Hydroperoxides are important reagents in organic synthesis and play a considerable role as intermediates in industrial processes. Thus tert-butylhydroperoxide is extensively used in Sharpless epoxidations\(^1\) of allylic alcohols and in the production of propylene oxide by the oxirane process.\(^2\) Nowadays the industrial synthesis of alcohols and in the production of propylene oxide by the oxirane process is a well-known reaction found in most basic textbooks of organic chemistry (Scheme 1). After protonation of the hydroxy group a concerted elimination of water and migration of the phenyl ring results in phenol and acetone. The same reaction sequence could also be achieved if \(\alpha,\alpha\)-dimethylbenzyl alcohol 2 was treated with hydrogen peroxide in acid medium.\(^3\)

We report here a novel outcome of the hydroperoxide rearrangement giving rise to \(\alpha\)-phenoxyhydroperoxide, geminal dihydroperoxide, and bis(hydroperoxy)-dialkylperoxide moieties. In connection with our investigation of optically active hydroperoxides\(^5\) the synthesis of racemic tertiary indane, 1,2,3,4-tetrahydroxybenzyl alcohol was approached. Instead, novel cyclic \(2\)-methylchroman-2-yl-hydroperoxide \(6\) was synthesized by Hock et al. by a laborious multistep procedure including autoxidation of the corresponding hydrocarbon.\(^6\) We try to synthesize hydroperoxides \(6\) in a direct manner by adopting the known procedure for the transformation of tertiary alcohols into corresponding hydroperoxides by treatment with aqueous hydrogen peroxide in the presence of catalytic amounts of acids.\(^7\) The starting bicyclic alcohols \(5\) can be considered as bridged analogues of \(\alpha,\alpha\)-dimethylbenzyl alcohol 2. Surprisingly, after treatment of \(5a, 5b\), or \(5c\) with hydrogen peroxide and a catalytic amount of sulfuric acid for 3 days, neither the anticipated bicyclic hydroperoxides \(6\) nor \(\alpha\)-hydroxyphenylalkyl ketones \(10\), as expected products derived from a hydroperoxide rearrangement analogous to the cumene hydroperoxide rearrangement according to Scheme 1, could be obtained. Instead, novel cyclic 2-methylchroman-2-yl-hydroperoxide \(11a\), \((\text{bis-hydroperoxy})\)-alkyl-phenols \(14\), and peroxide products presumably of structure \(15\) were obtained (Scheme 2). The structures of all products were confirmed by their spectroscopic data, and that of \(14c\) was confirmed by X-ray crystal analysis (see Figure 1).

The formation of products \(11, 14\) and \(15\) can be explained (Scheme 2) by primary substitution of the hydroxy group by hydrogen peroxide, giving rise to...
tertiary hydroperoxides, which suffer an acid-catalyzed migration of the phenyl substituent, affording a cyclic phenoxycarbenium ion. The latter add a second molecule of hydrogen peroxide to give the cyclic phenoxyhydroperoxide, which obviously is stable and was isolated as the main product in the case of the six-membered ring (route A). Seven-membered analogues could not be isolated but opened the heterocyclic ring after protonation of the ring oxygen atom. The resulting \( \text{o-hydroxyphenylalkyl-\(\text{o-hydroperoxy}\)} \) carbenium ions add a third molecule of hydrogen peroxide, generating geminal dihydroperoxides. For \( n = 2 \) not only geminal dihydroperoxides but also brown oils of limited stability were obtained, whose structure was assigned as 1:1 diastereomeric mixtures (meso-compound and racemate) of bridged bis(hydroperoxy)-dialkylperoxides by \( \text{H}^+ \) and \( \text{\(^{13}\)C NMR spectroscopy. These products could be formed by reaction of the intermediate carbenium ion with the geminal bishydroperoxide. Using the same reaction conditions for the seven-membered ring the expected tertiary hydroperoxide was obtained as main product together with some geminal dihydroperoxide. Obviously, the peroxide rearrangement by ring enlargement is hampered in this case by unfavorable eight-membered intermediates. Although semicyclic hemiacetals and \( \text{o-hydroxyphenylalkyl ketone} \), as expected products of the common hydroperoxide rearrangement in analogy to Scheme 1, were not observed, their transient appearance is not unlikely. However, as a result of their bridged structures they are in an equilibrium with the intermediate (Scheme 2). This equilibrium is continuously disturbed by irreversible transformation of into the hydroperoxide and further to bishydroperoxides until all of is consumed. The peroxides could either be formed by reaction of the bisdihydroperoxide with intermediate cations or by condensation of two molecules of under elimination of hydrogen.
Jefford et al. obtained geminal dihydroperoxides from the ketones and hydrogen peroxide. In general the hydroperoxides 5 were synthesized according to the early works of Criegee and the products were separated by column chromatography. The overall transformation of the tertiary alcohol 5 into the hydroperoxides 11, 14, and 15 represents a novel outcome of the well-known hydroperoxide rearrangement, as well as a novel route to such structural units. The extension of this method to other cyclic tertiary alcohols is currently underway.

### Experimental Section

**General.** Melting points were determined with a hot-stage apparatus and are uncorrected. 1H and 13C NMR spectra were recorded in CDCl3 at 300 and 75.5 MHz, respectively, with TMS as internal standard. Silica gel (0.04–0.063, MERCK) was used for column chromatography. Starting materials 5 and yields of products 6, 11, 14, and 15 (Table 1) are presented in a straightforward way by treatment of the alcohol 5b with hydrogen peroxide in the absence of acids. This is a preferable alternative to the hitherto known multistep procedure. So far α-alkoxyperoxide compounds were obtained from acetals and hydrogen peroxide, by autoxidation of ethers, or by ozonolysis of alkenes in the presence of aliphatic alcohols. Such structural moieties are found in potent antimalarials. Geminal dihydroperoxides are rare. They were synthesized according to the early works of Criegee and the hydroperoxide 5a is unlikely. Route B also could not account for the observed formation of 11. Finally, it is to be mentioned that the originally anticipated peroxide 6b was obtained in a straightforward way by treatment of the alcohol 5a with hydrogen peroxide in the absence of acids. This is a preferable alternative to the hitherto known multistep procedure. Recently J. efford et al. obtained geminal dihydroperoxides from ketals with hydrogen peroxides in the presence of H2SO4.

The overall transformation of the tertiary alcohol 5 into the hydroperoxides 11, 14, and 15 represents a novel outcome of the well-known hydroperoxide rearrangement, as well as a novel route to such structural units. The extension of this method to other cyclic tertiary alcohols is currently underway.

### Table 1. Starting Materials 5 and Yields of Products 6, 11, 14, and 15

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<tr>
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<th>14</th>
<th>15</th>
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<td>1a</td>
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<tr>
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<tr>
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<tr>
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<tr>
<td>7</td>
<td>Me</td>
<td>3d</td>
<td>(1:10)</td>
<td>d</td>
<td>56</td>
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</tr>
</tbody>
</table>

*In the absence of acid.*

2.22–2.28 (m, 1H), 1.80–1.84 (m, 1H), 1.62–1.70 (m, 2H), 1.37 (s, 3H); 13C NMR (75.5 MHz, CDCl3) δ = 138.9, 138.6, 129.5, 128.1, 126.8, 126.7, 83.4, 33.7, 30.3, 27.1, 20.9.

### General Procedure for Preparation of 6d, 11, 14, and 15 (Table 1): One drop of concentrated H2SO4 was added to a solution of 5 (20 mmol) in 50% aqueous hydrogen peroxide (14 mL) in a 25 mL apparatus and was stirred for 3 days. After dilution of the mixture with water (15 mL), extraction with Et2O (3 × 25 mL), and washing with saturated aqueous NaHCO3 solution and water, the organic phase was dried with (Na2SO4). The solvent was removed under vacuum, and the products were separated by column chromatography.

### Notes

Bis[1-hydroperoxy-1-ethyl-4-(2-hydroxyphenyl)-butyl]-peroxide (15c): brown oil; yield 36%; Rf (hexane/EtOAc, 7:3) 0.19; IR (film) 3400, 2946, 1456, 1179, 856, 588 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 9.52 (s, 1H), 9.51 (s, 1H), 6.96 – 7.05 (m, 4H), 6.65 – 6.79 (m, 4H), 5.46 (s, 1H), 5.37 (s, 1H), 2.57 – 2.58 (m, 4H), 1.57 – 1.76 (m, 12H), 0.80 – 0.85 (t, 6H); ¹³C NMR (75.5 MHz, CDCl₃) δ 153.6, 130.2, 130.0, 128.0, 127.9, 127.3, 127.2, 120.68, 120.66, 115.3, 115.1, 115.0, 29.8, 29.5, 28.9, 28.6, 23.6, 23.5, 22.9, 22.7, 8.0, 7.8; HRMS (LSIMS) calcd for (M⁺ + Na) 445.18384, found 445.18311

Crystal Structure Determination for Compound 14c.¹⁶
Crystals were obtained by crystallization from EtOH. A colorless crystal of 14c with the dimensions 1.20 × 0.56 × 0.40 mm³ was measured on a ST’OE IPDS diffractometer using Mo Kα radiation (λ = 0.71073 Å). Crystal data: C₁₂H₁₈O₅, MW = 242.26, orthorhombic space group P2₁2₁2₁; a = 11.749(2) Å, b = 11.931(3) Å, c = 26.770(6) Å, α = 90°, V = 3752.8(13) Å³, Z = 12, Dc = 1.286 mg/m³, F(000) = 1560, ρ(Mo Kα) = 0.100 mm⁻³. At 180(2) K in the range of 2.43° < θ < 25.25° 23321 reflections were measured (R(int) = 0.0458) of which 6770 were unique (R(int) = 0.1277). The structure was solved by direct methods and refined by least-squares procedure within the SHELX program system. The final residuals were wR2(all) = 0.0976, R1(all) = 0.0551 and R1(obs) = 0.0458. The maximum and minimum peaks in the final difmap were 0.277 and -0.255 e Å⁻³, respectively.

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