Comparison Between Ground and Excited State Reactivity of Cyclopropenes: Thermolysis and Far-U.v. (185 nm) Photolysis of Spiro[2.4]hept-1-ene

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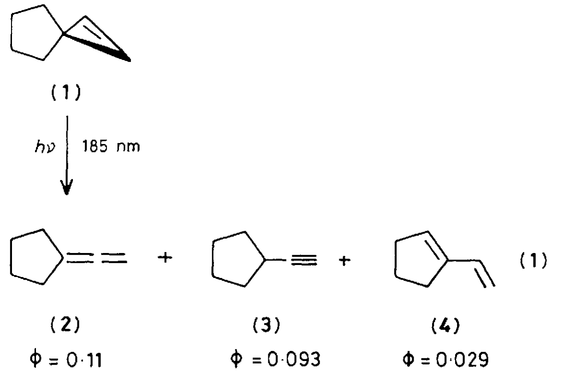
Differences in thermal and photochemical product distributions of spiro[2.4]hept-1-ene reflect state selective reactivity of S_0 and S_1 vinylcarbene intermediates.

The singlet photochemistry of cyclopropenes has continued to attract interest,[1–5] although efforts have largely been devoted to examples bearing substituents to provide a chromophore accessible at long wavelengths (λ >220 nm). Such substituents as phenyl, vinyl, or acyl on C(3) divert reactivity towards cyclization pathways forming indenes, cyclopentadienes, or furans, respectively. Only minor amounts of isomeric allenes are formed, and methylacetylene derivatives are conspicuously absent.[2–4] We report results of the solution-phase direct photolysis of spiro[2.4]hept-1-ene (**1**)† which exhibits reactivity intrinsic to the three membered ring, *i.e.*, isomerization to vinylidenecyclopentene (**2**), ethynylcyclopentane (**3**), and 1-vinylcyclopentene (**4**), equation (1). Additionally, a remarkable contrast is provided by the thermolysis of (**1**) which yields, instead, alkyne (**3**) and minor amounts of 1,3-diene (**4**) to the exclusion of allene (**2**) (Table 1). This difference in ground and excited state product distributions, we suggest, might reflect state selective reactivity of a vinylcarbene intermediate formed upon ring opening of the cyclopropene.

Direct photolyses of 10^{-2} M solutions of (**1**) in deoxygenated pentane where only the far-u.v. (185 nm) component of a low pressure mercury lamp (185 + 254 nm)[7] was absorbed† gave (**2**),[8] (**3**), and (**4**)[9] in yields of 34, 26, and 8.1%, respectively, as percentages of (**1**) which had reacted. Each product was isolated by preparative g.c. and identified by comparison of spectral data and g.c. retention times with authentic samples.‡[8,9] The yields cited were calculated from the ratio[7] {slope (product)/slope [(**1**) reacted]} × 100 using slopes from the linear portion of concentration *vs.* time plots at <8% conversions and, thus, reflect only primary photochemistry. Quantum yields were determined, equation (1), using *cis*-cyclo-octene as actinometer.[10]



Vapour phase thermolyses of (**1**) and (**2**) were conducted at 225 ± 2 °C in a sandbath using 12 × 120 mm thick-walled, base washed Pyrex tubes sealed at 10^{-2} mmHg. Reactions were quenched by quickly plunging the hot tubes into liquid nitrogen. Products (**2**)—(**4**), in yields summarized in Table 1, were identified by comparison (n.m.r., i.r., and g.c. retention times) with authentic samples.‡[8,9] The base prevented acid catalysis, resulting in abnormally high rates of disappearance of (**1**) and low yields (<10%) of (**3**) and (**4**) in a 1:3 ratio, respectively. Allene (**2**) was thermally stable (entry 4, Table 1), and its absence in pyrolyses of (**1**) cannot be due to decomposition or isomerization to (**3**) or (**4**).

The results for thermolysis of (**1**) are similar to those for 3,3-dimethylcyclopropene[11] which affords 3-methylbut-1-yne

Table 1. Yields from thermolyses of spiro[2.4]hept-1-ene (**1**) at 225 °C.

		Yield/%[a]				Conversion/
Reactant	Time/min	(**1**)	(**2**)	(**3**)	(**4**)	%
(**1**)[b]	20	67[d]	0	25	1.4	33
(**1**)[c]	30	56[d]	0	47	2.3	44
(**1**)[b]	60	28[d]	0	75	3.5	72
(**2**)[c]	60	0	97[d]	0	0	0

[a] Yields determined by g.c. using a 22 ft × ⅛ in column of 10% SP2100 on 100/120 mesh Supercoport at 90 °C. [b] Pyrex tube washed with conc. ammonium hydroxide and dried at 120 °C, 1 h. [c] Pyrex tube washed with ethanolic KOH and dried at 200 °C. [d] Recovered reactant.

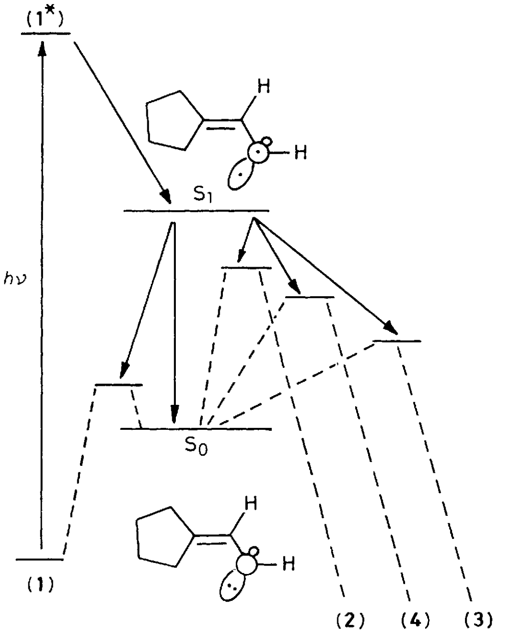


Figure 1. Pathways for decay of S_1 and reaction of S_0 vinylcarbenes.

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† Spiro[2.4]hept-1-ene, a new compound, gave satisfactory elemental analyses; n.m.r., ^{1}H, δ (CCl_4) 1.21—1.71 (m, 8H), 7.18 (quintet, *J ca.* 1 Hz, 2H); i.r. (CCl_4) 3.38, 3.48, 6.15, 6.92, and 9.80 μm; u.v. (pentane) λ 185 (ϵ 3311), 216 (1096), and 254 nm (<0.10). The synthesis was adapted from ref. 6.

‡ Ethynylcyclopentane was purchased from Alfa Products and purified by preparative g.c.

(90%) and 2-methylbuta-1,3-diene (10%), and are typical of the strong kinetic preference for methylacetylenes rather than allenes in pyrolyses of other cyclopropenes, *e.g.*, cyclopropene,[12] and its 1-methyl-,[11] and 1,3-diethyl-substituted[13] derivatives. The current mechanistic picture[1,12,14] for ground state reactivity involves reversible[12,13] ring opening to a σ^2 vinylcarbene (S_0 state)[15] followed by hydrogen migrations in a second rate-determining step. For the isomerization of cyclopropene to propyne (E_{act} = 37.5 kcal/mol[12]) and allene (E_{act} = 43.4 kcal/mol[12])§ the activation energies reflect the relative barrier heights of the 1,2-H shift processes.

To account for allene (**2**) as the major photoproduct, we suggest (Figure 1) ring opening of (**1***) to give an S_1 excited state of the vinylcarbene intermediate followed by radiationless decay to proximate maxima on the ground state surface corresponding to transition states in cyclopropene thermal isomerizations. The least favourable thermal pathway, that to (**2**), would offer the closest approach to the S_1 excited state potential surface and thus be photochemically preferred. A considerable fraction of the photoreaction, nonetheless, appears to derive from a contribution by the S_0 vinylcarbene since the thermolysis ratio of (**3**):(**4**) is not reversed. Finally, the thermolyses show that conversion of S_0 into S_1 vinylcarbenes does not occur.

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§ 1 kcal = 4.184 kJ.

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