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ELUCIDATION OF ORGANIC REACTION MECHANISMS BY DIRECT OBSERVATION OF THE INTERMEDIATE BY RAMAN LASER RAPID SPECTROMETRY.

L. Maciejewski[+], J. Brocard[+*], B. Sombret[++] and F. Wallart[++]

[+]Laboratoire de Chimie Organique 1, [++]Laboratoire de Spectrochimie IR et Raman Section de Lille
Université des Sciences et Techniques, BP 36 59650 Villeneuve d'Ascq France

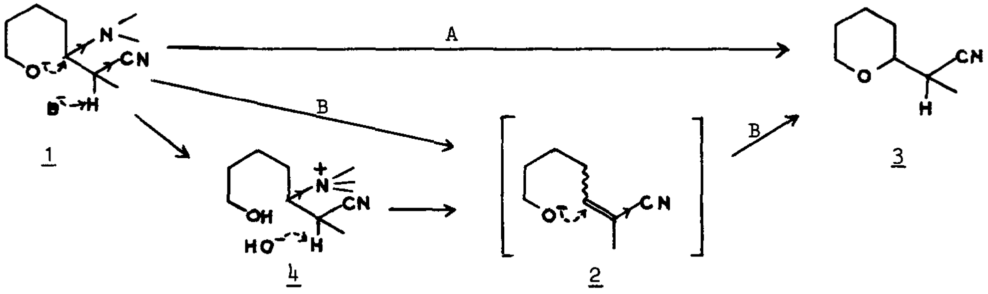
We have demonstrated the utility of Raman Laser rapid spectrometry in the detection of an unstable intermediate in an organic reaction by averaging a large number of spectra of the reaction mixture in the range of absorption of a characteristic Raman vibration mode.

The preliminary results obtained using Raman Laser rapid spectrometry (RLRS) have demonstrated the utility of this technique in the field of inorganic chemistry for the investigation of fast chemical reactions and for the study of transient species. To our knowledge the only applications of this technique to organic chemistry concerned the kinetic study of hydrogen chloride addition to a conjugated diene and the characterization of a radical cation (1). Here we present the application of RLRS for the elucidation of reaction mechanisms in organic chemistry.

2-Methyl 3-dimethylamino 7-hydroxy heptanonitrile 1 undergoes cyclization at 180° to 2-tetrahydropyranyl propionitrile 3 in the presence of a catalytic amount of sodium methoxide. Two possible mechanisms may be proposed for this reaction ;

A. An intramolecular nucleophilic substitution (SN2-type).

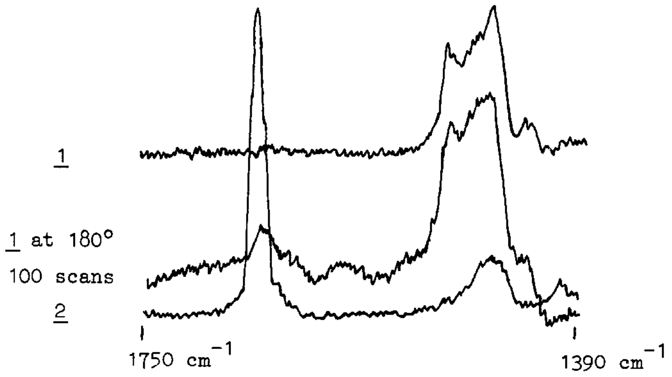
B. An elimination-addition process.



Since the amide ion is known to be a poor leaving group the elimination-addition process appears to be more likely. Precedents for such a mechanism already exist. For example the base catalysed substitution reaction of the amino group in β-amino ketones by alkoxy groups at 80° proceeds by way of an ethylenic intermediate (2). However, the elevated temperature (180°) at which 1 cyclizes to 3 and the relative 1-6 positions of the electrophilic and nucleophilic centres render the SN2-type direct substitution quite feasible.

The detection of 2 during the reaction would confirm the two-step mechanism . This intermediate can be separately prepared by heating the quaternary ammonium species 4 at 30° which consequently undergoes ring closure into 3 at temperatures above 60°. At 180° the temperature at which 1 cyclizes to 3, the lifetime of intermediate 2 will be very short and its concentration very low. The identification of 2 in the reaction medium is much facilitated by employing a concave holographic grating double monochromator to record the Raman line at 1652 cm^{-1} which is assigned to the stretching vibration mode of the conjugated double bond. The spectrometer employed is a prototype which comprises a new spectral scanning system which records a chosen spectral range during a period of 1 second. By recording and averaging 100 spectra it is possible to detect 2 in concentrations as low as 0.1 %.

Thus the liquid starting material 1 (0.5 ml) and a catalytic quantity of sodium methoxide in a Raman sample tube was set before the entrance slit of the spectrometer operating with a chosen spectral range of 1750 to 1390 cm^{-1}. The reaction mixture was then heated to 180° and 100 spectra were recorded and averaged over a period of 12 minutes.



The resulting spectrum exhibits a signal at 1650 cm^{-1} the intensity of which is weak but sufficient to identify the conjugated double bond and consequently the presence of the intermediate 2. This evidence strongly supports the two-step elimination-addition mechanism B for this cyclization reaction.

Further applications of this technique to organic chemistry are being investigated.

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