A New and Convenient Synthesis of Benzo[1,2 : 4,5]dicyclobutenes

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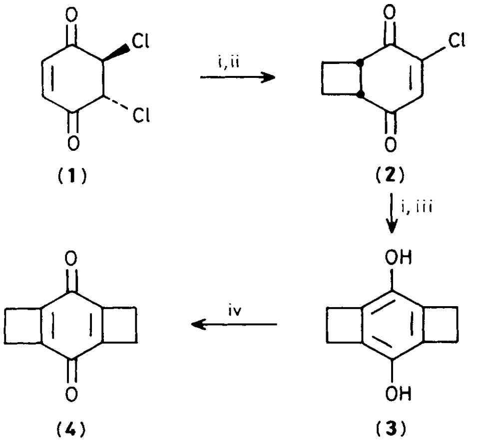
A new synthesis of the dicyclobuta-*p*-benzoquinone derivative (**4**) and the reactions of (**4**) or its masked quinone derivative (**7**) with organolithium followed by reduction provide a new route for the preparation of 3,6-dialkyl- and 6-alkyl-3-hydroxybenzo[1,2 : 4,5]dicyclobutenes (**6**) and (**9**).

Benzodicyclobutenes have received considerable attention because of their highly strained nature and the reactivity of the corresponding *o*-xylylenes, and especially as the key intermediate in the synthesis of multibridged [2_n]cyclophanes.[1] A few methods are known for the preparation of benzo[1,2 : 4,5]dicyclobutene and its derivatives, but the synthetic strategy is limited to the thermal SO_2-elimination from the corresponding disulphone[2] or the gas-phase pyrolysis of α,α′-dichlorodurene and its derivatives.[1,3] We report here a new and convenient synthetic method of the dicyclobuta-*p*-benzoquinone derivative (**4**) and a smooth and general conversion of (**4**) into 3,6-disubstituted benzo[1,2 : 4,5]dicyclobutenes (**6**) and (**9**).

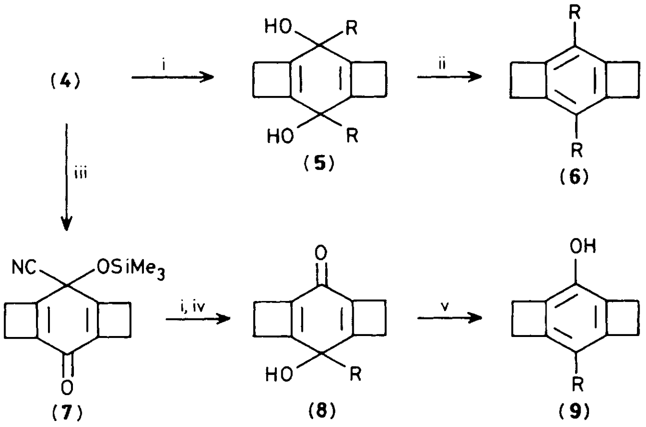
In a previous paper, we reported the synthesis of (**4**) in a low overall yield.[4] However, we have found another method for the synthesis of (**4**), which affords the *p*-benzoquinone derivative in much higher yield (Scheme 1). Photo[2 + 2]-addition of 5,6-dichlorocyclohex-2-ene-1,4-dione (**1**)[5] to ethylene (CH_2Cl_2, 0 °C, 4 h), followed by treatment with pyridine, gave the enedione (**2**) [74% based on (**1**), yellow oil, b.p. 83—86 °C at 0.2 mmHg, *m*/*z* 170 (M^+)].† Photoaddition of (**2**) to ethylene in a similar manner as above, followed by dehydrochlorination and enolization with LiF–Li_2CO_3 in dimethylformamide (DMF) afforded the hydroquinone (**3**) in 46% yield. Oxidation of (**3**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), as reported previously,[4] gave the quinone (**4**) in 74% yield.

For the synthesis of 3,6-disubstituted benzodicyclobutenes, (**4**) was first treated with an excess of MeLi at −78 °C for 1.5 h. The diol (**5a**) was obtained in 72% yield [colourless needles, m.p. 136.5—137.5 °C, *m*/*z* 192 (M^+)]. Reductive dehydroxylation of (**5a**) with $SnCl_2$–HCl in diethyl ether gave 3,6-dimethylbenzo[1,2 : 4,5]dicyclobutene (**6a**) in 93% yield, which showed spectroscopic data identical to those reported by Boekelheide.[6] In a similar manner, the reaction of (**4**) with BuLi and PhLi, followed by treatment with $SnCl_2$–HCl in diethyl ether, afforded 3,6-dibutyl- and 3,6-diphenylbenzo[1,2 : 4,5]dicyclobutenes (**6b**) and (**6c**), respectively [(**6b**), 48% based on (**4**), colourless crystals, m.p. 44—45 °C, *m*/*z* 242 (M^+); (**6c**), 43% based on (**4**), colourless prisms, m.p. 276—277 °C, *m*/*z* 282 (M^+)].

Although attempted mono-alkylation of (**4**) with 1 equiv. of RLi was unsuccessful, (**4**) could be converted into the corresponding *p*-quinols (**8**) using the silyloxynitrile protective group[7] (Scheme 2). Addition of trimethylsilyl cyanide to (**4**) in the presence of triphenylphosphine as catalyst afforded the Me_3SiCN-quinone adduct (**7**). Treatment of (**7**) without isolation with an excess of MeLi, followed by removal of the Me_3SiCN blocking group with silver fluoride in aq. tetrahydrofuran (THF), produced the *p*-quinol (**8a**) in 58% yield based on (**4**) [colourless crystals, m.p. 137—137.5 °C, *m*/*z* 176 (M^+)]. Reduction of (**8a**) with zinc in acetic acid afforded 3-hydroxy-6-methylbenzo[1,2 : 4,5]dicyclobutene (**9a**) in almost quantitative yield [colourless needles, m.p. 164.5—165.5 °C, *m*/*z* 160 (M^+); ^{1}H n.m.r. ($CDCl_3$) δ 1.98 (s, 3H), 3.01 (s, 8H), 4.41 (br. s, 1H); ^{13}C n.m.r. ($CDCl_3$) δ 11.1, 26.4, 27.6, 119.8, 127.5, 143.8, 144.1]. Similar treatment of (**7**) with BuLi and PhLi, followed by removal of the blocking group gave the corresponding quinols (**8b**) and (**8c**), respectively [(**8b**), 34% based on (**4**), colourless oil; (**8c**), 49% based on (**4**), colourless oil]. Reduction of (**8b**) and (**8c**) with zinc in acetic acid afforded 6-butyl- and 6-phenyl-3-hydroxy-



Scheme 1. *Reagents:* i, *hν*, CH_2=CH_2, CH_2Cl_2, 0 °C; ii, pyridine, CH_2Cl_2, room temp., 18 h; iii, LiF, Li_2CO_3, DMF, 120 °C, 18 h; iv, DDQ, MeCN, room temp., 30 min.



a; R = Me
b; R = Bu
c; R = Ph

Scheme 2. *Reagents:* i, RLi, THF–Et_2O, −78 °C, 2 h; ii, $SnCl_2 \cdot 2H_2O$, HCl, Et_2O, 0 °C to room temp.; iii, Me_3SiCN, PPh_3, MeCN, room temp., 18 h; iv, AgF, THF–H_2O, room temp., 20 h; v, Zn, AcOH, room temp., 1 h.

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† All new compounds exhibited spectroscopic and analytical data consistent with the assigned structure.

benzo[1,2 : 4,5]dicyclobutenes (**9b**) and (**9c**), respectively [(**9b**), 58%, colourless needles, m.p. 107—108.5 °C, *m/z* 202 (M^+); (**9c**), 65%, colourless prisms, m.p. 235.5—236.5 °C, *m/z* 222 (M^+)].

In summary, our method has enabled a relatively simple synthesis of both 3,6-dialkyl- and 6-alkyl-3-hydroxybenzo[1,2 : 4,5]dicyclobutenes (**6**) and (**9**) to be carried out using the dicyclobuta-*p*-benzoquinone derivative (**4**) as a key intermediate, and in principle should provide access to a variety of unusual 3,6-disubstituted benzo[1,2 : 4,5]dicyclobutenes.

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