PROBLEM 16

[SUPPL Problem 16 # 1]

Arabic compound numbers in TAPSOC,
Roman numerals in Supplementary material

In perspective

Perhaps because we are biased to think about unsaturated fatty acids as a distended succession of carbons forming relaxed linear chains, it may surprise you to learn that tetraene carboxylic esters like **1** contain considerable *strain energy*.

X-Ray evidence shows that there is a distortion of the bond angle (>130º vs the expected 120º) comprising CH_3 groups on C^4 and C^6 (fatty acid nomenclature). The C^8 methyl is also pushed out of the orderly coplanar structure, an effect that throws the C=C bond conjugation out of its hinges. Hence, tetraene esters like **I** resemble a pressed spring about to leap.

A variety of unusual reactions stem from this peculiar feature, two of which are the soul of this problem. The formation of **2** (TAPSOC problem 16) had the added interest of opening a short route to a biomimetic synthesis of a family of natural compounds, the *crispatenes*, the core of which is set up in just one step in compound **2** [1]. By contrast, tricyclic caged compound **3** is created upon changing the energy source from electronic excitation (hν) to heat.

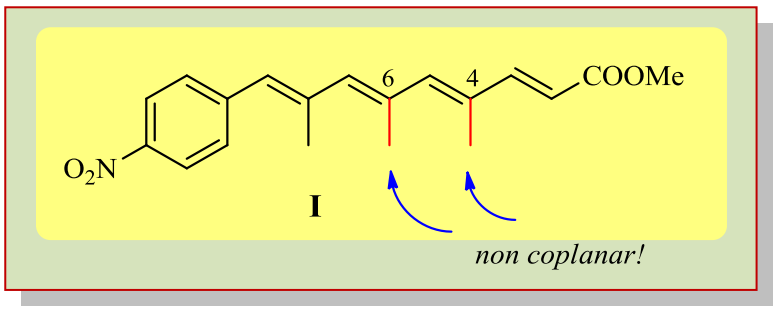

FIGURE SP16.1.1

An energy minimized (MM2, author) three dimensional rendering of this structure is included in TAPSOC webpage, problem 15, comp 16-I.mol for you to observe deviations from the expected coplanarity of methyls on C^4, C^6 and C^8.

REFERENCE/NOTE

[1] Palladium promoted cyclization of tetraenes has been used as well in the synthesis of these marine compounds. The stereochemistry of the multiple cyclization is of considerable interest. See, for example: Miller AK, Byun DH, Beaudry CM, Trauner D. Proc. Natl. Acad. Sci. 2003;101:12019-12023. DOI: 10.1073/pnas.0401787101.