Letters to the Editor

The formation of iminoxyl and nitroxyl radicals from *para*-quinonedioxime

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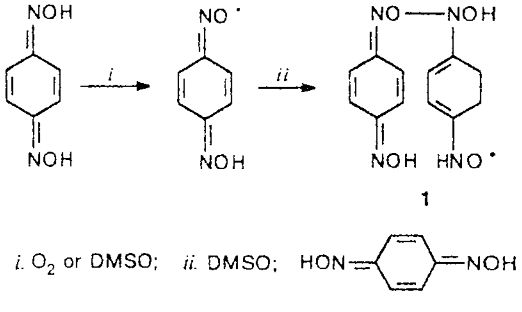
The formation of iminoxyl radicals in oxidation of oximes is described in the literature.[1–6] We established that solid samples of commercially available *para*-quinonedioxime reprecipitated from alcohol (methanol or ethanol) give a weak ESR signal with a *g*-factor of 2.0052, which was primarily assigned to dopant paramagnetic centers. However, an attempt to purify *para*-quinonedioxime more carefully by vacuum (10^{-2} Torr) sublimation at 60 °C resulted in quite unexpected phenomena: the intensity of the signal increased sharply to $2.8 \cdot 10^{18}$ sp/g, and the form of the signal corresponding to triaxial anisotropy became pronounced: $g_1 = 2.0076$, $g_2 = 2.0048$, $g_3 = 2.0021$, and $a_N = 2.6$ mT. These parameters are close to those presented for iminoxyl radicals in the solid phase obtained by γ-irradiation of polycrystalline oximes.[4] Double sublimation resulted in a subsequent 20-fold increase in the intensity of the ESR signal. An attempt to perform the third sublimation resulted in the self-ignition of the sample.

The ESR spectrum of a solution of *para*-quinonedioxime in DMSO exhibits a nitrogen triplet with the constant $a_N = 1.07$ mT and g = 2.0059, which is typical of aromatic nitroxyl radicals.[7] Calculated per gram of the substance, the concentration of the radicals in a solution of DMSO is twice as high as that in the solid sample.

We suppose that the existence of iminoxyl radicals in *para*-quinonedioxime can be related to its solid-phase oxidation by air oxygen. The amount of the iminoxyl radicals formed can be accumulated only to a certain concentration below which a considerable removal of the radicals from each other still prevents their disproportionation. As indicated above, triple vacuum sublimation is accompanied by ignition of the sample. An attempt to sublime *para*-quinonedioxime in air also results in its ignition. Perhaps this is associated with the formation of energetically unfavorable iminoxyl radicals in a sufficiently high concentration. The disproportionation of these radicals is accompanied by the release of a great amount of heat. It is most probable that DMSO also oxidizes *para*-quinonedioxime to iminoxyl radicals, which then add to neutral molecules to form nitroxyl radicals of the supposed structure (**1**). This results in the fact that the concentration of the radicals in solution calculated per gram of the substance is somewhat higher than that in the solid state.



1

i. O_2 or DMSO; *ii.* DMSO; HON=C_6H_4=NOH

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Reaction of trimethallylborane with bromopyridine — the first example of reversible 1,2-allylboration of pyridines

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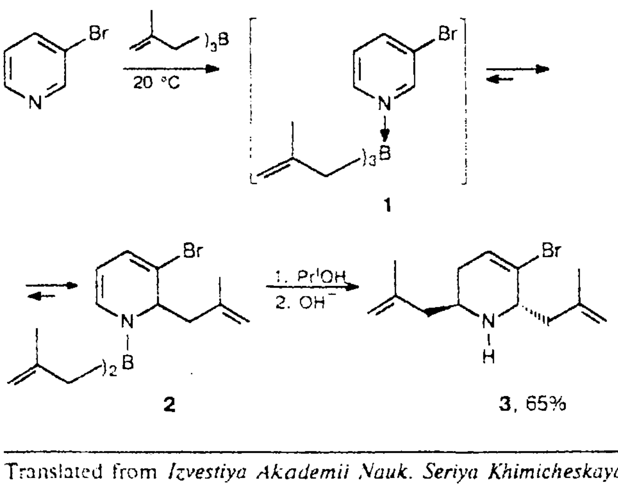
Triallyl- [1—3] and trimethallylborane[3,4] are strong Lewis acids and readily form 1 : 1 complexes with pyridine and its different derivatives. As a rule, these adducts are thermally stable but undergo complete rearrangement under the action of alcohols to give the corresponding *trans*-2,6-diallyl-1,2,3,6-tetrahydropyridines in 70—97% yields.[5,6]

We observed that trimethallylborane (but not triallylborane) reacts with 3-bromopyridine at room temperature to give the product of 1,2-addition (**2**). The reaction proceeds so rapidly that complex **1** has not been detected (^{1}H NMR) at 20 °C (Scheme 1).

Scheme 1



This reaction is the first example of 1,2-allylboration of a pyridine compound and is of basic significance for interpretation of the mechanism of the reductive *trans*-2,6-diallylation of pyridines. Previously,[5,6] this addition has been only postulated as one of the key stages of this multistage process. It is noteworthy that 1,2-addition of organometallic compounds, *e.g.*, RLi, to pyridine was known long ago[7] and is widely used in organic synthesis.

Subsequent treatment of compound **2** with propan-2-ol (−40—20 °C) and an alkali solution resulted in the formation of amine **3** with the *trans*-arrangement of methallyl groups (yield 65%).

Studying the properties of dienaminoborane **2**, we also established for the first time that 1,2-allylboration of at least 3-bromopyridine is a reversible process. This is confirmed by the following data. The treatment of compound **2** with pyridine (1 : 1) gives free 3-bromopyridine and pyridine adduct **4** (46%, ^{1}H NMR). The reaction of **2** with triallylborane results in the formation of trimethallylborane and complex **5**, which, as has been shown previously,[5,6] does not give the corresponding product of 1,2-addition even after long heating at 160 °C.

The processes presented in Scheme 2 are equilibrium processes and do not proceed to completeness, since the basicity of the pyridines involved in the reaction and the Lewis acidity of the two allylboranes differ insignificantly.

Compound **2**, b.p. 90—92 °C (1 Torr), $n_D^{20.5}$=1.5365, δ^{11}B 50.2. IR (thin layer), ν/cm^{-1}: 1564, 1632, 1640, 2968, 3072. Found (%): C, 61.36; H, 7.56;

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