

Preparation and Characterization of 6,6-Dimethylenefulvene

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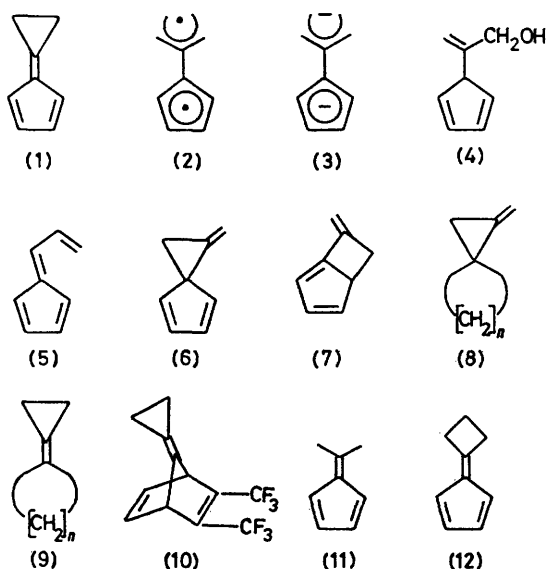
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Summary The highly strained cycloalkylfulvene, 6,6-dimethylenefulvene (**1**) has been generated *via* the gas phase pyrolysis of the spirotriene (**6**) and has been unambiguously characterized both spectroscopically and chemically.

A NUMBER of 6,6-cycloalkylfulvenes have been synthesized and spectroscopically characterized.¹ One of the most interesting of this series is the highly strained 6,6-dimethylenefulvene (**1**). The fulvene (**1**) is also a prime precursor of the trimethylenemethane biradical (**2**) which has been predicted by Herndon² to be representative of a class of

intermediates designated as 'closed shell' biradicals. This analysis also suggests stability for the dianion (**3**) in a manner reminiscent of the pentalene dianion.³

The fulvene (**1**) has been previously reported from the acid catalysed dehydration of the alcohol (**4**).⁴ Spectroscopically it was described only as an unstable red oil whose u.v. spectrum was strongly red shifted compared with other 6,6-dialkylfulvenes. This large red shift and the close similarity of the reported spectrum to that of 6-vinylfulvene (**5**) seemed quite remarkable. We therefore report the generation of (**1**) by another route and describe its spectral properties which differ significantly from those previously reported.⁴



yellow needles.† This material was subsequently identified as the desired fulvene (**1**) by its characteristic spectral data and chemical reactivity: ^1H n.m.r. δ (CDCl_3) 6.48 (m, 2H), 6.32 (m, 2H), and 1.40 (s, 4H); i.r. (CCl_4) 1770 cm^{-1} ; mass spectrum, m/e 108. The high frequency C-C stretching band at 1770 cm^{-1} is characteristic of cyclopropenes and methylenecyclopropanes and supports the assigned structure.⁷ Furthermore, reaction of (**1**) as a dilute solution in pentane with hexafluorobut-2-yne was rapid and quantitative to yield the Diels-Alder adduct (**10**): ^1H n.m.r. δ (CDCl_3) 6.97 (t, J 2 Hz, 2H), 4.31 (m, 2H) and 1.10 (brs, 4H); mass spectrum m/e 266. The u.v. spectrum of (**1**) was particularly interesting and showed a typical dialkylfulvene absorption with an intense, highly structured band centred at ca. 270 nm and a weaker broad band at 364 nm (Table).

TABLE

	$\nu_{\text{max}}/\text{cm}^{-1}$	$\lambda_{\text{max}}/\text{nm}$ (C_6H_{12})
(1)	1770	248sh, 256, 263, 273, 364
(5)	1625, 1596	277, 285, 295, 305, 395
(11)	1641	258, 265, 272, 281, 356
(12)	1680	260, 268, 277, 286, 360

We have recently described the synthesis of the spirotriene (**6**) by the low temperature photochemical cycloaddition of diazocyclopentadiene to allene.⁵ Since it is known that spirocyclic derivatives of the general type (**8**) can be thermally equilibrated *via* a formal 1,3-sigmatropic rearrangement with the tetrasubstituted olefins (**9**),⁶ this seemed to be a potential route to (**1**).

At 25°C in solution, (**6**) underwent a fast 1,5-sigmatropic ring expansion to the bicyclic triene (**7**)⁵ which promptly dimerized, rather than undergoing the desired 1,3-migration. However, when (**6**) was passed through a conditioned quartz tube at 400°C (0.04 mm), a new monomeric product crystallized in the cold trap (-78°C) as

It is significant that in spite of the considerable strain caused by the cyclopropane ring, the u.v. spectrum of (**1**) is extremely similar to those of the model dialkylfulvenes (**11**) and (**12**) and is strongly blue shifted relative to the conjugated isomer (**5**).

The fulvene (**1**) is stable at low temperatures as a crystalline solid or as a dilute solution in deoxygenated hydrocarbon solvents, but polymerizes explosively when warmed to room temperature as a neat liquid.

(Received, 11th January 1978; Com. 026.)

† Under these conditions none of the characteristic dimers (ref. 5) resulting from (**7**) could be detected in the pyrolysate.

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