Photolysis of *cis*-1,2-Dihydroxyindane Carbonate and *cis*-1,2-Dihydroxy-1,2,3,4-tetrahydronaphthalene Carbonate

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Cyclic carbonate esters **2** and **3** were prepared and the photochemistry studied. The direct irradiation of these esters produces 1,3-diradicals which undergo either ring closure to form epoxides, H migration to form ketones or Grob type fragmentation processes which lead to products *via* ring expansion or contraction.

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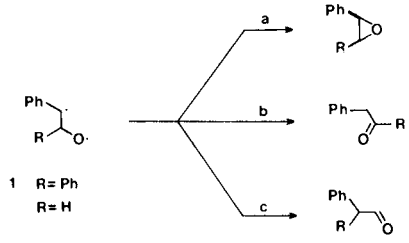
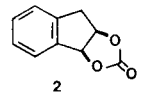
Although the photolysis of aryl substituted cyclic carbonate esters has been reported to yield aryl carbenes [1], we have found that the major pathway for the direct irradiation of both mono and vicinal diaryl cyclic carbonate esters is 1,3-diradical formation followed by a) ring closure, b) H migration or c) aryl migration as shown in equation 1 [2,3].



1 R=Ph
R=H

We have extended our studies to the fused ring systems *cis*-1,2-dihydroxyindane carbonate (**2**) and *cis*-1,2-dihydroxy-1,2,3,4-tetrahydronaphthalene carbonate (**3**) and



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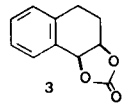


3

have found that in addition to the above mentioned pathways, intermediates from these cyclic carbonate esters can also undergo Grob type fragmentations to yield products through ring expansion or ring contraction.

The preparation of these cyclic carbonate esters was straightforward. Treatment of indene with formic acid and hydrogen peroxide produced *cis*-2-formyloxy-1-indanol [4] which was hydrolyzed to give *cis*-1,2-dihydroxyindane. Reaction of this compound with 1,1'-carbonyldiimidazole in refluxing benzene produced **2** in 80% yield. When 1,2-dihydronaphthalene was treated with formic acid and hydrogen peroxide, the *trans* diol was obtained. However, the reaction of 1,2-dihydronaphthalene with potassium permanganate in cold aqueous THF [5] gave the requisite diol in 35% yield which was then esterified as above to give **3** in 83% yield.

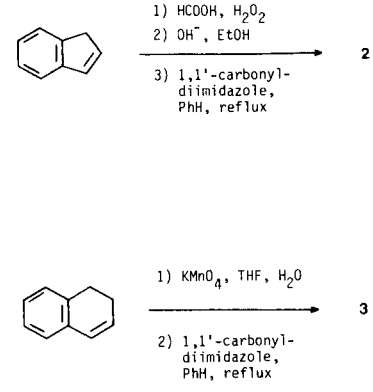
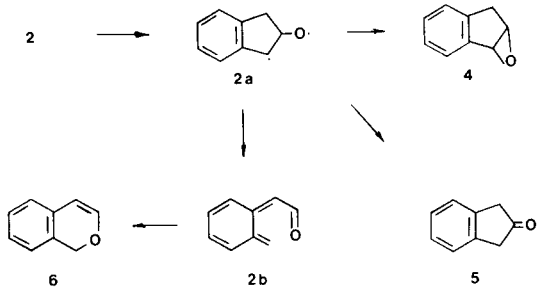


Figure 1. Preparation of Cyclic Carbonate Esters **2** and **3**.

We found that the direct irradiation of a nitrogen sparged solution of **2** in acetonitrile afforded indene oxide (**4**), 2-indanone (**5**) and isochromene (**6**) in a ratio of 1.6:1:1.7. Irradiation of **2** under sensitized conditions led to no reaction and the starting material was recovered unaltered.

Since **5** and **6** are known to be products of the photolysis of **4** [6], we were not sure if **5** and **6** were formed as primary photoproducts or as secondary photoproducts formed from indene oxide. However, analysis of the reaction mixture by hplc through the early stages of the photoylsis showed that **4-6** were all primary photoproducts. These are shown in Figure 2.

Thus, one can envision the loss of carbon dioxide from **2** in a singlet state process to produce **2a** which undergoes ring closure to epoxide **4**, H migration to ketone **5** or a Grob type fragmentation to quinoidal intermediate **2b** which then isomerizes to **6**.



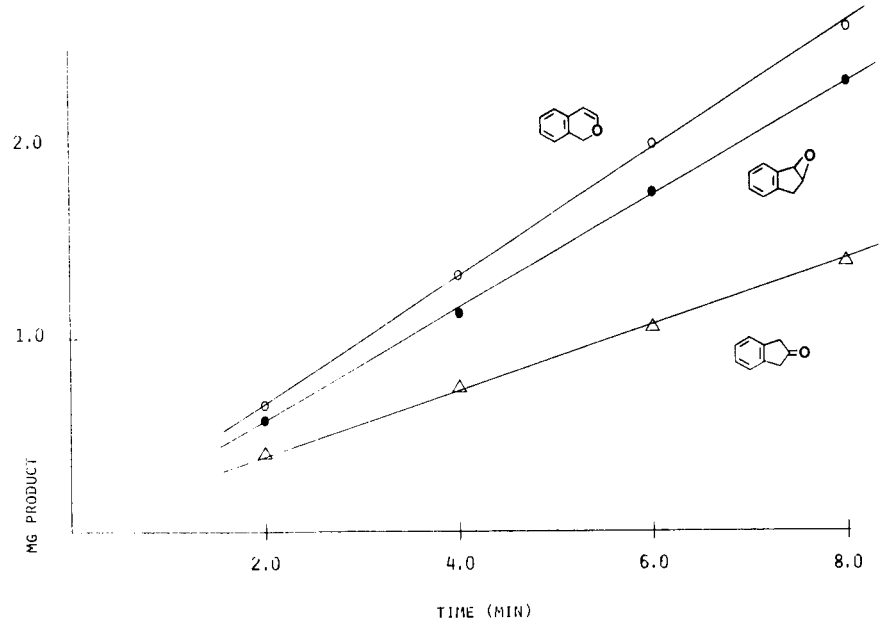
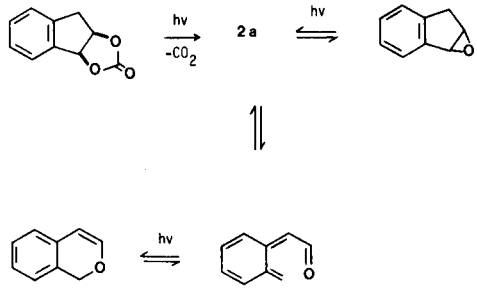


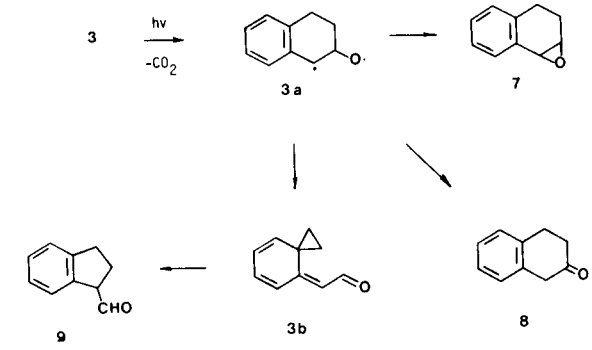
Figure 2. Plot of the Appearance of Photoproducts **4-6** with Respect to Time.

Quinoidal intermediates such as **2b** have been proposed in both the photolysis of **4** [7] and in the interconversion of substituted isochromenes to indene oxides [8]. Thus, intermediate **2b** can be formed from both **2** and **4** *via* the common intermediate **2a**.



Similarly, irradiation of **3** affords oxirane **7**, ketone **8** and aldehyde **9** in a ratio of 2.9:1.3:1. Again, analysis of the reaction mixture by hplc through the early stages of the photolysis revealed that products **7-9** are all primary photoproducts. Thus, analogous to the processes in equation 2, one can propose the formation of intermediate **3a** from **3** in a singlet state process which undergoes ring closure to form **7**, H migration to form **8** or undergoes a Grob type fragmentation to produce **3b** which then forms **9**.

Therefore, we have extended our studies on the generality of the photoextrusion of carbon dioxide from cyclic carbonate esters to form epoxides and ketones and have identified another decay pathway for the intermediate 1,3-diradicals.



EXPERIMENTAL

Melting points were taken with a Thomas Hoover melting point apparatus and are uncorrected. The nmr spectra were recorded with a Varian EM-360L spectrometer while infrared spectra were recorded with a Perkin Elmer 559B infrared spectrometer. Analysis of reaction mixtures by gc/ms were carried out with a Hewlett Packard 5992B gas chromatograph/mass spectrometer equipped with a 3′ x 1/8″ glass column of 2% OV-101. The gc parameters were set at: injector port = 120°; initial column temperature = 100° with temperature rising 6°/minute until a final temperature of 200° was reached. Retention times and mass spectra were compared to those of authentic samples. The hplc measurements were taken with a Tracor Model 900 liquid chromatograph equipped with a 254 nm uv detector and a reverse phase C-18 column. The solvent system was 50:50 methanol/water and toluene was used as an internal standard.

Indene, 2-indanone, 1,2-dihydronaphthalene, 2-tetralone and 1,1′-carbonyldiimidazole were all commercially available (Aldrich). The preparation of indene oxide [9], 1,2-epoxy-1,2,3,4-tetrahydronaphthalene [10], isochromene [11] and indane-1-carboxaldehyde [12] are all described in the literature.

Photochemical reactions were carried out using a Rayonet Photochemical Reactor (Southern New England Ultraviolet Co) equipped with either 8 RPR 2537 lamps or 4 RPR 3000 lamps. The reaction mixtures

were placed in quartz tubes fitted with a rubber septum and sparged with deoxygenated nitrogen for 30 minutes prior to irradiation.

cis-1,2-Dihydroxyindane Carbonate (**2**).

cis-1,2-Dihydroxyindane [13] (2.0 g, 13 mmoles) and 1,1'-carbonyldiimidazole (2.3 g, 14 mmoles) were added to 75 ml of benzene and heated under gentle reflux for 3 hours. Upon cooling, the organic phase was washed with water (2 x 40 ml) and then dried over sodium sulfate. The benzene was removed and the residue was recrystallized twice from benzene/hexane to 1.7 g of colorless crystals, mp 73-74°; ms: m/e (relative intensity) 176 (42, M^+), 132 (52), 104 (100); ^1H nmr (deuteriochloroform): 7.2 m 4H, 5.83 d 1H, J = 6 Hz, 5.30 m 1H, 3.23 d 2H, J = 4 Hz; ir (potassium bromide): 1775 (C=O).

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.18; H, 4.54. Found: C, 67.92; H, 4.60.

cis-1,2-Dihydroxy-1,2,3,4-tetrahydronaphthalene.

1,2-Dihydronaphthalene (1.30 g, 10 mmoles) in 20 ml of THF was treated with potassium permanganate (1.58 g, 10 mmoles) in water (60 ml) dropwise over a two hour period at 5° under a nitrogen atmosphere. After addition was complete, the solution was allowed to stir at room temperature for an additional three days. The solution was filtered and the residue was then washed with THF (3 x 30 ml). After removal of the THF, the diol was extracted with ether (3 x 50 ml). The combined ether extracts were dried over sodium sulfate and the solvent was removed to give the desired *cis*-diol, 0.57 g (35%), mp 100-101°, lit [13], 101°.

cis-1,2-Dihydroxy-1,2,3,4-tetrahydronaphthalene Carbonate (**3**).

Following the same procedure as above, 0.41 g of *cis*-1,2-dihydroxy-1,2,3,4-tetrahydronaphthalene (2.5 mmoles) was allowed to react with 0.41 g of 1,1'-carbonyldiimidazole (2.5 mmoles) to give 0.40 g (85%) of colorless crystals mp 80-81°; ms: m/e (relative intensity) 190 (59 M^+), 146 (100), 128 (47), 117 (96), 104 (42), 91 (49); ^1H nmr (deuteriochloroform): 7.26 m 4H, 5.63 d 1H, J = 9 Hz, 5.10 m 1H, 2.7 m 2H, 2.1 m 2H; ir (potassium bromide): 1785 (C=O).

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.47, H, 5.26. Found: C, 69.41, H, 5.33.

Photolysis of **2**.

A solution of **2** (250 mg, 1.4 mmoles) in purified acetonitrile (15 ml) was sparged with nitrogen and irradiated for 1.5 hours. The solvent was then removed and the nmr of the photolysate was taken. In addition to unaltered starting material, the spectrum revealed the doublet at 6.6 for the vinyl proton of isochromene, the singlet at 3.5 for 2-indanone, and the multiplet at 4.1-4.3 of indene oxide. The hplc retention times of the reaction mixture was compared to those of authentic samples and the amounts of each were determined by co-injection with a known amount of toluene.

Photolysis of **3**.

A solution of **3** in acetonitrile was photolyzed as described above. The nmr spectrum of the photolysate showed unaltered starting material, a doublet at 9.4 for the aldehyde proton of 9, singlet at 3.4 for the benzylic protons on 8 and the multiplet centered at 3.6 of epoxide **7**. The gc/ms trace of the photolysate had retention times and mass spectra identical to those of authentic samples. Quantitative analyses were carried out by hplc as described above.

Sensitized Photolyses.

For the sensitized irradiations, samples of 2 or 3 (1×10^{-2} in 4*M* acetone in acetonitrile) were irradiated for 8 hours at 300 nm. Removal of the solvent and analysis by nmr showed the presence of unaltered starting material.

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