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THERMAL CYCLOADDITION TO
cis,cis,cis,cis-1,3,5,7-CYCLONONATETRAENE

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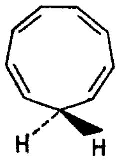
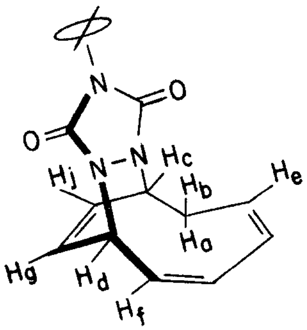
IN a recent report[1] dealing with the synthesis and isolation of the title compound (1), we briefly touched upon the reaction of this substance with 4-phenyl-1,2,4-triazoline-3,5-dione (2)[2] to the extent that we formulated a structure containing a monocyclic hydrocarbon segment. Presently, we detail additional information in this context which allows for a definitive structural assignment for the adduct.

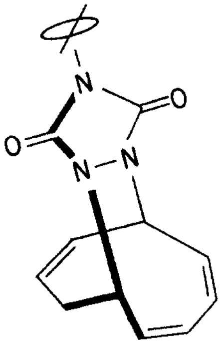
Admixture of equimolar quantities of 1 and 2 in methylene chloride at -78° results in the rapid consumption of the intensely colored dienophile and the formation of a white crystalline product (mp. 181-183°) in *ca.* 60% yield. Elemental analysis coupled with pertinent mass-spectral information, m/e 293 (parent; 65%) and m/e 118 (1; 74%), serves to effectively characterize this substance as a 1:1 adduct. In addition, this material displays prominent infrared (KBr) bands at 1750, 1690, 1420, 775 and 745 cm^{-1}, uv (CH_3CN) absorption in the form of a shoulder at 215 nm (ϵ 15,000) and an nmr ($CDCl_3$) spectrum consisting of a narrow multiplet at τ 2.60 (5 H), a complex array of peaks extending from τ 3.60 to τ 5.10 (8 H), and two broad multiplets centered at τ 7.05 (1 H) and τ 8.10 (1 H). The obvious lack of "aliphatic" resonance in the nmr spectrum, besides the signals due to the geminal protons of the methylene function, is uniquely consistent with a skeleton containing a monocyclic hydrocarbon segment. Furthermore, the complexity of the low-field absorption suggests an unsymmetrical structure. Indeed, the lack of molecular symmetry becomes quite apparent on examination of the 100 MHz nmr spectrum of this substance, depicted in Figure 1. Specifically, it is seen that the uppermost region of the low-field multiplet, which without doubt contains the resonances of the two "bridgehead" protons, now clearly consists of two well separated one-hydrogen multiplets. Hence, we conclude that the bridgehead positions are magnetically non-equivalent and consequently that of four possible structures for the cycloadduct only the two shown in 3 and 4 ought to be given serious consideration.[3]



1



3



4

Careful analysis[4] of the nmr spectrum taken at 100 MHz led to the assignments and coupling constants shown in Figure 1. These fully justify our preliminary rejection of a symmetrical arrangement and, in addition, serve to further limit our choice to 3 as the correct structure for the cycloadduct. Specifically, our results indicate that each of the two bridgehead hydrogens is substantially coupled to one of a pair of olefinic protons which are also strongly coupled to one another (J_{dg}= 6.2 Hz, J_{cj}= 7.0 Hz and J_{gj}= 10.0 Hz) and further that these key olefinic protons are not subject to additional coupling.

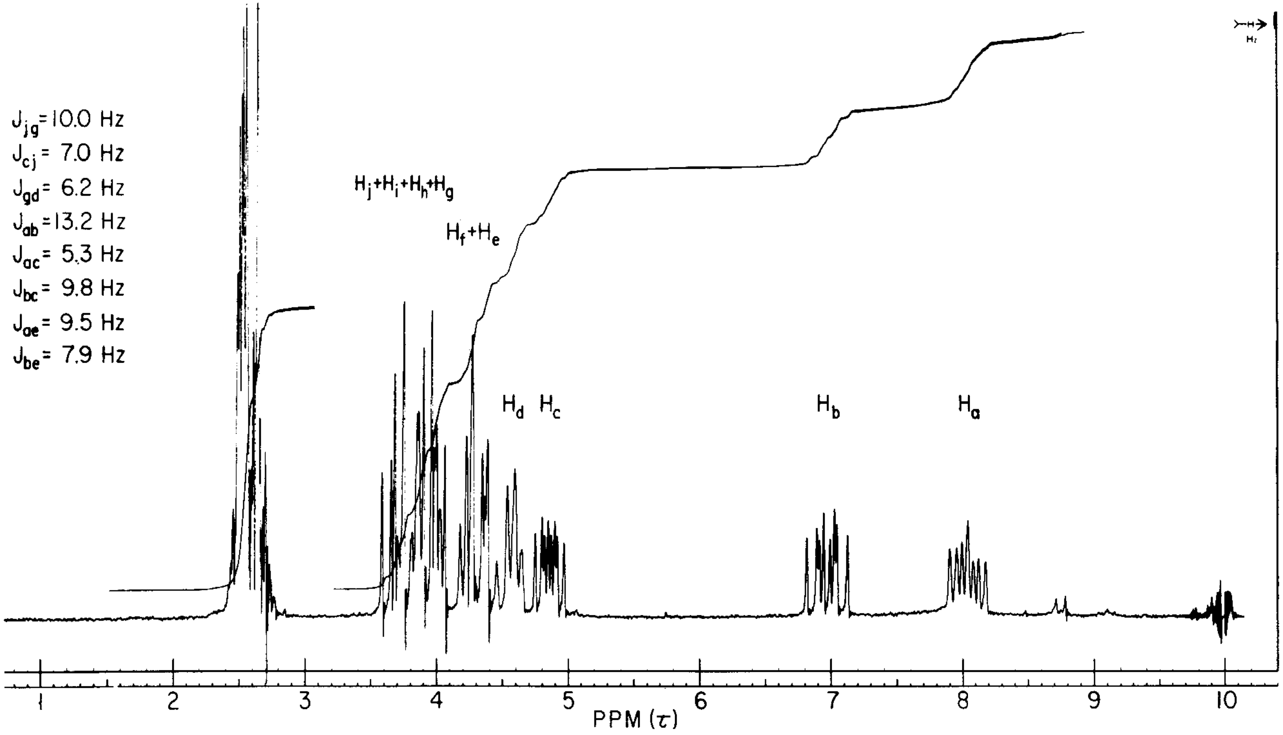


Figure I. 100 MHz Nmr Spectrum of Cycloadduct $\underset{\sim}{3}$

While entirely as anticipated for structure 3 this piece of information is decidedly inconsistent with the alternate structural arrangement which would only accomodate these facts through the highly unlikely combination of a vanishingly small vicinal coupling and a substantial 1,4 splitting (10.0 Hz) within the butadiene segment. Also, our data demand that the methylene hydrogens and the remote bridgehead proton be coupled to non-vicinal olefinic hydrogens. Again, 3 but not 4 satisfies this condition.

Finally a brief concluding remark regarding the preferred mode of cycloaddition to 1. While orbital symmetry factors are no doubt chiefly responsible for the failure of the tetraene to participate in a "2 + 6" process, they cannot possibly be implicated in the reluctance of this hydrocarbon to undergo either "2 + 8" or symmetrical "2 + 4" cycloaddition for the simple reason that such paths are symmetry-allowed, thermally. Instead, the non-occurence of such processes is in all probability due to conformational resistance of the reacting polyene segment to attain a co-planar arrangement in the transition state. In fact, examination of a "Dreiding" molecular model of 1 reveals quite clearly that formation of either of the two undetected symmetrical adducts would require extensive skeletal distortion. In contrast, very minor skeletal reorganization is anticipated in the formation of 3 on account of a nearly planar C_1 to C_4 butadiene segment in 1.

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REFERENCES AND REMARKS

(1) A. G. Anastassiou, V. Orfanos and J. H. Gebrian, Tetrahedron Letters, 4491 (1969).

(2) We elected this dienophile because of its unique tendency to undergo 1,4 addition with cyclooctatetraene; A. B. Evnin, R. D. Miller and G. R. Evanega, Tetrahedron Letters, 5863 (1968).

(3) The remaining two structures would arise from symmetrical addition of 2 onto 1 either in a "2 + 4" or in a "2 + 8" manner.

(4) This involved extensive spin decoupling.