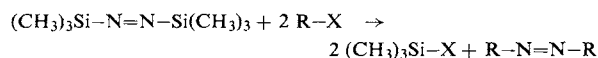# Bis(diphenylboryl)diimine [1]

By N. Wiberg and G. Schwenk [*]

In most cases silicon-nitrogen compounds are readily cleaved by Lewis acids at the Si—N bond[2]. Treatment of bis(trimethylsilyl)diimine[3] should thus lead to a synthesis of new derivatives of diimine, R—N=N—R:

$$(CH_3)_3Si-N=N-Si(CH_3)_3 + 2\ R-X \rightarrow$$
$$2\ (CH_3)_3Si-X + R-N=N-R$$

By using chlorodiphenylborane [R—X = (C₆H₅)₂B—Cl] in this way we obtained the first pure "azoborane"[4], namely, the brilliant yellow bis(diphenylboryl)diimine *(1)*. This compound completes the series of diimine derivatives R_2N_2 in which the two groups R attached to the diimine residue run from the element of the third to that of the seventh Group of the first short Period:

R_2N_2; R =

$\diagdown$B$\diagup$	$\diagdown$C$\diagup$	$\diagdown$N$\diagup$	—O	F
yellow	yellow-red	colorless	colorless	colorless
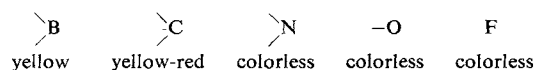
Compound *(1)* is not the sole product; about 70% of the reactants undergo an obscure reaction leading to nitrogen and an oil containing boron-nitrogen compounds of unknown composition.

The diimine *(1)* is polymeric, insoluble in the usual solvents, and extremely unreactive; thermal decomposition occurs only slowly above 400 °C, with loss of all the nitrogen. The compound is stable towards acids, but decomposes in the basic pyridine, giving up half its nitrogen. Two structural formulas *(1a)* and *(1b)* (Ph = C₆H₅) require consideration:

(1a)   *(1b)*
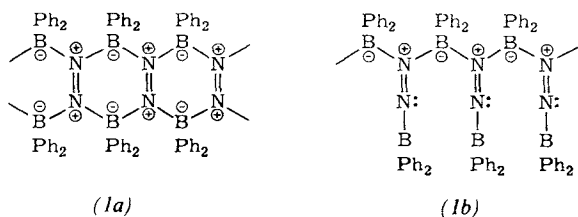
In *(1a)* the valency requirements of all the nitrogen and boron atoms are fully met; in *(1b)* only half the nitrogen and boron atoms are so satisfied, the other half having a free n-electron pair or an electron deficiency. The findings that organic azo compounds can be only singly protonated and that *(1)* dissolves in pyridine with decomposition are in favor of structure *(1b)*; this formula appears the more probable also because of the color of the compound which, as for other azo compounds, may depend on an n→π* electron transition [5].

Experimental:

Solutions of bis(trimethylsilyl)diimine (15.5 mmoles) and chlorodiphenylborane (31 mmoles) each in methylene dichloride (20 ml) are mixed at —40 °C, the reaction being carried out in the absence of oxygen. The mixture becomes deep blue for a short time and evolves nitrogen. When evolution of nitrogen is complete there is a clear yellowish-orange solution, from which analytically pure *(1)* separates slowly at —25 °C as a yellow precipitate.

[*] Priv.-Doz. Dr. N. Wiberg and Dipl.-Chem. G. Schwenk
Institut für Anorganische Chemie der Universität
8 München 2, Meiserstrasse 1 (Germany)

[1] Part 2 of Derivatives of Diimine. This work was supported by the Deutsche Forschungsgemeinschaft. — Part 1: [3].

[2] Cf., e.g. H. Nöth, Z. Naturforsch. 16b, 618 (1961); N. Wiberg and K. H. Schmid, Chem. Ber. 100, 748 (1967).

[3] N. Wiberg, W.-Ch. Joo, and W. Uhlenbrock, Angew. Chem. 80, 661 (1968); Angew. Chem. internat. Edit. 7, 640 (1968).
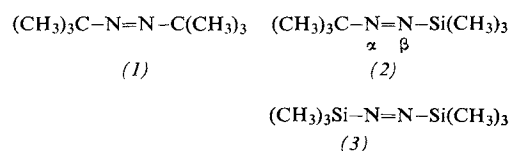
[4] It is probable that very impure azoboranes are formed on oxidation of hydrazines of the type R₂B—NH -NH—RB₂: H. Nöth, personal communication.

[5] M. B. Robin, R. Hart, and N. Kuebler, J. Amer. chem. Soc. 89, 1564 (1967).

ESR Spectra of Radical Anions of Aliphatic Azo Compounds: *tert*-Butyl and Trimethylsilyl Derivatives of Diimine[1]

By U. Krynitz, F. Gerson, N. Wiberg, and M. Veith [*]

Successive replacement of the tertiary carbon atoms of the relatively stable, pale yellow di(*tert*-butyl)diimine (azoisobutane) *(1)* [2] by the group-homologous silicon atoms leads by way of the less stable, red *tert*-butyl(trimethylsilyl)diimine *(2)* [3] to the extremely unstable, pale blue bis(trimethylsilyl)diimine *(3)* [4]:

$$(CH_3)_3C-N=N-C(CH_3)_3 \quad (CH_3)_3C-N=N-Si(CH_3)_3$$
$$\alpha\quad\beta$$
$$(1) \qquad\qquad\qquad (2)$$

$$(CH_3)_3Si-N=N-Si(CH_3)_3$$
$$(3)$$

In this paper, we report on the radical anions *(1)*⊖, *(2)*⊖, and *(3)*⊖ of these three compounds, which are of theoretical interest as simple π-electron radicals. In contrast to the situation with the known radical anions of aromatic azo compounds[5], the π-spin population in *(1)*⊖, *(2)*⊖, and *(3)*⊖ should be limited mainly to the azo group. This applies particularly to *(1)*⊖, whereas in the radical anions *(2)*⊖ and *(3)*⊖ the unpaired electron can be delocalized to some extent in unoccupied silicon orbitals of suitable symmetry [6].

The radical anions were prepared by reduction of *(1)*, *(2)*, and *(3)* with sodium or potassium in tetrahydrofuran (THF). THF was preferred to 1,2-dimethoxyethane as solvent since it was found that *(2)* and *(3)* are considerably less stable in the latter solvent. However, the radical anions *(1)*⊖ and *(2)*⊖ are remarkably stable: after standing for several hours at temperatures below 0 °C their concentration has decreased only slightly. This is only partially true for *(3)*⊖; although this radical anion is very stable when the counter ion is Na⁺, it decomposes even in a few minutes above —50 °C when the counter ion is K⁺. The ESR coupling constants for *(1)*⊖, *(2)*⊖, and *(3)*⊖ are listed in Table 1, where the assignments for $a_{N\alpha}$ and $a_{N\beta}$ in the case of *(2)*⊖ are based on

Table 1. Coupling constants (in gauss) of the magnetic nuclei in *(1)*⊖, *(2)*⊖, and *(3)*⊖. Solvent: THF.

Radical anion	Counter ion/ °C	$a_{N\alpha}$	$a_{N\beta}$	a_H	a_{13C} [a]	a_{29Si}
(1)⊖	Na⁺/0	8.24 ± 0.05	8.24 ±0.05	0.32 ±0.01	4.7 ±0.5	—
	K⁺/0	8.25 ± 0.05	8.25 ±0.05	0.32 ±0.01	4.8 ±0.5	—
(2)⊖	Na⁺/0	10.85 [b] ± 0.10	4.28 [b] ±0.05	[c]	[d]	[d]
	K⁺/0	10.40 [b] ± 0.10	4.57 [b] ±0.05	[c]	[d]	[d]
(3)⊖	Na⁺/0	6.62 ± 0.06	6.62 ±0.06	[c]	—	[d]
	K⁺/—80	6.25 ± 0.06	6.25 ±0.06	[c]	—	7.0 ±0.2

[a] Tertiary C atoms.   [b] Temperature-dependent coupling constants.   [c] Not resolved.   [d] Not unambiguously identified.

comparisons with $(1)^\ominus$ and $(3)^\ominus$ and on HMO calculations. The characteristic spectra are reproduced in Figures 1a—1d.

Not enough information is presently available for a detailed discussion of the ESR results (Table 1). In the first place, it is questionable whether the parameters that have been proposed for the relations between ^{14}N coupling constants and π-spin populations in other cases [7] may be used here. Secondly, the hybridization state of trimethylsilyl-substituted nitrogen atoms in (2) and (3) has not been clarified. Even with these limitations the following relations are evident:

1. The sums of the coupling constants $a_{N\alpha} + a_{N\beta}$ decrease along the series $(1)^\ominus$, $(2)^\ominus$, and $(3)^\ominus$: 16.5; 15.2 (15.0); 13.2 (12.5). The decreases correspond to the expectation that trimethylsilyl substituents should have an appreciable share of the π-spin population [6]. It is informative to compare the ^{14}N
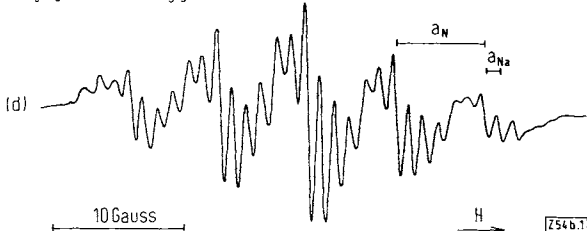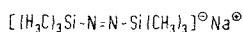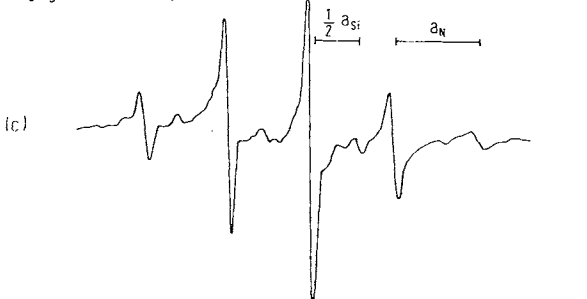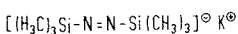
$$[(H_3C)_3C-N=N-C(CH_3)_3]^\ominus K^\oplus$$

(a)

$$[(H_3C)_3C-N=N-Si(CH_3)_3]^\ominus Na^\oplus$$
$$\alpha \quad \beta$$

(b)

$$[(H_3C)_3Si-N=N-Si(CH_3)_3]^\ominus K^\oplus$$

(c)

$$[(H_3C)_3Si-N=N-Si(CH_3)_3]^\ominus Na^\oplus$$

(d)

10 Gauss   H   [754b.1]
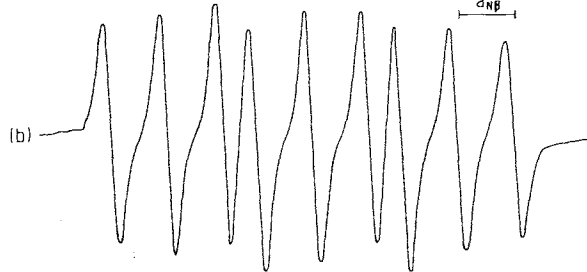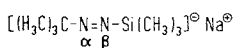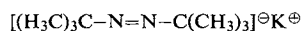
Fig. 1. ESR spectra of the radical anions $(1)^\ominus$ (a), $(2)^\ominus$ (b), and $(3)^\ominus$ (c and d).

Solvent: THF; temperature: 0 °C for a, b, and c, —80 °C for d.

coupling constants ($a_{N\alpha} = a_{N\beta}$) of the two symmetrical radical anions $(1)^\ominus$ and $(3)^\ominus$ with the corresponding values for the radical anion $(4)^\ominus$ of azobenzene [5]: $(1)^\ominus$ 8.25; $(3)^\ominus$ 6.25 (6.62); $(4)^\ominus$ 4.84 gauss. The capacity of trimethylsilyl substituents for sharing π-spin population is thus intermediate between the capacities of alkyl and of aryl substituents.

2. In contrast to radical anion $(1)^\ominus$, where a coupling constant $a_H(C-CH_3) = 0.32$ gauss could be measured (cf. Fig. 1a), the corresponding splittings could not be resolved in the spectra of $(2)^\ominus$ or $(3)^\ominus$ (cf. Figs. 1b, c, d). The reason for this probably lies in the small size of $a_H(Si-CH_3)$, which for $(3)^\ominus$ is likely to be at most 0.1 gauss in view of a line width of 0.6 gauss. This finding cannot yet be interpreted.

3. An additional hyperfine splitting was observed for $(3)^\ominus$ with Na^+ as counter ion: $a_{Na} = 1.05 \pm 0.05$ gauss (Fig. 1d). The splitting pattern (seven lines of relative intensities 1:2:3:4:3:2:1) corresponds to interaction with two equivalent ^{23}Na nuclei, a phenomenon that has already been found for ketyls in THF with Na^+ or Li^+ as counter ions [8]. Since the electronic structures of the azo and the keto group are related, similar associations might be involved in the two cases. An additional splitting by ^{39}K nuclei of two equivalent K^+ counter ions was not observed either for $(3)^\ominus$ or for the ketyls mentioned above, probably because of lack of association (larger volume of the K^+ ion) and/or of non-resolution (appreciably lower magnetic moment of the ^{39}K isotope). The former explanation is favored in the case of $(3)^\ominus$ by the almost identical line widths in the spectra concerned (Figs. 1c and 1d) and also by the stabilization, already indicated, of the radical anion by Na^+ counter ions.

[*] Dr. U. Krynitz and Prof. Dr. F. Gerson
Physikalisch-chemisches Institut der Universität
CH-4056 Basel, Klingelbergstrasse 80 (Switzerland)

Priv.-Doz. Dr. N. Wiberg and Dipl.-Chem. M. Veith
Institut für Anorganische Chemie der Universität
8 München 2, Meiserstrasse 1 (Germany)

[1] Also Part 3 of Derivatives of Diimines. This work was supported by the Schweizerischer Nationalfonds (Project No. 4651) and by the Deutsche Forschungsgemeinschaft. — Part 2: N. Wiberg and G. Schwenk, Angew. Chem. 81, 745 (1969); Angew. Chem. internat. Edit. 8, 755 (1969).

[2] E. Farenhorst and E. C. Kooyman, Recueil Trav. chim. Pays-Bas 75, 993 (1953).

[3] N. Wiberg and M. Veith, unpublished.

[4] N. Wiberg, W.-Ch. Joo, and W. Uhlenbrock, Angew. Chem. 80, 661 (1968); Angew. Chem. internat. Edit. 7, 640 (1968).

[5] E. T. Strom, G. A. Russell, and R. Konaka, J. chem. Physics 42, 2033 (1965).

[6] F. Gerson, J. Heinzer, H. Bock, H. Alt, and H. Seidl, Helv. chim. Acta 51, 707 (1968).

[7] E. W. Stone and A. H. Maki, J. chem. Physics 39, 1635 (1963).

[8] N. Hirota and S. I. Weissmann, J. Amer. chem. Soc. 82, 4424 (1960); A. H. Reddoch, J. chem. Physics 43, 3411 (1965).

O-Acylated Vinylogous Amides [1]

By H. G. Nordmann and F. Kröhnke [*]

Vinylogous amides (formamides) (2) react extremely smoothly with methylene-active compounds such as N-(p-bromophenacyl)pyridinium bromide (1) in acetic anhydride in a kind of vinylogous formylation to give vinylpyridinium salts of the type (3) [3].

O-Acylated vinylogous amides were assumed to occur as active intermediates in order to explain the unusually high reactivity of vinylogous amides in the above reaction [2,3]. We have now succeeded in isolating these compounds for the first time [4,5].

756

Angew. Chem. internat. Edit. / Vol. 8 (1969) / No. 10