Thermal Cycloaddition of Diphenylcyclopropenone to Tricyclo[6.2.0.0^{3,6}]deca-1,3(6),4,7,9-pentaene to Afford a Quadricyclanone Derivative, and Its Photochemical Conversion into Keten and Cyclopropene

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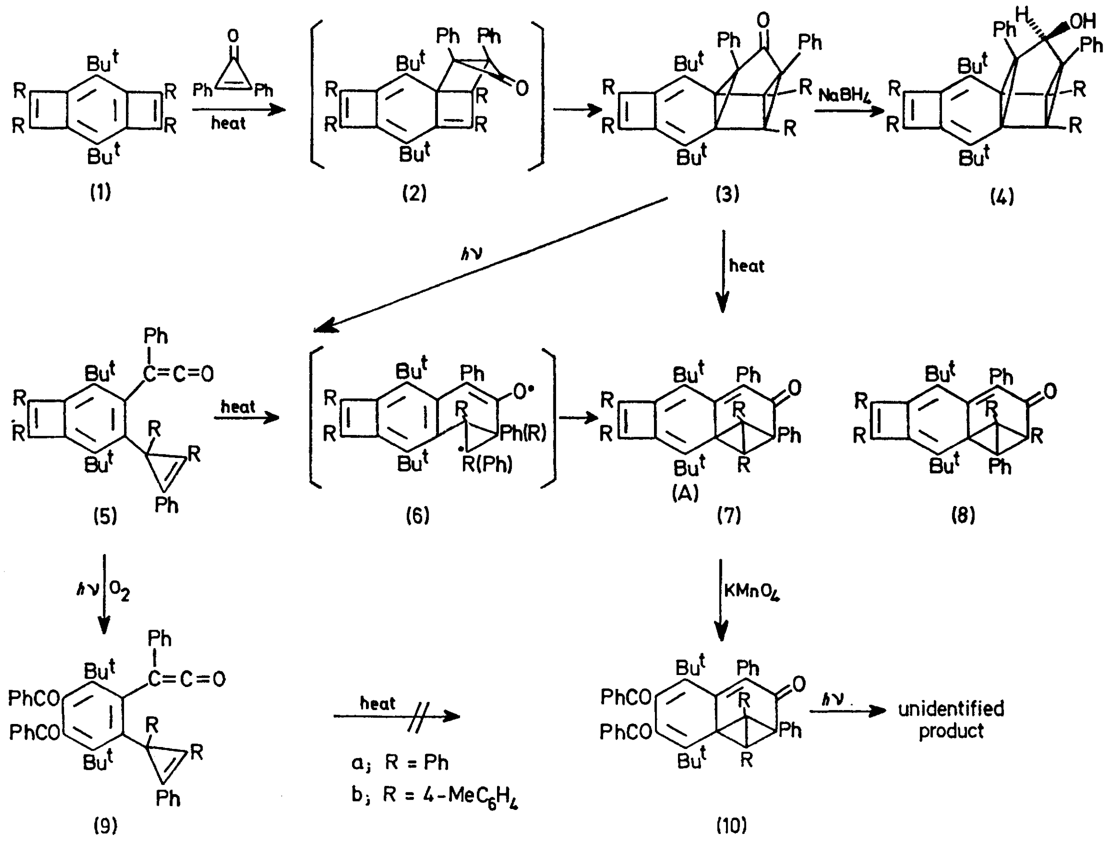
Summary Thermal cycloaddition of diphenylcyclopropenone to tricyclo[6.2.0.0^{3,6}]deca-1,3(6),4,7,9-pentaene (**1**) gave the quadricyclanone derivative (**3**), which on further heating and photolysis was converted into the bicyclobutane derivative (**7**) and the benzocyclobutene (**5**) bearing keten and cyclopropenyl groups, respectively; heating of (**5**) afforded (**7**).

OXIDATION of quadricyclanol has been so far the sole preparative route to quadricyclanone (**11**).[1] We now report a new preparative method for the quadricyclanone skeleton by thermal cycloaddition of diphenylcyclopropenone (DCP) to the cyclobutadiene ring. We also report some new reactions of the resulted quadricyclanone (**3**) and its derivatives.



Heating (**1a**)[2] and equimolar amounts of DCP under reflux in xylene under N_2 for 7 h afforded (**3a**)† as colourless prisms in 58% yield, m.p. 241—242 °C (decomp.), ν_{max} 1775 cm^{-1}; λ_{max} 244 (ϵ 24,800) and 306 nm (19,300), τ 9·19 (s, Bu^t). The presence of the symmetry plane of (**3a**) bisecting its carbonyl unit was proved by the following facts. The alcohol (**4a**) which was prepared by $NaBH_4$ reduction of (**3a**) no longer had this symmetry plane and showed two Bu^t singlet signals at τ 9·12 and 9·21. Furthermore, (**3b**) which was derived from (**1b**) and DCP in 77% yield showed two 4-Me signals in a 1 : 1 ratio at τ 7·76 and 7·83. The formation of (**3**) can be interpreted in terms of a ($_{\pi}2_s + {}_{\sigma}2_s$) cycloaddition of (**2**) which was initially produced by a ($_{\pi}4_s + {}_{\pi}2_s$) cycloaddition of (**1**) and DCP. However, the former cycloaddition would be nonconcerted, since thermal ($_{\pi}2_s + {}_{\sigma}2_s$) cyclisations are forbidden.[3]

Heating (**3a**) under reflux in 1,2-dichlorobenzene for 3 h afforded (**7a**) as yellow needles in 64% yield, m.p. 244—246 °C; ν_{max} 1680 cm^{-1}. Structure (**7a**), which has a symmetry plane bisecting the bicyclobutane ring, was assigned by analogy with the n.m.r. spectrum of (**7b**)

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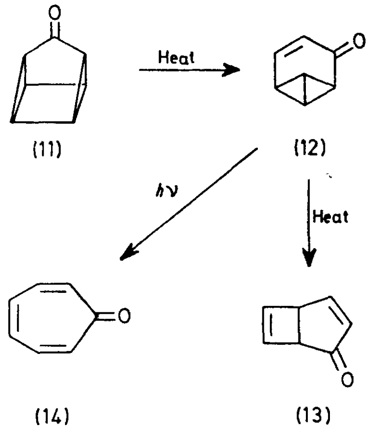
† I.r., u.v., and n.m.r. spectra were measured for Nujol mulls and solutions in $CHCl_3$ and $CDCl_3$, respectively. All new compounds gave satisfactory elemental analyses and mass spectral data.

derived from (**3b**) in 77% yield, in which the four 4-Me groups appeared as three singlets at τ 7·67, 7·68, and 7·78 in a 1:1:2 ratio. Of the two $\mathrm{Bu^t}$ signals of (**7a**) (τ 8·94 and 9·71) and of (**7b**) (8·92 and 9·71), those which appeared at the extremely high magnetic field could be assigned to $\mathrm{Bu^t}$(A), which is presumably shielded by the two benzene nuclei on the four-membered ring. Molecular models support this.



This thermal conversion of (**3**) into (**7**) is analogous to that of (**11**) into (**12**).[4] However, the photochemical reaction of (**3**) was interesting. Irradiation‡ of a solution of (**3a**) in benzene under N_2 for 3·5 h afforded (**5a**) as red needles in 95% yield, m.p. 201—202 °C; ν_{max} 2100 cm^{-1}; λ_{max} 456 nm (ε 1280). This u.v. band at longer wavelength is representative of a benzocyclobutene.[5] Similarly, irradiation of (**3b**) gave (**5b**) in 95% yield. Photo-oxidation of (**5a**) and (**5b**) in benzene for 0·5 h gave (**9a**) (86%) and (**9b**) (85%), respectively. Such an easy photo-oxidation is also representative of benzocyclobutenes.[5]

Interestingly, heating of (**5a**) under reflux in xylene under N_2 for 1 h gave (**7a**) in 68% yield. This novel cyclisation can be interpreted by the radical pathway which proceeds *via* (**6a**), even though the concerted ($_{\pi}4_s + _{\pi}2_s$) mode cannot be excluded. In either mechanism, two modes of cyclisation are expected for (**5b**) which has an unsymmetrically substituted cyclopropene ring. Heating of (**5b**) gave (**7b**) (17%) and (**8b**) (51%). In the case of a radical reaction, (**6b**) (substituent arrangement as shown in parentheses) would produce (**8b**). However, (**9**) was inert in the thermal reaction.

In contrast to the thermal and photochemical conversions of (**12**) into (**13**) and (**14**), respectively,[4] (**7**) was inert in both reactions, probably since such conversions of (**7**) would produce, unfavourably, benzocyclobutenes. This consideration was proven to be correct by photolysis of (**10**) which was prepared by $KMnO_4$ oxidation of (**7**). Irradiation of a solution of (**10a**) in benzene for 0·5 h afforded an unidentified isomer, $C_{57}H_{48}O_3$, as colourless prisms in quantitative yield, m.p. 269—270 °C, ν_{max} 1725 and 1670 cm^{-1}; τ 8·95 (s, $\mathrm{Bu^t}$). Similarly, photolysis of (**10b**) gave an isomer, $C_{61}H_{56}O_3$, in quantitative yield. Nevertheless, (**10**) was inert in the thermal reaction.

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‡ Irradiations were carried out at room temperature with a 100 W high-pressure mercury lamp through a Pyrex filter.

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