Tetrahedron Vol. 42, No. 5, pp. 1461 to 1468, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00
Pergamon Press Ltd.

CYCLOADDITION REACTIONS OF 5H-BENZOCYCLOHEPTENE WITH SINGLET OXYGEN AND WITH 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE, AND THE CHEMISTRY OF THE 5H-BENZOCYCLOHEPTENE ENDOPEROXIDES[1]

Basri Atasoy[2] and Metin Balcı *

Department of Chemistry, Faculty of Science, Atatürk University
Erzurum, Turkey

(*Received in UK* 17 *December* 1985)

Abstract- The cycloaddition reactions of 5H-benzocycloheptene with 4-phenyl 1,2,4-triazoline-3,5-dione (PTAD) and singlet oxygen has been investigated. ^{1}H-NMR spectra established structures formally derived from the cycloheptatriene valence isomer by (2+4)-Diels-Alder cycloaddition. The formation of these cycloheptatriene adducts is discussed in terms of cycloheptatriene-norcaradiene-equilibrium. The chemistry of the cycloheptatriene endoperoxide (6) was studied. Thermolysis of (6) gave a mixture of products; bis-epoxide, epoxy-ketone, and hydroxy-enone. However, base-catalyzed rearrangement of (6) gave diketone (14) instead of the expected hydroxy-enone. This observation is unprecedented. The formation-mechanism of (14) is also discussed.

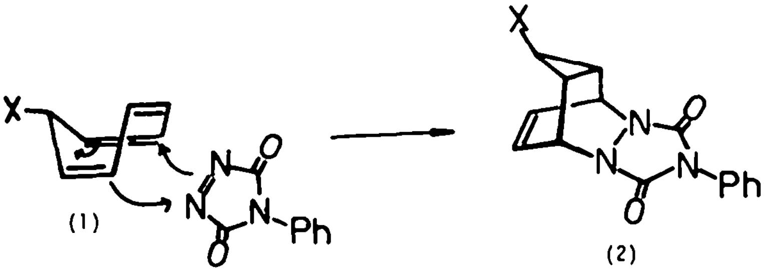
INTRODUCTION

Cycloheptatriene undergoes two dynamic processes, a) ring inversion and b) valence isomerization[3]. Both theoretical[4] and experimental[5] treatments of this equilibrium have continued to appear in the literature up to the present day. The valence isomers cycloheptatriene and norcaradiene have been detected by dynamic ^{1}H-NMR spectroscopy in the cases of a few 7-substituted cycloheptatrienes. Unsubstituted norcaradiene has not been detected previously[6]. Its existence is accepted from the cyloaddition reactions to cycloheptatriene (CHT), forming norcaradiene (NOR)-type adducts.

Recently, it has been shown that singlet oxygen is sufficiently reactive to intervene in the CHT-NOR equilibrium via cycloaddition[7]. The ratios of CHT-NOR endoperoxides qualitatively reflect the distribution of valence isomers in the 7-substituted cycloheptatrienes on the other hand, a powerful dienophile, N-phenyl triazoline-dione (PTAD) gives only norcaradiene adducts, irrespective of the electronic nature of the substituents[7]. More recently[8], the cycloaddition reactions of PTAD with 7,7-difluoro- and 7,7-dialkoxy-1,3,5-cycloheptatrienes have been studied. Since, these substituents have strong electron-withdrawing ability, they should shift the CHT-NOR equilibrium to the CHT-side. NOR- and CHT-type adducts were observed, depending on the electronic nature of these substituents.

The formation of NOR-type adducts in cycloaddition reactions has always been explained in terms of the addition of dienophiles with norcaradiene unit which is in equilibrium with cycloheptatriene. A possible alternative way for the formation of the NOR-adduct with PTAD is a homo-Diels-Alder addition to cycloheptatriene; this has not previously been considered (Eq. 1).

In order to obtain more insight into this problem, we decided to study first the addition of PTAD and singlet oxygen to a cycloheptatriene which does not bear any substituent at C-7 and which cannot equilibrate with its valence isomer. Therefore we chose for our studies 5H-benzocycloheptene (3). In the case of (3) one would not expect any homo-Diels-Alder adduct, since the resonance energy of the benzene ring will be lost on formation of the norcaradiene adduct.



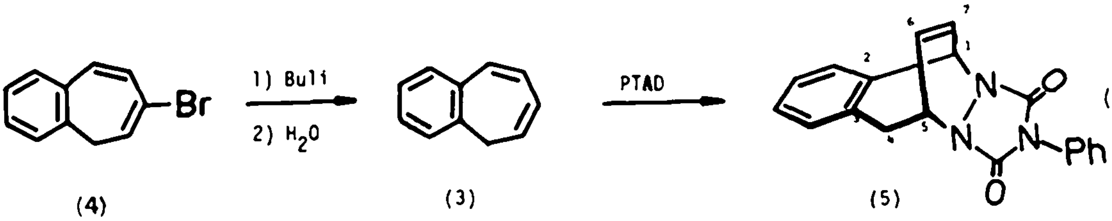
(Eq.1)

HOMO-DIELS-ALDER ADDITION

RESULT AND DISCUSSION

REACTION OF 5H-BENZOCYCLOHEPTENE WITH PTAD

5H-Benzocycloheptene has been synthesized by reduction of the known bromobenzocycloheptene[9] (4) with BuLi.



(Eq.2

When a mixture of (3) and PTAD in CH_2Cl_2 was reacted at ambient temperature a sole (2+4) adduct (5) was obtained in a yield of 55% after recrystallization from CH_2Cl_2/petroleum ether. The structure of this adduct was deduced from its ^{1}H-NMR spectrum. The methylene protons at C-4 show an AB-system at δ 3.0-3.95 ppm. Both parts of this AB-system are further split by H-5. The olefinic protons exhibit absorptions at δ 6.8 (t) and 6.4 (t) ppm. Bridgehead protons are at δ 5.25 ppm (H-5) and 5.65 ppm with the expected splitting patterns. The aromatic protons appeared as two separate singlets at δ 7.3 ppm (4H) and 7.65 ppm (5H).

The formation of CHT-type adduct (5) indicates that PTAD can add exclusively to a cycloheptatriene unit in which the cycloheptatriene is not substituted at C-7. Whatever the addition mechanism, leading to NOR-type adduct, can be,

i) cycloaddition of PTAD to norcaradiene, equilibrating with cycloheptatriene, or

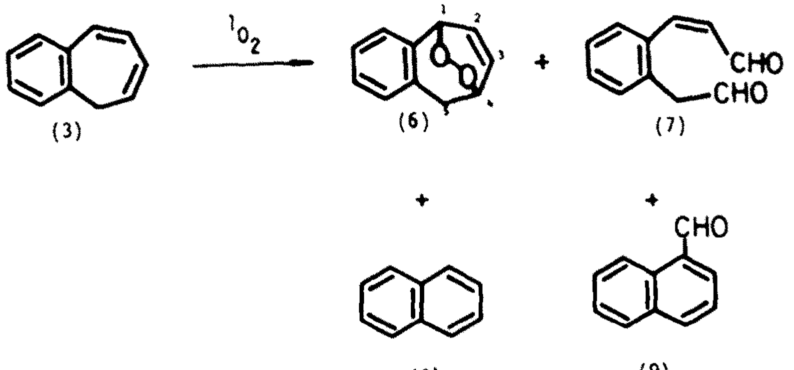
ii) homo-Diels-Alder addition,

we were not able to detect any trace of NOR-type adduct. As mentioned before, the formation of NOR-type adduct would cause loss of the benzene ring resonance energy. Therefore, we can conclude that PTAD can add to cycloheptatriene systems which do not equilibrate with their valence isomer, norcaradienes. However, in the case of equilibrium there is a competition between cycloheptatriene and norcaradiene units to react with PTAD. Since the diene unit in NOR has a planar structure, PTAD can add more easily to NOR than to the twisted diene unit in CHT.

REACTION OF 5H-BENZOCYCLOHEPTENE WITH SINGLET OXYGEN

The manifold aspects related to the photo-oxygenation of carbocyclic polyenes have been extensively investigated[10]. Then the reactions of singlet oxygen with cyclic polyenes might be expected to give the cycloaddition process[11]. For example, unsubstituted cycloheptatriene produces four types of adducts with singlet oxygen[12].

The photo-oxygenation of 5H-benzocycloheptene (3) was carried out by bubbling of oxygen in carbon tetrachloride while irradiating by a 150 Watt projector lamp in the presence of tetraphenylporphin as sensitizer. After 13 h of irradiation, ^{1}H-NMR monitoring indicated complete consumption of (3). ^{1}H-NMR spectrum of the crude material showed that the endoperoxide was formed, besides aromatic



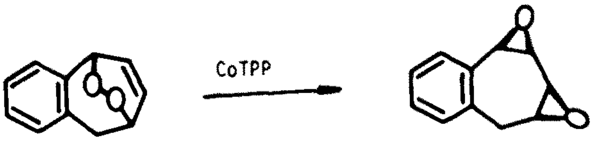
(3) (6) (7) (8) (9)

(Eq.3)

aldehydes. Careful silica gel chromatography of this mixture at 25°C, eluting with $CHCl_3$/petroleum ether (2:1), permitted the separation of naphthalene, α-naphthaldehyde, endoperoxide (6) and dialdehyde (7), respectively. Naphthalene and α-naphthaldehyde were characterized by comparison with authentic samples. Careful ^{1}H-NMR studies of the reaction mixture before column chromatography indicated the absence of α-naphthaldehyde, showing that it was formed during chromatography.

The structure of (6) was established on the basis of analytical and spectral data. The ^{1}H-NMR spectrum pattern of (6) was very similar to that of (5). The methylene protons gave rise to an AB-system at δ 2.8-3.8 ppm, further split by the adjacent bridgehead proton H-4. A doublet at δ 5.1 ppm was assigned to the bridgehead proton H-1 and a multiplet at δ 4.75 to H-4. Double resonance experiment were needed to assign the olefinic protons. Irradiation at the bridgehead proton H-1 caused a collapse of the triplet at δ 6.65 into a doublet. Therefore, the triplet at δ 6.65 was assigned to H-2 and the triplet at δ 6.35 to H-3. The aromatic protons gave a multiplet at δ 6.85-7.50 ppm.

For additional structural proof we relied on chemical transformation, the Cobalt-meso-tetraphenylporphyrin (CoTPP)-catalyzed rearrangement[13], as illustrated in Eq. 4. Recently, we showed the application of the CoTPP-catalyzed rearrangement to systems with strained or perturbed diene moieties which can form bis-epoxides in high yield[14]. We submitted the endoperoxide (6) to a CoTPP-catalyzed rearrangement and obtained the desired epoxide (11) in quantitative yield.

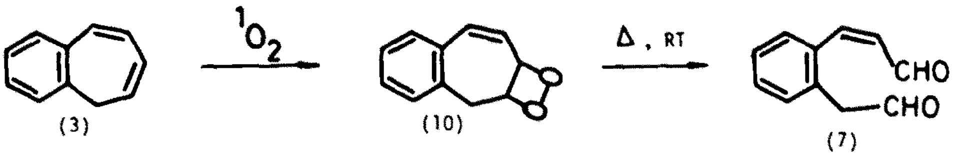


(6) (11)

(Eq.4)

Dialdehyde (7) could not be isolated pure; it was always contaminated with α-naphthaldehyde, and was always partly condensed to the naphthaldehyde during chromatography. The characteristic ^{1}H-NMR data of (7) could be discerned in the spectrum of the mixture. The aldehyde protons gave two peaks at δ 9.1 (t) and 9.3 (d) ppm and the methylene protons appeared at δ 3.75 as a doublet. The formation of (7) can be explained by ring cleavage of the dioxetane (10) which can originate from (2+2) cycloaddition of singlet oxygen to 5H-benzocycloheptene.

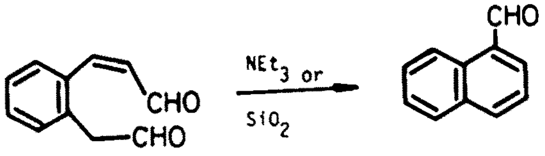
The photo-oxygenation of cycloheptatriene was also resulted in the formation of 5% benzaldehyde[12]. Recent low-temperature studies[15] have revealed that a 1,2-dioxetane is precursor to the benzaldehyde.



(3) (10) (7)

(Eq.5)

Since the methylene protons in (7) are activated by a carbonyl group and benzene ring, (7) can easily undergo condensation reactions. Treatment of (7) with triethylamine or stirring with SiO_2 in CH_2Cl_2 at room temperature formed α-naphthaldehyde exclusively.



(7) (9) (Eq.6)

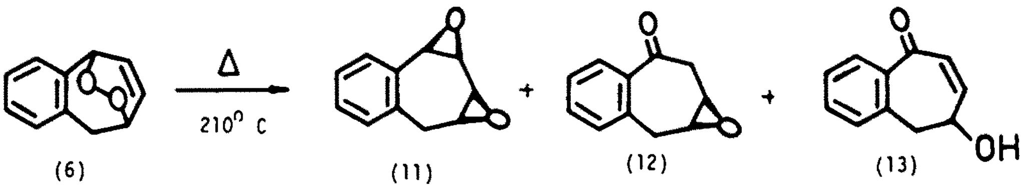
The origin of naphthalene formed during photo-oxygenation of (3) is obscure. A similar observation was also made in the cycloheptatriene system. Photo-oxygenation of cycloheptatriene formed, besides the endoperoxides, benzene in a yield of 5%[12]. The mechanism of its formation was not clarified.

As mentioned before, singlet oxygen can intervene in the cycloheptatriene-norcaradiene equilibrium and trap a norcaradiene concentration too small to detect even by dynamic ^1H-NMR. Photo-oxygenation of 5H-benzocycloheptene provided only the cycloheptatriene adduct. Our results indicate that the norcaradiene isomer is not in equilibrium with the 5H-benzocycloheptene. PTAD also gave only the cycloheptatriene adduct. Thus we observe for the first time non-divergent cycloaddition behaviour between PTAD and singlet oxygen. When an equilibrium between cycloheptatriene and norcaradiene does not arise, the two dienophiles, PTAD and singlet oxygen, react in a similar manner.

THERMOLYSIS OF ENDOPEROXIDE (6)

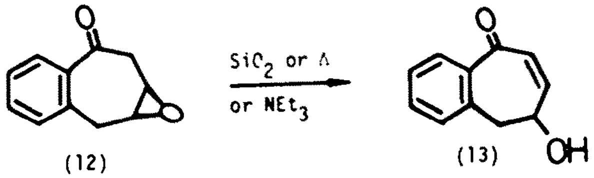
One of the commen reactions of unsaturated [n.2.2]bicyclic endoperoxides is the thermal cleavage of the weak oxygen-oxygen bond followed by addition of the oxygen radicals to the adjacent double bond to give bis-epoxides with syn-configuration. However, this reaction can form also some side products. One of these is the formation of epoxy-ketones[16]. Thermolysis of endoperoxides from strained or perturbed diene moiety is always accompanied by side reactions. Such side reactions have been observed recently in cycloheptatriene systems[17].

The thermolysis of (6) should be interesting in view of these side reactions. Therefore, we submitted endoperoxide (6) to thermolysis in a sealed tube. The thermal stability of endoperoxide (6) is quite high and heating at 210°C in toluene for 1 h was needed in order to destroy it completely. The major product of the thermolysis was the expected bis-epoxide (50%). The structure was established by comparison of the physical data of (11) which was formed by CoTPP-catalyzed rearrangement of (6). Bis-epoxide (11) was isolated and purified by silica gel column chromatography.



(6) (11) (12) (13) (Eq.7

Significant was the observation that the crude thermolysate mixture showed also the presence of (12) and (13). Attempt to isolate (12) by column chromatography failed. Presumably the silica gel catalyzes the isomerization of (12) to (13), since (12) possesses a β-γ-epoxy-ketone moiety.

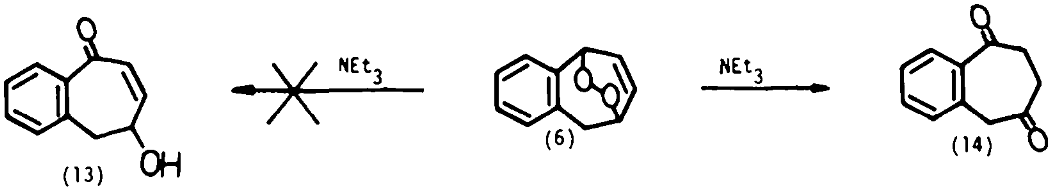


(12) (13) (Eq.8)

Control experiments revelead that the bis-epoxide (11) was stable under the thermolysis conditions, indicating that (12) and (13) are not secondary products arising from bis-epoxide (11). However, thermolysis of epoxy-ketone (12) under the same reaction conditions showed that the isomerization of (12) to (13) occurs. Therefore, we can conclude that hydroxy-enone (13) is a secondary product from (12). β-γ-Epoxy-ketones are also sensitive to bases. Treatment of (12) with triethylamine furnished (13) in quantitative yield.

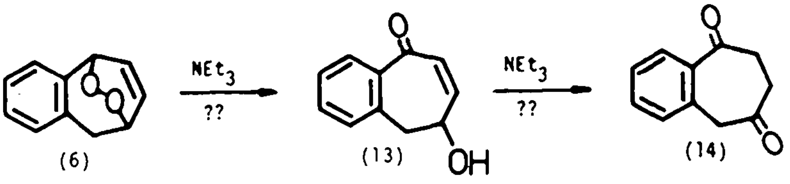
REACTION OF ENDOPEROXIDE (6) WITH NEt$_3$[18]

Base-catalyzed decomposition of peroxides and hydroperoxides exemplify a general type of elimination reaction which may be expected for compounds in which an anion or group X (capable of giving a relatively stable anion X$^-$) is attached to oxygen. The application of this reaction to bicyclic endoperoxides resulted in the formation of hydroxy-ketone which can further be converted into interesting compounds like diketones, dienones, etc. The triethylamine-catalyzed reaarrangement has successfully been applied to many systems[19].



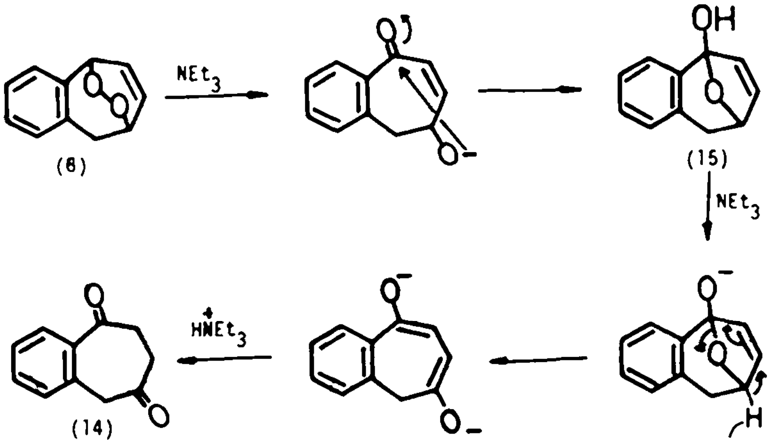
Therefore, we studied the triethylamine-catalyzed reaction of the endoperoxide (6) at 0°C. Surprisingly, we isolated the saturated diketone (14) instead of the expected hydroxy-ketone (13). Diketone (14) was characterized by its spectral data. The ^{1}H-NMR spectrum consisted of a singlet at δ 3.9 ppm (H-55'), and an AA'BB'-system at δ 2.5-3.3 ppm (H-22', H-33'). Three of the aromatic protons absorbed at δ 7.0-7.6 ppm, the fourth at δ 7.75-8.05 ppm. The low-field aromatic proton resonance is the result of the shielding effect of the carbonyl function. This indicates also the location of the carbonyl group. The IR spectrum with two carbonyl absorptions at 1715 and 1690 cm^{-1} is in agreement with the proposed structure. To the best of our knowledge this base-catalyzed reaction is unprecedented[20].

To explain the mechanism of this interesting transformation, it would be reasonable to assume that the first step is the formation of hydroxy-enone (13) which can undergo further isomerization (Eq. 9).



(Eq.9)

Hydroxy-enone (13) was isolated by thermolysis of (6) as a side product, so that we had the possibility to check the above mentioned mechanism. The hydroxy-enone was treated under the same reaction conditions with NEt$_3$. No reaction was detected. Therefore, the formation of (13) as an intermediate was eliminated. The base-catalyzed reaction carried out in an NMR tube. Monitoring of the reaction



SCHEME I

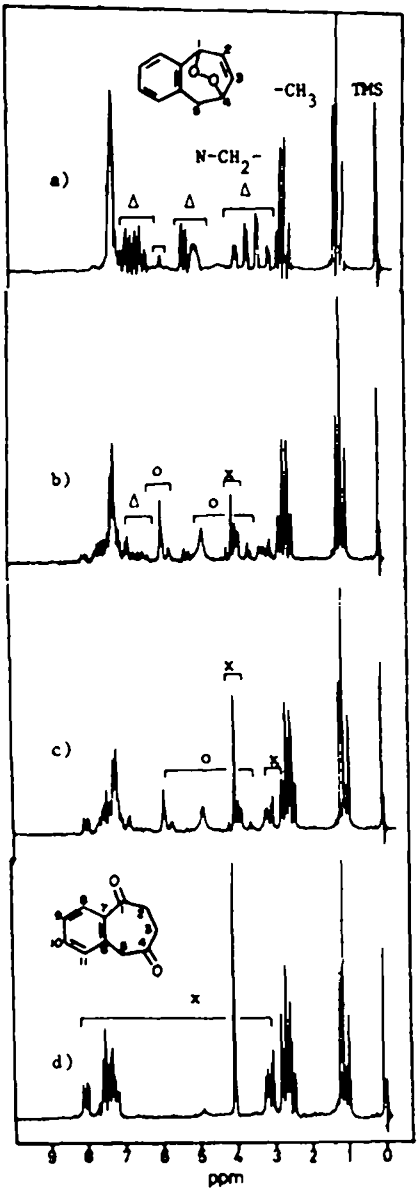


Figure 1. ^{1}H-NMR spectra from the triethylamine-catalyzed reaction of endoperoxide (6).
a) Endoperoxide/Triethylamine after 5 min. b) 100 min. c) 150 min. d) 240 min.
Δ) Resonances of the endoperoxides (6)
o) Resonances of the intermediate
x) Resonances of the diketone (14)

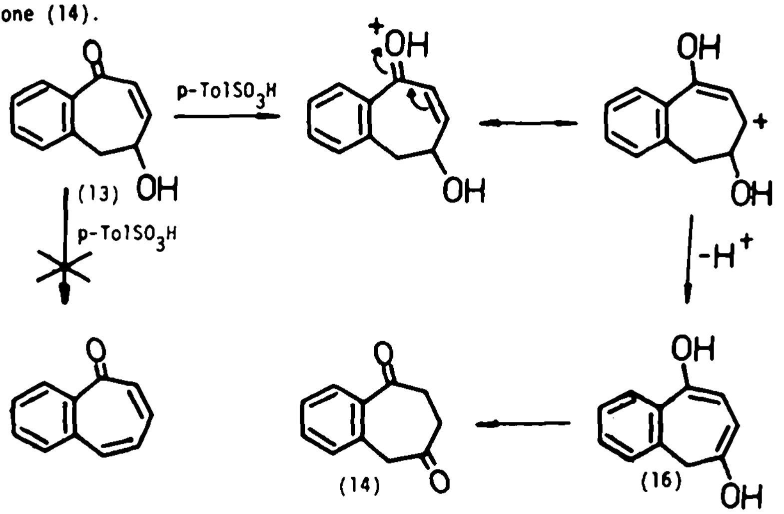
with ^{1}H-NMR indicated that the diketone (14) was not a primary product. As one can see from the ^{1}H-NMR spectra (Figure 1) at first an intermediate product was formed. From the spectra (spectrum c) we could extract some characteristic ^{1}H-NMR data from the intermediate. As can be seen in Figure 1c, the endoperoxide resonances disappeared. We observed peaks arising from the intermediate at δ 3.5-4.2 ppm, an AB-system (methylene protons), at δ 4.7-4.9 bridgehead and alcoholic protons and at δ 5.7-5.9 ppm, olefinic protons. Interesting feature of the AB-System is the coupling constant J_{gem} = 16.0 Hz. This coupling has dropped from 18 Hz in the endoperoxide which indicates the existence of ring strain or ring contraction. In the light of these parameters we suggest structure (15) for the intermediate, and a mechanism for the rearrangement as outlined on Scheme 1. Probably, the intermediate (15) can be transformed to a dienolate ion in which the removal of the bridgehead hydrogen and the ring-opening take place in a concerted reaction.

The effect of the solvent on the mode of this reaction has been also investigated. The polarity of the solvent did not change the reaction.

Independently, diketone (14) was also obtained by reaction of hydroxy-enone (13) with a catalytic amount of p-toluenesulfonic acid.

We attempted to generate 2,3-benzotropone in a simple way. To our surprise, we isolated diketone in quantitative yield.

The reaction mechanism is depicted in Scheme II. The intermediate bis-enol (16) can tautomerize cleanly into diketone (14).



SCHEME II

A similar observation has been made by Isler et al.[21] who reported isomerization of the hydroxyisophorone to the dione by refluxing a solution of hydroxyisphorone with a catalytic amount of TosOH in benzene.

EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, material were obtained from commercial suppliers and were used without further purification. Ether, tetrahydrofuran and benzene were distilled from sodium (potassium-benzophenone) immediately prior to use. Methylene chloride, triethylamine were distilled from calcium hydride prior to use. Boiling points and melting points are uncorrected.
Infrared spectra (IR) were determined with Perkin Elmer 377 infrared recording spectrophotometer. ^{1}H-NMR spectra were recorded with EM 360 Varian spectrometer. Mass spectra were recorded at the University of Florida.

5H-Benzocycloheptene$^{22)}$

To a solution of 7.5 g (34 mmole) of 7-bromo-5H-benzocycloheptene (4) in 100 ml of freshly distilled THF was added at -70°C under nitrogen atmosphere a solution of 38 ml buthyllithium (50 mmole) in hexane over 45 min. The reaction was allowed to come to -20°C over 1 h with stirring, and then recooled to -70° C at which point 10 ml of H_2O was added slowly. After allowing the reaction to come to room temperature a part of THF was removed under reduced pressure. To resulting mixture was added 100 ml of H_2O and 100 ml of petroleum ether. The layers were separated, the aqueous layer reextracted two times with 50 ml of petroleum ether and the combined organic layers washed with water and dried over Na_2SO_4. After removal of solvent under reduced pressure (15 mm Hg, 30°C) the oily residue was distilled at 20 mm Hg. The fraction between 115-120°C afforded 3.5 g (72%) colorless liquid.

Cycloaddition of PTAD to the 5H-Benzocycloheptene (3)$^{23)}$

To a stirred solution of 142 mg (1 mmol) of 5H-benzocycloheptene in 20 mL of CH_2Cl_2 was added at room temperature in small portions 175 mg (1 mmol) of the PTAC over a period of ca. 30 min.. After stirring at room temperature for 6 h, the solvent was rotoevaporated and the solid residue was purified by preparative TLC (silica gel) using $CHCl_3$/petroleum ether (1:1). Crystallization from CH_2Cl_2/petroleum ether gave white crystals (55%) : mp: 197-198°C ; MS (70 eV), m/e 317 (63.6 %), 198 (7.1), 177 (7.5), 155 (11.5), 143 (12.6), 142 (100), 141 (75.4), 129 (11.6), 128 (15.4), 119 (21.9), 115 (22.2), 91 (10.8), 77 (5.6). Anal. $C_{19}H_{15}O_2N_3$ (317.33) Calcd.: 71.91 C, 4.76 H, Found : C, 72.08; H, 4.68.

Photo-oxygenation of 5H-Benzocycloheptene (3)$^{23)}$

To a magnetically stirred solution of 1.5 g (10.5 mmol) of 5H-benzocycloheptene (3) in 150 mL of CCl_4 was given ca. 50 mg of tetraphenylporphyrine (TPP) as sensitizer. The solution was irradiated with a projector lamp (150 Watt) at room temperature while passing continuously a slow stream of dry oxygen gas. The progress of the photo-oxygenation was monitored by ^{1}H-NMR until essentially complete consumption of the starting material. After 13 h the reaction was completed. The solvent was rotoevaporated (15 mm Hg, 25°C) and the residue was chromatographed on silica gel (50 g) at 25°C, eluting with $CHCl_3$/petroleum ether (2:1).

1. Fraction : 40 mg (3%) naphthalene
2. Fraction : 197 mg (12%) α-naphthaldehyde
3. Fraction : ca. 1.0 mixture of endoperoxide (6) and α-naphthaldehyde
4. Fraction : 380 mg mixture of α-naphthaldehyde and dialdehyde (4:1).

Third fraction was rechromatographed on ca. 30 g silica gel eluting with $CHCl_3$/petroleum ether. After separation of α-naphthaldehyde as a first fraction, endoperoxide (6) was collected and the solvent was removed by rotoevaporation (15 mm Hg, 25°C) to give 720 mg (39%) of (6). Crystallization from CH_2Cl_2/petroleum ether gave colourless crystals (560 mg, 30%) ; mp : 94-95°C, MS (70 eV), m/e 174 (2.8%), 146 (16.9), 145 (100), 131(21.0), 129 (24.8), 128 (43.2), 127 (35.3), 117 (39.0), 116 (59.8), 115 (95.4), 104 (23.4). Anal. $C_{11}H_{10}O_2$ (174.19). Calcd.: C 75.48, H 5.79. Found : C 75.34, H 5.88.

CoTPP^{24}-catalyzed Rearrangement of (6)^{23}

To a magnetically stirred solution of 100 mg (0.575 mmol) of endoperoxide (6) in 10 mL of CH_2Cl_2 was added a solution of 5 mg cobalt-meso-tetraphenylporphyrine in 3 mL of CH_2Cl_2 at 10°C. After comlete addition (20 min.) the mixture was stirred for 1 h at room temperature. The solvent was rotoevaporated (15 mm Hg, 30°C). The residue was passed through 5 g silica gel, eluting with $CHCl_3$/petroleum ether (2:1). Rotoevaporation of the solvent gave the bis-epoxide (11) in quantitative yield (100 mg). Crystallization from CH_2Cl_2/petroleum ether gave colourless crystals. mp : 94-95°C. Anal. $C_{11}H_{10}O_2$ (174.19) Calcd. : C 75.48, H 5.79. Found : C 75.68, H 5.91.

Reaction of Dialdehyde (7) with NEt_3

To a magnetically stirred solution of 150 mg dialdehyde (7) and α-naphthaldehyde (isolated as last fraction from the photo-oxygenation reaction of (3)) mixture in 15 mL of CH_2Cl_2 was added a solution of 20 mg NEt_3 in 5 mL of CH_2Cl_2. The mixture was stirred for 30 min. at room temperature. The solvent was evaporated. ^{1}H-NMR spectrum of the oily residue showed the complete formation of α-naphthaldehyde as sole product in quantitative yield.

Reaction of Dialdehyde (7) with SiO_2

To a magnetically stirred solution of 200 mg dialdehyde (7) and α-naphthaldehyde mixture in 50 mL of CH_2Cl_2 was given 10 g silica gel. The mixture was stirred for 6 h at room temperature. Silica gel was filtered and the solvent was rotoevaporated. α-Naphthaldehyde was formed again in quantitative yield.

Thermolysis of Endoperoxide (6)

A solution of 250 mg (1.43 mmol) endoperoxide (6) in 5 mL of toluene was placed into a constricted test tube, sealed under vacuum, and heated at 210°C for 1 h. After cooling to room temperature the solvent was rotoevaporated and the residue analyzed by ^1H-NMR to assure complete transformation of endoperoxide (6). The thermolysate was submitted to silica gel (20 g) chromatography. Eluting with $CHCl_3$ afforded as first eluate the bisepoxide (11) in 50% yield. As second eluate, a mixture of epoxyketone (12) and hydroxy-enone (13) was isolated in 40% yield. Rechromatography of this eluate on silica gel, eluting with $CHCl_3$/petroleum ether (1:1) gave as a sole product, hydroxy-enone (13). Colourless liquid; IR ($CHCl_3$) 3600-3500, 3000, 1640, 1380, 1100 cm^{-1}. ^1H-NMR ($CDCl_3$) δ 2.5-3.0 (br. s, OH), 3.0-3.7 (AB-System, 2H), 4.3-4.7 (m, 1H), 6.0-6.8 (AB-System, 2H), 7.0-7.5 (m, 3H), 7.6-7.8 (m, 1H).

NEt_3-Catalyzed Reaction of Endoperoxide (6)[23]

To a magnetically stirred solution of 100 mg (0.575 mmol) of endoperoxide (6) in 5 mL of methanol (or CH_2Cl_2) was added a solution of 20 mg (0.2 mmol) of NEt_3 in 1 mL of methanol. The mixture was stirred at room temperature for 4 h. The reaction was monitored by TLC. The solvent was rotoevaporated to leave a colourless liquid. The product was passed through a short silica gel column, eluting with CH_2Cl_2. The solvent was rotoevaporated. Pure diketone (14) was obtained in quantitative yield. Colourless liquid; MS (70 eV) m/e 174 (100%), 146, (52.2), 145 (41.2), 131 (62.2), 119 (70.3), 118 (63.7), 91 (48.5), 90 (83.3), 88 (48.7). Anal. $C_{11}H_{10}O_2$ (174.19). Calcd.: C 75.84, H 5.79. Found C 74.92, H 5.68.

Reaction of the Hydroxy-enone (13) with NEt_3

To a magnetically stirred solution of ca. 50 mg (0.29 mmol) hydroxy-enone (13) in 20 mL of CH_2Cl_2 was given 50 mg of NEt_3. The mixture was stirred at room temperature for 8 h. The solvent was rotoevaporated and the residue analyzed by ^1H-NMR. The hydroxy-enone was unchanged.

Acid-catalyzed Reaction of Hydroxy-enone (13)

A mixture of 40 mg (0.23 mmol) of (13) and 5 mg (0.03 mmol) of p-toluenesulfonic acid in 5 mL of dry benzene was refluxed for 2 h. The organic layer was washed with water and dried over $MgSO_4$. After evaporation of the solvent and passing through a short silica gel column, diketone (14) was isolated in quantitative yield.

ACKNOWLEDGEMENT : The authors are indepted to the Department of Chemistry, Atatürk University for financial support of this work and wish to express their appreciation to Prof. Dr. W. M, Jones (University of Florida) for Mass spectral measurements and to Mr. Şahmettin Yıldız for his technical assistance.

REFERENCES

1) For a preliminary communication see: Balcı, M. ; Atasoy, B., *Tetrahedron Lett.*, 1984, 25, 4033.
2) Taken in part from the Ph.D. Dissertation of B. Atasoy, Atatürk University, Erzurum, May 1985.
3) For rewies see : a) Maier, G., *Angew. Chem.*, 1967, 79, 466. b) Kessler, H., "Methoden der Organischen Chemie" Houben-Weyl-Müller, 1972, 5/1d, 300. c) Balcı, M., *Doğa Bilim Dergisi, A*, 1982, 6, 53.
4) a) Hoffmann, R., *Tetrahedron Lett.*, 1970, 2907. b) Günther, H., *Tetrahedron Lett.*, 1970, 5173.
5) a) Ciganek, E., *J. Am. Chem. Soc.*, 1965, 87, 1149. b) Görlitz, M. ; Günther, H., *Tetrahedron*, 1967, 25, 4467. c) Wehner, R. ; Günther, H., *J. Am. Chem. Soc.*, 1975, 97, 923. d) Balcı, M. ; Fischer, H. ; Günther, H., *Angew. Chem.*, 1980, 92, 316.
6) The authentic norcaradiene has been recently prepared. Rubin, M. B., *J. Am. Chem. Soc.*, 1981, 103, 77
7) Adam, W. ; Balcı, M. ; Pietrzak, B., *J. Am. Chem. Soc.*, 1979, 101, 6285.
8) a) Welt, G. ; Fisher, P. ; Föhlisch, B., *Chem. Ber.*, 1982, 115, 3427. b) Heise, I. ; Leitich, J., *Chem Ber.*, 1985, 118, 332.
9) Mayor, C. ; Jones, W. M., *Tetrahedron Lett.*, 1977, 3855.
10) a) Kearns, D.R., *Chem. Rev.*, 1971, 71, 395. b) Frimer, A. A., ibid. 1979, 79, 359. c) Foote, C. S., *Acc. Chem. Res.*, 1968, 1, 104.
11) Gormann, A. A. ; Lowering, G. ; Rodgers, M.A. I., *J. Am. Chem. Soc.*, 1979, 101, 3050.
12) Adam, W. ; Balcı, M., *J. Am. Chem. Soc.*, 1979, 101, 7542.
13) Boyd, J. D.; Foote, C. S.; Imagawa, D. K., *J. Am. Chem. Soc.*, 1980, 102, 3641.
14) a) Balcı, M. ; Sütbeyaz, Y., *Tetrahedron Lett.*, 1983, 24, 311. b) ibid. 1983, 24, 4135.
15) Adam, W. ; Rebollo, H., *Tetrahedron Lett.*, 1981, 22, 3049.
16) Balcı , M., *Chem. Rev.* 1981, 81, 91.
17) Adam, W. ; Balcı, M., *J. Am. Chem. Soc.*, 1979, 101, 7548.
18) Kornblum, M. ; de la Mare, H. E., *J. Am. Chem. Soc.*, 1951, 73, 980.
19) Adam, W. ; Balcı, M ; Rivera, J., *Synthesis*, 1979, 807.
20) Similar rearrangement has been observed also in other cycloheptatriene systems. Balcı, M. ; Akbulut, N., unpublished results.
21) Isler, O. ; Lindlar, H. ; Montavon, M. ; Ruegg, R. ; Saucy, G. ; Zeller, P., *Helv. Chim. Acta.*, 1956, 39, 2041.
22) Wittig, G. ; Eggers, H. ; Duffner, P., *Ann. d. Chemie.*, 1958, 10, 619.
23) For further spectral data see ref. 1.
24) Rothemund, P. ; Menotti, A. R., *J. Am. Chem. Soc.*, 1948, 70, 1808.