Journal of Organometallic Chemistry, 51 (1973) C1–C2

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Preliminary communication

Synthesis and characterization of 1,3-dimethyl-2-phenyldiazaborolin

J.S. MERRIAM and K. NIEDENZU

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506 (U.S.A.)

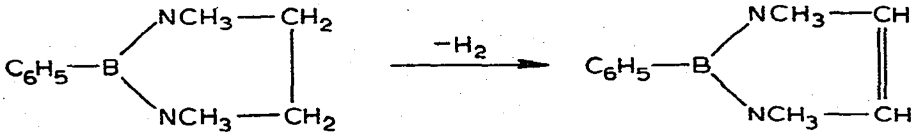
(Received January 8th, 1973)

SUMMARY

The preparation and characterization of the first diazaborolin, a system which is isoelectronic with the cyclopentadienide anion, is described.

Although the 1,3-diaza-2-boracycloalkanes have long been known[1], their chemistry has not yet been explored in great detail. One of the most interesting representatives of this class of compounds appears to be the five-membered heterocyclic system; previous preliminary studies[2] indicated that it can be dehydrogenated to yield a species, 1,3-diaza-2-borolin, which is isoelectronic with the cyclopentadienide anion. The potentially similar chemical behavior of the two cited isoelectronics offers attractive preparative and theoretical possibilities.

In the present work the synthesis and characterization of the first diazaborolin, 1,3-dimethyl-2-phenyldiazaborolin, (II), according to eq. (1) is described. Compound II was obtained by refluxing 1,3-dimethyl-2-phenyldiazaboracyclopentane[3] (1,3-dimethyl-2-phenyldiazaborolidine, (I), m.p. –84°, b.p. 210°) in argon atmosphere over 10% palladium-on-charcoal catalyst for 72 hours. The product was rectified by distillation to yield a colorless solid, m.p. 44–45°, b.p. 250–251° (745 mm).



(1)

(I) (II)

The structure of (II) is readily substantiated by the proton magnetic resonance spectrum of the compound. Whereas the methylene protons of (I) give a singlet, δ 3.10 ppm, the protons bonded to the annular carbon atoms of II exhibit a resonance signal with a chemical shift δ 6.14 ppm (relative to TMS). Also, the boron-11 magnetic resonance spectra (neat liquids, relative to boron trifluoride-etherate) of I (δ −32.2 ppm) and II (δ −25.6 ppm) are distinctly different, the latter chemical shift being in the order of that of *B*-triphenyl-*N*-trimethylborazine. This observation may be indicative of a similar degree of "aromaticity" for the two cited compounds.

Molecular orbital calculations comparing the diazaboroline system of II with the cyclopentadienide anion indicate similar π-donor abilities for the two species; using a ferrocene system as a model for the diazaboroline ligand, evaluation of overlap integrals (Offenhartz Method) indicates metal-to-ring bond lengths of 1.8 – 2.1 Å. These values compare favorably with metal-to-ring bond distances in metallocenes[4].

The mass spectra of I and II show significant differences in both peak intensities and fragmentation patterns. The parent peak P of I (m q 174) is 71.2% in relative abundance to the base peak $P-1$, whereas in the spectrum of II the parent peak (m/q 172) is also the base peak, with only 33.0% relative abundance for $P-1$. A strong indication of the chemical stability of the 1,3,2-diazaborolin system is also seen in the ready loss of a phenyl group from II under electron impact, whereas in the mass spectrum of I not only is there more ready fragmentation but a C_6H_5BN species is highly abundant but is not observed in the spectrum of II.

Current studies are directed towards the preparation of *B*-alkylated 1,3-diaza-2-borolins, metallocene analogs of this novel system, and the possibility of its utilization in Diels–Alder reactions.

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