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NICKEL MEDIATED FLASH ISOMERIZATION: A NEW APPROACH TO 1,4-BUT-1-ENE DIOL DERIVATIVES

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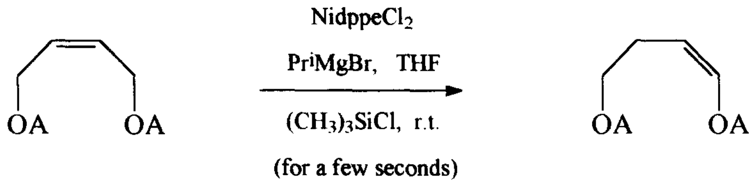
Abstract: Fast isomerization of cis 1,4-but-2-endiol derivatives (**1**) to 1,4-but-1-endiol derivatives (**2**) was carried out in mild conditions. The activity of the proposed Ni-hydride species is closely correlated with the nature of the protecting groups of the alcoholic functions of **1**, which are also responsible for the regio and stereo chemical aspects of the reaction.

The well known isomerization of allyl ethers in vinyl derivatives represents a key step in many functional group interconversions in strong conditions[1]. On the other hand, transition metal complexes are able to isomerize an allylic moiety in vinylic moiety[2], using high temperatures over long periods. During our research on the reactivity of 1,4-but-2-ene diol, employed in organic synthesis as a low cost C_4 synthon[3], we have developed a new catalytic system able to isomerize the double bond of this molecule in a few seconds at room temperature (Scheme 1).

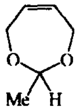
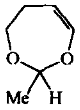
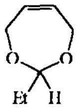
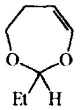
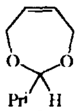
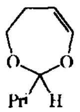
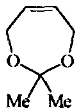
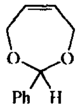
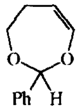
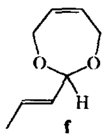
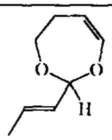
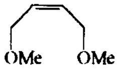
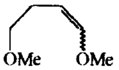
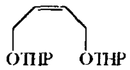
Scheme 1



A = protecting group

In a typical experimental procedure one molar equivalent of **1** in THF and 0.02 molar equivalents of Nickel 1,2-bis(diphenylphosphino)ethane dichloride ($NidppeCl_2$) were reacted, at 0 °C with two molar equivalents of a solution of *i*-propyl magnesium bromide, in the same solvent. After the formation of a reddish limpid solution, a catalytic amount (0.01 molar equivalent) of trimethyl silyl chloride was added at room temperature. After a few seconds the mixture was hydrolyzed with a saturated NH_4Cl solution and extracted with diethyl ether. After elimination of the solvent no by-products were present (g.c., NMR). The data obtained are collected in the Table.

Table

Run	Substrate[(a)]	Product[(b)]	Conversion[(c)]	Catalytic System[(d)]
1	 a		100	A, B
2	 b		100	A
3	 c		100	A
4	 d	—	0	A, B
5	 e		45	A, B
6	 f		35	A, B
7	 g		100	A
8	 h		100	A
9	 i	—	0	A, B
10	 l	—	0	A, B

[(a)] The starting dioxep-5-enes were synthetized by using well known procedures[4]; the dimethoxy derivative 1g was synthetized by employing cis 1,4-but-2-endiol in benzene, in the presence of catalytic amounts of 18-crown-6, NaOH and K_2CO_3 as described for analogous allyl alcohols[5]; the disilyl derivative 1h was obtained starting from cis 1,4-but-2-endiol, pyridine and 2 molar equivalents of TMS–Cl at room temperature[6].

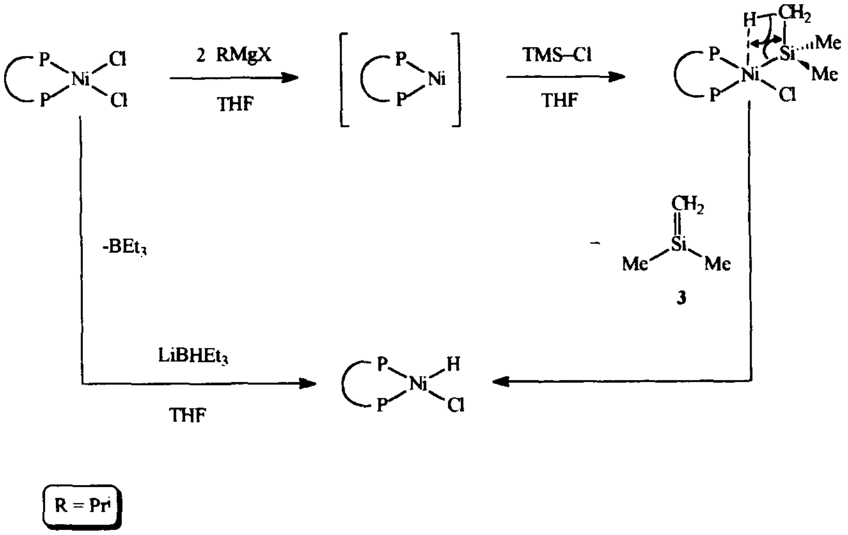
[(b)] All products present ^{1}H-NMR (200 MHz), ^{13}C-NMR (50 MHz), mass and IR spectra in close agreement with the structure assigned.

[(c)] The conversions were determined by g.c. analyses and ^{1}H-NMR and are referred to the use of catalytic system A.

[(d)] Catalytic system A was obtained as described in Scheme and in the text; catalytic system B was prepared by using NidppeCl_2 with one molar equivalent of Super-Hydride® (see Scheme 2).

The reaction seems to depend on the structure of the protecting group employed. The catalytic system does not react with isolated olefinic double bonds (see Table, run 10) and allyl ketals (see Table, run 6). Employing **1e**, a cis trans mixture of **2e** was obtained but using **1f** only the cis isomer was formed (IR, ^{1}H-NMR, ^{13}C- NMR). The catalytic species of a hydridic nature is probably obtained by an oxidative addition of TMS–Cl with Nidppe[7a,b] followed by a β elimination of hydride from the trimethylsilyl group[7c-f] (Scheme 2).

Scheme 2



This mechanistic purpose seems to be confirmed by the presence of silene **3**[8] (g.c.-mass) as a by-product when the catalytic system A was used. Moreover it must be emphasized that similar results were obtained by employing NidppeCl_2 and one molar equivalent of $LiBHEt_3$ as a catalyst, a well known approach to a Ni-H species[9]. Further research is in progress.

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