Tetrahedron Letters,Vol.26,No.32,pp 3869-3870,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

A NEW HETEROCYCLIC REARRANGEMENT: CONVERSION OF 2-VINYLPYRAZOLIUM SALTS INTO 1,2-DIHYDROPYRIMIDINES

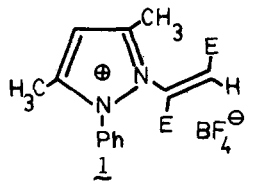
Antonio de la Hoz and Carmen Pardo*
Departamento de Química Orgánica, Facultad de Química,
Universidad Complutense, 28040-Madrid, Spain

José Elguero
Instituto de Química Médica,CSIC, Juan de la Cierva 3, 28006-Madrid, Spain

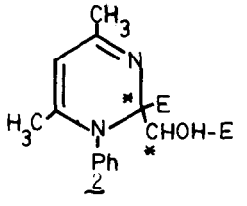
Summary: Treatment of 2-vinylpyrazolium salt 1 in basic medium yields the 1,2-dihydropyrimidine 2. The structure of 2 was established by analytical and spectroscopic methods.

Previously, we reported[1] the synthesis of N-vinylpyrazolium salts, novel compounds the reactivity of which was unknown.

One of these salts, 3,5-dimethyl-1-phenyl-2-(Z-1,2-dimethoxycarbonyl)vinylpyrazolium tetrafluoroborate 1, on treatment with saturated aqueous potassium carbonate at room temperature affords the 1,2-dihydropyrimidine 2 as a mixture of two diastereoisomers. All attempts to separate them were unsuccessful.



1



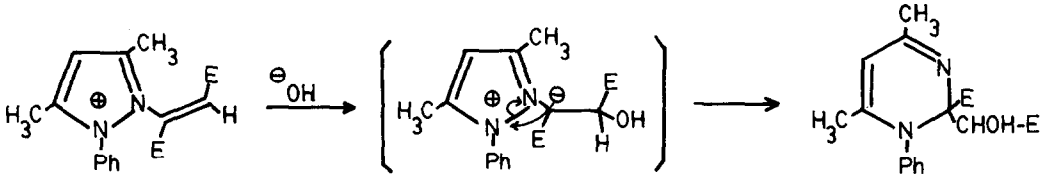
2

E=CO_2CH_3 *chiral centres

The structure of compound 2 was established by analytical and spectroscopic methods. Microanalysis and molecular weight 332, determined by mass spectroscopy, correspond to a molecular formula $C_{17}H_{20}N_2O_5$. In the mass spectrum of 2 the most important fragmentations correspond to the loss of fragments $CHOHCO_2CH_3$ (M-89 $^+$) and CO_2CH_3 (M-59 $^+$). The i.r. spectrum of 2 shows characteristic absorptions at 3280-2080 cm^{-1} (ν_{OH} strongly H-bonded) and 1730 and 1715 (two ν_{CO} of non-conjugated esters). ^1H and ^{13}C n.m.r. spectra clearly support the proposed structure 2. ^1H-n.m.r. ($DCCl_3$), δ(ppm from TMS): 1.59 and 1.62 (3H, d, J=0.7 Hz, CH_3-6); 2.06 and 2.10 (3H, s, CH_3-4); 3.39, 3.64, 3.66 and 3.68 (3H, s, CH_3O); 3.84 and 4.10 (1H, very broad signal, OH); 4.40 and 4.95 (1H, broad singlet, CHOH); 5.10 and 5.18 (1H, q, J=0.7 Hz, H-5); 7.20-8.02 (5H, m, Ph). Broad signals at 3.84

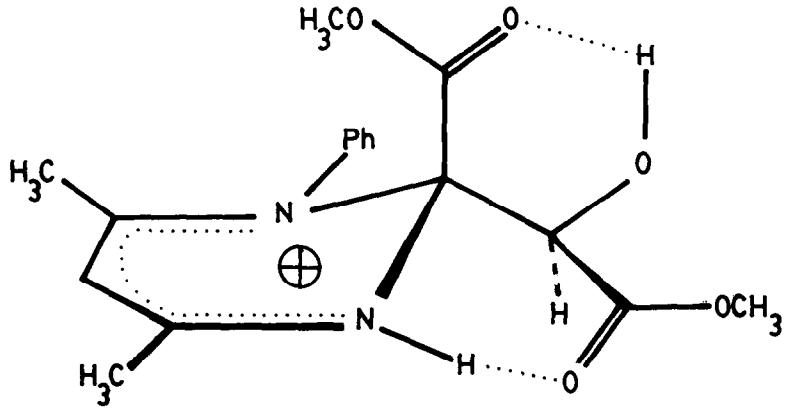
and 4.10 ppm disappear on addition of D_2O or TFAA and signals at 4.40 and 4.95 ppm become sharp singlets. This fact shows that the broadening of the CHOH signals is caused by a ^3J coupling with the OH. ^{13}C n.m.r. ($DCCl_3$), δ(ppm from TMS): 20.5 and 20.6 (CH_3-6); 23.8 (CH_3-4); 52.2, 52.4 and 52.6 (CH_3O); 72.1 and 73.0 (CHOH); 84.2 and 85.1 (C-2); 97.6 and 98.8 (C-5); 128.8-132.1 (C-o,m,p Ph); 139.6 (C-iPh); 151.6 and 152.5 (C-6); 166.9 and 167.1 (C-4); 170.4, 171.1, 171.5 and 172.5 (CO).

Transformation of salt 1 into the 1,2-dihydropyrimidine 2 involves a pyrazole ring expansion via the carbanion formed by nucleophilic attack by hydroxide on the exocyclic double bond, as shown in the scheme:



1 2

Treatment of 2 in acidic media (TFAA, HBF_4 or picric acid) yields only one of the two possible diastereoisomeric salts 3, the configuration of which should be RS(SR). Molecular models show that in the RS(SR) configuration there are two stabilizing hydrogen bonds which do not exist in the other diastereoisomer.



3

This report is the first example of ring expansion in pyrazolium salts. Previously, pyrazole ring expansions have been reported in carbene addition to pyrazoles and in the reaction of N-benzylpyrazoles and indazoles with sodium amide at high temperature.[2]

REFERENCES

1.- A. de la Hoz, E. Díez-Barra, C. Pardo, J. P. Declercq, G. Germain, M. van Meerssche and J. Elguero, Tetrahedron, 39, 2193 (1983).

2.- H. C. van der Plas, "Ring Transformations of Heterocycles", Academic Press, London, 1973, Vol. 1, pp. 274-275.

(Received in UK 17 June 1985)