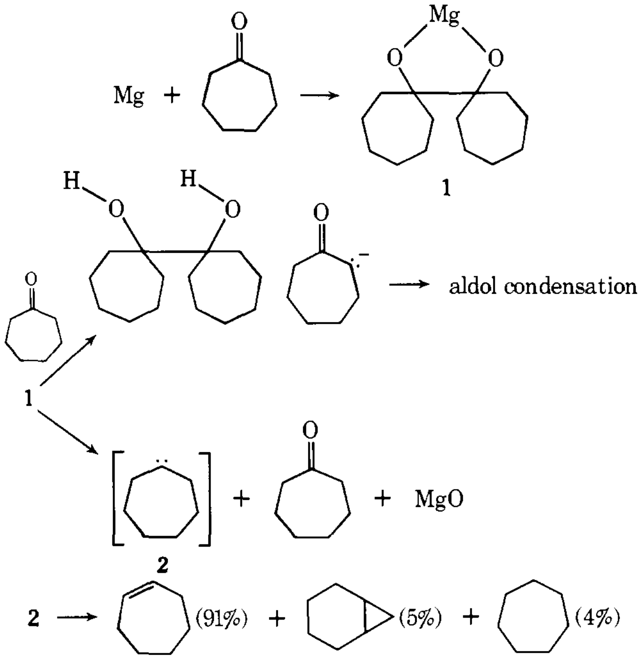
cloheptanone when the latter is subjected to aldol condensation conditions as described by Grignard and Colonge.[8] One should also note that although the aldol condensation of cycloheptanone is inadequately described in the literature, the aldol condensation of cyclohexanone is well known to yield a variety of products depending on reaction conditions.[9] For this reason a rigorous analysis of the balance of the oil was not attempted.

In light of these facts, we should like to suggest the following mechanism for the reaction of magnesium atoms with cycloheptanone.



Actually it is unlikely that **2** is a free species but is probably a highly complexed carbenoid. The ratio of cycloheptene to norcarane does not suggest a free carbene in light of the Friedman and Schechter work.[6]

We are extending our studies to other metals and other carbonyl compounds and shall report these results in due course.

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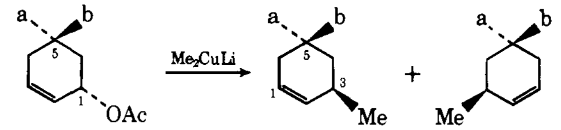
On the Stereochemistry of Conversion of Allylic Esters to Olefins with Lithium Dialkylcuprates

Sir:

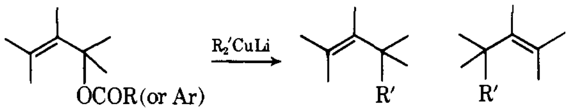
We wish to report that conversion of *cis*-and *trans*-5-methyl-2-cyclohexenyl acetate (**1**) to 3,5-dimethylcyclohexene (**2**) with lithium dimethylcuprate (Me_2CuLi) is stereospecific; *cis*-**1** gives *trans*-**2** and *trans*-**1** gives *cis*-**2**. Thus substitution occurs on the side of the ring opposite from the replaced acetate group. The two allylic positions become equivalent as shown by eq 1.



(1)

cis-**1**, a = Me; b = H ⟶ *trans*-**2**, a = Me; b = H
trans-**1**, a = H; b = Me ⟶ *cis*-**2**, a = H; b = Me

The conversion of allylic esters (**3**) to olefins by coupling with lithium dialkylcuprates was first reported by Crabbé and co-workers[1] and has been a key step in several subsequent investigations.[2,4] Coupling can occur at either end of the allylic system to give unrearranged (**4a**) or rearranged (**4b**) products.[3] Mixtures are generally formed; however, in some cases single isomers, either rearranged[1,2] or unrearranged,[4] are obtained. In one case isomeric allylic acetates gave essentially the same product distribution[2b] and it was concluded that the transformation involves formation of allylic radicals and subsequent transfer of an alkyl radical.[2b]

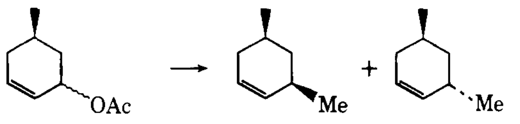


3 **4a** **4b**

(2)

Recently Corey and Mann[3] reported a case in which a cyclopentenyl allylic lactone reacts without rearrangement and with complete inversion to give the desired product. However, the system was designed to give the observed result and alternatives are precluded for steric reasons.

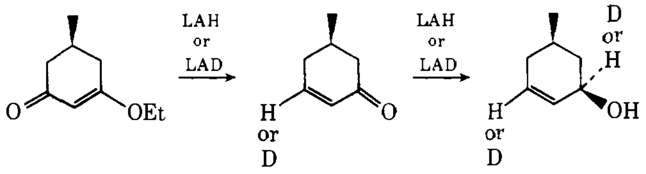
In this work we have converted the isomeric 5-methyl-2-cyclohexenyl acetates (**1**)[5a] to 1,3-dimethylcyclohexene (**2**). Configurations of the isomeric acetates were established previously.[5] Lithium dimethylcuprate was prepared by addition of methyllithium to a cold (0 °C) suspension of methylcopper (prepared from a butyl sulfide–copper iodide complex)[6] in ether. Reaction of **1** with 2 equiv of Me_2CuLi in ether at 0 °C for 24 h resulted in 90–95% conversion to **2**. The olefin was isolated by preparative GC and configurations were established by hydrogenation to the corresponding 1,3-dimethylcyclohexanes which were identified by comparison with authentic samples.[7] The pertinent data are summarized under eq 3. These data are averages of two to seven independent experiments. Isomeric compositions were determined by capillary GC (200 ft SE-30 for **2** and 300 ft UCON polar for **1**) which gave baseline resolution.



(3)

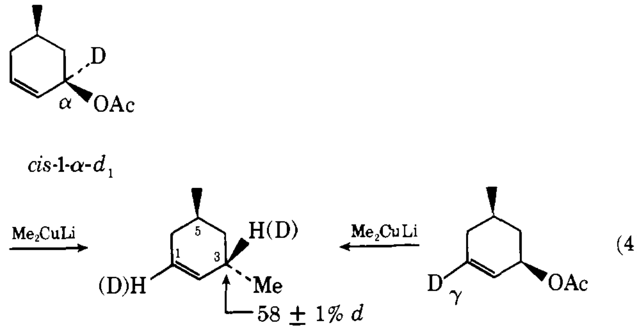
1		*cis*-2	*trans*-2
99.3 ± 0.1% *cis*-1	⟶	1.3 ± 0.2%	98.7 ± 0.2%
99.3 ± 0.1% *trans*-1	⟶	97.6 ± 0.1%	2.4 ± 0.1%
86.6 ± 0.1% *trans*-1	⟶	86.4 ± 0.2%	13.6 ± 0.2%

The conversion of α- and γ-deuterio-**1** to **2** was investigated to determine the amount of allylic rearrangement in this unbiased system. Synthesis of the 5-methyl-2-cyclohexenyl system involves two lithium aluminum hydride reductions.[5b] The final reduction gives 95% cis alcohol (**5**) from which pure *cis*-**5** can be obtained. This mixture can also be converted to *trans*-**5**.[5b,c] As illustrated, use of lithium aluminum deuteride in the appropriate step leads to either α- or γ-deutero-*cis*-**5**.



cis-**5**

As shown by eq 4, *cis*-**1**-α-d_1 (96.7 ± 1.6% *d*) and *cis*-**1**-γ-d_1 (98.4 ± 1.4% *d*) gave *trans*-**2**-d_1 with the same fraction of total deuterium at C_3. Total deuterium contents were determined from mass spectra.[8] Expanded Eu(fod)$_3$-shifted 100-MHz NMR spectra of the deuterated acetates **1**-d_1 showed they were discretely labeled as indicated. Unreacted *cis*-**1**-α-d_1 was isolated and found to be unchanged which shows that scrambling does not occur prior to reaction. The deuterium distribution in *trans*-**2**-d_1 was determined from the total deuterium (same as for *cis*-**1**-d_1) and relative peak areas (planimeter) for the C_3 and C_5 proton signals in expanded 270-MHz NMR spectra which gave baseline separation of both signals. The data indicate that **2**-d_1 derived from either α- or γ-deuterio-**1** has somewhat more than half of the label at C_3. This probably results from a systematic error in determining the deuterium distribution. In any case it appears that the reaction involves a symmetrical intermediate (allyl radical or π-allyl complex) in which the two allylic positions are equivalent.

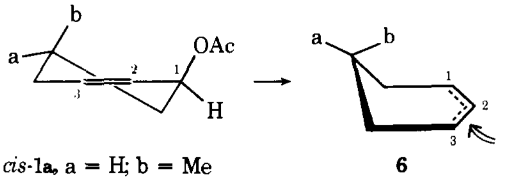


cis-1-α-d_1

(4)

trans-**2**-d_1 *cis*-1-γ-d_1

The data under eq 3 show that the 1 → 2 transformation is highly stereoselective. This system is unbiased with regard to substitution with and without allylic rearrangement. However, there may be an inconspicuous steric bias, unique to the cyclohexenyl system, that favors inversion of configuration. For reasons given earlier in another connection,[9] the quasi-axial conformation (**1a**) may be related to the best transition state for cleavage of the allylic bond. This leads to an allylic intermediate (**6**) with the out of plane C_5 carbon on the side from which the acetate group has departed. Clearly the oppposite side (**6**, arrow) is less hindered for capture to form product or an intermediate π-allyl complex.



cis-**1a**, a = H; b = Me
trans-**1a**, a = Me; b = H

6

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Capped Cyclodextrin

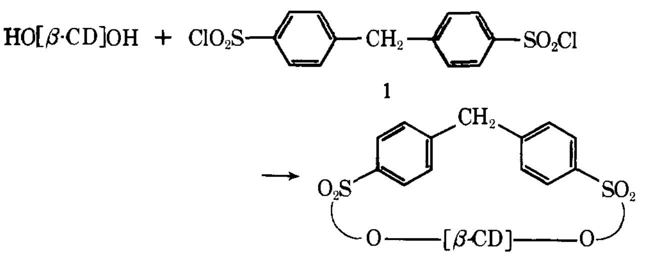
Sir:

Inclusion recognition or host-guest recognition has attracted the rapidly increasing interest of chemists since the first structural recognition of benzene derivatives by cyclodextrins in ester hydrolyses,[1] the remarkable regio recognition of anisole by cyclodextrin in chlorination,[2] or the beautiful chiral recognition of α-amino acids by certain crown ethers[3] has been reported.

However, only a few host molecules are known to recognize a guest molecule mostly via *hydrophobic interaction.* For development and understanding of the concept of host-guest recognition, new families of hydrophobic binding hosts must be added into the list of known hosts.

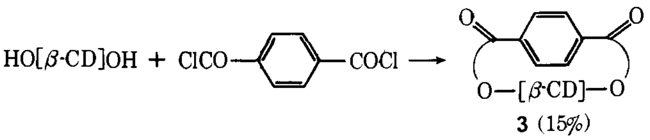
According to Nèmethy-Sheraga theory,[4] hydrophobic destabilization originates mostly in the entropically unfavorable orientation of water molecules on the surface of the hydrophobic guest (and/or host) dissolved in water. From this standpoint, the driving force of hydrophobic host-guest binding, or *hydrophobic interaction,* should be closely correlated with a decrease of the hydrophobic surface exposed in water. Thus, it may be reasonably expected that the capping of well-known cylindrical hosts should cause a remarkable strengthening of hydrophobic binding[5] as is schematically exemplified by Figure 1.

Now we wish to report the preparation of β-cyclodextrins (β-CD), capped by hydrophobic moieties, **2**, and **3**, which bind



1

2 (20%)



3 (15%)