The Sensitized Photooxidation of Cycloheptatriene (Tropilidene). Isolation and Thermal Isomerization of $(4\pi+2\pi)$ Cycloadduct, 8,9-Dioxabicyclo-[3.2.2]-2,6-nonadiene, and Preparation of Tropone[1]

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The sensitized photooxidation of cycloheptatriene (tropilidene) in methanol afforded $(4\pi+2\pi)$ cycloadduct; 8,9-dioxabicyclo[3.2.2]-2,6-nonadiene (**1**), 6-hydroxy-2,4-cycloheptadienone and 6-oxoheptadienal presumably derived from $(6\pi+2\pi)$ cycloadduct, and small amounts of tropone and benzaldehyde. Mechanism of their formation are discussed. It was found that the treatment of the photooxidation mixture with triethylamine afforded tropone in about 50% yield. Thermal isomerization of **1** in refluxing xylene afforded *cis*-3,9-dioxatricyclo-[6.1.0.0^{2,4}]-5-nonene, 8-oxabicyclo[5.1.0]-4-octen-3-one and 4-hydroxy-2,6-cycloheptadienone.

Kende and Chu have reported evidence that the oxidation of tropilidene by photochemically generated singlet oxygen gave $(4\pi+2\pi)$ and $(6\pi+2\pi)$ cycloadducts and hydroperoxide by isolating their hydrogenation products including cycloheptanol, 3-hydroxycycloheptanone and *cis*-1,4-cycloheptanediol.[3] However, they could not isolate any direct oxidation products. Meanwhile, the oxidation of tropilidene with peracetic acid gave monoepoxide, 8-oxabicyclo[5.1.0]-2,4-octadiene,[4] and its further oxidation with excess peracid afforded a mixture of diepoxides and triepoxides.[5]

We have studied the similar photooxidation reaction for the purpose of the isolation of the oxidation products and the preparation of tropone *via* photooxidation of tropilidene,[6] and we have isolated a $(4\pi+2\pi)$ cycloadduct; 8,9-dioxabicyclo[3.2.2]–2,6-nonadiene, 6-hydroxy-2,4-cycloheptadienone and 6-oxoheptadienals presumably derived from a $(6\pi+2\pi)$ cycloadduct, and have discussed the mechanisms of the formation of these products. We have also obtained tropone in considerable yield by the base treatment of the photooxidation mixture. Furthermore, it was found that the thermal reaction of $(4\pi+2\pi)$ cycloadduct in refluxing xylene afforded three isomeric rearranged products. The results are reported in this paper.

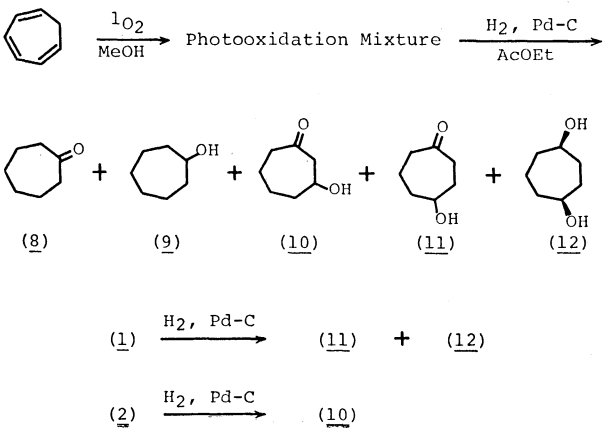
Results and Discussion

When a 1.5% solution of tropilidene in methanol was irradiated with visible light (6×20 W) in the presence of methylene blue for 2 days[7] while oxygen was slowly passed through the solution, $(4\pi+2\pi)$ cycloadduct (8,9-dioxabicyclo[3.2.2]-2,6-nonadiene) (**1**) (8.4%), 6-hydroxy-2,4-cycloheptadienone (**2**) (23.4%), tropone (**3**) (trace), benzaldehyde (**4**) (trace), *trans,trans*-6-oxoheptadienal (**5**) (0.4%), *trans,trans*-6-oxoheptadienal dimethylacetal (**6**) (0.63%) and a mixture of stereoisomer of 6-oxoheptadienal dimethylacetal (**7**) (0.55%) were isolated after repeated purification by column chromatography on silica gel.

When the photooxidation of tropilidene was performed in acetone in the presence of hematoporphyrin, benzaldehyde was obtained in 51% yield, and the reaction in a mixture of methanol and acetone (1:1) afforded the compound (**1**) in 15% yield.

The structures of the products were determined mainly by their spectroscopic data as well as some chemical transformations. ^{1}H-NMR spectrum of **1**, and ^{1}H-NMR parameter of the compounds (**1**, **2**, **5**, and **6**) were shown in Fig. 1, and Table 1, respectively.

Kende and Chu have reported[3] that catalytic hydrogenation of the total crude photooxidation mixture in ethyl acetate in the presence of 10% Pd–C afforded a mixture of cycloheptanone (**8**), cycloheptanol (**9**), 3-hydroxycycloheptanone (**10**), 4-hydroxycycloheptanone (**11**) and *cis*-1,4-cycloheptanediol (**12**). We have also isolated the same products[8] by the catalytic hydrogenation of the photooxidation mixture in the presence of 5% Pd–C, and furthermore we have obtained **11** and **12**, and **10** by the catalytic hydrogenation of **1**, and **2**, respectively.



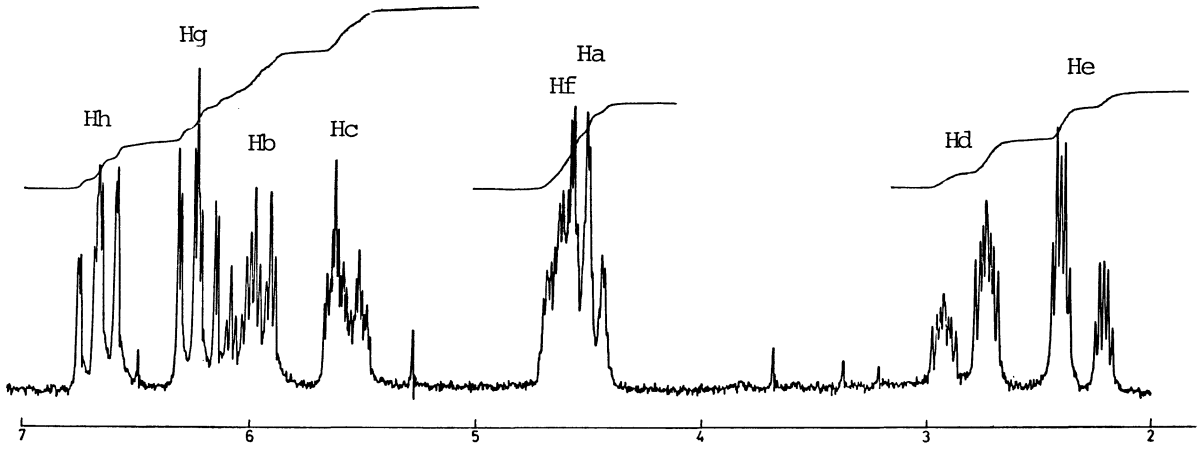


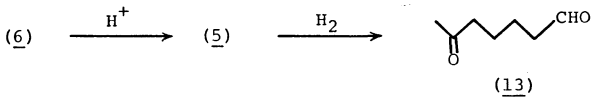
Fig. 1. ^{1}H-NMR spectrum of **1** in $CDCl_3$ (100 MHz).

Table 1. ^{1}H-NMR parameters of **1**, **2**, **5**, **6**, **15**, **27**, and **28**

Compound	^{1}H-NMR parameters (δ-values, J in Hz)[a]
1[b]	2.30 (He), 2.83 (Hd), 4.48 (Ha), 4.65 (Hf), 5.59 (Hc), 5.98 (Hb), 6.25 (Hg), 6.66 (Hh) $J_{ab}=7.0$, $J_{ac}=1.1$, $J_{ag}=1.2$, $J_{ah}=7.0$, $J_{bc}=10.5$, $J_{bd}=2.0$, $J_{be}=2.0$, $J_{bh}=0.5$, $J_{cd}=4.0$, $J_{ce}=4.0$, $J_{cf}=1.5$, $J_{de}=19.0$, $J_{df}=5.0$, $J_{ef}=2.0$, $J_{fg}=7.0$, $J_{fh}=1.2$, $J_{gh}=9.0$
2[b]	2.76 (Hf), 3.50 (Hg), 3.97 (OH), 4.73 (He), 6.00 (Hc), 6.05 (Ha), 6.55 (Hd), 6.65 (Hb) $J_{ab}=2.2$, $J_{af}=1.5$, $J_{bc}=7.6$, $J_{cd}=11.4$, $J_{ce}=2.0$, $J_{de}=4.0$, $J_{df}=3.0$, $J_{ef}=4.6$, $J_{eg}=12.8$, $J_{fg}=15.8$
5[b]	2.29 (CH_3), 6.3—6.6 (m, 2H), 6.9—7.3 (m, 2H), 9.63 (CHO)
6[b]	2.20 (CH_3), 3.25 (OCH_3), 4.82 (He), 5.92 (Hd), 6.07 (Ha), 6.40 (Hc), 6.98 (Hb) $J_{ab}=15.4$, $J_{bc}=10.7$, $J_{cd}=15.4$, $J_{ce}=1.2$, $J_{de}=4.0$
15[c]	2.3—2.9 (m, Hf, Hg), 2.90 (m, Hh), 3.07 (m, Ha), 3.35 (m, Hc), 3.48 (m, Hb), 5.68 (m, Hd, He)
27[c]	2.3—3.4 (m, 6H), 5.90 (d,d, J=12.0, 2.0, Ha), 6.47 (d,d,d, J=12.0, 7.0, 5.0, Hb)
28[b]	2.61 (He), 2.82 (Hd), 3.08 (OH), 4.69 (Hc), 6.03 (Ha), 6.14 (Hg), 6.61 (Hf), 6.71 (Hb) $J_{ab}=12.5$, $J_{ac}=2.0$, $J_{ag}=2.0$, $J_{bc}=2.5$, $J_{bd}=1.0$, $J_{cd}=11.0$, $J_{ce}=5.0$, $J_{cf}=0.5$, $J_{de}=17.0$, $J_{df}=4.5$, $J_{dg}=2.0$, $J_{ef}=7.0$, $J_{eg}=1.0$, $J_{fg}=12.0$

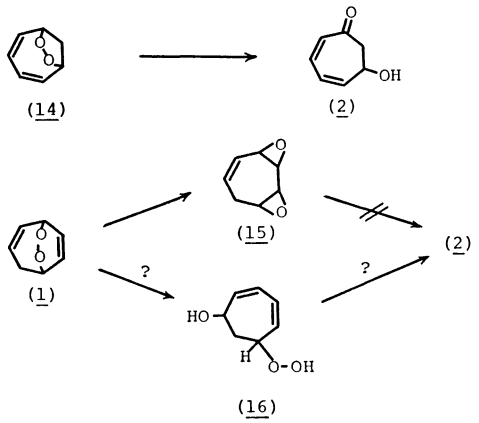
a) Refer the text for proton numberings. b) In $CDCl_3$. c) In CCl_4.

Hydrolysis of **6** with hydrochloric acid afforded the corresponding aldehyde (**5**), which can be converted to 6-oxoheptanal (**13**) upon catalytic reduction. Acid hydrolysis of **7** afforded **5** as one of the products.



The compound (**2**) must be resulted from the cleavage of dioxide ring of ($6\pi+2\pi$) adduct (**14**). But as less likely mechanism, Kende and Chu have pointed out that **2** could be arised by multiple rearrangement of ($4\pi+2\pi$) adduct (**1**) through an allylic diepoxide intermediate (**15**) or *via* S_N'-hydrolysis of **1** to 6-hydroperoxy-2,4-cycloheptadien-1-ol (**16**) in the reaction condition.

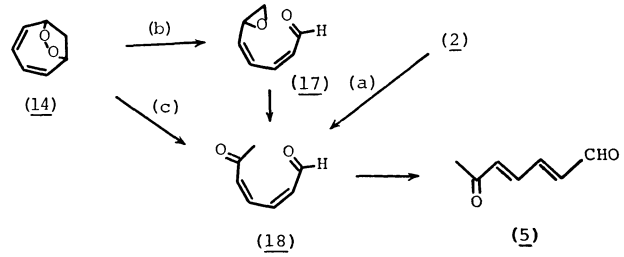
As will be described later, thermal isomerization of the adduct (**1**) did not give **2**, but gave diepoxide (**15**) as one of the products, and it was found that **15** does not change to **2**, but gradually changed to 4-hydroxy-2,6-cycloheptadienone on column of silica gel. Furthermore, the compound (**1**) did not change in aqueous methanol in the presence or absence of

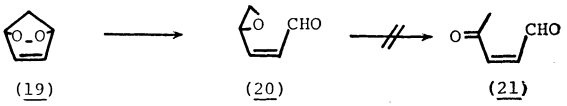


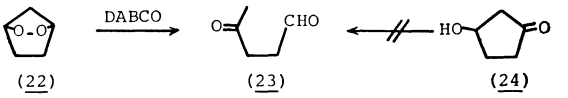
diluted perchloric acid by standing at room temperature for 5 days. Therefore, it is assumed that the compound (**2**) must not be resulted from ($4\pi+2\pi$) adduct (**1**), but must be resulted from the initially formed ($6\pi+2\pi$) adduct (**14**) as has been posturated by Kende.[3]

The formation of acyclic compounds (**5**—**7**) can be explained by the following three processes. Path (a) involves a retro-Aldol cleavage of the compound (**2**).

Path (b) involves a rearrangement of ($6\pi+2\pi$) adduct (**14**) to epoxyaldehyde (**17**) followed by isomerization to the aldehyde (**5**) *via* *cis,cis*-6-oxoheptadienal (**18**). Path (c) proceeds through the direct new peroxide rearrangement of **14** to **18** followed by *cis-trans* isomerization.

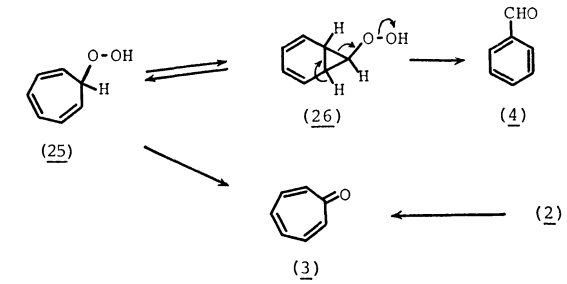




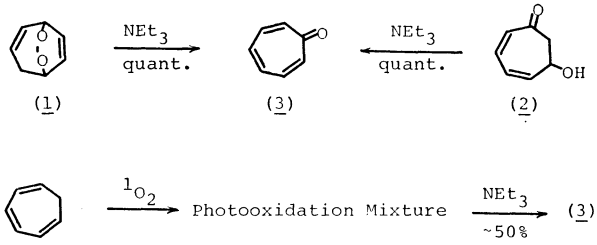


The possibility of path (a) may be ruled out since **2** does not change on standing in methanol. Ohloff *et al.*, and Adams *et al.* have isolated a epoxide (**20**) derived from 1,4-epidioxy-2-cyclopentene (**19**) during photooxidation of cyclopentadiene, however, they did not observe the formation of 4-oxopentenal (**21**).[9] Therefore, the path (c) is assumed to be more plausible for the formation of **5**—**7**, although further study is needed to establish a mechanism. Recently, it has been reported that 5,6-dioxabicyclo[2.2.1]heptane (**22**) underwent a rearrangement upon exposure to 1,4-diazabicyclo[2.2.2]octane to give levlinaldehyde (**23**) and that the possibility might arise *via* retro-aldol cleavage of 3-hydroxycyclopentanone (**24**) was ruled out.[10] The both rearrangements to ketoaldehydes (**5** and **23**) may proceed by the similar mechanism.

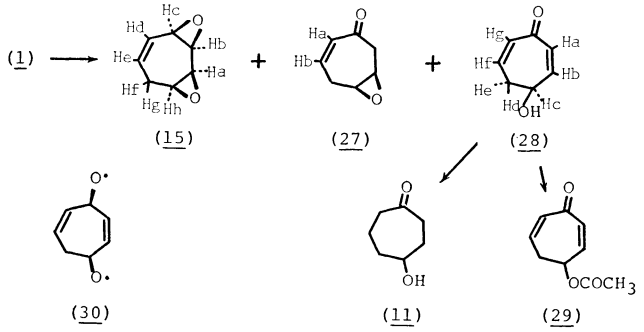
The mechanism of the formation of benzaldehyde can be explained by the rearrangement of the initially formed hydroperoxide (**25**) *via* norcaradiene intermediate (**26**). The formation of tropone can also be explained by the dehydration of **25**[3] and/or 6-hydroxy-2,4-cycloheptadienone (**2**).



When the compounds (**1** and **2**) were treated with triethylamine, tropone was formed in quantitative yields, respectively. Furthermore, it was found that when the crude photooxidation mixture was allowed to stand in the presence of triethylamine at room temperature for 12 h, tropone was obtained in about 50% yield from tropilidene. Therefore, the photooxidation of tropilidenes will become a useful synthetic method of tropone and its derivatives.



Since it has long been known that some epidioxy compounds are thermally and photochemically labile, and many interesting rearranged products have been derived from the epidioxy compounds, the thermal reaction of the compound (**1**), isolated for the first time, was studied. Heating of **1** in refluxing xylene afforded three isomeric products; *cis*-3,9-dioxatricyclo-[6.1.0.0^{2,4}]-5-nonene (**15**), 8-oxabicyclo[5.1.0]-4-octen-3-one (**27**) and 4-hydroxy-2,6-cycloheptadienone (**28**), in the yield of 25, 20, and 18%, respectively. The structure of the products including a stereochemistry of **15** was determined by the analyses of their NMR (Table 1) and the comparison of the NMR with those of their phenyl and methoxy derivatives obtained from phenyl- and methoxytropilidenes,[11] and general mechanistic consideration of the rearrangement of epidioxides.[12] Catalytic hydrogenation and acetylation of **28** afforded 4-hydroxycycloheptanone (**11**) and 4-acetoxy-2,6-cycloheptadienone (**29**).



Although Prinzbach and Rücker have already reported[5] the synthesis of *cis*-diepoxide (**15**) as a mixture with other epoxides the present work is the first time to isolate **15** in pure state.

During the purification of the compounds (**15** and **27**) using column chromatography on silica gel, they gradually changed to the hydroxyketone (**28**). Therefore, **28** may be formed as secondary product by the rearrangement of **15** and/or **27** which may be formed as primary rearranged products of **1** *via* biradical intermediate (**30**). It would also be considered that epoxyketone (**27**) also results from the rearrangement of the diepoxide (**15**),[13] however, **27** could not be detected during the purification of **15**. Upon treatment of these isomers with triethylamine, tropone was obtained in quantitative yields.

Experimental

The mp values are uncorrected. The IR spectra were recorded with Hitachi EPI 510 and Hitachi 215 grating spectrophotometer and for the UV spectra Hitachi EPS 035 and Hitachi 323 spectrophotometers. The mass spectra were obtained with a Hitachi RMU 60 mass spectrometer. The NMR spectra were recorded on Varian HA-100, A-60 and Hitachi R-22 spectrometers.

Sensitized Photooxidation of Cycloheptatriene. A solution of cycloheptatriene (3.5 g, 0.038 mol) and Methylene Blue (100 mg) in methanol (250 ml) was irradiated by visible light (6×20 watt) for 2 days at around 25 °C by cooling with water while oxygen was slowly passed through the solution. The solvent was removed under reduced pressure, the residue was extracted with ether and an oil (2.13 g) was obtained from the extract. The oil was submitted to column chromatography on silica gel (60 g) and eluted with chloroform. From the effluents, benzaldehyde (trace), adduct (**1**) (402.5 mg, 8.4%), a mixture of ring opening products, tropone (**3**) (trace), and 6-hydroxy-2,4-cycloheptadienone (**2**) (1.09 g, 23.4%) were obtained by the order of the effluents. A mixture of ring opening products were further purified by a column chromatography on silica gel using a mixture of benzene and ethyl acetate as solvent, and *trans,trans*-6-oxoheptadienal dimethylacetal (**6**) (40.6 mg, 0.63%), a mixture of stereoisomer of 6-oxoheptadienal dimethylacetal (**7**) (35.3 mg, 0.55%), and *trans,trans*-6-oxoheptadienal (**5**) (18.5 mg, 0.4%) were obtained. **1**; Colorless oil; IR (neat) 1640, 1058, 995, 975, 905, 880, 750 cm^{-1}; MS *m/e* 124 (M^+, 22), 106 (92), 105 (100), 96 (29), 95 (49), 81 (28), 78 (37), 77 (96). Found: C, 67.53; H, 6.62%. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.50%. **2**; Pale yellow oil; IR (CCl_4) 3430, 1658, 1640 cm^{-1}; UV λ_{max}^{MeOH} 240 nm (log ε, 3.38), 291 (3.66); MS *m/e* 124 (M^+, 23), 82 (27), 78 (15), 54 (100). Found: C, 67.83; H, 6.65%. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.50%.
5; Colorless needles, mp 40—42.5 °C; IR (CCl_4) 2820, 2740, 1690, 1590 cm^{-1}; UV λ_{max}^{MeOH} 274 nm (log ε, 4.44), 352 (2.54), 341 (2.52); MS *m/e* 124 (M^+, 96), 109 (100), 81 (96), 58 (86), 41 (91). Found: C, 67.78; H, 6.66%. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.50%. **6**; Colorless oil; IR (CCl_4) 1690, 1675, 1600 cm^{-1}; UV λ_{max}^{MeOH} 265.5 nm (log ε, 4.48), 330 (2.70); MS *m/e* 170 (M^+, 9), 139 (32), 127 (23), 95 (24), 81 (22), 75 (36), 44 (100). Found: C, 63.45; H, 8.18%. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29%. **7**; Colorless oil; IR (CCl_4) 1690, 1580 cm^{-1}; MS *m/e* 170 (M^+).

*Catalytic Hydrogenation of **1**, **2**, and **5**.* a) A solution of **1** (200 mg, 1.61 mmol) in ethyl acetate (20 ml) was submitted for a catalytic hydrogenation in the presence of 5% Pd–C (10 mg) at room temperature and atmospheric pressure, and about 120 ml of hydrogen was absorbed. The catalyst was filtered off, the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel using ethyl acetate as solvent. From the effluents, 4-hydroxycycloheptanone (**11**) (158 mg, 1.23 mmol, 76.4%) and 1,4-cycloheptanediol (**12**) (40 mg, 0.31 mmol, 19.3%) were obtained.[8]
b) A solution of **2** (100 mg, 0.8 mmol) in ethyl acetate (10 ml) was hydrogenated in the presence of 5% Pd–C (5 mg), and worked up the same as in the above procedure. 3-Hydroxycycloheptanone (**10**) was obtained in almost quantitative yield.[8]
c) A solution of 5 (30 mg) in ethyl acetate was hydrogenated in the presence of 5% Pd–C, and 6-oxoheptanal (**13**) was obtained as colorless oil in almost quantitative yield by purification using column chromatography on silica gel. The compound showed bp 100 °C/0.1 mmHg; IR (CCl_4) 2930, 1715, 1370 cm^{-1}; MS *m/e* 128 (M^+), and was identified by the comparison of its IR and NMR spectra with those of 6-oxoheptanal obtained by oxidation of 1-methylcyclohexene with ozone.

Formation of Tropone from the Photooxidation Products. a) A crude photooxidation mixture (2.62 g) obtained by oxidation of cycloheptatriene (3.5 g) in methanol (250 mg) in the presence of Methylene Blue (90 mg) was dissolved in methanol (50 ml) containing triethylamine (1 ml), and the solution was allowed to stand at room temperature for 12 h. The solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture of chloroform and 3% methanol as solvent, and tropone (2.01 g, *ca.* 50%) was obtained. b) A solution of **1** (200 mg) and triethylamine (0.5 ml) in methanol (30 ml) was allowed to stand at room temperature for 12 h. The solvent was removed under reduced pressure, and tropone was obtained in almost quantitative yield.

*Thermal Reaction of **1**.* A solution of **1** (602 mg, 4.86 mmol) in anhydrous xylene (30 ml) was refluxed under nitrogen atmosphere for 2 days. The solvent was removed under reduced pressure, the residue was submitted to column chromatography on silica gel (40 g) and eluted with a mixture of benzene and ethyl acetate (9:1), and in the order of the effluents, diepoxide (**15**) (150.5 mg, 1.21 mmol, 24.9%), ketoepoxide (**27**) (119.5 mg, 0.96 mmol, 19.8%), and ketoalcohol (**28**) (107 mg, 0.86 mmol, 17.8%) were obtained. The compounds (**15** and **27**) were gradually changed to **28** during further purification by chromatography on silica gel. **15**; Colorless crystals, mp 23—25 °C; IR (neat) 940, 915, 905, 840 cm^{-1}; MS *m/e* 124 (M^+, 4), 95 (35), 68 (87), 67 (47), 66 (100). Found: C, 67.50; H, 6.60%. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.50%. **27**; Colorless oil; IR (neat) 1670, 820 cm^{-1}; UV λ_{max}^{MeOH} 228 nm (log ε, 3.89), 275 (2.63); MS *m/e* 124 (M^+, 5.5), 96 (42), 95 (29), 81 (28), 68 (100), 67 (26). Found: C, 68.02; H, 6.30%. **28**; Colorless oil; IR (CCl_4) 3430, 1650, 1615, 1430 cm^{-1}; UV λ_{max}^{MeOH} 232.5 nm (log ε, 4.06), 240 (3.97), 303 (3.11), 312 (3.08); MS *m/e* 124 (M^+, 28), 106 (47), 96 (54), 95 (91), 78 (77), 55 (54), 28 (100). Found: C, 67.94; H, 6.55%.
Acetate (**29**); Colorless oil; IR (neat) 1745, 1650, 1615 cm^{-1}.

References

1) This work was presented partly at the 6th symposium on the chemistry of non-benzenoid aromatic compounds, Fukuoka, October, 1973, and at the National Meeting of the Chemical Society of Japan, Tokyo, April, 1975.
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6) a) Schenck had reported without any description of the condition and the yield that the photooxidation of cycloheptatriene gave tropone; G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957); b) Many general synthetic methods of tropone have been reported; *cf.* T. Nozoe *et al.*, "Daiyuki Kagaku (Comprehensive Organic Chemistry)," ed by M. Kotake, Vol. 13, Tokyo (1960); F. Pietra, *Chem. Rev.*, **73**, 293 (1973); K. Takase, "Shin-Gikken Kagaku Koza," ed by Chemical Society of Japan, Vol. 14, (1977), p. 901.
7) Progress of the reaction was monitored by GLC analysis

on an SE-30 column, and at the end of the reaction, color of the solution was still deep blue.

8) IR and NMR of **10** were in agreement with those of 3-hydroxycycloheptanone kindly provided by Prof. H. Nozaki, Kyoto University; H. Nozaki, M. Kurita, and R. Noyori, *Tetrahedron Lett.*, **1968**, 2025. Authentic *cis*-1,4-cycloheptanediol and 4-hydroxycycloheptanone were prepared by the reduction of 8,9-dioxabicyclo[3.2.2]-6-nonene and 4-hydroxy-2,6-cycloheptadienone (**28**), respectively.

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