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ISOLATION OF ENAMMONIUM SALT AND ITS REARRANGEMENT TO THE CORRESPONDING IMINIUM SALT

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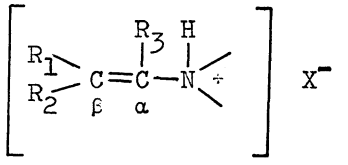
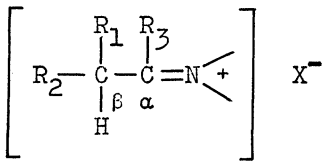
1-(β-Methylstyryl)-2-methylpiperidinium chloride was isolated and characterized. This is the first case of the isolation of the enammonium salt. The enammonium salt was found to change easily to the corresponding iminium salt at room temperature.

Enamines are known to be very useful starting materials for various organic syntheses.[1] One of their reactions is a formation of the salts with acids. The protonation on nitrogen or the β-carbon of the enamine to give the salt (I) or (II) is possible.



Enammonium salt (I)



Iminium salt (II)

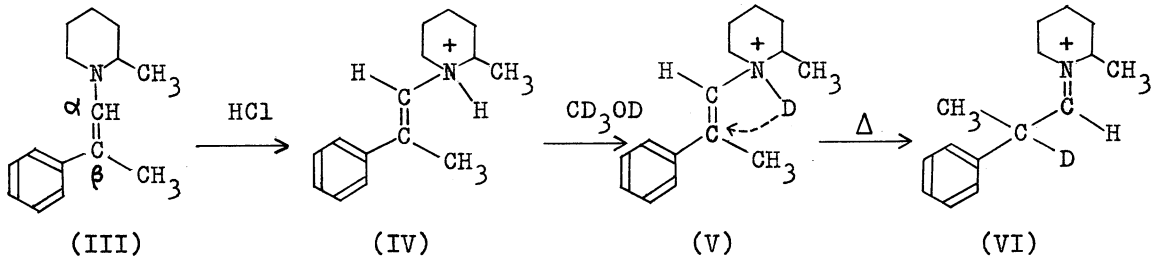
It has been shown that the protonation takes place rapidly on nitrogen and is followed by a transfer of the proton to the carbon, but the enamine salts so far isolated have been demonstrated to have the iminium salt structure (II).[2] The evidence for N protonation has been based on the reaction of ozone, diazomethane or lithium aluminum hydride with N-protonated salts under cooling. This paper deals with the isolation and identification of N-protonated salt as fine needles and its

rearrangement to the corresponding iminium salt.

Dry HCl gas was bubbled into a benzene solution (1.5 ml) of 1-(β-methylstyryl)-2-methylpiperidine (III) (0.5 g) under cooling in an ice-salt bath. Precipitated needles were pressed on a porous plate in a dry-box, desiccated, and dissolved again in chloroform. The solution was concentrated in a stream of dry nitrogen gas under cooling, and white needles separated out gradually. The recrystallized salt was separated from the solution by filtration, washed with dry benzene, and dried under vacuum. The salt was highly hygroscopic and decomposed to 2-phenylpropanal and 2-methylpiperidine hydrochloride on exposure to air. In a dry solvent at room temperature, it easily changes to the corresponding iminium salt.

NMR spectra of the enamine (III) and the isolated salt in CD_3OD are shown in Fig. 1-(a) and (b). Chemical shifts are indicated in δ value using TMS as an internal standard. In Fig. 1-(a), two olefin proton signals (5.75 and 5.99 ppm) and two olefin methyl proton signals (1.95 and 2.10 ppm) are observed. The area ratio of 5.75 ppm signal : 5.99 ppm signal is 8 : 92 which coincides well with the ratio of 1.95 ppm signal : 2.10 ppm signal (10 : 90). Allyl couplings (1.5 Hz) are also observed between the corresponding olefin and methyl signals. These results show that the enamine (III) is a mixture of two geometrical isomers, one of which is present predominantly over the other one. The predominant one seems to have a structure where the phenyl and the 2-methylpiperidino groups are situated each other in trans positions. In Fig. 1-(b), the allyl coupling constant, 1.5, Hz was also observed between the signal at 6.27 ppm and that at 2.48 ppm. These signals can reasonably be assigned to the olefin proton and the methyl protons. This means that the isolated salt has the same partial structure, $N\text{-}CH\text{=}C\text{-}CH_3$, as the enamine (III). On the basis of the above results, the spectrum (Fig. 1-(b)) was assigned the structure of the enammonium salt (IV). The methyl signals at 2.10 ppm in the spectrum (a) was shifted to lower field, 2.48 ppm, in the spectrum (b). This seems to assist the partial structure of the enammonium salt, $N^+H\text{-}CH\text{=}C\text{-}CH_3$. The occurrence of the proton exchange was shown by the appearance of the signal at 5.10 ppm assignable to CD_3OH in the spectrum (b). When the CD_3OD solution of the salt (IV) was heated up to 50°C, the signals of the NMR spectrum changed from (b) to (c). Spectrum (c) is identical to that of the iminium salt reported in a previous paper.[3] The signal at 1.70 ppm in the spectrum (c) was singlet, and allyl coupling could not be observed. This means that the salt (IV) is easily deuterated in CD_3OD to the N-deuterated salt (V), which is subsequently rearranged to the corresponding iminium salt (VI). The

sequences of the reactions shown in Scheme 1 are consistent with the generally accepted mechanism of the iminium salt formation. The enamine (III), the enammonium salt (IV), and the iminium salt (VI) are easily soluble in $CDCl_3$, but this solvent is inferior to CD_3OD in the resolution.



(III) (IV) (V) (VI)

Scheme 1

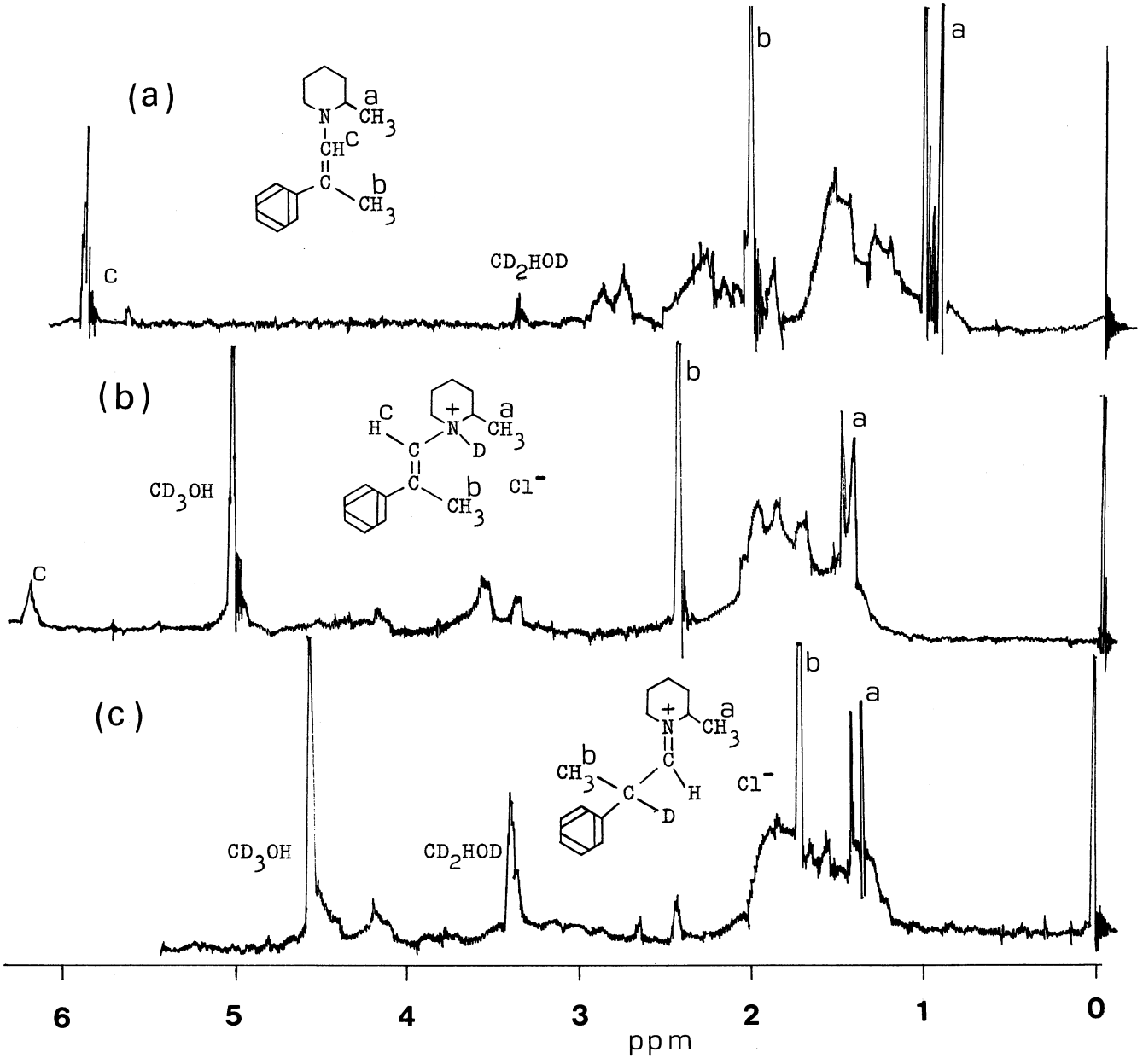


Fig. 1.

The complex bands appeared in 2350-2600 cm^{-1} in the IR spectrum of the enammonium salt (IV) were assignable to the ammonium structure, N^{+}-H . In the case of nicotine hydrochloride, it was reported that the band attributable to the ammonium structure was observed in the region of 2350-2440 cm^{-1}.[4] The absorption band, 1637 cm^{-1}, due to the double bond stretching in the IR spectrum of the enamine (III) was shifted by 21 cm^{-1} and 34 cm^{-1} toward higher frequencies in those of the enammonium salt and the iminium salt (VI), respectively. Leonard and Gash reported a shift of 20-50 cm^{-1} toward higher frequencies when an enamine was converted to its iminium salt.[5] All these observations strongly support that the isolated salt has the enammonium salt structure (IV).

This seems to be the first case of the isolation of the enammonium salt and the observation of its rearrangement to the corresponding iminium salt. Up to the present, it has been thought that the enammonium salt would be too labile to be isolated. The stability of the enammonium salt (IV) may be attributed to the conjugation of the C=C double bond with benzene ring.

References

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