

Regioselectivity in the Di- π -methane Rearrangement; Alternative Processes in the Photochemistry of Halogeno-1,4-dienes

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Summary In the di- π -methane rearrangement, the order of migratory preference is: dihalogenovinyl > diphenylvinyl > dicyanovinyl; a new photorearrangement of 1,4-dienes and a novel rearrangement occurring during photoaddition of benzophenone to a 1,4-diene are reported.

THE regioselectivity of the di- π -methane rearrangement¹ of 1,4-dienes such as (1) is ascribed to the relative abilities of the terminal substituents to stabilise the carbonyl centres in the cyclopropyldicarbonyl species (A). If substituent X is more stabilising than phenyl, cleavage of bond a leads to (2), whereas if phenyl is more stabilising (3) is formed *via* cleavage of bond b.

Direct irradiation† of each of the dienes (**1a—d**) led to regioselective formation of a single vinylcyclopropane in each case. The dicyanodiene (**1a**) rearranged by diphenylvinyl migration, rather than dicyanovinyl, to yield (**2a**). In contrast, the halogeno-dienes (**1b**), (**1c**), and (**1d**) underwent dihalogenovinyl migration, rather than diphenylvinyl, to form (**3b**), (**3c**), and (**3d**), respectively. This sequence of migratory preferences (*i.e.* dihalogenovinyl > diphenylvinyl > dicyanovinyl) shows that the order for stabilisation of the carbinyl centres in the cyclopropyl-dicarbonyl species (**A**) ($X = \text{cyano or halogeno}$) is cyano > phenyl > halogeno.

Sensitised irradiation† of the dicyanodiene (**1a**) and difluorodiene (**1b**) does not lead to formation of (**2a**) or (**3b**), respectively. Hence these dienes undergo di- π -methane rearrangement from their singlet excited states. Benzophenone sensitisation† of (**1a**) led to no reaction, whereas a benzophenone adduct was formed from (**1b**). Structure (**4**) has been assigned to this adduct, formation of which involves skeletal rearrangement. A likely mechanism for its formation involves attack by benzophenone triplet at the difluoromethylene group of (**1b**) to yield the bridged biradical (**B**) which then rearranges to (**4**). An alternative possibility utilising the triplet biradical (**C**) to attack benzophenone seems implausible² since ring closure of (**C**) to form (**2b**) would be expected to compete effectively with benzophenone addition. The vinylcyclopropane (**2b**) was not formed under conditions of either direct or sensitised irradiation.

The triplet excited‡ dichlorodiene (**1c**) rearranged to the vinylcyclopropane (**3c**). Another isomeric compound, possibly the cyclopropene (**5c**) or the cyclobutene (**6c**)‡ was produced in low yields from (**1c**) under conditions of both direct and sensitised irradiation.

Though the dibromodiene (**1d**) did undergo di- π -methane rearrangement on direct irradiation,† the product (**3d**) was a minor one. The major reaction produced (**7**), absent from the sensitised reaction, by singlet excited state dehydrobromination. Another product (**5d**), produced in low yields from the direct and sensitised reactions,† was isomeric with (**1d**) and possibly may have either the structure (**5d**) or (**6d**).‡

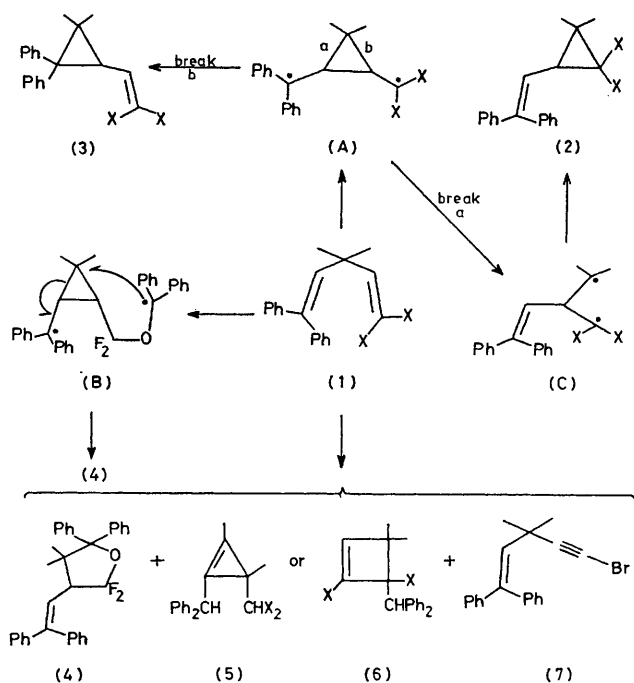
† Direct irradiations were carried out for solutions of (**1a**) in benzene, (**1b**) in cyclohexane, and (**1c**) and (**1d**) in *t*-butyl alcohol. Sensitised irradiations were carried out for solutions containing benzophenone in benzene. The halogenodienes also produced small amounts of other unidentified products as well as appreciable amounts of intractable oils.

‡ These compounds exhibit similar u.v. spectra [*e.g.* for the dibromide: λ_{max} (hexane) 220 (sh, ϵ 11,400), 252 (589), 259 (617), 265 (513), 269 (sh, 356), and 282 (180) nm] and very similar, disconcertingly simple, ¹H n.m.r. spectra [*e.g.* for the dichloride: δ (CCl₄) 0.87 (s, 3H), 1.26 (s, 3H), 4.98 (s, 1H), 5.97 (s, 1H), and 7.12–7.47 (m, 10H)]. Further structural proof for these compounds is being sought.

¹ H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, 1970, **92**, 6267; for a review of the rearrangement see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531.

² Different triplet *vs.* singlet regioselectivities for ring-opening of a cyclopropyl-dicarbonyl species such as (**A**) are rare, though not unknown: P. Baekström, *J.C.S. Chem. Comm.*, 1976, 476.

The formation of these cycloalkene products is not yet understood. They appear to be primary photoproducts, being detectable during the early stages of the reactions; control experiments show that they are not formed from photovinylcyclopropane precursors under the reaction conditions.



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