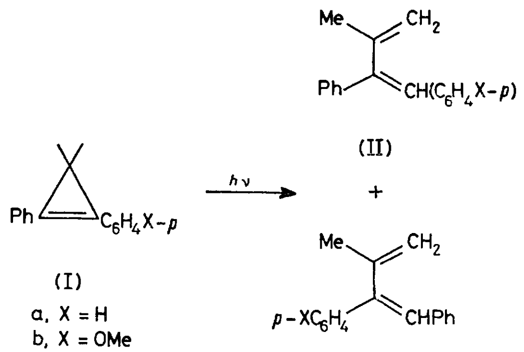
Electronic Excited States of Small Ring Compounds. Substituent Effects on the Photochemical Ring Cleavage of 3,3-Dimethyl-1,2-diarylcyclopropenes

By Richard M. Morchat and Donald R. Arnold*

(*Photochemistry Unit, Department of Chemistry, University of Western Ontario, London, Ontario* N6A 5B7 *Canada*)

Summary The mixture of dienes formed upon direct irradiation of 3,3-dimethyl-1,2-diarylcyclopropenes [1-phenyl-2-*p*-methoxyphenyl (Ib) and 1-phenyl-2-*p*-cyanophenyl (Ic)] indicates regioselective cleavage of the cyclopropene bond bearing the electron donating aryl ring.

Direct irradiation of 3,3-dimethyl-1,2-diphenylcyclopropene (Ia) leads to formation of the isomeric dienes (IIa) (*E* and *Z*). This reaction does not occur from the triplet state of (Ia) obtained by photosensitization (triplet–triplet transfer).[1] It seems likely, therefore, that the initial intermediate in this ring cleavage process is a singlet rather than the more stable triplet state.[2] We report here the irradiation of the *para*-methoxy and *para*-cyano derivatives (Ib and c) which were studied to define the factors which influence the ring cleavage process. The results are summarized in the Table. There is a marked preference for formation of the dienes which result from cleavage of the cyclopropene bond adjacent to the aryl ring which donates electrons.

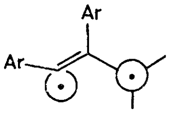


(I)

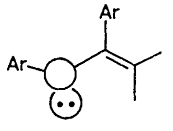
a, X = H
b, X = OMe
c, X = CN

(II)

(III)



(s′)



(s″)

TABLE. Substituent effects on the photochemical ring cleavage of 3,3-dimethyl-1,2-diarylcyclopropenes[a]

		(II)		(III)	
	Φ[b]	*Z*	*E*	*Z*	*E*
(Ia)[c]	0·045	75	25	—	—
(Ib)	0·046	26	48	11	15
(Ic)	0·048	<1	<1	62	38

[a] Irradiations were carried out at 10 °C through a $BiCl_3$ filter which absorbs wavelengths < 357 nm, in benzene–pyridine (9 : 1) solution. Product ratios were constant between 25 and 80% conversion. [b] Quantum yield for the disappearance of cyclopropene at low conversion, determined spectroscopically. The yield of dienes after complete conversion was high (> 90%) in every case. [c] See ref. 1.

The structure assignment of the new dienes rests upon analysis of their spectra (i.r., u.v., n.m.r., and mass) and combustion analysis. Furthermore, acid catalysed decomposition of the vinyl diazo precursors of the cyclopropenes gave (IIa—c). While acid catalysed decomposition of the cyclopropenes (Ia and c) also gave (IIa and c), (Ib) gave only (IIIb) under these conditions. This is consistent with protonation of the cyclopropene to give the more stable cyclopropyl cation which then opens to the allyl cation. Subsequent loss of a proton gives the observed dienes. The configuration of the isomeric pairs was established by observing a nuclear Overhauser effect; the 1-vinyl proton shows enhanced absorption upon irradiation of the allylic methyl of the isomers having the *Z*-configuration.

Detailed theoretical calculations have been carried out to characterize possible intermediates in the cleavage of the parent molecule, cyclopropene.[3] Two closely spaced planar singlets were recognized; a 1,3-diradical-like singlet (s′) which correlates with the ground state and is presumably involved in the thermal cleavage of cyclopropenes, and a lower-lying state, vinylcarbene-like (s″), which correlates with the cyclopropene excited singlet. The vinylcarbene can be viewed as the result of heterolytic cleavage and rotation of the dimethylmethylene carbon. Both electrons occupy an in-plane (σ) orbital with only two electrons in the conjugated π-orbital. In view of the rather low quantum yields for the ring cleavage and the likelihood that the process is reversible[4] it is difficult to attribute the observed variation in product ratio to one particular step. Nevertheless, as the parent molecule can serve as a model for heavily substituted derivatives, these concepts can be used to explain the observed regioselectivity.

In the vinylcarbene intermediate (s″) the aryl ring on the carbene carbon would be conjugated with the electron deficient π-system. The observed product distribution then follows the expected stability of the alternative vinylcarbenes; that is, *para*-methoxyphenyl is favoured relative to phenyl and phenyl is favoured over *para*-cyanophenyl at the carbene carbon. An alternative explanation suggested by Padwa to explain related results is less readily applied since it requires knowledge of the substituent effect acting inductively on the stability of the adjacent vinyl radical.[5] Furthermore, Padwa discusses the problem in terms of the 1,3-diradical-like intermediate (s′) which correlates with the ground not the excited singlet state.

This work was supported by the National Research Council (Canada).

(*Received, 27th April* 1978; *Com.* 443.)

---

[1] J. A. Pincock, R. Morchat, and D. R. Arnold, *J. Amer. Chem. Soc.*, 1973, **95**, 7536.

[2] D. R. Arnold, R. W. Humphreys, W. J. Leigh, and G. E. Palmer, *J. Amer. Chem. Soc.*, 1976, **98**, 6225.

[3] J. H. Davis, W. A. Goddard III, and R. G. Bergman, *J. Amer. Chem. Soc.*, 1976, **98**, 4015; 1977, **99**, 2427; L. Salem and C. Rowland, *Angew. Chem. Internat. Edn.*, 1972, **11**, 92; J. A. Pincock and R. J. Boyd, *Canad. J. Chem.*, 1977, **55**, 2482; S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, 1969, **14**, 305.

[4] J. A. Pincock and A. A. Moutsokapas, *Canad. J. Chem.*, 1977, **55**, 979.

[5] A. Padwa, T. Blacklock, D. Getman, and N. Hatanaka, *J. Amer. Chem. Soc.*, 1977, **99**, 2344.