tained. The $^1$H NMR spectrum of the reaction mixture showed the recovery of (*E* and *Z*)-**7a** (6.1%, *E*:*Z* = 2.1:1). **22**: $^1$H NMR δ 1.78–1.98 (3 H, m), 2.69 (2 H, t, *J* = 6.2 Hz), 2.80 (2 H, t, *J* = 6.9 Hz), 6.15 (1 H, d, *J* = 8.0 Hz), 7.11–7.52 (9 H, m); IR (liquid film) 3545 (br), 3400 (br), 1605 (s), 1115 (s), 1095 (s), 1075 (s), 1025 (s), 995 (s), 925 (s), 840 (s), 760 (s), 750 (s), 700 (s), 660 cm$^{-1}$ (s); mass spectrum, *m*/*z* (relative intensity) 286 ($M^+$, $C_{18}H_{17}O^{37}Cl$, 3), 284 ($M^+$, $C_{18}H_{17}O^{35}Cl$, 9), 294 (14), 231 (10), 118 (31), 107 (100), 91 (25); exact mass calcd for $C_{18}H_{17}O^{37}Cl$ 286.0939 and $C_{18}H_{17}O^{35}Cl$ 284.0969 (found 286.0938 and 284.0970).

**Reaction of Menthone with (2-Methylpropenyl)lithium.** To a THF (5 mL) solution of menthone (168.6 mg, 1.09 mmol) was added 1.10 mmol of 2-propenyllithium (0.196 M in THF–pentane) at 0 °C, and the mixture was stirred for 5 min. After the usual workup the crude mixture was analyzed by capillary GLC (PEG-20M). Reaction of menthone with *n*-BuLi was performed by a similar procedure.

**Reaction of Menthone with ((2,3-Benzo-2-cyclohexylidene)methyl)magnesium Chloride.** The Grignard reagent was prepared by refluxing a THF (7.5 mL) mixture of magnesium turnigs (144 mg, 6.00 mmol) and **7a** (*E*:*Z* = 84:16) (538 mg, 3.01 mmol) in the presence of several milligrams of iodine. To this was added 924 mg (5.92 mmol) of menthone, and the mixture was heated under reflux for 0.5 h. The usual workup followed by flash chromatography (1–10% ether in petroleum ether) gave 178.2 mg (20%) of (*E*)-**21** and 11.7 mg (1.3%) of (*Z*)-**21**.

**Acknowledgment.** Support of this work by Grant-in-Aid for Special Project Research from the Japan Ministry of Education, Science and Culture (No. 61225014) is gratefully acknowledged.

**Registry No.** **4a**·K, 22379-62-0; **4a**·Li, 15082-42-5; **4a**-$d_2$, 114507-60-7; **4b**·K, 73447-13-9; **4c**·K, 95465-43-3; **4d**·K, 2245-69-4; **4e**·K, 114507-39-0; **4f**·K, 54637-77-3; **4f**·Li, 4111-51-7; **4f**-*1*-*d*, 114507-68-5; **4g**·K, 78278-74-7; **4g**·Li, 15675-21-5; **4g**-*3*-*d*, 114507-71-0; **5a**, 513-37-1; **5b**, 3017-69-4; (*E*)-**6a**, 68089-82-7; (*Z*)-**6a**, 68089-83-8; **66**, 57124-78-4; (*E*)-**7a**, 114507-40-3; (*Z*)-**7a**, 114507-41-4; **7b**, 91092-18-1; **8a**, 95465-44-4; **8a**-$d_2$, 114507-61-8; (*E*)-**8c**, 114507-45-8; (*Z*)-**8c**, 114507-46-9; **8d**, 95465-56-8; **8e**, 95465-46-6; **8f**, 62217-47-4; **8h**, 114507-49-2; **8i**, 6244-46-8; (*E*)-**8j**, 114507-50-5; (*Z*)-**8j**, 114507-51-6; (*E*)-**8k**, 114507-52-7; (*E*)-**8k**-*d*, 114507-70-9; (*Z*)-**8k**, 114507-53-8; (*Z*)-**8k**-*d*, 114507-69-6; (*E*)-**8n**, 114507-56-1; (*E*)-**8n**-*d*, 114507-73-2; (*Z*)-**8n**, 114507-57-2; (*Z*)-**8n**-*d*, 114507-72-1; (*E*)-**8m**, 114507-54-9; (*Z*)-**8m**, 114507-55-0; **9a**, 95465-55-7; **9b**, 5445-30-7; **9c**, 19780-41-7; (*E*)-**10b**, 114507-43-6; (*Z*)-**10b**, 114507-44-7; (*E*)-**10g**, 114507-47-0; (*Z*)-**10g**, 114507-48-1; **11**·Li, 95465-51-3; **11**·K, 95465-47-7; **11**-*d*·K, 114507-58-3; **12**, 95465-48-8; **12**-*d*, 95483-62-8; **13**, 95465-49-9; **14**, 95465-50-2; **15**, 114507-59-4; **16**, 53282-30-7; **17**, 95465-54-6; **18**, 114507-63-0; (*E*)-**20**, 114507-64-1; (*Z*)-**20**, 114507-65-2; **19**, 114507-42-5; (*E*)-**21**, 114507-66-3; (*Z*)-**21**, 114507-67-4; **22**, 114507-74-3; 1-methoxy-3-methyl-1-phenyl-2-butene-*1*,*2*-$d_2$, 114507-62-9; 1-methoxy-3-methyl-1-phenyl-2-butene, 83605-31-6; menthone, 89-80-5; ((2,3-benzo-2-cyclohexylidene)methyl)magnesium chloride, 114507-75-4; 1-(4-chlorophenyl)-1-methoxy-3-methyl-2-butene, 114507-76-5.

# Formation of 1-Phenyl-2,3-dioxabicyclo[2.2.1]heptane in the Reaction of 1,3-Dibromo-4-phenylcyclopentane with Hydrogen Peroxide in the Presence of Silver Trifluoroacetate†

Kimio Takahashi,‡ Motoo Shiro,§ and Morio Kishi*,‡

*Shionogi Research Laboratories, Shionogi & Co., Ltd., Fukushima-ku, Osaka 553, Japan*

*Received November 17, 1987*

Reaction of 1,3-dibromo-4-phenylcyclopentane (**23**), prepared from 4-hydroxycyclopent-2-en-1-one (**10**) in a stereocontrolled manner, or its stereoisomer **24** with anhydrous hydrogen peroxide in the presence of silver trifluoroacetate in ether gave 1-phenyl-2,3-dioxabicyclo[2.2.1]heptane (**25**) mainly as a rearranged product. The expected 5-phenyl-2,3-dioxabicyclo[2.2.1]heptane (**8**) and phenylcyclopentenyl hydroperoxides **26** and **27** were also formed in this reaction. An authentic sample of endoperoxide **8** was prepared by using peroxide transfer reaction between bis(tri-*n*-butyltin) peroxide and bistriflate of *cis*-diol **35**. The stereochemistry of the endoperoxide **8** and related compounds in this series was confirmed by correlation with the data from X-ray crystallographic analysis of the diacetate of diol **21** obtained from endoperoxide **8** by stannous chloride reduction.

Since the time prostaglandin endoperoxides $PGG_2$ (**1**) and $PGH_2$ (**2**) were isolated and characterized by Hamberg and Samuelsson[1] in 1973, the chemistry of endoperoxides has been studied extensively.[2,3] Several methods have been developed for the synthesis of endoperoxides. The simplified endoperoxide 2,3-dioxabicyclo[2.2.1]heptane (**3**) was synthesized as a model compound for PG endoperoxides **1** and **2**. Salomon and Salomon[4] reported the synthesis of **3** by peroxide transfer reaction between the bistriflate of cyclopentane-1,3-diol and bis(tri-*n*-butyltin) peroxide. Porter and Gilmore[5] reported synthesis of **3** by intramolecular cyclization of 3-bromocyclopentane 1-hydroperoxide, or by the double displacement reaction of 1,3-dibromocyclopentane with hydrogen peroxide in the presence of silver acetate. Adam and Eggelte[6] reported a simple synthesis of **3** from cyclopentadiene using singlet oxygen followed by diimide reduction. Recently, **3** was synthesized from bicyclo[2.1.0]pentane via *tert*-butyl peroxymercuriation by Bloodworth and Hargreaves.[7] The trapping of triplet cyclopentane-1,3-diyl with oxygen to

† All compounds described in this paper are racemic, and one series of enantiomers is depicted for convenience.

‡ Laboratory of Organic Chemistry.

§ Laboratory of Physical Chemistry.

(1) Hamberg, M.; Samuelsson, B. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 899. Also see: Hamberg, M.; Svensson, J.; Wakabayashi, T.; Samuelsson, B. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 345.

(2) Review: Porter, N. A. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic: New York, 1980; Vol. IV, pp 261–294.

(3) Review: Saito, I.; Nittala, S. S. In *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; pp 311–374.

(4) Salomon, R. G.; Salomon, M. F. *J. Am. Chem. Soc.* **1977**, *99*, 3501.

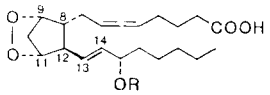
(5) Porter, N. A.; Gilmore, D. W. *J. Am. Chem. Soc.* **1977**, *99*, 3503.

(6) Adam, W.; Eggelte, H. J. *J. Org. Chem.* **1977**, *42*, 3987.

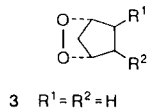
(7) Bloodworth, A. J.; Hargreaves, N. *Tetrahedron Lett.* **1987**, *28*, 2783.

0022-3263/88/1953-3098$01.50/0 

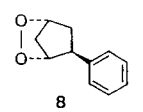
yield single-chain endoperoxide **4** was reported by Wilson, Adam, and collaborators.[8] Formation of 8,12(PG numbering)-cis-disbustituted endoperoxide **5** from an acyclic hydroperoxide using radical cyclization was reported by O'Connor's group.[9] Corey and his group[10] reported the synthesis of the cis-disubstituted endoperoxide **6** by radical



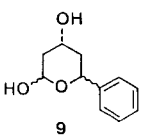
1 R=OH ($PGG_2$)
2 R=H ($PGH_2$)



3 $R^1=R^2=H$
4 $R^1=H$, $R^2=$
5 $R^1=Et$, $R^2=$
6 $R^1=CH_2CH(OMe)_2$, $R^2=$
7 $R^1=$ Ph, $R^2=H$



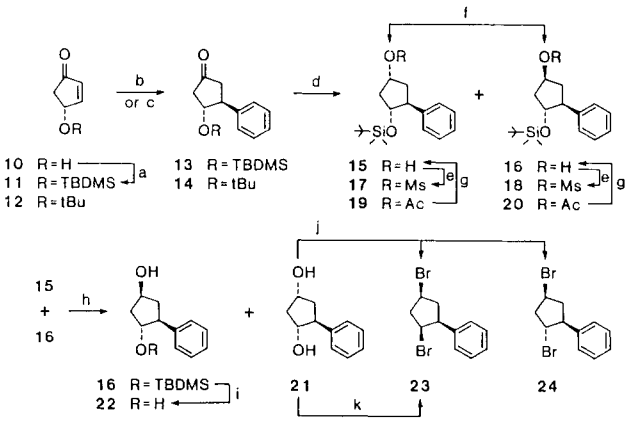
8



9

cyclization of a mercuric compound. Total synthesis of $PGH_2$ (**2**) was accomplished by the displacement reaction of a substituted 1,3-dibromocyclopentane derivative with potassium superoxide by Johnson and collaborators[11] and independently by Porter and collaborators[12,13] using hydrogen peroxide. Then, total synthesis of $PGG_2$ (**1**) was also reported by Porter's group[14] in a similar way. Because $PGH_2$ (**2**) is a pivotal compound in prostaglandin biosynthesis,[15] many model reactions of endoperoxides have been reported.[2,3] Noyori and collaborators reported the palladium(0)[16] or ruthenium(II)[17] catalyzed reaction of $PGH_2$ methyl ester to primary PGs, methyl (5*Z*,8*E*,10*E*,12*S*)-12-hydroxy-5,8,10-heptadecatrienoate (HHT), and malonaldehyde. Porter and Mebane[18] reported on the synthesis of **7** and transformation of **7** to $PGI_2$ type compounds by a one electron transfer reaction[19] with ferrous sulfate. Recently, we have been studying endoperoxide **8** as a $PGH_2$ model compound on the assumption that the $C_{13}$–$C_{14}$ double bond of the $\omega$ side chain of **2** would play an important role in the bioconversion of the bicyclic moiety of **2** into that of thromboxane $A_2$. Transformation of **8** to stereoisomers of 2,4-dihydroxy-6-phenyltetrahydropyran (**9**), a thromboxane B type compound, was achieved by the action of ferrous sulfate.[20] In the course of synthesizing **8**, we have chosen the reaction of 1,3-dibromo-4-phenylcyclopentane (**23**) with anhydrous hydrogen peroxide in the presence of silver trifluoroacetate, because among various methods for synthesis of endoperoxides, reaction of 1,3-dibromocyclopentane derivatives with hydrogen peroxide in the presence of silver cation was used widely and seemed to be the most feasible. However, we obtained rearranged endoperoxide **25** as a major product instead of the desired endoperoxide **8**. In this article, we wish to report on the formation of "rearranged" endoperoxide **25** in the reaction of dibromide **23** and **24** with hydrogen peroxide.

**Scheme I**[a]



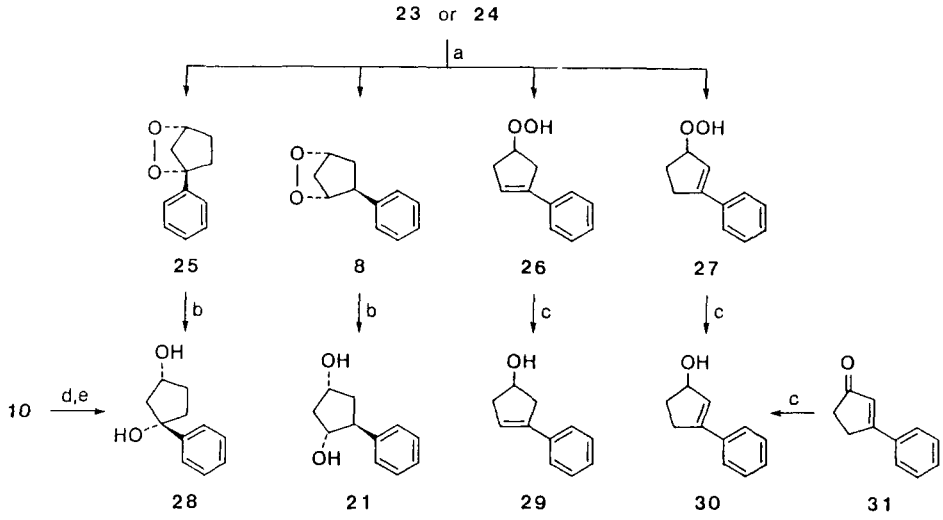
[a] (a) Acetylacetone *tert*-butyldimethylsilyl enol ether, *p*-TsOH, DMF; (b) $Ph_2CuLi$, ether; (c) PhCu, *n*-$Bu_3P$, ether; (d) L-Selectride, THF (e) MsCl, $Et_3N$, $CH_2Cl_2$; (f) CsOAc, benzene, 18-crown-6; (g) NaOMe, MeOH; (h) *n*-$Bu_4NF$, THF; (i) 0.1 N HCl, MeCN; (j) $Ph_3P$, $CBr_4$, $CH_2Cl_2$; (k) 2-chloro-3-ethylbenzoxazolium tetrafluoroborate, $Et_4NBr$, $Et_3N$, $CH_2Cl_2$.

## Results and Discussion

1,3-Dibromo-4-phenylcyclopentanes **23** and **24** were synthesized from commercially available 4-hydroxycyclopent-2-en-1-one (**10**) as shown in Scheme I. The hydroxy group of **10** was protected with the *tert*-butyldimethylsilyl group by use of the *tert*-butyldimethylsilyl enol ether of acetylacetone[21] in the presence of a catalytic amount of *p*-toluenesulfonic acid in dimethylformamide to give the corresponding silyl ether **11** in 83% yield. The yield is superior to that obtainable by silylation with *tert*-butyldimethylsilyl chloride under basic conditions.[22] Reaction of the protected enone **11** with diphenyllithium cuprate[23] gave the ketone **13** in 57% yield as a crystalline compound. Similarly, reaction of the enone **12**,[24] available from cyclopentadiene, with phenylcopper in the presence of tri-*n*-butylphosphine[25] afforded the ketone **14** in 71% yield, also as a crystalline compound. The trans relationship between the introduced phenyl and *O*-silyl group was confirmed by X-ray crystallographic analysis of diacetate **33** derived from **13** (vide infra). Reduction of the ketone **13** was done with various hydride reagents, but stereoselective formation of *cis*-diol derivative **15** was not successful. The results from NMR spectroscopic analysis of the hydride reduction products were as follows [reagent, the yield of alcohols, the ratio of **15** to **16**]: sodium borohydride, 89%, 54:46; zinc borohydride, 82%, 73:27; diisobutylaluminum hydride, 91%, 54:46; L-Selectride

(8) Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 929. Wilson, R. M.; Schnapp, K. A.; Merwin, R. K.; Ranganathan, R.; Moats, D. L.; Conrad, T. T. *J. Org. Chem.* **1986**, *51*, 4028.
(9) O'Connor, D. E.; Mihelich, E. D.; Coleman, M. C. *J. Am. Chem. Soc.* **1981**, *103*, 223; **1984**, *106*, 3577.
(10) Corey, E. J.; Shimoji, K.; Shih, C. *J. Am. Chem. Soc.* **1984**, *106*, 6425. Corey, E. J.; Shih, C.; Shih, N-Y.; Shimoji, K. *Tetrahedron Lett.* **1984**, *25*, 5013.
(11) Johnson, R. A.; Nidy, E. G.; Baczynski, L.; Gorman, R. R. *J. Am. Chem. Soc.* **1977**, *99*, 7738.
(12) Porter, N. A.; Byers, J. D.; Mebane, R. C.; Gilmore, D. W.; Nixon, J. R. *J. Org. Chem.* **1978**, *43*, 2088.
(13) Porter, N. A.; Byers, J. D.; Holden, K. M.; Menzel, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 4319.
(14) Porter, N. A.; Byers, J. D.; Ali, A. E.; Eling, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 1183.
(15) Review: Nelson, N. A.; Kelly, R. C.; Johnson, R. A. *Chem. Eng. News* **1982**, *60* (Aug 16), 30.
(16) Suzuki, M.; Noyori, R.; Hamanaka, N. *J. Am. Chem. Soc.* **1981**, *103*, 5606.
(17) Suzuki, M.; Noyori, R.; Hamanaka, N. *J. Am. Chem. Soc.* **1982**, *104*, 2024.
(18) Porter, N. A.; Mebane, R. C. *Tetrahedron Lett.* **1982**, *23*, 2289.
(19) Turner, J. A.; Herz, W. *Experientia* **1977**, *33*, 1133.
(20) Takahashi, K.; Kishi, M. *J. Chem. Soc., Chem. Commun.* **1987**, 722.
(21) Veysogln, T.; Mitschel, L. A. *Tetrahedron Lett.* **1981**, *22*, 1299.
(22) Tanaka, T.; Kurozumi, S.; Toru, T.; Miura, S.; Kobayashi, M.; Ishimoto, S. *Tetrahedron* **1976**, *33*, 1713.
(23) Posner, G. *Org. React.* **1972**, *19*, 1.
(24) Scwartz, J.; Loots, M. J.; Kosugi, H. *J. Am. Chem. Soc.* **1980**, *102*, 1333.
(25) Suzuki, M.; Suzuki, T.; Kawagishi, T.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 1247.

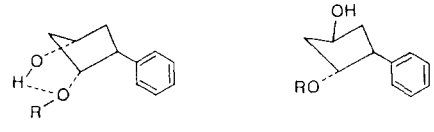
**Scheme II**[a]




[a] (a) Anhydrous $H_2O_2$, $CF_3COOAg$, ether; (b) $SnCl_2$, EtOH, $H_2O$; (c) $NaBH_4$, MeOH; (d) PhLi, THF, (e) $H_2$, $PtO_2$, AcOEt.

(Aldrich), 84%, 75:25; lithium thexyllimonyl borohydride, 80%, 80:20.

Although separation of the two epimers **15** and **16** by silica gel chromatography was very difficult, these were separated effectively after the next step. Treatment of the mixture of **15** and **16**, prepared by L-Selectride reduction



15 R = TBDMS
21 R = H



16 R = TBDMS
22 R = H

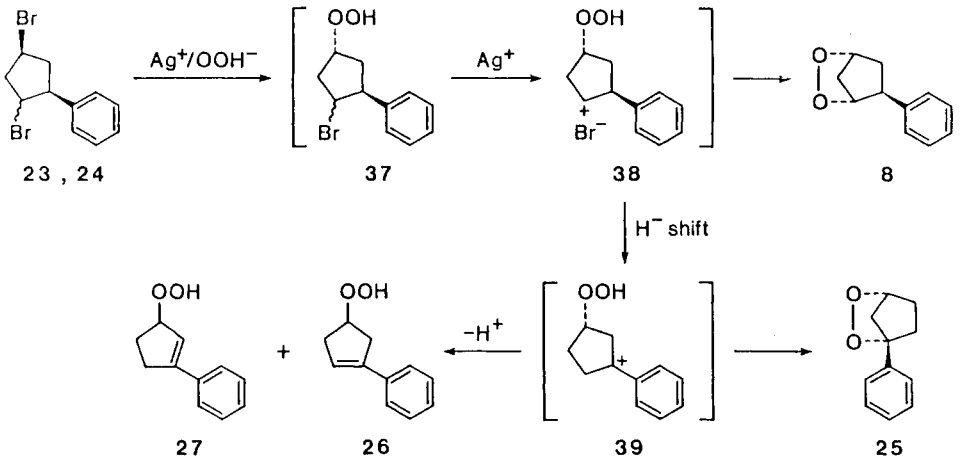
of **13**, with tetra-*n*-butylammonium fluoride gave unchanged silyl ether **16** and deprotected diol **21**, which were easily separated by silica gel chromatography. Recovered **16** was deprotected with 0.1 N hydrochloric acid in acetonitrile, yielding *trans*-diol **22**. Moreover, the undesirable trans isomer **16** was inverted to cis compound **15** in the following manner. Alcohol **16** was mesylated with mesyl chloride and triethylamine, and the resulting mesylate **18** was treated with cesium acetate[26] in the presence of 18-crown-6 in refluxing benzene. The inverted acetate **19** thus obtained was methanolyzed with sodium methoxide in methanol to afford the additional alcohol **15**. Thus, the preparative method leading to *cis*-diol **21** was established. Similarly, alcohol **15** was inverted to the epimer **16** via mesylate **17** and acetate **20**. Stereochemistry of these isomers was assigned on the basis of hydrogen bonding observed by IR spectroscopy.[27] Absorption bands arising from intramolecular hydrogen bonding were observed at 3538 and 3557 $cm^{-1}$ in the IR spectra of compound **15** and **21** in carbon tetrachloride ($2.8 \times 10^{-4}$ M solution), respectively. On the other hand, only absorptions arising from free hydroxyl were observed in the IR spectra of compound **16** and **22** at 3626 and 3619 $cm^{-1}$, respectively. The above stereochemical assignments were confirmed by X-ray crystallographic analysis of diacetate **33**, prepared from diol **21**.

In the next stage, conversion of the *cis*-diol **21** to *cis*-dibromide **23** was attempted. Treatment of *cis*-diol **21** with triphenylphosphine and carbon tetrabromide in dichloromethane gave two unstable dibromides in rather low yield (26% for the less polar compound, and 20% for the more polar one). On the other hand, bromination of *cis*-diol **21** with 2-chloro-3-ethylbenzoxazolium tetrafluoroborate,[14,28] tetraethylammonium bromide, and triethylamine in dichloromethane afforded a single isomer of dibromide, identical with the more polar compound in the first bromination reaction. Although the stereochemistry of these two bromides is still uncertain, dibromide prepared in the latter reaction was assigned as the *cis*-dibromide **23** and the other isomer as the trans **24** from the analogy to bromination of prostaglandin $F_{2\alpha}$ by the same method. Treatment of mesylate **32**, prepared from **21**, with LiBr[11] gave a mixture of **23** and **24** in lower yield.

Next, synthesis of endoperoxide **8** from dibromide **23** was attempted. Reaction of the dibromide **23** with anhydrous hydrogen peroxide[29,30] in the presence of silver trifluoroacetate in ether at 0 °C gave four unstable peroxides **8**, **25**, **26**, and **27**, which were positive to the ferrous thiocyanate[31] and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine[32] tests (Scheme II). The products were purified with silica gel chromatography at 0 °C. The desired endoperoxide **8** was obtained from the early fraction as a mixture with isomeric endoperoxide **25** in 35% yield, favoring **25** in a ratio of 1:6. Further purification of this mixture gave pure **25** as a colorless oil. The $C_4$ bridgehead proton appeared as a broad singlet at 4.82 ppm in the NMR spectrum. The molecular ion was observed at $m/z$ 176 in the mass spectrum. Reduction of the mixture of **25** and **8** with stannous chloride gave separable diols **28** and **21**, which were identical with authentic samples of **28** and **21**, respectively. An authentic sample of diol **28** was prepared by the reaction of the enone **10** with 2 equiv of phenyllithium, followed by catalytic hydrogenation. Hydroperoxides **26** and **27** were isolated in 9% and 8% yield, respectively, from the latter fraction of the chromatography of the dibromide reaction products. Compounds **26** and **27** exhibited hydroperoxide proton NMR signals at 7.94 and 7.85 ppm, respectively. Molecular ions from these molecules were observed at $m/z$ 176. IR spectra showed

(26) Torisawa, Y.; Okabe, H.; Ikegami, S. *Chem. Lett.* **1984**, 1555.
(27) Eliel, E. L.; Pillan, C. *J. Am. Chem. Soc.* **1955**, *77*, 3600.
(28) Mukaiyama, T.; Shoda, S.; Watanabe, Y. *Chem. Lett.* **1977**, 383.
(29) Hurd, C. D.; Puterbaugh, M. P. *J. Am. Chem. Soc.* **1930**, *52*, 950.
(30) Corey, E. J.; Niwa, H.; Falk, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 1586.
(31) Bundy, G. L.; Baldwin, J. M.; Peterson, D. C. *J. Org. Chem.* **1983**, *48*, 977.
(32) Ronald, R. C. *J. Org. Chem.* **1985**, *50*, 5084.

**Scheme III**

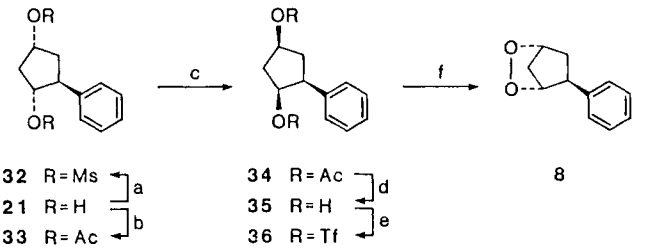



absorption peaks arising from the hydroperoxy groups at 3510 $cm^{-1}$. Reduction of the two peroxides **26** and **27** with sodium borohydride gave 3-phenylcyclopentenols **29** and **30**, respectively. Alcohol **29** was identified by comparison of its physical data with those published.[33] An authentic sample of isomer **30** was prepared from known enone **31**[34] by sodium borohydride reduction.

Reaction of the other dibromide **24** with hydrogen peroxide in the presence of silver trifluoroacetate under exactly the same conditions as described above for **23** afforded the same products (**8**, **25**, **26**, and **27**) in almost the same yields and distribution as those from **23**. These findings suggest that the reactions proceeded through a common intermediate. The possible reaction pathways are shown in Scheme III. The reaction is likely initiated by hydroperoxide substitution of the bromine atom that is farthest from the phenyl group to form **37**. This is likely because the other bromine is deactivated toward substitution due to the negative inductive effect of the phenyl group. The formation of ion pair **38** as the common intermediate would follow with a hydride shift leading to tertiary benzylic cation **39** as a major pathway. Intramolecular cyclization of **38** producing **8** would be a minor pathway. It was reported that, in the 2-phenylcyclopent-1-yl carbenium system, phenyl coordination to the adjacent developing carbenium is not an important pathway and 1,2-hydride shift predominates to form the benzylic cation.[35] The cation **39** could lead to the formation of endoperoxide **25** and hydroperoxides **26** and **27** by intramolecular cyclization and deprotonation, respectively.

Although endoperoxide **8** was not obtained in a pure form in the above reactions, it was identified by comparison with the authentic material prepared in a different way as shown in Scheme IV. Thus, *cis*-diol **21** was mesylated with 2 equiv of mesyl chloride and triethylamine. The mesylate **32** thus obtained was treated with excess cesium acetate in the presence of 18-crown-6 in refluxing toluene to give the inverted diacetate **34**. Methanolysis of the diacetate **34** to diol **35** and treatment of the resulting diol **35** with triflic anhydride in pyridine gave unstable bistriflate **36**. Without purification, the bistriflate **36** was subjected to peroxide transfer reaction[4] with bis(tri-*n*-butyltin) peroxide, prepared from tri-*n*-butyltin methoxide and anhydrous hydrogen peroxide. This yielded a crystalline endoperoxide **8** of mp 40–42 °C (from petroleum ether) as the sole isolable product, although the yield was

**Scheme IV**[a]




[a] (a) MsCl, $Et_3N$; (b) $Ac_2O$, py; (c) CsOAc, 18-crown-6, toluene; (d) NaOMe, MeOH; (e) $Tf_2O$, py; (f) $(n\text{-}Bu_3SnO)_2$, $CH_2Cl_2$.

not satisfactory (6%). The molecular ion of **8** was observed at $m/z$ 176 in the mass spectrum. Bridgehead protons appeared at 4.66 and 4.85 ppm as broad singlets in the NMR spectrum. Reduction of this peroxide **8** with stannous chloride afforded diol **21**.

In conclusion, the reaction of 1,3-dibromo-4-phenylcyclopentane (**23**) (prepared from the enone **10** in a stereocontrolled manner) or its stereoisomer **24** with hydrogen peroxide in the presence of silver trifluoroacetate produced 1-phenyl-2,3-dioxabicyclo[2.2.1]heptane (**25**) as a major product, accompanied with the expected 5-phenyl-2,3-dioxabicyclo[2.2.1]heptane (**8**) and hydroperoxides **26** and **27** as minor products. The formation of ion pair **38** and subsequent hydride shift to benzylic cation **39** is proposed as the common reaction pathway in these reactions.

## Experimental Section

Melting points were determined on a Yanagimoto micro apparatus and are uncorrected. A Hitachi 260-10 or JASCO-J-0056 spectrophotometer was used to obtain IR spectra. NMR spectra were obtained with a Varian EM-390 (90 MHz) or Varian XL-200 (200 MHz) spectrometer in $CDCl_3$ with $Me_4Si$ as the internal reference unless otherwise mentioned. Mass spectra were determined with a Hitachi RMU-8 spectrometer (70 eV). Elemental analyses were performed by the analytical department of these laboratories. Lobar Columns (Merck, silica gel 60, 230–400 mesh) were used for column chromatography with a FMI RP-SY Lab Pump and a Waters R-403 differential refractometer. TLC plates were purchased from E. Merck and peroxides were detected by a spray of either ferrous thiocyanate or *N,N,N',N'*-tetramethyl-*p*-phenylenediamine dihydrochloride. HPLC analyses were carried out on a LiChrosorb SI 60 column (Merck, 10 μm, 4.6 mm × 250 mm) in normal-phase operation and a Develosil ODS-7 column (Nomura Chemical Co., 7 μm, 4.6 mm × 250 mm) in reverse-phase operation. This unit contained a Reodyne injector, a Knauer pump, and an Oyobunko Uvilog UV detector.

**4-[(*tert*-Butyldimethylsilyl)oxy]cyclopent-2-en-1-one (11).** A mixture of 4-hydroxycyclopent-2-en-1-one (**10**) (2.08 g, 21.24 mmol), acetylacetone *tert*-butyldimethylsilyl enol ether (5.00 g,

(33) Padwa, A.; Alexander, E. *J. Am. Chem. Soc.* **1970**, *92*, 1976.
(34) House, H. O.; Wasson, R. L. *J. Am. Chem. Soc.* **1957**, *79*, 1488.
(35) Kim, C. J.; Brown, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 5043, 5051.

23.36 mmol), p-TsOH (100 mg, 0.53 mmol), and DMF (21 mL) was stirred at room temperature for 15 h. The mixture was poured into aqueous $NaHCO_3$ and extracted with hexane. The organic layer was dried ($Na_2SO_4$) and evaporated. Chromatography of the residue with hexane/AcOEt (80/20) as the eluent gave **11** (3.71 g, 83%) as a colorless oil: IR (film) 1715 $cm^{-1}$; NMR $\delta$ 7.34 (1 H, dd, $J$ = 2, 7 Hz, $C_3$-H), 6.10 (1 H, dd, $J$ = 1, 7 Hz, $C_2$-H), 4.93 (1 H, m, $C_4$-H), 2.57 (1 H, dd, $J$ = 6, 19 Hz, $C_5$-H), 2.04 (1 H, dd, $J$ = 3, 19 Hz, $C_5$-H), 0.87 (9 H, s, $CMe_3$), 0.09 (6 H, s, $SiMe_2$), which was identical with a sample prepared by the reported[22] procedure.

**(3*R**,4*S**)-3-[(*tert*-Butyldimethylsilyl)oxy]-4-phenylcyclopentan-1-one (13).** A solution of the enone **11** (5.30 g, 25 mmol) in ether (50 mL) was added to a stirred solution of $Ph_2CuLi$, prepared from CuI (9.50 g, 50 mmol) and PhLi (1.8 M in ether–cyclohexane, 55.5 mL, 100 mmol), at −70 °C. The mixture was stirred at 0 °C for 2 h and was poured into aqueous $NH_4Cl$ and extracted with hexane. The organic layer was dried ($Na_2SO_4$), evaporated, and chromatographed. Elution with hexane/AcOEt (9/1) afforded **13** (4.12 g, 57%): mp 53–54 °C (EtOH/$H_2O$); IR ($CHCl_3$) 1742 $cm^{-1}$; NMR $\delta$ 7.30 (5 H, br s, ArH × 5), 4.32 (1 H, q, $J$ = 6 Hz, $C_3$-H), 3.50–3.15 (1 H, m, $C_4$-H), 3.00–2.11 (4 H, m, $C_2$-$H_2$, $C_5$-$H_2$), 0.81 (9 H, s, $CMe_3$), and −0.12 and −0.21 (each 3 H, each s, $SiMe_2$); MS, $m/z$ 275 ($M^+$ − Me), 233 ($M^+$ − Bu). Anal. Calcd for $C_{17}H_{26}O_2Si$: C, 70.30; H, 9.02. Found: C, 70.02; H, 9.06.

**(3*R**,4*S**)-3-(*tert*-Butyloxy)-4-phenylcyclopentan-1-one (14).** Under an Ar atmosphere, $n$-$Bu_3P$ (22.88 mL, 92 mmol) was added to a stirred suspension of CuI (7.60 g, 40 mmol) in ether (320 mL) at room temperature. PhLi (1.9 M in ether–cyclohexane, 21.06 mL, 40 mmol) was slowly added to the above mixture at −78 °C. After 0.5 h, a solution of the enone **12** (6.16 g, 40 mmol) in ether was added to this solution. The mixture was stirred at −78 °C for 1.5 h, and aqueous $NH_4Cl$ was added at −40 °C. The layers were separated at room temperature. The organic layer was washed with brine, dried ($Na_2SO_4$), and evaporated, giving an oil (37.1 g). Silica gel (70–230 mesh) chromatography with hexane/AcOEt (80/20) as the eluent yielded **14** (6.606 g, 71%): mp 68–69 °C (EtOH/$H_2O$); IR ($CHCl_3$) 1735 $cm^{-1}$; NMR $\delta$ 4.12 (1 H, dd, $J$ = 7, 14 Hz, $C_3$-H), 3.32 (1 H, dt, $J$ = 8, 8 Hz, $C_4$-H), 2.96–2.02 (4 H, m, $C_2$-$H_2$, $C_5$-$H_2$), and 1.02 (9 H, s, $CMe_3$). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.73; H, 8.72.

**Reduction of Ketone 13 with L-Selectride.** L-Selectride (1.0 M in THF, 17.0 mL) was added to a stirred solution of the ketone **13** (4.10 g, 14.138 mmol) in THF (30 mL) at −78 °C, and the solution was stirred for 30 min. Aqueous $NH_4Cl$ (1.0 mL), 10% aqueous NaOH (10 mL), and 30% $H_2O_2$ (3.0 mL) were added at 0 °C, and the mixture was stirred at 0 °C for 30 min and then extracted with hexane. The organic layer was dried ($Na_2SO_4$), evaporated, and chromatographed with hexane/AcOEt (80/20) as the eluent to yield **15** and **16** (3.46 g, 84%), in a ratio of 75:25, which was used in the next step without separation.

**(1*R**,3*R**,4*S**)-3-[(*tert*-Butyldimethylsilyl)oxy]-4-phenylcyclopentan-1-ol (15).** A mixture of the acetate **19** (14 mg, 0.042 mmol), NaOMe (4.5 mg, 0.084 mmol), and MeOH (1.0 mL) was stirred at room temperature for 1 h. $CH_2Cl_2$ and aqueous $NH_4Cl$ were added and the layers were separated. The organic layer was washed with water, dried ($Na_2SO_4$), and evaporated. Chromatography of the residue with hexane/AcOEt (80/20) as the eluent afforded **15** (9 mg, 73%) as a colorless oil: IR ($CCl_4$) 3636 and 3538 $cm^{-1}$; NMR $\delta$ 7.40–7.10 (5 H, m, ArH × 5), 4.60–4.25 and 4.25–4.00 (each 1 H, each m, $C_1$-H, $C_3$-H), 3.50–3.20 (1 H, m, $C_4$-H), 2.65–1.65 (4 H, m, $C_2$-$H_2$, $C_5$-$H_2$), 0.80 (9 H, s, $CMe_3$), and −0.10 (6 H, s, $SiMe_2$); MS, $m/z$ 277 ($M^+$ − Bu).

**(1*S**,3*R**,4*S**)-3-[(*tert*-Butyldimethylsilyl)oxy]-4-phenylcyclopentan-1-ol (16) and (1*R**,3*R**,4*S**)-4-Phenylcyclopentane-1,3-diol (21).** (a) $n$-$Bu_4NF$ (1.0 M in THF, 13.01 mL) was added to a solution of the mixture of alcohols **15** and **16** (3.80 g, 13.01 mmol) in THF (38 mL) at room temperature. After stirring for 3 h, the mixture was diluted with $CH_2Cl_2$ and washed with water. The organic layer was dried ($Na_2SO_4$), evaporated, and chromatographed. Elution with hexane/AcOEt (85/15) gave unreacted **16** (239 mg, 6%): colorless oil; IR ($CCl_4$) 3626 $cm^{-1}$; NMR $\delta$ 7.32 (5 H, br s, ArH × 5), 4.61–4.40 (1 H, m, $C_1$-H), 4.40–4.25 (1 H, m, $C_3$-H), 3.30–2.80 (1 H, m, $C_4$-H), 2.70–1.60 (4 H, m, $C_2$-$H_2$, $C_5$-$H_2$), 0.80 (9 H, s, $CMe_3$), and −0.20 and −0.28 (each 3 H, each s, $SiMe_2$). Anal. Calcd for $C_{17}H_{22}O_2Si$: C, 69.81; H, 9.65. Found: C, 69.36; H, 9.37. Elution with AcOEt afforded diol **21** (1.399 g, 58%): mp 81–82 °C (AcOEt/hexane); IR ($CCl_4$) 3619 and 3557 $cm^{-1}$; NMR $\delta$ 7.25 (5 H, br s, Ar H × 5), 4.60–4.35 (1 H, m, $C_1$-H), 4.35–4.00 (1 H, m, $C_3$-H), 3.50–3.20 (1 H, m, $C_4$-H), 2.80 and 2.60 (each 1 H, each br s, OH × 2), 2.55–1.66 (4 H, m, $C_2$-$H_2$, $C_5$-$H_2$); MS, $m/z$ 178 ($M^+$). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.99; H, 7.80.

(b) Acetate **20** (41 mg, 0.12 mmol) was treated with NaOMe (7.0 mg, 0.13 mmol) in MeOH (1.0 mL) at room temperature for 1 h. $CH_2Cl_2$ and aqueous $NH_4Cl$ were added and the layers were separated. The organic layer was dried ($Na_2SO_4$) and evaporated, and the residue was chromatographed with hexane/AcOEt (85/15) to give **16** (19 mg, 54%), which was identical with the sample described in (a).

**(1*R**,3*R**,4*S**)-3-[(*tert*-Butyldimethylsilyl)oxy]-1-[(methylsulfonyl)oxy]-4-phenylcyclopentane (17).** $Et_3N$ (51 mg, 0.5 mmol) and MsCl (57 mg, 0.5 mmol) were added to a stirred solution of the mixture of epimers **15** and **16** (120 mg, 0.41 mmol) in $CH_2Cl_2$ (5.0 mL) at 0 °C. The mixture was stirred at room temperature for 15 h and then extracted with $n$-hexane. The organic layer was dried ($Na_2SO_4$), evaporated, and recrystallized from $CH_2Cl_2$/hexane, yielding **17** (82 mg, 54%): mp 85–86 °C; IR ($CHCl_3$) 1355 $cm^{-1}$; NMR $\delta$ 7.30 (5 H, br s, ArH × 5), 5.44–5.26 (1 H, m, $C_1$-H), 4.22–3.96 (1 H, m, $C_3$-H), 3.34–3.02 (1 H, m, $C_4$-H), 3.12 (3 H, s, SMe), 0.82 (9 H, s, $CMe_3$), and −0.18 and −0.20 (each 3 H, each s, $SiMe_2$); MS, $m/z$ 313 ($M^+$ − Bu). Anal. Calcd for $C_{18}H_{30}O_4SSi$: C, 58.34; H, 8.16. Found: C, 58.11; H, 8.01.

**(1*S**,3*R**,4*S**)-3-[(*tert*-Butyldimethylsilyl)oxy]-1-[(methylsulfonyl)oxy]-4-phenylcyclopentane (18).** $Et_3N$ (69 mg, 1.67 mmol) and MsCl (191 mg, 1.67 mmol) were added to a stirred solution of the alcohol **16** (407 mg, 1.39 mmol) in $CH_2Cl_2$ (4.0 mL) at 0 °C. After stirring at 0 °C for 2 h, the mixture was washed with water, dried ($Na_2SO_4$), and evaporated. The residue was chromatographed with hexane/AcOEt (80/20) as the eluent, yielding **18** (430 mg, 84%) as a colorless oil: IR ($CHCl_3$) 1355 $cm^{-1}$; NMR $\delta$ 7.30 (5 H, br s, Ar H × 5), 5.40–5.10 (1 H, m, $C_1$-H), 4.35–4.15 (1 H, m, $C_3$-H), 3.02 (3 H, s, SMe), 3.10–1.90 (5 H, m, $C_2$-$H_2$, $C_4$-H, $C_5$-$H_2$), 0.76 (9 H, s, $CMe_3$), and −0.20 and −0.28 (each 3 H, each s, $SiMe_2$); MS, $m/z$ 313 ($M^+$ − Bu). Anal. Calcd for $C_{18}H_{30}O_4SSi$: C, 58.34; H, 8.16. Found: C, 58.20; H, 8.07.

**(1*R**,3*R**,4*S**)-1-Acetoxy-3-[(*tert*-butyldimethylsilyl)oxy]-4-phenylcyclopentane (19).** A mixture of the mesylate **18** (400 mg, 1.081 mmol), CsOAc (623 mg, 3.243 mmol), 18-crown-6 (143 mg, 0.54 mmol), and benzene (10 mL) was refluxed for 2.5 h. The cooled mixture was extracted with hexane and washed with water, and the organic layer was dried ($Na_2SO_4$). Evaporation of the solvent and chromatography of the residue with hexane/AcOEt (90/10) as the eluent gave **19** (354 mg, 98%) as a colorless oil: IR ($CHCl_3$) 1740 $cm^{-1}$; NMR $\delta$ 7.35 (5 H, br s, ArH × 5), 5.40–5.15 (1 H, m, $C_1$-H), 4.20–3.91 (1 H, m, $C_3$-H), 3.40–3.05 (1 H, m, $C_4$-H), 2.75–1.60 (4 H, m, $C_2$-$H_2$, $C_5$-$H_2$), 2.05 (3 H, s, Ac), 0.79 (9 H, s, $CMe_3$), and −0.20 and −0.30 (each 3 H, each s, $SiMe_2$); MS, $m/z$ 277 ($M^+$ − Bu).

**(1*S**,3*R**,4*S**)-1-Acetoxy-3-[(*tert*-butyldimethylsilyl)oxy]-4-phenylcyclopentane (20).** Mesylate **17** (74 mg, 0.2 mmol) was treated with CsOAc as above to yield the acetate **20** (41 mg, 61%) as a colorless oil: IR (film) 1740 $cm^{-1}$; NMR $\delta$ 7.30 (5 H, br s, ArH × 5), 5.42 (1 H, m, $C_1$-H), 4.34–3.96 (1 H, m, $C_3$-H), 3.15–1.75 (5 H, m, $C_2$-$H_2$, $C_4$-H, $C_5$-$H_2$), 2.08 (3 H, s, Ac), 0.78 (9 H, s, $CMe_3$), and −0.18 and −0.28 (each 3 H, each s, $SiMe_2$); MS, $m/z$ 277 ($M^+$ − Bu).

**(1*S**,3*R**,4*S**)-4-Phenylcyclopentane-1,3-diol (22).** A mixture of the silyl ether **16** (380 mg, 1.30 mmol), 0.1 N HCl (1.0 mL), and MeCN (3.8 mL) was stirred at room temperature for 3 h. The mixture was diluted with $CH_2Cl_2$ and washed with water. The organic layer was washed with aqueous $NaHCO_3$, dried ($Na_2SO_4$), and evaporated. Chromatography of the residue with AcOEt gave **22** (185 mg, 80%): mp 103–104 °C (AcOEt); IR ($CCl_4$) 3623 $cm^{-1}$; NMR $\delta$ 7.25 (5 H, br s, ArH × 5), 4.50–4.15 (2 H, m, $C_1$-H, $C_3$-H), 2.95–1.56 (5 H, m, $C_2$-$H_2$, $C_4$-H, $C_5$-$H_2$), and 2.75 (2 H, br s, OH × 2); MS, $m/z$ 178 ($M^+$). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.80; H, 7.85.

**(1*S**,3*S**,4*S**)-1,3-Dibromo-4-phenylcyclopentane (23) and (1*S**,3*R**,4*S**)-1,3-Dibromo-4-phenylcyclopentane (24).** (a) A mixture of the diol **21** (18 mg, 0.1 mmol), $Ph_3P$ (104 mg, 0.4 mmol), $CBr_4$ (66 mg, 0.2 mmol), and $CH_2Cl_2$ (1.0 mL) was stirred at room temperature for 15 h. The solvent was evaporated and

the residue was chromatographed with hexane/AcOEt (90/10), yielding **24** (6 mg, 29%) as an oil: NMR δ 7.40–7.10 (5 H, m, ArH × 5), 4.85–4.55 (2 H, m, $C_1$-H, $C_3$-H), 3.90–3.60 (1 H, m, $C_4$-H), 3.40–2.30 (4 H, m, $C_2$-$H_2$, $C_5$-$H_2$); MS, *m/z* 302, 304 ($M^+$). Further elution gave **23** (8.0 mg, 26%): mp 56–57 °C; NMR δ 7.32 (5 H, br s, ArH × 5), 4.70–4.20 (2 H, m, $C_1$-H, $C_3$-H), and 3.40–2.60 (5 H, m, $C_2$-$H_2$, $C_4$-H, $C_5$-$H_2$); MS, *m/z* 302, 304 ($M^+$).

(b) A solution of the diol **21** (36 mg, 0.2 mmol) in $CH_2Cl_2$ (2.0 mL) was added to a stirred mixture of 2-chloro-3-ethylbenzoxazolium tetrafluoroborate (135 mg, 0.5 mmol), $Et_4NBr$ (84 mg, 0.4 mmol), $Et_3N$ (51 mg, 0.5 mmol), and $CH_2Cl_2$ (2.0 mL) at 0 °C. After stirring for 1 h, the mixture was diluted with $CH_2Cl_2$ and washed with water, and the organic layer was dried ($Na_2SO_4$) and evaporated. Chromatography with hexane/AcOEt (90/10) of the residue afforded **23** (24 mg, 39%), which was identical with the sample described in method (a).

**(1*R**,4*R**,5*S**)-5-Phenyl-2,3-dioxabicyclo[2.2.1]heptane (8), (1*S**,4*R**)-1-Phenyl-2,3-dioxabicyclo[2.2.1]heptane (25), 1-Hydroperoxy-3-phenylcyclopent-3-ene (26), and 1-Hydroperoxy-3-phenylcyclopent-2-ene (27).** (a) A solution of anhydrous $H_2O_2$ (1.83 M in ether, 5 mL) and $CF_3COOAg$ (530 mg, 2.4 mmol) was added to a solution of the bromide **23** (or **24**) (183 mg, 0.6 mmol) in ether (1.8 mL) at 0 °C. After the mixture was stirred for 0.5 h at 0 °C, hexane was added to the mixture. The organic layer was washed with ice–water, dried ($Na_2SO_4$), evaporated, and chromatographed at 0 °C. Elution with hexane/AcOEt (90/10) gave a mixture of **8** and **25** (38 mg, 35%, **8**/**25** = 1/6 by NMR). Purification of the mixture by repeated chromatography gave **25** as a colorless oil: NMR δ 7.55–7.15 (5 H, m, ArH × 5), 4.82 (1 H, br s, $C_4$-H), and 2.70–1.85 (6 H, m, $CH_2$ × 3); MS, *m/z* 176 ($M^+$). Further elution with the same solvent gave **26** (10 mg, 9%) as a colorless oil: IR ($CHCl_3$) 3510 $cm^{-1}$; NMR δ 7.94 (1 H, s, OOH), 7.55 (5 H, m, ArH × 5), 6.06 (1 H, t, *J* = 3 Hz, $C_4$-H), 5.15–4.96 (1 H, m, $C_1$-H), and 3.02–2.65 (4 H, m, $C_2$-$H_2$, $C_5$-$H_2$); MS, *m/z* 176 ($M^+$). Further elution gave **27** (8.0 mg, 8%) as a colorless oil: IR ($CHCl_3$) 3510 $cm^{-1}$; NMR δ 7.85 (1 H, s, OOH), 7.55–7.20 (5 H, m, ArH × 5), 6.20 (1 H, m, $C_2$-H), 5.42–5.18 (1 H, m, $C_1$-H), and 3.10–1.70 (4 H, m, $C_4$-$H_2$, $C_5$-$H_2$); MS, *m/z* 176 ($M^+$).

(b) Triflic anhydride (338 mg, 1.20 mmol) in $CH_2Cl_2$ (1.0 mL) was added to a stirred solution of the diol **35** (89 mg, 0.5 mmol) and pyridine (95 mg, 1.20 mmol) in $CH_2Cl_2$ (5.0 mL) at 0 °C. After 30 min, the mixture was washed with water, dried ($Na_2SO_4$), and evaporated to give **(1*S**,2*S**,4*S**)-1-phenyl-2,4-bis[[(trifluoromethyl)sulfonyl]oxy]cyclopentane (36)** as an unstable material, which was used in the next step without purification: NMR δ 7.33 (5 H, br s, ArH × 5), 5.80–5.24 (2 H, m, $C_2$-H, $C_4$-H), 3.50–3.20 (1 H, m, $C_1$-H), 2.90–2.50 (4 H, m, $C_3$-$H_2$, $C_5$-$H_2$). A solution of **36** in $CH_2Cl_2$ (1.0 mL) was added to a solution of $(n\text{-}Bu_3SnO)_2$, prepared from $n$-$Bu_3SnOMe$ (321 mg, 1 mmol) and anhydrous $H_2O_2$ (1.83 M in ether, 0.6 mL) at 0 °C. After the mixture was stirred for 1 h at 0 °C, the solvent was evaporated and the residue was chromatographed with hexane/AcOEt (90/10) at 0 °C, yielding **8** (5 mg, 6%): NMR δ 7.55–7.15 (5 H, m, ArH × 5), 4.85 and 4.66 (each 1 H, each br s, $C_1$-H, $C_4$-H), 3.55–3.30 (1 H, m, $C_5$-H), 2.55–1.80 (4 H, m, $C_6$-$H_2$, $C_7$-$H_2$); MS, *m/z* 176 ($M^+$), which was identical with the sample described above.

**(1*S**,3*R**)-1-Phenylcyclopentane-1,3-diol (28).** (a) PhLi (2.0 M in ether–cyclohexane, 10 mL) was added dropwise to a stirred solution of the enone **10** (980 mg, 10 mmol) in THF (30 mL) at −78 °C, and the mixture was stirred at this temperature for 0.5 h. The mixture was poured on ice, acidified with AcOH, and extracted with $CH_2Cl_2$. The organic layer was washed with aqueous $NaHCO_3$, dried ($Na_2SO_4$), and evaporated. The residue was recrystallized from $CH_2Cl_2$/hexane to give **1-phenylcyclopent-2-ene-1,4-diol** (1.05 g, 60%): mp 94–95 °C; IR ($CHCl_3$) 3560 $cm^{-1}$; NMR δ 7.32 (5 H, br s, ArH × 5), 6.03 (2 H, s, vinyl H × 2), 4.86–4.64 (1 H, m, $C_4$-H), 3.75 and 3.52 (each 1 H, each br s, OH × 2), 2.62 (1 H, dd, *J* = 6, 15 Hz, $C_5$-H), 2.12 (1 H, dd, *J* = 3, 15 Hz, $C_5$-H). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.84; H, 6.96. A mixture of the diol described above (352 mg, 2 mmol) and $PtO_2$ (23 mg) in AcOEt (20 mL) was stirred under $H_2$ atmosphere (1 atm) at room temperature for 0.5 h. The catalyst was removed by filtration through a pad of Celite and the filtrate was evaporated. The residue was recrystallized from ether/hexane to give **28** (306 mg, 86%): mp 71–72 °C; IR ($CHCl_3$) 3570 and 3390 $cm^{-1}$; NMR δ 7.55–7.25 (5 H, m, ArH × 5), 4.66–4.32 (1 H, m, $C_3$-H), 3.00 (2 H, br s, OH × 2), 2.45–1.95 (6 H, m, $CH_2$ × 3); MS, *m/z* 178 ($M^+$). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.03; H, 7.98.

(b) A mixture of the endoperoxides **8** and **25** (38 mg, 0.216 mmol) was added to a stirred mixture of EtOH (1.0 mL), phosphate buffer (pH 7.0, 1.0 mL), and $SnCl_2$ (60 mg, 0.316 mmol) at 5 °C. After 1 h, the mixture was extracted with ether, and the organic layer was dried ($Na_2SO_4$) and evaporated. The residue was chromatographed with $CH_2Cl_2$/MeOH (96/4) to yield **28** (13 mg, 34%), which was identical with authentic material prepared in (a). Further elution gave diol **21** (1.0 mg, 3%), which was identical with authentic material described above.

**1-Hydroxy-3-phenylcyclopent-3-ene (29).** $NaBH_4$ (1.0 mg, 0.026 mmol) was added to a stirred solution of the hydroperoxide **26** (10 mg, 0.057 mmol) in MeOH (1.0 mL) at 0 °C. After 5 min, $CH_2Cl_2$ was added and the mixture was washed with water. The organic layer was dried ($Na_2SO_4$), evaporated, and chromatographed with hexane/AcOEt (50/50) to yield **29** (6 mg, 66%): mp 80–81 °C (lit.[33] mp 80–82 °C); IR ($CHCl_3$) 3570 $cm^{-1}$; NMR δ 7.55–7.20 (5 H, m, ArH × 5), 6.10 (1 H, br s, $C_4$-H), 4.80–4.50 (1 H, m, $C_1$-H), 3.20–2.30 (4 H, m, $C_2$-$H_2$, $C_5$-$H_2$); MS, *m/z* 160 ($M^+$).

**1-Hydroxy-3-phenylcyclopent-2-ene (30).** (a) The hydroperoxide **27** (8 mg, 0.046 mmol) was treated with $NaBH_4$ as above to give **30** (5 mg, 69%): mp 98–99 °C; IR ($CHCl_3$) 3560 $cm^{-1}$; NMR δ 7.55–7.20 (5 H, m, ArH × 5), 6.15 (1 H, br s, $C_2$-H), 4.94 (1 H, br s, $C_1$-H), and 3.10–1.65 (4 H, m, $C_4$-$H_2$, $C_5$-$H_2$); MS, *m/z* 160 ($M^+$).

(b) $NaBH_4$ (14 mg, 0.38 mmol) was added to a solution of the enone **31**[34] (60 mg, 0.38 mmol) in MeOH (1.0 mL) at 0 °C. After 10 min of stirring, the mixture was extracted with $CH_2Cl_2$, washed with water, dried ($Na_2SO_4$), and evaporated. Chromatography of the residue with hexane/AcOEt (50/50) afforded **30** (54 mg, 89%), which was identical with the sample described in (a).

**(1*R**,3*R**,4*S**)-1,3-Bis[(methylsulfonyl)oxy]-4-phenylcyclopentane (32).** $Et_3N$ (1.149 g, 11.38 mmol) and MsCl (1.303 g, 11.38 mmol) were added to a solution of the diol **21** (844 mg, 4.74 mmol) in $CH_2Cl_2$ (8 mL) at 0 °C, and the mixture was stirred for 1 h. The mixture was washed with water, dried ($Na_2SO_4$), and evaporated. The residue was recrystallized from AcOEt/hexane to yield **32** (1.377 g, 87%): mp 106–107 °C; IR ($CHCl_3$) 1360, 1330, and 1180 $cm^{-1}$; NMR δ 7.30 (5 H, br s, ArH × 5), 5.40–5.20 (1 H, m, $C_1$-H), 5.10–4.86 (1 H, m, $C_3$-H), 3.80–3.55 (1 H, m, $C_4$-H), 3.04 and 3.68 (each 3 H, each s, SMe × 2), and 3.00–2.00 (4 H, m, $C_2$-$H_2$, $C_5$-$H_2$); MS, *m/z* 238 ($M^+$ − $MeSO_3H$). Anal. Calcd for $C_{13}H_{18}O_6S_2$: C, 46.69; H, 5.43; S, 19.18. Found: C, 46.31; H, 5.29; S, 18.92.

**(1*R**,3*R**,4*S**)-1,3-Diacetoxy-4-phenylcyclopentane (33).** A mixture of the diol **21** (60 mg, 0.337 mmol), $Ac_2O$ (1.0 mL), and pyridine (1.0 mL) was allowed to stand at room temperature for 15 h and evaporated. Chromatography of the residue with hexane/AcOEt (80/20) gave **33** (85 mg, 96%): mp 52–53 °C (ether/hexane); IR ($CHCl_3$) 1725 $cm^{-1}$; NMR δ 7.26 (5 H, br s, ArH × 5), 5.35–4.95 (2 H, m, $C_1$-H, $C_3$-H), 3.46 (1 H, dt, *J* = 7, 9 Hz, $C_4$-H), 2.90–1.60 (4 H, m, $C_2$-$H_2$, $C_5$-$H_2$), and 2.08 and 1.98 (each 3 H, each s, Ac × 2); MS, *m/z* 203 ($M^+$ − OAc). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.66; H, 6.84.

**(1*S**,3*S**,4*S**)-1,3-Diacetoxy-4-phenylcyclopentane (34).** A mixture of the bismesylate **32** (1.50 g, 4.49 mmol), CsOAc (5.12 g, 26.95 mmol), 18-crown-6 (0.59 g, 2.25 mmol), and toluene (45 mL) was refluxed for 8 h. The mixture was diluted with hexane, washed with water, and dried ($Na_2SO_4$). Evaporation and chromatography with hexane/AcOEt (80/20) afforded **34** (759 mg, 65%) as an oil: IR (film) 1730 $cm^{-1}$; NMR δ 7.30 (5 H, br s, ArH × 5), 5.42–5.10 (2 H, m, $C_1$-H, $C_3$-H), 3.36–3.04 (1 H, m, $C_4$-H), 2.75–1.95 (4 H, m, $C_2$-$H_2$, $C_5$-$H_2$), 2.06 and 1.80 (each 3 H, each s, Ac × 2); MS, *m/z* 262 ($M^+$).

**(1*S**,3*S**,4*S**)-4-Phenylcyclopentane-1,3-diol (35).** A mixture of the diacetate **34** (759 mg, 2.89 mmol), NaOMe (375 mg, 6.95 mmol), and MeOH (15 mL) was stirred at room temperature for 1 h. $CH_2Cl_2$ and aqueous $NH_4Cl$ were added to the mixture and the organic layer was dried ($Na_2SO_4$) and evaporated. The residue was recrystallized from AcOEt, yielding **35** (418 mg, 81%): mp 124–125 °C; IR ($CHCl_3$) 3560 $cm^{-1}$; NMR δ 7.32 (5 H, br s, ArH × 5), 4.52–4.18 (2 H, m, $C_1$-H, $C_3$-H), 3.30–3.00 (1 H, m, $C_4$-H), 2.70–1.85 (4 H, m, $C_2$-$H_2$, $C_5$-$H_2$), 2.05 and 1.75 (each

1 H, each br s, OH × 2); MS, $m/z$ 178 ($M^+$). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.80; H, 7.85.

**X-ray Results.** Crystal data of compound **33**: $C_{15}H_{18}O_4$, MW = 262.3, monoclinic, space group $P2_1/c$, $a$ = 10.924 (7) Å, $b$ = 8.125 (5) Å, $c$ = 17.187 (9) Å, $\beta$ = 112.82 (5)°, $V$ = 1406 (1) Å$^3$, $Z$ = 4, $D_c$ = 1.239 g cm$^{-3}$. The structure was solved by direct methods and refined by a block-diagonal least-squares technique to $R$ = 0.048 for 2076 reflections, excluding the hydrogen atoms of one of the methyl groups.

**Supplementary Material Available:** Perspective view, tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for compound **33** (5 pages). Ordering information is given on any current masthead page.

# Notes

## Regiochemistry of Formation, Stereochemistry, and Interconversion of α-*tert*-Butyl(4- or 5-nitro-*N*-methyl-2-pyrrolyl)methyl Sulfones and Sulfinates[1]

Trevor W. Hambley,[†] Michael C. Harsányi,[‡] and Robert K. Norris*[,‡]

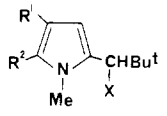
*Departments of Organic Chemistry and Inorganic Chemistry, The University of Sydney, 2006, N.S.W., Australia*

*Received December 7, 1987*

In a recent paper we reported that the chlorides **1** and **2** reacted with nucleophiles or with methanol to give substitution products by an $S_N1$ process.[2] When we treated the above chlorides with sodium *p*-toluenesulfinate (**3**), complex reaction products resulted, and it appeared that simple substitution reactions were not taking place. We now report the results of the reaction of **1** and **2** with the salt **3**.

### Results and Discussion

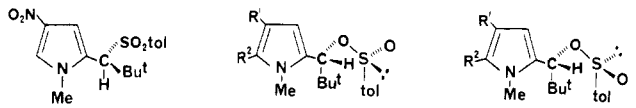
**Reaction of the Chlorides 1 and 2 with Sodium *p*-Toluenesulfinate (3).** Treatment of the chloride **1** with the salt **3** in DMF at 60 °C for 15 min gave a mixture of four compounds, as judged from the *N*-methyl and *tert*-butyl resonances in the $^1$H NMR spectrum of the crude reaction mixture, in ca. 92% yield [estimated by reference to added TNT (2,4,6-trinitrotoluene)]. On the basis of



| | $R^1$ | $R^2$ | X |
|---|---|---|---|
| 1 | $NO_2$ | H | Cl |
| 2 | H | $NO_2$ | Cl |
| 4 | $NO_2$ | H | OH |
| 5 | $NO_2$ | H | *p*-$MeC_6H_4SO_2$ |
| 7 | $NO_2$ | H | *p*-$MeC_6H_4S$ |
| 8 | H | $NO_2$ | *p*-$MeC_6H_4SO_2$ |
| 10 | H | $NO_2$ | OH |
| 11 | H | $NO_2$ | OCHO |

spectroscopic and chemical evidence presented below these products were assigned as the alcohol **4** (6%), the sulfone **5** (28%), and the two diastereomeric sulfinic esters **6a** (36%) and **6b** (22%). Duplicate reactions varied slightly

Na$^+$ *p*-$MeC_6H_4SO_2^-$
**3**



**5a**

| | $R^1$ | $R^2$ |
|---|---|---|
| **6a** | $NO_2$ | H |
| **9a** | H | $NO_2$ |

| | $R^1$ | $R^2$ |
|---|---|---|
| **6b** | $NO_2$ | H |
| **9b** | H | $NO_2$ |

in the relative proportion of these products (±4%). The benzylic and aromatic region of the $^1$H NMR spectrum obtained from a typical mixture resulting from this reaction is given in Figure 1a. The reaction products on standing for ca. 17 h in $CDCl_3$ at room temperature changed into a simple mixture of the alcohol **4** (20%) and the sulfone **5** (71%). The sulfone **5** could be isolated readily from any reaction mixture resulting from treatment of **1** with **3** so long as the mixture was left for 15–20 h before recrystallization. Sulfone **5** had the required elemental composition and was unambiguously prepared from the sulfide **7** (previously isolated from the reaction of chloride **1** with *p*-toluenethiolate ion)[2] by oxidation with *m*-chloroperbenzoic acid in dichloromethane. The $^1$H NMR spectrum of **5** is given in Figure 1b. In previous studies in our laboratories, it has been found that sulfones of the type Ar′CH-*t*-$BuSO_2$Ar exhibit dynamic $^1$H NMR phenomena around the Ar′–CH bond.[3-5] This sulfone did not exhibit DNMR effects, and it appeared reasonable that it was "locked" into the less hindered conformation **5a**, in which the *N*-methyl group was remote from the bulky substituents on the benzylic carbon. This conclusion was confirmed by NOE experiments. Irradiation of the benzylic proton (H1) gave significant enhancement of the signals from the *N*-methyl group (9.7%), the *tert*-butyl group (10.6%), and also the signal from the two protons on the benzene ring ortho to the $SO_2$ group (6.1%). Irradiation of the *N*-Me group gave a 3.7% enhancement of H1, a 3.3% of H5′ and a 0.8% enhancement of the signal for the two ring protons ortho to the sulfonyl group respectively. Irradiation of the *tert*-butyl group enhancement of the signal for H1 (2.2%) and H3′ (2.3%). The significant interactions of H1 and the *N*-Me group with

[†] Department of Inorganic Chemistry.
[‡] Department of Organic Chemistry.

(1) This research was supported by a grant from the Australian Research Grants Scheme (to R.K.N.) and has been abstracted from the Ph.D. Thesis of Michael C. Harsányi, The University of Sydney, November, 1987.

(2) Harsányi, M. C.; Norris, R. K. *Aust J. Chem.* **1987**, *40*, 2063–2083.
(3) Norris, R. K.; Randles, D. *Aust. J. Chem.* **1979**, *32*, 1487–1509.
(4) Barker, S. D.; Norris, R. K. *Aust. J. Chem.* **1983**, *36*, 81–95.
(5) Field, L. D.; Hambley, T. W.; Jacobs, B. D.; Wilson, K.; Norris, R. K. *Aust. J. Chem.*, in press.

0022-3263/88/1953-3104$01.50/0 