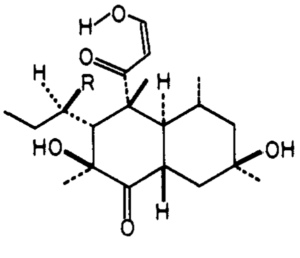
(3 H, d, $J = 6.8$ Hz), three quaternary CH_3 at δ 1.26, 1.40, 1.57 (each 3 H, s), $O{=}CCH_2CH_2OH$ group at δ 2.82 (1 H, dt, $J = 18$ Hz, 4 Hz), 3.11 (1 H, dq, $J = 18$ Hz, 3 Hz), 3.76–3.85 (1 H, m), 3.87–3.97 (1 H, m). Treatment of **2** with Ac_2O in pyridine gave monoacetate **3**, $C_{23}H_{38}O_6$[3] mp 103.5–108.0 °C, IR ν_{max} (KBr) 3530, 1750, 1710 cm^{-1}. The similarity of the spectral data of betaenone B (**2**) with those of betaenone A (**1**) suggests that structurally **2** is closely related with **1**. The structure **2** for betaenone B was deduced from extensive decoupling measurements in ^1H NMR spectra of the derivatives of **2** and verified by conversion of **2** to **1** as follows. Oxidation of **2** with pyridinium chlorochromate afforded an oily aldehyde, **4** [MS, m/z 366 (M^+); IR ν_{max} (neat) 1700 cm^{-1}; ^1H NMR (400 MHz) 5.98 (1 H, d, $J = 4.9$ Hz), 7.74 (1 H, d, $J = 4.9$ Hz), 15.13 (1 H, br, s)], which was treated with KOH–MeOH to afford a crystalline compound [mp 150–154 °C; $[\alpha]_D$ +64.8° (c 0.56, $CHCl_3$)] whose spectral data and behavior on TLC are identical with those of betaenone A (**1**). Very recently stemphyloxin (**5**), which is closely related to the aldehyde **4**, was isolated from leaf spot disease fungus (*Stemphylium botryosum*) of tomato.[8]



4 R = CH_3

5 R = CH_2OH

The absolute configuration of betaenone B (**2**) was determined by ORD and CD measurements. Since the B ring of betaenone B (**2**) has a chair conformation from the coupling constants[9] of signals due to C-5, C-9, and C-10 protons in the ^1H NMR spectrum and since under high dilution conditions (0.44×10^{-4} M in CCl_4) the IR spectrum showed an absorption band at 3480 cm^{-1} due to an intramolecular hydrogen bond, twisted cyclohexane conformation was indicated for the A ring of **2**. From a molecular model, it is understandable that steric effects arising from two axially oriented substituents at C-3 ($CH_3CH_2C(CH_3)H$–) and C-4 (CH_3) would be considerably lessened in such a twisted conformation. Such a conformation of **2** is expected to have a positive octant effect. In fact, ORD and CD measurements exhibited a positive octant effect and a positive curve, respectively, so the absolute configuration of betaenone B should be as depicted in **2**, and betaenone A is thus **1**. Substitutional patterns of **1** and **2** indicate that biogenetically these compounds are derived via the polyketide pathway. Physiological activities of and biogenetic pathway to betaenones and other metabolites[10] from the same fungus will be investigated.

Acknowledgment. We are grateful to Dr. S. Naito, Hokkaido National Agricultural Experimental Station, Sapporo, for a generous gift of the strain *Phoma betae* Fr. PS-13.

Registry No. 1, 85269-22-3; **2**, 85269-23-4; **3**, 85269-24-5; **4**, 85269-25-6.

Supplementary Material Available: Listings of atomic coordinates and bond distances of betaenone A (1 page). Ordering information is given on any current masthead page.

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[8] Strobel, G. A. 7th World Congress on Animal, Plant and Microbial Toxins, Brisbane, July 1982. Barash, I.; Pupkin, G.; Netzer, D.; Kashman, Y. *Plant Physiol.* **1982**, *69*, 23.

[9] ^1H NMR (400 MHz) δ 2.31 (1 H, dt, $J = 14$ Hz, 3 Hz, eq 9-H), 2.49 (1 H, dd, $J = 14$ Hz, 11 Hz, 5-H), 2.66 (1 H, ddd, $J = 14$ Hz, 11 Hz, 3 Hz, 10-H).

[10] Several phytotoxins related to aphidicolins were recently isolated: Ichihara, A.; Oikawa, H.; Hayashi, K.; Hashimoto, M.; Sakamura, S., to be submitted for publication.

Oxidatively Assisted Hydrolysis of Allylic Iodides to Rearranged Allylic Alcohols. A New Example of [2,3] Sigmatropic Rearrangement

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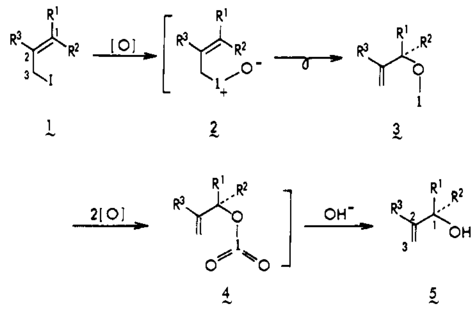
[2,3] sigmatropic rearrangement of allylic amine oxides,[1] sulfoxides,[2] and selenoxides[3] has long received widespread interest because of its theoretical and synthetic importance, but no such rearrangement has been known for allylic halogen oxides. This communication proposes a hitherto unknown rearrangment of allylic iodoso compound **2** to allylic hypoiodite **3**, which occurs when allylic iodides **1** are oxidized with peracid to give rearranged allylic alcohols **5** (eq 1). To our knowledge, this reaction represents the first example of a sigmatropic rearrangement involving allylic halogen oxides. It was developed to furnish a new regiospecific method for preparing **5** from **1** (eq 1).



(1)

Recently, interest has been directed to a facile conversion of a simple alkyl iodide into the corresponding alcohol by oxidation with *m*-chloroperbenzoic acid (*m*-CPBA) followed by hydrolysis.[4] This reaction was applied to convert allylic iodide **6** into allylic alcohol **7** in our previously developed synthetic route to the 1-oxacephem skeleton[5,6] (Scheme I). Contrary to our expectation, allylic alcohol **7** was formed in only moderate yield and accompanied by a large amount of aldehyde **8**.[7] However, substantial improvement was effected by performing the reaction in a two-phase system using excess amounts of a peracid and an inorganic base (Table I).

In addition to such a significant change in the reaction conditions, we observed the following distinct differences in reaction mode between the previously reported procedures[4a,b] and the present one. First, whereas $^1/_3$ equiv of iodine was liberated in the oxidation of saturated alkyl iodides, no iodine but 1 equiv of sodium iodate was formed in the oxidation of allylic iodides. Second, while only 1.33 equiv (2.0 equiv in practice)[4a,b] of peracid

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[1] Thyagarajan, B. S.; Hillard, J. B.; Reddy, K. V. *Tetrahedron Lett.* **1974**, 1999–2002.

[2] (a) Bickart, P.; Carson, F. W.; Jacobus, J.; Miller, E. G.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4869–4876. (b) Tang, R.; Mislow, K. *Ibid.* **1970**, *92*, 2100–2104. (c) Evans, D. A.; Andrews, G. C.; Sims, C. L. *Ibid.* **1971**, *93*, 4956–4957. (d) For a general review, see: Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147–155.

[3] (a) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 7154–7155. (b) For a general review, see: Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22–30.

[4] (a) Reich, H. J.; Peake, S. L. *J. Am. Chem. Soc.* **1978**, *100*, 4888–4889. (b) Macdonald, T. L.; Narasimhan, N.; Burka, L. T. *Ibid.* **1980**, *102*, 7760–7765. (c) Cambie, R. C.; Chambers, D.; Lindsay, B. G.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc., Perkin Trans 1* **1980**, 822–827. (d) Davidson, R. I.; Kropp, P. J. *J. Org. Chem.* **1982**, *47*, 1904–1909.

[5] Nagata, W. *Philos. Trans. R. Soc. London, Ser. B* **1980**, *B289*, 225–230.

[6] Yoshioka, M.; Tsuji, T.; Uyeo, S.; Yamamoto, S.; Aoki, T.; Nishitani, Y.; Mori, S.; Satoh, H.; Hamada, Y.; Ishitobi, H.; Nagata, W. *Tetrahedron Lett.* **1980**, *21*, 351–354.

[7] See supplementary material for this information.

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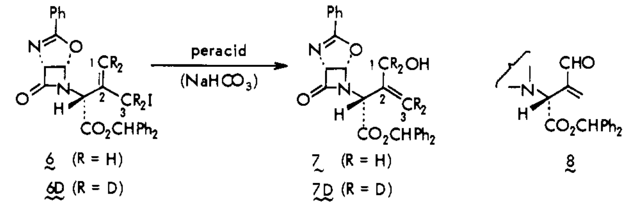
Table I. Peracid Oxidation of Allylic Iodide **6** to Allylic Alcohol **7**

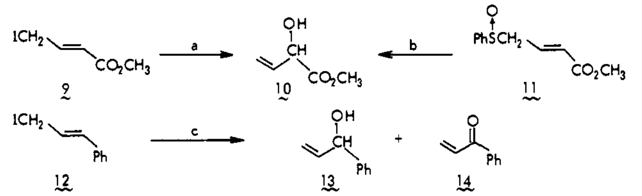
peracid equiv[a]	inorg base (equiv)	solvent	temp, °C	time, h	yield, %
m-CPBA (4.0)	$NaHCO_3$ (2.0)	$EtOAc-H_2O$ (2:1)	rt	2	88[b]
m-CPBA (4.0)	$NaHCO_3$ (2.0)	$CH_2Cl_2-H_2O$ (2:1)	5-10	1	82[b]
$PhCO_3H$ (4.5)	$NaHCO_3$ (2.0)	$EtOAc-H_2O$ (2:1)	rt	3	88[c]
o-$HO_2CC_6H_4CO_3H$ (5.0)	$NaHCO_3$ (2.0)	$EtOAc-H_2O$ (tr)	rt	2.5	84[c]
CH_3CO_3H[d] (6.0)	$NaHCO_3$ (2.0)	$EtOAc-H_2O$ (1:1)	rt	17	93[c]
CH_3CO_3H[d] (6.0)	$NaHCO_3$ (2.0)	$CH_2Cl_2-H_2O$ (1:1)	rt	7	93[c]

[a] Excess amounts of peracid were used to overcome their competing decomposition catalyzed with the base. [b] Isolated yield. [c] Determined by HPLC analysis. [d] Commercially available 40% peracetic acid was used.

Scheme I



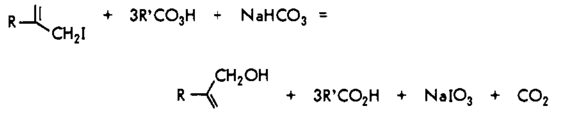
Scheme II



[a] *m*-CPBA, EtOAc or CH_2Cl_2/aqueous Na_2CO_3, 5-20 °C, 1 h. [b] Ph_3P, $CH_3OH-C_6H_6$, reflux, 7 h. [c] *m*-CPBA, $CHCl_3$, $HO(CH_2)_2OH$/aqueous Na_2CO_3, −13 to −17 °C.

are necessary for the saturated system, at least 3 equiv (4–6 equiv in practice) of peracid are necessary for the allylic system.[8] Moreover, evidence against carbonium ion intermediacy postulated for the oxidation of alkyl iodides,[4] but support for possible incorporation of an allylic rearrangement in the present oxidation was obtained by a rigorously performed deuterium-scrambling experiment.[7] Thus, while the double bond at C_1-C_2 in **6D**[7] was shifted to C_2-C_3 in **7D**, the deuterium contents[7] of 15–17% and 25–27%, respectively, at C_1 and C_3 were retained throughout the reaction. Direct evidence for this view was obtained from the following examples, which demonstrate also the general applicability of the present reaction. Oxidation of methyl *trans*-γ-iodocrotonate (**9**)[9] afforded the rearranged, deconjugated allylic alcohol **10**[10] in 65–67% yield[11,12] (Scheme II). Remarkably, no isomeric methyl γ-hydroxycrotonate was detected in the products. Cinnamyl iodide (**12**)[13] was also oxidized, at a lower temperature of -13 to -17 °C, to give 63%[11] of phenylvinylcarbinol (**13**)[14] and 10%[11] of phenyl vinyl ketone (**14**).[15] Again, no cinnamyl alcohol was formed in this reaction.

On the basis of these findings, we propose the following tentative reaction pathway (eq 1) and stoichiometry (eq 2) for the present



(2)

reaction. In this pathway, initially formed unstable iodoso compound **2** is assumed to rearrange to hypoiodite **3** in a [2,3] sigmatropic manner by analogy with the structurally related selenoxide.[3a] Intermediate **3** undergoes further oxidation to give iodate **4**, which is finally hydrolyzed to allylic alcohol **5** and iodate anion.

Finally, the efficiency of the present reaction was compared with the well-known Mislow[2a,b]–Evans[2c,d] reaction. Methyl γ-phenylthiocrotonate *S*-oxide (**11**)[7] was heated with triphenylphosphine in methanol and benzene. In both reactions, the rearranged alcohol **10** was formed in comparable yields, but the Mislow–Evans reaction required the very drastic condition of 7-h refluxing in contrast with the 1-h standing at 5–20 °C in our process.

Acknowledgment. We sincerely appreciate the discussions of the NMR studies by the late Dr. K. Tori and J. Nishikawa and the mass spectrum analyses done by Dr. Y. Nakagawa and H. Iwatani.

Registry No. **6**, 67977-89-3; **7**, 67977-88-2; **9**, 65495-78-5; **10**, 5837-73-0; **12**, 59625-54-6; **13**, 4393-06-0.

Supplementary Material Available: Spectral and combustion data for **8** and **11**, deuterium distribution data for **6D** and **7D**, and data for preparation of **6D** and **11** (2 pages). Ordering information is given on any current masthead page.

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[8] More recently Davidson and Kropp[4d] observed that the number of molar equivalents of oxidant for complete oxidation depends on the substrate system.

[9] Gershon, H.; Shanks, L.; Gawiak, D. E. *J. Med. Chem.* **1976**, *19*, 1069–1072.

[10] Palm, R.; Ohse, H.; Cherdron, H. *Ang. Chem., Int. Ed. Engl.* **1966**, *5*, 994–1000.

[11] As determined by GC analysis.

[12] In a typical procedure, aqueous Na_2CO_3 (4.68 g, 44.2 mmol, in 100 mL of H_2O) was added to a stirred solution of **9** (10.0 g, 44.2 mmol) in CH_2Cl_2 (200 mL). To this mixture was added *m*-CPBA (35.9 g, 0.177 mol) portionwise at 5 °C under stirring and nitrogen stream (slightly exothermic reaction). The reaction mixture was further stirred vigorously at room temperature for 1 h. $NaIO_3$ (8.7 g, 99%) was removed by filtration. After the usual workup, the product containing 67% (GC) of **10** was distilled at 58–66 °C (12–13 mmHg) to give 2.59 g (51%) of pure **10**.

[13] Kaiser, C.; Burger, A.; Zirngibl, L.; Davis, C. S.; Zirkle, C. L. *J. Org. Chem.* **1962**, *27*, 768–773.

[14] Duveen, D. I.; Kenyon, J. *J. Chem. Soc.* **1939**, 1697–1701.

[15] Franzen, V. *Ann. Chem.* **1957**, *602*, 199–208.

Pentadienyl Dithiocarbamate as a 1,5-Dianion Equivalent. Versatile Reagent for Polyene Synthesis[1]

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Although thioallylic anions have become recognized as an increasingly important tool in synthetic aliphatic chemistry,[2] thiopentadienyl anions are as yet much less explored for organic

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[1] Presented in part at the 45th Annual Meeting of the Chemical Society of Japan, Apr 1982, Tokyo, and at the 4th International Congress on Organic Synthesis, IUPAC, Aug 1982, Tokyo, Japan.

[2] Biellman, J. F.; Ducey, J. B. *Org. React.* **1982**, *27*, 1.

0002-7863/83/1505-2909$01.50/0