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THERMAL CYCLOADDITION OF 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE TO 7,7-CARBOMETHOXY-7H-BENZOCYCLOHEPTENE AND 7,7-DIMETHYL-7H-BENZOCYCLOHEPTENE

CYCLOHEPTATRIENE-NORCARADIENE EQUILIBRIUM

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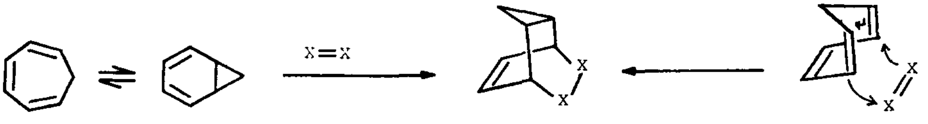
Summary: Cycloaddition reactions of 7,7-carbomethoxy-7H-benzocycloheptene and 7,7-dimethyl-7H-benzocycloheptene with 4-phenyl-1,2,4-triazoline-3,5-dione have been investigated. The formation of products is discussed in terms of cycloheptatriene-norcaradiene equilibrium.

Cycloheptatriene undergoes two dynamic processes, valence isomerization and ring inversion[1]. The valence isomers cycloheptatriene and norcaradiene have been detected by ^{1}H-NMR spectroscopy in the cases of a few substituted cycloheptatrienes[2]. The existence of unsubstituted norcaradiene[3] is accepted from the cycloaddition reactions to cycloheptatriene, forming norcaradiene-type adducts. For example, a powerful dienophile, N-phenyltriazolinedione (PTAD) gives with 7-substituted cycloheptatrienes only norcaradiene-type adducts, irrespective of the electronic nature of substituents[4]. Since norcaradiene valence isomer is expected to react with PTAD significantly faster (because of the planar diene moiety) than cycloheptatriene isomer one obtains only norcaradiene-type adducts. In cases where cycloheptatriene can not equilibrate with its valence isomer PTAD adds also to the cycloheptatriene unit[5].

A possible alternative way to the norcaradiene adduct with PTAD by a $(2\pi+2\pi+2\pi)$-cycloaddition (Homo-Diels-Alder addition) has never been discussed. More recently, Leitich and Sprintschnik have shown that cycloaddition of maleic an-

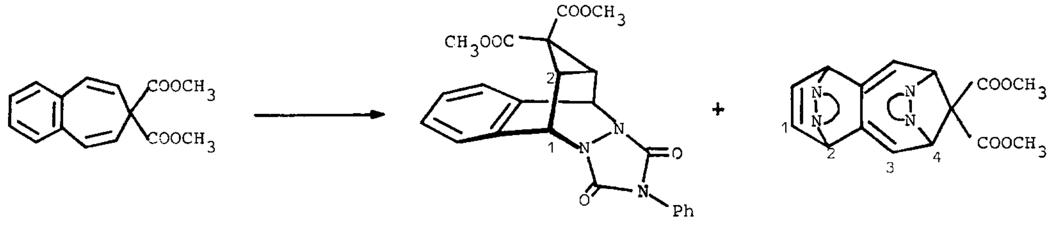


$(2\pi+4\pi)$ Cycloaddition to norcaradiene

$(2\pi+2\pi+2\pi)$ Cycloaddition to cycloheptatriene hyride to 7H-benzocycloheptene arises via $(2\pi+2\pi+2\pi)$ Homo-Diels-Alder addition On the other hand the addition product of maleic anhydride to 7H-benzocycloheptene-7,7-dicarbonitrile appears to be formed via $(2\pi+4\pi)$ cycloaddition to norcaradiene[6]. This finding prompted us to communicate our preliminary results in this field.

In order to have more insight into this problem we have chosen 7,7-carbomethoxy-7H-benzocycloheptene (1) and 7,7-dimethyl-7H-benzocycloheptene (2) for our studies. (1) and (2) were synthesized as reported in the literature[7].

Treatment of (1) with PTAD in CH_2Cl_2 at ambient temperature afforded two major products[8] (3) and (4) in yields of 30% and 45%, respectively. The structure of (3) was established on analytical and spectral evidence. The simplicity of the 400 MHz ^1H-NMR spectrum of (3) indicated the formation of a highly symmetrical adduct. The bridgehead protons and cyclopropane protons show an AA'XX' system at δ 2.75 ppm (A-part, H_2 2H) and 5.88 ppm (X-part, H_1 2H). Methoxyl protons give rise to two singlets 3.12 ppm and 3.75 ppm as expected according to the unsymmetrical orientation of these groups. Aromatic protons appear as a multiplet at 7.13-7.43 ppm (9H). 100.6 MHz ^{13}C-NMR spectrum showed in the sp^3 region only five singnals which could be assigned to bridgehead, cyclopropane, and methoxyl protons[9]. Finally, the X-ray structure analysis[10] of (3) confirms these spectral findings (Figure 1). The 400 MHz ^1H-NMR spectrum of (4) is also highly symmetrical. The bridgehead protons (H_2, 2H) and olefinic protons (H_1, 2H) show an AA'XX' system at 5.27 ppm and 6.69 ppm. Other protons (H_4) and (H_3) appear as an AX system at 5.25 ppm and 6.36 ppm (J_{AX}=7.6 Hz). Two singlets at 3.45 ppm and 3.77 ppm were assigned to methoxyl protons. Aromatic protons appear as a multiplet at 7.30-7.64 ppm. Also 100.6 MHz ^{13}C-NMR spectrum was completely in agreement with the proposed structure.



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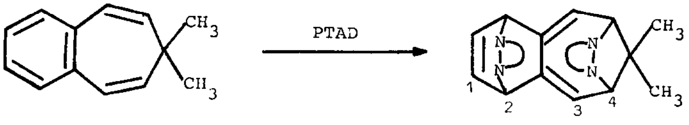

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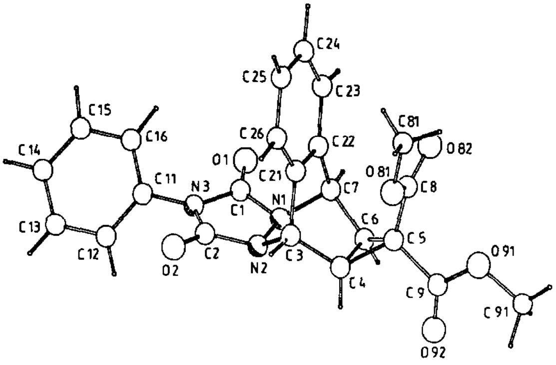
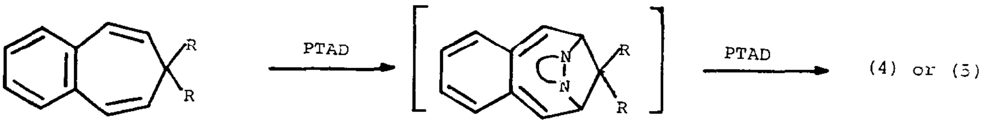


Figure 1. X-ray structure of (3)

Finally, the mass spectrum of (4) (M^+=608) clearly demonstrates the addition of two moles PTAD to (1). However, on the basis of these spectral data we were not able to determine the stereochemical configuration of this molecule

7,7-Dimethyl-7H-benzocycloheptene (2) reacted with PTAD under the same reaction condition as reported for (1). Only (5) could be separated as the sole isolable product in a yield of 45%. Careful examination of the ^{1}H-NMR spectrum did not indicate the formation of a norcaradiene-type adduct. The ^{1}H-NMR spectrum of this adduct displays similar pattern as the spectrum of (4). Olefinic protons (H_1, 2H) and bridgehead protons (H_4, 2H) appear at 4.3 ppm and 6.23 ppm as an AX system. The singlet at 1.37 ppm was assigned to the methyl protons[11].

The products (4) and (5) probably are formed by a (2π+6π) or (2π+10π) cycloaddition to the cycloheptatriene unit forming ortho quinod structure which can be trapped easily by a second mol of PTAD to give (4) and (5).



R = $COOCH_3$
= CH_3

6

It is well known that benzoannelation of cycloheptatriene at the C_3-C_4 positions shifts the cycloheptatriene-norcaradiene equilibrium to the side of cycloheptatriene[1]. On the other hand, substituents like -COOR, and -CH_3 groups at C_7 can stabilize the norcaradiene structure[12]. But the effect of the annelated benzene ring will be more dominating than the effect of substituents, since in the formation of a norcaradiene structure the resonance energy will be lost. Therefore, the formation of (3) could be explained on the basis of a $(2\pi+2\pi+2\pi)$-Homo-Diels-Alder cycloaddition. However the fact that (2) does not form any norcaradiene adduct may indicate:

a) that (3) has been formed by addition of PTAD to the norcaradiene isomer of (1), since a carbonyl group can stabilize the norcaradiene structure better than a methyl group <u>or</u>

b) that the endo-methyl group prevents the formation of the $(2\pi+2\pi+2\pi)$ cycloaddition product due to a steric interaction between the methyl group and the benzene ring.

Further investigations are currently under way to examine the effect of the methyl group.

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8) In addition to (3) and (4) we isolated a mixture of two minor products.
9) (3) : decom. p.: 192-194^{o}C; 100 MHz ^{13}C-NMR ($CDCl_3$/TMS) 168.39, 164.14, 156,06, 130.85, 129.69, 128.92, 125,26, 124,98, 55.71, 53.45, 52.03, 37.83, 24.52.; IR ; IR ($CHCl_3$) 1780, 1755, 1740, 1710, 1600, 1440, 1365, 1310, 1275, 1135, 1100, 985, 940, 390 cm^{-1}. M = 433.
   (4) : decomp. p.: 218-220^{o}C; 100 MHz ^{13}C-NMR ($CDCl_3$/TMS) 168.76, 164.68, 155.45, 154.79 133.23, 131.40, 131.52, 131.23, 129.26, 128.93, 128.61, 128.25, 126.04, 125.83, 62.89, 57.85, 57.64, 54.48, 53.73,; IR (KBr) 1765, 1740, 1730, 1715, 1705, 1600, 1500, 1440, 1400, 1350, 1290, 1260, 1240, 1130, 1100, 1030, 870. M = 608.
10) The detailed X-ray structure analysis will be reported later.
11) (5) : decomp. p.: 215^{o}C, IR (KBr) 1755, 1730, 1680, 1600, 1540, 1500, 1400, 1350, 1280 1240, 1230, 1140, 1050, 1020, 890, 840, 770, 690, 640 cm^{-1}. M =520.
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