Reduction of 2,2,6,6-Tetramethylpiperidine Nitroxide Radical *via* Complex Formation with Copper(II) Perchlorate

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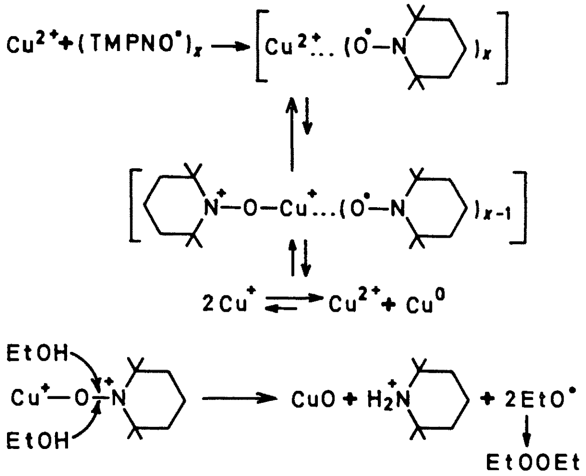
Summary Room temperature reaction of 2,2,6,6-tetramethylpiperidine nitroxide radical with copper(II) perchlorate in triethyl orthoformate yields the corresponding piperidinium perchlorate, *via* formation of an unstable copper complex

IN view of the increasing interest in nitroxide free radicals[1] and such applications as spin labelling for probing biological structures,[2] we report the unusual interaction of 2,2,6,6-tetramethylpiperidine nitroxide free radical (TMPNO·) with copper(II) perchlorate at room temperature in triethyl orthoformate leading to a labile complex which gradually decomposes to yield 2,2,6,6-tetramethylpiperidinium perchlorate (I), elemental copper, and mixed copper oxides Nitroxide radicals have been reduced to amines, but only by using strong reducing agents, while under mild conditions the corresponding hydroxylamine is obtained[3] To our knowledge this is the first example of the formation of an amine salt under relatively mild conditions

TMPNO was prepared by the method of Rassat *et al*,[4] further purified by vacuum sublimation and its structure and purity confirmed by means of its e s r, n m r, i r, and visible spectra[4] In a typical experiment 0 007 mole of the ligand and 0 00175 mole of copper(II) perchlorate hydrate were separately dissolved in triethyl orthoformate, an efficient dehydrating agent,[5] the resulting solutions were mixed at room temperature, and an orange-yellow solid precipitated immediately with simultaneous evolution of heat The precipitate is unstable, gradually darkens, and a mirror of elemental copper forms on the walls of the container while an off-white crystalline solid also precipitates After five days, the solid residue is removed and washed with benzene The benzene-insoluble solid consists mainly of elemental copper, copper oxides, and the off-white solid which is soluble in nitromethane or acetone (yield 36%). Recrystallization from nitromethane yields a water-white crystalline solid, 2,2,6,6-tetramethylpiperidinium perchlorate (I), which explodes at 305° without melting † The compound is diamagnetic, its i r spectrum exhibits the characteristic NH_2^+ bending vibration[6] at 1589 cm^{-1} and the ν_3 band of ionic ClO_4^-[7] at *ca* 1100 cm^{-1} (broad), n m r (D_2O) shows two singlets at τ 8 34 and 8 63 with integration ratio 1 : 2 3 This is consistent with formulation of this compound as (I) if an overlap of the signals of NH_2^+ and CH_3 protons at τ 8 63 is assumed, and the protons of the three methylene groups are responsible for the signal at τ 8 34‡ The conductance of a 10^{-3}M- solution of (I) in nitromethane at 25° (Λ_M = 104 $ohm^{-1}cm^2mole^{-1}$) clearly indicates that it is a 1 : 1 electrolyte in solution

This unusual reaction was encountered during the preparation of a series of crystalline complexes of TMPNO with



SCHEME

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† Elemental analysis was correct for (I)

‡ Piperidine (Sadtler, JEOL, High Resolution n m r Spectra, No 100—135) exhibits signals for the -NH proton at τ 8 75, and for the protons at the 3-, 4-, and 5- ring positions at τ 8 51

the perchlorates of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Zn^{II}, all of which appear to form stable complexes of the "suspect" ligand type. Spin-pairing between the free electrons of nitroxide radicals and the *d* electrons of Co^{II} [8] and Cu^{II} [9] has been established. The copper(II) perchlorate complex, on the other hand, although originally precipitating as an orange–yellow solid, does not appear to be stable.

A possible mechanism for the reaction is shown in the Scheme. Initially a complex of the type $Cu(TMPNO\cdot)_x(ClO_4)_2$ ($x \leqslant 4$)[10] is formed. From the magnetic properties[8,9] of nitroxide free-radical complexes of d^n metal ions, the metal ion in the complex is effectively d^{n+1}. In the complexes of Mn, Fe, Co, and Ni, the metal ion is in the formal oxidation state +1 with a possible co-ordination number of 4 or higher.[8,11] In the case of Cu^{II}, an actual reduction to +1 may occur, since the relative stabilities of Cu^{I} and Cu^{II} are strongly dependent on environmental changes (nature of ligands, anions, and solvents).[12] The formed complex would then be relatively unstable and elemental copper could be formed by disproportionation. In addition, formation of Cu^{II} and Cu^{0} from Cu^{I} is favoured in the presence of perchlorate ions.[12] The Cu^{I} nitroxide adduct could then be involved in a hydrogen abstraction reaction with the alcohol formed from the hydrolysis of triethyl orthoformate, in a manner similar to that suggested by Brackman and Gaasbeck.[13] The presence of the peroxide EtOOEt has not been confirmed, but it was established that aldehydes are not formed during the course of the reaction.

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