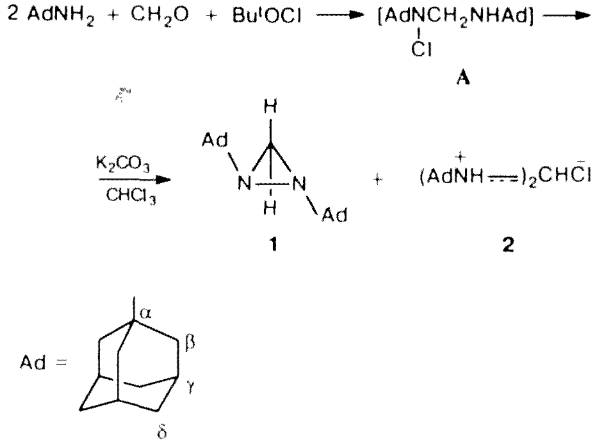

stirring to a solution of $AdNH_2$ (0.5 g, 3.3 mmol) in $CHCl_3$ (20 mL) at 0–5 °C. Then the mixture was boiled for 48 h until the characteristic signal of HN of AdNHCl at 4.05 ppm (in $CDCl_3$) disappeared from the ^1H NMR spectrum of the sample. After the separation of the precipitate and evaporation of the solvent, the residue was dissolved in $CHCl_3$ (5 mL). After 2 h (at 20 °C) precipitated crystals of product **2** (12 mg, 2.1 %) were separated. ^1H NMR ($CDCl_3$), δ: 1.68 (br.q, 12 H, δ-CH_2, AB spectrum, $\Delta\nu$ = 30.0, ^2J = −12.2 Hz), 1.85 (br.s, 12 H, β-CH_2), 2.17 (br.s, 6 H, γ-CH), 7.37 (t, 1 H, NCHN, ^3J = 12.9 Hz), 10.31 (br.d, 2 H, HN).

Product **1** was isolated from the mother liquor by chromatography on a column with silica gel (100–160 mm, eluent $CHCl_3$–CCl_4, 1 : 1). Diaziridine **1** (51 mg, 9.8 %) was obtained after two crystallizations from acetone, m.p. 195 °C, R_f = 0.38 ($CHCl_3$–CCl_4, 1 : 1). Found (%): N, 9.19. $C_{21}H_{32}N_2$. Calculated (%): N, 8.96. Partial MS (EI, 70 eV), m/z (I_{rel} (%)): 312[M]$^{+\cdot}$ (51.8), 177[M−Ad]$^+$ (6.1), 135 [Ad]$^+$ (100), 42 [M-2Ad]$^{+\cdot}$ (49.7). ^1H NMR ($CDCl_3$), δ: 1.56 (br.s, 12 H, β-CH_2), 1.59 (br.q, 12 H, δ-CH_2, AB spectrum, $\Delta\nu$ = 21.1, ^2J = −12.2 Hz), 2.04 (br.s, 6 H, γ-CH), 2.55 (s, 2 H, NCH_2N). ^{13}C NMR ($CDCl_3$): 29.41 (d, γ-C, ^1J = 132.2 Hz), 36.76 (t, δ-C, ^1J = 128.0 Hz), 39.55 (t, NCH_2N, ^1J = 173.0 Hz), 39.66 (t, β-C, ^1J = 128.0 Hz), 54.15 (s, α-C).

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References

1. R. Ohme, E. Schmitz, and P. Dolge, *Chem.Ber.*, 1966, **99**, 2104.
2. R. G. Kostyanovsky, V. A. Korneev, I. I. Chervin, V. N. Voznesensky, Yu. V. Puzanov, and P. Rademacher, *Mendeleev Commun.*, 1996, 106.

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Chlorine dioxide as a novel mild oxidant of allylic alcohols

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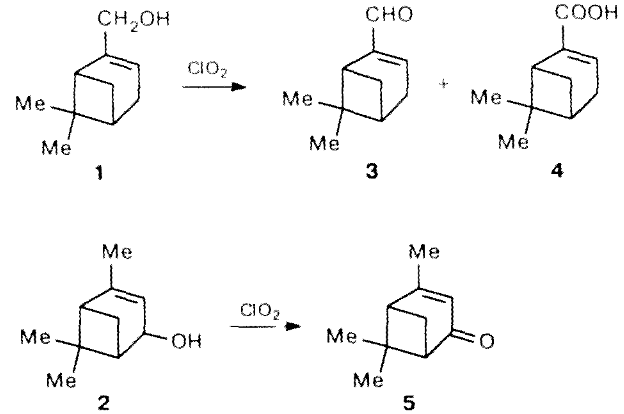
In addition to the known methods for oxidizing allylic alcohols to the corresponding carbonyl compounds,[1] we suggest a new method, oxidation with chlorine dioxide, which has not been previously used in organic synthesis. Being a highly reactive oxidation reagent, ClO_2 is widely used in the paper and pulp industry for whitening cellulose.[2] The mechanism and products of the oxidation of model lignin compounds (styrene and stilbene derivatives) with chlorine dioxide have been studied in recent works.[3]

The terpenols myrtenol (**1**) and *trans*-verbenol (**2**), whose oxidation results in the formation of myrtenal (**3**), myrtenic acid (**4**), and verbenone (**5**), respectively, were chosen as substrates.



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GLC analysis was performed on an LKhM-80 chromatograph, argon was used as the carrier-gas, and a column was filled with 5 % SKTFT-50 on Chromaton N-AW-DMCS. Peaks were identified by comparison with known compounds, and the contents of the components were determined by internal normalization. IR spectra were recorded on a Specord M-80 instrument, and ^{1}H NMR spectra were recorded on a Tesla instrument (100 MHz).

Oxidation of 1. Myrtenol **1** (0.45 g in 10 mL of CCl_4) was oxidized by gaseous ClO_2 at 50 °C for 45 min. The reaction was monitored by TLC on Silufol UV-336 plates with hexane—diethyl ether (5 : 2) was as the eluent. Then the oxidation product was cooled and dried over anhydrous Na_2SO_4, the solvent was distilled off, and the residue was analyzed by GLC. The degree of conversion of **1** was 61 %; myrtenal **3** (41 %) and myrtenic acid **4** (4 %) were formed. The oxidation product was twice treated in a separatory funnel with a 3 % aqueous solution of NaOH. Neutral compounds were extracted with diethyl ether. The alkaline layer was treated with 10 % H_2SO_4 to the acidic reaction with Congo, compound **4** was extracted with diethyl ether, washed, and dried over Na_2SO_4, and the solvent was evaporated. IR (KBr), ν/cm^{-1}: 3100—2500 (C—OH); 1690 (C=O); 1630 ($R^1R^2C=CR^3H$); 1280 (C—O). ^{1}H NMR ($CDCl_3$), δ: 0.798 (s), 1.34 (s, 6 H, CMe_2); 2.455 (m, 4 H, 2 CH_2); 2.78 (t, 2 H, 2 CH); 6.989 (m, 1 H, CH=); 11.1 (br.s, 1 H, OH).

Oxidation of 2. *trans*-Verbenol **2** (0.4 g in 10 mL of ethanol) was oxidized by gaseous ClO_2 at –20 °C for 30 min. TLC showed that the reaction ceased when the alcohol was entirely absent in the reaction mixture. According to GLC, the conversion of compound **2** was 100 %; the oxidation product consisted only of verbenone (**5**).

References

1. P. Müller, in: *The Chemistry of Functional Groups. Supplement E: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur Analogs. Part I*, Ed. S. Patai, Interscience—Wiley, Chichester, 1980, 469—506; H. Masao, K. Toshiyuki, and M. Takashi, *Synth. Commun.*, 1994, **24**, 1823; J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1952, 1094; R. Sheldon and J. Van Doorn, *J. Catalysis*, 1973, **31**, 427.
2. T. A. Tumanova and I. E. Flis, *Fiziko-khimicheskie osnovy otbelki tsellyulozy* [*Physicochemical Foundations of Whitening of Cellulose*], Lesnaya Prom-st', Moscow, 1972, 103 (in Russian).
3. C. Brage, T. Eriksson, and J. Gierer, *Holzforschung*, 1995, 49.

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