3,4,8,9-Tetramethyltetracyclo[4,4,0,$0^{3,9}$,$0^{4,8}$]decane-1,6-dioic Anhydride. A Photosensitized $\pi^2+\pi^2_s$ Intramolecular Cycloaddition

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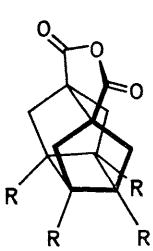
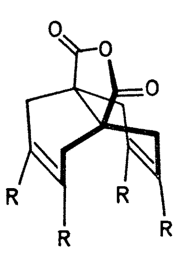
Summary Photosensitized cycloaddition of the 1 : 2 Diels–Alder adduct of acetylene dicarboxylic acid and 2,3-dimethylbuta-1,3-diene affords (I) in 44% yield: this represents the simplest synthesis of this tetracyclo[4,4,0,$0^{3,9}$,$0^{4,8}$]decane ring system.

INTEREST in the synthesis of strained polycyclic ring systems has resulted in numerous publications in the literature. There is only one report describing the synthesis of the novel tetracyclo[4,4,0,$0^{3,9}$,$0^{4,8}$]decane system.[2] The method involved at least seven steps with subsequent reduction in the overall yield. We report a new, simple route to this tetracyclodecane ring system involving the intramolecular photosensitized cycloaddition of suitably oriented double bonds.[3]



(I) R = Me



(II)

The Diels–Alder reaction of 2,3-dimethylbuta-1,3-diene and acetylene dicarboxylic acid leads smoothly to the anhydro-1 : 1 adduct, 4,5-dimethyl-3,6-dihydrophthalic anhydride [76%; m.p. 167·5—168·5°; i.r. (Nujol) ν_{max} 1850 and 1780 cm^{-1}; ^1H n.m.r.† δ 1·77 (s, 6H), 3·01 (s, 4H)]. Reaction of this adduct with a second mole equiv. of the diene in a sealed tube at 190° affords 3,4,8,9-tetramethylbicyclo[4,4,0]decane-1,6-dioic anhydride, (II) [91%; m.p. 152—153·5°; i.r. (Nujol) ν_{max} 1845 and 1770 cm^{-1}; ^1H n.m.r. δ 1·67 (s, 12H), 2·20 (d, 4H, J 14·5 Hz), 2·38 (d, 4H)]. In agreement with other work,[4] dimethyl acetylenedicarboxylate yields only a 1 : 1 adduct with the diene. A 1 : 2 adduct was not obtained even at elevated temperatures.

A solution of (II) in acetone was photolysed at 20° under nitrogen with a 450 w Hanovia lamp for 2 days. Removal of the solvent followed by column chromatography through silica gel afforded a crystalline material [representing a conversion of 44% of (II) by ^1H n.m.r. integration; m.p. 210—211°; i.r. (Nujol), ν_{max} 1850 and 1785 cm^{-1}; ^1H n.m.r. δ 1·05 (s, 12H), 1·38 (d, 4H, J 11 Hz), 1·98 (d, 4H)]. (There was no visible reaction with a solution of Br_2 in CCl_4). It is

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† All ^1H n.m.r. measurements were made on a Hitachi-Perkin-Elmer Model R-20 NMR spectrometer operating at 60 MHz. Spectra were obtained in $CDCl_3$ solution and line positions are reported as p.p.m. (δ) downfield from Me_4Si used as an internal standard. Line positions and coupling constants were determined by first-order analysis of the spectra. Satisfactory chemical analyses were obtained for all compounds described in this work.

not clear at the present time whether the conversion of (II) into (I) can be increased with longer irradiation times or whether the yield obtained represents the photoequilibrium ratio between (I) and (II). The upfield shift of the ^1H n.m.r. signals due to the methyl protons is consonant with the transformation (II) → (I). Such a process is photochemically allowed according to rules postulated for such processes, and has been designated as a $\pi_s^2 + \pi_s^2$ cycloaddition.[5] Precedents for such processes are numerous.[3,6]

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