CHEMISTRY LETTERS, pp. 133-134, 1979. Published by the Chemical Society of Japan

MAGNESIUM OXIDE AS AN EFFECTIVE CATALYST FOR MIGRATION OF EXO-CYCLIC DOUBLE BOND

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Exo-double bonds of 2-methylene-4,4,6-trimethylbicyclo[4,2,0]-octane ($\underset{\sim}{1}$), $\Delta^{7(13)}$-protoilludene ($\underset{\sim}{3}$), $\Delta^{2(3),7(13)}$-illudadiene ($\underset{\sim}{5}$), and $\Delta^{2(10)}$-pinene ($\underset{\sim}{7}$) were effectively migrated to the endo positions over MgO catalyst.

A simple and beneficial method for migrating an exo-double bond to endo position will make the Wittig reaction more valuable in the synthesis of olefinic compounds. Usually, the double bond is migrated by acid-catalyzed reaction.[1] On the other hand, base-catalyzed double bond migrations are scarecely known in organic synthesis except with strong homogeneous bases such as t-BuOK in dimethyl-sulfoxide. We wish to report that the migration of the double bond proceeds by a simple procedure using magnesium oxide as a heterogeneous basic catalyst.[2]

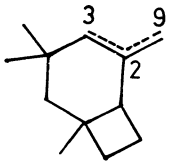
Magnesium oxide catalyst was prepared from magnesium hydroxide (Kanto Chemical Co.) by outgassing at 773 K for 2-3 h and was stored in a sealed glass ampoule. The reactant that had been degassed was admitted to the catalyst through a breakable seal. The whole reaction system was kept at the reaction temperature to prevent the reaction mixture from being condensed. The products were collected in a liquid nigtogen trap and subjected to gas chromatographic and mass spectrometric analyses.

Results are given in Table 1. All reactions were very clean and proceeded quantitatively. Especially, the reaction of illudadiene ($\underset{\sim}{5}$)($\Delta^{2(3),7(13)} \rightarrow \Delta^{2(3),7(8)}$) is notable, because any other methods[3] could not give such an excellent result.

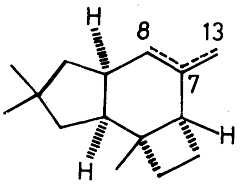
Since magnesium oxide exhibits basic property on the surface, it is considered that the reactions are initiated by abstraction of the allylic proton by the basic center on the catalyst to form carbanion species favoring an endo-cyclic double bond formation.

Table 1. Double bond migration over MgO Catalyst

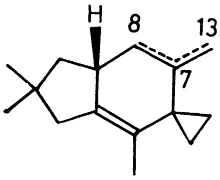
Substrate	Weight of substrate g	Weight of catalyst g	Reaction temp. K	Reaction time h	Product	Yield
1	0.10	0.1	383	1	2	quantitative
3	1.2	2.0	438	1.5	4	quantitative
5	0.15	0.15	423	2	6	quantitative
7	0.05	0.2	373	2	8	quantitative



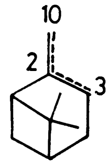
1:$\Delta^{2(9)}$
2:$\Delta^{2(3)}$



3:$\Delta^{7(13)}$
4:$\Delta^{7(8)}$



5:$\Delta^{7(13)}$
6:$\Delta^{7(8)}$



7:$\Delta^{2(10)}$
8:$\Delta^{2(3)}$

References and Notes

1) Among the acid-catalyzed migrations, boiling in toluene for several hours with a small amount of I_2 was the most convenient and effective method for our synthetic work. However, this method is not effectively applicable to the present cases.

2) K. Tanabe, "Solid Acids and Bases," Kodansha, Tokyo-Academic Press, New York, London (1978).

3) For the reaction of 3→4, I_2 actas as an efficient catalyst and gave a 93 % yield[4]. However, a trace of iodo compound, a byproduct of the reaction, was often contained in the product, and difficult to be removed. The pure sample of 4 was easily prepared by means of the present method.

4) K. Hayano, Y. Ohfune, H. Shirahama and T. Matsumoto, Tetrahedron Lett., 1991 (1978).

(Received December 4, 1978)