



PALLADIUM-CATALYZED ALLYLATION OF α -(*o*-CARBORAN-1-YL)ACETOPHENONE WITH ALLYL CARBONATES

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Cite this: *INEOS OPEN*, 2024, 7 (4–5), 132–133
DOI: 10.32931/io2450a

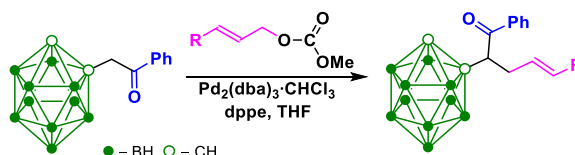
Received 16 October 2024,
Accepted 15 November 2024

<http://ineosopen.org>

Abstract

The reactions of palladium-catalyzed allylation of *o*-carboranylacetophenone with allyl carbonates lead to the formation of allylation products in good yields. Depending on the structure of the reagents and their ratio, both monoallylation and diallylation products can be obtained.

Key words: carboranes, allyl carbonates, palladium-catalyzed allylation.



The chemistry of carboranes and their derivatives has been actively developing since the early 1960s. Due to the unusual electronic structure of an icosahedral moiety, its large volume and high thermal stability, as well as a high content of the boron atoms, both the compounds themselves and methods for their modification are of considerable theoretical and practical interest [1–6].

One of the important approaches to the formation of carbon–carbon bonds is the palladium-catalyzed allylation, since the introduction of an allyl group into organic molecules opens up opportunities for its further functionalization [7–12].

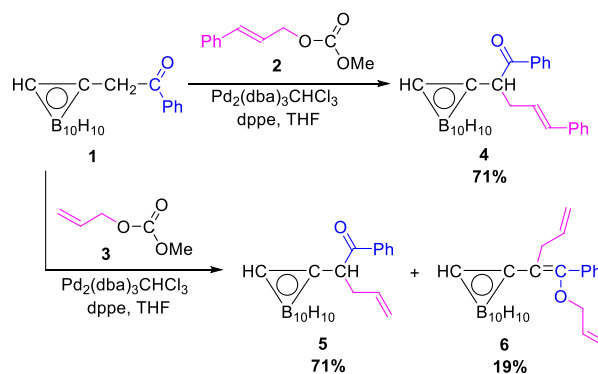
In this short communication, we demonstrate a new approach to modify the α -position of the side chain in substituted *o*-carboranes, which could prove promising for the preparation of unknown or difficult to access types of carborane derivatives.

We studied Pd-catalyzed allylation of α -(*o*-carboran-1-yl)acetophenone **1**, in which the CH₂ group was activated by the second (in addition to *o*-carboranyl) strong electron-withdrawing benzoyl group. Allyl carbonates **2** and **3** were used as reagents (Scheme 1). It is known that allyl carbonates are more reactive in such reactions than, for example, allyl acetates, since they contain a better leaving group [13]. In addition, the use of allyl carbonates allows the reactions to proceed under neutral conditions [14]. The reactions were carried out in the presence of a catalyst obtained from Pd₂(dba)₃·CHCl₃ and dppe taken in a 1:5 ratio [15]. The interaction of ketone **1** with cinnamyl methyl carbonate **2** led to the formation of expected allylation product **4** in 71% yield (Scheme 1).

The result of the reaction of allyl carbonate **3** with ketone **1** depends on the ratio of the reagents. At an equimolar ratio, only the expected allylation product **5** is formed. However, the conversion of initial ketone **1** is low and, according to the ¹H NMR spectroscopic analysis, its content in the reaction mixture is four times greater than that of the allylation product.

If a two-fold excess of the carbonate was taken for the reaction, then a mixture of monoallylation product **5** and diallyl-substituted product **6** was obtained in a 1.4:1 ratio. At a three-

fold excess of the carbonate, a mixture of the mono- and diallylation products was formed in a 6.5:1 ratio, which was established by ¹H NMR spectroscopy. Both products were separated by column chromatography on silica gel and isolated in pure form.



Scheme 1. Palladium-catalyzed allylation of α -(*o*-carboran-1-yl)acetophenone with allyl carbonates.

A molecular structure of diallylation product **6** was elucidated by X-ray diffraction (Fig. 1). Product **6** does contain two allyl groups; however, while the first one is expectedly located at the α -position to the carboranyl moiety, the second one formed the *O*-allyl ether of the enol derived from monoallylated ketone **5**.

We believe that there are several factors promoting the transfer of the reaction center during repeated allylation, the combined action of which led to the formation of allyl ether **6**. α -Deprotonation of the monoallylation product should lead to the formation of a tertiary α -carbanion, which is less favorable than the formation of a secondary carbanion at the stage of the formation of the monoallyl-substituted derivative. In addition, the repeated allylation at the α -position should lead to the generation of a quaternary carbon center at this position, which is especially unfavorable for steric hindrances due to the presence of a very bulky carboranyl substituent. The formation

of the enol, accompanied by a change in the hybridization of the α -carbon atom from sp^3 to sp^2 , also leads to a decrease in steric strains at the α -position in the product. Finally, the formation of the enol form of the monoallylation product is facilitated by the formation of a long conjugated chain involving the C=C bond of the enol, the aromatic ring, and the carboranyl moiety.

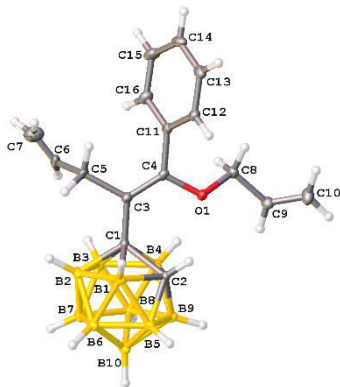


Figure 1. General view of compound **6** in the representation of non-hydrogen atoms as thermal ellipsoids ($p = 30\%$); the minor components of the disordered allyl group are omitted.

Thus, the Pd-catalyzed allylation of *o*-carborane derivative **1** under the action of allyl carbonates leads to mono- and/or diallylation products in good yields. The presence of the allyl group in these products provides opportunities for further modification, which can be used to obtain various functional *o*-carborane derivatives.

Acknowledgements

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (agreement no. 075-00277-24-00) using the equipment of the Center for Molecular Composition Studies of INEOS RAS.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the crystallographic data for compound **6**, the NMR spectra of compounds **4**, **5**, and **6**. For ESI, see DOI: 10.32931/io2450a.

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