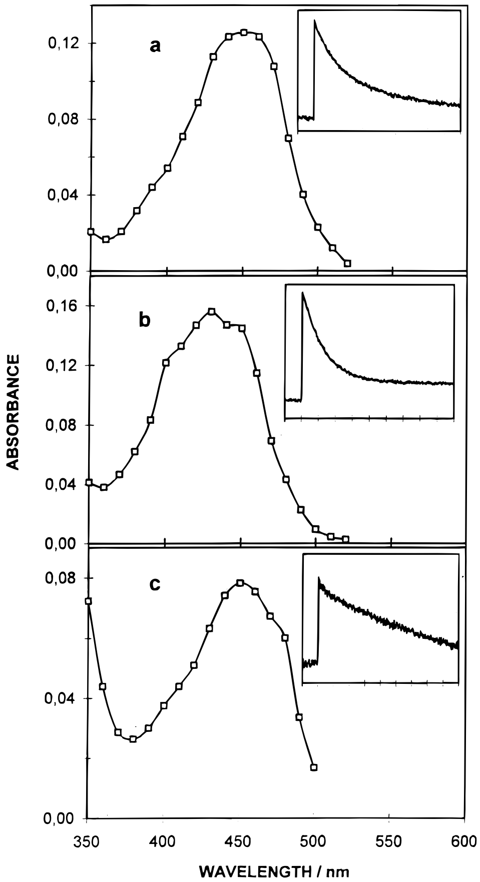

Figure 1. End of pulse spectra obtained by 266 nm flashing of the dihydronaphthalenes **3** (a), **5** (b), and **8** (c) in acetonitrile. Insets: kinetic trace for the decay at the absorbance maximum (a) for **3** at 450 nm, 100 ms per division; (b) for **5** at 430 nm, 10 ms per division; and (c) for **8** at 450 nm, 200 ms per division.

Table 1. Rate Constants (k) for the Decay of the Flash-Photolytically Observed Transients and Quantum Yield for Irreversible Quantum Yield (Φ)

substrate	k, s^{-1}	$\Phi_{-(\text{substrate})}$	product proportion
3	4.2	$\Phi_{-3} \leq 3 \times 10^{-3}$	
5	440 (80)[a]	$\Phi_{-5} = 0.13$ (0.115)[a]	**6** (100%)
8	0.8 (0.75)[a]	$\Phi_{-8} = 0.21$ (0.19)[a]	**9** (62%), **10** (38%)

[a] For **5**- or **8**-d_2.

close to that observed for the corresponding shift of octatrienes (6.4−7.7).[13,14] This is actually the expected value for a linear C−H−C geometry in the excited state.[15]

Irradiation of the *cis* 2-benzyl derivative **8** gave again a mixture of alkenes **9**, along with the isomeric *trans* dihydronaphthalene **10**. With the α,α-D_2 derivative, deuterium was selectively incorporated at the methylene group α to the cyano function (Scheme 1). Again, a transient was detected and attributed to polyene **11** (see Figure 1c). It was similar in intensity to the previous cases, and, thus Φ_e was ca 0.1 also in this case. However, the decay was slower than with **4** ($k = 0.8$ s^{-1}) and the deuterium effect was negligible within the experimental error. The steady state quantum yield (sum of that for isomerization and that for ring opening to **9**) was again close to Φ_e. In this case both reactions, thermally allowed disrotatory ring closure and sigmatropic H shift, lead to distinct products, respectively the *trans* 1,2-disubstituted dihydronaphthalene **10** and the alkenes **9**.[16] These occurred with a comparable efficiency. Thus, both k_c and k_s contributed significantly to the observed transient decay rate in this case, viz., electrocyclic cyclization competed with sigmatropic rearrangement with the polyene **11** but not with isomeric **7**. Furthermore, the latter reaction was ca 10^3 times slower with **11** than with **7** (see insets in Figure 1b,c). This could be rationalized as due to different conformations of the two compounds. MO calculations (semiempirical AM1)[17] showed that the energy minimum for **7** lay at a conformation well suited for hydrogen transfer with the benzylic hydrogen colinear with the relevant π orbital (in accord with the observed deuterium effect), whereas the minimun for **11** had the central C−C bond in the butadiene moiety rotated outward. Thus both electrocyclic and sigmatropic reactions were subjected to a conformational barrier.

In conclusion, methylenepropylidenecyclohexadienes are generated by photoinduced ring opening of 1,2-dihydronaphthalenes. There structure is supported by correspondence of the visible spectrum with expectation, as well as by the observed thermal reactions (ring closure with **4**, various rearrangement with **7** and **11**). Ring opening is a general reaction, since formation of a color upon irradiation of other derivatives of **1** has been previously reported.[3,7,8] Under the chosen condition, secondary photochemical reactions are avoided and thermal processes of these polyenes are cleanly observed. Thermal reclosure occurs at room temperature in tenths of seconds through one of the fastest known hexatriene ring closure reactions.[18] When there is an allylic hydrogen atom, a [1,7]-sigmatropic shift occurs and is by 2 orders of magnitude faster than the electrocyclic reactions. This is similar to the difference measured in non-benzo-fused trienes,[2b,c,14] but occurs here at room temperature and is many orders of magnitude faster. As it appears for **11**, in this temperature range a conformational barrier strongly hinders both reactions. The thermal and photochemical reactivity of the polyenes **4**, **7**, and **1** will be the subject of further quantitative studies.

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(16) The measured quantum yield for isomerization to **10** was a minimal value, since some *E*/*Z* isomerization of the alkene may have taken place during the steady state irradiation before reclosure..

(17) Austin M1.

(18) The only fastest related ring closure is that observed with the *o*-xylylene obtained from 9,9,10-triphenyl-9,9a-dihydroanthracene, see ref 9.