

# Synthesis of the first stable carborane containing simple enol

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A carborane-containing stable simple enol — 1-(2-isopropyl-*o*-carboran-1-yl)-1-phenyl-2-mesityl-2-hydroxyethylene — has been synthesized. This enol does not isomerize to the starting ketone or keto-enol mixture even after prolonged heating in benzene in the presence of CF<sub>3</sub>COOH.

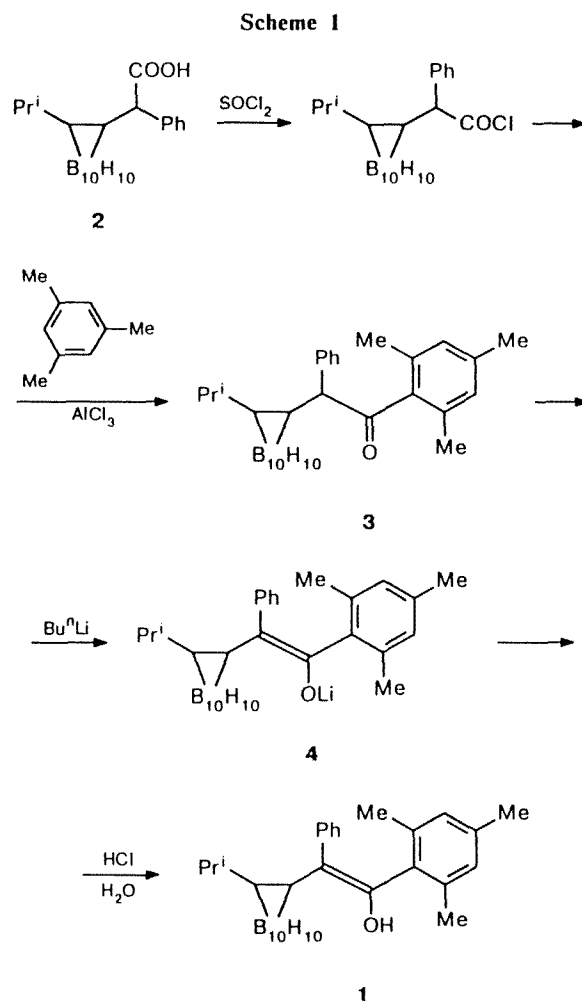
**Key words:** carborane-containing ketones and enols; synthesis; isomerization.

Sterically hindered groups, such as 2,4,6-trimethylbenzyl (mesityl, Mes) are usually used to stabilize simple enols. As a rule, stable enols contain no less than two mesityl groups, for example: Mes<sub>2</sub>C=C(OH)Mes, Mes(R)C=C(OH)Mes, Mes<sub>2</sub>C=C(OH)Ar.<sup>1</sup>

In the present work, a stable simple enol (**1**) containing one mesityl group and one bulky 1-isopropyl-*o*-carboranyl group was synthesized. The synthesis of enol **1** from (2-isopropyl-*o*-carboran-1-yl)phenylacetic acid (**2**) was carried out (Scheme 1).

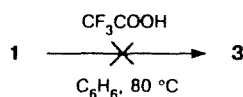
Ketone **3**, whose structure was confirmed by IR spectroscopy data, is smoothly formed from the chloro acylchloride acid **2** and mesitylene in the presence of AlCl<sub>3</sub> in a Friedel—Crafts reaction. A yellow enolate, soluble in the reaction mixture, is readily obtained by the action of Bu<sup>n</sup>Li on the solution of ketone **3** in an ether-benzene mixture at 10–15 °C. Enol **1** was obtained as colorless crystals by adding the enolate solution to a dilute solution of HCl. Enol **1** neither contains impurities of the starting ketone **3**, a product of addition of Bu<sup>n</sup>Li at the carbonyl group, nor a secondary alcohol, a product of CO group reduction. It is of interest that the reaction of Bu<sup>n</sup>Li with ketone **3** proceeds only in the direction of the formation of enolate **4**. The structure of enol **1** was confirmed by IR and NMR spectra as well as by elemental analysis. In accordance with the IR spectrum, enol **1** contains a double bond ( $\nu(\text{C}=\text{C})$  1630 cm<sup>-1</sup>) and two hydroxyl groups, one associated and one free (the corresponding bands at  $\nu$  3383 and 3487 cm<sup>-1</sup>). As follows from the <sup>1</sup>H NMR spectrum, the mesitylene group of enol **1** rapidly rotates in the NMR time-scale at 20 °C; therefore, the two *ortho*-methyl groups are revealed as a singlet signal. This is in agreement with the fact that the two *meta*-hydrogens also correspond to one signal. This allows one to assume that the structure of enol **1** is such that the *o*-carboranyl group and the OH-group are in the *cis*-position.

The hydroxyl group of enol **1** is strongly acidic since its signal in the NMR spectrum is shifted downfield



( $\delta$  9.08) compared with the OH signal in Mes<sub>2</sub>C=C(OH)Mes ( $\delta$  6.11).<sup>3</sup> This is likely to be associated with the strong electron-acceptor character of the *o*-carboranyl group.

Enol **1** is not converted into the starting ketone **3** by heating in benzene for 12 h at 80 °C, or by heating under the same conditions in the presence of catalytic amounts of CF<sub>3</sub>COOH; this means that there is no keto-enol equilibrium under those conditions.



In this regard, enol **1** is like the enol (Ph<sub>2</sub>Mes)<sub>2</sub>C=C(OH)Me that is not converted into ketone under analogous conditions.<sup>3</sup>

Thus, we have obtained the first carborane containing, stable, simple enol **1**, not capable of turning into the starting ketone **3** under the conditions of acidic catalysis. This example shows that the bulky *o*-carboranyl group, like bulky organic aromatic groups, can be used for obtaining stable, simple enols.

### Experimental

IR spectra were recorded on a UR-20 instrument; <sup>1</sup>H NMR spectra were recorded on a Bruker WP-200SY spectrometer in acetone-d<sub>6</sub>. The <sup>1</sup>H chemical shifts are given with reference to SiMe<sub>4</sub>. The course of the reaction was monitored by TLC on Silufol plates.

**[1-(2-Isopropyl-*o*-carboran-1-yl)-1-phenyl]methyl mesityl ketone (3).** A solution of [1-(2-isopropyl-*o*-carboran-1-yl)-1-phenyl]acetic acid (3.4 g, 11 mmol) in 15 mL of dry benzene, 5 mL SOCl<sub>2</sub>, and -0.05 mL DMFA was boiled until HCl evolution was completed. After removing the solvent *in vacuo*, 15 mL of dry mesitylene were added to the residue, and then AlCl<sub>3</sub> (1.6 g, 12 mmol) was added with stirring. The mixture was heated on a water bath until HCl evolution was completed and a precipitate formed. The cooled reaction mixture was decomposed by a 5 % HCl solution (50 mL), the organic layer was separated, and the water layer was extracted with benzene (20 mL). The organic solutions were combined and dried (MgSO<sub>4</sub>). Ketone **3** (2.4 g, 52 %) was obtained after distillation of the solvent *in vacuo* and crystallization; m.p. 166–168 °C (heptane–toluene). Found (%): C, 62.79;

H, 8.12; B, 24.99. C<sub>22</sub>H<sub>34</sub>B<sub>10</sub>O. Calculated (%): C, 62.56; H, 8.06; B, 25.59. IR spectrum, ν/cm<sup>-1</sup>: 1707 (CO); 2600 (BH).

**1-(2-Isopropyl-*o*-carboran-1-yl)-1-phenyl-2-mesityl-2-hydroxyethylene (1).** Bu<sup>n</sup>Li (2 mL, 2.3 mmol, 1.14 M) in benzene was added to a solution of ketone **3** (0.9 g, 2.1 mmol) in 15 mL of an ether–benzene (2 : 1) mixture with stirring under an Ar atmosphere at 5–10 °C, and a light-orange solution was obtained. Then, the temperature was raised to 20 °C; the solution was poured into dilute hydrochloric acid (20 mL, 5 % solution) and extracted with ether (2×10 mL). The ether extracts were dried with MgSO<sub>4</sub>. Enol **1** (0.85 g, 96 %) was obtained after distillation of the solvent *in vacuo* and crystallization; m.p. 192–193 °C (benzene–heptane). Found (%): C, 62.18; H, 8.09; B, 25.80. C<sub>22</sub>H<sub>34</sub>B<sub>10</sub>O. Calculated (%): C, 62.56; H, 8.06; B, 25.59. IR, ν/cm<sup>-1</sup>: 1630 (C=C); 1615, 1603 (Ph); 2600 (BH); 3383 (OH assoc.); 3487 (OH not assoc.). <sup>1</sup>H NMR, δ: 1.14 (d, 6 H, (CH<sub>3</sub>)<sub>2</sub>CH, *J* = 6.8 Hz); 2.04 (s, 3 H, *p*-CH<sub>3</sub>–Mes); 2.25 (s, 6 H, *o*-CH<sub>3</sub>–Mes); 2.85 (hept, 1 H, (CH<sub>3</sub>)<sub>2</sub>CH, *J* = 6.8 Hz); 6.59 (s, 2 H, Mes); 6.99–7.29 (m, 5 H, Ph); 9.08 (br.s, 1 H, OH).

**Attempts to isomerize 1 into 3.** *A.* A solution of enol **1** (0.1 g, 0.2 mmol) in 5 mL of dry benzene was boiled for 12 h. TLC did not detect ketone in the reaction mixture, and only the starting enol was present.

*B.* A solution of enol **1** (0.1 g, 0.2 mmol) in 5 mL of dry benzene and 0.1 mL CF<sub>3</sub>COOH was boiled for 12 h. TLC did not detect ketone in the reaction mixture, and only the starting enol was present.

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