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# SYNTHESIS OF 1-ALKOXY-1,3-DIENES BY MEANS OF TRANSETHERIFICATION

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*RESUM*

En aquest treball es demostra que el procés de la transeterificació des d'1-metoxibutadiè utilitzant 2-butanol és un bon mètode per a sintetitzar diens que poden ser estereoselectius en reaccions de tipus Diels-Alder. Una anàlisi teòrica d'aquesta reacció mitjançant el mètode basat en la teoria d'orbitals moleculars AM1 dóna suport també a l'eficàcia d'aquesta reacció.

*RESUMEN*

En este trabajo se demuestra que el proceso de la transeterificación desde 1-metoxibutadieno utilizando 2-butanol es un buen método para la síntesis de dienos que pueden ser estereoselectivos en reacciones de tipo Diels-Alder. Un análisis teórico de esta reacción con el método basado en la teoría de orbitales moleculares AM1 es otro argumento a favor de la eficacia de la reacción.

*ABSTRACT*

The transetherification from 1-methoxybutadiene using 2-butanol is shown to be a good method for synthesizing dienes which can be stereoselective in Diels-Alder reactions. A theoretical analysis by means of the AM1 molecular orbital-based method provides the clues for the success of this reaction.

**Keywords**: 1-Alkoxy-1,3-Dienes, Transetherification, AM1 Method.

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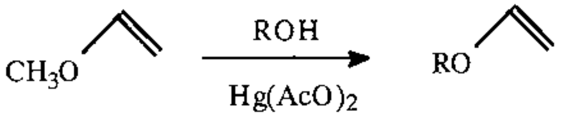
## INTRODUCTION

In most studies of the Diels-Alder reaction related with stereochemical control, the dienophile and the catalyst have been used as inductors of stereoselectivity (1). Although use of chiral dienes can be found in the literature (2,3), as a general rule they have shown only moderate stereoselectivity.

Earlier papers have described the transetherification of alkyl vinyl ethers catalyzed by mercury acetate, $Hg(OAc)_2$ (Scheme I) (4); further, the study of its mechanism has been also published (5). For this process no racemization has been found when quiral secondary alcohols are used (6), and its yield varies as a function of the pair of entering and leaving alcohols.



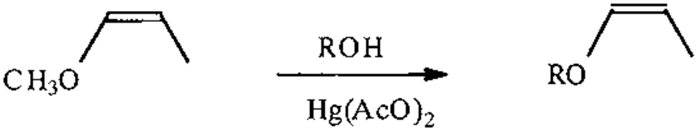
1

**2a-d**

R=
a: (R)-2-butyl
b: (S)-2-butyl
c: (-)-menthyl
d: (R)-1-phenylethyl

***Scheme I***

In the present paper we have studied the viability of using the above procedure involving transetherification catalyzed by $Hg(AcO)_2$ for the synthesis of new and structurally simple quiral dienes from 1-alkoxydienes. We have studied, from both theoretical and experimental points of view, the transetherification of 1-methoxybutadiene using as model of secondary alcohol the racemic 2-butanol (Scheme 2).



3a,b

4a,b

R: 2-buthyl
a: cis
b: trans

***Scheme 2***

## THEORETICAL METHODOLOGY

The theoretical study, previous to experiments, has been carried out by means of the AM1 molecular orbital-based semiempirical method (7), which has been shown to provide reasonable results for a wide variety of organic reactions. In particular, the parameterization of Hg (8) has led to correct results in other studies. The theoretical procedure consisted thus of completely optimizing reactants, products and intermediates, so relative energies be available. For the sake of comparison, the study has been carried out also on the vinylic transetherification.

## EXPERIMENTAL RESULTS AND DISCUSSION

The comparative energetic study, depicted in Figure 1, shows that one of the intermediates is very stable for both processes, namely the vinyl (a) and butadienyl (b) transetherifications; this intermediate is found below reactants for process (a), as opposite to the intermediate for process (b), which is found above them. Furthermore, the positively-charged species are found at high energies; the species involving 2-BuO is more stable, by ca. 2 kcal/mol, than the original species involving MeO.

For process (b), the intermediate resulting from 1,4-addition turns out to be thermodynamically more favoured by 5.55 kcal/mol than the intermediate arising from a 1,2-addition, as expected. The most plausible evolution of the intermediate of a 1,2-addition would be reversion to reactants. Thus, the formation of a 2-alkoxybutadiene may be reasonably discarded from a mechanistic point of view.

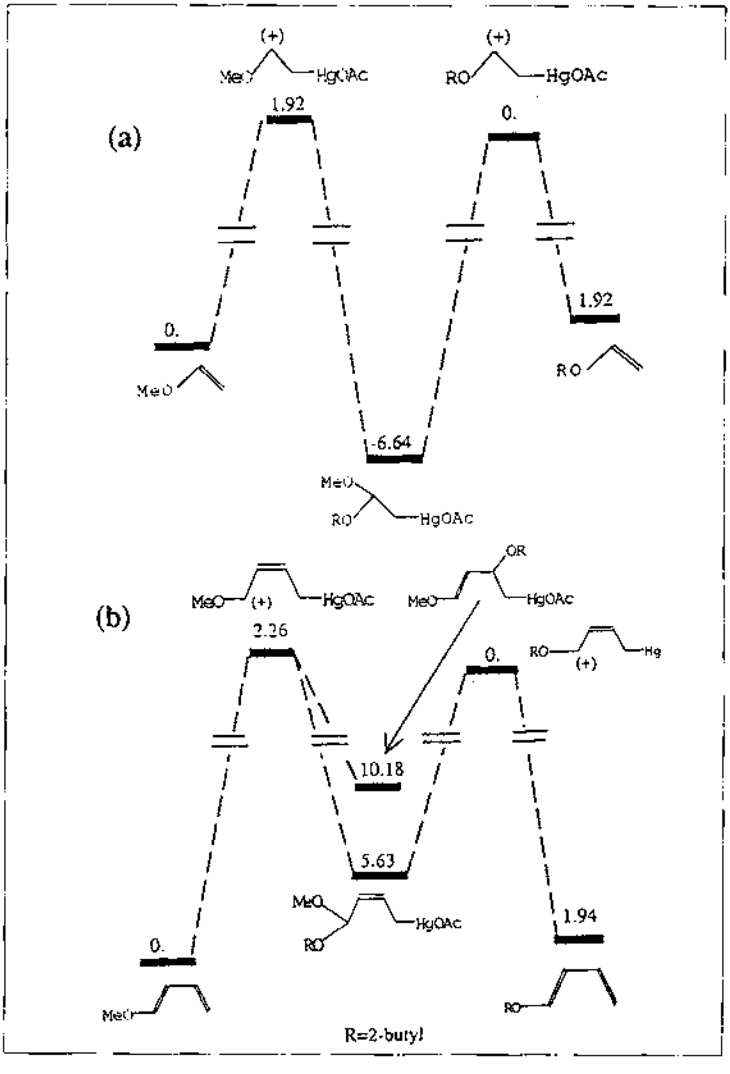


*Figure 1.* *Schematic diagram for energies (in kcal/mol) of reactants, intermediates and products of the vinyl (a) and butadienyl (b) transetherifications. Note that all energies are relative to the reactant, except for energies of protonated systems, which are given relative to the most stable protonated structure*

These results, which have been confirmed by experimental data, lead to think that the behaviour of both equilibrium reactions, vinyl and butadienyl transetherifications, are similar. We have not found any reason to think that under the same reaction conditions, using the same chiral alcohols and the same catalyst as those used in the vinyl transetherification may lead to racemization, which is not found in the latter case.

The transetherification reaction was experimentally carried out using commercially available 1-methoxybutadiene (mixture of both stereoisomers) and 2-butanol (racemic) through heating the mixture (1:1.2 ratio) at 40 °C during 4 hours in the presence of 5% mercury acetate. The yield of 26% (integration by gas chromatography) did not change meaningfully when the time doubled or the temperature raised to 50 °C. It is worth mentioning that the homologous vinylic transetherification (3) has reportedly a yield of 30%.

The analysis of the product by mass spectroscometry gave $M^{+}$=126 (20%); furthermore, $^{1}$H- and $^{13}$C-NMR allowed to identify the products as 1-*sec*-butoxy-1,3-butadiene (*cis/trans* ratio 4:5). The possibility of one of the products being 2-*sec*-butoxy-1,3-butadiene was definitely discarded by means of a SEFT $^{13}$C-NMR experiment, which showed that there is only one ethylenic $CH_2$ per molecule. Finally, the stability of both ethers was tested in a silica gel chromatography column, thus demonstrating the viability of separating the cis and trans isomers by this method.

In summary, the results obtained after the present transetherification are very similar to those obtained in vinyl transetherification, so the procedure described provides an easy way to synthesize new and structurally simple quiral 1-alkoxy-1,3-dienes. Further work will deal with the synthesis of various of such chiral dienes, and with testing its usefulness for yielding enantiomeric or diastereomeric excesses.

## SPECTROSCOPIC DATA.

Compounds 4a,b were identified by $^{1}$H-NMR (400 MHz, d-acet, standard $SiMe_4$), $^{13}$C-NMR (100 MHz, d-acet, Standard $SiMe_4$), and mass spectra. Data for 4a: m/z: 126 ($M^{+}$, 21), 70 (100), 69 (30), 57 (13). $^{1}$H-NMR (d-acct) (: 0.90, $H_8$ (t, $J_{87}$=7.3 Hz, 3H); 1.17, $H_9$ (d, $J_{96}$=6.2 Hz, 3H); 1.53, $H_7$ (m, 2H); 3.80, $H_6$ (m, 1H); 4.77, $H_4$ (dd, $J_{43}$=11.2 Hz, $J_{42}$=2.4 Hz, 1H); 4.96 (dd, $J_{53}$=16.8 Hz, $J_{54}$=2.4 Hz, 1H); 5.02, $H_2$ (dd, $J_{23}$=10.9 Hz, 1H); 6.12, $H_1$ (d, $J_{12}$=6.1 Hz, 1H); 6.64, $H_3$ (m, 1H). $^{13}$C-NMR (d-acet) (: 9.8, 20.2, 29.9, 80.6, 107.5, 112.3, 131.3, and 146.8. Data for 4b: m/z: 126 ($M^{+}$, 20), 70 (100), 69 (31), 57 (12). $^{1}$H-NMR (d-acet) (: 0.89, $H_8$ (t, $J_{87}$=7.3 Hz, 3H); 1.17, $H_9$ (d, $J_{96}$=6.2 Hz, 3H); 1.56, $H_7$ (m, 2H); 3.84, $H_6$ (m, 1H); 4.68, $H_4$ (dd, $J_{43}$=10.3 Hz, $J_{45}$=2.4 Hz, 1H); 4.90, $H_5$ (dd, $J_{53}$=17.2 Hz, 1H); 5.56, $H_2$ (dd, $J_{21}$=11.3 Hz, $J_{23}$=10.6 Hz, 1H); 6.21, $H_3$ (m 1H); 6.60, $H_1$ (d, 1H). $^{13}$C-NMR (d-acet) (: 9.8, 19.8, 29.9, 79.2, 109.1, 110.6, 134.9, and 151.5.

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## References

CARRUTHERS, W., "Cicloaddition Reactions in Organic Synthesis", Pergamon Press , 1990.

MASAMUNE, S., CHOY, W., PETERSEN, J.S., and SITA, L.R., ANGEW. Chem., Internat. Ed. Engl., *1985*, 24, 1.

CHARLTON, J.L., Tetrahedron Lett., *1985*, 26, 3413.

WATANABE, W.H. and COULON, L.E., J. AM. Chem. Soc., *1957*, 79, 2828.

YUKI, H., HATADA, K. and NAGATA, K., BULL. Chem. Soc. Jpn., *1970*, 43, 1817.Chiellin, E., Gazz. Chim. Ital., *1972*, 102, 830.

LIOTARD, D.A., HEALY, E.F., RUIZ, J.M. and DEWAR, M.J.S., AMPAC, Version 2.1, Austin, TX , 1989.

DEWAR, M.J.S. and JIE, C., Organometallics, *1989*, 9, 1547.