$[C_6H_6]_n$ Hydrocarbons. Tetracyclic $C_{12}H_{12}$ Compounds from $C_{18}H_{18}$ Precursors[1]

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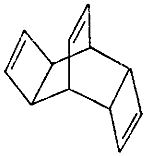
Summary Photochemical rearrangement of the polycyclic homotropylidene carbonate (**4**) yields the heptacyclic carbonates (**5**), (**6**), and (**8**), from which the tetracyclo-$[4,4,2,0^{2,5},0^{7,10}]$dodecatrienes (**1**)—(**3**) are synthesized.

WITHIN the series of $[C_6H_6]_2$ hydrocarbons,[2] compounds (**1**)—(**3**) constitute a sub-group, differing only in the spatial arrangement of the cyclobutene units. The properties of compound (**1**) and (**2**) are well established, but compound (**3**) has so far resisted isolation or spectroscopic detection.[3] When the stereochemically homogeneous carbonate (**4**)[4] is irradiated in ethanol,† a mixture of the stereoisomeric heptacyclic carbonates (**5**), (**6**), and (**8**) is formed quantitatively.‡ Compound (**5**) can be separated from this mixture by recrystallization from acetone. Compound (**5**) and the isomer mixture of (**6**) and (**8**) were characterized by i.r. (ν_{CO} 1795 cm^{-1} KBr) and mass (M^+ m/e 294) spectroscopy, and elemental analysis. Compound (**5**) can be differentiated from the mixture (**6**)–(**8**) by ^{1}H n.m.r. spectroscopy (60 MHz; $CDCl_3$, Me_4Si): compound (**5**), δ 1·46 (2H, 3- and 8-H), 2·15 (2H, 2- and 9-H), 6·2 (2H, 15- and 16-H), and 6·33 (2H, 12- and 13-H); compounds (**6**) and (**8**), δ 1·70 (2H, 3- and 8-H), 1·85 (2H, 2- and 9-H), 5·78 (2H, 12- and 13-H), and 5·85—6·35 (2H, 15- and 16-H). In (**6**)–(**8**) the olefinic cyclobutene protons are shifted to high field relative to (**5**). The cyclobutane protons 2-H, 9-H and 3-H, 8-H are anisochronous in (**5**) and have nearly identical chemical shifts in (**6**) and (**8**). If the carbonate mixture is treated according to the sequence in the Scheme,[5] followed by pyrolysis of the $C_{18}H_{18}$ hydrocarbons (160°; 8 h; in C_6H_6) a mixture of the olefins (**1**)—(**3**) and benzene is formed. Compounds (**1**)—(**3**) were characterized by ^{1}H n.m.r. spectroscopy. Compound (**1**), δ 5·62 (2H, 3- and 4-H), 6·03 (2H, 11- and 12-H), and 6·27 (2H, 8- and 9-H); compound (**2**): δ 5·8 (2H, 11- and 12-H) and 5·84 (4H, 3-, 4-, 8-, and 9-H); compound (**3**): δ 2·63 (2H, 1- and 6-H), 2·67 (4H, 2-, 5-, 7-, and 10-H), 5·96 (4H, 3-, 4-, 8-, and 9-H), and 6·46 (2H, 11- and 12-H).



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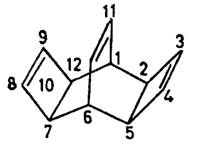

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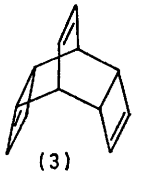

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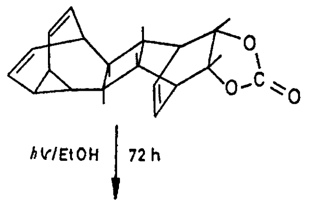

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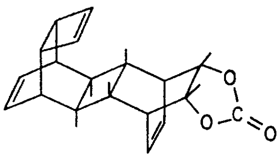

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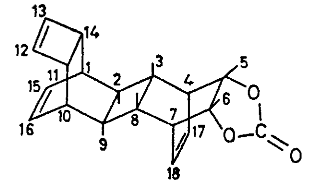

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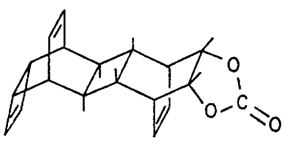

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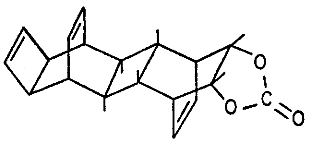

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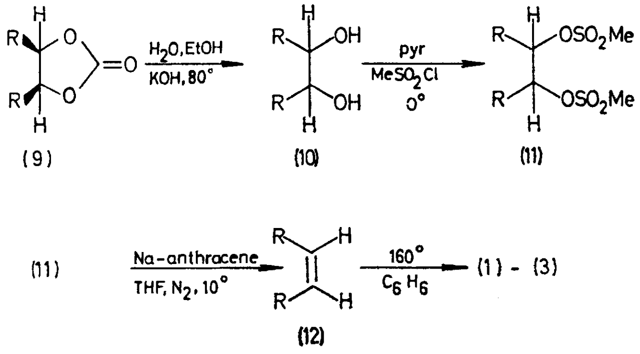
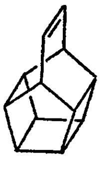


SCHEME



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† Hanovia, 679A36, 450 Watt, Corex filter.

‡ The stereoisomer (**7**) was not detectable spectroscopically. The ratio of (**5**) to (**6**)–(**8**) is 2·5 : 1.

Starting from (**5**), pure compound (**3**) can be isolated by the same procedure. The chemical shift of the cyclobutene protons in (**3**), δ 5·96, clearly demonstrates the promixity of the two double bonds which make (**3**) prone to polymerization. Benzophenone-sensitized irradiation of (**3**) in ether yields quantitatively the known cage compound (**13**) [δ ($CDCl_3$) 6·26 (2H, sextet) and 3·07 (4H, m)].[6] With $AgBF_4$ in $CHCl_3$, (**13**) isomerises at room temperature.

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[5] For the reaction (**11**) → (**12**) see: J. C. Carnahan, jun., and W. D. Closson, *Tetrahedron Letters*, 1972, 3447.

[6] E. LeGoff and S. Oka, *J. Amer. Chem. Soc.*, 1969, **91**, 5665.