(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.

Acknowledgment. We are grateful to the National Natural Science Foundation of China and to the Chinese Academy of Sciences for their financial support of this research.

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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Received January 23, 1992

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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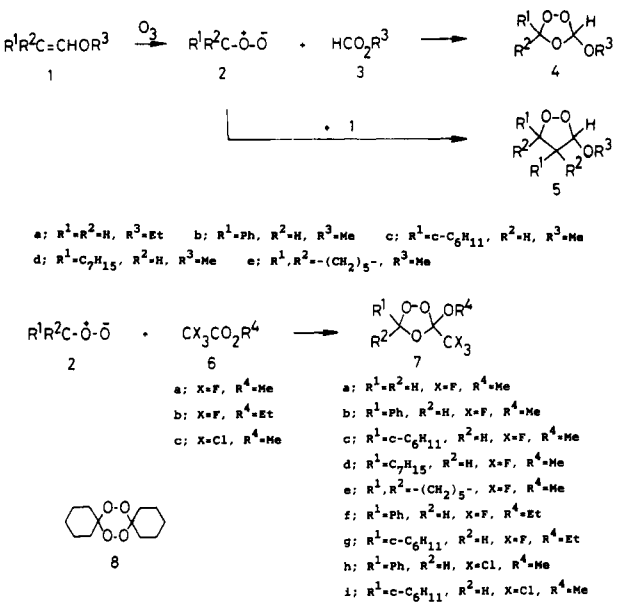
0022-3263/92/1957-3487$03.00/0

Scheme I

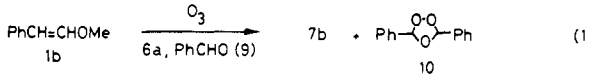


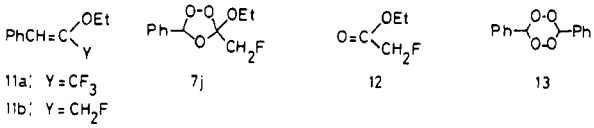
(**6a**) gave a product mixture from which only ca. 0.6% of cross-ozonide **7a** (derived from cycloaddition of formaldehyde *O*-oxide (**2a**) with **6a**) was obtained. Major products were the parent ozonide **4a** (cycloaddition with ethyl formate (**3a**)) and the 1,2-dioxolane **5a** (cycloaddition with **1a**),[2c] which were isolated in yields of 15.4 and 34.5%, respectively (Scheme I).

It was assumed that the yields of cross-ozonide may be increased by a large excess of the trapping agent **6a** in conjunction with enhanced solvent polarity. Therefore, the same reaction was carried out in diethyl ether and with 10 equiv of **6a** at −70 °C. Certainly, the yield of the crossed ozonide **7a** increased to 1.7%, but the major products were again **4a** (11.1%) and **5a** (60%). These results demonstrate that the order of dipolarophilicity toward formaldehyde *O*-oxide (**2a**) follows the sequence **1a** > **3a** > **6a**, although we cannot exclude the possibility that the order of **3a** > **6a** would be due to the cage effects in the recombination between **2a** and **3a**.

A remarkably different order of reactivity was observed for alkyl- and aryl-substituted carbonyl oxides **2b–d**. Ozonolyses of vinyl ethers **1b–d** were conducted in the presence of 10 equiv of alkyl trihalolacetates **6a–c** in ether at −70 °C. Under these conditions, the following isolated yields of cross-ozonides could be obtained: 67% of **7b**, 48% of **7f**, 18% of **7h**, 59% of **7c**, 48% of **7g**, 19% of **7i**, and 49% of **7d** (Scheme I). It is also worth noting that the ^{1}H NMR spectra of the crude products did not show the formation of normal ozonides **4b–d** or 1,2-dioxolanes **5b–d**, suggesting that of the three sets of 1,3-dipolarophiles **1b–d**, **3** (R^3 = Me or Et), and **6a–c**, the α-halo-substituted esters **6a–c** were the most reactive toward carbonyl oxides **2b–d**.[3] By contrast, ozonolysis of (methoxymethylene)cyclohexane (**1e**) in the presence of **6a** under the same conditions gave a complex mixture containing the cyclohexane *O*-oxide dimer (1,2,4,5-tetroxane) **8**, yet none of the expected cross-ozonide **7e** was detected.

These results, in conjunction with the above-mentioned low yield of cross-ozonide from the ozonolysis of ethyl vinyl ether in ethyl acetate,[2,7] indicate that the introduction of halogen substituents in the α-position of esters imparts enhanced dipolarophilicity toward carbonyl oxides. Consistent with this, a competition reaction revealed that the reactivity of methyl trifluoroacetate (**6a**) is very similar to that of benzaldehyde (**9**); the ozonolysis of **1b** in the presence of **6a** and **9** (5 equiv for each) resulted in the formation of **7b** (32%) and stilbene ozonide **10** (25%) (eq 1). Furthermore, as the differences in the yields of **7b** (67%) and **7h** (18%), as well as **7c** (59%) and **7i** (19%) suggest, fluorine exerts a considerably stronger effect upon the dipolarophilicity of the carbonyl group than chlorine.

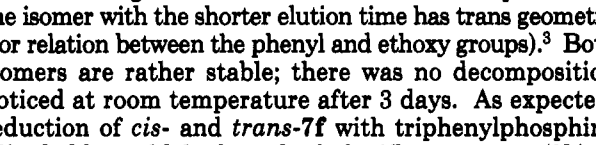




In further experiments we have ozonized substrates 2-ethoxy-2-(trifluoromethyl)styrene (**11a**) and 2-ethoxy-2-(fluoromethyl)styrene (**11b**), in order to test whether 3-α-(halomethyl)-3-alkoxy-1,2,4-trioxolanes can be also obtained from the parent olefins, i.e., by reaction of benzaldehyde *O*-oxide with α-fluoro-substituted esters **6b** or **12** in a ratio of ca. 1:1, and to assess a possible influence of the degree of α-fluorination of esters upon their potential for ozonide formation. These reactions were carried out both in pentane solutions and on polyethylene, since the latter conditions are known to be conducive to ozonide formation.[8]

Ozonolysis of **11a** on polyethylene gave two stereoisomeric ozonides, *cis*- and *trans*-**7f**, in a ratio of 60:40; they were isolated in yields of 27 and 26%, respectively. Ozonolysis of **11a** in pentane gave a mixture of *cis*- and *trans*-**7f** as the major products, and of *cis*- and *trans*-stilbene ozonide (**10**) as minor products, from which 1% of *trans*-**7f** and 10% of *cis*-**7f** was isolated. The stereochemical assignments are based on the assumption that the isomer with the shorter elution time has trans geometry (for relation between the phenyl and ethoxy groups).[3] Both isomers are rather stable; there was no decomposition noticed at room temperature after 3 days. As expected, reduction of *cis*- and *trans*-**7f** with triphenylphosphine afforded benzaldehyde and ethyl trifluoroacetate (**3b**) in a molar ratio of ca. 1:1.

Ozonolysis of **11b** on polyethylene or in pentane did not afford detectable amounts of the corresponding ozonide **7j**. In the crude reaction products, the following product distributions were determined by ^{1}H NMR analysis: ethyl fluoroacetate (**12**) (65%), *cis*-**10** (10%), *trans*-**10** (12%), 3,6-diphenyl-1,2,4,5-tetroxane (**13**) (8%) and benzaldehyde (5%) from the ozonolysis in pentane and **12** (65%), and benzaldehyde (23%) and benzoic acid (12%) from the ozonolysis on polyethylene.



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(7) Ozonolysis of **1b** in methyl acetate at −78 °C gave a mixture of 3,6-diphenyl-1,2,4,5-tetroxane (**13**) (10%), benzaldehyde (**9**) (35%), and benzoic acid (7%).
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These results are indicative of a pronounced effect of the degree of α-fluorination of ester fragments upon their potential for ozonide formation. Furthermore, they show that α-trifluoro-substituted acetates are prone to undergo [3 + 2] cycloaddition with carbonyl oxide to give ozonide in a 1:1 stoichiometry.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on Bruker 250, JNM-PS-100, and JNM-GSX-400 instruments. Unless otherwise mentioned the spectra were recorded in $CDCl_3$.

Ozonolysis of 1a in Pentane in the Presence of 6a. A solution of 2.0 g (27 mmol) of **1a** and 13.0 g (100 mmol) of **6a** in 40 mL of pentane was treated with 27 mmol of ozone at −78 °C. Residual ozone was flushed out with N_2, the solution was warmed up to rt, and pentane was distilled off at 0 °C and 90 Torr to leave 2.2 g of a colorless liquid residue. From the latter, 500 mg (15.4%) of **4a**, 27 mg (0.6%) of **7a**, and 1.1 g (34.5%) of **5a** were isolated by flash column chromatography (column 1.2 × 30 cm; 20 g of silica gel; pentane/ether, 44:1).

3-Ethoxy-1,2,4-trioxolane (4a): colorless liquid; ^1H NMR δ 1.26 (t, J = 7.1 Hz, 3 H), 3.63–3.82 (m, 2 H), 4.93 (s, 1 H), 5.48 (s, 1 H), 6.08 (s, 1 H); ^{13}C NMR δ 14.85, 60.67, 93.88, 111.95. These data correspond with those reported for **4a**.[9]

3-Methoxy-3-(trifluoromethyl)-1,2,4-trioxolane (7a): colorless liquid; ^1H NMR δ 3.58 (s, 3 H), 5.30 (s, 1 H), 5.58 (s, 1 H); ^{13}C NMR δ 50.65 (s), 96.57 (s), 117.47 (q, J = 42.8 Hz), 119.43 (q, J = 286.0 Hz); EI-MS m/z (relative intensity) 174 (5.7) M^+, 142 (55.3) $[M - O_2]^+$, 69 (100) $[CF_3]^+$.

Reduction of 7a. A solution of 18 mg of **7a** in 0.3 mL of $CDCl_3$ was admixed with 0.1 mL of a $CDCl_3$ solution containing triphenylphosphine and kept at ca. 4 °C for 2 d. ^1H NMR analysis showed the presence of **6a** (δ 3.98) and of formaldehyde (δ 9.72).

3-Ethoxy-1,2-dioxolane (5a): colorless liquid; ^1H NMR ABMNX system with δ 2.59, 2.76, 3.94, 4.24, 5.32 and δ 1.23, 3.50, 3.82 for the ethyl group; ^{13}C NMR δ 14.85, 42.47, 63.51, 66.08, 101.75; EI-MS m/z (relative intensity) 118 (6.1) M^+, 85 (100) $[M - OOH]^+$, 73 (26.1) $[M - OC_2H_5]^+$; CI-MS 119 (87.8) $[M + 1]^+$. The ^1H and ^{13}C NMR data correspond with those reported for **5a**.[2c]

General Procedure for Ozonolysis of 1a–e in Diethyl Ether in the Presence of 6a–c. Solutions containing 2 mmol of the respective vinyl ether **1** and 20 mmol of the respective α-halo ester **6** in 20 mL of diethyl ether were treated with 2 mmol of ozone at −70 °C. The solvent was evaporated at rt and 15 Torr, and the residue was separated by column chromatography (column 1.2 × 30 cm; 20 g of silica gel; hexane/ether, 95:5). The ozonides **7b,f,g** were obtained as mixtures of two stereoisomers (the ratio, ca. 9:1; the chemical shift (δ) of the characteristic signal of the minor isomer in ^1H NMR spectra: **7b**, 6.29 (s); **7f**, 6.29 (s); **7g**, 5.21 (d, J = 5.0 Hz). Treatment of the isomer mixtures of **7b,f,h** with triphenylphosphine in $CDCl_3$ led to quantitative formation of the corresponding mixtures of aldehydes and alkyl trihaloacetates). Despite several attempts, however, pure samples of the minor isomers of the ozonides could not be isolated. Thus, for these ozonides the physical properties of only the major isomers are cited herein.

Ozonolysis of 1a (2.0 g) in the presence of 6a (34.0 g) in 10 mL of ether afforded 2.7 g of liquid residue from which 360 mg (11.1%) of **4a**, 81 mg (1.7%) of **7a**, and 1.9 g (60%) of **5a** were isolated.

Ozonolysis of 1b in the presence of 6a afforded 495 mg of liquid residue from which 337 mg (67%) of **7b** was isolated.

3-Methoxy-3-(trifluoromethyl)-5-phenyl-1,2,4-trioxolane (7b): colorless liquid; ^1H NMR (CCl_4) δ 3.67 (s, 3 H), 6.37 (s, 1 H), 7.3–7.7 (m, 5 H); IR 3030, 2960, 1465, 1395, 1373, 1320, 1205, 1165, 1090, 1035, 955, 918, 845, 820, 755, 698, 622 cm^{-1}. Anal. Calcd for $C_{10}H_9F_3O_4$: C, 48.01; H, 3.63. Found: C, 48.47; H, 3.48.

Ozonolysis of 1c in the presence of 6a afforded 500 mg of liquid residue, from which 302 mg (59%) of **7c** was isolated.

3-Cyclohexyl-5-methoxy-5-(trifluoromethyl)-1,2,4-trioxolane (7c): colorless liquid; ^1H NMR ($CDCl_3$) δ 1.1–1.9 (m, 11 H), 3.56 (s, 3 H), 5.34 (d, J = 4.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.22, 25.25, 25.88, 26.57, 26.75, 38.52, 50.50, 110.03, 114.41 (q, J = 37 Hz), 119.31 (q, J = 286 Hz); IR 2940, 2860, 1455, 1370, 1335, 1200, 1160, 1090, 965, 885, 820, 735 cm^{-1}. Anal. Calcd for $C_{10}H_{15}F_3O_4$: C, 46.88; H, 5.90. Found: C, 46.52; H, 5.97.

Ozonolysis of 1d in the presence of 6a afforded 510 mg of liquid residue, from which 267 mg (49%) of **7d** was isolated.

3-Heptyl-5-methoxy-5-(trifluoromethyl)-1,2,4-trioxolane (7d): colorless liquid; ^1H NMR (CCl_4) δ 0.8–1.9 (m, 15 H), 3.55 (s, 3 H), 5.51 (t, J = 4.2 Hz, 1 H); IR 2940, 2860, 1460, 1200, 1095 cm^{-1}. Anal. Calcd for $C_{11}H_{19}F_3O_4$: C, 48.53; H, 7.03. Found: C, 48.81; H, 6.96.

Ozonolysis of 1e in the presence of 6a afforded 350 mg of liquid residue. Column chromatography on silica gel (elution with ether/hexane, 1:20) gave first the cyclohexanone oxide dimer **8** (61 mg, 27%): mp 132–133 °C (lit.[10] mp 123–126 °C), the physical properties being identical with those of the authentic sample prepared by cyclohexanone and hydrogen peroxide.[10] Further elution with ether/hexane (1:10–1:1) resulted in the recovery of the unidentified products (200 mg).

Ozonolysis of 1b in the presence of 6b afforded 350 mg of liquid residue, from which 253 mg (48%) of **7f** was isolated.

Ozonolysis of 1c in the presence of 6b afforded 420 mg of liquid residue, from which 259 mg (48%) of **7g** was isolated.

3-Ethoxy-3-(trifluoromethyl)-5-cyclohexyl-1,2,4-trioxolane (7g): colorless liquid; ^1H NMR ($CDCl_3$) δ 1.29 (t, J = 7.0 Hz, 3 H), 1.0–2.0 (m, 11 H), 3.94 (q, J = 7.0 Hz, 2 H), 5.34 (d, J = 4.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.32, 25.85, 25.78, 26.51, 27.22, 27.40, 39.15, 60.15, 110.47, 114.93 (q, J = 37 Hz), 119.94 (J = 287 Hz); IR 2920, 2850, 1445, 1100, 980, 880, 780 cm^{-1}. Anal. Calcd for $C_{11}H_{17}F_3O_4$: C, 48.89; H, 6.34. Found: C, 49.43; H, 6.12.

Ozonolysis of 1b in the presence of 6c afforded 3.7 g of liquid residue, from which 108 mg (18%) of **7h** was isolated.

3-Methoxy-3-(trichloromethyl)-5-phenyl-1,2,4-trioxolane (7h): mp 86–88 °C; ^1H NMR ($CDCl_3$) δ 3.76 (s, 3 H), 6.58 (s, 1 H), 7.3–7.8 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 51.64, 97.77, 107.40, 120.51, 128.38, 128.45, 128.85, 131.67; IR 2955, 1462, 1317, 1207, 1185, 1140, 1067, 1035, 1012, 803, 750 cm^{-1}. Anal. Calcd for $C_{10}H_9Cl_3O_4$: C, 40.10; H, 3.03. Found: C, 40.51; H, 3.13.

Ozonolysis of 1c in the presence of 6c afforded 3.7 g of liquid residue, from which 116 mg (19%) of **7i** was isolated.

3-Cyclohexyl-5-methoxy-5-(trichloromethyl)-1,2,4-trioxolane (7i): colorless liquid; ^1H NMR (CCl_4) δ 1.0–1.8 (m, 11 H), 3.71 (s, 3 H), 5.49 (d, J = 5.0 Hz, 1 H). Anal. Calcd for $C_{10}H_{15}Cl_3O_4$: C, 39.30; H, 4.91. Found: C, 39.45; H, 4.85.

A Competition Reaction between Methyl Trifluoroacetate (6a) and Benzaldehyde (9). To a solution of **1b** (268 mg, 2 mmol), **6a** (1.28 g, 10 mmol), and **9** (1.06 g, 10 mmol) in ether (20 mL) was passed a slow stream of ozone at −70 °C. After evaporation of the solvent, the products were separated by column chromatography (column 1.5 × 30 cm; 30 g of silica gel; benzene/hexane, 1:4). The first faction contained **7b** (79 mg, 32%). From the second fraction was obtained a 1:1 mixture of *cis*-**10** (δ 6.33, s) and *trans*-**10** (δ 6.36, s) (57 mg, 25%).

Ozonolysis of 11a. (a) Ozonolysis on Polyethylene. A 1.04-g (4.81-mmol) sample of **11a**[11] on 80 g of polyethylene was ozonized at −75 °C for 8 h. The products were extracted with diethyl ether and ether was removed at rt at ca. 12 Torr to leave 1.03 g of a residue. ^1H NMR analysis showed the presence of 37% of *cis*-**7f**, 56% of *trans*-**7f**, and 7% of **11a**. Separation by column chromatography (column 3 × 60 cm; 110 g of silica gel; pentane/ether, 30:1) gave first 315 mg (26%) of *trans*-**7f** and then 332 mg (27%) of *cis*-**7f**.

***trans*-3-Ethoxy-3-(trifluoromethyl)-5-phenyl-1,2,4-trioxolane (*trans*-7f)**: mp 48–51 °C; ^1H NMR δ 1.33 (t, J = 7.10 Hz, 3 H), 4.13 (qm, J = 7.86 and 2.28 Hz, 2 H), 6.32 (s, 1 H), 7.41–7.59 (m, 5 H); ^{13}C NMR (at −10 °C) δ 14.60 (qt, J = 127.3 and 2.8 Hz), 59.88 (tq, J = 146.4 and 4.4 Hz), 106.41 (broad d, J = 179.4 Hz), 114.27 (q, J = 35.9 Hz), 119.43 (q, J = 286.3 Hz), 127.80 (dd, J = 161.7 and 6.9 Hz), 127.85 (t, J = 7.3 Hz), 129.00 (dd, J = 160.0 and 7.0 Hz), 131.74 (dt, J = 160.8 and 7.3 Hz). Anal. Calcd for $C_{11}H_{11}F_3O_4$: C, 50.08; H, 4.20. Found: C, 50.62; H, 4.31.

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***cis*-3-Ethoxy-3-(trifluoromethyl)-5-phenyl-1,2,4-trioxolane (*cis*-7f)**: mp 66–68 °C; ^{1}H NMR δ 1.34 (t, J = 7.10 Hz, 3 H), 4.06 (qm, J = 7.81 and 2.26 Hz, 2 H), 6.42 (s, 1 H), 7.37–7.64 (m, 5 H); ^{13}C NMR (at −10 °C) δ 14.61 (qt, J = 127.5 and 2.8 Hz), 59.83 (tq, J = 146.2 and 4.5 Hz), 106.72 (dt, J = 176.7 and 4.5 Hz), 114.72 (q, J = 36.8 Hz), 119.83 (q, J = 286.9 Hz), 128.52 (t, J = 7.3 Hz), 128.90 (dd, J = 162.4 and 7.2 Hz), 128.38 (d, J = 163.0 Hz), 131.69 (dt, J = 161.3 and 7.3 Hz).

Reduction of Ozonide 7f. Solutions containing 40 mg of either *cis*-7f or *trans*-7f in 0.3 mL of $CDCl_3$ were admixed with 0.1 mL of $CDCl_3$ solutions containing triphenylphosphine and kept in an NMR tube at rt for 15 h and 2 d, respectively. ^{1}H NMR analysis showed in each case the presence of **6b** (δ 1.37, t, J = 7.15 Hz; 4.39, q, J = 7.16 Hz) and of benzaldehyde (**9**) (δ 10.03, s) in a molar ratio of ca. 1:1.

(b) Ozonolysis in Pentane. A solution of 1.18 g (5.46 mmol) of **11a** in 80 mL of pentane was ozonized at −75 °C. The solvent was evaporated at rt and 13 Torr to leave 1.1 g of a residue. ^{1}H NMR analysis showed the presence of 10% of *cis*-7f (δ 6.32, s), 74% of *trans*-7f (δ 6.42, s), 8% of *cis*-10 (δ 6.33, s), and 8% of *trans*-10 (δ 6.36, s). Separation by column chromatography (conditions as above) gave 14 mg (1%) of *cis*-7f, 145 mg (10%) of *trans*-7f, and 84 mg of a mixture consisting of *cis*-7f, *cis*-10, and *trans*-10 in a ratio of 1:4:5.

Ozonolysis of 11b. (a) Ozonolysis on Polyethylene. A 0.30-g (1.67-mmol) sample of **11b**[11] on 24 g of polyethylene was ozonized at −75 °C for 2 h, and the products were worked up as described above for **11a** to leave 190 mg of a residue. ^{1}H NMR analysis showed the presence of **12** (65%, δ 4.85, d, J = 47.11 Hz), **9** (23%; δ 10.02, s), and benzoic acid (12%).

(b) Ozonolysis in Pentane. A solution of 150 mg (0.83 mmol) of **11b** in 40 mL of pentane was ozonized at −75 °C, and the product was worked up as described above for **11a** to leave 127 mg of a residue. ^{1}H NMR analysis showed the presence of **12** (65%), *cis*-**10** (10%), *trans*-**10** (12%), **13** (8%; δ 6.93, s) and **9** (5%). Separation by column chromatography (column 3 × 60 cm; 20 g of silica gel; pentane/ether, 20:1) gave 42.4 mg (48%) of **12** (δ 1.32, t, J = 7.15 Hz, 3 H; 4.29, q, J = 7.15 Hz, 2 H; 4.85, d, J = 47.11 Hz, 2 H), 25 mg (13%) of a 3:7 mixture of *cis*-**10** (δ 6.33, s) and *trans*-**10** (δ 6.36, s), 6 mg (3%) of **13** (mp 201–202 °C; δ 6.93, s, 2 H; 7.40–7.54, m, 10 H), and 3 mg (4%) of **9** (δ 7.47–7.67, m, 3 H; 7.88–7.90, m, 2 H; 10.02, s, 1 H).

Acknowledgment. Masatomo Nojima thanks the Deutscher Akademischer Austauschdienst for a travel grant and Woo-Sun Kim and Karl Griesbaum are grateful to the Deutsche Forschungsgemeinschaft for financial support and for a travel grant.

Registry No. **1a**, 109-92-2; **1b**, 4747-15-3; **1c**, 66051-10-3; **1d**, 120872-41-5; **1e**, 19096-89-0; **4a**, 90150-47-3; **5a**, 97674-27-6; **6a**, 431-47-0; **6b**, 383-63-1; **6c**, 598-99-2; **7a**, 140928-35-4; **7b** (isomer 1), 140928-36-5; **7b** (isomer 2), 140928-44-5; **7c**, 140928-37-6; **7d**, 140928-38-7; **7f**-*trans*, 140928-39-8; **7f**-*cis*, 140928-40-1; **7a** (isomer 1), 140928-41-2; **7a** (isomer 2), 140928-45-6; **7h**, 140928-42-3; **7i**, 140928-43-4; **8**, 183-84-6; **9**, 100-52-7; *cis*-**10**, 21072-45-7; *trans*-**10**, 21072-46-8; **11a**, 5942-75-6; **11b**, 6043-54-5; **12**, 459-72-3; **13**, 16204-37-8; $PhCO_2H$, 65-85-0.

Asymmetric Type-II Photocyclization of Acrylylureas

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Received December 30, 1991

Type-II photocyclization is an important and well-studied photochemical reaction.[1] An asymmetric version of this type of reaction in the crystalline state is quite remarkable.[2] Yet in solution, there has been no conclusive results on asymmetric type-II cyclization. Some preliminary investigations on asymmetric type-II photocyclization of chiral ketones bearing asymmetric centers on γ-positions were carried out in solution.[3]

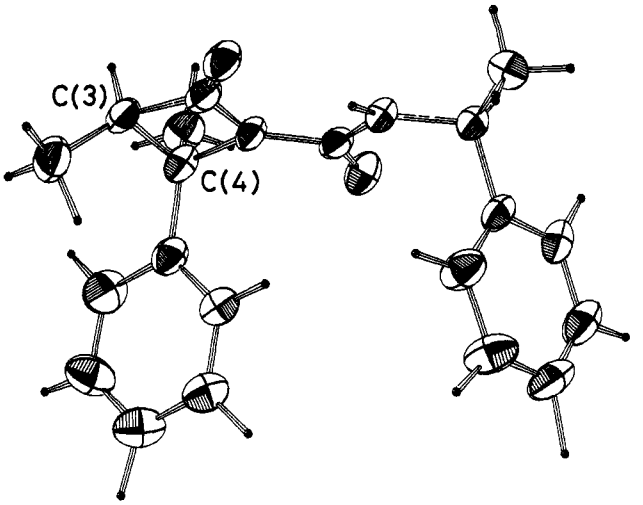

Figure 1. ORTEP view of **2a**.

In order to have a better understanding of the mechanism of type-II photocyclization in solution, and also to achieve a complete retention of the original configuration of the γ-carbon atom after cyclization, we designed photocyclization of acrylylureas **1a–11**[4] bearing two chiral (1-phenylethyl)amino groups. One of the chiral centers connected to the imido nitrogen atom is for the reaction site, the attached hydrogen to this chiral center will be abstracted by the excited enone double bond, and the remaining chiral 1-phenylethylamino group is for determination of the absolute configuration of the photoproducts.

As reported for α,β-unsaturated amides, photocyclization gave 2-azetidinones.[5] The cyclization was efficiently sensitized by benzophenone or *p*-methoxyacetophenone in benzene externally irradiated in a Pyrex test tube by a 450-W high-pressure mercury lamp under bubbling of

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