Direct Photolysis at 185—254 nm of Cyclo-octa-1,3-diene and Cyclohepta-1,3-diene. Wavelength-independent Photobehaviour

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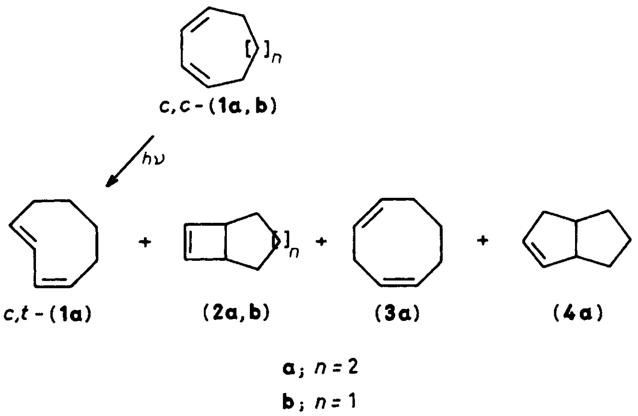
In sharp contrast to the wavelength-dependent photobehaviour of simple mono-alkenes, the photochemistry of conjugated dienes was found to be independent of excitation wavelength in the region 185—254 nm.

We have recently reported that the photochemistry of simple alkenes, *e,g,* 2,3-dimethylbut-2-ene and oct-2-ene, is wavelength-dependent in the solution phase, giving a different distribution of products in the wavelength range 185—228 nm.[1] This indicates that several excited singlet states of the alkenes are involved simultaneously, and that the photochemical processes compete well with internal conversion between the singlet states to give the corresponding photoproduct from each excited state. Srinivasan *et al.* have also shown that weakly interacting bichromophoric alkenes, including non-conjugated dienes, exhibit wavelength-dependent photobehaviour.[2] Thus, contrary to earlier assumptions,[3] the photochemistry of simple and of at least some bichromophoric alkenes appears to be wavelength-dependent, although the scope and limitations of this phenomenon are not fully established. In this context, it is important to reinvestigate the photochemistry of conjugated dienes in the light of the above-mentioned recent results, using a wide range of excitation wavelengths; such investigations should afford a further insight into the nature of the excited states of conjugated dienes. We now report results on the solution-phase photochemistry of *cis,cis*-cyclo-octa-1,3-diene [*c,c*-(**1a**)] and *cis,cis*-cyclohepta-1,3-diene [*c,c*-(**1b**)] at 185—254 nm.



Direct irradiation of pentane solutions of *c,c*-(**1a**) (10 mM) was performed at 185, 229, and 254 nm to give the *cis,trans*-isomer [*c,t*-(**1a**)] as the major product, along with smaller amounts of (**2a**)—(**4a**) (Table 1). Although the same photoreaction at 248 nm has been reported to give similar products,[4] the most significant finding here is that, in contrast to the wavelength-dependent photobehaviour of mono-alkenes[1] and non-conjugated dienes,[2] the product distribution at the early stage of the photoreaction is relatively invariant over the excitation-wavelength range of 185—254 nm and the relative importance of the products remains unchanged. Irradiation at 185, 229, and 254 nm of *c,c*-(**1b**) (10 mM) gave the cyclized product (**2b**) in excellent yield, but additional products were not formed, even at 185 nm.

This wavelength-independent photochemistry of the conjugated dienes is unexpected from previous work. The most unusual feature of conjugated dienes, compared with mono-alkenes or non-conjugated dienes, is the low-lying $\pi_2 \rightarrow \pi_3^*$ transition around 220—245 nm, while the $\pi_1 \rightarrow \pi_3^*$ or $\pi_2 \rightarrow \pi_4^*$ band is located at *ca.* 185 nm and the weak $\pi_2 \rightarrow$ 3s and $\pi_2 \rightarrow$ 3p Rydberg transitions also fall in the region 185—200 nm.[5] The wavelength-independent photobehaviour of the conjugated dienes may be rationalized by assuming that, unlike non-conjugated dienes and mono-alkenes, conjugated dienes do not afford any products from the upper excited singlet, which suffers instead very fast internal conversion to the lowest excited singlet (π_2, π_3^*) which in turn gives rise to the products. This assumption seems plausible since the good spatial overlap between the π_1–π_4 MOs in

Table 1. Direct photolysis at 185—254 nm of *c,c*-(**1a**) and *c,c*-(**1b**) in pentane.

	Irradiation[a]			Yield (%)[b]			
Alkene	λ/nm	Time/min	Conv. (%)	*c,t*-(**1**)	(**2**)	(**3**)	(**4**)
c,c-(**1a**)	185	60	18	79	4.0	1.9	[c]
		120	38	62	7.8	2.6	0.5
	229	5	7	87	8.1	[d]	[d]
		20	21	83	10	1.9	[c]
	254	20	19	89	3.2	2.8	0.6
		120	44	64	10	4.0	1.0
c,c-(**1b**)	185	20	11	[c]	88	[c]	[c]
		60	30	[c]	92	[c]	[c]
	229	5	23	[c]	98	[c]	[c]
		10	46	[c]	93	[c]	[c]
	254	10	33	[c]	95	[c]	[c]
		20	68	[c]	96	[c]	[c]

[a] Light sources; 185 nm: 30 W mercury resonance lamp fitted with an Acton 185N interference filter; 229 nm: 16 W cadmium resonance lamp; 254 nm: 30 W mercury resonance lamp fitted with a Vycor filter. [b] Chemical yield based on the diene consumed. [c] <0.5% yield. [d] Yield not determined owing to the low conversion.

conjugated dienes may facilitate the internal conversion between the π,π* singlets, although the internal conversion between π,π* and π,3s or π,3p singlets will be much slower owing to their minimal spatial overlap, as is the case with mono-alkenes. The present results suggest also that the photochemistry of biologically interesting polyenes, *e.g.* retinal and precalciferol, should be wavelength independent as far as the π,π* excitation is concerned. This seems essential for biological systems, since wavelength-dependent photochemistry giving unexpected product(s) may result in malfunction.

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