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The Sensitized Photooxidation of Methoxycycloheptatrienes. The Synthesis of α-, β-, and γ-Tropolones[1]

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The sensitized photooxidation of 7-methoxycycloheptatriene (7-methoxytropilidene) afforded [4+2] cycloadduct (**2**), tropone, benzaldehyde and their 2-methoxy derivatives. Thermal isomerization of **2** followed by the treatment with alumina yielded 4-methoxytropone. The photooxidation of 1-methoxytropilidene gave 4-hydroxytropone and *o*-methoxybenzaldehyde, and the photooxidation of 3-methoxytropilidene followed by the treatment with triethylamine afforded 3-methoxytropone, tropone, and *o*-methoxybenzaldehyde. Characterization of the products and the mechanisms of the reactions are discussed.

Recently, we have reported that the oxidation of cycloheptatriene (tropilidene) by photochemically generated singlet oxygen afforded [4+2] cycloadduct, and other products derived from [6+2] cycloadduct, and that tropone can be efficiently obtained *via* the photooxidation of tropilidene.[3]

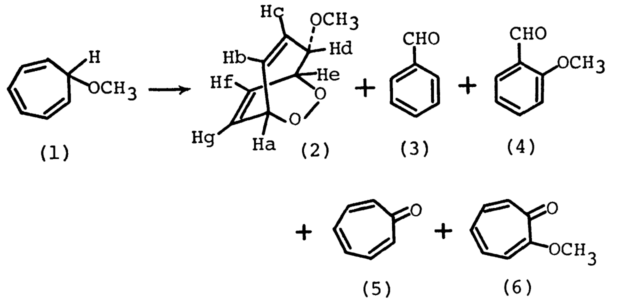
Mori and Takeshita have also reported on the photooxidation of tropilidene, methoxytropilidene, and bitropyl sensitized by α-dicarbonyl compounds to isolate [4+2] and [6+2] cycloadducts.[4]

More recently, Adam and Balci have isolated [6+2] cycloadduct and two kinds of [4+2] cycloadducts derived from norcaradiene and cycloheptatirene by the separation of photooxidation product of tropilidene at low temperature.[5]

We have studied the photooxidation of three kinds of methoxytropilidenes to isolate and characterize the oxidation products and to derive to hydroxytropones, especially to 3- and 4-hydroxytropones (β- and γ-tropolones, respectively) which have been prepared with some difficulty. The results are reported in this paper.

Results and Discussion

Photooxidation of 7-Methoxytropilidene. The photooxidation of 7-methoxytropilidene (**1**) was performed in acetone with visible light (60 W×3) at room temperature in the presence of hematoporphyrin as sensitizer, and the products were separated by silica gel chromatography to afford five products; [4+2] cycloadduct (**2**, 40—50%), benzaldehyde (**3**, 10%), *o*-methoxybenzaldehyde (**4**, 5%), tropone (**5**, trace), and 2-methoxytropone (**6**, trace). The compounds (**3**—**6**) were characterized by direct comparison of their spectroscopic data with those of the authentic samples. The compound (**2**) was obtained as colorless oil, shows a parent ion peak at 154 in the mass spectrum, and strong IR absorption bands (neat) at 1085, 970, and 750 cm^{-1}. ^{1}H-NMR spectrum of **2** in CDCl$_3$ is shown in Fig. 1 and the each signal and coupling constant can be assigned with the help of double resonance



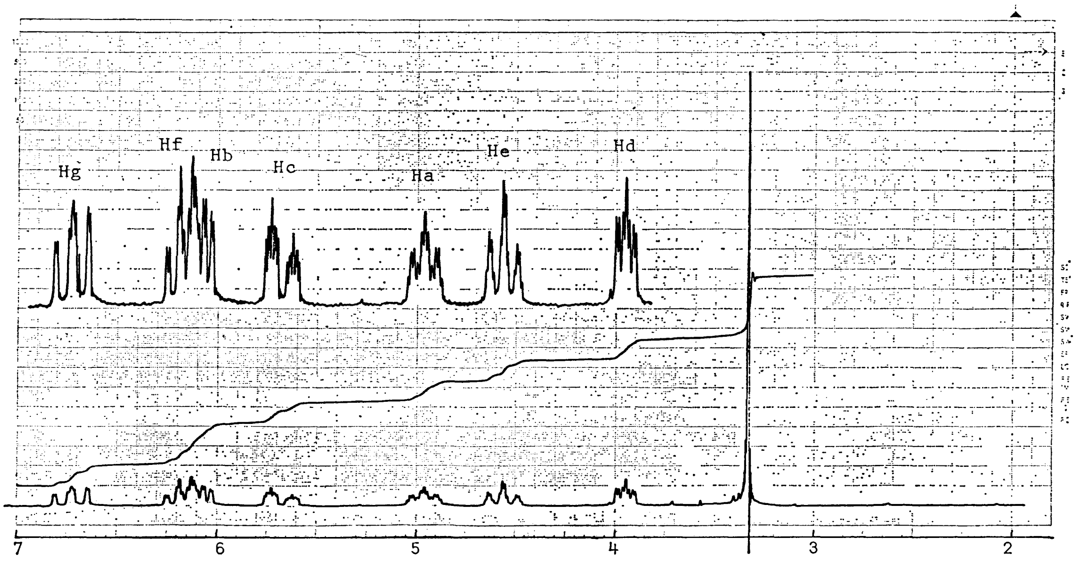
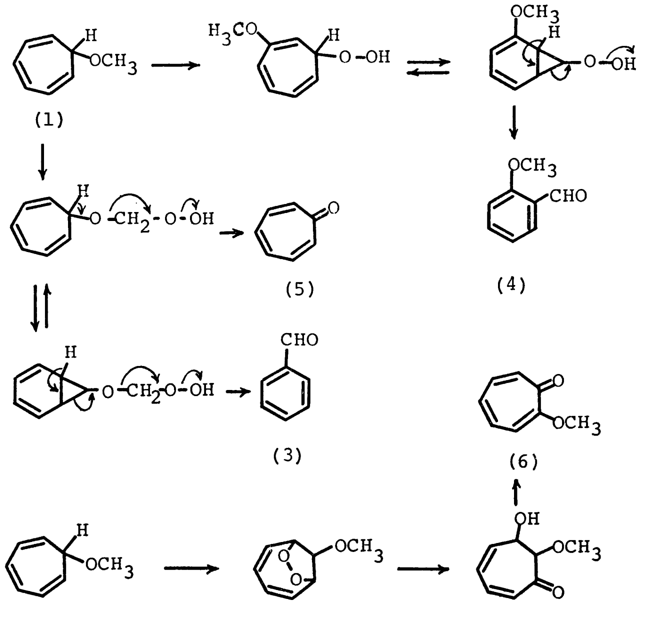


Fig. 1. ^{1}H-NMR spectrum of 2 in CDCl$_3$ (100 MHz).

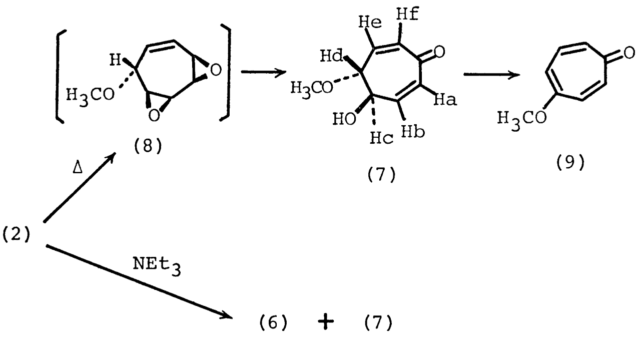
experiments, and the parameters are shown in Table 1. From these data the structure of the compound (**2**) was determined as [4+2] cycloadduct, 4-methoxy-6,7-dioxabicyclo[3.2.2]nona-2,8-diene, shown in scheme including a stereochemistry of methoxyl group.

We tentatively proposed the mechanisms, involving peroxides and [6+2] cycloadduct as intermediates, of the formation of the products (**3**—**6**) as follows.

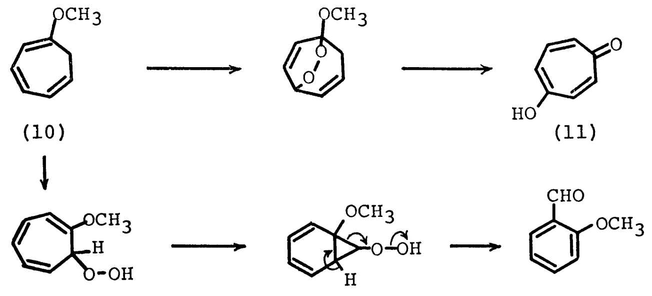


The adduct (**2**) was thermally isomerized in xylene to give 4-hydroxy-5-methoxy-2,6-cycloheptadien-1-one (**7**) in 60% yield, whose structure including a stereochemistry was determined by ^{1}H-NMR spectrum data shown in Table 1. The compound (**7**) is considered to be formed *via* diepoxide (**8**) which could not be isolated in this case.[6] The treatment of **7** with alumina afforded 4-methoxytropone (**9**)[7,8] in 58% yield. Furthermore, the treatment of **2** with triethylamine afforded **7** (34%) and 2-methoxytropone (**6**) (34%).

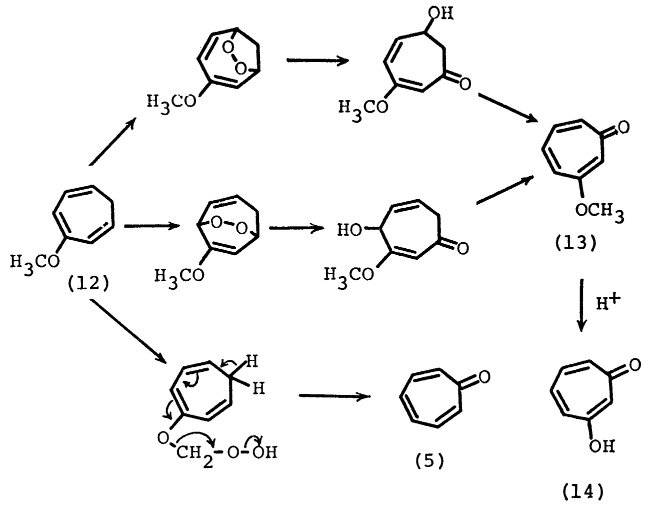
From these results, it was found that 4-methoxytropone (**9**) can be effectively synthesized in moderate yield starting from 7-methoxytropilidene *via* photooxidation.



Photooxidation of 1-Methoxytropilidene. The photooxidation of 1-methoxytropilidene (**10**)[9] was performed in a similar manner to 7-methoxytropilidene in acetone in the presence of hematoporphyrin. The removal of the solvent just after the oxidation was completed caused explosion, and no clear product was obtained. However, working up after the solution of the oxidation was allowed to stand at room temperature for a week, gave two products; 4-hydroxytropone (γ-tropolone) (**11**)[7,8] and *o*-methoxybenzaldehyde (**4**) in 34% and 12% yields, respectively by chromatographic separation, and any *endo*-peroxides could not be isolated. The mechanisms of the formation of these compounds were tentatively proposed as follows.



Photooxidation of 3-Methoxytropilidene. The photooxidation of 3-methoxytropilidene[9] in methanol in the presence of Methylene Blue afforded only *o*-methoxybenzaldehyde after the direct separation using silica gel chromatography. However, the treatment of the crude photooxidation products with triethylamine afforded 3-methoxytropone (**13**),[8,10] tropone (**5**), and *o*-methoxybenzaldehyde in 16%, 24%, and 5% yield, respectively. 3-Methoxytropone (**13**) can be easily hydrolyzed by acids to give 3-hydroxytropone (β-tropolone) (**14**).[10a] The mechanism of the formation of the tropones was tentatively considered as follows which involves the formation of [4+2] or [6+2] cycloadduct and peroxide at methoxyl carbon as intermediates.



Experimental

The mp values are uncorrected. The IR spectra were recorded with Hitachi EPI 510 and Hitachi 215 grating spectrophotometer. The mass spectra were obtained with Hitachi RMU 60 mass spectrometer. The NMR spectra were recorded on Varian HA-100, A-60, and Hitachi R-20 spectrometers.

TABLE 1. ^{1}H-NMR PARAMETERS OF **2** AND **7**

Compound	^{1}H-NMR parameters (δ values, J in Hz)[a)]
2[b)]	3.34 (OCH_3), 3.93 (H_d), 4.55 (H_e), 4.96 (H_a), 5.68 (H_c), 6.07 (H_f), 6.18 (H_b), 6.78 (H_g) $J_{ab}=7.0$, $J_{ac}=1.3$, $J_{af}=1.2$, $J_{ag}=7.0$, $J_{bc}=10.5$, $J_{bd}=1.8$, $J_{bg}=0.5$, $J_{cd}=3.5$, $J_{ce}=1.5$, $J_{de}=6.5$, $J_{df}=0.5$, $J_{ef}=7.0$, $J_{eg}=1.1$, $J_{fg}=9.0$
7[c)]	2.9 (OH), 3.51 (OCH_3), 3.48, 3.65 (H_c, H_d), 5.92, 5.97 (H_a, H_f), 6.47, 6.50 (H_b, H_e) $J_{ab}=13.0$, $J_{ac}=2.0$, $J_{af}=2.0$, $J_{bc}=2.0$, $J_{cd}=10.5$, $J_{de}=2.0$, $J_{df}=2.0$, $J_{ef}=13.0$

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

Sensitized Photooxidation of 7-Methoxytropilidene. A solution of 7-methoxytropilidene (10.0 g, 0.082 mol) and hematoporphyrin (132 mg) in acetone (400 ml) was irradiated by visible light (60 W × 3) for 6 days at below 30 °C by cooling with water while oxygen was slowly passed through the solution. The solvent was removed under reduced pressure, the residue was submitted to column chromatography on silica gel and eluted with chloroform. From the effluents, benzaldehyde (869 mg, 8.2 mmol, 10%), *o*-methoxybenzaldehyde (558 mg, 4.1 mmol, 5%), an adduct (**2**, 5.44 g, 34.3 mmol, 43.5%), tropone (trace), and 2-methoxytropone (trace) were obtained by the order of the effluents. **2**; Colorless oil, IR (neat) 1085, 970, 750 cm^{-1}; MS *m/e* 154 (M^+, 18), 122 (57), 94 (100), 84 (71), 81 (52), 68 (73), 66 (73); Found: C, 62.42; H, 6.46%. Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.54%.

Thermal Reaction of **2**. A solution of **2** (600 mg, 3.9 mmol) in anhydrous xylene (30 ml) was refluxed under nitrogen atmosphere for 15 h. The solvent was removed under reduced pressure, the residue was submitted to column chromatography on silica gel and eluted with chloroform, and keto alcohol (**7**, 360 mg, 2.34 mmol, 60%) was obtained. **7**; Colorless oil, IR (neat) 3450, 1660, 1618 cm^{-1}; MS *m/e* 154 (M^+, 2.9), 122 (47.1), 109 (35.3), 95 (35.3), 94 (100). 2,4-Dinitrophenylhydrazone; reddish crystals, mp 156—157 °C, Found: C, 50.17; H, 4.14; N, 16.71%. Calcd for $C_{14}H_{14}O_6N_4$: C, 50.30; H, 4.22; N, 16.76%.

Treatment of **7** *with Alumina.* A solution of **7** (200 mg, 1.3 mmol) in chloroform was adsorbed on alumina column (10 g). After 2 h, the column was eluted with ethyl acetate to give 4-methoxytropone (102 mg, 0.75 mmol, 58%), colorless crystals, mp 28—29 °C, which was identified by direct comparison of spectroscopic data with those of the authentic sample.

Reaction of **2** *with Triethylamine.* A solution of **2** (429 mg, 3.2 mmol) in dichloromethane (30 ml) was refluxed for 25 h in the presence of triethylamine (5 drops). The solvent was removed under reduced pressure, a solution of the residue in chloroform was submitted to chromatography on silica gel and eluted with chloroform–methanol (2%). From the effluents, keto alcohol (**7**, 158 mg, 1.1 mmol, 34.4%) and 2-methoxytropone (138 mg, 1.1 mmol, 34.4%) were obtained.

Sensitized Photooxidation of 1-Methoxytropilidene. A solution of 1-methoxytropilidene (1.0 g, 8.2 mmol) and hematoporphyrin (30 mg) in acetone (100 ml) was photochemically oxidized for 2 days in a similar manner to 7-methoxytropilidene. After the oxidation, the solution was allowed to stand at room temperature for a week. The solvent was removed under reduced pressure and 4-hydroxytropone (**11**, 382 mg, 34.1%), mp 211 °C (dec) was obtained as crystalline substance. The residue was separated by chromatography on silica gel and *o*-methoxybenzaldehyde (137.5 mg, 12.3%) was obtained. 4-Hydroxytropone (**11**) was identified by direct comparison of the physical data with those of the authentic sample.

Photooxidation of 3-Methoxytropilidene. A solution of 3-methoxytropilidene (**12**, 1.0 g, 8.2 mmol) and Methylene Blue (50 mg) in methanol (100 ml) was photochemically oxidized for 2 days in a similar manner to 7-methoxytropilidene. The solvent was removed under reduced pressure. A solution of the residue in methanol (70 ml) was added triethylamine (1.5 ml) and allowed to stand at room temperature for 10 h. The solvent was removed under reduced pressure, the residue was submitted to chromatography on alumina and eluted with chloroform. From the effluents, *o*-methoxybenzaldehyde (55.8 mg, 5%), tropone (213 mg, 24%), and 3-methoxytropone (**13**, 210.5 mg, 16%), colorless oil, were obtained. 3-Methoxytropone (**13**) was identified by the comparison of the spectroscopic data with those of the authentic sample.

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