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A RING-EXPANSION AND SOME REACTIONS OF 4,6-DIMETHYLBENZOCYCLOBUTEN-1-ONE

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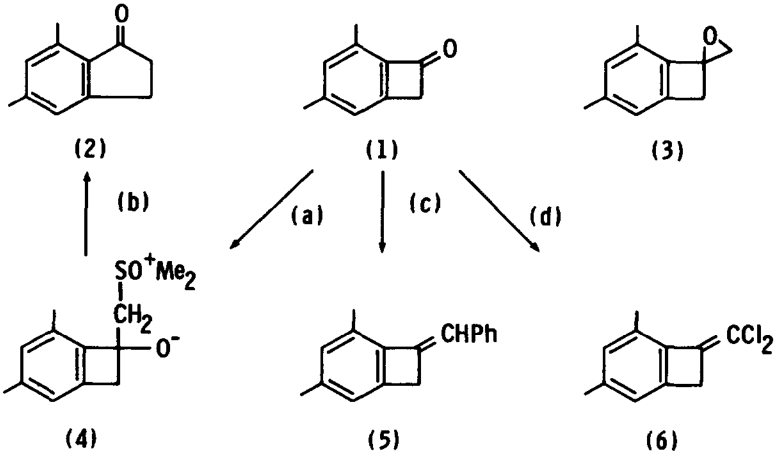
In the course of experiments to synthesise derivatives of benzocyclobutene, using the carbonyl function of 4,6-dimethylbenzocyclobuten-1-one (1), the latter compound was treated with dimethyloxosulphonium methylide in dimethylsulphoxide at room temperature (45 min.) and then at 50° (1 hr.). The product was not the expected epoxide (3) but 5,7-dimethylindan-1-one (2) which was obtained in high yield (>50%), m.p. 76-77° (lit.[1] m.p. 76-77°), τ($CDCl_3$) 7.69 (s,3H), 7.48 (s,3H), 7,4 (m,2H) 7.05 (m,2H), 3.18 (s,1H), 3.0 (s,1H), 2,4,-dinitrophenylhydrazone, m.p. 277-279° (lit.[2] m.p. 277-278°). Reduction of the indanone with sodium borohydride in ethanol gave 5,7-dimethylindan-1-ol, m.p. 95-96°, τ($CDCl_3$) 8.5 (broad, 1H exchangeable with D_2O), 7.7 (s,3H), 7.6 (s,3H), multiplets at 7.7 and 7.05 (2H in each), 4.7 (m,1H), 3.05 (m,2H). With dimethylsulphonium methylide (1) gave a complex mixture, but the expected epoxide (3) was not identified. Rearrangement of (3) might be expected to give the isomeric 2-indanone through migration of the phenyl group, but probably an initial adduct such as (4) undergoes fission at the 1-2 bond and the product cyclises to give (2).

The strain in the benzocyclobutene system is known to lead to fission of the 1-2 bond under basic conditions [3,4], and as a further example of this we obtained 2,4,6-trimethylbenzophenone from the reaction of (1) with phenylmagnesium bromide in ether. Benzocyclobutenones usually undergo normal reactions with Grignard reagents [4,5], and from (1) and benzylmagnesium bromide we obtained the expected carbinol as an oil, M^+ 238; this was dehydrated (toluene-*p*-sulphonic acid in boiling benzene) to give 1-benzylidene-4,6-dimethylbenzocyclobutene (5) m.p. 56-57°, τ ($CDCl_3$) ca. 7.5 (2s,6H), 6.1 (s,2H), 3.5 (s,1H), 3.17 (s,2H), 2.5-3 (m,5H). The ylid from triphenylphosphine and carbon tetrachloride[6] did not cause ring-opening of (1), the product being 1-dichloromethylene-4,6-dimethylbenzocyclobutene (6), m.p. 33-34°, τ ($CDCl_3$) 7.88 (s,3H), 7.74 (s,3H), 6.7 (s,2H), 3.37 (s,2H) M^+ 212. The IR spectrum (strong band at 1670 cm^{-1}) excludes the isomeric indene structure.

Since enolisation of (1) would generate the energetically unfavourable benzocyclobutadiene structure, the methylene group does not exhibit normal reactivity. It failed to condense with *p*-chlorobenzaldehyde and *p*-dimethylaminobenzaldehyde under acidic and basic conditions respectively, and with formaldehyde and secondary amines under Mannich conditions. Bromination of (1) in acetic acid gave 3 (or 5)-bromo-4,6-dimethylbenzocyclobuten-1-one, m.p. 159-161°, τ ($CDCl_3$) 7.6 (s,3H), 7.54 (s,3H), 6.2 (s,2H), 2.8 (s,1H), and further bromination of this compound left the methylene group unsubstituted; this is in contrast with the reported[7] mono- and dibromination of benzocyclobuten-1-one with N-bromosuccinimide.



(a) $CH_2{:}SOMe_2$ (b) spontaneous (c) $PhCH_2MgBr$, then H^+ (d) $Cl_2C{:}PPh_3$

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