m/e (rel int): 85 (53), 129 (100), 211 (13), 253 (52), 268 (33). HRMS calcd for $C_{16}H_{33}BO_2$: 268.2574. Observed: 268.2589.

Pinacol Cyclohexylboronate (2l). A clear oil (1.53 g, 73%) was obtained from cyclohexene (10 mmol, 0.82 g) after flash column chromatography (solvent, 2% ether in hexane). IR (neat): 2978 (s), 1449 (s), 1371 (s), 1311 (s), 1258 (s), 1146 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.72–1.55 (m, 4 H), 1.40–1.27 (m, 6 H), 1.24 (s, 12 H), 1.04–0.93 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 82.6, 27.9, 27.1, 26.7, 24.7, 22.1 (bs). MS (EI, 70 eV) *m/e* (rel int): 124 (100), 129 (24), 195 (38), 210 (7). HRMS calcd for $C_{12}H_{23}BO_2$: 210.1791. Observed: 210.1783.

(*exo*)-Pinacol 2-Norbornylboronate (2m). A clear oil (1.20 g, 54%) was obtained from norbornene (10 mmol, 0.94 g) after flash column chromatography (solvent, 2% ether in hexane). IR (neat): 2994 (s), 1452 (s), 1372 (s), 1266 (s), 1225 (s), 1187 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.29 (bs, 1 H), 2.22 (bs, 1 H), 1.58–1.42 (m, 4 H), 1.39–1.29 (m, 1 H), 1.29–1.13 (m, 15 H), 0.92–0.85 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 82.7, 38.7, 38.1, 36.7, 32.2, 29.3, 25.8 (bs), 24.7, 12.4 (bs). MS (EI, 70 eV) *m/e* (rel int): 136 (57), 165 (14), 207 (100), 222 (5). HRMS calcd for $C_{13}H_{23}BO_2$: 222.1791. Observed: 222.1785.

Registry No. 1, 25015-63-8; **2a**, 83947-55-1; **2b**, 126688-98-0; **2c**, 141091-29-4; **2d**, 141091-30-7; **2e**, 83947-56-2; **2f**, 141091-31-8; **2g**, 141091-32-9; **2h**, 141091-33-0; **2i**, 141091-35-2; **2j**, 141091-37-4; **2k**, 141091-38-5; **2l**, 87100-15-0; **2m**, 141091-39-6; **3e**, 74213-48-2; **4h**, 141091-34-1; **4i**, 141091-36-3; PivCl, 3282-30-2; BH_3·SMe_2, 13292-87-0; HexC≡CH, 629-05-0; $Cl(CH_2)_3C$≡CH, 14267-92-6; $I(CH_2)_3C$≡CH, 2468-55-5; PhC≡CH, 536-74-3; $NC(CH_2)_3C$≡CH, 14918-21-9; *t*-$BuOCO_2(CH_2)_3C$≡CH, 140872-91-9; PrC≡CMe, 764-35-2; PhC≡CMe, 673-32-5; OctCH=CH_2, 872-05-9; $HO(CH_2)_3C$≡CH, 5390-04-5; pinacol, 76-09-5; 1-ethynyl-1-methoxycyclohexane, 5240-36-8; 1-ethynyl-1-cyclohexene, 931-49-7; cyclohexene, 110-83-8; norbornene, 498-66-8.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of the products (28 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Reversal of Regiochemistry of Wacker-Type Reactions Oriented by Heteroatoms

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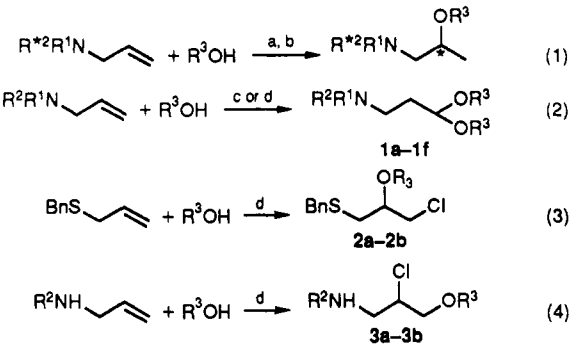
As one of the most widely used organometallic reactions, the Wacker process plays a very important role not only in the petrochemical industry but also in synthetic chemistry and especially in the synthesis of fine chemicals.[1-3] Although the application of this process is well-known with regard to the production of acetaldehyde from ethylene, the corresponding reactions of higher olefins usually afford methyl ketones rather than aldehyde, following the Markovnikov rule of addition.[2] Only a few reports have appeared of preferential aldehyde formations, and most of these involve olefins bearing an electron-withdrawing group wherein the direction of polarization of the terminal double bond is altered.[4] Because the formation of aldehydes and their derivatives via the attack at the terminal carbon of a terminal double bond is one of the important processes currently attracting attention in synthetic organic chemistry,[5] we report here a heteroatom-oriented Wacker-type reaction resulting in acetal as the main reaction product rather than the usual methyl ketone product.

During the course of studying the asymmetric oxypalladation of allylamine (eq 1),[6] we discovered that the addition of lithium or strontium carbonate changed the reaction course from eq 1 to eq 2, affording dimethyl acetal



(a) Li_2PdCl_4, K_2CO_3, (b) $NaBH_4$/THF, (c) Li_2PdCl_4, Li_2CO_3, or $SrCO_3$, (d) 10% Li_2PdCl_4/300% $CuCl_2$

as the major product rather than the expected 2-methoxypropylamine. We then examined this reaction with various substrates under the typical conditions of the Wacker process, using Li_2PdCl_4 with excess cupric chloride as cooxidant. The results of these reactions are listed in Table I, and the following conclusions can be drawn.

In the presence of $CuCl_2$, all reactions proceeded in the mode of a Wacker-type reaction. The difference in products (acetal, ketal, or chloro ether) is due to the directing influence of the heteroatoms. In the case of allyl and butenyl tertiary amines (entries 1–7) and of butenyl and pentenylsulfides (entries 9, 10), the acetals were obtained exclusively in good yields with no evidence of the formation of ketal. For allylic substrates with heteroatoms of stronger coordinating ability (S ≫ NH > N), the stabilized intermediates of the Wacker reactions were intercepted by Cu(II) to afford alkoxychlorinated products (chloro ethers, entries 11–14).

According to the regiochemistry of oxypalladation of allylic and homoallylic systems,[7,8] the nucleophile would be expected to attack the inner carbon atom of the double bond of allyl amines or sulfides and the external carbon atom of the double bond of the 3-butenylamine, 3-butenyl sulfide, or 4-pentenyl sulfide.[9] The above regiochemistry of the palladation reaction holds true in the presence of Cu(II) in several systems. Thus, for entries 7, 9, and 10, the nucleophiles were directed to the external carbon atom of the double bond of 3-butenylamine and sulfide and of

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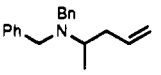
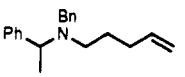
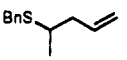
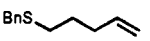
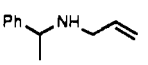
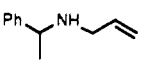
Table I. The Wacker Reaction of Allylamine and Other Substrates[a]

entry	substrate[b] R¹	substrate[b] R²	nucleophile[b] R³	time (h)	yield[c] (%) acetal	chloro ether	ketal
1	Bn	Bn	Me	10	81.0, **1a**		
2	Bn	Bn	Et	20	80.8, **1b**		
3	Bn	$PhCHCH_3$	Me	10	81.5, **1c**		
4	Me	$PhCHCH_3$	Me	8	76.4, **1d**		
5	Et	Et	Et	70	84.5, **1e**		
6	Bn	Bn	$(CH_2OH)_2$[d]	70	74.0, **1f**		
7			Me	72	68.5, **4**		
8			Me	72	45.4, **5**		48
9			Me[e]	60	55.0, **6**		
10			Me[e]	60	56.2, **7**		
11			Me[e]	36		87.7, **2a**	
12			Et[e]	48		83.9, **2b**	
13			Me[f]	72	10.4	82.1, **3a**	
14			Et[f]	96	<5	88.8, **3b**	

[a] 10% Li_2PdCl_4, 300% $CuCl_2$. Excess nucleophile (alcohol) is used as solvent, except when indicated otherwise. The reaction temperatrure was 50 °C, except when indicated otherwise. [b] R^1, R^2, and R^3 refer to those in eqs 2–4. [c] Isolated yield. [d] THF:ethylene glycol = 5:1. [e] 20% Li_2PdCl_4 and 300 % $CuCl_2$ were used as catalysts in entries 9–12. [f] The reaction temperature was −10 °C. At higher temperature, the yield of acetals was increased, for example, 23% acetal at 50 °C for entry 13.

4-pentenyl sulfide. This directing influence of the N atom, although less strong than S, can still be observed in the case of 4-pentenylamine (entry 8), and a 1:1 product ratio of acetal and ketal was obtained. For entries 11, and 12, the nucleophiles were directed to the inner carbon in allyl sulfide.

The above regiochemistry does not hold in the case of allylamines (entries 1–6 and 13–14). For these substrates, the nucleophile was directed to the external carbon atom rather than to the inner carbon atom as expected. Please also note that the positions of the alkoxy groups in the products of the reaction with allyl sulfide and allyl secondary amine are different, as shown in eqs 3 and 4. This was confirmed by LAH reductive cleavage of the Cl atom and verified by NMR as well as MS analysis of the dechlorinated ethers. Similar reaction of tertiary allyl amine using benzoquione instead of Cu(II) as cooxidant only gave a mixture of ketal and ketone. It seems that Cu(II) not only plays the role of a cooxidant but also exerts an influence on the regiochemistry of the reaction. But the role of Cu(II) in the change of regiochemistry is still obscure.[10]

In conclusion, the regiochemistry of the Wacker reactions of tertiary 2-propenyl- and 3-butenylamine and of 3-butenyl and 4-pentenyl sulfides is reversed, as compared with the Wacker reaction of ordinary higher olefins, affording acetals in high yield. The heteroatom-directed transformations exemplified here may be useful in synthetic chemistry. For example, it provides a means for introducing a $-(CH_2)_nCHO$ group (n = 2, 3) onto the N atom by first allylation and then Wacker oxidation. This may provide a facile means for the synthesis of β- or γ-amino acids as well as of β- or γ-amino alcohols. Studies further defining the scope and the potential in synthesis and the asymmetric inductions are in progress.

(10) During the revision of our manuscript, we noticed a very recent report of Murahashi (*Chem. Commun.* **1991**, 1599). In this report, the Wacker reaction of *N*-allylamides also provides aldehyde as main products (aldehyde:ketone = 9:1) by using O_2 as cooxidant.

Experimental Section

^1H NMR spectra were recorded on a Jeol FX-90Q or a XL-200 spectrometer. Tetramethylsilane served as an internal standard. Mass spectra were recorded by using a Finnigan 4021 (low-resolution) or a Finnigan 8430 (high-resolution) mass spectrometer. IR spectra were recorded on a ShimadzuIR-440 instrument. All solvents such as THF or alcohols were purified by using normal methods.

General Procedure. In a side-armed Pyrex tube with a magnetic stirring bar were placed lithium tetrachloropalladate (26.2 mg, 0.1 mmol) and cupric chloride (403.5 mg, 3 mmol). The tube was evacuated on a vacuum line at 50 °C. A solution of substrate (1 mmol) in 5 mL of solvent was added under argon gas, and the mixture was stirred at 50 °C and traced by TLC. After the reaction was complete, excess sodium sulfide was added and the mixture stirred for 20 min and extracted with 4 × 40 mL of ether. The extracts were combined, washed with 10 mL of 10% aqueous sodium hydroxide solution and 10 mL of water, and dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure, and the crude product was purified and separated by preparative TLC. The purity of these purified new compounds listed below was judged to be >90% by ^1H NMR spectral determinations.

***N*,*N*-Dibenzyl-3,3-dimethoxypropylamine (1a)**: ^1H NMR ($CDCl_3$) δ 1.76 (m, 2 H), 2.52 (m, 2 H), 3.18 (s, 6 H), 3.54 (m, 4 H), 4.38 (t, 1 H, J = 5.8 Hz), 7.30 (m, 10 H); MS (EI, m/e) 299 (M^+ 0.88), 284 (23.49), 210 (75.23), 181 (7.11), 118 (8.90), 91 (100.00); IR (cm^{-1}) 695, 715, 1060, 1120, 1440, 1499, 1600, 2800–3000. Anal. Calcd for $C_{19}H_{25}NO_2$: C, 76.22; H, 8.42; N, 4.68. Found: C, 76.23; H, 8.67; N, 4.29.

***N*,*N*-Dibenzyl-3,3-diethoxypropylamine (1b)**: ^1H NMR ($CDCl_3$) δ 1.10 (t, 6 H, J = 6.4 Hz), 1.74 (m, 2 H), 2.58 (m, 2 H), 3.56 (m, 8 H), 4.54 (t, 1 H, J = 6.0 Hz), 7.40 (m, 10 H); MS (EI, m/e) 328 (M^+ + 1, 18.10), 327 (M^+, 4.21), 298 (26.13), 244 (11.24), 210 (100.00); IR (cm^{-1}) 700, 740, 1060, 1120, 1440, 1499, 1600, 2800–3000. Anal. Calcd for $C_{21}H_{29}NO_2$: C, 77.02; H, 8.93; N, 4.28. Found: C, 77.31; H, 8.88; N, 4.15.

***N*-Benzyl-*N*-(α-methylbenzyl)-3,3-dimethoxypropylamine (1c)**: ^1H NMR ($CDCl_3$) δ 1.38 (d, 3 H, J = 6.8 Hz), 1.70 (m, 2 H), 2.50 (m, 2 H), 3.16 (2s, 2 × 3 H), 3.50 (s, 2 H), 3.86 (q, 1 H, J = 6.8 Hz), 4.32 (t, 1 H, J = 6.0 Hz), 7.25 (m, 10 H); MS (EI, m/e) 313 (M^+, 4.74), 298 (62.31), 224 (62.52), 120 (58.26), 105

(100.00), 91 (87.77); IR (cm^{-1}) 700, 740, 1060, 1120, 1440, 1495, 1600, 2800–3000. Anal. Calcd for $C_{20}H_{27}NO_2$: C, 76.64; H, 8.68; N, 4.47. Found: C, 76.45; H, 8.65; N, 4.43.

***N*-Methyl-*N*-(α-methylbenzyl)-3,3-dimethoxypropylamine (1d)**: ^1H NMR (CD_3COCD_3) δ 1.32 (d, 3 H, J = 7.2 Hz), 1.70 (m, 2 H), 2.16 (s, 3 H), 2.40 (m, 2 H), 3.23 (s, 6 H), 3.56 (q, 1 H, J = 7.2 Hz), 4.40 (t, 1 H, J = 5.4 Hz), 7.34 (m, 5 H); MS (EI, m/e) 238 (M^+ + 1, 17.4), 222 (58.90), 148 (72.73), 134 (14.71), 105 (100.00), 44 (58.41); IR (cm^{-1}) 700, 740, 1200, 1445, 1490, 1600, 2800–3000. Anal. Calcd for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.65; H, 9.77; N, 5.89.

***N*,*N*-Diethyl-3,3-diethoxypropylamine (1e)**: ^1H NMR (DMSO-d_6) δ 1.06 (m, 12 H), 1.62 (q, 2 H), 2.44 (m, 6 H), 3.50 (m, 4 H), 4.52 (t, 1 H, J = 5.8 Hz); MS (EI, m/e) 204 (M^+ + 1, 14.80), 194 (7.01), 174 (22.79), 116 (8.36), 58 (11.60); IR (cm^{-1}) 600 1080, 1220, 1360, 1440, 1650, 1700, 2800–3000.

***N*,*N*-Dibenzyl-2-(1′,3′-dioxa-2′-cyclopentyl)ethylamine (1f)**: ^1H NMR ($CDCl_3$) δ 1.93 (m, 2 H), 2.46 (m, 2 H), 3.49 (m, 4 H), 3.70 (m, 4 H), 4.77 (t, 1 H, J = 5.0 Hz), 7.24 (m, 10 H); MS (EI, m/e) 298 (M^+ + 1, 100.0), 297 (M^+, 24.49), 210 (78.89), 134 (3.83); IR (cm^{-1}) 700, 740, 1120, 1445, 1495, 1600, 2800–3000. Anal. Calcd for $C_{19}H_{23}NO_2$: C, 76.74; H, 7.80; N 4.71. Found: C, 76.50; H, 7.92; N, 4.92.

***N*,*N*-Dibenzyl-5,5-dimethoxypentyl-2-amine (4)**: ^1H NMR ($CDCl_3$) δ 1.04 (d, 3 H, J = 7.2 Hz), 1.30 (m, 2 H), 1.68 (m, 2 H), 2.76 (m, 1 H), 3.28 (s, 6 H), 3.60 (m, 4 H), 4.23 (t, 1 H, J = 5.4 Hz), 7.36 (m, 10 H); MS (EI, m/e) 328 (M^+ + 1, 0.60), 312 (12.20), 224 (100.00), 105 (23.97), 91 (75.00); IR (cm^{-1}) 695, 740, 1050, 1120, 1440, 1495 1600, 2800–3000. Anal. Calcd for $C_{21}H_{29}NO_2$: C, 77.02; H, 8.92; N, 4.20. Found: C, 77.28; H, 8.79; N, 3.93.

***N*-Benzyl-*N*-(α-methylbenzyl)-5,5-dimethoxypentylamine (5)**: ^1H NMR ($CDCl_3$) δ 1.30 (d, 3 H, J = 7.2 Hz), 1.34 (m, 6 H), 2.36 (m, 2 H), 3.12 (s, 6 H), 3.48 (s, 2 H), 3.84 (q, 1 H, J = 7.2 Hz), 4.20 (t, 1 H, J = 5.4 Hz), 7.27 (m, 10 H); MS (EI, m/e) 342 (M^+ + 1, 49.3), 310 (61.37), 224 (100.00), 120 (20.30), 105 (45.45), 91 (18.85); IR (cm^{-1}) 700, 740, 1050, 1120, 1445, 1495, 1600, 2800–3000. Anal. Calcd for $C_{22}H_{31}NO_2$: C, 77.39; H, 9.15; N, 4.10. Found: C, 77.38; H, 9.37; N, 3.83.

Benzyl 5,5-dimethoxypentyl-2-yl sulfide (6): ^1H NMR ($CDCl_3$) δ 1.26 (d, 3 H J = 7.2 Hz), 1.78 (m, 3 H), 2.59 (m, 2 H), 3, 10 (s, 6 H), 3.68 (s, 2 H), 4.42 (t, 1 H, J = 5.2 Hz), 7.22 (m, 5 H); MS (EI, m/e) 255 (M^+ + 1, 2.64), 222 (10.62), 148 (61.32), 131 (16.39), 105 (100.00), 91 (51.79); IR (cm^{-1}) 690, 740, 1060, 1120, 1375, 1445, 1590, 2800–3000; HRMS m/e calcd for $C_{13}H_{19}OS$ (M − 31) 223.1166, found 223.1157.

Benzyl 5,5-dimethoxypentyl sulfide (7): ^1H NMR ($CDCl_3$) δ 1.20, 1.48 (m, 6 H), 2.32 (t, 2 H, J = 5.2 Hz), 3.10 (s, 6 H), 3.60 (s, 2 H), 4.22 (t, 1 H, J = 5.2 Hz), 7.16 (m, 5 H); MS (EI, m/e) 255 (M^+ + 1, 5.41), 223 (93.27), 131 (100.00), 101 (26.12), 91 (21.96), 75 (84.53); IR (cm^{-1}) 690, 750, 1050, 1100, 1445, 1580, 2800–3000; HRMS m/e calcd for $C_{14}H_{22}O_2S$ (M − 31) 223.1166, found 223.1157.

3-Chloro-2-methoxypropyl benzyl sulfide (2a): ^1H NMR ($CDCl_3$) δ 2.60 (d, 2 H, J = 4.0 Hz), 3.32 (s, 3 H), 3.36 (m, 1 H), 3.59 (d, 2 H, J = 4.0 Hz) 3.72 (s, 2 H), 7.26 (m, 5 H); MS (EI, m/e) 232 (M^+ + 2, 5.50), 230 (M^+, 11.66), 198 (7.88), 163 (7.26), 122 (19.98), 91 (100.00); IR (cm^{-1}) 690, 740, 1080, 1410, 1435, 1475, 1580, 2800–3000; HRMS m/e calcd for $C_{11}H_{15}OClS$ (M + 2) 232.0502, found 232.0494.

3-Chloro-2-ethoxypropyl benzyl sulfide (2b): ^1H NMR ($CDCl_3$) δ 1.17 (t, 3 H, J = 6.0 Hz), 2.61 (d, 2 H, J = 4.0 Hz), 3.42–3.68 (m, 5 H), 3.74 (s, 2 H), 7.26 (m, 5 H); MS (EI, m/e) 246 (M^+ + 2, 4.46), 244 (M^+, 15.84), 201 (9.45), 199 (20.53), 122 (22.85), 91 (100.00); IR (cm^{-1}) 690, 740, 900, 1080, 1320, 1420, 1480, 1580, 1670, 2800–3000; HRMS m/e calcd for $C_{12}H_{17}OClS$ 244.0688, found 244.0687.

***N*-(α-Methylbenzyl)-2-chloro-3-methoxypropylamine (3a)**: ^1H NMR ($CDCl_3$) δ 1.16 (d, 3 H, J = 6.0 Hz), 1.54 (s, 1 H, NH), 2.40 (m, 2 H), 3.19 (s, 3 H), 3.40 (m, 4 H), 7.14 (s, 5 H); MS (EI, m/e) 230 (M^+ + 3, 18.8), 229 (M^+ + 2, 100.00), 228 (M^+ + 1, 53.00), 192 (5.53), 134 (16.34), 105 (47.74); IR (cm^{-1}) 690, 740, 1080, 1330, 1350, 1430, 1590, 1660, 2700, 3000, 3200–3500; HRMS m/e calcd for $C_{12}H_{18}NOCl$ 227.1073, found 227.1075.

***N*-(α-Methylbenzyl)-2-chloro-3-ethoxypropylamine (3b)**: ^1H NMR ($CDCl_3$) δ 1.24 (t, 3 H, J = 6.4 Hz), 1.34 (d, 3 H, J = 6.4 Hz), 1.84 (s, 1 H, NH), 2.62 (m, 2 H), 3.10 (m, 1 H), 3.56 (m, 5 H), 7.28 (s, 5 H); MS (EI, m/e) 244 (M^+ + 3, 4.24), 233 (M^+ + 2, 100.00), 232 (M^+ + 1, 12.80) 134 (11.44), 105 (21.66); IR (cm^{-1}) 690, 740, 1060, 1120, 1360, 1440, 2800–3000, 3200–3500; HRMS m/e calcd for $C_{13}H_{20}NOCl$ 241.1234, found 241.1235.

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Registry No. **1a**, 140927-73-7; **1b**, 140927-74-8; **1c**, 140927-75-9; **1d**, 140927-76-0; **1e**, 3616-60-2; **1f**, 140927-77-1; **2a**, 140927-78-2; **2b**, 140927-79-3; **3a**, 140927-80-6; **3b**, 140927-81-7; **4**, 140927-87-3; **5**, 140927-88-4; **6**, 140927-89-5; **7**, 140927-90-8; methanol, 67-56-1; ethanol, 64-17-5; ethyene glycol, 107-21-1; *N*,*N*-dibenzyl-2-propenylamine, 22014-91-1; *N*-benzyl-*N*-(α-methylbenzyl)-2-propenylamine, 140927-82-8; *N*-methyl-*N*-(α-methylbenzyl)-2-propenylamine, 140927-83-9; *N*,*N*-diethyl-2-propenylamine, 5666-17-1; *N*,*N*-dibenzyl-4-penten-2-ylamine, 140927-84-0; *N*-benzyl-*N*-(α-methylbenzyl)-4-pentenylamine, 140927-85-1; benzyl 4-penten-2-yl sulfide, 140927-86-2; benzyl 4-pentenyl sulfide, 39984-76-4; benzyl 2-propenyl sulfide, 6937-97-9; *N*-(α-methylbenzyl)-2-propenylamine, 66896-61-5.

Supplementary Material Available: ^1H NMR spectra of all new compounds (14 pages). Ordering information is given on any current masthead page.

3-(Trihalomethyl)-3-alkoxy-1,2,4-trioxolanes

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Introduction

Esters exhibit generally poor 1,3-dipolarophilicity toward carbonyl oxides.[2] Thus, ozonolysis of ethyl vinyl ether in ethyl acetate as solvent afforded only 11% of the expected cross-ozonide 3-ethoxy-3-methyl-1,2,4-trioxolane,[2c] and ozonolysis of 1-methoxy-2-alkyl- or 1-methoxy-2-aryl-substituted ethylenes in solution did not provide any of the corresponding ozonides, even if the reactions were carried out in the presence of the reactive ester methyl formate.[3] By contrast, ozonolyses of the same substrates on polyethylene did provide the corresponding ozonides in each case.[3] These ozonides were, however, labile toward silica gel, and hence, considerable losses occurred during the isolation by column chromatography, resulting in low yields of isolated products.

Since it is known that α-halo substituents considerably increase the reactivity of aldehydes and ketones toward carbonyl oxides,[3-6] it was of interest to us whether α-halo substituents may also lead to enhanced dipolarophilicity in esters. To this end, we have ozonized substrates **1a–e** in the presence of methyl trifluoroacetate (**6a**), as well as substrates **1b** and **1c** in the presence of ethyl trifluoroacetate (**6b**) or methyl trichloroacetate (**6c**) in an attempt to generate the corresponding ozonides **7** by competition of the activated esters **6** with the esters **3** for the carbonyl oxide fragments **2** (Scheme I).

Results and Discussion

Ozonolysis of ethyl vinyl ether (**1a**) at −78 °C in pentane and in the presence of ca. 4 equiv of methyl trifluoroacetate

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