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ULTRASONICALLY IMPROVED REDUCTIVE PROPERTIES OF AN AQUEOUS Zn-NiCl$_2$ SYSTEM-2. REGIOSELECTIVITY IN THE REDUCTION OF (-)-CARVONE

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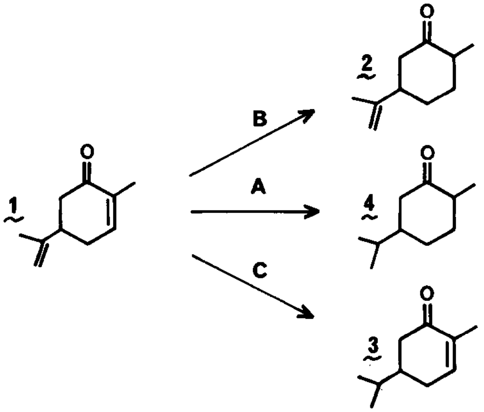
Summary : While the previously described reductive system Zn-NiCl$_2$ leads to the non-selective hydrogenation of the two olefinic bonds of (-)-carvone 1, the two selective hydrogenation products (+)-dihydrocarvone 2 and carvotanacetone 3 are obtained in good yield with the same reagent under modified experimental conditions.

Hydrogenation of the olefinic bond of an α-enone is a widely used reaction in synthesis. To achieve this goal the reaction should possess a high functional and regio selectivity if other reducible functions are present in the target molecule[1]. (-)-Carvone 1 which possesses several insaturations was chosen as a test for the reducing ability of the zinc-nickel chloride system described in the accompanying note. Several methods have been proposed to obtain selectively dihydrocarvone 2[2] or carvotanacetone 3[3]. This work describes the possible modifications in the hydrogenation of 1 with the zinc-nickel chloride catalyst by simple variations of experimental conditions.



	Time/hours Stirring	Ultrasound	Yield^a(b)
System A	12	3	**4** : 100(96)
System B	24	1.5	**2** : 98(95)
System C	6		**3** : 88(83)-**4** : 12

Figure 1 : Reduction of (-)-carvone - a : G.C. yield ; **b** : Isolated yield.

With a catalytic system A[4] using Zn-NiCl$_2$,6H$_2$O(9:1,mol:mol) in an aqueous alcoholic medium, 1 is rapidly transformed to carvomenthone 4 (figure 1). The two olefinic bonds are simultaneously reduced in good yield. The comparison between stirring and ultrasonic assistance shows an important acceleration and a more complete reaction when ultrasound is applied. However, the process appears to be non-selective. It is possible to obtain essentially pure dihydrocarvone 2 from 1 if the reaction is run in the presence of amino compounds. This constitutes our system B. A regioselectivity pattern different from that of system A results from buffering the medium with ammonia-ammonium chloride in the pH range 6-10, but is not observed with other basic or acidic additives. Triethylamine can replace NH_3/NH_4Cl with similar results. Ultrasounds increase markedly the rate of the reaction (figure 1). Under such conditions, the next step is the concomitant reduction of both the carbonyl and terminal olefinic group of 2.

Carvotanacetone 3 is obtained preferentially by the regioselective reduction of the terminal olefin of 1 with a preformed reagent Zn-$NiCl_2$, containing stoichiometric amounts of each constituent, under a hydrogen atmosphere : system C. In the absence of hydrogen, no reaction occurs and 1 is recovered unchanged. For this hydrogenation to proceed stirring appears much preferable to sonication which gives low rates and erratic yields.
This negative effect can be caused by cavitational degassing of the liquid phase, preventing thus any contact between the reaction partners[5]. The next step is the preferential hydrogenation of the conjugated olefin.

These experimental results show some potentialities of the Zn-$NiCl_2$ system in selective hydrogenation. Some ultrasound effects, promoting or inhibiting a reaction, are pointed out. It appears that at least two different pathways are involved in these processes. For one of them which makes use of dissolved hydrogen and reduced nickel, the reduction occurs preferentialy on the terminal unhindered olefin. The ultrasound irradiation brings a negative factor in this reaction. The second way is undoubtely promoted by ultrasounds and leads to the hydrogenation of the conjugated double bond. Presently this system is not fully understood and requires further investigations.

References and notes :

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2. (a) F. Camps, J. Coll, J. Guitard, Tetrahedron, 42, 4603 (1986).
   (b) E. Keinan, H. Greenspoon, J. Am. Chem. Soc., 108, 7314 (1986).
3. A.S. Hallsworth, H.B. Hembest, I.T. Wrigley, J. Chem. Soc., 1969 (1957).
4. For the general procedure, see the accompanying note, ref 7. System A : Zinc dust 2.4 g (36,7 ag.), then $NiCl_2,6H_2O$ 1 g (4.2 mmol) are added to 7 ml of 2-methoxyethanol, 7 ml of water and 6.38 mmol of (-)-carvone, and submitted to sonication at 30°C.
   System B : Zinc dust 1.5 g (23 ag) then $NiCl_2,6H_2O$ 400 mg (1.68 mmol) are added to the solvents mixture (2-methoxyethanol 8 ml ; Buffer (1M)NH_4OH/NH_4Cl, pH=8, 6 ml) containing 6.38 mmol of (-)-carvone, and sonicated at 30°C.
   System C : The stoichiometric reagent, 6.4 mmol, is formed by stirring at 40°C (zinc 420 mg, $NiCl_2,6H_2O$ 1.53 g) under a hydrogen atmosphere in 2-methoxyethanol (7 ml) and water (7 ml) for 2h. 6.38 mmol of the substrate are then reacted for 6 hours at 40°C.
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