(racemic sulfoxide); mp 74.5 °C (pure *S* enantiomer); $[\alpha]^{27}_D = -54°$ (*c* 1.98, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.40 (s, 3 H), 2.69 (s, 3 H), 7.28–7.55 (AA'BB'm, 4 H); ^1H NMR analysis with the chiral shift reagent, (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol indicated the sulfoxide to be enriched in the *S* enantiomer (i.e., 30% ee).

Preparation of 1-Chloroalkyl Hydroperoxides by the Addition of Hydrogen Chloride to Carbonyl Oxides

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Carbonyl oxides, formed as intermediates in ozonolysis, are well-known to react with "participating solvents" such as water, alcohols, hydrogen peroxide, alkyl hydroperoxides, carboxylic acids, ammonia, amines, and hydrogen cyanide to yield α-heteroatom-substituted hydroperoxides.[1] We have previously made 1,1-dichloroalkyl hydroperoxides by the addition of anhydrous hydrogen chloride to α-chlorinated carbonyl oxides.[2,3] We report here the first examples of 1-chloroalkyl hydroperoxides, prepared by the analogous addition of HCl to carbonyl oxides that do not already have an α-chlorine atom.

The lack of selectivity in the cleavage of the primary ozonide from unsymmetrical olefins and the formation of a highly reactive aldehyde or ketone alongside the desired carbonyl oxide would be disadvantageous in attempts to obtain the title compounds selectively. We prepared the 1,1-dichloroalkyl hydroperoxides from symmetrical double-bond-dichlorinated olefins; the byproduct, an acid chloride, reacted slowly enough with the hydroperoxides that it could be stripped out of the mixture after the reaction. In general it is possible to obtain carbonyl oxides selectively from unsymmetrical olefins when one double-bond carbon has an electron-withdrawing substituent such as a halogen or an alkoxy group (eq 1). If there is a

$$R^1R^2C{=}CClR^3 + O_3 \rightarrow \underset{\mathbf{1}}{R^1R^2C^+OO^-} + R^3COCl \quad (1)$$

chlorine atom on C-1 of a terminal olefin, there is the additional advantage that the acid chloride is formyl chloride, which rapidly decomposes into carbon monoxide and hydrogen chloride. This is the strategy that we have used in the present work to examine the reaction of HCl with a number of carbonyl oxides, most of which have no electronegative substituent in the α position.

In Tables I and II we show the olefins that we have subjected to ozonolysis in methyl formate in the presence of HCl and the carbonyl oxides presumed to be intermediates in the reactions. Table I has the carbonyl oxides that were found to add HCl, and Table II those that did not do so. Carbonyl oxides **1a–e** are clearly formed under these conditions and readily add HCl (eq 2).

$$1 + HCl \rightarrow \underset{\mathbf{2}}{R^1R^2CClOOH} \quad (2)$$

Hydroperoxide **2b** proved to be stable enough to be distilled and to give fair elemental analyses. This stability is comparable with that of the analogous α-methoxy hydroperoxide $ClCH_2CH(OCH_3)OOH$, which has been described by others.[4] The β-brominated hydroperoxide **2c** was not distilled, but it was similarly stable. The methoxy and acetoxy analogues **2d** and **2e** were more labile; thus, although some NMR samples of **2d** were unchanged after 1 h at 35 °C, others decomposed with the evolution of considerable heat when allowed to warm above 0 °C.

The lower part of Table I shows some chlorinated hydroperoxides that have previously been reported (**2g–i**) and one (**2f**) made in this study, in all of which the carbonyl oxide already has an α-chlorine substituent.

The yield of trichloromethyl hydroperoxide (**2g**) is unknown; since the ozonolysis of C_2Cl_4 is very slow, the alternative preparation of **2g** by light-induced oxidation of chloroform is preferable.[5] Nevertheless, the known ester $CCl_3OOCOCH_3$ was prepared in detectible amounts by prolonged treatment of C_2Cl_4 with ozone in the presence of HCl and acetyl chloride; it was identified by comparison with authentic material.[5]

Except for the simplest carbonyl oxide, **1a**, all those so far found to add HCl have electron-withdrawing groups in either the α or the β position. That this is not a sufficient criterion, however, is attested by the failure of carbonyl oxide **1m** to produce $C_6H_5CCl_2OOH$. It is uncertain just how the failure occurs in this example: in the formation of **1m**, in the addition of HCl, or in some instability of the hydroperoxide once formed.

In some of the other cases, the course of the reaction was clearer. Thus, ozonolysis of 1-methoxycyclopentene gave the same products (polymers) with HCl as without.[6] This appeared also to be the case for β-bromostyrene (benzaldehyde and diphenyltetroxane as the main products). Ozonolysis of two olefins that are expected to yield the carbonyl oxide $(CH_3)_2C^+OO^-$ (**1k**) failed to give any evidence for the formation of $(CH_3)_2CClOOH$ (**2k**). Instead, the major product was acetone peroxide (the cyclic dimer or trimer of **1k**). In this context it must be mentioned that other workers, carrying out the ozonolysis of 2-methyl-3-chloro-2-butene on the surface of polyethylene, found evidence from NMR spectra and product studies for the formation of the acetate ester of hydroperoxide **2k**.[7] It was suggested that the ester arose by rearrangement of the normal ozonide; in contrast to the esters of the 1,1-dichloroalkyl hydroperoxides we have previously described, however, it was both thermally and chemically unstable, reacting spontaneously with either water or silica gel. If hydroperoxide **2k** is equally sensitive, it may well not have survived our reaction conditions.

The only α-chlorinated hydroperoxides that we have been able to acetylate with acetyl chloride are **2g–i**, and all of the esters have been described previously.[2,3,5,8] The failure of the others to yield acetates cannot in all cases be due to instability of the hydroperoxides: **2b**, for example, is stable for days in acetyl chloride at 4 °C. This resistance toward acetylation with acetyl chloride is particularly surprising in light of the fact that 1,1-dichloroethyl hydroperoxide was readily acetylated in good yield when allowed to stand in acetyl chloride.[3]

These results led us to question the assigned structures, but the spectroscopic evidence for them is strong (the

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Table I. Carbonyl Oxides Giving Hydroperoxides with HCl

starting olefin	carbonyl oxide	hydroperoxide
CH_2=CHCl	**1a**, CH_2OO	**2a**, $ClCH_2OOH$
$ClCH_2CH$=CHCl	**1b**, $ClCH_2CHOO$	**2b**, $ClCH_2CHClOOH$
$BrCH_2CH$=CHCl	**1c**, $BrCH_2CHOO$	**2c**, $BrCH_2CHClOOH$
CH_3OCH_2CH=CHCl	**1d**, CH_3OCH_2CHOO	**2d**, $CH_3OCH_2CHClOOH$
CH_3COOCH_2CH=CHCl	**1e**, CH_3COOCH_2CHOO	**2e**, $CH_3COOCH_2CHClOOH$
CHCl=CHCl	**1f**, ClCHOO	**2f**, Cl_2CHOOH
CCl_2=CCl_2	**1g**, Cl_2COO	**2g**, Cl_3COOH
CH_3CCl=$CClCH_3$	**1h**, CH_3CClOO	**2h**, CH_3CCl_2OOH
C_2H_5CCl=$CClC_2H_5$	**1i**, C_2H_5CClOO	**2i**, $C_2H_5CCl_2OOH$

Table II. Carbonyl Oxides Not Giving Hydroperoxides with HCl

starting olefin	presumed carbonyl oxide
CH_3CH=CHCl	**1j**, CH_3CHOO
$(CH_3)_2C$=CHCl	**1k**, $(CH_3)_2COO$
$(CH_3)_2C$=$CClCH_3$	**1k**, $(CH_3)_2COO$
C_6H_5CH=CHBr	**1l**, C_6H_5CHOO
C_6H_5CCl=$CClC_6H_5$	**1m**, C_6H_5CClOO
1-CH_3O-c-C_5H_7	**1n**, $CH_3OCO(CH_2)_3CHOO$

infrared spectrum of **2b**, for example, has an OH-stretch absorption at 3510 cm^{-1}, and in most cases the OH proton was visible in the ^1H NMR spectrum); we have also been able to confirm the presence of the hydroperoxide group by another derivatization. Apparently the reaction of the hydroperoxides **2a–e** with acetyl chloride is very slow, and any ester formed is too unstable to be detected.

Thus, introduction of gaseous formaldehyde into a solution of the hydroperoxide **2b** leads to the formation of **3b**, a rather stable substance. Analogous addition products were prepared from **2a** and **2c–f** (eq 3). The addition of aldehydes to hydroperoxides is an established reaction, and in a number of cases the products are at least as stable as the hydroperoxides themselves.[4,9]

$$\mathbf{2} + HCHO \rightarrow \underset{\mathbf{3}}{R^1R^2CClOOCH_2OH} \quad (3)$$

$$\mathbf{3} + AcCl \rightarrow \underset{\mathbf{4}}{R^1R^2CClOOCH_2OAc} + HCl \quad (4)$$

There are a few reports in the literature of the esterification of such addition products.[10] Treatment of compounds **3a–d,f** with acetyl chloride yields the acetate esters **4a–d,f** (eq 4). Acetyl chloride reacted with **3g** to give the ester of **2g**, not **3g**. One product from the attempted acetylation of **3e** appeared from the NMR spectra to be the expected ester **4e**, but after distillation it was found to contain only trace amounts of chlorine. Attempts to increase the yields of the esters by adding bases led to decomposition of the peroxides. This is expected, since the hydroperoxide–aldehyde addition products are known to be unstable toward base.[11]

The ^1H and ^{13}C NMR spectra of compounds **2b–e**, **3b–e**, and **4b–d** form a self-consistent set. The proton of the CHCl group resonates at ca. δ 6.1 and is coupled differently to the diastereotopic protons of the neighboring CH_2 group; it is little affected by the addition of formaldehyde. The carbon of the CHCl group falls in the narrow range δ 93.6–96.5 in **2b–e** and experiences a small γ shift in **3b–e** and **4b–d**. Most distinctive is $^1J_{CH}$ of this carbon, which is consistently 178–183 Hz. We are not aware of any ^{13}C NMR spectra in the literature for formaldehyde-addition products of hydroperoxides. The OCH_2O carbon at δ 92.4–93.0 falls near the range of the CHCl carbons in **3b–e**, but it is readily distinguished by both its multiplicity and its lower $^1J_{CH}$ (166–167 Hz); on esterification it experiences a small upfield shift, and its coupling constant increases to 171 Hz. The protons of the OCH_2O group exhibit the expected downfield shift (ca. 0.5 ppm) on esterification. These chemical-shift and coupling-constant effects are almost identical with those shown by the mono- and diacetates (**6** and **7**) of bis(hydroxymethyl) peroxide (**5**), which were made for comparison.

The resonance of the $CHCl_2$ proton in **2f** may easily be overlooked, since it is nearly (sometimes exactly) the same as that of chloroform. The $^1J_{CH}$ value of 205 Hz in **2f** is also remarkably close to that of chloroform at 208 Hz.[12]

Experimental Section

All chemicals and solvents were from Merck, Darmstadt, Federal Republic of Germany. 1,3-Dichloropropene (DCP) was a mixture of the cis and trans isomers. Ozone was generated with a Fischer Model 502 generator, and the mixture of HCl and O_3 gases was made by adding HCl from a lecture bottle to the O_3 stream through a T-connector. Elemental compositions and molecular weights (MW) by vapor pressure osmometry (VPO) were determined by the laboratory of F. Pascher, Remagen-Bandorf, Federal Republic of Germany. Molecular weights by cryoscopy (cry) in benzene were determined with an apparatus from Knauer, Oberursel, Federal Republic of Germany. NMR spectra were made in $CDCl_3$ solution on a Varian CFT-20 (^{13}C), its 80-MHz modification (^1H) or a Perkin-Elmer R32 (90-MHz ^1H). IR spectra were made of CCl_4 solutions on a Perkin-Elmer Model 577 spectrometer. GCMS spectra were made on a Hewlett-Packard Model 5995A.

1-Chloro-3-methoxypropene (ca. 1:1 cis/trans mixture) was prepared by methanolysis of DCP.[13] 1-Chloro-3-acetoxypropene (cis/trans) was made by treating DCP with NaOAc, not in ethanol, as in the literature,[14] but in AcOH. 1-Chloro-3-hydroxypropene[15] (cis/trans) was prepared by basic hydrolysis of the acetate. 1-Chloro-3-bromopropene (cis/trans) was prepared from the alcohol by a procedure described for allenyl alcohols.[16] The NMR spectra indicated up to 25% of the starting alcohol as an impurity.

1,2-Dichloroethyl Hydroperoxide (2b). A solution of 5.0 g (45.1 mmol) of DCP in 100 mL of dry methyl formate was saturated with anhydrous hydrogen chloride at −10 °C and treated with a stream of ozone and hydrogen chloride until it became blue (ca. 75 min). Removal of solvent under vacuum at 0 °C left an oil that could be distilled (25 °C, 0.3 Torr) to yield 2.51 g (42.5%). Active oxygen (iodometric in acetic acid): 11.25%, calcd 12.22%. Elemental Anal. Calcd for $C_2H_4Cl_2O_2$ (MW 130.95): C, 18.34; H, 3.08; O, 24.43; Cl, 54.14. Found: C, 18.22; H, 3.54; O, 25.6; Cl, 50.3. MW: found (cry) 142; (VPO) 269. ^1H NMR: δ 9.0 (br, OH), 6.09 (dd, J = 8.1, 4.2 Hz, CHCl), 3.85 (dd, J = 11.5, 8.1 Hz,

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H-2α), 3.72 (dd, J = 11.5, 4.2 Hz, H-2β). ^{13}C NMR: 96.3 (J_{CH} = 181 Hz, CHCl), 43.6 (J_{CH} = 156 Hz, CH_2Cl). IR: strong absorptions at 3510, 1430, 1355, 1182, 1100, 1042, and 700 cm^{-1}.

The other hydroperoxides were prepared similarly, but at −20 °C.

Chloromethyl Hydroperoxide (2a). ^1H NMR: δ 7.5 (br s, OH), 5.80 (s, CH_2Cl). ^{13}C NMR: δ 85.7 (J_{CH} = 176 Hz).

1-Chloro-2-bromoethyl Hydroperoxide (2c). ^1H NMR: δ 8.9 (br s, OH), 6.08 (dd, J = 8.1, 4.2 Hz, CHCl), 3.85 (dd, J = 11.5, 8.1 Hz, H-2α), 3.69 (dd, J = 11.5, 4.3 Hz, H-2β). ^{13}C NMR: δ 95.8 (J_{CH} = 182 Hz, CHCl), 30.3 (J_{CH} = 157 Hz, CH_2Br).

1-Chloro-2-methoxyethyl Hydroperoxide (2d). ^1H NMR: δ 8.5 (br, OH), 6.08 (dd, J = 6.6, 4.7 Hz, CHCl), 3.80 (dd, J = 11.8, 6.8 Hz, H-2α), 3.76 (dd, J = 11.7, 4.7 Hz, H-2β), 3.45 (s, OCH_3). ^{13}C NMR: δ 96.2 (J_{CH} = 180 Hz, CHCl), 72.7 (J_{CH} = 151 Hz, $MeOCH_2$), 59.7 (J_{CH} = 143 Hz, OCH_3).

1-Chloro-2-acetoxyethyl Hydroperoxide (2e). ^1H NMR: δ 8.5 (br s, OH), 6.05 (dd, J = 7.8, 4.0 Hz, CHCl), 4.57 (dd, J = 12.3, 7.8 Hz, H-2α), 4.34 (dd, J = 12.4, 4.0 Hz, H-2β), 2.13 (CH_3). ^{13}C NMR: δ 171.6 (C=O), 95.0 (J_{CH} = 178 Hz, CHCl), 63.9 (J_{CH} = 153 Hz, $AcOCH_2$), 20.6 (J_{CH} = 130 Hz, CH_3).

Dichloromethyl Hydroperoxide (2f). ^1H NMR: δ 9.0 (br s, OH), 7.27 (s, $CHCl_2$). ^{13}C NMR: δ 99.5 (J_{CH} = 205 Hz).

1,2-Dichloroethyl Hydroxymethyl Peroxide (3b). Hydroperoxide **2b** was prepared as above from 1.0 g of technical DCP, and the solvent was removed under vacuum. The oil was redissolved in 25 mL of CH_2Cl_2 and cooled to 0 °C. Formaldehyde was generated by slowly warming 0.5 g of paraformaldehyde in a small flask with a flame. A stream of N_2 was passed through this flask and into the solution of hydroperoxide until all the paraformaldehyde had volatilized. This took about half an hour. After another half hour at 0 °C, the solvent was removed under vacuum. From a ^{13}C NMR spectrum the purity of the product was estimated at ca. 80%. It could be chromatographed on silica gel with 20% ethyl acetate in $CHCl_3$, but the purity was not improved. On attempted distillation under vacuum, the product decomposed with evolution of a gas. ^1H NMR: δ 6.1 (dd, J = 3–4, 6–7 Hz, CHCl), 5.28 (s, OCH_2O), 4.5 (br, OH), 3.6–4.1 (m, CH_2Cl). ^{13}C NMR: δ 95.1 (J_{CH} = 183 Hz, CHCl), 93.1 (J_{CH} = 167 Hz, OCH_2O), 44.2 (J_{CH} = 157 Hz, CH_2Cl). IR: strong absorptions at 3600, 1430, 1180, and 700 cm^{-1} as well as a group of absorptions between 950 and 1110 cm^{-1}.

The addition of formaldehyde to the other hydroperoxides was carried out at −20 °C.

Chloromethyl Hydroxymethyl Hydroperoxide (3a). ^1H NMR: δ 5.84 (t, J = 1.0 Hz, CH_2Cl), 5.24 (t, J = 1.0 Hz, OCH_2O), OH proton not observed. ^{13}C NMR: δ 92.9 (J_{CH} = 167 Hz, OCH_2O), 83.6 (J_{CH} = 177 Hz, CH_2Cl).

1-Chloro-2-bromoethyl Hydroxymethyl Peroxide (3c). ^1H NMR: δ 6.15 (dd, J = 8.0, 4.5, CHCl), 5.28 (br s, J = 0.7 Hz, OCH_2O), 3.82 (dd, J = 11.5, 8.0 Hz, H-2α), 3.70 (dd, J = 11.5, 4.6 Hz, H-2β), OH proton not observed. ^{13}C NMR: δ 94.1 (J_{CH} = 183 Hz, CHCl), 92.5 (J_{CH} = 166 Hz, OCH_2O), 30.7 (J_{CH} = 157 Hz, CH_2Br).

1-Chloro-2-methoxyethyl hydroxymethyl peroxide (3d) was obtained as a mixture with **2d**. ^1H NMR: δ 8.35 (br s, OH), 6.18 (m, CHCl), 5.25 (d, J = 0.9 Hz, OCH_2O), 3.6–4.0 (m, $MeOCH_2$), 3.46 (s, CH_3O). ^{13}C NMR: δ 94.3 (J_{CH} = 180 Hz, CHCl), 92.4 (J_{CH} = 166 Hz, OCH_2O), 73.1 (J_{CH} = 146 Hz, $MeOCH_2$), 59.5 (J_{CH} = 143 Hz, CH_3O).

1-Chloro-2-acetoxyethyl Hydroxymethyl Hydroperoxide (3e). ^{13}C NMR: δ 170.9 (C=O), 93.6 (J_{CH} = 181 Hz, CHCl), 93.0 (J_{CH} = 166 Hz, OCH_2O), 64.1 (J_{CH} = 153 Hz, $AcOCH_2$), 20.6 (J_{CH} = 130 Hz, CH_3).

Dichloromethyl hydroxymethyl hydroperoxide (3f) was not obtained pure; the NMR spectrum was poorly resolved. ^1H NMR: δ 7.31 (s, $CHCl_2$), 5.93 (br s, OH), 5.34 (s, OCH_2O).

Trichloromethyl Hydroxymethyl Peroxide (3g). ^1H NMR: δ 5.45 (s, OCH_2O), 3.6 (br s, OH). ^{13}C NMR δ 113.7 (CCl_3), 93.6 (J_{CH} = 168 Hz, OCH_2O).

1,2-Dichloroethyl Acetoxymethyl Peroxide (4b). The peroxide **3b** was prepared as above from 0.50 g of DCP, but not chromatographed. Stripped of solvent, it was redissolved in 5 mL of acetyl chloride and held at 7 °C for 3 h. The volatiles were removed at aspirator vacuum, and the residual oil was chromatographed on silica gel with a 1:1 mixture of hexane and $CHCl_3$. The combined peroxide fractions (0.56 g, 62%) were distilled in a miniature sublimator to yield a few drops for analyses. Anal. Calcd for $C_5H_8Cl_2O_4$ (MW 203.00): C, 29.58; H, 3.96; O, 31.53; Cl, 34.93. Found: C, 29.24; H, 4.01; O, 32.1; Cl, 34.3. MW (cry): found 197. ^1H NMR: δ 6.04 (dd, J = 8, 4.5 Hz, CHCl), 5.72 (s, OCH_2O), 3.90 (dd, J = 12, 8 Hz, H-2α), 3.80 (dd, J = 12, 4.5 Hz, H-2β), 2.13 (s, CH_3). ^{13}C NMR: δ 169.8 (C=O), 94.7 (J_{CH} = 182 Hz, CHCl), 89.8 (J_{CH} = 171 Hz, OCH_2O), 43.9 (J_{CH} = 154, CH_2Cl), 20.9 (J_{CH} = 130 Hz, CH_3). IR: strong absorptions at 1770, 1210, and 1000–1035 cm^{-1}. GCMS: m/e 107/109, 77/79 (base peak), 73, and 49/51.

The other esters were prepared similarly.

Chloromethyl Acetoxymethyl Peroxide (4a). Anal. Calcd for $C_4H_7ClO_4$ (MW 154.55): C, 31.08; H, 4.57; O, 41.41; Cl, 22.94. Found: C, 31.01; H, 4.59; O, 41.3; Cl, 22.9. MW (cry) 164; (VPO) 180. ^1H NMR: δ 5.78 (t, J = 1.0 Hz, $ClCH_2$), 5.69 (t, J = 1.0 Hz, OCH_2O), 2.15 (s, CH_3). ^{13}C NMR: δ 169.9 (C=O), 90.0 (J_{CH} = 171 Hz, OCH_2O), 83.1 (J_{CH} = 176, $ClCH_2$), 20.9 (J_{CH} = 130 Hz, CH_3). IR: strong absorptions at 1760, 1210, and 1010 cm^{-1} and moderate ones at 1365, 1305 and 685 cm^{-1}.

1-Chloro-2-bromoethyl Acetoxymethyl Peroxide (4c). Anal. Calcd for $C_5H_8ClBrO_4$ (MW 247.44): C, 24.27; H, 3.25; O, 25.86; Cl, 14.33; Br, 32.29. Found: C, 24.08; H, 3.28; O, 25.9; Cl, 14.4; Br, 32.2; MW (cry) 250. ^1H NMR: δ 6.09 (ddt, J = 8.1, 4.6, 0.8 Hz, CHCl), 5.72 (t, J = 0.8 Hz, OCH_2O), 3.75 (dd, J = 11.5, 8.1 Hz, H-2α), 3.70 (dd, J = 11.5, 4.6 Hz, H-2β), 2.15 (s, CH_3). ^{13}C NMR: δ 169.7 (C=O), 94.3 (J_{CH} = 183 Hz, CHCl), 89.8 (J_{CH} = 171 Hz, OCH_2O), 30.4 (J_{CH} = 157 Hz, $BrCH_2$), 20.9 (J_{CH} = 130 Hz, CH_3). IR: strong absorptions at 1765, 1207, and 1000 cm^{-1}.

1-Chloro-2-methoxyethyl Acetoxymethyl Peroxide (4d). Anal. Calcd for $C_6H_{11}ClO_5$ (MW 198.61): C, 36.28; H, 5.58; O, 40.28; Cl, 17.85. Found: C, 36.30; H, 5.74; O, 41.1, Cl, 17.2; MW (cry) 198. ^1H NMR: δ 6.09 (ddt, J = 6.5, 5.3, 0.6 Hz, CHCl), 5.71 (t, J = 0.5 Hz, OCH_2O), 3.73 (m, H-2α,β), 3.42 (s, CH_3O), 2.13 (s, CH_3). ^{13}C NMR: δ 169.9 (C=O), 95.0 (J_{CH} = 180 Hz, CHCl), 89.9 (J_{CH} = 171 Hz, OCH_2O), 73.5 (J_{CH} = 146 Hz, OCH_2C), 59.6 (J_{CH} = 140 Hz, CH_3O), 20.9 (J_{CH} = 126, CH_3).

Dichloromethyl Acetoxymethyl Peroxide (4f) (containing AcOH and unidentified products). ^1H NMR: δ 7.29 (t, J = 1.1 Hz, $CHCl_2$), 5.77 (d, J = 1.1 Hz, OCH_2O), 2.15 (s, CH_3). ^{13}C NMR: δ 169.7 (C=O), 97.4 (J_{CH} = 205 Hz, $CHCl_2$), 90.0 (J_{CH} = 171 Hz, OCH_2O), 20.7 or 20.8 (J_{CH} = 130 Hz, CH_3).

Caution. *Bis(hydroxymethyl) peroxide is reported to be extremely explosive,*[17] *and the acetate ester of trichloromethyl hydroperoxide has caused several explosions in our laboratory. The new compounds reported here should be assumed to be both explosive and toxic.*

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Registry No. **1a**, 78894-19-6; **1b**, 138434-04-5; **1c**, 138434-05-6; **1d**, 138434-06-7; **1e**, 138434-07-8; **1f**, 138434-08-9; **1j**, 68941-70-8; **1k**, 65339-02-8; **1l**, 138458-85-2; **1m**, 138458-86-3; **1n**, 138434-17-0; **2a**, 138434-09-0; **2b**, 138434-10-3; **2c**, 138434-11-4; **2d**, 138434-12-5; **2e**, 138434-13-6; **2f**, 138434-14-7; **2g**, 94089-33-5; **3a**, 40323-32-8; **3b**, 138434-18-1; **3d**, 138434-20-5; **3e**, 138434-21-6; **3f**, 138434-22-7; **3g**, 138434-23-8; **4a**, 138434-24-9; **4b**, 138434-25-0; **4c**, 138434-26-1; **4d**, 138434-27-2; **4**, 138434-28-3; **6**, 138434-29-4; **7**, 22721-77-3; **8a**, 138434-30-7; **8f**, 138434-31-8; **9**, 764-41-0; **10**, 138434-32-9; DCP, 542-75-6; CH_2=CHCl, 75-01-4; $BrCH_2CH$=CHCl, 3737-00-6; CH_3OCH_2CH=CHCl, 2806-79-3; CH_3COOCH_2CH=CHCl, 13042-00-7; CHCl=CHCl, 540-59-0; CH_3CH=CHCl, 590-21-6; $(CH_3)_2C$=CHCl, 513-37-1; $(CH_3)_2C$=$CClCH_3$, 17773-65-8; C_6H_5CH=CHBr, 103-64-0; C_6H_5CCl=$CClC_6H_5$, 13700-82-8; 1-CH_3O-c-C_5H_7, 1072-59-9.

Supplementary Material Available: ^1H and ^{13}C NMR resonances of 1-chloro-3-methoxypropene, 1-chloro-3-acetoxypropene, 1-chloro-3-hydroxypropene, and 1-chloro-3-bromopropene; tabulated long-range ^{13}C–^1H coupling constants for **2a,b**, **3a,b**, **4a,b**; preparation and tabulated NMR spectra of **6** and **7**; a discussion of the formation and NMR spectra of chloromethyl hydroperoxymethyl peroxide (**8a**) and dichloromethyl chloro-

(17) Wieland, H.; Sutter, H. *Chem. Ber.* **1930**, *63*, 66.

hydroperoxymethyl peroxide (8f); a discussion of the ozonolysis of 1,4-dichloro-2-butene (9) in the presence of HCl to yield 1,2-dichloroethyl 1'-hydroxy-2'-chloroethyl peroxide (10); ^{1}H NMR spectra of **2a** + **8a**, **2b–e**, **2f**, **3a–d,f,g**, **4a,b,d**, and **6**; ^{13}C NMR spectra of **2a** + **8a**, **2b–f**, **3a–d,g**, **4a,b,d,f**, and **6**; and IR spectra of **2b**, **3b**, and **4b** (42 pages). Ordering information is given on any current masthead page.

Practical Synthesis of an Enantiomerically Pure Intermediate of the Lactone Moiety of Mevinic Acids

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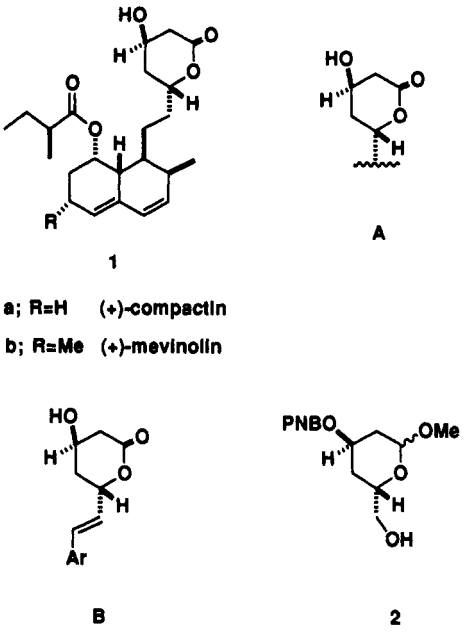
Since the recognition of hypercholesterolemia as a risk factor of atherosclerosis and coronary heart disease,[1] there have been multiple efforts to identify chemical entities capable of regulating the plasma level of this sterol.[2] Mevinic acids[3] are part of a family of fungal metabolites that have attracted considerable attention due to their biological activities as inhibitors of 3-hydroxy-3-methylglutaryl coenzyme A (HMG-CoA) reductase, the rate-limiting enzyme in cholesterogenesis in man.[4,5] Compactin[6] (**1a**) and mevinolin[4b,7] (**1b**) (Chart I) are two prominent members of this family of clinically useful hypocholesterolemic agents. The key structural feature common to all mevinic acids[3] is the β-hydroxyvalerolactone function A which, in its open form, closely mimics mevalonic acid, a crucial intermediate in the terpenoid biosynthetic pathway leading to cholesterol.

Structure–activity relationships in previous series revealed[8] that the chiral lactone moiety, A, is essential for strong biological activity, whereas the hexahydronaphthalene half allows more structural variations. Recent reports[9] on the discovery of active analogues, B, which retain the lactone portion of mevinic acids have increased the potential interest of enantiospecific routes to suitable chirons.[10]

Chart I



In view of the nature of the lactone portion, a number of syntheses involved starting materials derived from carbohydrates.[11] Shorter chains derived from chiral, nonracemic hydroxy acids and similar sources have also been used.[12] The lactone moiety has also been constructed by employing a hetero-Diels–Alder approach, a protocol extensively investigated by Danishefsky and co-workers.[13]

A practical approach to incorporate the key chiral hydroxy lactone portion A in the synthesis of the natural compounds **1a,1b** or the analogues B is to employ the masked lactols as precursors of electrophilic species. Consequently, the synthesis of multigram amounts of methyl 2,4-dideoxy-3,6-bis(*O*-*p*-nitrobenzoyl)-D-*erythro*-hexopyranosides **2** from D-glucose using a few simple and high yielding steps is of considerable interest.

2,3:5,6-di-*O*-isopropylidene-D-glucose diethyl dithioacetal (**3**) is readily available from D-glucose using standard methods.[14,15] Compound **3** (Scheme I) was transformed

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(14) Compound **3** has been previously prepared (75% yield) by reaction of D-glucose diethyldithioacetal and 4 equiv of 2-methoxypropene (Grindley, T. B.; Wickramage, Ch. *Carbohydr. Res.* **1987**, *167*, 105). In our hands, the simplest manner to carry out this operation was to dissolve the crude dithioacetal[15] in acetone. Allowing the solution to stand for 5–6 h at rt affords the required diacetonide **3**, certainly due to the presence of residual acid from the previous step acting as a catalyst.

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