the value of $[\alpha]_A$ or that of $[\alpha]_E$ or both are different in acetone from the corresponding values in methanol and in methylene chloride, i.e., that there is a substantial intrinsic solvent effect as well as a conformational effect on rotation.

Experimental Section

3-Thianone[4] was enantioselectively oxidized to the corresponding *S*-oxide by Sharpless' reagent.[6] The resulting 3-thianone *S*-oxide, 61% ee (chiral shift reagent) was reduced with sodium borohydride[4] to a mixture of *cis*- and *trans*-3-hydroxythiane *S*-oxide from which the first-eluting cis isomer was obtained by flash chromatography ($CHCl_3$/MeOH, 14:1).

The mole fractions (x_A, x_E) of conformers A and E (Scheme I) in CD_2Cl_2 and CD_3COCD_3 were obtained from the concentration-dependent vicinal H–O–C–H coupling constants (J_{obs}) by using the equation $J_{obs} = J_A x_A + J_E x_E$, where $x_E + x_A = 1$. J_A and J_E were taken from proton NMR spectra of 1 in CD_2Cl_2 and in CD_3COCD_3 at −80 °C at concentrations where both A and E conformers were readily seen: $J_A = 9.7$ Hz, $J_E = 4.8$ Hz in CD_2Cl_2; $J_A = 9.2$ Hz, $J_E = 4.2$ Hz in CD_3COCD_3. (That $x_E = 1.0$ at all concentrations in methanol was concluded from the invariance of the coupling constants of the carbinol hydrogen, H(3), which is a near-triplet of triplets with coupling constants of 10.4, 10.0, 3.9, and 3.9 Hz.) $[\alpha]^{25}{}_D$ was measured at various concentrations; for the plot in Figure 3, the corresponding x_E was obtained from the linear regression of the plot of x_E vs log *c* (Figure 2), $r = 0.999$.

Acknowledgment. This work was supported by NSF Grant CHE-8703060. E.B. is grateful for a NATO fellowship.

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(6) Pitchen, P.; Duñach, E.; Deshmukh, M. N.; Kagan, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 8188.

Reversed Regiochemistry in the Hydroboration of Vinylarenes Catalyzed by Neutral Rhodium Complexes and the Related Asymmetric Version†

Jinfang Zhang, Boliang Lou, Guangzhong Guo, and Lixin Dai*

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

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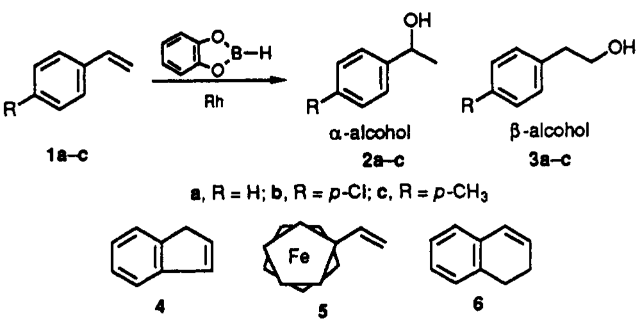
Introduction

Since its discovery in 1956, the unique olefin hydroboration reaction has became one of the most widely used synthetic reactions.[1] Through the efforts of Brown and co-workers, and many others, the versatility of hydroboration has been repeatedly demonstrated. Thus, many new types of reagents have been introduced, including some which have shown enantioselectivities as high as 100% with certain olefins.[2] When Noth and Mannig[3] reported a catalyzed hydroboration for the first time, a new facet of hydroboration was revealed. The recent reports of Burgess,[4] Hayashi,[5] and Suzuki[6] prompted us to disclose our own results on the catalyzed hydroboration of vinylarenes.[7]

Results and Discussion

In the catalyzed hydroboration of styrenes, Hayashi[5] obtained a very high enantioselectivity with reversed regiochemistry. He claimed that high Markovnikov selectivity was only observed with cationic rhodium complexes and in the presence of tertiary phosphine ligands, whereas Wilkinson's catalyst or $[Rh(COD)_2]BF_4$ without phosphine ligands afforded the anti-Markovnikov products.

Scheme I



Surprisingly, in the present study, in contrast to the results of Hayashi, the α-alcohol was obtained as the major product of the catalyzed hydroboration of styrene with catecholborane (CB) in the presence of Wilkinson's catalyst. The results of catalyzed hydroboration in the presence of Wilkinson's catalyst compared to those of uncatalyzed hydroboration are summarized in Table I.

Substrates 1–6 were all vinylarenes. The catalyzed hydroboration of all these substrates followed a Markovnikov pathway leading to the α-alcohol almost exclusively. This was opposite to that of uncatalyzed hydroboration. In the uncatalyzed reactions, substrates 1–5 showed a high propensity to form β-alcohols. 1,2-Dihydronaphthalene (6) was the only substrate which afforded an α-alcohol as the major product, in the α:β ratio of 90:10. In this case, the catalyzed reaction enhanced the regioselectivity to 98:2 (entry 7). The reversed regiochemistry of all the substrates could further be reinforced by the addition of 4 mol % of a Lewis acid, such as $SnCl_2$, $Ti(OR)_4$, $ZnCl_2$, or BF_3. For example, with styrene, the α:β ratio changed from 90:10 to 98:2, with yields over 90%.

Another neutral rhodium catalyst, $[RhCl(COD)]_2$, was also examined. Without the presence of tertiary phosphine, or in the presence of Lewis acids, the major product was still the β-alcohol. For example, in the presence of $SnCl_2$ the α:β ratio was 33:67. However upon the addition of 2 mol % of triphenylphosphine, the ratio changed to 59:41. With 4 mol % of phosphine, the regiochemistry reversed completely to an α:β ratio of 98:2.

Next, $[RhCl(COD)]_2$, with DIOP or BINAP as chiral

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† Dedicated to Prof. Wang Yu on the occasion of his 80th birthday.

(1) (a) Brewster, J. H. *Aldrichimica Acta* **1987**, *20*(1), 3. (b) Matteson, D. S. *Synthesis* **1986**, 973. (c) Pelter, A.; Smith, K.; Brown, H. C. *Boron Reagents*; Academic: London, 1989.

(2) (a) Madal, A. K.; Jadhav, P. K.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 3543. (b) Brown, H. C.; Jadhav, P. K. *J. Org. Chem.* **1981**, *46*, 5047. (c) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1977**, *99*, 5514. (d) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *J. Org. Chem.* **1982**, *47*, 5047. (e) Masamune, S.; Kim, B. M.; Peterson, J. S.; Sato, T.; Veenstra, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 4549.

(3) Mannig, D.; Noth. H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878.

(4) (a) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5179. (b) Burgess, K.; Ohlmeyer, M. J. *Tetrahedron Lett.* **1989**, *30*, 5857. (c) Burgess, K.; Ohlmeyer, M. J. *Tetrahedron Lett.* **1989**, *30*, 5861.

(5) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426.

(6) Sato, M.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1990**, *31*, 231.

(7) After submission of this manuscript, a report of mechanistic study of the Rh-catalyzed hydroboration of alkenes appeared (Evans, D. A.; Fu, G. C. *J. Org. Chem.* **1990**, *55*, 2280). It reported that the Rh-catalyzed hydroboration of styrene also gave the α-alcohol as the main product.

(8) Brown, H. C.; Nelson, D. J.; Scouten, C. G. *J. Org. Chem.* **1983**, *48*, 641.

(9) Vishnakarma, L. C.; Fry, A. *J. Org. Chem.* **1980**, *45*, 5306.

(10) Marshall, P. A.; Prager, R. H. *Austr. J. Chem.* **1979**, *32*, 1251.

(11) Losterzo, C.; Ortaggi, G. *J. Organomet. Chem.* **1982**, *234*, C28.

(12) Boaz, N. W. *Tetrahedron Lett.* **1989**, *30*, 2061.

(13) Seebach, D.; Daum, H. *Chem. Ber.* **1974**, *107*, 1748.

0022-3263/91/1956-1670$02.50/0

Table I. Hydroboration of Vinylarenes with Catecholborane Catalyzed by Wilkinson's Catalyst Compared to Uncatalyzed Hydroboration[a]

		catalyzed		uncatalyzed		
entry	substrate[b]	yield,[d] %	product ratio,[c] $\alpha:\beta$	reagent[e]	yield,[d] %	product ratio,[c] $\alpha:\beta$
1	**1a**[f]	87	86:14	CB		8:92[1c]
2	**1a**[g]	88	94:6	$BH_3 \cdot THF$		19:81[1c]
3	**1b**	93	99:1	BH3·Me_2S	92	22:78
4	**1c**	88	97:3	$BH_3 \cdot Me_2S$	92.5	3:97
5	**4**	91.5	99:1	$BH_3 \cdot Me_2S$	85	16:84
6	**5**	86	95:5	$BH_3 \cdot Me_2S$	100	10:90
7	**6**	98	98:2	$BH_3 \cdot THF$	90	90:10[11]

[a] The reaction was performed in THF solution, at room temperature. The catalyst was $RhCl(PPh_3)_3$. [b] Mole ratio substrate:CB:catalyst = 1.0:2.0:0.02. [c] The product ratio was determined by capillary GLC (0.2 mm × 50 m SE-54, 150–230 °C) and was verified by ^1H NMR (60 MHz). For entry 6, the ratio was determined only by ^1H NMR. [d] Isolated yield. [e] All results with $BH_3 \cdot Me_2S$ were obtained in the present study. Product ratios reported in the literature were as follows: for entry 3, with $BH_3 \cdot THF$, 27:73;[8] for entry 4, with 9-BBN, 2.6:97.4;[9] for entry 5, with $BH_3 \cdot THF$, 14:86; with $TxBH_2$, 1:99[10] for entry 6, with $BH_3 \cdot THF$, 3:97.[11] [f] The reaction temperature was 30 °C. [g] The reaction temperature was 5 °C. All other reactions, except for entry 1, were performed at 10 °C.

Table II. Asymmetric Hydroboration of Vinylarenes with Catecholborane Catalyzed by $[RhCl(COD)]_2$[a]

entry	substrates	conditions	yield,[b] %	% ee[c] (configuration)	$[\alpha]_D$ (solvent)[d] of products
1	**1a**	(2*R*)-(−)-DIOP, $SnCl_2$, −78 °c, 1 day	84.5	48 (*R*)	+25° (CH_2Cl_2)
2	**1a**	(2*S*)-(−)-BINAP, $AlCl_3$, −40 °C, 4 days	85	94 (*S*)	−49.1° (CH_2Cl_2)
3	**1a**	(2*S*)-(−)-BINAP, −78 °C, 4 days	63	92 (*S*)	−48.5° (CH_2Cl_2)
4	**1b**	(2*S*)-(−)-BINAP, −78 °C, 3 days	95	91 (*S*)	−45.6° (Et_2O)
5	**1c**	(2*S*)-(−)-BINAP, −78 °c, 3 days	95	96 (*S*)	−52.5° ($CHCl_3$)
6	**4**	(2*S*)-(−)-BINAP, −40 °C, 1 week	20.4	19	
7	**5**	(2*S*)-(−)-BINAP, −78 °c, 4 days	79	18.4 (*R*)	−5.9° (benzene)

[a] The reactions were performed in DME, with 2 mol % of catalyst present. [b] Isolated yield. [c] The ee value and absolute configuration were determined by comparison with optical rotations reported in the literature and were verified by the ^1H NMR spectra of the acetylated products in the presence of chiral $Eu(hfc)_3$ shift reagent. For entry 6, the determination was made by ^1H NMR. [d] Literature values for the optical rotations of optically pure products were as follows: (*S*)-(−)-**2a**, $[\alpha]^{23}_D$ −52.5° (CH_2Cl_2);[5] (*R*)-(+)-**2b**, $[\alpha]^{21}_D$ +49.9° (Et_2O);[5] (*R*)-(+)-**2c**, $[\alpha]^{22}_D$ +56.0° (neat);[5] (*R*)-*1*-Indanol (entry 6), $[\alpha]_D$ −34°;[12] (*S*)-1-ferrocenyl-1-ethanol, $[\alpha]_D$ +32°.[13]

phosphine ligands, was employed as a catalyst to determine what kind of asymmetry would be induced. The results are summarized in Table II. The enantioselectivity observed with styrene and substituted styrenes with BINAP as a chiral ligand was high, with enantiomeric excesses (ee) ranging between 91 and 96 (Table II, entries 2–5). The enantioselectivity observed with indene and vinylferrocene were not high. However, the catalyzed asymmetric hydroboration was remarkable for the nonstoichiometric use of chiral ligands.

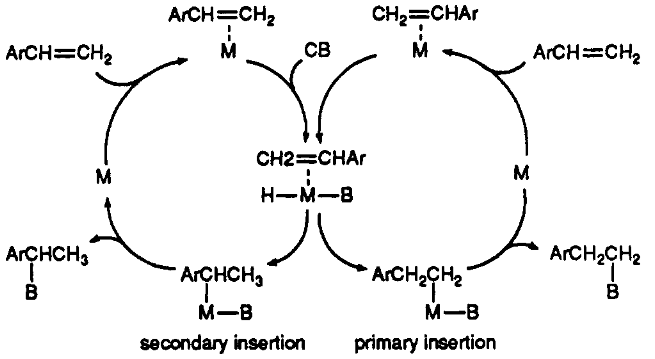
The catalytic process can be described by Scheme II. The formation of a B–M–H species has been described.[3] The insertion of an olefin to M–H bond (or M–B bond) may occur in two different ways: primary insertion and secondary insertion. The bias toward secondary insertion displayed here can also be explained by invoking the presence of η^3-benzylrhodium intermediates.[14]

Experimental Section

^1H NMR spectra were recorded with a Varian EM 360 spectrometer. Tetramethyl silane served as an internal standard. Mass spectra were recorded with a Finnegan 4021 instrument; infrared spectra were recorded with a Shimidzu IR-440 instrument. A Hewlett-Packard 5880A capillary gas chromatograph was used to determine the ratio of α-alcohol to β-alcohol. Optical rotations were measured with a Perkin-Elmer 241 polarimeter.

All reactions were performed under an atmosphere of dry nitrogen and were monitored by thin-layer chromatography (silica GF, Shanghai Institute of Materia Medica). Tetrahydrofuran (THF) and 1,2-dimethylethane (DME) were dried over sodium wire and then were distilled from $LiAlH_4$. $RhCl(PPh_3)_3$, (−)-DIOP, and $BH_3 \cdot Me_2S$ were purchased from Aldrich, (−)-BINAP from Tokyo Kasei. $[RhCl(COD)]_2$ and catecholborane (CB) were prepared by known procedures.

Scheme II



M = unsaturated $RhClL_2$ species
B = $BO_2C_6H_4$

Typical Procedure for Catalyzed Hydroboration. *p*-Chlorostyrene. $RhCl(PPh_3)_3$ (23 mg, 2 mol %) was added to a bottle under N_2 and then THF (1.5 mL) and freshly distilled *p*-chlorostyrene (0.15 mL, 1.25 mmol) were added. The color of the solution was dark red. The mixture was stirred for 10 min, and then CB (0.15 mL) was added drop-by-drop. The color of the mixture became lighter. The mixture was stirred for 4–5 h, or overnight, until reaction was complete. EtOH (95%, 0.5 mL) was then added to destroy excess CB. Then 3 N aqueous NaOH (2 mL) and 30% H_2O_2 (1 mL) were added. After standing for 1 day, the mixture was extracted with ethyl ether. Solvent was evaporated from the extract, and the ratio of α- and β-alcohol was determined by capillary gas chromatography. After purification by thin-layer chromatography (petroleum ether/ethyl ether, 5:2), 0.183 g (93%) of product was obtained.

Typical Procedure for Catalyzed Asymmetric Hydroboration. *p*-Methylstyrene. $[RhCl(COD)]_2$ (6.4 mg, 1 mol %) and (*S*)-(−)-BINAP (16 mg, 2 mol %) were placed in a dried bottle under N_2. DME (2 mL) was added, and the mixture was stirred for a few minutes. The color of the solution became red. The mixture was cooled to −78 °C and was stirred for 10 min. Then

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(14) Hughes, R. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 5, p 506.

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.

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

Toshiya Sugimoto, Norinaga Nakamura, Masatomo Nojima,* and Shigekazu Kusabayashi

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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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 ^{1}H 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

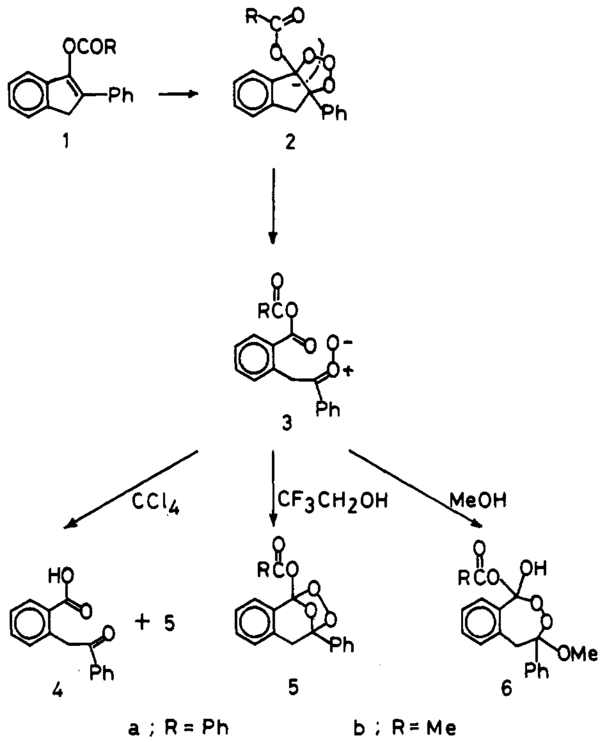
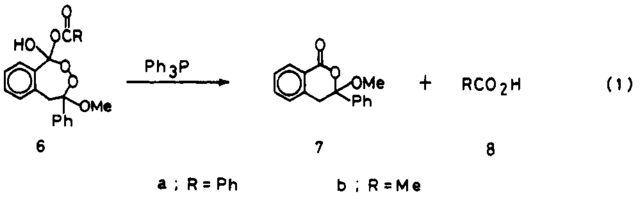


Table I. Ozonolysis of 2-Phenyl-3-(acyloxy)-1*H*-indenes **1a,b** and 1-Phenyl-2-(benzoyloxy)acenaphthylene (**9**)[a]

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.



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(1) La Barge, M. S.; Keul, H.; Kuczkowski, R. L.; Wallasch, M.; Cremer, D. *J. Am. Chem. Soc.* **1988**, *110*, 2081 and references therein.

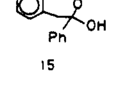
(2) (a) Bunnelle, W. H.; Meyer, L. A.; Schlemper, E. O. *J. Am. Chem. Soc.* **1989**, *111*, 7612. (b) Bunnelle, W. H. *Ibid.* **1989**, *111*, 7613.

(3) Odinokov, V. N.; Kukovinets, O. S.; Khalilov, L. M.; Tolstikov, G. A.; Kosnikov, A. Y.; Lindeman, S. V.; Struchkov, Y. T. *Tetrahedron Lett.* **1985**, *26*, 5843.

(4) (a) Griesbaum, K.; Volpp, W.; Huh, T. *Tetrahedron Lett.* **1989**, *30*, 1511. (b) Griesbaum, K.; Volpp, W.; Huh, T.; Jung, I. C. *Chem. Ber.* **1989**, *122*, 941. (c) Griesbaum, K.; Kim, W.; Nakamura, N.; Mori, M.; Nojima, M.; Kusabayashi, *J. Org. Chem.* In press.

(5) Wojciechowski, B. J.; Chiang, C.; Kuczkowski, R. L. *J. Org. Chem.* **1990**, *55*, 1120.

(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**.



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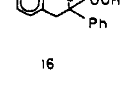

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