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CYCLOHEPTATRIENE-NORCARADIENE-EQUILIBRIUM

CYCLOADDITION REACTIONS OF THE 1.2-BENZOCYCLOHEPTATRIENE WITH SINGLET OXYGEN AND 4-PHENYL-1.2.4-TRIAZOLIN-3.5-DIONE

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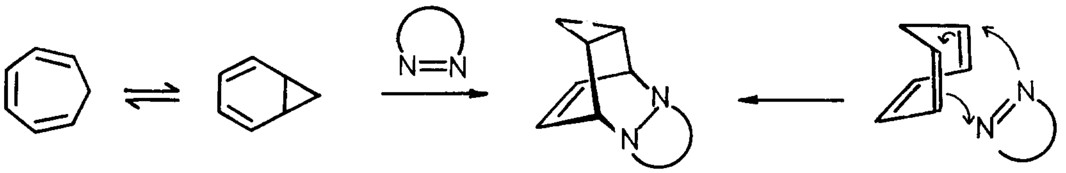
Summary: Cycloaddition reactions of the 1.2-benzocycloheptatriene with singlet oxygen and 4-phenyl-1.2.4-triazolin-3.5-dione (PTAD) have been studied. For the first time, addition of the PTAD to a cycloheptatriene derivative has been observed.

Cycloheptatriene undergoes two dynamic processes, ring inversion and valence isomerization.[1] Both theoretical[2] and experimental treatments of this equilibrium have continued to appear in the literature up to the present day. Both valence isomers, cycloheptatriene and norcaradiene have been detected by variable-temperature NMR spectroscopy in a few 7-substituted cases.[3] In the case of unsubstituted cycloheptatriene, norcaradiene itself has not been detected previously. Its existence is accepted from the cycloaddition reactions to cycloheptatriene, forming norcaradiene-type adducts. The authentic norcaradiene has been prepared via photodecarbonylation of tricyclo$[3.2.2.0^{2.4}]$non-6-ene-8.9-dione by means of matrix isolation at -196 °C.[4]

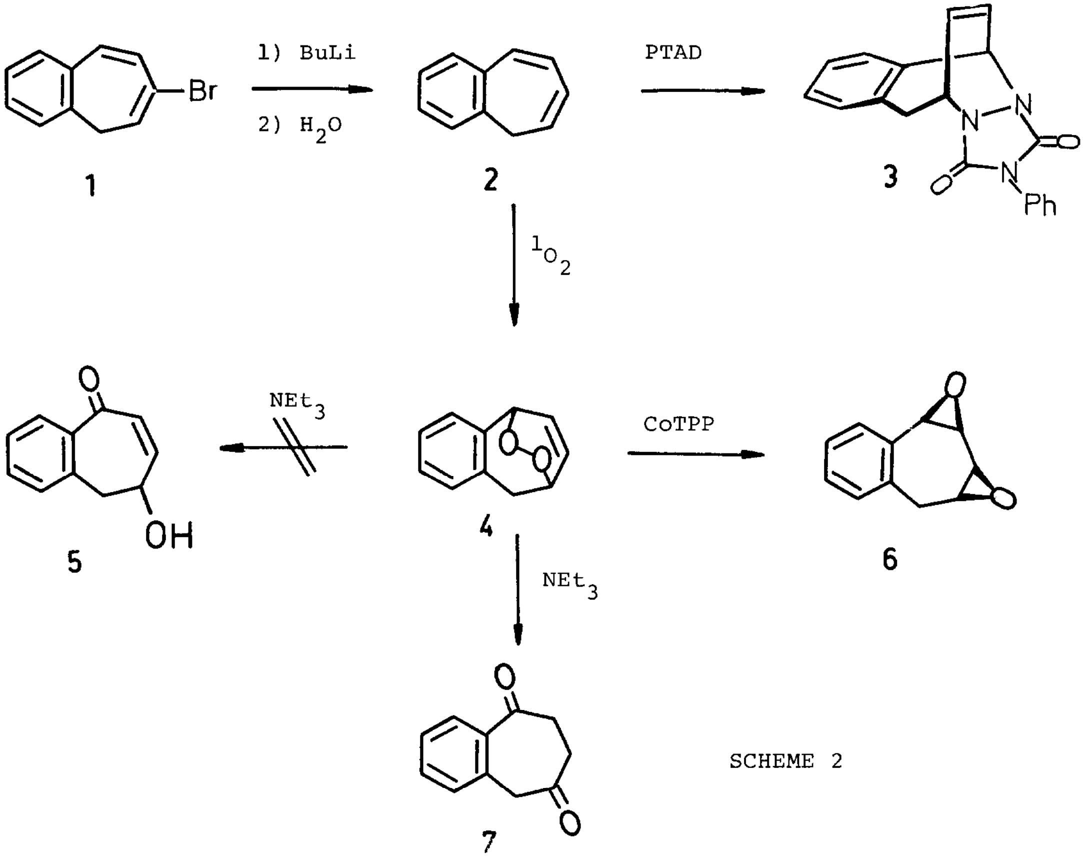
Recently, it has been shown that singlet oxygen is sufficiently reactive to intervene in the cycloheptatriene-norcaradiene equilibrium via cycloaddition.[5] Thus, ratios of cycloheptatriene and norcaradiene endoperoxides qualitatively reflect the distribution of the valence isomers in the 7-substituted cycloheptatrienes. However, N-phenyltriazolindione (PTAD) gives only norcaradiene products with cycloheptatrienes irrespective of the electronic nature of the 7-substituents.[5]



SCHEME 1

$[2+4]$ Cycloaddition to Norcaradiene

$[2+4]$ Homo-Cycloaddition to Cycloheptatriene



SCHEME 2

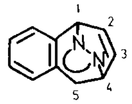
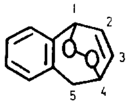
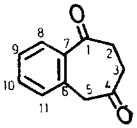
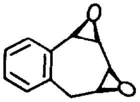
Formation of the norcaradiene-type adducts has been always explained in terms of the addition of dienophiles with the norcaradiene unit which is in equilibrium with cycloheptatriene. An addition of the PTAD with cycloheptatriene unit has never been observed.[5,6] A possible alternative way for the norcaradiene-adduct with PTAD by Homo-Diels-Alder aaddition has never been considered (Scheme 1).

In order to have more insight to this problem, at first we have decided to study whether PTAD can cycloadd with cycloheptatriene unit or not. Therefore we have chosen 1.2-benzocycloheptatriene which does not equilibrate with its valence isomer, for our studies.

1.2-Benzocycloheptatriene has been synthesized by reduction of the bromo compoun (1) with BuLi. From the reaction of (2) with PTAD in CH_2Cl_2 at ambient temperature we have obtained one adduct.[8] The structure of (3) follewed from its characteristic NMR spectrum which is similar to spectrum of (4). We were able to assign the ^1H-NMR spectrum of (3) completely. The data are presented in table 1.

1.2-Benzocycloheptatriene (2) has been submitted to the usual photooxygenation conditions, using tetraphenylporphine as sensitizer in carbontetrachloride at room temperature. ^1H-NMR studies revealed that the endoperoxide (4) was formed besides some aromatic aldehydes. The structure (4) was assigned on the basis of extensive double resonance experiments.

TABLE 1 : Selected physical data of (3), (4), (6), and (7).

	^{1}H-NMR ($CDCl_3$)		IR cm^{-1}
	δ ppm	J	
	*3.0-3.95 AB System* $H_{55'}$, *5.25 m* H_4, *5.65 dd* H_1 *6.4 br.t* H_3 , *6.8 br.t (4H)* *7.3 br.s (4H), 7.65 br.s (5H)*	J_{12}: 6.8 Hz, J_{23}: 8.4 Hz J_{34}: 6.6 Hz, J_{45}: 3.0 Hz $J_{45'}$: 4.1 Hz, J_{55}: 18 Hz J_{13}: 1.1 Hz, J_{24}:1.3 Hz	*1760, 1710* *1490, 1405* *1270, 1140* *770, 710*
	*2.8-3.8 AB System* $H_{55'}$, *4.75 m* H_4 , *5.1 br.d* H_1 *6.35 t* H_2 , *6.65 t* H_3 *6.85-7.5 m (4H)*	J_{12}: 6.9 Hz, J_{23}: 8.6 Hz J_{34}: 7.6 Hz, J_{45}: 4.1 Hz $J_{45'}$: 3 Hz, $J_{55'}$: 17.8 Hz J_{14}: 1.0 Hz, J_{24}: 1.3 Hz	*1490, 1450* *1410, 1185* *990, 770* *750, 730*
	*2.5-3.3 AA'BB' System* H_2 H_3 *(4H) , 3.9 s* H_5 *(2H)* *7.0-7.6 m* H_9 H_{10} H_{11} *7.75-8.05 m* H_8		*1715, 1675* *1600, 1315* *1275, 965* *890*
	*2.65-3.3 m methylenic (2H)* *and epoxide (1H) , 3.3-3.85* *epoxide (2H) , 4.0 d epoxide* *(1H) , 6.8-7.4 aromatic (4H)*		*3000, 2940* *1495, 1450* *1275, 1200* *965, 890*

As additional structural proof we have relied on chemical transformations, including a) base-catalyzed rearrangement, b) CoTPP-catalyzed rearrangement. Base-catalyzed rearrangement[9] has formed the unexpected diketone (7) quantitatively, instead of the expected hydroxy-ketone (5). To the best of our knowledge, this base-catalyzed rearrangement is unprecedented.[10] The formation mechanism of this diketone is currently under investigation.

CoTPP-catalyzed rearrangement[11] of (4) has given exclusively the bisepoxide in high yield.

As already mentioned before, singlet oxygen can intervene the cycloheptatriene-norcaradiene equilibrium and detect even too small norcaradiene concentration which is not possible by dynamic ^{1}H-NMR. Photooxygenation of 1.2-benzocycloheptatriene provided only cycloheptatriene adduct. Our results support that the norcaradiene isomer is not equilibrating with 1.2-benzocycloheptatriene. By the reaction of PTAD with (2) we have obtained for the first time a cycloheptatriene adduct. This observation is novel.

These results indicate that tha PTAD can add to cycloheptatriene unit. Herewith we observed for the first time the non-divergent cycloaddition behaviour between the PTAD and singlet oxygen dienophiles. In the case of 1.2-benzocycloheptatriene we have not expected a Homo-Diels-Alder addition since the resonance energy of benzene ring will be lost upon formation of norcaradiene-type adduct.

In order to clear the addition mechanism of the PTAD to cycloheptatriene derivatives, forming norcaradiene-type adduct, some specific studies are underprogress

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