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Synthetic Photochemistry. XXIII.[1] The Photoreduction of Dioxetanes to *cis*-1,2-Glycols: ^{18}O-Labelling Experiments

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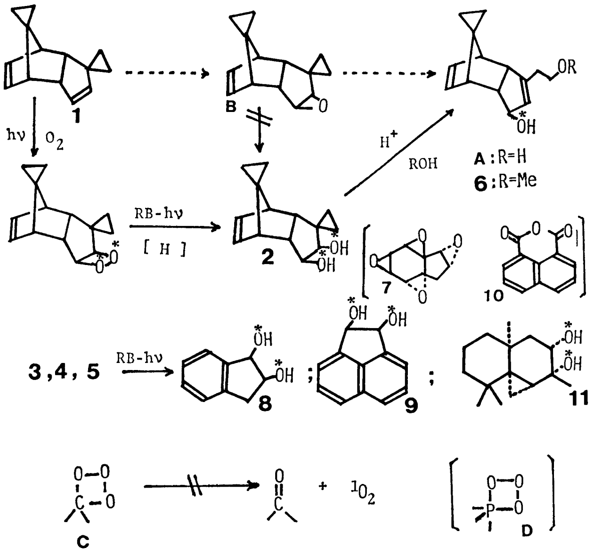
Synopsis. The Rose Bengal-sensitized photooxidation of some dioxetane-forming olefins, the Diels-Alder dimer of spiroheptadiene, indene, acenaphthylene, and thujopsene, under an $^{18}O_2$-atmosphere yielded the labelled analogs of the previously characterized *cis*-1,2-glycols. According to the mass-spectral analysis, both oxygens of the glycols were derived from the oxygen molecule.

Recently, we have shown the formation of *cis*-1,2-glycols in the Rose Bengal (RB)-sensitized photooxygenation of certain dioxetane-forming olefins.[2-4] It was deduced that the intermediate dioxetanes were involved in this reductive step. Should this be the case, both the oxygen atoms must come from the molecular oxygen. However, an accompanying formation of a *seco*-cyclopropane glycol (**A**), even in low yields, in the reaction of dispiro[cyclopropane-1,3′-tricyclo[5.2.1.0^{2,6}]deca-4′,8′-diene-10′,1″-cyclopropane] (**1**) arises the question that an epoxide (**B**) may be a precursor of both **A** and the *cis*-1,2-glycol (**2**). Consequently, to provide independent evidence, we have carried out ^{18}O-labelling experiments with **1**, indene (**3**),[4,5] a frequently studied dioxetane-forming olefin, and acenaphthylene (**4**),[4] as well as with thujopsene (**5**), a sesquiterpenoid cyclopropane derivative.[3]

Following the previous method,[2] the irradiation of **1** was performed by means of a tungsten lamp with a relatively large amount of RB, *ca.* 1.4 mmol/cm^3, in a mixed solution of methanol and pyridine under a 99%-enriched $^{18}O_2$-atmosphere[6] for 51 h by cooling with running water; the product mixture was then fractionated by silica-gel column chromatography to give the solvolyzed methoxy alcohol (**6**), 3%, and the glycol (**2**), 10%. The mass-spectral determination of **2** revealed an incorporation of two ^{18}O-atoms in the molecule with a more than 62% isotopic purity. Because of the weakness of the intensities of the molecular ions (less than 1% of the total ions), the peaks at *m*/*e*: 220 ($C_{14}H_{18}O^{18}O$) and 218 ($C_{14}H_{18}O_2$) were obscured under the noise level, and so the given figures (see Experimental) for the intensities of these weak peaks might be higher than the actual isotopic contents. At this stage, it can merely be pointed out that the solvolytic formation from **B** must be a minor path.



Scheme 1.

Next, a similar $^{18}O_2$-photooxygenation was carried out with indene (**3**); when the oxygenation was carried out at −40 °C in methanol, the major product was identified as the tetraepoxide (**7**), which was previously reported to be formed in the oxidation in aprotic solvents.[7] However, when the oxygenation was carried out at *ca.* 15—25 °C, after a work up by silica-gel column chromatography of the reaction mixture,[2,4] the desired *cis*-1,2-indandiol (**8**) was obtained in an 18% yield, together with other, previously identified products.[4,5] The mass-spectral analysis of **8** again confirmed the incorporation of two ^{18}O-atoms, with the relative intensity of *m*/*e*: 150, 152, and 154 being 2.3:1.7:96.

Although the relative rate of the oxygenation of acenaphthylene (**4**) is known to be very small, we have also carried out an $^{18}O_2$-experiment. The results were entirely the same as those of **8**; the *cis*-1,2-diol (**9**), obtained in a 24% yield, was shown to be $C_{12}H_8$-$^{18}O_2$, the relative intensity of the peaks at *m*/*e*: 186:188:190 being 8:6:86. The major product in this case was 1,8-naphthalic anhydride (**10**) (58%), whose mass spectrum indicated the incorporation of three ^{18}O-atoms.

As has previously been described, the solvolysis of the epoxy derivatives is known to give not only *trans*-1,2-diols, but, also the *cis*-glycols, **8** and **9**;[4] the present experiments can be employed to evaluate such solvolytic formation of *cis*-1,2-glycols by analyzing the mono-^{18}O-labelled products. The results show that this process is merely a side path; in the cases of **8** and **9**, a mass spectrometry gave estimates of *ca.* 2% and 6%. Consequently, the possible involvement of the epoxides in the sensitized photooxygenative formation of **8** and **9** has been unambiguously eliminated, and in turn, the intermediacy of the dioxetanes for the *cis*-glycol formation has been established.

Finally, the RB-sensitized photooxygenation of **5** was carried out in methanol under a recovered $^{18}O_2$-atmosphere, contaminated with $^{16}O_2$; after a usual work-up using silica gel column chromatography afforded the *cis*-glycol (**11**)[3] in a 15% yield, together with other products characterized previously. The mass-spectral determination of **11** clarified the incorporation of two ^{18}O-atoms in the molecule; the relative intensity of the molecular ions for 238:240:242 was 54:4:42, where the peak due to the mono-^{18}O-labelled **11** was very weak compared to the peaks of the other isomers, providing firm evidence for eliminating a trioxetane precursor (**C**).[8] Should this be the case, these three peaks should have a ratio of *ca.* 7:4:5 on the basis of the observed ^{16}O:^{18}O ratio of 5:4. At the same time, it may be difficult for any mechanism involving two oxygen molecules to explain these isotope distributions.

Experimental

*RB-Sensitized Photooxidation of **1** with $^{18}O_2$. Isolation of **2** and **6**:* A mixed solution of methanol (20 cm^3) and pyridine (5 cm^3) containing **1** (735 mg) and RB (115 mg) was repeatedly degassed and flushed with nitrogen under reduced pressure at −70 °C, after which 99%-$^{18}O_2$ gas (100 cm^3) was introduced into the reaction vessel by means of a gas buret. The irradiation was performed by means of a 500-W tungsten lamp for 51 h at 15—20 °C with vigorous stirring of the solution by the use of a magnetic bar. The reaction was checked occasionally by the volumetric analysis of O_2-consumption. The mixture was then warmed *in vacuo* to remove the solvent, and the residue was chromatographed on a silica-gel column; together with the recovered **1** (265 mg), the vinyloxirane and the dialdehyde,[9] the glycol **2** (colorless needles, mp 56—57 °C (57 mg, 10%) [Found: *m/e*, 218(4.3), 219(3.7), 220(2.8), 221(1.6), 222(11.6)]), and methoxy alcohol (6)(a colorless oil (18 mg, 3%) [Found: *m/e*, 232(27.8, 233(8.2), 234(100), 235(26.5), 236(7.5)]), were isolated.

*RB-Sensitized Photooxidation of **3**. Formation of **7**:* A methanol solution (20 cm^3) of **3** (735 mg) was similarly irradiated with RB (135 mg) at −40 °C for 10.5 h. The only product consisted of colorless crystals (mp 175—176 °C (lit,[7] 178.5—180.5 °C)), whose NMR spectrum was identical with that of **7** [Found: *m/e*, 188.0567 (10.4, M$^+$, Calcd for $C_9H_8{}^{18}O_4$: 188.0592), 183(4.4), 185(1.7), 186(1.1), 187.0522 (100, M$^+$−1, Calcd for $C_9H_7{}^{18}O_4$: 187.0514, and $C_9H_9O^{18}O_3$ requires 187.0628)].

*RB-Sensitized Oxidation of **3** with $^{18}O_2$. Isolation of **8**:* A methanol solution (20 cm^3) of **3** (500 mg) was irradiated at 15—25 °C by means of a 500-W tungsten lamp in the presence of RB (100 mg) under an $^{18}O_2$-atmosphere for 8.5 h. The reaction mixture was then evaporated *in vacuo* to remove the solvent, and the residue was chromatographed on a silica-gel column; fractions eluted from hexane–ethyl acetate (8:2) contained two methoxy hydroperoxides, homophthalaldehyde and its cyclic acetal,[4] but no further characterization was attempted. From hexane-ethyl acetate (6:4), **8** (colorless crystals, mp 102.5—103 °C, 90 mg (18%) [Found: *m/e*, 154.0766 (M$^+$, Calcd for $C_9H_{10}{}^{18}O_2$: 154.0766)]) was isolated.

*RB-Sensitized Photooxidation of **4** with $^{18}O_2$. Isolation of **9** and **10**:* A methanol solution (12 cm^3) of **4** (430 mg) was irradiated at 15—25 °C by means of a 500-W tungsten lamp in the presence of RB (70 mg) under an $^{18}O_2$ atmosphere for 55 h. The reaction mixture was then evaporated *in vacuo* to remove the solvent, and the residue was chromatographed on a silica-gel column to give, after the elution of the recovered **4** (200 mg), colorless needles (mp 213—214 °C, **9**, 70 mg (24%) [Found: *m/e*, 190.0767 (M$^+$, Calcd for $C_{12}H_{10}{}^{18}O_2$: 190.0766)). The relative intensity of *m/e*: 186:188:190=8:6:86], and 1,8-naphthalenedicarboxylic anhydride (**10**), mp 268—270 °C, 178 mg (58%) [Found: *m/e*, 204 ($C_{12}H_6{}^{18}O_3$)].

*RB-Sensitized Photooxygenation of **5**. Formation of **11**:* A mixed solution of methanol (8 cm^3) and acetone (6 cm^3) containing **5** (535 mg) and RB (75 mg) was irradiated by means of a 500-W tungsten lamp under an $^{18}O_2$-atmosphere (45%) for 35 h at 20—25 °C. The mixture was then chromatographed on a silica-gel column to give, after the elution of the recovered **5** (238 mg), colorless needles (mp 63—65 °C, **11** (53 mg, 15%) [Found: *m/e*, 242.2009 (M$^+$, Calcd for $C_{15}H_{26}{}^{18}O_2$: 242.2015)). The relative intensities of *m/e*: 240:241:242=54:4:42; *m/e*: 220:222=45:55].

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