Boronitroxides

Sir:

Since the discovery of Fremy's salt,[1] a great number of nitroxides have been interpreted.[2] However, no nitroxides bearing a covalent boron–nitrogen bond have been described.

We now report ESR spectral data of the first boronitroxides detected during the reaction of various nitroso compounds with alkali metal borohydrides.

In a typical run, a solution (0.1 M) of the nitroso compound and the metal borohydride[3] (0.2–0.8 M) in a degassed polar aprotic solvent is prepared at room temperature and immediately set in the cavity of a Varian E 109 ESR spectrometer. These solutions yield instantaneously strong signals due to the previously unknown boronitroxides $RN(O\cdot)BH_3^-M^+$ (**1**) for all R studied except R = *t*-Bu· (see Table I and Figure 1).

For 2-methyl-2-nitrosopropane (MNP), the detection of **1** (R = *t*-Bu·) at room temperature is immediate only by using concentrations of at least 0.2 M for $NaBH_4$ and 0.4 M for KBH_4. For other concentrations, the sample must be heated at 60 °C for a few minutes in order to observe signals of **1** (R = *t*-Bu·) free from all admixture. However, the instantaneous formation of **1** at room temperature is observed even with MNP, when the nitroso compound is allowed to react with sodium or potassium borohydride in dry degassed dicyclohexyl-18-crown-6 benzene solution.

The ESR spectra for boronitroxides consist of two overlapping spectra for the two isotopes of boron (Figure 1). The predominate spectrum consists of 40 observable lines over the 48 lines theoretically expected by interaction of the unpaired electron with the ^{14}N nucleus ($I = 1$), the ^{11}B nucleus ($I = {}^3/_2$, 80.42% natural abundance), and a set of three equivalent ^1H nuclei ($I = {}^1/_2$). The secondary spectrum arises from interaction of the unpaired electron with the ^{14}N nucleus, the ^{10}B nucleus ($I = 3$, 19.58% natural abundance), and three equivalent ^1H nuclei. All the ESR spectra have been computer simulated, and the hyperfine splitting (hfs) constants of Table I give the best fit between calculated and experimental spectra. When the set of three equivalent protons is replaced by a set of three equivalent deuterons (using $NaBD_4$), satisfactory agreement between calculated and experimental spectra is obtained by assuming $a_H/a_D = 6.514$, the ratio of proton to deuteron gyromagnetic ratios.

The boronitroxide structure **1** is supported by the magnitude of the hfs constants and *g* value which are very close to those of carbon homologues.[4] Nitrogen and boron hfs constants of respectively ca. 20 and 12 G have been reported[5] for various dialkyl nitroxides complexed with boron trihalide; these values rule out the occurrence of a dialkyl or diaryl nitroxide complexed with borane in the present study.

The boronitroxides **1** have been shown to be very persistent in the temperature range 20–100 °C, and the hfs constants do not exhibit any significant temperature dependence. These species are quickly destroyed by mineral and carboxylic acids and seem to be unreactive toward electrophiles like acetone or propylene oxide.

The thermal instability of dialkyl nitroxides having at least one hydrogen atom on one of the α carbon atoms has been interpreted[6] in terms of an irreversible bimolecular decay process leading to a hydroxylamine and a nitrone. Since such a process is unlikely in the case of boronitroxides **1**, it explains the increase of persistence of the signals and thus substantiates the proposed structure.

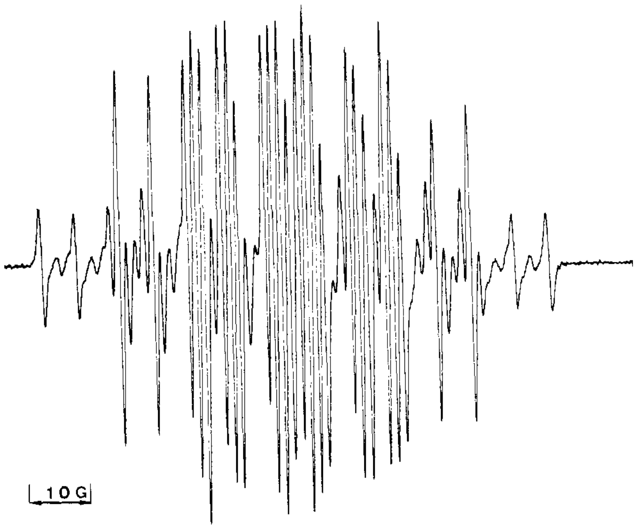

Figure 1. ESR experimental spectrum obtained from a mixture of MNP (0.1 M), KBH_4 (0.2 M), and dicyclohexyl-18-crown-6 (0.2 M) in dry degassed benzene solution at 25 °C.

The formation of boronitroxides **1** could be tentatively explained[7] by two different reactions (eq 1 and 2).

$$RNO^-\cdot M^+ + BH_3 \rightarrow RN(O\cdot)BH_3^-M^+ \quad (1)$$

$$RNO + BH_3^-\cdot M^+ \rightarrow RN(O\cdot)BH_3^-M^+ \quad (2)$$

The detection of a boronitroxide during the reaction of 2,4,6-tri-*tert*-butyl-3,5-dideuterionitrosobenzene ($t\text{-}Bu_3NB\text{-}d_2$) with sodium borohydride or sodium borodeuteride (entries 12 and 13, Table I) supports borane radical anion $BH_3^-\cdot$ as an intermediate. This radical resembles closely the methyl radical,[8] and its trapping on $t\text{-}Bu_3NB\text{-}d_2$ (eq 2) is expected to occur at the nitrogen atom,[9] leading to the observed nitroxide structure, while the very crowded $t\text{-}Bu_3NB\text{-}d_2$ radical anion should react with borane (eq 1) to form a boron–oxygen bond, leading to an *N*-alkoxyanilino radical.[10]

As in the case of the free-radical chain mechanism in the reduction of 7,7-dibromonorcarane[11] and aryl halides[12] with sodium borohydride in DMF, the origin of borane radical anion is not clear, but it seems reasonable to suggest that the role of BH_4^- would be that of an electron-transfer reagent to the nitroso compound in the process.

Further work is in progress in order to give details on the mechanism of formation and chemical reactivity of this new class

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(1) E. Fremy, *Ann. Chim. Phys.*, **15**, 459 (1845).

(2) A. R. Forrester in "Landolt-Börnstein. Magnetic Properties of Free Radicals", K. H. Hellwege, Ed., Springer-Verlag, Berlin, 1979, Vol. 9, Part C 1, Chapter 6.

(3) No ESR signals are observed with $NaB(C_6H_5)_4$; $NaBH_3CN$ or $NH_4BF_4\cdot LiBH_4$ is ineffective and gives little, if any, of the desired nitroxides.

(4) For example, in the case of methyl 1,1,3,3-tetramethylbutyl nitroxide, the following hfs constants have been reported in CH_2Cl_2: a_N 15.1 G, $a_{H(CH_3)}$ 12.1 G, $a_{^{13}C(CH_3)}$ 6.1 G: R. Brière, H. Lemaire, and A. Rassat, *J. Chem. Phys.*, **48**, 1429 (1971). For methyl tertiary alkyl nitroxides, the *g* value lies in the range 2.0059–2.0065 for measurements in solvents in the polarity range benzene to chloroform.[2]

(5) T. B. Eames and B. M. Hoffman, *J. Am. Chem. Soc.*, **93**, 3141 (1971).

(6) K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Am. Chem. Soc.*, **93**, 902 (1971).

(7) When the reaction between MNP and sodium borohydride or sodium borodeuteride is carried out in a protic solvent like EtOH or a 1:1 mixture (v/v) of DMF–EtOH, the six-line spectrum characteristic of the *tert*-butyl hydronitroxide is observed together with the spectrum of the di-*tert*-butyl nitroxide (DTBN). The formation of *tert*-butyl hydronitroxide could be accommodated according to

$$BH_4^- + t\text{-}BuNO \rightarrow t\text{-}BuN(OH)H \xrightarrow[\text{or } t\text{-}BuNO]{O_2} t\text{-}BuN(O\cdot)H$$

as recently reported: B. Kalyanaraman, E. Perez-Reyes, and R. P. Mason, *Tetrahedron Lett.*, 4809 (1979). However, the intervention of the MNP radical anion cannot be ruled out: $BH_4^- + t\text{-}BuNO \rightarrow t\text{-}BuNO^-\cdot + BH_4\cdot \rightarrow t\text{-}BuN(O\cdot)H$. DTBN could result from trapping by MNP of *t*-Bu· radical formed from MNP by photochemical (daylight) decomposition [Th. A. J. W. Wajer, A. Mackor, and Th. J. De Boer, *Tetrahedron*, **23**, 4021 (1967)] and/or by decomposition of MNP radical anion. For examples of electron-transfer reactions between nitroso compounds and nucleophiles as well as the formation of DTBN in such reactions, see: I. I. Bilkis and S. M. Shein, *Tetrahedron*, **31**, 969 (1975).

(8) T. A. Claxton, M. J. Godfrey, and N. A. Smith, *J. Chem. Soc., Faraday Trans. 2*, **68**, 181 (1972).

(9) S. Terabe and R. Konaka, *J. Chem. Soc., Perkin Trans. 2*, 369 (1973).

(10) M. P. Crozet, E. Flesia, J-M. Surzur, M. Boyer, and P. Tordo, *Tetrahedron Lett.*, 4563 (1975).

(11) J. T. Groves and K. Way Ma, *J. Am. Chem. Soc.*, **96**, 6527 (1974).

(12) J. A. Barltrop and D. Bradbury, *J. Am. Chem. Soc.*, **95**, 5085 (1973).

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Table 1. ESR Spectral Data of Boronitroxides RN(O·)BH$_3^-$M$^+$

reducing agent	nitroso compd[a]	a_N	a_B	$a_{H(D)}$	g value
NaBH$_4$[b]	MNP	14.1[c]	5.7[c]	12.7[c]	2.0057
KBH$_4$	MNP	13.7	5.6	12.6	2.0057
NaBD$_4$	MNP	14.0	5.7	1.9	2.0057
KBH$_4$[d]	MNP	13.9	5.5[e] 1.8	12.6	2.0059
NaBH$_4$	ND	13.4	5.9	12.6	2.0057
KBH$_4$	ND	13.1	5.9	12.4	2.0058
NaBD$_4$	ND	13.4	5.9	1.9	2.0059
NaBH$_4$	2,3,4,5,6-MeNB	13.4	6.1	13.0	2.0057
NaBH$_4$	NB-d_5	9.4	4.8	9.9	2.0054
NaBH$_4$	2,3,4,5,6-OMeNB	12.6	5.7	12.1	2.0057
NaBD$_4$	2,3,4,5,6-OMeNB	12.6	5.7	1.8	2.0059
NaBH$_4$	t-Bu$_3$NB-d_2	12.7	6.1	11.6	2.0057
NaBD$_4$	t-Bu$_3$NB-d_2	12.7	6.1	1.8	2.0059

[a] MNP, 2-methyl-2-nitrosopropane; ND, nitrosodurene; 2,3,4,5,6-MeNB; 2,3,4,5,6-pentamethylnitrosobenzene; NB-d_5; 2,3,4,5,6-pentadeuterionitrosobenzene; 2,3,4,5,6-OMeNB; 2,3,4,5,6-pentamethoxynitrosobenzene; t-Bu$_3$NB-d_2; 2,4,6-tri-*tert*-butyl-3,5-dideuterionitrosobenzene. [b] Unless otherwise noted, all reactions were carried out at 25 °C in DMF with RNO (0.1 M) + MBH$_4$ (0.2–0.8 M). Similar results are observed for aromatic nitroso compounds in DME, Me$_2$SO, HMPA-THF (1:1), acetonitrile, pyridine, and ethylenediamine. [c] Hyperfine splitting constants are given in gauss. [d] MNP (0.1 M), KBH$_4$ (0.2 M), and dicyclohexyl-18-crown-6 (0.2 M) in benzene. [e] Hfs constants for ^{11}B and ^{10}B.

of paramagnetic "ate" complexes.

Notes Added in Proof: During the submission of our manuscript, the reaction of sodium borohydride with alcohols in the presence of nitrosodurene has been described: D. Rehorek, R. Herzschuh, and H. Hennig, *Inorg. Chim. Acta*, **44**, 75 (1980). In our opinion, the ESR spectrum observed and assigned to C$_6$H(CH$_3$)$_4$N(O·)BH$_2$ (a_N = 22.67 G, $a_{H(2H)}$ = 15.63 G, and $a_{^{11}B}$ = 7.08 G) has been misinterpreted. We observed the same kind of spectrum in our experiments by using a mixture of DMF–EtOH. This spectrum has been computer simulated and the following hfs constants give a very good fit with the experimental curve (a_N = 14.39 G, $a_{H(3H)}$ = 14.39 G, and $a_{^{11}B}$ = 6.67 G), thus this spectrum is attributable to C$_6$H(CH$_3$)$_4$N(O·)BH$_3^-$Na$^+$. We will comment on Rehorek's study in a forthcoming paper.

Acknowledgments. We thank Professors Nathan Kornblum and Jean-Marie Surzur for helpful discussions. This work was supported by the Centre National de la Recherche Scientifique through Grants LA 109 and AI 32538.

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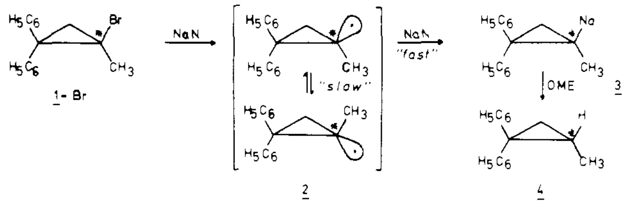
Received March 28, 1980

Alternative Pathways in the Reactions of Cyclopropyl Halides with Alkali Metal Naphthalenes

Sir:

From the reaction of sodium naphthalene (NaN) with optically active 1-methyl-2,2-diphenylcyclopropyl bromide (**1**-Br) in dimethoxyethane (DME), leading to 1,1-diphenyl-2-methylcyclopropane (**4**)[1] with 29% net retention of configuration, Jacobus and Pensak concluded[2] that single electron transfer (SET) from a naphthalene radical anion (MN) to a cyclopropyl radical like **2** competes successfully with the ring inversion of **2** (Scheme I).

Scheme I



Scheme II

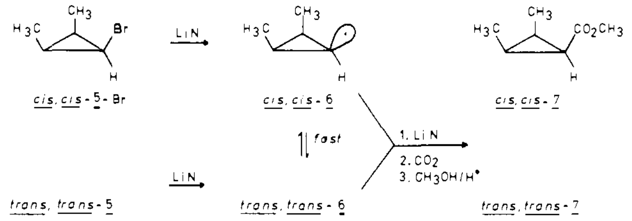


Table I. Ratios of *cis*-**11**/*trans*-**11** from the Reactions of 10-Hal with MN in THF at Room Temperature[a]

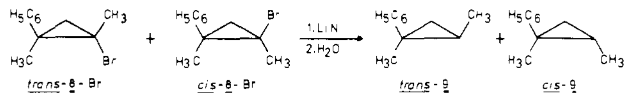
MN	*cis*-**10**-Cl	*cis*-**10**-Cl/ *trans*-10-Cl 40:60	*cis*-**10**-Br	*cis*-**10**-Br/ *trans*-10-Br 68:32
LiN	45:55	45:55	45:55	45:55
NaN	40:60	40:60	40:60	40:60
KN	39:61	39:61	39:61	39:61

[a] Ratios were determined by VPC; estimated error ±3%. *Normal addition:* MN (0.9 M) in THF is added dropwise to 10-Hal (1.0 M) in THF, followed by hydrolysis after 1 min; yields of **11** were 78 ± 14%.[6]

In contrast to these findings, we have reported[3] that 1-bromo-*cis*,*cis*-2,3-dimethylcyclopropane (*cis*,*cis*-**5**-Br) and its isomer *trans*,*trans*-**5**-Br, respectively, reacted with LiN in tetrahydrofuran (THF) after carboxylation and methylation to the identical 21:79 mixture of the carboxy methylates *cis*,*cis*- and *trans*,*trans*-**7**. Consequently, in the case of the secondary cyclopropyl radicals *cis*,*cis*- and *trans*,*trans*-**6** ring inversions are much faster than SET from MN (Scheme II).[4]

The object of this communication is to demonstrate two things: (1) Inversions of free secondary and tertiary cyclopropyl radicals are always faster than bimolecular SET reactions with MN; net retention is not observed. (2) Net retention as observed in the case of **1**-Br does *not* result from a sequence as outlined in Scheme I.[2] In order to show this, we performed the following experiments.

Reaction of 78:22 and 25:75 mixtures, respectively, of *r*-1-bromo-1-methyl-*c*-2-methyl-*t*-2-phenylcyclopropane (*trans*-**8**-Br) and its isomer *cis*-**8**-Br with LiN in THF at 20 °C led after hydrolysis to the identical 45:55 mixture of the cyclopropanes *trans*- and *cis*-**9**.[5] This demonstrates that the equilibration of



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[1] The precursor of **4** is the configurationally stable **3**, which is immediately protonated with retention of configuration in solvents like DME and THF: Walborsky, H. M.; Impastato, F. J.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3283; and see ref 7.

(2) Jacobus, J.; Pensak, D. *J. Chem. Soc. D* **1969**, 400.

(3) Boche, G.; Schneider, D. R. *Tetrahedron Lett.* **1978**, 2327. A rate constant $k = 1.6 \times 10^9$ L·mol^{-1}·s^{-1} was assumed for the SET reactions of MN with cyclopropyl radicals.[10]

(4) Identical reactions with *cis*- and *trans*-1-bromo-2-phenylcyclopropane, respectively, confirmed this result.[3]

(5) *trans*- and *cis*-**8**-Br were prepared in analogy to Kitaotani, K.; Hiyama, T.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3288: bp 42–44 °C (10^{-2} torr); ^{1}H NMR (CCl$_4$) δ 1.43 (s, CH$_3$ at C^1 of *trans*-**8**-Br); 1.95 (s, CH$_3$ at C^1 of *cis*-**8**-Br). The isomer ratio was determined by transformation with *n*-butyllithium into *trans*- and *cis*-**9** (VPC analysis): bp 64–68 °C (10 torr); ^{1}H NMR (CCl$_4$) δ 0.74 (br s, CH$_3$ at C^2 of *trans*-**9**), 1.18 (br s, CH$_3$ at C^2 of *cis*-**9**).

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