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BROMO-1-ETHOXY-7-NORBORNYLMAGNESIUM
A STABLE ALICYCLIC β-ALKOXY-SUBSTITUTED GRIGNARD COMPOUND

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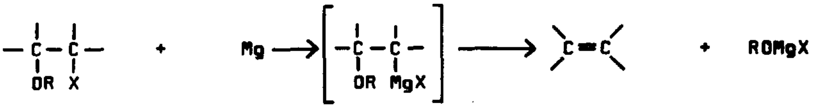
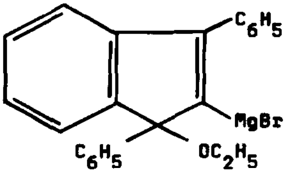
It is well known that β-alkoxyalkyl Grignard compounds cannot be prepared from the corresponding halide and magnesium; instead a ready elimination reaction under the formation of alkenes occurs[1]:



To our knowledge the only example of a stable β-alkoxy-substituted Grignard compound is the recently reported bromo-1-ethoxy-1.3-diphenyl-2-indenylmagnesium (I)[2]:

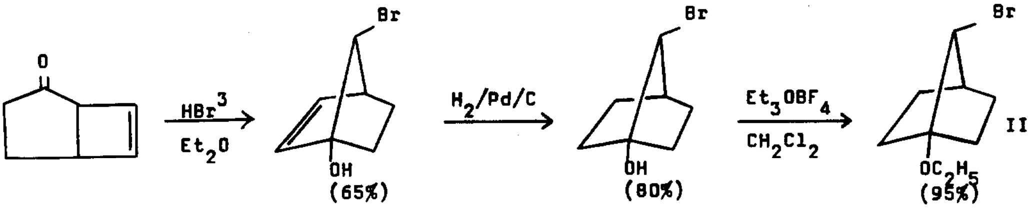


I

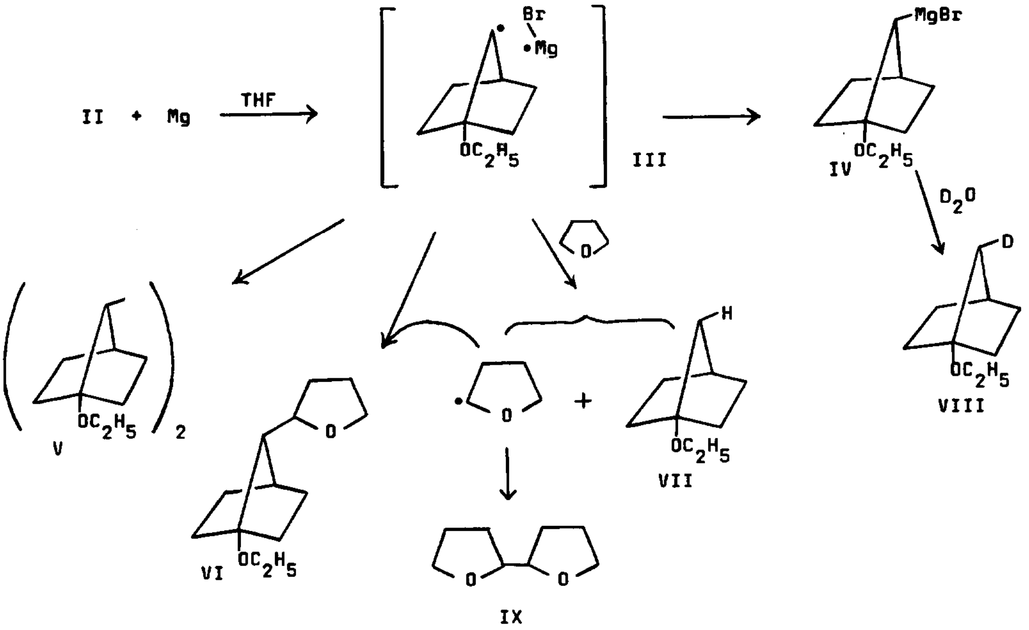
The normal β-elimination is said not to take place in this specific case because the activation energy for the formation of the five membered ring allene would be too high.

We wish to report an example of a β-alkoxy-substituted Grignard compound, which is stable because elimination is prohibited by Bredt's rule.

The starting material for our investigation, 1-ethoxy-bromonorbornane (II), was synthesized in the following way:

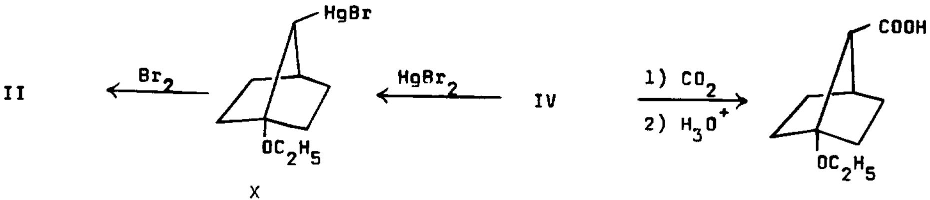


Under rigorous exclusion of oxygen and moisture in a sealed glass apparatus II reacted with magnesium in tetrahydrofuran without the aid of a catalyst. After sedimentation of the voluminous black residue of metallic magnesium a clear, water-white solution was obtained, which contained bromo-ethoxy-7-norbornylmagnesium (IV; 10 - 20%) as evidenced by treatment with deuterium-oxide, mercury(II) bromide and carbondioxide and by the NMR spectrum.



After deuterolysis and working up by preparative GLC (Apiezon L) compounds V (12%), VI (1.5%), VII + VIII (48%), IX (6%) and unreacted II (1.5%) were isolated and identified by their NMR and mass spectra. According to spectral analysis the mixture of VII and VIII contained the two compounds in a 3 : 1 ratio. Of V two isomers with identical mass spectra were isolated; evidently these are the two possible diastereomers. According to the NMR spectrum VI also consisted of two (diastereo)isomers.
The formation of V, VI, VII and IX can be rationalized by a radical process occuring via III during the attack of magnesium on II[4].

Reaction of the Grignard solution with mercury(II)bromide and with carbon dioxide yielded X (m.p. 110°) and XI (m.p. 64-66°) respectively. They were identified by elemental analysis, NMR and mass spectra[5]. The structure of X was confirmed by reconverting it to II with bromine.



X

XI

The remarkable stability of IV was proven by heating the Grignard solution for two days at 80°: no change was observed in the NMR spectrum including a signal at approximately 0 ppm, which can be assigned to H^7 of III. However a decrease of the intensity of this signal was observed after heating the sample at 130° during two days; the course of this decomposition reaction will be further investigated.

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Bibliography

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5. The mass spectrum of X did not show a molecular ion peak; the highest fragment was found at m/e 390.9600; calculated for $(X \text{ minus } C_2H_5)^+$ m/e 390.9621.