freshly distilled *p*-methylstyrene (0.17 mL, 1.3 mmol) was added, and the mixture was stirred for another 30 min. CB (0.15 mL, 1.59 mmol) was added drop-by-drop. The mixture was stirred at −78 °C for 3 days. Then 3 N aqueous NaOH (3 mL) and 30% H_2O_2 (0.5 mL) were added, and the mixture was stirred for 12 h. The mixture was extracted with diethyl ether. Evaporation of solvent and purification by TLC gave 0.0445 g of recovered *p*-methylstyrene and 0.1185 g (95%) of α-*p*-methylphenethyl alcohol: $[\alpha]^{10}{}_{D}$ −52.5° (*c* 1.18, $CHCl_3$), 96% ee.

Acknowledgment. We thank the Chinese Academy of Sciences and the Chinese National Foundation of Natural Sciences for financial support.

Ozonolysis of 2-Phenyl-3-(acyloxy)-1*H*-indenes and 1-Phenyl-2-(benzoyloxy)acenaphthylene. Intramolecular Carbonyl Oxide–(Acyloxy)carbonyl Cycloaddition

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Alkoxy and acyloxy ozonides (3-alkoxy- and 3-(acyloxy)-1,2,4-trioxolanes) constitute a new class of cyclic peroxides that have generated much interest. The alkoxy ozonides have been prepared by both intermolecular[1] and intramolecular[2,3] cycloaddition of a carbonyl oxide, generated by alkene ozonolysis in solution, to an ester. An alternative method is ozonolysis of vinyl ethers and vinyl acetates on polyethylene. By this method the corresponding alkoxy and acyloxy ozonides can be prepared very efficiently.[4] Very recently Kuczkowski and coworkers found that ozonolysis of vinyl acetate in $CDCl_3$ afforded 3-acetoxy-1,2,4-trioxolane (34% yield) and 3-acetoxy-1,2-dioxolane (51% yield).[5] We report here an example of the intramolecular addition of a carbonyl oxide moiety to a remote (acyloxy)carbonyl group.

Ozonolysis of 2-phenyl-3-(benzoyloxy)-1*H*-indene (**1a**) in carbon tetrachloride gave a complex mixture of products, from which ozonide **5a**, 2-(benzoylmethyl)benzoic acid (**4**), and benzoic acid (**8a**) were isolated in yields of 17%, 34%, and 42%, respectively (Scheme I and Table I). A significant increase in the ozonide yield (to 57%) was obtained when the reaction was performed in a protic electrophilic solvent system—trifluoroethanol/methylene chloride. In methanol/methylene chloride, however, capture of the ozonolysis intermediate by the protic nucleophilic solvent predominated. The ^1H NMR spectrum of the mixture of crude products showed the presence of a methanol-captured product in ca. 70% yield. The isolated yield was, however, only 40% because of the instability of the product on silica gel. Because treatment with triphenylphosphine gave the lactone **7** and benzoic acid (**8a**) (eq 1), this compound was tentatively identified as the hemiperacetal **6a**.[6] Exactly the same behavior was observed with 2-phenyl-3-acetoxy-1*H*-indene (**1b**) (Table I).

Scheme I

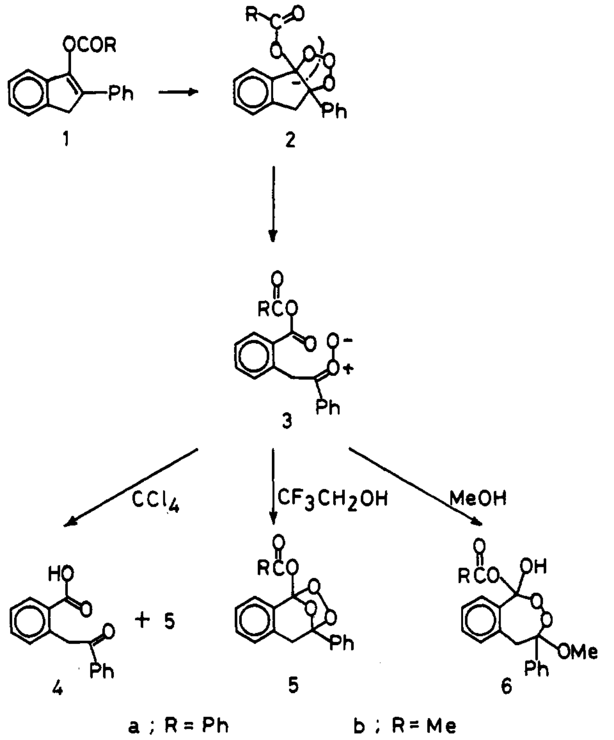
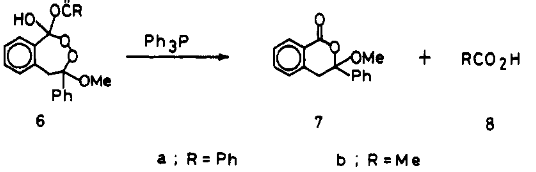


Table I. Ozonolysis of 2-Phenyl-3-(acyloxy)-1*H*-indenes 1a,b and 1-Phenyl-2-(benzoyloxy)acenaphthylene (9)[a]

substr	solvent	reactn temp, °C	products (% yield)
1a	CCl_4	0	**5a** (17), **4** (34), **8a** (42)[b]
1a	CF_3CH_2OH/CH_2Cl_2	0	**5a** (57)
1a	CH_3OH/CH_2Cl_2	0	**6a** (42)
1a	CH_3OH/CH_2Cl_2	−70	**6a** (41)
1b	CCl_4[c]	0	**5b** (5), **4** (38)[d]
1b	CF_3CH_2OH/CH_2Cl_2	0	**5b** (65)
1b	CH_3OH/CH_2Cl_2	−70	**6b** (73)[e]
9	CCl_4	0	**11** (58), **12** (20), **8a** (14)[f]
9	CH_2Cl_2	0	**11** (69), **12** (12)
9	CF_3CH_2OH/CH_2Cl_2	0	**11** (51), **12** (42), **13** (35)
9	CH_3OH/CH_2Cl_2	−70	**11** (70), **12** (9), **14** (8)[f]

[a] Treatment of a substrate with 2 equiv of ozone, unless otherwise noted. [b] **1a** was recovered in 7% yield. [c] Reaction with 1.6 equiv of ozone. [d] **1b** was recovered in 18% yield. [e] **4b** was not isolated in a pure state. [f] **9** was recovered in 5% yield.



(1)

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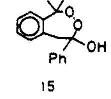
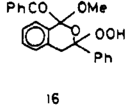
(6) As one of the reveiwers has suggested, we cannot rigorously exclude the possibility that the methanol-derived product is the isomeric hemiperacetal **15** or the isochroman derivative **16**.



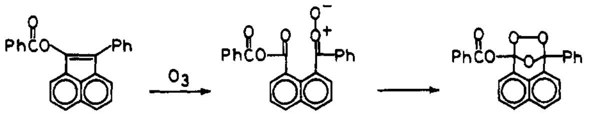
15



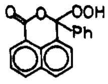
16

Based on the known directive effects in the cleavage of primary ozonides,[5,7] **1** should produce the carbonyl oxide intermediate **3**, via the primary ozonide **2** (Scheme I). The (acyloxy)carbonyl moiety is a poor 1,3-dipolarophile and, therefore, intramolecular cyclization of **3** to **5** did not occur efficiently in carbon tetrachloride. In trifluoroethanol/methylene chloride, however, solvation of the polar carbonyl oxide moiety by the protic solvent enhanced the electrophilicity of the carbonyl oxide carbon of the intermediate **3**, thereby facilitating intramolecular cycloaddition to yield the ozonide **5**.[8]

The behavior of 1-phenyl-2-(benzoyloxy)acenaphthylene (**9**) was remarkably different from that of **1**. The ozonolysis of **9**, which should initially produce the carbonyl oxide intermediate **10**, provided exclusively the ozonide **11** in fair yield, regardless of whether carbon tetrachloride, methylene chloride, trifluoroethanol/methylene chloride, or methanol/methylene chloride was used as solvent (Table I and eq 2). As byproducts, mixtures of the hydroperoxy-substituted lactone **12**, benzoic acid (**8a**), trifluoroethyl benzoate (**13**) and the methoxy-substituted lactone **14** were obtained, with the composition the solvent.



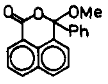
9 10 11 (2)



12

$PhCO_2CH_2CF_3$

13



14

The rigid carbonyl oxide intermediate **10** has a conformation favorable for intramolecular [3 + 2] cycloaddition and, consequently, ozonide formation could not be suppressed, even by the efficient trapping solvent methanol. This is in agreement with the observation that ozonolysis of 2-phenyl-1*H*-indene in methanol/methylene chloride at −70 °C gave methanol-derived products, including the corresponding hemiperacetal, in good yield.[9] The corresponding ozonide was the predominant product in the case of 1-phenylacenaphthylene.[8]

Experimental Section

Preparation of Starting Materials 1a,b and 9. Typical Procedure. Compounds **1a,b** and **9** were prepared by the method of Dehmlow et al.[10] To a stirred mixture of NaH (346 mg) and 1,2-dimethoxyethane (10 mL), under N_2, was added a dimethoxyethane (40 mL) solution of 2-phenylindanone (3 g) over 15 min. A solution of benzoyl chloride (2.02 g) in dimethoxyethane (50 mL) was then added over 2 h. The reaction mixture was poured into ice/water and was extracted with ether. The ether extract was washed with brine and dried (Na_2SO_4). After evaporation of the solvent from the extract, column chromatography of the residue on silica gel (benzene) gave **1a**, **1b** and **9**.

2-Phenyl-3-(benzoyloxy)-1*H*-indene: mp 119–120 °C (methylene chloride/hexane); IR 1740, 1255, 1245 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.92 (s, 2 H), 7.0–8.3 (m, 14 H). Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.79; H, 5.14.

2-Phenyl-3-acetoxy-1*H*-indene (1b, ca. 45%): mp 111–112 °C (methylene chloride/hexane); IR 1770, 1200, 1185 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 3.80 (s, 2 H), 7.1–8.0 (m, 9 H). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.74; H, 5.63.

1-Phenyl-2-(benzoyloxy)acenaphthylene (9, ca. 60%): mp 146–147 °C (methylene chloride/hexane); IR 1735, 1255 cm^{-1}. Anal. Calcd for $C_{25}H_{16}O_2$; C, 86.19; H, 4.63. Found: C, 86.20; H, 4.44.

Ozonolysis of 1a in Carbon Tetrachloride. A carbon tetrachloride solution (20 mL) of **1a** (300 mg) was treated with 2 equiv of ozone at 0 °C. (With 1 equiv of ozone, uptake was incomplete and ca. 35% of unreacted was recovered.) After evaporation of the solvent, the products were separated by column chromatography on silica gel. Elution with benzene initially gave **1a** (21 mg, 7%). Subsequent elution yielded 2-phenyl-3-(benzoyloxy)-1*H*-indene ozonide (**5a**) (58 mg, 17%): mp 124–125 °C (methanol at ca. 50 °C; prolonged heating in refluxing methanol caused complete decomposition)); ^1H NMR ($CDCl_3$) δ 3.71 (d, *J* = 18 Hz, 1 H), 3.92 (d, *J* = 18 Hz, 1 H), 7.2–8.2 (m, 14 H); ^{13}C NMR δ 38.72 (1 C), 110.56 (1 C), 118.28 (1 C), 121.79–134.21 (18 C), 161.46 (1 C); IR 1740 cm^{-1}. Anal. Calcd for $C_{22}H_{16}O_5$: C, 73.33; H, 4.48. Found: C, 73.05; H, 4.50.

Elution with ether gave 2-(benzoylmethyl)benzoic acid (**4**) (80 mg, 34%): mp 165–166 °C (methylene chloride/hexane); ^1H NMR ($CDCl_3$) δ 4.73 (s, 2 H), 7.2–8.1 (m, 9 H); IR 3430, 3050, 1685, 1410, 1270, 1215 cm^{-1}. Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74.42; H, 5.04.

Finally, benzoic acid (**8a**) was obtained (49 mg, 42%). Because the IR and NMR spectra of the mixture of crude products did not show the presence of carboxylic acid **4**, it seemed likely that this compound was produced by decomposition of unidentified ozonolysis products on silica gel.

Ozonolysis of 1a in Methanol/Methylene Chloride. A 1:1 methanol/methylene chloride solution (20 mL) of **1a** (300 mg) was treated with 2 equiv of ozone at −70 °C. The mixture was poured into water and was extracted with ether. After evaporation of the solvent from the extract, the crude products were triturated with ether/hexane to give 98 mg of 3-(benzoyloxy)-3-hydroxy-7-methoxy-7-phenyl-4,5-benzo-1,2-dioxepan (**6a**): mp 90–93 °C (hexane); ^1H NMR ($CDCl_3$) δ 3.09 (d, *J* = 14 Hz, 1 H), 3.39 (s, 3 H), 3.70 (d, *J* = 14 Hz, 1 H), 6.7–8.2 (m, 14 H) (no signal due to the OH proton could be detected); ^{13}C NMR ($CDCl_3$) δ 45.82 (1 C), 51.22 (1 C), 109.96 (1 C), 126.20–135.91 (19 C), 173.57 (1 C) (the signal for C-3 should appear in the aromatic region); IR 3400, 1750 cm^{-1}. Anal. Calcd for $C_{23}H_{20}O_6$: C, 70.40; H, 5.14. Found: C, 70.49; H, 5.16.

The residue, containing substantial amounts of the hemiperacetal **6a**, was purified by column chromatography on silica gel (ether/benzene). However, only a small amount (35 μg) of **6a** was isolated, together with a complex mixture of unidentified products.

Ozonolysis of 1b in Carbon Tetrachloride. A carbon tetrachloride solution (20 mL) of **1b** (300 mg) was treated with 1.6 equiv of ozone at 0 °C. After evaporation of the solvent, the residue was purified by column chromatography on silica gel. Elution with benzene initially gave **1b** (53 mg, 18%). Subsequent elution gave 2-phenyl-3-acetoxy-1*H*-indene ozonide (**5b**) (19 mg): mp 130–132 °C (methylene chloride/hexane); IR 1790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (s, 3 H), 3.67 (d, *J* = 18 Hz, 1 H), 3.88 (d, *J* = 18 Hz, 1 H), 7.1–7.8 (m, 9 H). Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.45; H, 4.73. Found: C, 68.31; H, 4.74. Elution with 1:1 ether–benzene gave **4** (109 mg, 38%).

Ozonolysis of 1b in Methanol/Methylene Chloride. A 1:1 methanol/methylene chloride solution (20 mL) of **1b** (1 mmol, 250 mg) was treated with 2 equiv of ozone at −70 °C. The ^1H NMR spectra of the crude product mixture showed the presence of the methanol-derived product **6b** (ca. 70%): ^1H NMR (CCl_4) δ 1.82 (s, 3 H), 2.95 (d, *J* = 14 Hz, 1 H), 3.28 (s, 3 H), 3.60 (d, *J* = 14 Hz, 1 H), 6.5–7.9 (m, 9 H), 10.22 (s, 1 H). Because **6b** was unstable on silica gel, column chromatography on silica gel gave a complex mixture of unidentified products. Treatment of the reaction mixture containing 154 mg of **6b** with 1 equiv of triphenylphosphine in benzene at 20 °C for 15 h gave 3-phenyl-3-methoxy-3,4-dihydro-1*H*-2-benzopyran-1-one (**7**) (120 mg): mp 139–140 °C (methylene chloride/hexane); ^1H NMR ($CDCl_3$) δ 3.17 (s, 3 H), 3.38 (s, 2 H), 7.2–8.3 (m, 9 H); IR 1715 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.18; H, 5.50. Product **7** was also obtained, in quantitative yield, from the reaction of **6a** with triphenylphosphine.

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Ozonolysis of 9 in Trifluoroethanol/Methylene Chloride. A 1:1 trifluoroethanol/methylene chloride solution (20 mL) of **9** (200 mg) was treated with 2 equiv of ozone at 0 °C. After workup, the products were separated by column chromatography on silica gel. Elution with benzene gave trifluoroethyl benzoate (**13**): oil; IR 1740, 1295, 1255, 1165, 705 cm^{-1}; ^{1}H NMR (CCl_4) δ 4.67 (q, $J = 8$ Hz, 2 H), 7.3–7.7 (m, 3 H), 8.0–8.1 (m, 2 H). Elution with 1:50 ether/benzene gave 1-phenyl-2-acetoxyacenaphthylene ozonide (**11**, 116 mg, 51%): mp 137–138 °C (methanol, 50 °C); ^{1}H NMR ($CDCl_3$) δ 6.99 (d, $J = 6$ Hz, 1 H), 7.2–8.1 (m, 14 H), 8.19 (d, $J = 6$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 112.09 (1 C), 119.43 (1 C), 119.54 (1 C), 125.00–134.21 (21 C), 161.74 (1 C); IR 1760 cm^{-1}. Anal. Calcd for $C_{25}H_{16}O_5$: C, 75.75; H, 4.07. Found: C, 75.74; H, 3.89. Elution with ether gave 3-phenyl-3-hydroperoxynaphtho[1,8-*cd*]pyran-1(3*H*)-one (**12**) (71 mg, 42%): mp 183–185 °C (ethyl acetate/hexane); IR 3270, 1690, 1300 cm^{-1}; CIMS (isobutane) *m/e* 293 ($M^+ + 1$); ^{1}H NMR (CD_3COCD_3) δ 7.4–8.5 (m, 11 H), 11.72 (s, 1 H); ^{13}C NMR (CD_3COCD_3) δ 110.15 (1 C), 121.08 (1 C), 127.27–130.39 (12 C), 132.83 (1 C), 134.88 (1 C), 140.45 (1 C), 163.33 (1 C). Anal. Calcd for $C_{18}H_{12}O_4$; C, 73.97; H, 4.14. Found: C, 73.90; H, 3.96.

Ozonolysis of 9 in Methanol/Methylene Chloride. A 1:1 methanol/methylene chloride solution (20 mL) of **9** (300 mg) was treated with 2 equiv of ozone at −70 °C. After workup, the products were separated by column chromatography on silica gel. Elution with benzene initially gave 15 mg (5%) of **9**. Continued elution gave the ozonide **11** (240 mg, 70%). Elution with 1:50 ether/benzene gave 3-phenyl-3-methoxynaphtho[1,8-*cd*]pyran-1(3*H*)-one (**14**) (19 mg, 8%): oil; IR 1710, 1275, 705 cm^{-1}; ^{1}H NMR (CCl_4) δ 3.91 (s, 3 H), 7.2–8.1 (m, 11 H). Anal. Calcd for $C_{19}H_{14}O_3$: C, 83.21; H, 5.11. Found: C, 83.50; H, 5.08. Elution with 1:5 ether/benzene gave **12** (22 mg, 9%).

Acknowledgment. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining ^{13}C NMR and mass spectra.

Registry No. **1a**, 131080-08-5; **1b**, 131080-09-6; **4**, 2881-31-4; **5a**, 131080-11-0; **5b**, 131080-13-2; **6a**, 131080-12-1; **6b**, 131080-14-3; **7**, 131080-15-4; **8a**, 65-85-0; **9**, 131080-10-9; **11**, 131080-16-5; **12**, 131080-17-6; **13**, 1579-72-2; **14**, 22422-09-9; 2-phenyl-1-indanone, 16619-12-8.

Isomerization Equilibria of 2*H*- and 4*H*-Thiopyrans

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2*H*- and 4*H*-thiopyrans have been the subject of numerous studies;[1] nevertheless, little is known about their relative thermodynamic stability, especially from a quantitative standpoint.[2–4]

Recently we provided the first quantitative data on the reversible isomerization of a number of 4-methoxy-4*H*-thiopyrans into the corresponding 2-methoxy-2*H* isomers.[5–7] However these data, owing to possible geminal interactions between the methoxy group and the ring sulfur atom, might depend only to a limited extent on the intrinsic stability of the heterocyclic systems. This prompted us to investigate a number of isomerization equilibria, shown in Scheme I, in which the migration of hydrogen, instead of the methoxy group, is involved. The results of such an investigation are reported herein.

Scheme I

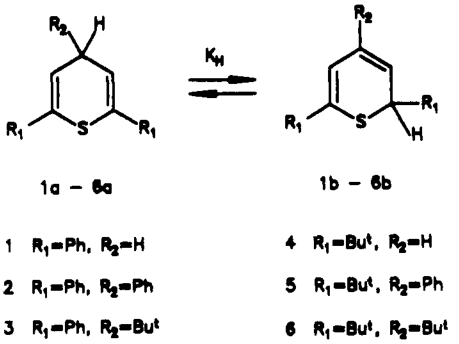

Table I. Equilibrium Constants[a] for the Isomerization of 4*H*-Thiopyrans into 2*H*-Thiopyrans

thiopyran	K_H[b]	K_{OMe}[c]
1	0.16[d]	0.52[e]
2	7.1[d]	33[e]
3	0.24[d]	0.80[e]
4	1.8[f]	3.2[g]
5	36[f]	94[h]
6	4.2[f]	4.2[g]

[a] Corrected for statistical factors. [b] In CD_3CN. [c] At 25 °C in MeOH. K_{OMe} values have been calculated from equilibrium data referring to the attachment of MeO^- to the corresponding thiopyrylium cations. [d] At 25 °C. [e] Reference 6. [f] At 100 °C. [g] Reference 7. [h] Reference 5.

Results and Discussion

Isomerization of the thiopyran mixtures (for their preparation and composition, see the Experimental Section) was carried out in CD_3CN in the presence of the corresponding thiopyrylium cation. This catalyzes the isomerization by a hydride transfer mechanism,[4] as shown in Scheme II. However, despite the catalyst, the equilibration processes were very slow. The 2,6-diphenyl-substituted thiopyrans **1–3** required from ca. 5 to 15 days to equilibrate at 25 °C, whereas the 2,6-di-*tert*-butyl-substituted thiopyrans **4–6** could be equilibrated, in a reasonable elapse of time (up to ca. 10 days), only at 100 °C. In each of the two series the order of the rate of equilibration as a function of the substituent R^2 was H > Ph > *t*-Bu. This pattern, which suggests the operation of steric effects, can be easily explained by the mechanism depicted in Scheme II. Indeed in order for the hydride transfer to occur the thiopyran and the thiopyrylium ion must closely approach each other, the approach becoming more difficult as the steric hindrance of the substituents increases.

In Table I are reported the statistically corrected equilibrium constants for the isomerization process K_H. These were evaluated dividing the final ratios of the isomers [2*H*]/[4*H*] by the factor 4 in the case of the thiopyrans **1** and **4**, and by the factor 2 in all the other cases. Indeed one has to consider that the 4*H*-thiopyrans **1a** and **4a** have a 2-fold axis of symmetry passing through the

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