

ORGANIC SONOCHEMISTRY - SOME ILLUSTRATIVE EXAMPLES OF A NEW FUNDAMENTAL APPROACH

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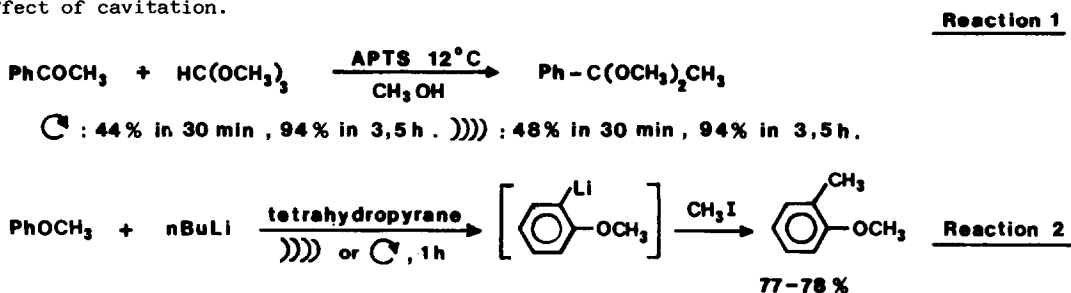
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Abstract : The sonochemical behaviour of several organic reactions, selected according to their mechanisms, has been examined. Their experimental evolution follows the prediction developed previously, that sonication promotes reactions proceeding through radical pathways.

In the accompanying paper¹, we develop a new interpretation of sonochemistry, with the purpose of rationalising the somewhat confuse present situation, and sketching a more accurate theory. The validity of this new formulation was tested with reactions, which had not yet been studied under sonochemical conditions.

Acid catalysed ketalisation² of acetophenone (reaction 1) was studied comparatively under stirring and under sonication. The two kinetic curves of the ketal formation coincide within experimental error.

The deprotonation of anisole with n-butyl lithium² (reaction 2) followed by quenching (without sonication) with excess methyl iodide was in the same way shown to be insensitive to the effect of cavitation.



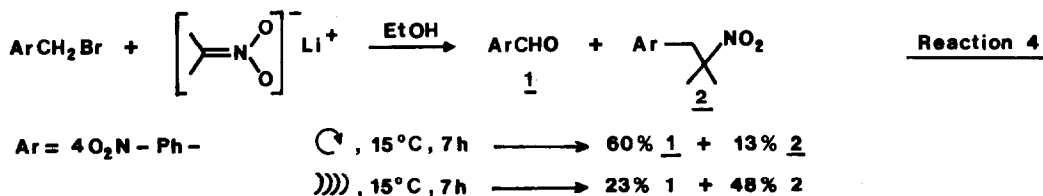
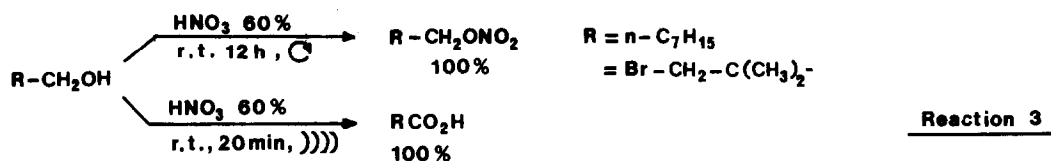
These examples illustrate the statement that reactions known (till now) to follow an ionic mechanism should be rather insensitive to the effects of ultrasounds. On the other hand, these effects have a favourable role in radical processes, as shown by the preliminary results described in the two following examples.

Reaction of 60% nitric acid with octanol and 3-bromo,2,2-dimethylpropanol proceeds slowly under stirring at room temperature to give a quantitative yield of the nitrate esters.

The same mixture, under sonication (cleaning bath, room temp.), turns rapidly red-yellow then green to afford in 20 min a quantitative yield of the acids (reaction 3). The mechanism of this oxidative process has been shown to involve nitrogen dioxide or its protonated form, i.e. a radical or a radical cation³. Sonication of the nitrate esters does not yield the acids.

Our second example of sonochemical switching is provided by the reaction of the lithium salt

of 2-nitropropane with p-nitrobenzylbromide. An ionic mechanism leads to the O-alkylation product rearranged to the aldehyde 1, while the C-alkylated compound 2 results from a DAISSET chain process⁴, according to the terminology of Chanon⁵. These experiments in deoxygenated ethanol solution in the dark showed that by stirring, p-nitrobenzaldehyde 1 is obtained in 60% yield accompanied by 13% of 2-(p-nitrobenzyl)-2-nitro-propane 2.



Under identical conditions, the sonicated experiment yields 48% of the C-alkylation product and 23% of the aldehyde. Obviously the ultrasonic irradiation has a direct influence on the relative rates of the reactions, probably by stimulating the single electron transfers. With these results, sonication appears to influence directly the mechanisms of reactions. The role of ultrasonic waves, in contrast to generally accepted ideas, is not restricted to a mechanical one named by many authors as "ultrasonic agitation". Along these guidelines, finding new applications for synthetic purposes should become easier. Furthermore, the sensitivity of a reaction to the effects of sonic waves can also be considered as a test for the existence of a "radical" (in a broad sense) pathway, which gives to sonication the value of an investigation method for the elucidation of reaction mechanisms.

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Literature

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