Tetrahedron Letters No.19, pp. 1363-1367, 1965. Pergamon Press Ltd.
Printed in Great Britain.

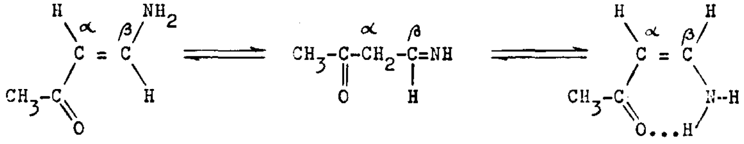
IMINE-ENAMINE TAUTOMERISM. VIII. THE IMINE TAUTOMER AS AN INTERMEDIATE IN THE CIS-TRANS ISOMERIZATION OF ENAMINO-KETONES

Janusz Dąbrowski and Jacek Terpiński
Department of Organic Chemistry, Polytechnical Institute
Warsaw, Poland.

(Received 19 February 1965; in revised form 19 March 1965)

From the theoretical point of view, amino derivatives of β-dicarbonyl compounds with nitrogen bearing at least one hydrogen atom can exist in different tautomeric forms similar to keto and enol forms of the parent dioxo compounds. However, as yet the imino form with no conjugated bonds have not been observed experimentally despite many attempts to detect it using different techniques /1-5/.[*]

Certainly this is energetically the most unfavourable form of all conceivable ones. Nevertheless, the existence of very small amounts of this form can not be excluded a priori. In particular this form is likely to arise as an intermediate in the cis-trans isomerization of enamino-ketones, e. g.:



---

[*] The observation of Holtzclaw, Collman and Alire /6/, who claimed to have observed considerable amounts of the keto-imine form, $CH_3COCH_2C/CH_3/=NH$, have not been confirmed by our experiments neither by Weinstein and Wyman /7/.

The prototropic character of the cis-trans isomerization of enamino-ketones was already suggested basing on the low value / 15 kcal/mole / of activation energy /8/ and the clear / though not measured / kinetic isotope effect on this process /3/.

The isomerization occurs spontaneously at room temperature /9,3,8/ which means that there would be a continuous exchange of hydrogen between the nitrogen and the α-carbon, if the proposed mechanism were correct.

To clear up this question methyl-β-aminovinyl ketone was kept dissolved for three days in an excess of deuterium oxide and than extracted and distilled. The NMR spectrum of the distillate / FIG 2 / was compared with the spectrum of the starting compound / FIG 1 / already discussed in our previous paper /10/ in which the splitting of the α-proton signal into a doublet was attributed to a coupling with the β-proton and the splitting of the β-proton signal into a sextet - to a coupling with the α-proton and the two amino protons.

The decrease in intensity of the H_α signal and the change of the H_β sextet into a broad singlet* confirm the exchange of the α-hydrogen for deuterium and the integration fix it to about 65 per cent.

In order to obtain further evidences methyl-β-amino-α,β-dideuterio-vinyl ketone was kept at room temperature with usual water and the NMR spectrum of the product measured / FIG 3 /. In this case the signal of the α-proton appeared showing that the α-deuterium was washed out to about 70 per cent. Accordingly to what was expected this signal was not splitted.

---

* because of the incomplete exchange of the α-hydrogen and the amino hydrogens an superposition of diverse multiplets results in the broadening of this signal.

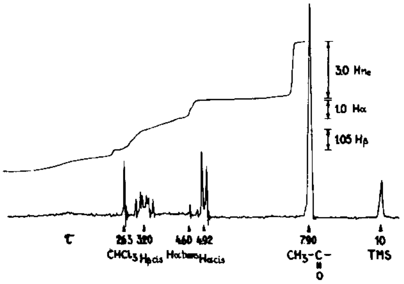


FIG 1

NMR spectrum of methyl-β-aminovinyl ketone in $CDCl_3$.

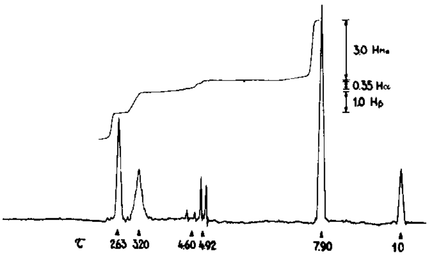


FIG 2

NMR spectrum of methyl-β-aminovinyl ketone after beeing kept with D_2O for three days.

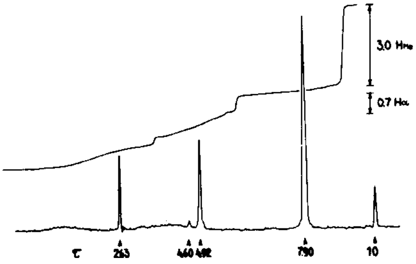


FIG 3

NMR spectrum of methyl-β-amino-α,β-dideuteriovinyl ketone after the exchange reaction with H_2O.

The uncapable of isomerization N,N-dimethyl derivative remained unaffected by deuterium oxide in a control experiment which is especially important in view of the tendency of enamino-ketones for electrophilic substitution at the α-carbon /11/.

The results presented here are, to the authors knowledge, the first experimental evidence of the existence of the imino tautomer of enamino-ketones.

On the other hand it must be taken into account that the rate of exchange observed here is not very high whereas the isomerization itself proceeds rather quickly[*]. For this reason one has to assume the existence of other mechanismes of the cis-trans isomerization in addition to that proceeding *via* unconjugated imino form. The investigations will be continued.

Aknowledgements. - Thanks are due to Professor W. Polaczkowa for her kind interest in this work, to Professor T. Urbański for his permission to use the NMR spectrometer and to Mr. L. Stefaniak, M. Sc., for measuring the spectra. Financial support from the Institute of Organic Synthesis, Polish Academy of Sciences, is gratefully aknowledged.

REFERENCES

1. K. Auwers and W. Susemihl, *Ber.* **63**, 1072 /1930/.
2. N. K. Kochetkov and J. Dąbrowski, *Zhur. Obschei Khim.* **26**, 3081 /1956/.
3. J. Dąbrowski, *Spectrocim. Acta* **19**, 475 /1963/.

---

[*] This fact was established previously for neat substances /9,8/ and their solutions in non-polar solvents /3/; we confirmed by refractometric measurement that it proceeds rapidly also in water solution.

4. G. Dudek and G. Volp, *J. Am. Chem. Soc.* **85**, 2697 /1963/.

5. G. Dudek and E. Dudek, J. Am. Chem. Soc. **86**, 4283 /1964/.

6. H. Holtzclaw, J. Collman and R. Alire, *J. Am. Chem. Soc.* **80**, 1100 /1958/.

7. J. Weinstein and G. Wyman, *J. Org. Chem.* **23**, 1618 /1958/.

8. J. Dąbrowski and J. Terpiński, *Bull. acad. polon. sci. Class III* **9**, 779 /1961/.

9. A. N. Nesmeyanov, N. K. Kochetkov and J. Dąbrowski, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk* **1955**, 179.

10. J. Dąbrowski, J. Terpiński and K. Kamieńska, *Roczniki Chem.*, in print.

11. N. K. Kochetkov, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk* **1954**, 47.

12. N. K. Kochetkov, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk* **1953**, 991.