Deoxygenation Reaction of Phenyl Nitronyl Nitroxides with the Strong Acceptors $TCNQF_4$ and TCNQ†

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The reaction of certain phenyl nitronyl nitroxide derivatives with strong acceptors such as $TCNQF_4$ or TCNQ in appropriate solvents give the corresponding imine nitroxide derivatives by an anomalous deoxygenation reaction with acceptors in a selective manner.

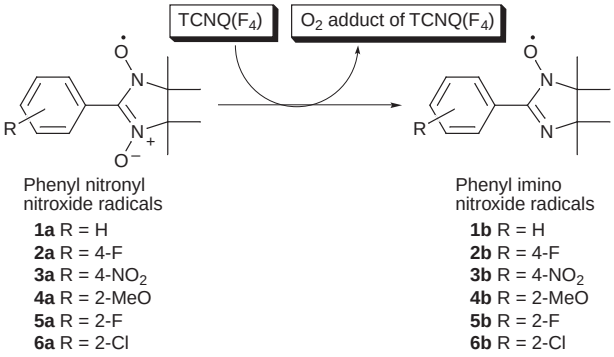
Nitronyl nitroxide radicals (4,4,5,5-tetramethyimidazoline-1-oxyl-3-oxides) are a well-known class of stable radicals used as spin probes for biological studies and/or are promising substrates for organomagnetic materials and a number of derivatives has been prepared for both purposes.[1] It is also known that imine nitroxide radicals can generally be obtained from the corresponding nitronyl nitroxides by treatment with triphenylphosphine or nitrous acid as deoxygenating agents.[2] Akaike *et al.*[3] and Joseph *et al.*[4] have independently reported interesting deoxygenation reactions of some nitronyl nitroxide derivatives with ·NO produced in biological systems and Sugimoto *et al.* have reported in a more recent publication that certain nitronyl nitroxides could be easily reduced to the corresponding imine nitroxides simply by standing the substrates in *n*-heptane or acetone solution at room temperature.[5]

TCNQ (7,7,8,8-tetracyanoquinodimethane) and $TCNQF_4$ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) are classical, strong organic acceptors[6] with cyanide functionality, and are used mainly as the components of CT complexes with appropriate donors to afford functional materials such as organic conductors.

During the course of our studies on the development of new organomagnetic materials based on nitroxide radicals,[7] we found recently that some TEMPO radicals[8] are able to form CT complexes with appropriate acceptors such as $TCNQF_4$ or DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone). On the other hand, similar attempts to prepare CT complexes from nitronyl nitroxides with $TCNQF_4$ or TCNQ in solution were fruitless, but imine nitroxide radicals were found to be obtained in place of CT complexes. Here we report an anomalous deoxygenation reaction of various phenyl nitronyl nitroxides by using $TCNQF_4$ or TCNQ to prepare imine nitroxide radicals which are also significant in biological[9] as well as materials science.[7]

When an acetonitrile solution of phenyl nitronyl nitroxide **1a**[10] was treated with an equimolecular amount of $TCNQF_4$, imine nitroxide **1b** was found to be formed in place of the corresponding CT complex, as revealed by FAB-MS as well as EPR measurements. It appeared to be interesting that reductive deoxygenation took place *in solution* by using a strong acceptor, *i.e.* a strong oxidative reagent, while Sugawara *et al.* obtained a DDQ complex from dimethylaminonitronyl nitroxide by mixing each component in the solid state.[11]

We then investigated the scope and limitation of the deoxygenation reaction by applying it to various nitronyl nitroxide radicals (Scheme 1). The deoxgenation reaction of **1a** proceeded smoothly in acetonitrile, tetrahydrofuran or ethanol in 2–5 min and rather gradually in acetone, affording **1b** as the sole isolated product after column chromatography on Al_2O_3, but no reaction was observed in nonpolar solvents such as dichloromethane or benzene. As shown in Table 1, neither the reaction time nor the variation of solvent employed seriously affected the yield of **1b**. Moreover, the weaker acceptor TCNQ was found to be similarly effective in the reaction, although the reaction with TCNQ proceeds rather slowly and hence needs more reaction time. On the contrary, no deoxygenation could be observed when **1a** was treated with DDQ, which suggests that the dicyanoalkene unit plays an indispensable role in the reaction.



Scheme 1

The reaction could also be applied to other phenyl nitronyl nitroxide derivatives (**2a–6a**)[12] with substituents in *o*- or *p*-positions to form the corresponding imino nitroxides **2b–6b** as shown in Table 1. Thus, although the isolated yields were not so high in each case, the reaction was found to be applicable to various phenyl nitronyl nitroxide derivatives with electron-donating or electron-withdrawing groups in the *o*- or *p*-positions of the radical substituent. It is to be noted that each reaction was found to be fast and that the radicals could be readily isolated without tedious separation although the yields were moderate, with one being comparable to conventional methods.[3] However, no imino nitroxide derivatives, but rather uncharacterizable mixtures of products, could be isolated when the same reaction was applied to ethyl nitronyl nitroxide.

In summary, we have found a new deoxygenation reaction for phenyl nitronyl nitroxide radicals by using strong acceptors such as $TCNQF_4$ or TCNQ in appropriate

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Table 1 Deoxygenation reaction of **1a–6a** by acceptors[a]

Substrate	Acceptor	Solvent	*t*/min	Yield(%)
1a	$TCNQF_4$	CH_3CN	2	57
1a	$TCNQF_4$	CH_3CN	30	54
1a	$TCNQF_4$	THF	5	34
1a	$TCNQF_4$	EtOH	5	45
1a	$TCNQF_4$	CH_3COCH_3	15	35
1a	TCNQ	CH_3CN	10	30
1a	TCNQ	CH_3CN	15	45
2a	$TCNQF_4$	CH_3CN	5	21
2a	TCNQ	CH_3CN	10	53
3a	$TCNQF_4$	CH_3CN	10	62
3a	TCNQ	CH_3CN	15	26
4a	$TCNQF_4$	CH_3CN	2	37
4a	TCNQ	CH_3CN	20	72
5a	$TCNQF_4$	CH_3CN	2	35
5a	TCNQ	CH_3CN	20	62
6a	$TCNQF_4$	CH_3CN	2	56
6a	TCNQ	CH_3CN	20	63

[a] Equimolar amount of acceptors in solvent (5–15 cm^3) was added to a solution of substrates (0.052–0.13 mmol) in solvent (5 cm^3) at room temperature.

solvents, which provides a method to obtain imino nitroxide radicals although $TCNQF_4$ or TCNQ themselves are the strong acceptors and are usually considered to be reagents for electron abstraction, *i.e.* oxidation reactions.

Experimental

Reaction of **1a** *with* $TCNQF_4$.—To a stirred solution of $TCNQF_4$ (14 mg, 0.056 mmol) in acetonitrile (5 cm^3) was added **1a** (13 mg, 0.11 mmol) in acetonitrile (5 cm^3). The blue colour of the reaction mixture turned immediately to deep green and then gradually to brownish orange; after 2 min, the mixture was concentrated *in vacuo*. The brownish orange oil thus obtained was purified by column chromatography (Al_2O_3) using benzene as eluent to give **1b** as the sole isolated product of a pale orange oil (6.8 mg, 57%) and no other products, including the oxygen-adduct of $TCNQF_4$, were recovered. $\lambda_{max}(CH_2Cl_2)$/nm: 444 br (ϵ/dm^3 mol^{-1} cm^{-1} 1490), 305 sh (14200) and 276 (27400). EPR (benzene): multiplet, $g = 2.006$, $a_N = 0.91$ and 0.34 mT. *m/z* (EI-HRMS) Found: 217.1417. Calcd. for $C_{13}H_{17}ON_2$: 217.1341. In a similar manner, radicals **2b–6b** have been prepared.

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