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A NEW METHOD FOR THE PREPARATION OF BICYCLO[2.1.1]HEXENES

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Bicyclo[2.1.1]hexenes are important for the study of highly strained ring systems and undergo interesting thermal and solvolytic rearrangements. Most syntheses of these compounds involve the preparation of a bicyclo[2.1.1]hexane derivative with subsequent introduction of the double bond. Although many standard β-elimination reactions of bicyclo[2.1.1]hexyl derivatives fail to give bicyclo[2.1.1]hexenes a modified Bamford-Stevens reaction,[1,2] dehydrobromination[3] and dechlorination[4] reactions have been successfully utilized for the preparation of bicyclo[2.1.1]hexenes. Other approaches have involved the solvolysis of bicyclo[2.2.0]hexenyl *p*-nitrobenzenesulfonate[5] and carbonium ion rearrangements of bicyclo[3.1.0]hexane derivatives.[6] We sought a general method for the preparation of bicyclo[2.1.1]hexenes in which the double bond was introduced simultaneously with the construction of the basic ring system. To achieve this goal we have examined the Ramberg-Bäcklund rearrangement[7] of the 2-chloro-3-thiabicyclo[3.1.1]heptane 3,3-oxides **1a** and **1b**. We now wish to report our initial results which indicate that this route provides a useful method for the preparation of bicyclo[2.1.1]hexenes **2**.

The known[8] mixture of *cis*- and *trans*-1,3-cyclobutane dicarboxylic acids **3a** was converted to the anhydride **4a** in 93% yield by refluxing with acetic anhydride Reduction of **4a** with lithium aluminum hydride[8] and treatment of the resulting cis-diol **5a** with methanesulfonyl chloride gave the dimesylate **6a**, (mp 92-94°, 89%). The dimesylate was converted to the volatile sulfide **7a** (mp 68-71.5°, 55%) by reaction with sodium sulfide in hexamethylphosphoramide. Chlorination of **7a** with N-chlorosuccinimide followed by oxidation with m-chloroperbenzoic acid gave the α-chlorosulfone **1a**. When treated with a slurry of sodium tert-amyl-oxide in diphenyl ether, bicyclo[2.1.1]hexene (**2a**) was produced in 68% yield by direct distillation from the reaction mixture under reduced pressure.[11]

Using a similar sequence of reactions from the known diacid **3b**[9,10] the α-chlorosulfone **1b** was prepared. When subjected to the Ramberg-Bäcklund reaction under the conditions utilized for **1a**, **1b** produced 5,5-dimethylbicyclo[2.1.1] hexene (**2b**) in 40% yield.[11]

Because a number of 1,3-cyclobutane dicarboxylic acids are known (e.g., the truxinic acids) this method will allow the preparation of a variety of substituted bicyclo[2.1.1]hexenes. Such studies are now in progress and will be reported at a later date.

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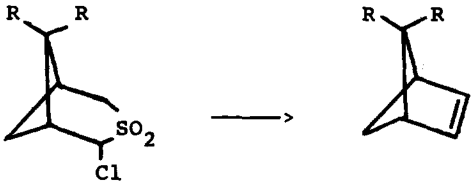
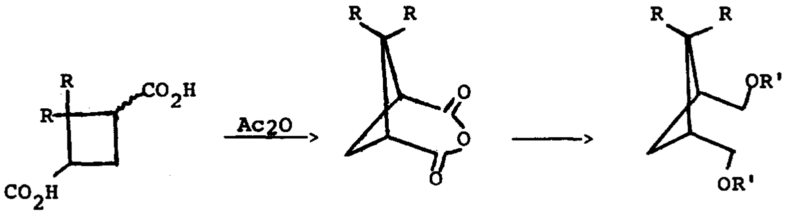
Formulae



1a (R = H)
b (R = Me)

2a (R = H)
b (R = Me)

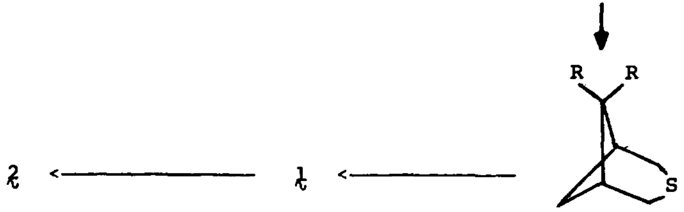


3a, R = H
b, R = Me

4a, R = H
b, R = Me

5a, R,R' = H
b, R = Me, R' = H

6a, R = H, R' = Ms
b, R = Me, R' = Ms



7a, R = H
b, R = Me

References and Notes

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11. The spectral properties of the bicyclo[2.1.1]hexenes **2a** and **2b** were identical with those reported in the literature.