Dispiro[2,2,2,2]deca-4,9-diene: Preparation and Reactions

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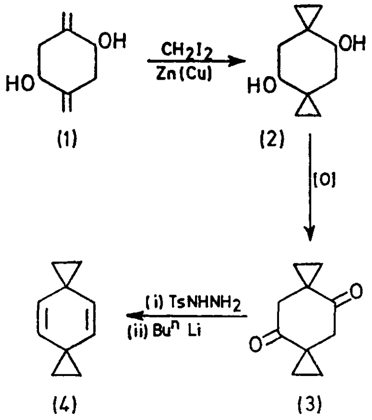
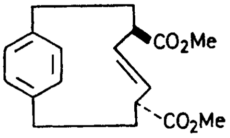
Summary Dispiro[2,2,2,2]deca-4,9-diene (**4**) is prepared and its chemical and physical properties are examined; the reaction with dimethyl *trans,trans*-muconate affords the cycloadduct (**5**).

De Meijere has recently reported the preparation of dispiro[2,0,2,4]deca-7,9-diene,[1] which has prompted us to report our results on the preparation and reactions of dispiro-[2,2,2,2]deca-4,9-diene (**4**), where the cyclopropane rings and the double bonds are aligned in the bisected conformation.[2]



2,5-Dimethylenecyclohexane-1,4-diol (**1**)[3] was cyclopropanated with methylene iodide and a Zn–Cu couple[4] to dispiro[2,2,2,2]deca-4,9-diol (**2**) (50%), m.p. 219—220°,† which was subsequently oxidized with Jones reagent[5] to the diketone (**3**) (69%), m.p. 81—82°. Treatment of the ditosylhydrazone of (**3**) with excess of Bu^{n}Li[6] afforded (**4**) as highly volatile, colourless plates melting at 121—122° (64%), *m/e* 132 (M^+); τ (CCl_4): 5·20 (s, 4H) and 9·33 (s, 8H). Alternatively, pyrolysis of the bisxanthate of (**2**) at 300° under reduced pressure also afforded (**4**). The compounds obtained from the two independent preparations were identical in all respects.



(5)

The u.v. maximum of (**4**), λ_{max} (n-hexane) 222 nm (log ϵ 4·30), is at a longer wavelength than that of tetracyclopropylethylene, λ_{max} (n-hexane) 219 nm (log ϵ 4·08).[7] However, the possibility of cyclic delocalisation of electrons in the six-membered ring in (**4**) is ruled out by the n.m.r. spectrum. The signal due to the olefinic protons of (**4**) (τ 5·20) appears at a higher field than that for the 4-H in spiro[2,5]oct-4-ene (τ 5·10).[8] Thus, no diamagnetic ring current is observed in (**4**).

Compound (**4**) was moderately thermally stable; its half-life at 160° was *ca.* 1 h. The major product of thermal decomposition in diglyme was *p*-diethylbenzene (75%).

Compound (**4**) reacted smoothly with dimethyl *trans,-trans*-muconate in benzene at 160° to give a colourless crystalline cycloadduct (**5**) (54%), m.p. 144—145°; *m/e* 302

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† Satisfactory analytical results were obtained for all new compounds.

(M^+).‡ Comparison of the n.m.r. and u.v. spectra with those of reported [8]paracyclophane derivatives[9] confirm the paracyclophane structure of (**5**).

This cycloaddition can be considered formally as a [$\sigma 2 + \pi 2 + \sigma 2 + \pi 4$] process, although it is not known whether the cycloaddition proceeds in a concerted manner or stepwise.

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‡ Though the stereochemistry of the product has not been fully established, the n.m.r. is best accounted for by the configuration in which the methoxycarbonyl groups are *trans* with respect to the 12-C ring, and the double bond on the bridge is also *trans*.

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