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3,4-DICARBOMETHOXYBICYCLO[3.2.2]NONATRIENE

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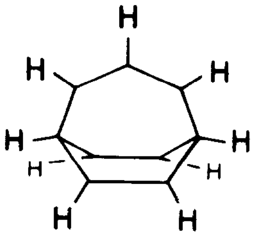
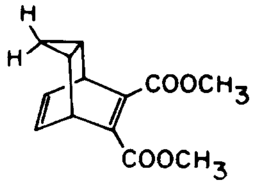
We here report the unanticipated, if also the first, isolation of a molecule possesing the bicyclo[3.2.2]nonatriene skeleton, an attractive precursor of the theoretically intriguing system, I.[*]



I



II

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[*] This incomplete representation reflects our current reluctance to specify a more detailed electron distribution or geometry for the cation, anion, or radical. Nor do we presume, now, to judge the relative importance of each of the three. Both synthetic efforts and calculations (R. Hoffmann) are in progress.

Dimethyl acetylenedicarboxylate reacts with 1,3,5-cycloheptatriene in refluxing toluene to produce II, as reported, (1) but also an isomer (2) (12%, m.p. 92-93°, $\lambda_{max}^{CH_3CN}$ 245 mμ (ε 4084), λ_{max}^{KBr} 5.76, 5.87, 6.08 μ, τ^{CCl_4} 2.70 (doublet of doublets, J = 1.8 and 10.5 c.p.s., relative area 1), 3.3-4.2 (seven multiplets, relative area 4.02), and singlets at 6.38 and 6.39 p.p.m. superimposed on multiplets (relative area 8.97)). The vicinal relationship of α,β-unsaturated and saturated ester functions is established both by the n.m.r. spectrum of the derived tetrahydrodiester (m.p. 44.5-46.5°, doublets at $\tau^{C_6D_6}$ 2.68 and 6.10 p.p.m., J = 9.0 and 5.0 c.p.s. respectively, normalized areas 1.00 : 1.00) and by the infrared of the derived hexahydroanhydride (m.p. 133-136°, λ_{max}^{KBr} 5.33, 5.54 μ). Clearly consistent, the assignment III is fully confirmed by oxidation (RuO_4 - $NaIO_4$ (3) followed by $NaMnO_4$) of the tetrahydrodiester to trans-1,4-cyclohexanedicarboxylic acid.

A reasonable (but not unique) formulation of the reaction process is suggested by sigmatropic (4) precedents in related systems (5).

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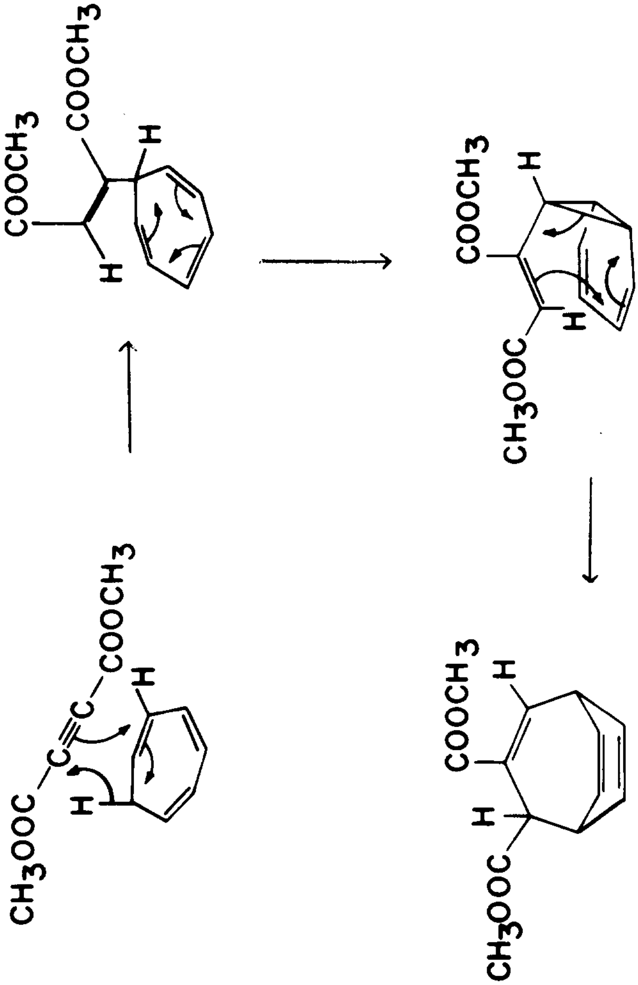
CH3OOC
C
C
COOCH3
H
H
COOCH3
COOCH3
H
H
COOCH3
CH3OOC
H
H
COOCH3
CH3OOC
H
H

III

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