Reaction of Pentacyclo[4,4,0,$0^{2,5}$,$0^{3,8}$,$0^{4,7}$]dec-9-ene with Diethyl Azodicarboxylate; Synthesis of *cis*-9,10-Dihydronaphthalene

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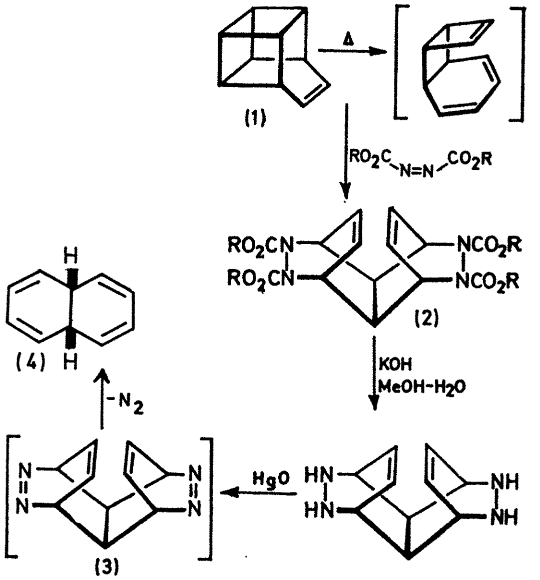
Summary Treatment of pentacyclo[4,4,0,$0^{2,5}$,$0^{3,8}$,$0^{4,7}$]dec-9-ene with two equivalents of diethyl azodicarboxylate affords a 1 : 2 adduct which undergoes hydrolysis–decarboxylation reactions giving rise to *cis*-9,10-dihydronaphthalene.

RECENT interest in the use of pentacyclo[4,4,0,$0^{2,5}$,$0^{3,8}$,$0^{4,7}$]-dec-9-ene (basketene)[1] (**1**) as an intermediate for the syntheses of polycyclic hydrocarbons[2] prompts us to report the reaction of (**1**) with diethyl azodicarboxylate.

When (**1**) and diethyl azodicarboxylate (2·5 : 1 mol ratio) were heated at 76° in carbon tetrachloride for ten days, adduct (**2**) was precipitated out of the solution as a light yellow solid. After being washed with hexane and recrystallized from ethanol, crystalline (**2**) was obtained [80% yield; m.p. 190—191°; τ ($CDCl_3$) 3·5—4·2 (m, 4H), 4·9—5·5 (m, 4H), 5·77 (q, 8H), 7·07 (br s, 2H), 8·75 (t, 12H); ν_{max} (KBr) 1698 cm^{-1} (C=O)]. Hydrolysis–decarboxylation of (**2**) under nitrogen with hot potassium hydroxide in aqueous methanol gave the corresponding hydrazine. Exposure of this compound to yellow mercuric oxide or air resulted in immediate oxidation with the formation of nitrogen and



cis-9,10-dihydronaphthalene (**4**) [overall yield 60% from (**2**)]. The n.m.r. spectrum of (**4**) displayed two sets of first-order doublets centred around τ 4·09 and 4·38 (8H), 6·68, (br s, 2H);[4] and naphthalene, as reported,[4] was obtained by prolonged heating of (**4**) at 120°. Since it has been well documented that 1,4-bis-allylic azo-compounds[3] such as 2,3-diazabicyclo[2,2,2]octa-2,5-diene decompose rapidly at room temperature (a symmetry-allowed retro-Diels–Alder process), we have postulated that under the present reaction conditions oxidation of hydrazine initially gives the bis-azo-compound (**3**) which, in turn, fragments to (**4**) and nitrogen.

The formation of (**4**) clearly indicates that adduct (**2**) has the structure shown. In addition, the present reactions provide a useful method for the preparation of (**4**) which has been known to be an important precursor[5] of other $[CH]_{10}$ hydrocarbons. We are studying reactions involving (**2**) as an intermediate for the synthesis of pentaprismane.[6]

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