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# THE REACTION OF 2-CHLOROBICYCLO[2.2.1]HEPTENE WITH METHYLLITHIUM

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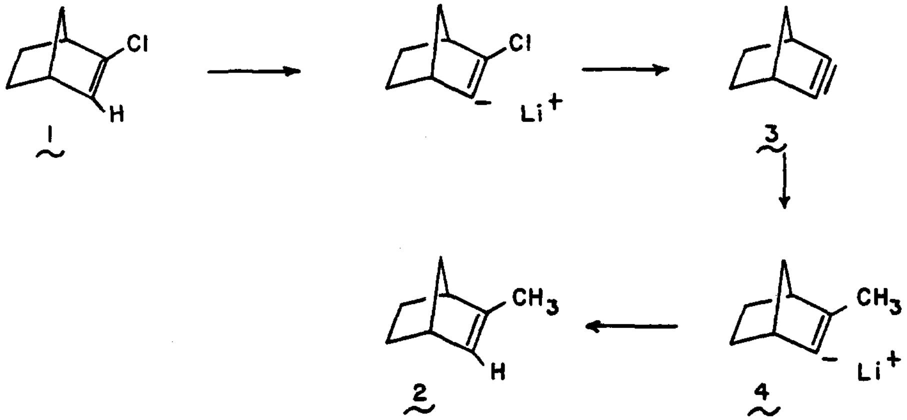
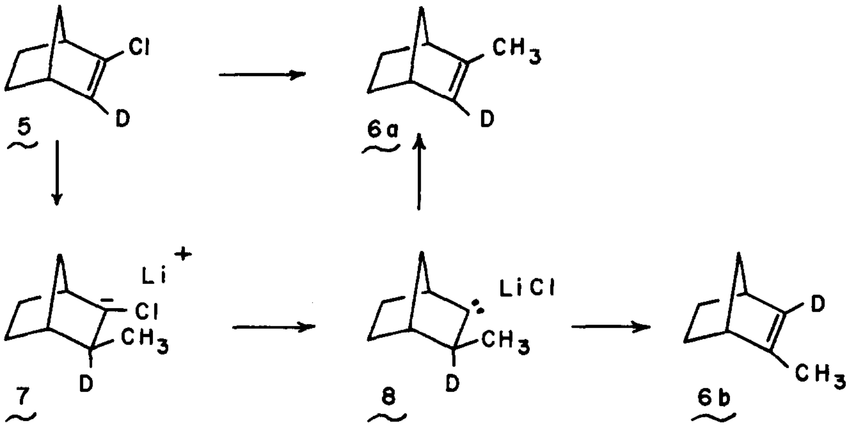
The reaction of methyllithium with 2-chlorobicyclo[2.2.1]heptene (1) has been reported to produce 2-methylbicyclo[2.2.1]heptene (2) in 73% yield.[2] This appeared to be a unique example of a substitution of a vinylic chloride by an alkyl group through reaction with an organolithium reagent. Whereas, alkyllithium reagents were not noted for such substitution reactions, the replacement of vinylic halides through reaction with aryllithium had ample precedent.[3,4] This substitution of halide by aryl was established to proceed *via* dehydrohalogenation of the vinylic halide to an alkyne and subsequent addition of the aryllithium to the acetylenic linkage.[3] In view of this background, we deemed it of interest to determine whether bicyclo[2.2.1]heptyne (3) was an intermediate in the conversion of 1 into 2. We now wish to report the results of this mechanistic study.

If the reaction of 2-chlorobicyclo[2.2.1]heptene (1) with methyllithium proceeded *via* 3, the first part of the process would involve removal of the vinylic proton followed by loss of chloride. Addition of methyllithium to 3 should then produce 4, which on hydrolysis should

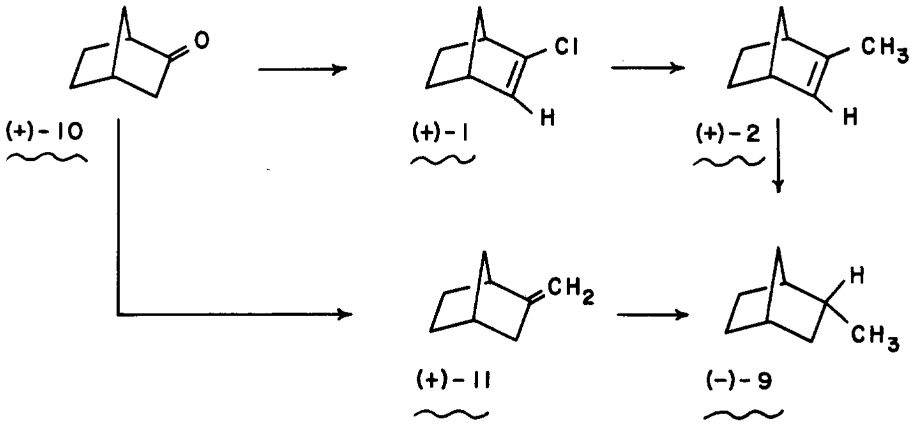


yield **2**. The simplest test of this process would be a work-up with deuterium oxide which would be expected to give 2-methyl-3-deuteriobicyclo[2.2.1]heptene. When **1** was stirred with five equivalents of ethereal methyllithium for 8 days, followed by the addition of deuterium oxide, no deuterium incorporation was observed. Since it could be argued that inadvertent hydrolysis of **4** had occurred during the course of this relatively slow reaction, we prepared 2-chloro-3-deuteriobicyclo[2.2.1]heptene (**5**).[5] Treatment of **5** with methyllithium as described



above, followed by aqueous work-up, resulted in no loss of deuterium in the product. Within experimental error **6** was labelled to the same extent as **5**, which ruled out the intermediacy of **3** (and of any other symmetrical intermediate). On the basis of the results discussed thus far, it could be suggested that methyllithium added to **5** to produce **7**, which on α-elimination gave **8**. In principle, **8** could serve as a precursor of either **6a** (by methyl migration) or of **6b** (by deuterium migration). On the basis of the established preference for hydrogen migration over methyl migration,[6] it would appear that the mechanism described would lead primarily to **6b**. Unfortunately, the labelling experiment carried out with **5** does not permit a distinction to be made between **6a** and **6b**.

In order to determine whether inversion or retention of configuration had occurred in the reaction of **1** with methyllithium, we prepared (+)-(1S)-2-chlorobicyclo[2.2.1]heptene [**(+)-1**], $[\alpha]_D^{25}$ + 1.3 ± 0.1° (c 9.72, $CHCl_3$) according to the method of McDonald and Steppel.[7] Treatment of **(+)-(1S)-1** under the standard conditions described above gave 2-methylbicyclo[2.2.1]heptene [**(+)-2**], $[\alpha]_D^{25}$ + 2.0 ± 0.1° (c 10.2, $CHCl_3$). In order to determine the absolute configuration and degree of optical retention (or inversion) of this product, the sample was catalytically reduced to yield *endo*-2-methylbicyclo[2.2.1]heptane [**(-)-9**], $[\alpha]_D^{25}$ - 9.2 ± 0.2° (c 6.63, $CHCl_3$). A sample of (+)-(1S)-bicyclo[2.2.1]heptan-2-one [**(+)-10**], which was identical in rotation to that used in the preparation of **(+)-1**, was converted into (+)-(1S)-2-methylenebicyclo[2.2.1]heptane [**(+)-11**], $[\alpha]_D^{25}$ + 33 ± 5° (c 6.0, $CHCl_3$) through reaction with methylenetriphenylphosphine. Reduction of **(+)-11** gave (-)-(1S)-2-*endo*-methylbicyclo[2.2.1]heptane [**(-)-9**], $[\alpha]_D^{25}$ - 9.4 ± 0.2° (c 7.05, $CHCl_3$). The agreement of the reduction products of **(+)-11** and **(+)-2** in both sign and degree of rotation established that the reduction product from **(+)-2** was (-)-(1S, 2R)-*endo*-2-methylbicyclo[2.2.1]heptane. This required that **(+)-2** also have the 1S configuration. Thus, the reaction proceeded with retention of configuration The agreement of the rotations of the samples of **(-)-9** indicated that, within experimental error, the replacement of chlorine by methyl had occurred with complete retention of stereochemistry.



In summary we have demonstrated that the highly unusual reaction of methyllithium with a vinyl chloride to give replacement does not proceed *via* either a cycloalkyne or an addition-α-elimination process. It would appear that a direct coupling reaction is involved.[8]

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## References and Footnotes

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4. For a general review see R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, N. Y., 1967, Chapter 8.

5. The details of the preparation of **5** will be presented in a full paper on this subject.

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7. R. N. McDonald and R. N. Steppel, *J. Amer. Chem. Soc.*, **92**, 5664 (1970).

8. The exact nature of this "coupling" reaction cannot be elucidated on the basis of the data currently available.