Synthetic Photochemistry. XVIII.[1] A Sensitizer Dependence in the Photooxidation of Indene and Acenaphthylene. The Occurrence of *cis*-1,2-Glycol Formation in a Rose Bengal-sensitized Reaction

Toshihide HATSUI and Hitoshi TAKESHITA*

Reaeseach Institute of Industrial Science, 86, Kyushu University, Hakozaki, Fukuoka 812

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Upon Rose Bengal-sensitized photooxygenation, indene and acenaphthylene afforded substantial amounts of the expected *cis*-glycols by means of the reduction of the intermediate dioxetanes. The formerly proposed structure of one of the isomeric methoxy hydroperoxides was revised on the basis of the chemical and spectral evidence.

Recently, we have found a new photochemical oxygenation process by which to form *cis*-1,2-glycols by means of the reduction of the intermediate dioxetanes.[2-4] To demonstrate the general applicability of this new process, we have carried out the experiments with indene (**1**) and acenaphthylene (**2**); the results will be described herein. Our selection of **1** as the reactant is due to the fact that, since the 1960's, the singlet oxygen oxidation of **1** has been investigated by many workers, and it is known to be the first dioxetane-forming arylolefin.[5,6] On the other hand, **2**, with no allylic hydrogen, should form only the cycloadducts.

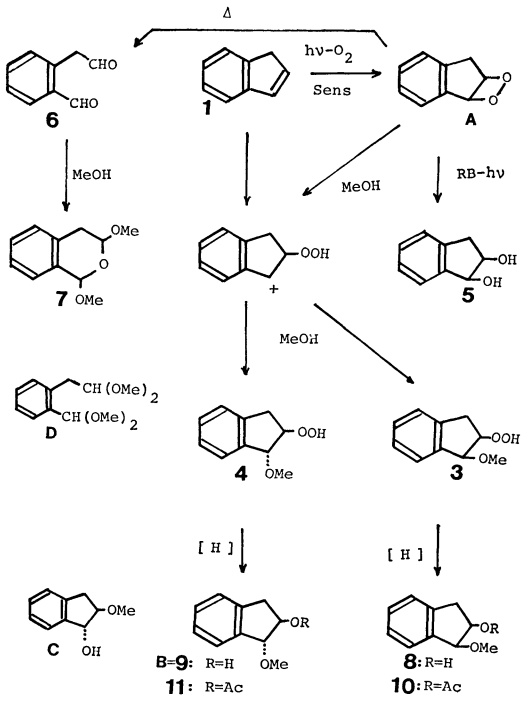
When a methanolic solution of **1** was irradiated by means of a tungsten lamp at 15—20 °C with a relatively large amount of Rose Bengal (RB) under an oxygen atmosphere, the occurrence of KI-starch positive species was indicated; in fact, the silica gel column chromatography of the mixture afforded a pair of methoxy hydroperoxides (**3**, 17%, and **4**, 34%), together with *cis*-1,2-indandiol (**5**, 21%),[7] homophthalaldehyde (**6**, a trace amount), and cylic acetal (**7**, 25%). Both **3** and **4** were hydroperoxy derivatives, for sodium borohydride reduction gave the 2-methoxy-1-indanols (**8** and **9**) the latter of which was characterized as *p*-nitrobenzoate. Although the NMR spectra of **8** and **9** were too ambiguous for us to assign the methine protons of oxygen functions, those of their acetates (**10** and **11**) provided clear information for use in determining the location and stereochemistry. The structure of **5** was evident on the basis of the NMR analysis as well as the chemical correlation with its diacetate. The occurrence of **6** was assured by the NMR analysis of its reduction product, 2-[2-(hydroxymethyl)phenyl]-ethanol (**12**).

The photooxidation of **1** with Methylene Blue (MB) in methanol disclosed similar product distributions, except for the absence of **5**.

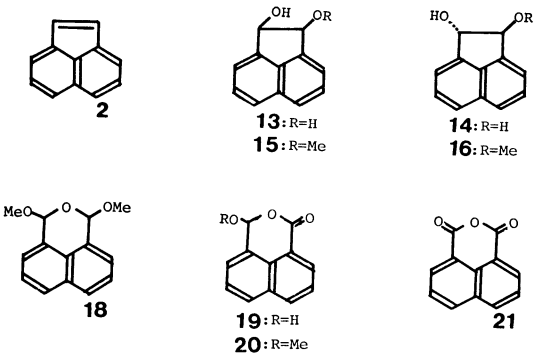
Subsequently, we have carried out the oxygenation with **2**. Thus, a methanol solution of **2** was irradiated by means of a 500-W tungsten lamp in the presence of RB under an oxygen atmosphere. The four products thus formed were identified and characterized as *cis*- (**13**, 45%) and *trans*-2-methoxy-1-acenaphthenols (**14**, 2%)[8] and *cis*- (**15**, 5%) and *trans*-2-methoxy-1-acenaphthenediols (**16**, 18%). The *cis-trans* isomerism in **15** and **16** was deduced from the different magnitudes of the spin-spin coupling constants and the indication of the internal hydrogen-bond for the methoxy-alcohol function of **15**, as well as the *m*-chloroperbenzoic acid (MCPA)-oxidation of **2**, where **16** was the major product (**16**:**15**=63:37).

However, the reaction products of **2** with MB were entirely different from those with RB; except for the *cis-cisoid-cis*-dimer (**17**, 5.3%) of **2**,[9] all the oxygenation products were related to a dioxetane, *i.e.*, 1,8-naphthalenedicarbaldehyde cyclic acetal (**18**, 22%), hydroxynaphthalide (**19**, 14%),[10,11] and methoxynaphthalide (**20**, 7%),[10,12] and 1,8-naphthalenedicarboxylic anhydride (**21**, 17%).[13] **18** was independently prepared from **13** by periodic acid-oxidation in methanol. **19** and the other carboxylic derivatives are probably secondary products produced by the autooxidation of unisolable 1,8-naphthalenedicarbaldehyde. The occurrence of *cis*-glycols from **1** and **2** was again confirmed only in the RB-sensitized photooxygenation; this sensitizer dependence for the substrates constitutes another example of the RB-sensitized photoreduction process of dioxetanes.

Previously, Kearns *et al.*[5] obtained a pair of methoxyindanols in the MB-sensitized photooxygenation of **1** and assigned them the structures of *trans*-1-methoxy-2-indanol (**B**) and *trans*-2-methoxy-1-indanol (**C**) on



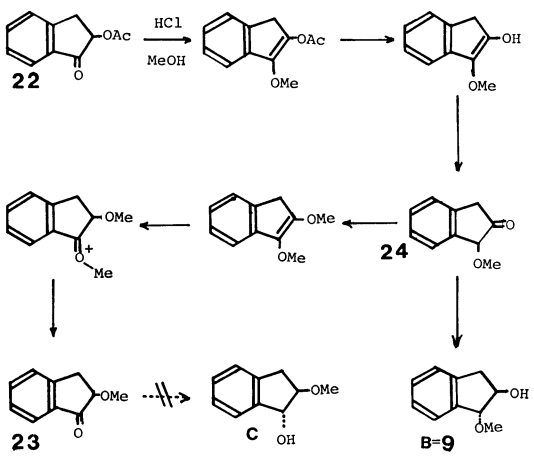
Scheme 1.



Scheme 2.

the basis of chemical correlations, following the previously known route.[14] Later, Foote *et al.*[6] suported this assignment for the structures of products derived from indene, except for that of acetal, to which Foote gave the **7** structure instead of the **D** originally given by Kearnes. The present results, however, showed some discrepancies; our **9** corresponds to **B**, but **8** does not correspond to **C**, and the structure of **7** agreed with the results of Foote. Since obtaining these indanols led Hasty and Kearns to claim a chemical trapping of the peroxirane[15] and has been cited in recent literature,[16,17] the settlement of this problem is important. The previous route of derivation involves the solvolytic substitution of 2-acetoxy-1-indanone;[18] the stable benzylic cation formed as the intermediate might therefore cause a shuffling of the substituents. Consequently, the reported formation of 2-methoxy-1-indanol based on this derivation seems to be unconvincing.

According to our reinvestigations, 2-acetoxy-1-indanone (**22**),[14,18] whose preparation from 2-bromo-1-indanone involved no rearrangement, was shown to give 2-methoxy-1-indanone (**23**, a quantitative yield) by the action of 3% hydrogen chloride in methanol under reflux for 90 min, but under less drastic conditions (40 °C for 45 min), **23** and 1-methoxy-2-indanone (**24**) were formed in a ratio of 1:1, while the additional heating of the mixture for 40 min at 40 °C caused the disappearance of **24**. In any case, we have not succeeded in finding the conditions by which to obtain



Scheme 3.

24 as a single solvolysate. Obviously, **23** is a thermodynamically stable product, while **24** is a kinetically controlled transient product, and not a simple substitution reaction, as is illustrated in Scheme 3.

The present result, the absence of an anti-Markovnikov methoxy hydroperoxide, should not only indicate the invalidity of the peroxirane hypothesis deduced on this structural basis, but should suggest also the necessity to reinvestigate the structural aspects of a related observation, *i.e.*, the formation of regioisomeric methoxy hydroperoxides from the peroxiranes of 1,3-pentadiene and 2,5-dimethyl-2,4-hexadiene.[15]

Experimental

*RB-sensitized Photooxygenation of **1** in Methanol.* A methanol solution (30 cm^3) of 1 (674 mg) and RB (221 mg) was irradiated by means of a 500-W tungsten lamp at 15—20 °C for 48 h under an oxygen atmosphere. The mixture was then diluted with water and extracted with CH_2Cl_2. The extract was fractionated on a silica-gel column with hexane–ethyl acetate to give, first, a colorless oil (529 mg; 51%), which, together with a small amount of **6**, consisted mainly of **3** and **4** [δ[19]: 2.88 (1H, dd, J=17, 4 Hz), 3.32 (1H, dd, J=17, 7 Hz), 3.51 (3H, s), 4.80 (2H, m), 7.20 (4H, m), and 8.88 (1H, OH)] in a ratio of 1:2; subsequently, fractionation gave **5**, colorless crystals (mp 102.5—103 °C (lit,[7] 99—101 °C); 185 mg (21%) [δ: 2.86 (1H, dd, J=16.5, 3.5 Hz), 3.00 (1H, dd, J=16.5 6 Hz), 3.33 (2H, br. OH), 4.32 (1H, m), 4.84 (1H, d, J=5 Hz), and 7.20 (4H, m)]), together with **7**, a colorless oil (280 mg (25%) [δ: 2.92 (2H, m), 3.56 (3H, s), 3.59 (3H, s), 5.06 (1H, m), 5.64 (1H, s), and 7.2 (4H, s)]).

*Diacetate of **5**.* Prepared by acetic anhydride in pyridine as colorless needles; mp 48—48.5 °C (lit,[7] 50.8—51.6 °C) [δ: 2.06 (3H, m), 2.08 (3H, s), 3.17 (2H, m), 5.51 (1H, td, J=6.3, 5.4 Hz), 6.19 (1H, d, J=5.4 Hz), and 7.26 (4H, m)].

*Sodium Borohydride Reduction of the Mixture of RB-sensitized Photooxygenation Products of **3**.* The photooxidation mixture obtained from **1** (609 mg) with RB (164 mg) for 24 h was directly reduced with $NaBH_4$ (10 mg) at room temperature. The mixture was then evaporated *in vacuo*, and the residue was chromatographed on a silica-gel column. The products identified were **7** (123 mg; 12%), **8** (72 mg; 8.4%) [Found: M. W., 164.0820. Calcd for $C_{10}H_{12}O_2$: 164.0837. δ: 2.85 (1H, br., OH), 3.02 (2H, m), 3.52 (3H, s), 4.53 (2H, m), and 7.25 (4H, m). δ (C): 39.0, 57.0, 72.4, 84.1, 125.5, 126.5, 128.9, 139.7, and 141.0. ν: 3560. 1110, 1100, 1080 cm^{-1}]), **9** (180 mg; 21%) [Found: *m/e*, 164. δ: 2.72 (1H, dd, J=16, 5.2 Hz), 2.8 (1H, br. OH), 3.24 (1H, dd, J=16, 6.8 Hz), 3.52 (3H, s), 4.44 (1H, m), 4.58 (1H, d, J=4 Hz), and 7.20 (4H, m). ν: 3620, 3440, 1095 cm^{-1}]), and **5** (23 mg; 3%).

*Acetate (**10**) of **8**.* Prepared by the use of acetic anhydride in pyridine as a colorless oil [δ: 2.10 (3H, s), 3.12 (2H, d, J=6 Hz), 3.44 (3H, s), 4.72 (1H, d, J=5 Hz), 5.44 (1H, dt, J=6, 5 Hz), and 7.24 (4H, m). δ(C): 21.1, 35.9, 57.5, 74.3, 82.7, 125.0, 125.3, 126.9, 128.9, 139.8, and 170.9. ν: 1740, 1240 cm^{-1}].

*Acetate (**11**) of **9**.* Prepared similarly as a colorless oil [δ: 2.06 (3H, s), 2.81 (1H, dd, J=16.7, 4 Hz), 3.50 (1H, dd, J=16.7, 6.8 Hz), 3.52 (3H, s), 4.77 (1H, d, J=3.2 Hz), 5.39 (1H, ddd, J=6.8, 4, 3.2 Hz), and 7.25 (4H, m), δ(C): 21.0, 36.8, 56.9, 78.8, 87.9, 124.9, 125.3, 126.9, 129.0, 139.7, 140.3, and 170.3].

p-*Nitrobenzoate of* ***9***. Prepared by the treatment of *p*-nitrobenzoyl chloride in pyridine at room temperature as pale yellow needles; mp 84.5—85 °C [Found: C, 65.16; H, 4.68, N, 4.54%. Calcd for $C_{17}H_{15}O_5N$: C, 65.17 H, 4.82; N, 4.47%].

MB-sensitized Photooxygeanation of ***1***. A methanol solution (25 cm³) of **1** (540 mg) and MB (60 mg) was irradiated by means of 500 W tungsten lamp for 28 h under an oxygen atmosphere. The mixture was then directly reduced with $NaBH_4$ to decompose the peroxy derivatives. After the evaporation of the whole mixture, the residue was chromatographed on a silica-gel column to give **7** (59 mg; 6.5%), **12** (a colorless oil; 185 mg (27%) [δ: 2.85 (2H, t, J=6 Hz), 3.70 (2H, br. OH), 3.76 (2H, t, J=6 Hz), 4.53 (2H, s), and 7.20 (4H, m). δ(C): 35.0, 62.4, 62.8, 126.4, 128.1, 129.2, 129.9, 137.8, and 138.9]), **8** (150 mg; 20%), and **9** (153 mg; 20%).

*Bis(*p-*nitrobezoate) of* ***12***. Prepared by the usual manner as colorless prisms; mp 133.5—134 °C (lit,[20] 134—135 °C) [δ: 3.23 (2H, t, J=7 Hz), 4.51 (2H, t, J=7 Hz), 5.49 (2H, s), 7.32 (4H, m), 8.16 (4H, m), and 8.18 (4H, s)].

RB-sensitized Photooxygenation of ***2***. A mixed solution (30 cm³) of methanol and acetone (1:2) of **2** (504 mg) and RB (100 mg) was similarly irradiated by means of a tungsten lamp under an oxygen atmosphere for 90 h at 15—20 °C. The reaction mixture was then heated at 30 °C *in vacuo* to remove the solvents. The residue was chromatographed on a silica-gel column. The recovered **2** (300 mg) was obtained by elution with hexane–ethyl acetate (95:5); subsequent elution with hexane–ethyl acetate gave colorless needles of **15** (mp 91.5—92.5 °C; 14 mg (5%) [Found: C, 77.99; H, 6.11%. Calcd for $C_{13}H_{12}O_2$: C. 77.98; H, 6.04%. δ: 3.26 (1H, d, J=7 Hz, OH), 3.62 (3H, s), 5.01 (1H, d, J=6 Hz), 5.50 (1H, dd, J=7, 6 Hz), and 7.4—7.8 (6H, m). ν: 3430, 1102, 780 cm⁻¹]), a colorless oil, **16** (49 mg (18%) [Found: C, 77.77; H, 6.06%. δ: 3.15 (1H, br., OH), 3.48 (3H, s), 4.90 (1H, d, J=2 Hz), 5.31 (1H, d, J=2 Hz), and 7.2—7.7 6H, m). ν: 3620, 3430, 1110, 775 cm⁻¹]), colorless needles, **13** (mp 213—214 °C (lit,[9] 218—219 °C), 101 mg (45%) [δ: 2.76 (2H, br., OH), 5.50 2H, br. d, J=7 Hz), and 7.2—7.8 (6H, m). ν: 3330, 3200, 1110, 775 cm⁻¹]), and colorless needles, **14** (mp 158—160 °C (lit,[8] 160—163 °C), 6 mg (2%) [δ: 3.3 (2H, br., OH), 6.42 (2H, br. s), 7.4—7.6 (4H, m), and 7.7—7.9 (2H, m). ν: 3360, 985 cm⁻¹]).

Acetylation of ***13***. This yielded colorless prisms; mp 132—134 °C (lit,[8] 134.5—136.5 °C) [δ: 2.12 (6H, s), 6.60 2H, s), and 7.4—7.8 (6H, m). ν: 1775, 1240, 775 cm⁻¹]).

Acetylation of ***14***. This yielded a colorless oil (lit,[8] a colorless oil) [δ: 2.09 (6H, s), 6.54 (2H, s), and 7.4—7.9 (6H, m). ν: 1745, 1370, 1240 cm⁻¹].

MB-sensitized Photooxygenation of ***2***. A mixed solution (30 cm³) of methanol and acetone (1:2) of **2** (500 mg) and MB (60 mg) was similarly irradiated under an oxygen atmosphere for 177 h. The mixture was then heated *in vacuo* to remove the solvent, and the residue was purified through a silica-gel column; from the hexane eluent, a photodimer of **2** (**17**) as colorless needles (mp 233—235 °C (lit,[9] 232—234 °C); 13 mg) and the recovered **2** (256 mg) were thus obtained. Subsequently eluted from hexane–ethyl acetate were a dimethyl acetal of 1,8-naphthalenedicarbaldehyde, **18** (a colorless oil, 77 mg; 22%), a methoxy lactone, **20** (pale yellow prisms; mp 105—106.5 °C (lit,[10] 104 °C), 23 mg (7%) [δ: 3.66 (3H, s), 6.42 (1H, s), 7.45—7.75 (3H, m), 7.90 (1H, m), 8.08 (1H, dd, J=9, 1 Hz), and 8.40 (1H, dd, J=7, 1 Hz). ν: 1728, 1090, 1000 cm⁻¹]), a hydroxy lactone, **19** (pale yellow needles, mp 175—176 °C (lit,[12] 167 °C), 43 mg (14%) [δ: 6.86 (1H, s), 7.35—7.95 (4H, m), 8.08 (1H, dd, J=8, 1 Hz), and 8.37 (1H, dd, J=7, 1 Hz). ν: 3280, 1680, 1120, 1005, 925, 775 cm⁻¹]), and 1,8-naphthalenedicarboxylic anhydride, **21** (pale yellow needles, mp 268—270 °C (lit,[13] 271—272 °C), 55 mg; 17%).

*2-Acetoxy-1-indanone (****22****)* was prepared from 2-bromo-1-indanone in accordance with Ishiwara's procedure.[18] Its purity was confirmed by the NMR [δ: 2.16 (3H, s), 3.04 (1H, dd, J=17, 5 Hz), 3.60 (1H, dd, J=17, 8 Hz), 5.38 (1H, dd, J=8, 5 Hz), and 7.25—7.8 (4H, m)].

*Preparation of 2-Methoxy-1-indanone (****23****).* *a)*: To a methanolic 3% HCl solution (10 cm³), **22** (107 mg) was added and refluxed for 90 min. After the evaporation of the solvent, the residual mixture (95 mg) was analyzed by means of the NMR [δ: 3.00 (1H, dd, J=16, 4 Hz), 3.48 (1H, dd, J=16, 7 Hz), 3.61 (3H, s), 4.17 (1H, dd, J=7, 4 Hz), and 7.2—7.8 (4H, m)] spectrum and found to be practically pure 2-methoxy-1-indanone (**23**).

b): Similarly, **22** (80 mg) in the methanolic hydrogen chloride (8 cm³, 3%) was heated at 40 °C for 45 min. The NMR spectrometry of the mixture indicated it to be *ca.* a 1:1-mixture of **23** and 1-methoxy-2-indanone (**24**) [δ: 3.50 (2H, s), 3.57 (3H, s), 4.75 (1H, s), and 7.2—7.8 (4H, m)]. Upon prolonged heating at 40 °C with the additional introduction of a 3% methanolic HCl (5 cm³), **24** disappeared from the mixture.

MCPA-oxidation of ***2*** *in Methanol*. A methanolic solution (10 cm³) of **2** (100 mg) and MCPA (120 mg) was kept at room temperature for 24 h. Subsequently, the silica gel column chromatography of the mixture afforded **15** (31 mg; 37%), and **16** (50 mg; 60%), together with the recovered **2** (37 mg).

Cleavage of ***13*** *with Periodic Acid*. A methanol solution (5 cm³) of **13** (25 mg), containing HIO_4 (70 mg) and water (1 cm³) was kept at room temperature for 1 h. The mixture was then neutralized by $NaHCO_3$ and chromatographed on a silica-gel column to give **18** (18 mg; 49%), identical with the sample obtained by photooxygenation.

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