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To cite this version:

Vincent Terrasson, José Giner Planas, Damien Prim, Clara Vinas, Francesc Teixidor, et al.. Cooperative effect of carborane and pyridine in the reaction of carboranyl alcohols with SOCl2: halogenation versus oxidation. IMEBoron, 2008, Platja d’Aro, Spain. hal-02913342

HAL Id: hal-02913342
https://hal.science/hal-02913342
Submitted on 8 Aug 2020

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Cooperative effect of carborane and pyridine in the reaction of carboranyl alcohols with SOCl₂: halogenation versus oxidation.

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Organic chlorides are key compounds in organic synthesis since they serve as intermediates in a wide variety of reactions. These molecules are commonly obtained by the reaction of an alcohol with thionyl chloride, one of the most employed halogenating reagents. With the aim to synthesize new α-carborane derivatives for material science and catalytic applications, we have prepared new carboranyl alcohols and carried out their reactions with thionyl chloride. If alcohols bearing a phenyl substituent gave the expected chlorinated compounds in good yields, those substituted with a pyridine ring surprisingly afforded the ketones as the only products under the same reaction conditions.

Following an adaptation to known procedures, we have prepared the series of four new carboranyl methylalcohols bearing a phenyl 1a-b or a pyridine substituent 2a-b (Scheme 1).

These alcohols were obtained in good to excellent yields (Table 1) and fully characterized by spectroscopic methods.

Molecular structures for 1a and 2a have been determined by X-ray structure analysis (Figure 1).

Whereas no intramolecular contacts are found in 1a, there is a clear intramolecular O-H...N hydrogen bond in 2a.

Reactions of the phenylmethylalcohol derivatives 1 a-b with an excess of SOCl₂ under reflux conditions afforded the expected chlorides 3 a-b in excellent yields (Scheme 2).

Surprisingly, the pyridymethyl alcohols 2 a-b did not afford the expected chlorides under the same conditions but gave the ketones 4 a-b (Scheme 3).

Chlorides 3 a-b and ketones 4 a-b have been unambiguously characterized by spectroscopic methods. Molecular structures for 3a and 4a have been determined by X-ray structure analysis (Figure 2).

Oxidation of the alcohols 2 a-b to the ketones 4 a-b is clearly affected by both the pyridine and carborane moieties in the same molecule since either 1 a-b or the organic counterpart (2-pyridyl)phenylmethanol exclusively afford the chloride products (Schemes 2 and 4).

When the reaction of 2a with SOCl₂ was monitored by NMR, the complete conversion of the alcohol to the intermediate I was observed within 5 min at room temperature. Further transformation according to Scheme 6 was only obtained by heating the reaction medium.

Halogenation versus oxidation in these compounds can be interpreted as a competition between nucleophilic addition of Cl⁻ versus proton abstraction at the benzylic position (Schemes 5 and 6). NMR data of the intermediate II clearly show that the benzylic proton is more acidic than that for the starting alcohol 2a (δ = 7.29 ppm compared to 5.11 ppm). This is probably due to the positive charge at the pyridine ring in II. This charge effect (making the benzylic proton more acidic) combined with the bulkiness of the carboranyl fragment hindering the nucleophilic attack of Cl⁻ could explain this unusual oxidation reaction.

References


We thank CICYT (Project MAT2006-05339), Generalitat de Catalunya (2005SGR00709), Spanish Government (Ref. to J.G.P.), MENRT-France (grant to V.T.), CNRS, Université de Versailles and UK EPSRC for financial support.