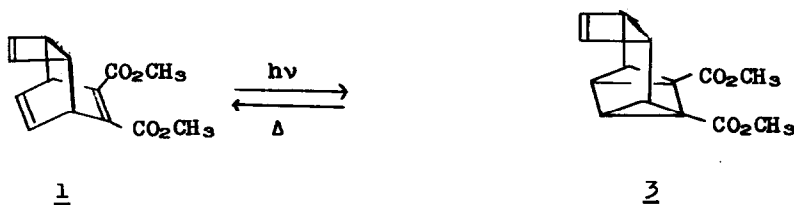


INTERNAL PHOTOLYTIC 2+2 CYCLOADDITION OF THE
CYCLOOCTATETRAENE-DIMETHYL ACETYLENEDICARBOXYLATE ADDUCT

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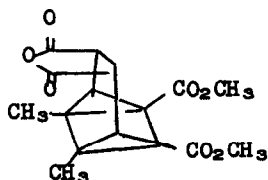
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The recent publication of Miller and Hedaya¹ on the photochemistry of 7,8-dicarbomethoxytricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (1) leads us to report our rather different results. They found that 1 gave dimethyl phthalate, syn-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (2), and cyclooctatetraene upon photolysis at room temperature, -20°, and liquid nitrogen temperature. That 2 arises from cyclobutadiene was deduced from isolation of cyclobutadiene-diene adducts, and decreased yields of 2, in the presence of piperylene or isoprene. They report looking for thermally labile 7,8-9,10 closure product 3 at -20°, but observe no closure.

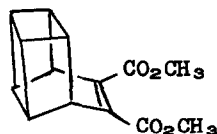


Photolysis of 1 in deuteriochloroform at -50° with either 313 nm light (Bausch and Lomb "high intensity" monochrometer) or a vycor-filtered Hanovia 450 w. lamp gave up to 61% conversion (34 hr, 0.44 M in a sealed nmr tube) to a thermally labile material showing nmr signals at δ 6.43(s,2H), 3.81(s,6H), 3.30(m,2H), 1.83-2.43(complex,4H), which is reasonable for 3. The major side product was dimethyl phthalate. The half-life of the unstable material was 16 min at 2.3°, which makes it somewhat less stable than the closed cyclohexadiene ($t_{1/2} = 12$ min at 19°) and cycloheptadiene ($t_{1/2} = 90$ min at 21.5°) adducts reported by Prinzbach, Ebenbach, and Philippoussian^{2,2}, but somewhat more stable than the more highly substituted

analogue 4.³ We could detect no other product than 1 from the thermal opening of



4



5

3, although 5 could have been formed by a thermally allowed⁴ $2s+2a+2a$ process. Interestingly, no 5 was observed photolytically either, although dihydro-1 (the cyclooctatetraene-maleic anhydride adduct) does undergo this photochemical closure when photosensitized.⁵ Cleavage to dimethylphthalate and cyclobutadiene is clearly faster than 3,4-9,10 cycloaddition. The failure of Miller and Hedaya to observe 7,8-9,10 cycloaddition may be due to a wavelength effect--their low temperature experiments were apparently carried out at 254 nm.

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