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ULTRASOUND IN ORGANIC SYNTHESIS 17[1]
MECHANISTIC ASPECTS OF THE CONJUGATE ADDITIONS TO α-ENONES IN AQUEOUS MEDIA

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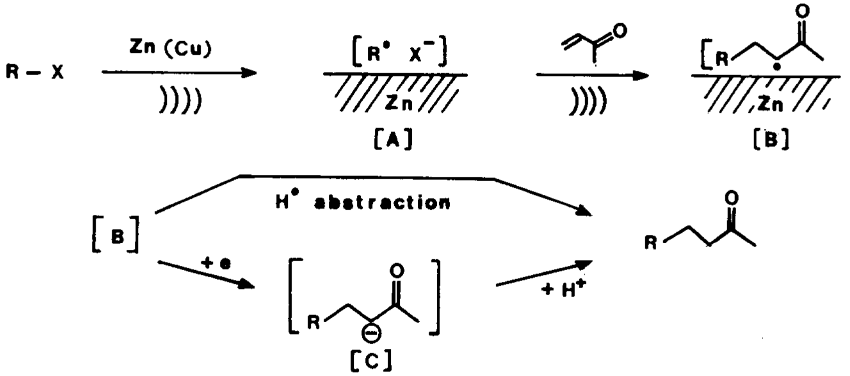
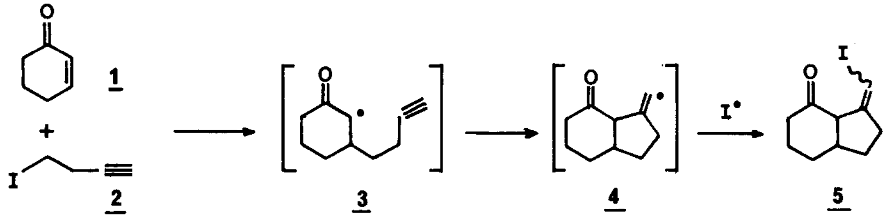
Abstract : A free radical mechanism occuring on the metal surface seems highly probable in the conjugate addition of alkyl groups to α-enones in the presence of zinc-copper couple, under sonochemical aqueous conditions.

In the accompanying note[1], we describe an optimisation process for the conjugate additions of alkyl groups to α-enones under sonochemical aqueous conditions. The compatibility of the reaction with water render highly probable a free radical mechanism in strong similarity with those demonstrated for Giese's "tin method"[2] and organoborane method[3]. The mechanism which can be proposed is represented in the Scheme below. In the first step, a single electron transfer (SET) occurs from the metal surface to the carbon halogen bond, generating the adsorbed radical A . The next steps of the sequence also take place at the metal surface as indicated in the following. In the first step, the role of the sonic waves should be an important acceleration of the SET, in analogy with related known processes[4]. Owing to the important solvents effects, it can be considered that species A is associated not only to the metal, but also to a solvent cage.

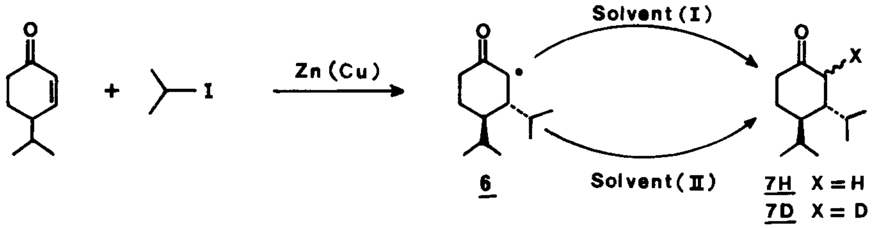


The maximum yield of the adduct is obtained in a water-rich solvent with an important degree of structure organisation. The solvent cage around radical A should be rigid and particularly sensitive to an ultrasonic breakage, as assumed by Mason and coworkers[5]. An efficient and rapid cleavage favors the addition process, leading to the α-keto radical, at the expenses of side reactions such as hydrogen abstraction or Wurtz-type coupling. This addition step is however relatively slow, as S(+)2-octyl iodide leads to racemic adducts[1].

Detection of species B was attempted using intra- and inter- molecular trapping experiments. The bicyclic ketone 5, although isolated in low yield (5%)[6], results from the reaction of I$^{\bullet}$ with radical 4, which itself is formed by a 5- exo dig cyclisation of the postulated radical 3. A similar situation has been described by Curran et al[7].



The evolution of the radical when no cyclisation can occur was examined as shown below.



In solvent(I) : $(CH_3)_2\underset{D}{C}-OH, H_2O \longrightarrow$ 7H

In solvent(II) : $C_2H_5-OD, D_2O \longrightarrow$ 7D

A radical such as 6 should abstract a deuterium atom from the solvent (I). Experimentally this is not the case, but a D^+ ion is abstracted from system (II). The intermediate α-keto radical 6 is then rapidly reduced at the metal surface to the enolate which protonates in a fast step, as no aldol is detected when the reaction solvent is acetone-water.

A confirmation is obtained that all the sequence takes place on the metal surface. In the case of a free radical B in solution, hydrogen (or deuterium) trapping should be much faster than reduction, and a reverse selectivity should be expected for the formation of 7H and 7D. Extensions and synthetic applications of this selective procedure are presently under study.

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References :

1. J.L. Luche, C. Allavena, Tetrahedron Lett., accompanying note.
2. B. Giese Angew. Chem. Int. Ed. Engl., 1985, 24, 553.
3. H.C. Brown, M.M. Midland, Angew. Chem. Int. Ed. Engl., 1972, 11, 692. For a recent related paper see : K. Nozaki, K. Oshima, K. Utimoto, Tetrahedron Lett., 1988, 29, 1041.
4. J.C. de Souza Barboza, C. Petrier, J.L. Luche, J. Org. Chem., 1988, 53, 1212.
5. T.J. Mason, J.P. Lorimer, B.P. Mistry, Tetrahedron, 1985, 41, 5201.
6. Polymeric material, unseparable in TLC, was extensively formed.
7. D.P. Curran, M.H. Chen, J. Am. Chem. Soc., 1987, 109, 6558.

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