

this indicated a total recovery of 39%, based on initial moles of cyclohexene. The distillation was not carried to completion, however, since the presence of the peroxide was anticipated.

Small-scale experiments (2 mmol) carried out in the above manner with or without 0.1 mmol of hydroquinone showed, by GLC analysis (10% UCW-98 on 80-100-mesh Gas Chrom Q), that hydroquinone completely suppressed the formation of **5c**, but that the amount of **5b** was unchanged.

Oxidation of Cyclooctene (6). Cyclooctene (20 mmol) was reacted with 10 mmol of SeO_2 and 40 mmol of *tert*-butyl hydroperoxide in 40 mL of CH_2Cl_2 at 25 °C for 48 h. The aqueous Na_2CO_3 quench to remove SeO_2 was followed by reduction of the excess hydroperoxide with Na_2SO_3 .¹⁷ Standard workup and chromatography on silica gel (5% ethyl acetate in hexanes) gave 2-cycloocten-1-ol **6a**, identified by spectral comparison to authentic material,¹⁸ and a mixture of the ether **6b** and peroxide **6c**. A LiAlH_4 reduction of this mixture afforded, after hydrolysis, a mixture of **6a** and 3-*tert*-butoxy-1-cyclooctene (**6b**) from which the latter was obtained pure by chromatography: NMR (CCl_4) δ 5.5 (m, 2, olefinic H), 4.4 (br m, 1, CHOR), 1.15 (s, 9, *tert*-butyl); IR (CCl_4) 3020 (w, olefinic CH), 1200 (s) cm^{-1} . Medium-pressure chromatography (Merck LiChroprep Si-60) on the mixture of the nonpolar products afforded a sample of pure 3-(*tert*-butylper-

oxy)-1-cyclooctene (**6c**): NMR (CCl_4) δ 5.6 (m, 2, olefinic H), 4.85 (br m, CHOR), 1.25 (s, 9, *tert*-butyl).

Oxidation of Cyclododecene (7). Cyclododecene (16 mmol) was oxidized with 8 mmol of SeO_2 and 32 mmol of *tert*-butyl hydroperoxide under the same conditions described above for cyclooctene. Chromatography of the crude oil afforded pure 2-cyclododecen-1-ol (**7a**), identical with an authentic sample¹⁸ by NMR and IR, 2-cyclododecen-1-one, identified by spectral comparison to a sample prepared by MnO_2 oxidation of **7a**, and a mixture of **7b** and **7c**. The latter compounds were obtained in pure form by the methods described above for cyclooctene. 3-*tert*-butoxy-1-cyclododecene (**7b**): NMR (CCl_4) δ 5.45 (m, 2, olefinic H), 3.40 (br m, 1, CHOR), 1.18 (s, 9, *tert*-butyl); IR (CCl_4) 3020 (olefinic CH), 1200 (s) cm^{-1} . 3-*tert*-(Butylperoxy)-1-cyclododecene (**7c**): NMR (CCl_4) δ 5.45 (m, 2, olefinic H), 4.25 (br m, 1, CHOR), 1.22 (s, 9, *tert*-butyl). Conversion of the alcohol **7a** to the acetate with acetic anhydride in pyridine at 25 °C and analysis by GLC on an OV-101 capillary column revealed the *E/Z* ratio to be 77:23 when starting from (*E*)-cyclododecene and 80:20 when starting from (*Z*)-cyclododecene.

Acknowledgment. We are grateful to the National Science Foundation for financial support. B.C. thanks the Centre National de la Recherche Scientifique and NATO for fellowship support.

Registry No. 1, 127-91-3; **2a**, 19894-98-5; **2b**, 81971-88-2; **2c**, 81971-89-3; **3b**, 82009-31-2; **4b**, 81971-90-6; **4c**, 81971-91-7; **5**, 110-83-8; **5a**, 822-67-3; **5b**, 40648-13-3; **5c**, 51437-25-3; **6**, 931-88-4; **6a**, 3212-75-7; **6b**, 81971-92-8; **6c**, 81971-93-9; (*E*)-**7**, 1486-75-5; (*Z*)-**7**, 1129-89-1; (*E*)-**7a**, 6221-49-4; (*Z*)-**7a**, 41513-26-2; (*E*)-**7a** acetate, 51533-21-2; (*Z*)-**7a** acetate, 69798-87-4; **7b**, 81971-94-0; **7c**, 81971-95-1; selenium dioxide, 7446-08-4; *tert*-butyl hydroperoxide, 75-91-2; 2-cyclododecen-1-one, 42858-38-8.

Dye-Sensitized Photooxidation of Silyl Diazo Compounds. Intramolecular Oxygen Transfer of Carbonyl Oxides

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Received December 30, 1981

The dye-sensitized photooxidation of silyl diazo compounds produced the corresponding silyl ketones and silyl esters, and the latter may be formed by the rearrangement of silyl-substituted carbonyl oxides. The reactions of a carbonyl oxide with various silyl ketones were also studied. The dye-sensitized photooxidation of diphenyldiazomethane in the presence of silyl ketones gave silyl esters together with benzophenone by reactions of a carbonyl oxide with the silyl ketones accompanying 1,2-anionic rearrangement of the silyl group.

A carbonyl oxide is a well-known Criegee-type intermediate in ozonolysis of alkenes or alkynes,¹ and recently its important role in biological systems has been recognized.² The most clean formation of carbonyl oxides involves the reaction of singlet oxygen with diazo compounds³ or the direct carbene reaction with ground-state molecular oxygen.⁴ Carbonyl oxides react intermolecularly with several substrates such as alkanes,⁵ alkenes,⁶ sulfides,⁷

sulfoxides,^{7,8} and aromatic compounds⁹ and can transfer an oxygen atom to their substrates. Although many types of intermolecular reactions of carbonyl oxides have been reported, intramolecular ones seem to be less investigated so far.¹⁰ Here, we report the detailed study on the dye-sensitized photooxidation of silyl diazo compounds and suggest the formation of silyl-substituted carbonyl oxides

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