CHEMISTRY LETTERS, pp. 101-104, 1989.

Periselectivities in Thermal Addition of Tropone to Allenic Esters

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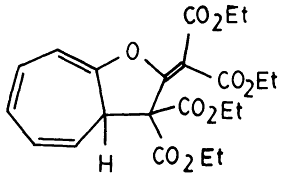
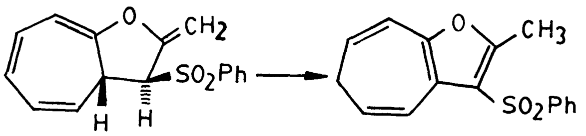
Unlike the reactions of tropone with tetraethylallenetetracarboxylic ester and phenylsulphonylpropa-1,2-diene reported in the literature (which yield 2+8 cycloadducts), thermal additions involving tropone and ethyl penta-2,3-dienoate, ethyl hexa-2,3-dienoate and ethyl 4-methylhexa-2,3-dienoate occur predominantly in a 2+4 manner. The reactions are of mechanistic significance.

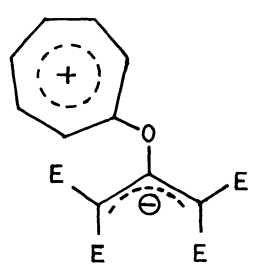
Thermal cycloaddition reactions involving tropone, and monoolefines,[1)] enamines[2)] and sulphene[3)] have been reported to furnish 2+8 and/or 2+4 adducts, albeit, the structural, steric and electronic factors which control the manner of addition are not yet fully understood. A unique 2π addend in these reactions is the allene molecule. However, to our knowledge, only two reports of such additions involving allenes have appeared in the literature. These relate to reactions of tropone with tetraethylallenetetracarboxylic ester[4)] and phenylsulphonylpropa-1,2-diene,[5)] which furnish exclusively the respective 2+8 adducts, A and B, in moderate yields; the dipolar intermediate (C) has been suggested to be implicated in the formation of A. In this communication, we describe thermal addition reactions involving tropone and 3 allenic esters i.e., ethyl penta-2,3-dienoate (1a), ethyl-hexa-2,3-dienoate (1b) and ethyl 4-methylhexa-2,3-dienoate (1c) which, unlike the above two reported reactions, furnish principally the 2+4 adducts.



(A)



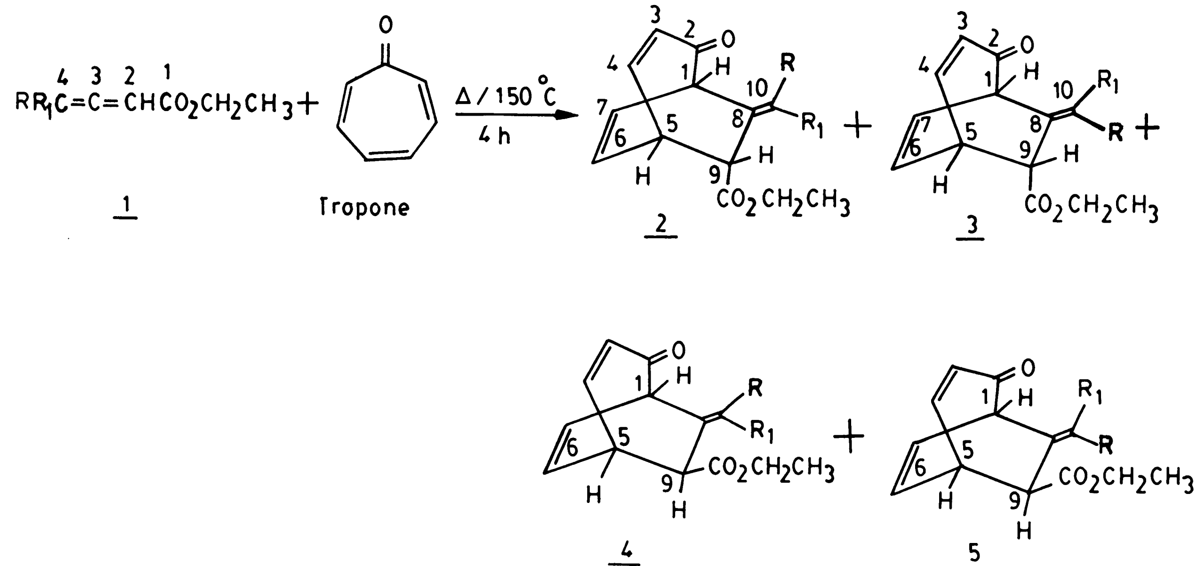
(B)



(C)

Heating a mixture of tropone (4 mmol, 435 mg) and ethyl penta-2,3-dienoate6) (1a, 4 mmol, 500 mg) at 150 °C (neat, under N_2) for 4 h gave a dark material which, on chromatography (silica gel, hexane-benzene 9:1 to 1:1 eluant), furnished the 2+4 adducts, 2a,3a,4a,and 5a (280 mg; total yield, 30%) and, in small quantity (40 mg, 4%), a 2+8 adduct (6).7)

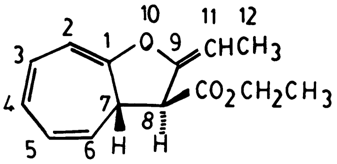
Similar reactions of tropone with ethyl hexa-2,3-dienoate (1b) and ethyl-4-methylhexa-2,3-dienoate (1c) led to formation of the respective endo- and exo-adducts: 2b:3b:4b:5b=14:1.5:5.5:1 (total yield 28%); 2c:3c:4c:5c=20:1.5:5.5:1 (total yield, 30%). The structure and stereochemistry of the adducts (2a-c to 5a-c) were established from various spectral data (^{1}H NMR, ^{13}C NMR, UV, IR, Mass).1,8,9) However, the orientation of tropone molecule in the adducts was



1 Tropone 2 3

4 5

a : R = H; R1 = CH3–
b : R = H; R1 = CH3CH2–
c : R = CH3–; R1 = CH3CH2–

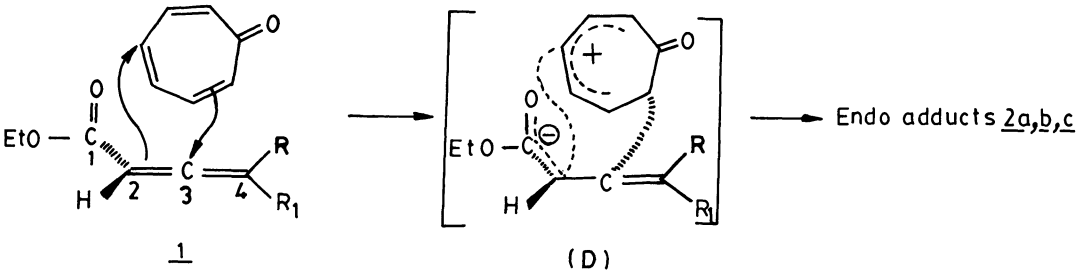


6

ascertained from the absence of coupling between C_9-H and C_1-H; the latter hydrogen (2a; δ 3.92) was identified from its LR coupling, $^{4}J_{1,3}$ 2.0 Hz with C_3-H (δ 5.90). The spectral data of 6 were in conformity with that of other known 2+8 adducts of tropone;3,5) here, low value of $^{3}J_{7,8}$ 3.5 Hz revealed trans C_7-H, C_8-H relationship in 6.

In the context of A and B, the reasons for divergent behaviour of tropone in reactions with 1a-c are not yet clear. However, we reflect that intervention of dipolar intermediates such as C (leading to 2+8 adducts) may have been suppressed in the present reactions on account of diminished electropositive character of C_3

in 1a, 1b and 1c as compared to tetraethylalleneteracarboxylic ester4) and phenylsulphonylpropa-1,2-diene.5) This finds support in the high field chemical shift of central allenic carbon (C_3) in 1a (δ 212.3), 1b (δ 211.4), and 1c (δ 209.5) with respect to C_2 in tetraethylallenetetracarboxylic ester (δ 227.4).4) The above view is also in consonance with the present observation of formation of a minor 2+8 adduct (6) in reaction of 1a (having a methyl group at C_4) as contrasted with the reactions of 1b and 1c where complete suppression of 2+8 adducts takes place. However, the observed endo-selectivity and selectivity in orientation of the tropone molecule in the adducts may have involved transition state such as D, albeit, it may be stated that, in such reactions involving addition of an electron-deficient diene to electron-deficient dienophiles, differential in the energetics of a two step - and a concerted mechanism may not be high.10)



We thank the CSIR, Government of India, for financial support to MPSI.

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6) Allenic esters (1a-c) were prepared according to literature method [R.P. Gandhi, M.P.S. Ishar, and A. Wali, Tetrahedron Lett., 1987, 6679] .

7) The reported yields of the adducts are based on starting amount of allenic esters. No reaction took place when tropone and 1a were refluxed in benzene

for 5 h. However, under the present conditions, 18-20% unreacted tropone was recovered. A GCMS analysis of the reaction mixture, done on a Jeol-JMS-D-300 instrument (SE-30, 3 mm X 3 M, 120-250 ^{o}C, 10^{o}/min, helium 1.4 kg/cm^{2}), revealed the presence of five 1:1 adducts (retention times, 7.4, 7.7, 8.0, 8.5, and 9.0 mts.) and two 1:2 adducts of tropone with **1a** (retention times, 14.7 and 15.0 mts.); the latter two adducts (yield, 8%) have been identified spectrally and are based on addition of a molecule of **1a** to the exocyclic double bond in the endo-adducts, **2a** and **3a**. Other peaks in the gas chromatogram corresponded to tropone, and dimers and trimers of **1a** (mass).

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(Received October 11, 1988)