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The Reaction of Nitrogen Dioxide with N-Benzylidene-t-butylamine N-Oxide. Formation of a White Solid Adduct and Its Properties

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The reaction of N-benzylidene-t-butylamine N-oxide (PBN) with NO_2 gave white diamagnetic solid $C_{11}H_{16}N_2O_4$ in addition to greenish blue free radical species. The white solid was shown to decompose quantitatively into the starting PBN and nitric acid when it was dissolved in water.

In pursuit of possible application to the analysis of environmental nitrogen oxides, several radical reagents have been reacted towards NO_x. Boocock and coworkers reported the selective reaction of 2-phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl (PTIO) with NO forming NO_2.1) The reaction has been applied to the analysis2) and the removal3) of NO. The spin trapping reaction by use of N-benzylidene-t-butylamine N-oxide (PBN) (**1**) has been applied to a wide variety of carbon-centered free radicals. However, its reactions with nitric oxides have not been examined extensively. Pryor and coworkers postulated the production of $PBNO_x$ (2) by the reaction of NO_2 with PBN4) without determining the structure of the other products.

In the aim of finding out a reagent which reacts selectively with either of NO_x species, we were intrigued in the reactions of several radical reagents with nitric oxides. Thus PBN was treated with NO and NO_2 in several solvents. Nitrogen monoxide (NO) was shown to be inert to this nitrone. When gaseous NO_2 was introduced to the hexane solution of PBN, white solid separated out from the solution. Elemental analysis showed it to be $C_{11}H_{16}N_2O_4$, which corresponds to a nitrate of PBN (3). The solid substance is diamagnetic and decomposes evolving brown gas (very probably NO_2) at its melting point. In order to further characterize the white solid, spectral and other physical properties were determined. The results are given in Table 1.

Table 1. Elemental Analysis and Physical and Spectral Properties of the White Solid PBN-NO_2 Adduct

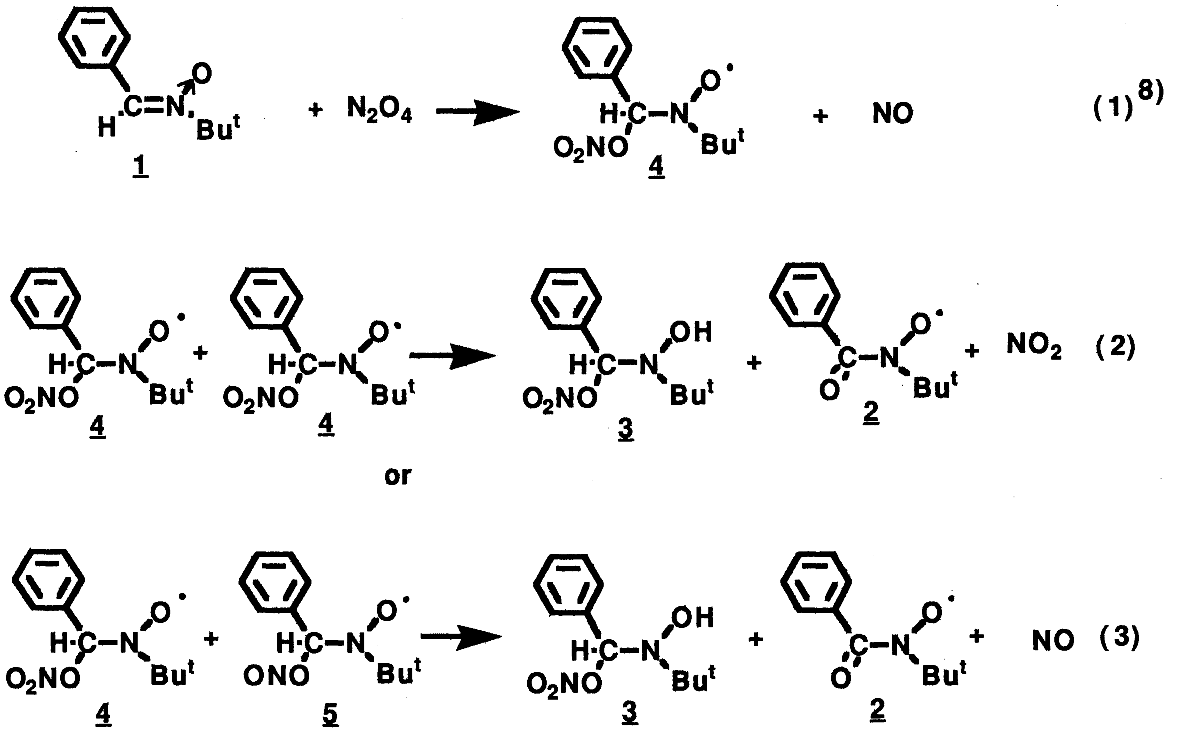
Elemental analysis	Found: C, 54.83%; H, 6.51%; N, 11.75% Calcd for $C_{11}H_{16}N_2O_4$: C, 54.99%; H, 6.71%; N, 11.75%
Melting point	68-69 °C(decomp.)
NMR Spectra (in methanol-d_4)	^1H (ppm from TMS): 1.22(s,3H,t-Bu), 1.59(s,6H,t-Bu), 5.37(s,1H, Ph-CH-), 7.37(m,5H, Ph) ^{13}C (ppm from TMS): 28.1(2CH_3,t-Bu), 31.2(1CH_3,t-Bu), 104.7(1C,Ph-CH-), 127.8(2C,m-Ph), 129.2(2C,o-Ph),129.5(1C,p-Ph), 139.6(1C,ipso-Ph) ^{14}N (ppm from $NaNO_3$): 210($\Delta\nu_{1/2}$:57Hz,N-OH), 264 ($\Delta\nu_{1/2}$:14Hz,-ONO_2) ^{17}O (ppm from H_2O): -340(-ONO_2)$^{6)}$
UV spectra	300 nm (2.0x10^4) in hexane; 293 nm (1.96x10^4) in methanol
IR spectra (NO_2)	1638 cm^{-1}, 1370 cm^{-1} (KBr pellet)$^{7)}$
MS spectrum	Trimethylsilylated derivative: m/z=312 (M^+)
Electric conductivity	5.1x10^{-4} S cm^{-1} in 1.0x10^{-2}M methanol soln.

The postulated structure **3** was supported convincingly by the spectral data. The hydroxylamino proton can be expected to be enough acidic to be ionized in water as revealed by its conductivity.

As the precipitation of the white solid proceeds, the solution got gradually colored greenish blue and became paramagnetic, intimating the simultaneous formation of a hexane-soluble free radical species. Its ESR spectrum has a triplet characteristic to nitroxyl free radicals. The relatively small hyperfine splitting constant (a_N = 8.1 G) suggested the presence of a nitroxyl carrying an electron-withdrawing substituent in the neighborhood of radical center, very seemingly benzoyl-t-butylnitroxyl **2**.

Intuitionally the nitrate-nitroxyl **4** is supposed to be formed from NO_2 and the nitrone **1** through the following pathway (Eq. 1). Disproportionation of **4** followed by the liberation of NO_2 (Eq. 2) or a similar reaction between **4** and **5** (Eq. 3) produces PBN-nitrate **3**.

Formation of the keto-nitroxyl **2** from the NO_2-adduct **5** had been proposed previously by Pryor and



Scheme 1. Reaction path forming PBN-nitrate.

coworkers.[4)] Thus the paramagnetic species in the solution can be assumed very probably to be 2. The hyperfine splitting constant agrees with the reported value for 2 (a_N = 7.9 G)[5)] within the experimental error.

The ease of formation of PBN-nitrate 3 was examined in several solvents, viz. carbon tetrachloride, chloroform, benzene, acetone, and methanol. Runs in CCl_4 gave 3 as precipitates; while those in methanol gave white solid after evaporation of the solvent. In solvents other than methanol, the greenish blue color developed by the introduction of NO_2. The color is quite similar to that observed with the hexane solution. The reaction in methanol proceeds without forming paramagnetic species; the solution remaining colorless throughout the reaction. The peculiar role of methanol can be explained in terms of its reducing ability to supply hydrogen atom necessary for the conversion of the nitrate-nitroxyl 4 to 3. The paramagentic solution usually contains several components which gave PBN, benzaldehyde, benzoic acid etc. as the ultimate descendants.

PBN-nitrate 3 is stable in crystalline state and also in methanol solution. However, it tends to decompose gradually in other solvents. In order to characterize the degradation products and to pursue the decomposition process, the solid 3 was dissolved in water and kept at a constant temperature of 25 °C. The solution was extracted at intervals with hexane, and the extract was analyzed by gas chromatography. The measurement on the extract sampled immediately after dissolution showed that PBN was recovered quantitatively (100%). The aqueous layer was revealed to contain nitrate ion but not nitrite ion by use of the brucine/concentrated sulfuric acid test for NO_3^- and the Griess-Romijn test for NO_2^-. The yield of the recovered PBN decreased gradually as a function of time (the half life-time; 1.6×10^4 s). As remarked previously, the degradation products, such as benzaldehyde and benzoic acid, increased their intensities as time elapsed.

In conclusion, the reaction producing solid PBN-nitate **3** proceeds very fast and quantitatively in hexane, which can possibly be applied to the selective determination and removal of NO_2.

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6) ^{17}O NMR chemical shift of $C_2H_5ONO_2$ in reference to H_2O is -340 ppm.
7) The characteristic NO_2 stretching vibrations of covalent nitrates appear in the ranges 1650-1620 and 1270-1290 cm^{-1}. With ionic organic nitrates the bands appear in the ranges 1410-1340 cm^{-1}. L. J. Bellamy, " The Infra-red Spectra of Complex Molecules," 3rd ed, Chapman and Hall, London (1975), pp. 337-345.
8) Dinitrogen tetroxide can react with PBN after dissociative disproportionation to NO_3 and NO. However, this was not confirmed unequivocally.

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