

Reductive Coupling of 6-Dimethylaminofulvenes furnishing 6,6'-Bifulvenyls

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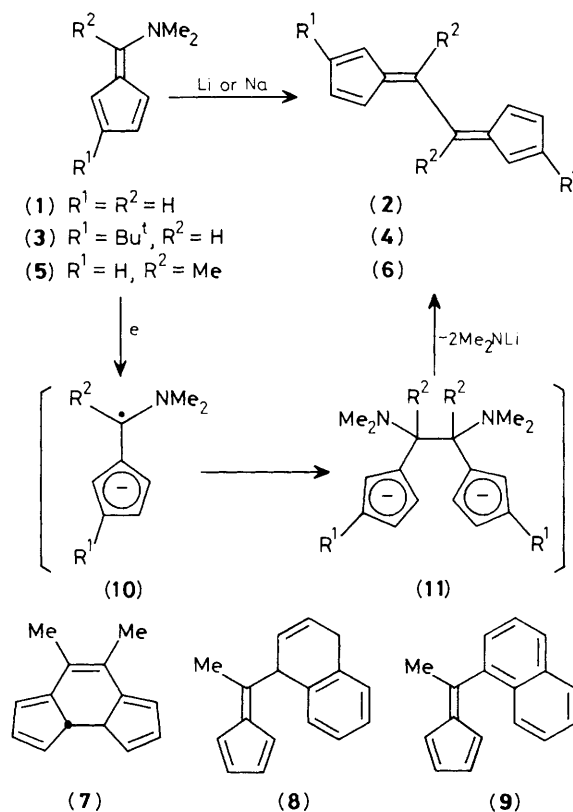
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Reaction of 6-dimethylaminofulvenes with alkali metals affords 6,6'-bifulvenyls or cyclised products thereof probably through coupling of their anion radicals at C-6 followed by deamination.

Alkali metal reduction of fulvenes has been reported to give, *via* anion radicals, an ethane-1,2-biscyclopentadienide arising from coupling at C-6, hydrocarbon dimers coupled in the five-membered ring, or dihydrofulvenes depending on the reaction conditions and the structure of the fulvene.¹⁻³ The synthetic utility of these reactions has not been greatly exploited, however, except for the preparation of a two-carbon bridged ferrocene.² We report here that alkali metal reduction of 6-dimethylaminofulvenes yields 6,6'-bifulvenyls (1,2-biscyclopentadienylidene ethanes) or dihydro-*as*-indacenes derived therefrom, providing a novel and simple method for synthesising these compounds, which are of particular theoretical and synthetic interest.

When 6-dimethylaminofulvene (**1**) was treated with 1.2 equiv. of lithium naphthalenide in tetrahydrofuran (THF) at 0 °C under nitrogen, the green colour of the solution due to the reagent rapidly changed to dark red. After 10 min, extractive work-up followed by chromatographic separation (silica gel, 0 °C, pentane elution) gave 6,6'-bifulvenyl (**2**)⁴ in 90% yield. Metallic lithium and sodium were also effective, but the reaction was slower and the yield lower (Li powder, 30 min, 62%; Na chips, 2 h, 32%). The high yield of (**2**) is remarkable in view of poor yield (3-6%)⁴ by the previous method. The reaction can be applied to substituted 6-dimethylaminofulvenes. Thus, similar reaction of 2-*t*-butyl-6-dimethylaminofulvene (**3**) afforded the bifulvenyl (**4**)⁵ in 35% yield. With 6-dimethylamino-6-methylfulvene (**5**), however, the expected bifulvenyl (**6**) was not isolated; instead its electrocyclic product, 4,5-dimethyl-8a,8b-dihydro-*as*-indacene (**7**),[†] and the novel fulvene derivative (**8**) were obtained, each in 20% yield, the latter compound being transformed to 6-methyl-6-

(1-naphthyl)fulvene (**9**)⁶ on treatment with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (37% yield). It is known that the bifulvenyl (**2**) undergoes ready electrocyclicisation at ambient temperature to give *trans*-8a,8b-dihydro-*as*-indacene.⁴ Electrocyclisation of (**6**) seems even easier than that of (**2**), for



† Spectral data for (**7**): ¹H n.m.r. (C₆D₆, 400 MHz) δ 2.02 (s, 6H), 2.62 (s, 2H), 6.46 (d, *J* 2.2 Hz, 2H), 6.56 (d, *J* 5.3 Hz, 2H), 6.76 (dd, *J* 5.3, 2.2 Hz, 2H); ¹³C n.m.r. (CDCl₃) 14.64, 57.11, 122.18, 126.45, 133.49, 134.45, 152.30.

which increased steric congestion by the methyl groups in the *transoid* form may be responsible.

The key intermediate for the bifulvenyl formation is the anion radical (10) which selectively couples at C-6 forming dianion (11) followed by deamination. Retarded coupling of the 6-methylated anion radical due to the steric effect of the methyl group may have allowed its concomitant reaction with the anion radical of naphthalene giving (8).

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