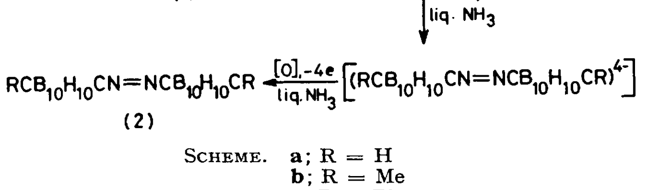
Preparation of Azocarbaboranes: Oxidation of 1-Amino-*o*-carbaborane Anion in Liquid Ammonia

By Tetsushi Totani,* Katsutoshi Aono, Hiroshi Nakai, and Motoo Shiro

(*Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka,* 553 *Japan*)

Summary 1-Amino-*o*-carbaborane anions, (*o*-$RCB_{10}H_{10}CNH_2$)$^{2-}$ in liquid NH_3 have been found to be oxidized with $KMnO_4$ to give the symmetrically substituted 1-azo-*o*-carbaboranes, $RCB_{10}H_{10}CN{=}NCB_{10}H_{10}CR$ (R = H, Me, Ph).

Although a large number of 1,2-dicarba-*closo*-dodecaborane(12) (*o*-carbaborane) derivatives have been synthesized,[1] azo and hydrazo carbaboranes containing a nitrogen–nitrogen linkage are not known. We attempted to obtain the title compounds by general azotization procedures but were unsuccessful probably because of the highly electron-deficient nature of the *o*-carbaborane cage. We now report a method for the preparation of the new azocarbaboranes (**2a**—**c**) by reduction of *o*-$RCB_{10}H_{10}CNH_2$ (**1a**—**c**) to the dianion (*o*-$RCB_{10}H_{10}CNH_2$)$^{2-}$ with Na metal in liquid NH_3 followed by oxidation[2] as shown in the Scheme.



Scheme. **a**; R = H
b; R = Me
c; R = Ph

In a typical run, $MeCB_{10}H_{10}CNH_2$ (**1b**)[3] (2·8 mmol) in liquid NH_3 was treated with Na (5·6 mg equiv.) at −63 °C under nitrogen and the resulting dianion solution was oxidized with finely powdered $KMnO_4$ (5·6 mmol). After evaporation of most of the NH_3 at ambient temperature, toluene was added at *ca.* −60 °C.† Residual NH_3 in the reaction mixture was then removed completely under reduced pressure. The green mixture was filtered, and washed with benzene. The filtrate was concentrated to afford a white to pale yellow solid, which can be recrystallized from CH_2Cl_2–C_6H_{14} [(**2b**), $MeCB_{10}H_{10}CNNCB_{10}H_{10}CMe$, m.p. 225 °C, 79% yield based on (**1b**)]. Compound (**2b**) exhibited a molecular cut-off at *m/e* 346 corresponding to the $(^{12}C_6{}^1H_{26}{}^{14}N_2{}^{11}B_{20})^+$ ion, and elemental analyses were consistent with the formula $C_6H_{26}N_2B_{20}$. Compounds (**2a**) (m.p. *ca.* 270 °C, sublimes, 58% yield) and (**2c**) (m.p. 243—244·5 °C, 73% yield) have also been prepared in the same way from (**1a**) and (**1c**), respectively. ^1H N.m.r. spectra of the azo compounds showed signals which were attributed to the substituents bonded to carbon [(**2a**) δ (Me_4Si) 4·27 (s, br, CH), (**2b**) δ 2·26 (s, CMe), (**2c**) δ 7.20 (m, CPh)]. Each compound gave an intense Raman line, at 1545 cm^{-1} for (**2a**), 1550 cm^{-1} for (**2b**), and 1555 cm^{-1} for (**2c**), characteristic of the stretching vibration of a symmetrically substituted –N=N– bond. Electronic spectra of these compounds showed an absorption at λ_{max} 364 nm (ϵ 32) for (**2a**), λ_{max} 375 nm (ϵ 22) for (**2b**), and λ_{max} 392 nm (ϵ 58) for (**2c**) giving rise to the R-band of azo groups (in 1,2-dimethoxyethane).‡ ^1H N.m.r. spectroscopy provided no evidence for the formation

---

† *Caution:* When the reaction mixture was concentrated to dryness without addition of toluene or other inert solvents, detonation occurred.

‡ The molecular structure of (**2b**) has been determined by *X*-ray crystallography and full details will be published elsewhere. These results confirm that the molecular conformation of (**2b**) is *trans*.

of the *cis*-isomer of (**2b**) because a sharp methyl resonance was detected suggesting only a single isomer. Compounds (**2a**—**c**) were readily reduced with $LiAlH_4$ in ether at room temperature to produce hydrazo-*o*-carbaboranes, $RCB_{10}H_{10}$-$CNHNHCB_{10}H_{10}CR$ (**3a**—**c**), in moderate yields (*ca*. 60%). [(**3a**) R = H: m.p. 250 °C, sublimes; (**3b**) R = Me: m.p. 233—237 °C; (**3c**) R = Ph: m.p. 195—196 °C].§ Under conditions for oxidation of $(o\text{-}MeCB_{10}H_{10}CNH_2)^{2-}$ and $(o\text{-}PhCB_{10}H_{10}CNH_2)^{2-}$ so far studied for the preparation of azo compounds, the corresponding 1-substituted hydrazo-*o*-carbaboranes (**3b**) and (**3c**) have been isolated only in traces. Attempts to obtain these hydrazo carbaboranes by reducing the amount of $KMnO_4$ used resulted in the formation of the azocarbaboranes (minor) additional to the original amines (major product) which would be reproduced *via* oxidation of the unreacted dianions, $(RCB_{10}H_{10}$-$CNH_2)^{2-}$. In the oxidation of (**1a**), a slightly higher yield of (**3a**) was obtained (19%), but this direct oxidative procedure does not appear to be appropriate for the preparation of hydrazo compounds.

We thank Dr. Y. Matsui of this laboratory for measuring laser Raman spectra and helpful discussions.

(*Received*, 9*th July* 1979; *Com.* 737.)

---

§ The hydrazo-*o*-carbaboranes (**3a**—**c**) gave satisfactory elemental analyses and spectral data (i.r., n.m.r., mass).

[1] R. N. Grimes, 'Carboranes,' Academic Press, New York, 1970; E. L. Muetterties, 'Boron Hydride Chemistry,' Academic Press, New York, 1975.

[2] M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. N. Cohen, *Inorg. Chem.*, 1963, **2**, 1111; L. I. Zakharkin, V. N. Kalinin, and V. V. Gedymin, *J. Organometallic Chem.*, 1969, **16**, 371.

[3] L. I. Zakharkin and V. N. Kalinin, *Zhur. obshchei. Khim.*, 1965, **35**, 1882.