

PHOTOCHEMISTRY OF β -IONYLIDENEACETONITRILE AND RELATED COMPOUNDS.

DIRECT CONVERSION OF A CYCLOHEXADIENE TO TRANS-HEXATRIENE.¹

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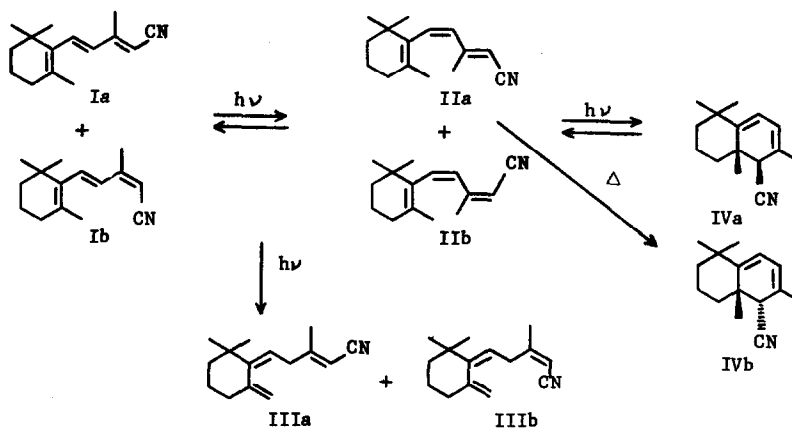
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Photocyclization of butadiene giving excited cyclobutene is highly endothermic thus energetically an unlikely process,³ while on symmetry grounds the process is an allowed one.⁴ It is now believed that the spectroscopic excited state of cyclobutene is not involved in this photocyclization reaction.^{3b} Clearly, the reverse reaction is not restricted on energy ground. It will, therefore, be interesting to examine experimentally whether ring opened products are indeed formed initially in an electronically excited state.

During our course of studies of reactions of ionyl and ionylidene compounds, we have examined in some detail the photochemical electrocyclic reaction of hexatriene and cyclohexadiene. The ring opening reaction is again both energetically and symmetry allowed. The cyclohexadiene system also absorbs in a more convenient range for experimental work. Our results described below appears to demand the explanation of formation of excited triene as the initial step of the photo-reaction.

Direct irradiation (2537 Å) of hexane solution of an isomeric mixture of 7-trans- β -ionylideneacetonitrile (Ia,b) leads to facile geometric isomerization to the 7-cis isomers (IIa,b)⁵ with concurrent accumulation of isomeric irreversible products from 1,5-sigmatropic hydrogen migration (IIIa,b).⁶ Another isomeric compound appears after significant accumulation of the 7-cis trienes. Its formation is reversible. After prolonged irradiation all triene

isomers and the new product are converted to a mixture of III. The new product is a cyclohexadiene with the structure shown (IVa). The epimer of IVa, IVb, is not present in the



irradiation mixture⁷ but can be obtained from thermal cyclization of IIa. The structures of all the compounds were assigned based on their spectroscopic data. The characteristic features in nmr spectra are summarized in Table I.

Table I. Characteristic NMR Absorption Peaks
in Compounds I-IV^{a,b}

Compounds	Characteristic Proton Signals (δ')				
	5-CH ₃ or exo-methylene	H ₇	H ₈	9-CH ₃	H ₁₀
Ia	1.74	6.50(d)	6.08(d) J = 16 Hz	2.14	5.09
Ib	1.68	6.50(d)	6.68(d) J = 16	2.00	5.02
IIa	1.47	6.16(d)	5.98(d) J = 12	2.05	5.24
IIb		6.21(a)	6.48(d) J = 12	1.90	5.03
IIIa	4.50(1H,d) 4.91(1H,m)	5.11(t) J = 7	2.93(2H,d)	1.96	5.01
IIIb	4.58(1H,d) 4.91(1H,m)	5.11(t) J = 7	3.20(2H,d)	1.80	5.01
IVa		5.78	5.78	1.92	
IVb	1.11	5.70	5.82 J = 5.5	1.82	2.51

a. Taken on HA-100. b. Solvent = CDCl₃.

Compound IV allows us to examine the initial electronic state formed in the ring opening reaction. Hexane solutions of IVb were irradiated. The initial products formed are the isomeric triene nitriles, and again the hydrogen migration products become predominant after longer irradiation periods. The action plot of the photo-reaction is shown in Figure I.⁸ It

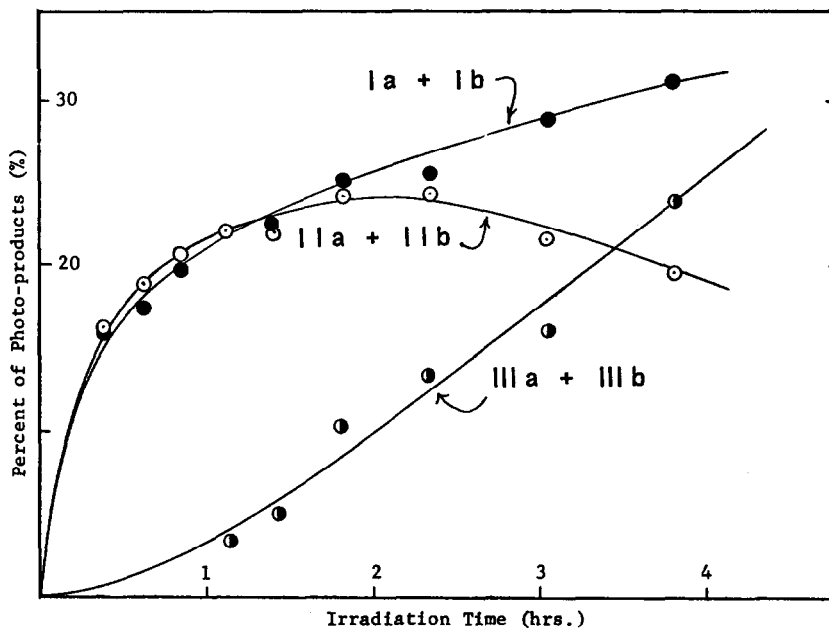
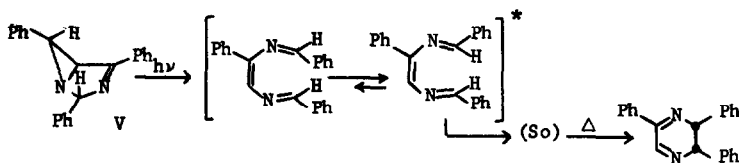


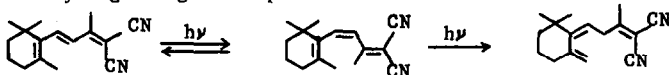
Figure I. Action plot of direct irradiation of IVb with 2537 Å

is immediately obvious that the two 7-trans isomers of the triene nitrile (Ia,b) as well as the 7-cis isomers are primary photoproducts, and not from secondary photo-isomerization of the latter. From symmetry grounds, direct formation of I from photo-ring opening of IV is, of course, not expected. The results, however, can be easily rationalized by assuming ring opening to cis-triene nitrile still in its excited singlet state. Formation of the 7-trans isomers is simply a natural consequence of chemical radiationless deactivation in the form of geometric isomerization. Therefore, what seem to be "two-photon" products are in fact formed with one quantum of light.

Interestingly, similar explanations can be used to account for several reported reactions. Central trans isomers of alloocimene were formed together with isomers from ring opening of α -pyronene.⁹ The conversion of diaza bicyclohexene V could involve direct formation of the isomerized enedimene followed by thermal ring closure.^{10,11}



References

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7. The epimer is not formed because IIb cannot exist in the required conformation for cyclization. Therefore we have found that the related dinitrile does not cyclize and only gives hydrogen migration products.
 
8. For clarity, only the sums of the isomeric pairs in I, II, III are shown. Plots with individual geometric isomers, expectedly, showed similar trend.
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