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New Synthesis of Benzocyclobutene and Annelated Benzocyclobutenes

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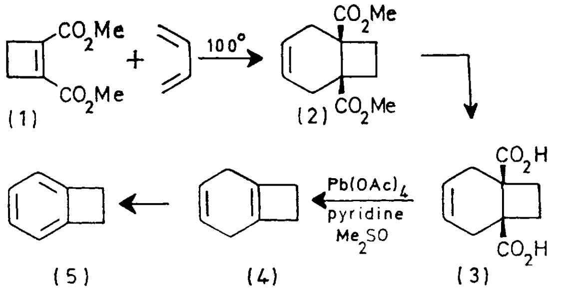
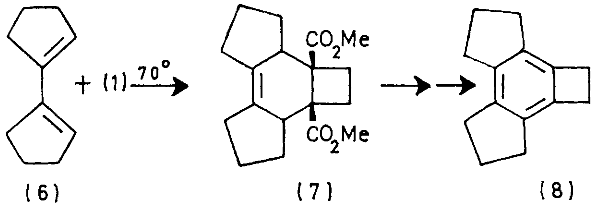
Summary Benzocyclobutene (**5**) and a bis-annelated derivative (**8**) have been synthesized by the Diels-Alder addition of dimethyl cyclobut-1-ene-1,2-dicarboxylate (**1**) to an appropriate diene and subsequent aromatization of the resulting six-membered ring.

Recently there have appeared several methods for the large-scale preparation of benzocyclobutene.[1] Although these procedures allow for straight-forward, high-yield synthesis of the parent compound, they are not readily adapted to various substituted derivatives. We have developed a new route to benzocyclobutene and believe that our approach should lend itself well to the synthesis of molecules in which one or two additional small rings are fused to the benzene nucleus.





The dicarboxylate (**1**) may be prepared from dimethyl $\alpha\alpha'$-dibromoadipate[2] according to the method of McDonald and Reitz.[3] When this material is sealed in a combustion tube with excess of butadiene and a small amount of hydroquinone for 2 days at 100° a single product is formed.[4] Flash distillation provides pure (**2**) (73%), b.p. 67—69° at 0·03 mmHg. Although both ester functions in (**2**) are sterically hindered, they may be readily hydrolysed by refluxing overnight with KOH in aqueous MeOH to afford the diacid (**3**) (80%). Treatment of (**3**) with $Pb(OAc)_4$ (1 equiv.)in Me_2SO containing pyridine (2 equiv.)[5] gives a pro-

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duct which is mainly bicyclo[4,2,0]octa-1(6),3-diene (**4**) contaminated with a small amount of benzocyclobutene (**5**). If the amounts of $Pb(OAc)_4$ and pyridine are doubled, a 57% yield of (**5**) may be obtained directly, τ (CCl_4) 3·04 (4H, m) and 6·86 (4H, s).[1] Cyclohexa-1,4-diene was converted smoothly into benzene under similar oxidizing conditions.

When 1,1′-bicyclopentenyl (**6**)[6] is substituted for butadiene in this sequence, cycloaddition occurs readily after several hours at 70°, to give an adduct which may be recrystallized from a minimum amount of hexane at low temperature, m.p. 79—80°. The ease with which (**6**) participates in Diels–Alder reactions has been previously established[7] and accounts for the milder conditions required for this step. Total conversion of (**7**) into the corresponding diacid requires 60 h of refluxing with KOH. The final bis-decarboxylation and subsequent aromatization take place in 18% yield to give compound (**8**) as the major product contaminated by a small amount of material believed to be the cyclohexa-1,4-diene precursor to (**8**).

The dicyclopentobenzocyclobutene (**8**) was purified by preparative gas chromatography to give a crystalline material, m.p. 90—91°. The assigned structure is consistent with a very intense parent peak in the mass spectrum at m/e 184 and the n.m.r. spectrum: τ (CCl_4) 6·96 (4H, s), 7·31 (8H, t, J 7 Hz), and 7·99 (4H, quintet, J 7 Hz).

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