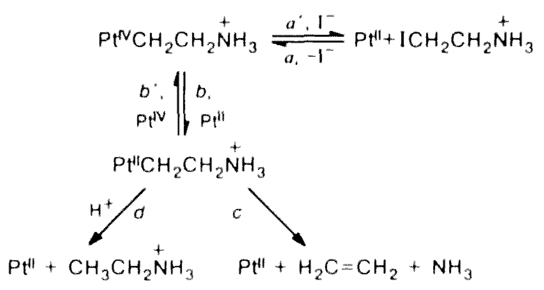
Scheme 1



nium group gives ethylene (stage *c*). The competition of reaction (*c*) and the stage of the complementary oxidation (*b*) explains the retardation effect of the Pt^{IV} additions. By analogy with the published data,[2] the reaction of protodemetallation (stage *d*) is included in Scheme 1, since the formation of ethylene is completely suppressed when 0.001 *M* $HClO_4$ is added to the reaction mixture instead of the phosphate buffer.

The discovered reaction is similar to the known (see, *e.g.*, Ref. 3) reactions of the decomposition of platinum(II) β-aminoethyl complexes in nonaqueous media. To perform this reaction, $Pt^{IV}CH_2CH_2NH_3^+$ should be preliminarily reduced to the corresponding Pt^{II} derivative, since stabilization of the resulting olefin by π-complexation is possible only in this state.

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References

1. V. V. Zamashchikov, S. A. Mitchenko, and S. M. Slinkin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 518 [*Russ. Chem. Bull.*, 1994, **43**, 478 (Engl. Transl.)].
2. S. A. Mitchenko and V. V. Zamashchikov, *Kinet. Katal.*, 1989, **30**, 297 [*Kinet. Catal.*, 1989, **30** (Engl. Transl.)].
3. G. Balacco and G. Natile, *J. Chem. Soc. Dalton Trans.*, 1990, 3021.

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1,2-Di(1-adamantyl)diaziridine

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It has been previously believed[1] that 1,2-di-*tert*-butyldiaziridine could not form due to steric hindrances of cyclization. However, this compound has been recently obtained, although in a low yield (6.2 %).[2]

In this work, the more sterically hindered 1,2-di(1-adamantyl)diaziridine **1** has been synthesized. Compound **1** is of interest as an object for the study of the inversion of N atoms and as a precursor of the unknown 1,2-di(1-adamantyl)hydrazine. *N,N'*-Di(1-adamantyl)formamidine hydrochloride (**2**) was isolated as the second product. The formation of compound **2** can be presented as the result of 1,2-dehydrochlorination of the common intermediate **A** or of the direct reaction of $AdNH_2$ with $CHCl_3$.

The NMR spectrum of diaziridine **1** has a record high-field shift (39.55 ppm) of the signal of the ring carbon atom for the series of known 1,2-dialkyldiaziridines (by 18.2 and 2.4 ppm compared to those of the di-Me and di-Bu^t analogs, respectively), which is explained by the maximum compression of the HCH angle of the ring.[2]

Synthesis of compounds 1 and 2. Paraform aldehyde (54 mg, 1.8 mmol), Bu^tOCl (0.18 g, 1.65 mmol), and finely powdered K_2CO_3 (1 g, 7.2 mmol) were added with rigorous

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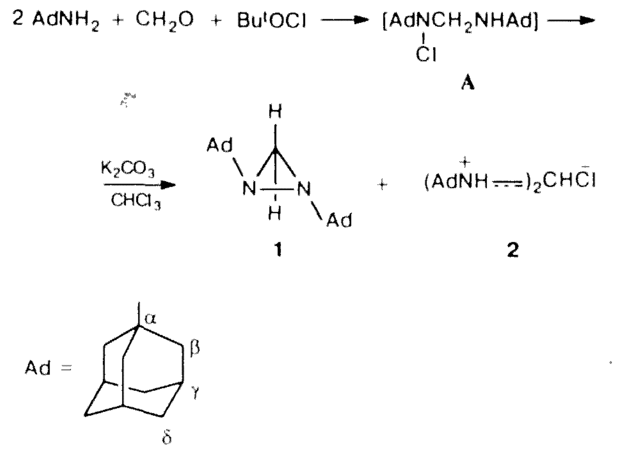

stirring to a solution of $AdNH_2$ (0.5 g, 3.3 mmol) in $CHCl_3$ (20 mL) at 0—5 °C. Then the mixture was boiled for 48 h until the characteristic signal of HN of AdNHCl at 4.05 ppm (in $CDCl_3$) disappeared from the ^1H NMR spectrum of the sample. After the separation of the precipitate and evaporation 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 $[M\text{-}2Ad]^{+\cdot}$ (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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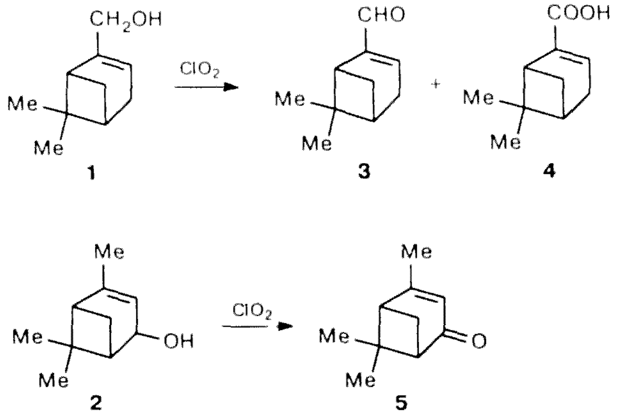
In addition to the known methods for oxidizing allylic alcohols to the corresponding carbonyl compounds,[1] we suggest a new method, oxidation with chlorine dioxide, which has not been previously used in organic synthesis. Being a highly reactive oxidation reagent, ClO_2 is widely used in the paper and 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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