ON THE MECHANISM OF THE REACTION OF

NITRIC OXIDE WITH TRIALKYLBORANES

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Very recently three different mechanisms were proposed[1,2,3] for the reaction of nitric oxide with trialkylboranes at room temperature.

In our preliminary studies[2], we found that nitric oxide appeared to function as an ambident nucleophile in its reactions with trialkylboranes, with an attack on the boron atom by either the nitrogen or the oxygen atom of NO. Moreover, which mechanism predominates depends on the temperature. Both N- and O- attack operate in varying degrees between -70° and $+70^{\circ}$C.
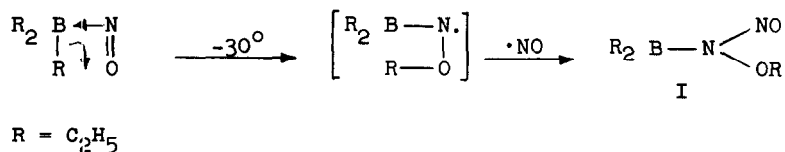
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[1] M. H. Abraham, J. H. N. Garland, J. A. Hill and L. F. Larkworthy, Chem. & Ind. (London) 1615 (1962).

[2] S. J. Brois, Abstracts of Papers presented at the 144th meeting of the American Chemical Society, Los Angeles, Calif., March 31 - April 5, 1963, p. 32M.

[3] M. Inatome and L. P. Kuhn, Preprints of Papers presented at the International Symposium on Boron-Nitrogen Chemistry, Duke University, Durham, North Carolina, April 23-25, 1963, p. 110.
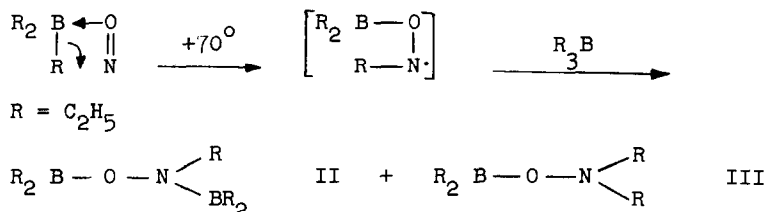
At low temperatures, e.g. -30°, principal N-attack on boron yields product I[4] in approximately 70% yield:

$$R_2 \; \overset{B \longleftarrow N}{\underset{R \downarrow O}{|}} \quad \xrightarrow{-30°} \quad \left[R_2 \; \overset{B \longrightarrow N.}{\underset{R \longrightarrow O}{|}} \right] \quad \xrightarrow{\cdot NO} \quad R_2 \; B \longrightarrow N \underset{OR}{\overset{NO}{<}}$$

$$\text{I}$$

$$R = C_2H_5$$

In the proposed four-center reaction, the migration of the alkyl group may or may not be synchronous with N-attack. The radical intermediate then couples very rapidly with nitric oxide to give I.

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[4]The structure of I, b.p. 88-89°(10mm), $n^{20}D$ 1.4301, which will be described in detail in the full account, is based on a satisfactory elemental analysis, and on its spectra. Its infrared spectrum shows absorptions at 6.83, 7.73, 8.05, 8.5 and 9.35μ which appear diagnostic for nitrosamines [R. N. Haszeldine and J. Jander, J. Chem. Soc., 691(1954)] . In cyclohexane, I had λ max at 227 and 292 mμ; the latter band shifts to 285 mμ in methanol. The NMR spectrum of I (neat) obtained on a Varian A60 Spectrometer discloses a quadruplet and triplet at 5.85 and 8.27 τ (EtO⁻ group) and a complex multiplet (J/δ = 0.30) between 9.17 and 9.8 τ (Et_2B group). Decomposition of I with concentrated sulfuric acid yielded nitrous oxide, ethane and ethylene.

At higher temperatures, a reversal in the mode of
nucleophilic attack by nitric oxide occurs. Thus, at 70°
predominant O-attack on boron gives II and III[5] in approximately
48 and 32 mole % yields, respectively:

$$R = C_2H_5$$

$R_2\,B - O - N \Big\langle \begin{smallmatrix} R \\ BR_2 \end{smallmatrix}$ II   + $R_2\,B - O - N \Big\langle \begin{smallmatrix} R \\ R \end{smallmatrix}$ III

The formation of approximately 8 mole % yield of
hydrocarbon (R = Butyl) consisting of 5.3% 1-butene, 2.1% butane,
0.4% trans-2-butene and 0.2% cis-2-butene suggests that the
alleged intermediate, $R_2\overset{\bullet}{B}ONR$, interacts with R_3B to yield II and
alkyl radical. Apparently R· not only couples with R_2BONR to form
mainly III but undergoes partial disproportionation at 70°. It
is particularly significant that hydrocarbon formation becomes
negligible at lower temperatures and essentially equivalent
amounts of II and III are formed (see Table I).

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[5]Structures II and III are based on satisfactory elemental
analyses, and spectra consistent with these structures. The
infrared spectra of II and III were characterized by a strong
$\rangle$B-O- absorption band at about 7.4μ. The proton spectrum
of II (neat) disclosed an Et-N$\langle$ group (quadruplet and triplet
at 6.73 and 8.90 τ) and two Et_2B- groups (doublet at 9.10 τ).
II reacted exothermically with water to give ethylboronous
acid and Et_2BONHEt (IV). The structure of IV based on
molecular weight determinations and spectral studies will
be discussed in the full account. The NMR spectrum of II
(neat) showed methylene and methyl resonances at 7.35 and
9.0 τ (Et_2N-). Of particular significance is the singlet
resonance signal at 9.1τ for the protons of the Et_2B- group.
NMR spectra of model compounds having the Et-B-O- structure,
viz., Et_2BOH, EtB(OH)$_2$ and ethyl boroxine also exhibited a
sharp singlet for the CH_3CH_2-B$\langle$ protons (S. J. Brois and
B. E. Hudson, to be published). Acid hydrolysis of III gave
Et_2BOH and Et_2NOH.

I

TABLE

Effect of Temperature on Product Composition

Temperature °C	Relative mole % product[a]		
	I	II	III
-30	70	14	16
0	56	22	22
20	26	38	36
70	15	50	35

[a]Relative mole percentages of products I, II and III
($R = C_2H_5$) were obtained by electronic integration of
their respective C- and N-methylene proton resonance
signals. Values are accurate to within $\pm$ 3 mole %.

The present results illustrated in Table I clearly
show that the course of the nucleophilic attack by the ambident
NO molecule is extremely temperature dependent. Both the N-
and O-attack mechanisms are operative at temperatures ranging
from $-70°$ to $+70°$. It is tentatively proposed, that the unique
behavior of NO as a ambident nucleophilic agent may be related
to its temperature-dependent magnetic moment.

Contrary to our findings, Abraham and co-workers[1]
postulated a mechanism in which NO is bonded to boron through
oxygen:

$$R_2B \diagup ON^\cdot \rightarrow R_2B-O-N^\cdot \rightarrow R_2B-O-N^\cdot \xrightarrow{NO} R_2B-O-N\diagdown^R_{NO}$$
$$V$$
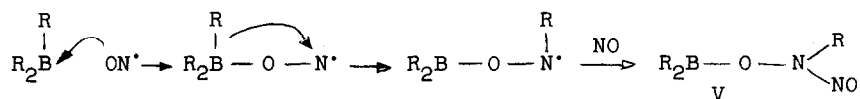
R = Isobutyl

The attack of the second molecule on nitric oxide, which
presumably could precede the 1, 3-shift, yields product V.

By way of further contrast, Inatome and Kuhn[3] interpreted this reaction in terms of a five-step mechanism in which nitric oxide is initially bonded to boron via nitrogen:

$$R_3B + NO \longrightarrow R_3BNO \tag{1}$$

$$R_3BNO + NO \longrightarrow RNO + R_2BNO \tag{2}$$

$$R_2BNO + R_3B \longrightarrow [R_2BNOBR_3] \longrightarrow \underset{VI}{R_2BNROBR_2} \tag{3}$$

$$2\ R_2BNO \longrightarrow \underset{VII}{\begin{array}{c} R_2B-N \rightarrow O \\ \| \\ O \leftarrow N-BR_2 \end{array}} \longrightarrow \underset{VIIA}{\begin{array}{c} R_2B-N-O \\ |\ \|\ | \\ O-N-BR_2 \end{array}} \tag{4}$$

$$RNO + R_3B \longrightarrow [RNOBR_3] \longrightarrow \underset{VIII}{R_2NOBR_2} \tag{5}$$
$$\longrightarrow \underset{IX}{RNHOBR_2} + \text{Butene-1}$$

R = Butyl

The initial adduct formed in Step 1 apparently reacts with NO to yield a C-nitroso and B-nitroso compound. The latter is reported[3] to dimerize (step 4) to yield product VII, a B-nitroso dimer presumably stabilized by the resonance form VIIA. The hypothetical B-nitroso and C-nitroso compounds react (steps 3 and 5) with R_3B to yield products VI (not isolated) and VIII respectively. The authors[3] propose that $RNOBR_3$ collapses (step 5) via an intramolecular hydrogen transfer from carbon to nitrogen to give the minor products, $RNHOBR_2$ (IX) and butene-1.

On the basis of our evidence[2], however, the latter mechanisms[1,3] are seriously questioned. It appears from our data that both reaction pathways lead to products with incorrect structures. Specifically, structure proposed by Abraham

et al.[1] and structure VII $(R_2BNO)_2$ [6], suggested by Inatome

and Kuhn[3] are in error. In the five-step sequence proposed

by Inatome and Kuhn the intermediate B-nitroso compound

(R_2BNO), being the monomer of VII is likewise erroneous.

Recent NMR studies of reaction mixtures obtained at room

temperature indicate that IX (step 5) is not a reaction product

but is in fact the hydrolysis product of VI. Moreover, the

mechanism of Inatome and Kuhn does not explain the small

amounts of butane and 2-butenes formed in the reaction at

room temperature. A full account of the present work will

be published elsewhere.

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[6]The nitrosamine I $(R = C_4H_9)$, corresponds to the product
b.p. 84° (2.5 mm), ultraviolet spectrum λ_{max}^{CCl4} 293
and $\lambda_{max}^{CH_3OH}$ 228 mμ which Inatome and Kuhn[3] erroneously
characterized as VII, the B-nitroso dimer.