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Cooperative Effect of Carborane and Pyridine in the Reaction of Carboranyl Alcohols with Thionyl Chloride: Halogenation versus Oxidation

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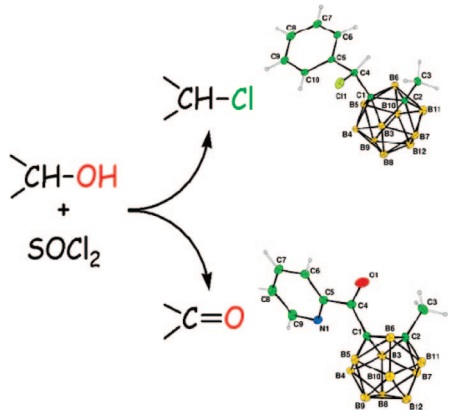

Thionyl chloride ($SOCl_2$) acts as halogenation reagent in its reaction with 1-[phenyl(hydroxy)methyl]-2-R-1,2-dicarba-*closo*-dodecaborane **1a**,**b** but unexpectedly behaves as an oxidant for 1-[2′-pyridyl(hydroxy)methyl]-2-R-1,2-dicarba-*closo*-dodecaboranes **2a**,**b**. The synthesis and characterization of all new compounds, including structure determinations of **1a**, **2a**, 1-[phenyl(chloro)methyl]-2-methyl-1,2-dicarba-*closo*-dodecaborane **3a**, and 1-[2′-pyridyl(oxo)methyl]-2-methyl-1,2-dicarba-*closo*-dodecaboranes **4a** are reported and the possible pathways are discussed.

Carbon-containing polyhedral boranes (*carboranes*) are extremely stable cage molecules that have been known for over 30 years. The icosahedral carborane *closo*-$C_2B_{10}H_{12}$ derivatives containing organic functional groups have found applications in a number of diverse fields such as material's science, boron carriers for boron neutron capture therapy, agents for the extraction of metal ions, in conducting organic polymers, ligands for metals, and more recently in supramolecular chemistry.[1] Organic halides are key intermediates in organic synthesis. Their transformations to useful compounds are well documented and they serve as intermediates in a wide variety of reactions and rearrangements.[2] Alcohols are the most common precursors to halides, with thionyl chloride ($SOCl_2$) being one of the most common halogenation reagents employed.[3] It is well-known that $SOCl_2$ reacts with alcohols to form chlorosulfite esters (seldom isolated)[4] that further convert to the desired chlorides and HCl and SO_2 in an excess of $SOCl_2$. Organic bases such as pyridine are often added to the reaction mixture because it provides a substantial concentration of chloride ion needed for the final reaction of the chlorosulfite intermediate.[3] However, the reaction also proceeds in the absence of bases and under heating conditions. As part of our work directed toward the synthesis and catalytic applications of *o*-carborane derivatives (1,2-dicarba-*closo*-dodecaborane) and benzhydrylamines,[5] we were interested in the preparation of new chloride derivatives of the *o*-carborane as useful intermediates for further transformations. Thus, we set out to prepare a new series of carboranyl chloride compounds by the reaction of the corresponding alcohols with $SOCl_2$. We report here on a rare example of $SOCl_2$-mediated alcohol oxidation in secondary alcohols having both carboranyl and pyridyl substituents.

Following an adaptation to known procedures,[6] we have prepared the series of carboranyl methylalcohols bearing a phenyl (**1a**,**b**) or a pyridine (**2a**,**b**) substituent as the starting compounds (Scheme 1). The new alcohols have been characterized by analytical and spectroscopic methods and the molecular structures for **1a** and **2a** have been determined by X-ray structure analysis (Figures 1 and 2). NMR data for the alcohols correlated well with that of other related carboranyl alcohols.[6] For example, the NMR data showed OH proton resonances at δ 2.44−2.50 (br s, concentration independent) for **1a** and δ 5.31−5.34 (d, concentration independent) for **2a**. Proton resonances for the CH groups in **1a** and **2a** appeared at δ 5.10 (concentration independent) as a singlet and a doublet, respectively. Full assignment of the proton resonances for **1b** and **2b** can be done by comparison of their NMR spectra with that of **1a** and **2a**. $^{11}B\{^1H\}$ NMR spectra for all compounds are consistent with a

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(1) See for example: (a) Planas, J. G.; Teixidor, F.; Viñas, C.; Light, M. E.; Hursthouse, M. B. *Chem. Eur. J.* **2007**, *13*, 2493, and references cited therein. (b) Teixidor, F., Viñas, C. In *Science of Synthesis*; Thieme: Stuttgart, Germany, 2005; Vol. 6, p 1235, and references cited therein. (c) Grimes, R. N. *J. Chem. Educ.* **2004**, *81*, 658. (d) Plešek, J. *Chem. Rev.* **1992**, *92*, 269.

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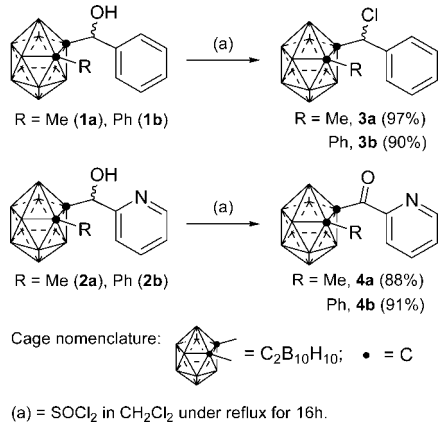
SCHEME 1. Synthesis of Compounds 3 and 4



closo-icosahedral geometry for the boron cage.[7] The $^{13}C\{^1H\}$ NMR spectra for all compounds also show characteristic peaks for the two cage−carbon vertices, phenyl, pyridine, and hydroxy methyl CH.

The higher chemical shift for the OH signals in the ^1H NMR in **2a**,**b** with respect to **1a**,**b** (vide supra) is consistent with the presence of a hydrogen bond of the type O−H···N in **2a**,**b** in solution.[8] The concentration independence of the OH proton resonances for the two model compounds (**1a** and **2a**) showed that there is no significant self-association of the alcohols in solution, and clearly indicates the intramolecular nature of the O−H···N hydrogen bond in **2a**.[9] The fact that the coupling between the two protons of the CHOH group in **2a** is observed confirms that the intramolecular hydrogen bond is retained in solution and probably avoids free rotation of the pyridyl fragment through the −C(H)(carboranyl)(OH) rotor.[10] IR spectra of the new alcohols in KBr exhibit broad stretching frequencies for O−H at 3390−3550 and 3355−3395 for **1a**,**b** and **2a**,**b**, respectively. The lower frequency of the O−H stretching mode for **2** in comparison with that of **1** is also consistent with the presence of O−H···N hydrogen bonding in the pyridyl(hydroxy)methyl derivatives in the solid state.[11] The existence of intramolecular O−H···N hydrogen bonding was confirmed by X-ray crystallographic analysis (Figure 1).

Reactions of the phenylmethyl alcohol derivatives **1a**,**b** with an excess of $SOCl_2$ under reflux conditions afforded the expected chloride derivatives **3a**,**b** in excellent yields. The new chloro derivatives have been characterized by analytical and spectroscopic methods and the molecular structure for **3a** has been determined by X-ray structure analysis (Figure 2). NMR data for these compounds show the disappearance of the OH proton and a characteristic downfield shift of the CHCl proton with respect to the corresponding CHOH in **1a**,**b**.

Surprisingly, the pyridylmethyl alcohols **2a**,**b** did not afford the expected chloro derivatives under the same reaction conditions as the phenyl counterparts but gave the ketones **4a**,**b** as the only reaction products (Scheme 1). The new ketone derivatives have been unambiguously characterized by analytical and spectroscopic methods and the molecular structure for **4a** has been determined by X-ray structure analysis (Figure 2). ^1H NMR data show the disappearance of both the OH and the CH proton signals for these compounds. In addition, characteristic signals for the C═O fragment are clearly observed in their $^{13}C\{^1H\}$ NMR spectra (δ 183−185) and IR (1693−1690 cm^{-1} in KBr).

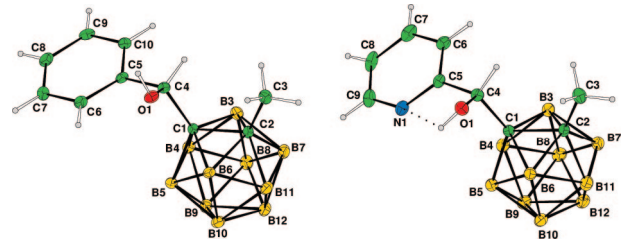


FIGURE 1. Molecular structures of **1a** (left) and **2a** (right). Thermal ellipsoids set at 35% probability; cluster hydrogen atoms are omitted for clarity.

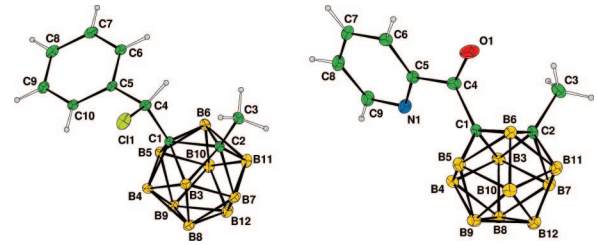


FIGURE 2. Molecular structures of **3a** (left) and **4a** (right). Thermal ellipsoids set at 35% probability; cluster hydrogen atoms are omitted for clarity.

The molecular structures for **1a**, **2a**, **3a**, and **4a** (Figures 1 and 2) are in agreement with the NMR data. Crystal and data collection can be found in the Supporting Information. The molecular structures for both alcohols show typical icosahedrons with very similar bond distances and angles, also similar to those in other carboranyl alcohols.[12] However, whereas no close intramolecular contacts are found in **1a**, there is a clear intramolecular O−H···N hydrogen bond in **2a** (d(O···N), 2.900(2) Å; ∠(OHN), 141.4°). The structural data for **3a** clearly show that chlorination took place at the carbon atom linking the carborane cage and the phenyl fragment (Figure 2). The bond length and angles in this molecule are those expected for icosahedral disubstituted 1,2-*o*-carboranes.[8] As for **4a** (Figure 2), its structural data unambiguously show that oxidation of the alcohol to the ketone has taken place. Carbon−oxygen bond length of 1.205(3) Å and a C1C4C5 angle of 121.7(2)° are consistent with a double C═O bond.[13] The structural data for **4a** correlate well with the only other simple carboranyl ketone reported.[14]

Oxidation of **2a**,**b** to the ketones **4a**,**b** is clearly affected by both the pyridine and carborane moieties in the same molecule since either **1a**,**b** (Scheme 1) or the organic counterpart (2-pyridyl)(phenyl)methanol affords the chloride products exclusively (SI). The oxidation is certainly an unusual reaction

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(10) Coupling is maintained even at 55 °C ($CDCl_3$).
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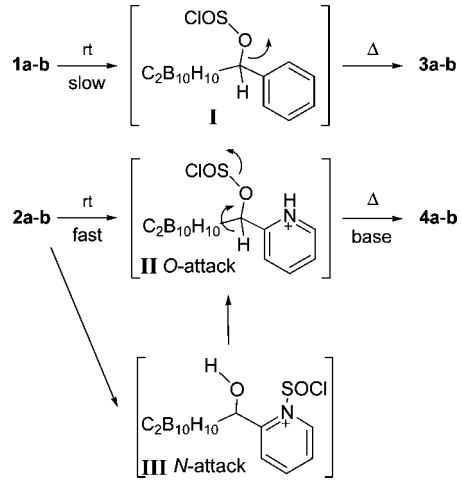
SCHEME 2. Postulated Mechanisms for the Reaction with $SOCl_2$



pathway regarding the extensive literature on the halogenation of alcohols by $SOCl_2$. To understand the reaction pathway, we have monitored the halogenation and oxidation reactions by in situ NMR spectroscopy. Thus, reaction of **1a** with an excess of $SOCl_2$ (10 equiv) takes place in $CDCl_3$ at room temperature to give the chloro derivative **3a** very slowly (50% conversion after 5 days).[15] A clear homogeneous solution was obtained and no reaction intermediates were observed. On the other hand, when $SOCl_2$ (5.1 equiv) was mixed with a solution of **2a** in $CDCl_3$ at room temperature, a new soluble compound **II** was formed within 5 to 10 min. Conversion of **II** to the corresponding ketone **4a** was only observed when the NMR sample was warmed at 55 °C (Scheme 2).[16] The marked difference in the reaction rate between **1a** and **2a** with $SOCl_2$ is worth noting. The faster reaction of **2a** with $SOCl_2$ could be explained either by an enhanced nucleophilicity of the oxygen (*O*-attack intermediate **II**, Scheme 2), due to the presence of an intramolecular O−H···N hydrogen bond, or by the nucleophilic catalysis of the pyridine ring (*N*-attack intermediate **III**).[17] Although the highly reactive intermediate **III** was not observed during the NMR experiments, we cannot exclude its formation, followed by intramolecular rearrangement to intermediate **II**. The latter intermediate (**II**) is not stable enough to be isolated and could not be fully characterized. However, its formation is evidenced by ^{1}H NMR with concomitant appearance of a pyridinium salt signal for the NH^+ proton (δ 18, br s), disappearance of the OH proton signal, and downfield shift of the benzylic proton (δ 7.29 ppm, s). These data suggest that the alcohol has reacted to give the chlorosulfite ester intermediate as proposed in Scheme 2.

Halogenation versus oxidation reaction in these compounds can be interpreted as a competition between nucleophilic addition of Cl^- to the methylene carbon (intermediate **I**) versus proton abstraction (intermediate **II**) from the same carbon under the reaction conditions (Scheme 2). Whatever the nature of the intermediate **II**, NMR data clearly show that the CH proton in this intermediate is more acidic than that for the starting alcohol (**2a**). This is probably due to the positive charge at N in **II** and could explain the ease of H abstraction. If we assume that chlorosulfite ester intermediates **I** and **II** are formed in the reaction of both **1** and **2** with $SOCl_2$ (Scheme 2), respectively, the absence of a positive charge in **I** would render the CH proton less acidic and make the Cl^- addition more favorable than proton abstraction. Different reaction pathways for charged and uncharged N-containing heterocycles have been reported.[18] However, this charge effect alone cannot account for the different reaction pathway in our case since the organic (2-pyridyl)(phenyl)methanol, having the pyridyl fragment, does form the chloro derivative exclusively.[19] Thus, in order to obtain the ketone derivatives, both the pyridinyl and carboranyl fragments must be present in the alcohol molecules. Although we do not have clear evidence for the mechanism, the oxidation pathway could be a combination of a charge effect (making the CH proton more acidic) and the bulkiness of the carboranyl fragment hindering the nucleophilic attack of the Cl^- anion to the CH carbon. We are currently studying the reactivity of the new carboranyl choride and ketone derivatives.

Experimental Section

Synthesis of *closo*-1-CH(Cl)(C_6H_5)-2-CH_3-1,2-$C_2B_{10}H_{10}$ (3a). General procedure: An excess of $SOCl_2$ (1 mL) was added to a CH_2Cl_2 solution (3 mL) of **1a** (239 mg, 0.905 mmol) and the mixture was stirred at reflux conditions for 16 h. The reaction mixture was then poured onto a cold saturated aqueous solution of K_2CO_3 (20 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic phases were dried over $MgSO_4$ and filtered. Chromatographic separation on silica gel (eluent: cyclohexane/ethylacetate 9:1, R_f 0.6) of the residue obtained upon evaporation of the filtered solution afforded pure **3a** as a pale yellow solid (248 mg, 0.877 mmol, 97%).

3a: mp 82 °C; ^{1}H NMR ($CDCl_3$) δ 7.42 (br s, 5H, C_6H_5), 5.20 (br s, 1H, C*H*Cl), 2.26 (s, 3H, C_c−CH_3); ^{1}H{^{11}B} NMR ($CDCl_3$), only signals due to B−H protons are given, δ 2.85 (br s, 1H), 2.55 (br s, 1H), 2.36 (br s, 2H), 2.34−2.25 (br s, 2H), 2.18 (br s, 1H), 2.10 (br s, 1H), 1.97 (br s, 1H), 1.46 (br s, 1H); ^{11}B NMR ($CDCl_3$) δ −2.2 (d, ^1J(B,H) = 148, 1B), −5.3 (d, ^1J(B,H) = 151, 1B), −7.0 to −12.8 (br m, 8B); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 137.8, 129.7, 128.6, 128.3 (C_6H_5), 80.9 (C_c), 76.2 (C_c), 60.6 (*C*HCl), 23.2 (C_c−*C*H_3); selected IR (KBr, cm^{-1}) ν 2592, 2556 (BH), 692; MS (CI-CH_4, *m*/*z*, %) 283 ([M + H]$^+$, 50), 247 ([M + H − HCl]$^+$, 100). Anal. Calcd for $C_{10}B_{10}H_{19}Cl$ (282.82): C 42.47, H 6.77. Found: C 42.61; H 6.83.

Synthesis of *closo*-1-CH(Cl)(C_6H_5)-2-C_6H_5-1,2-$C_2B_{10}H_{10}$ (3b). The general procedure described for **3a** was followed, using **1b** (100 mg, 0.306 mmol) to obtained **3b** as a pale yellow solid (95 mg, 0.275 mmol, 90%) by column chromatography (eluent: cyclohexane/ethylacetate 9:1, R_f 0.65).

3b: mp 126 °C; ^{1}H NMR ($CDCl_3$) δ 7.80−7.77 (m, 2H, C_6H_5), 7.61−7.48 (m, 3H, C_6H_5), 7.35−7.28 (m, 3H, C_6H_5), 7.17−7.14 (m, 2H, C_6H_5), 4.54 (s, 1H, C*H*Cl); ^{11}B NMR ($CDCl_3$) δ −1.4 (d, ^1J(B,H) = 156, 1B), −3.8 (d, ^1J(B,H) = 161, 1B), −7.8 to −12.3 (br m, 8B); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 137.8, 131.5, 131.4, 129.9, 129.5, 129.3, 128.3, 128.2 (C_6H_5), 86.3 (C_c), 85.3 (C_c), 60.0 (*C*HCl); selected IR (KBr, cm^{-1}) ν 2602, 2587, 2556 (BH), 702. Anal. Calcd for $C_{15}B_{10}H_{21}Cl\cdot 0.5H_2O$ (353.90): C 50.91, H 6.27. Found: C 50.78, H 6.19.

(15) No reaction was observed after 3 h with only 2 equiv of $SOCl_2$.

(16) Leaving the reaction mixture to stand at room temperature for several hours resulted in the precipitation of the pyridinium salt **2a**·HCl. The latter has been fully characterized (SI).

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(19) Monitoring the reaction of (2-pyridyl)(phenyl)methanol with $SOCl_2$ by NMR clearly shows the fast formation of a pyridinium salt (d 16.4 br s, 1H) as the sole product at room temperature. Further heating or addition of a base gives the final chloro derivative (SI).

Synthesis of *closo*-1-C(O)(C_6H_5)-2-CH_3-1,2-$C_2B_{10}H_{10}$ (4a). The general procedure described for **3a** was followed, using **2a** (100 mg, 0.377 mmol) to obtained **4a** as a white solid (88.0 mg, 0.335 mmol, 88%) by column chromatography (eluent: cyclohexane/ethylacetate 9:1, R_f 0.40).

4a: mp 78 °C; ^{1}H NMR ($CDCl_3$) δ 8.70 (br d, ^3J(H,H) = 4.2, 1H, NC_5H_4), 7.85 (td, J(H,H) = 7.5, 1.8, 1H, NC_5H_4), 7.75 (dt, J(H,H) = 7.8, 0.9, 1H, NC_5H_4), 7.50 (ddd, J(H,H) = 7.5, 4.5, 1.2, 1H, NC_5H_4), 2.12 (s, 3H, C_c-CH_3); ^{1}H{^{11}B} NMR ($CDCl_3$), only signals due to B−H protons are given, δ 2.86 (br s, 2H), 2.50 (br s, 1H), 2.44 (br s, 2H), 2.33 (br s, 2H), 2.28 (br s, 2H), 2.19 (br s, 1H); ^{11}B NMR ($CDCl_3$) δ −0.1 (d, ^1J(B,H) = 149, 1B), −5.5 (d, ^1J(B,H) = 150, 1B), −8.5 to −10.1 (br m, 8B); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 185.0 (*C*O), 153.1, 148.4, 136.9, 126.9, 124.1 (NC_5H_4), 24.4 (C_c-CH_3); selected IR (KBr, cm^{-1}) ν 2662, 2577 (BH), 1693 (CO); MS (CI-NH_3, *m*/*z*, %) 264 ([M + H]$^+$, 100). Anal. Calcd for $C_9B_{10}H_{17}NO$ (263.35): C 41.05, H 6.51, N 5.32. Found: C 40.81, H 6.25, N 5.02.

Synthesis of *closo*-1-C(O)(C_6H_5)-2-C_6H_5-1,2-$C_2B_{10}H_{10}$ (4b). The general procedure described for **3a** was followed, using **2b** (120 mg, 0.366 mmol) to obtained **4b** as a white solid (108 mg, 0.334 mmol, 91%) by column chromatography (eluent: cyclohexane/ethylacetate 9:1, R_f 0.35).

4b: mp 117 °C; ^{1}H NMR ($CDCl_3$) δ 8.67 (d, ^3J(H,H) = 4.7, 1H, NC_5H_4), 7.73−7.60 (m, 3H, C_6H_5 and NC_5H_4), 7.47−7.23 (m, 5H, C_6H_5 and NC_5H_4); ^{11}B NMR ($CDCl_3$) δ 0,4 (d, ^1J(B,H) = 149, 1B), −3,3 (d, ^1J(B,H) = 135, 1B), −8.4 to −11.1 (br m, 8B); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 183.1 (*C*O), 152.9, 148.2, 136.7, 126.9, 124.1 (NC_5H_4), 131.0, 130.8, 130.4, 128.4 (C_6H_5), 84.7 (C_c), 80.8 (C_c); selected IR (KBr, cm^{-1}) ν 2597, 2582, 2556 (BH), 1690 (CO); MS (CI-NH_3, *m*/*z*, %) 326 ([M + H]$^+$, 100). Anal. Calcd for $C_{14}B_{10}H_{19}NO\cdot0.5H_2O$ (334.43): C 50.28, H 6.03, N 4.19. Found: C 49.93, H 5.68, N 4.11.

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Supporting Information Available: Full experimental procedures, characterization data, ^{1}H and ^{13}C NMR spectra for all compounds, and crystallographic details and CIF files for compounds **1a**, **2a**, **3a**, and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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