X-RAY CRYSTALLOGRAPHIC STRUCTURES OF 9-METHYL-3-OXA-2,6,8-TRIPHENYL-5-AZATRICYCLO[4,2,1,$0^{2,6}$]NON-7-ENE 6-HYDROXY-1,6,7-TRIPHENYLAZABICYCLO[3,3,0]OCTA-2,7-DIENE AND 6-HYDROXY-4-METHYL-1,6,7-TRIPHENYLAZABICYCLO[3,3,0]OCT-7-ENE: PRODUCTS FORMED BY REARRANGEMENTS OF N-VINYLPYRIDINIUM PSEUDOBASES

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Abstract — The reaction of hydroxide ion with 1-vinyl or 1-propenyl-2,4,6-triphenylpyridinium salts produces an unusual rearrangement to 3-oxa-2,6,8-triphenyl-5-azabicyclo[4,2,1,$0^{2,6}$]non-7-ene or the corresponding 9-methyl derivative as shown by spectroscopic and X-ray crystallographic techniques.

We recently discovered[1] a remarkable series of unprecedented rearrangements which occur when 1-vinyl- (1a) and 1-propenyl-2,4,6-triphenylpyridinium salts (1b) react with hydroxide ion. The formation of the cage compounds (4a,b) and (9) can be explained by electrocyclic ring opening of the initial adducts (2a,b) to give (3a,b) which undergo prototropic tautomerism to the divinylogous amides (6a,b). We formulate the cyclization of (6a,b) as an electrocyclic $[\pi 4s + \pi 2s + \pi 2a]$ thermally-allowed process of hitherto unrecognized type yielding (4a) or in the case of the methyl derivative, a mixture of the isomers (4b) and (9).

The structures of these cage compounds (4a,b,9) were originally deduced from spectroscopic data[1] but in view of their novelty, we considered it important to confirm them by an X-ray determination. This has now been done for (9).

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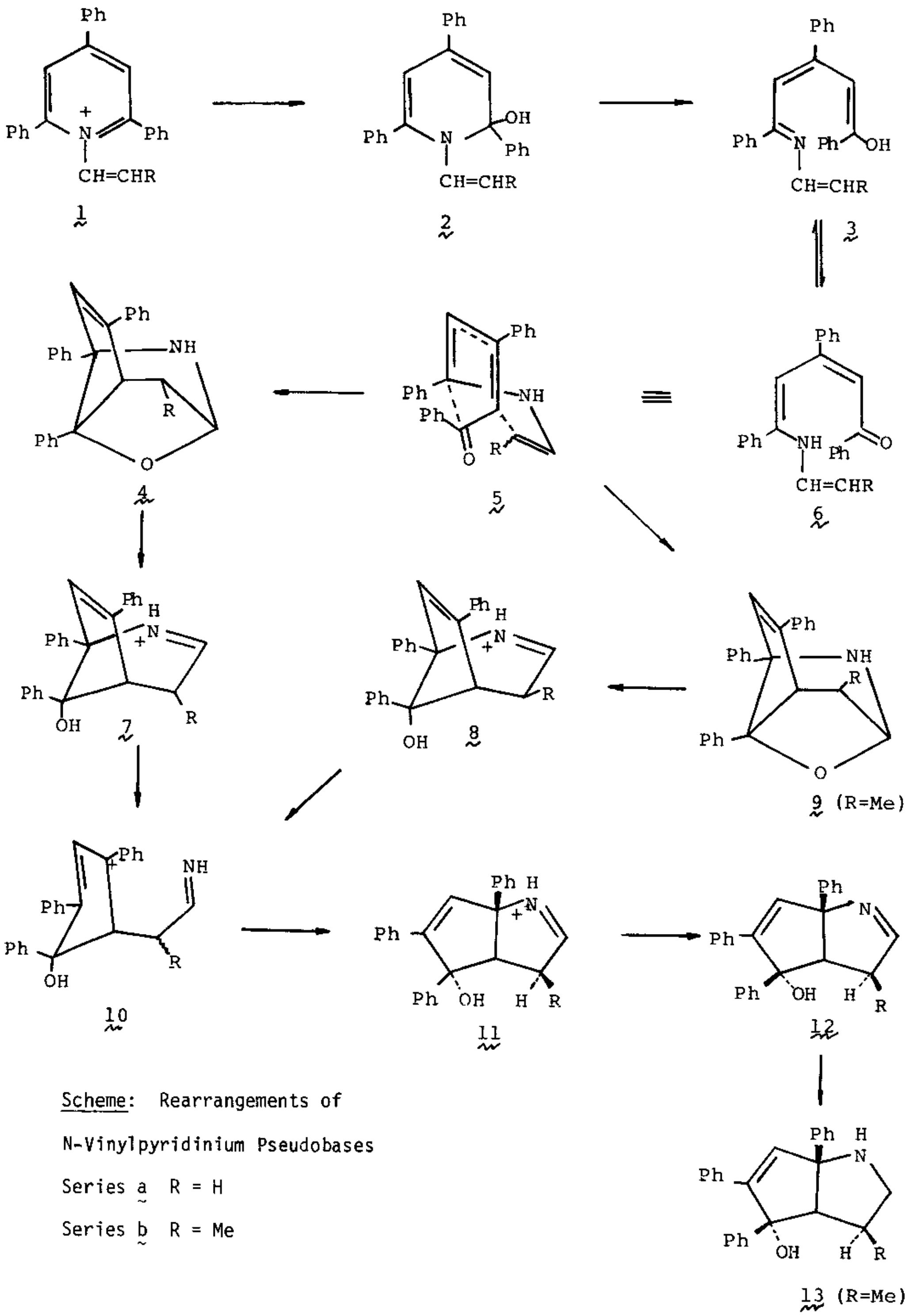

<u>Scheme</u>: Rearrangements of N-Vinylpyridinium Pseudobases

Series a R = H

Series b R = Me

Crystals of (9) are monoclinic space group $P2_1/n$ with a = 12.957(4), b = 12.180(2), c = 13.413(4)Å and β = 110.69(2)°. There are four molecules per cell. A total of 2606 reflections were measured and 1949 were used in the analysis.[2] The final R value was 0.046. A stereoview of the molecule is given in Fig. 1.

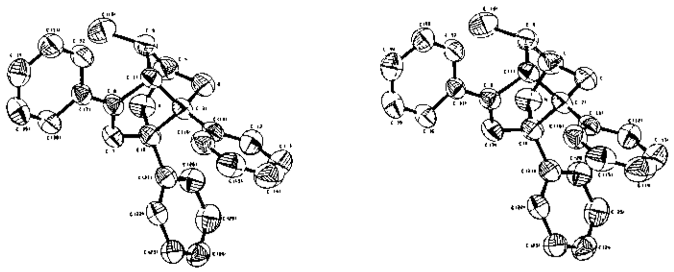

Figure 1. An ORTEP stereo drawing of (9) showing the atomic numbering and thermal ellipsoids.

Further rearrangements of (4) and (9) occur on acid treatment. The first products to be isolated are salts (11a,b) which were deprotonated to yield the corresponding imine free bases (12a,b). Imine (12b) underwent borohydride reduction to (13). The 1,3-rearrangements of the nitrogen atom in (4, 9) to (11a,b) are conceptually visualized as proceeding via the intermediates (10a,b). This interpretation is in keeping with the X-ray determined crystal structures of (11b) and (12a).

Compound (12a) crystallizes with a molecule of ethanol in the triclinic space group $P\bar{1}$ (from intensity statistics and the structure determination) with two molecules per unit cell. The dimensions are a = 10.182(7)Å, b = 10.268(5)Å, c = 10.875(3)Å and α = 101.95(3)°, β = 96.83(4)° and γ = 101.57(5)°. A total of 1793 reflections were measured and 1735 were used in the analysis.[2] The final R value was 0.098.

Compound 13 crystallizes in the orthorhombic space group $Pn2_1a$ with four molecules per unit, all with dimensions of a = 8.875(2)Å, b = 10.793(4)Å and c = 21.560(6)Å. A total of 1444 reflections were measured and 1212 were used in the analysis.[2] The final R value was 0.055. A stereoview of the molecule is given in Figure 2.

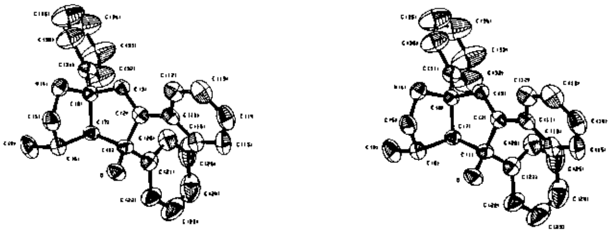

Figure 2. An ORTEP stereo drawing of (13) illustrating the atomic numbering and thermal ellipsoids.

The distances and angles in the three compounds are not unusual. There is a C-C double bond between C(7)-C(8) in (9) [1.328(4)Å] which is shifted to C(2)-C(3) in (12a) [1.326(14)Å] and in (13). [1.321(10)Å], consistent with the reaction scheme. The five-membered rings in (12a) and (13) are not planar, with the saturated rings in (13) being significantly distorted from planarity. The dihedral angle between the two five-membered rings is 59.4° in (12a) and 73.4° in (13). In both cases the oxygen is on the same side of the five-membered, C(1)-C(2)-C(3)-C(8)-C(7), as is the five-membered N containing ring, again consistent with the proposed mechanism.

REFERENCES AND NOTES

1. a. A. R. Katritzky and O. Rubio, J. Org. Chem. in press. b. Compounds (9) and (13) were recrystallized from *n*-hexane and abs. ethanol, respectively. Compound (12a) was obtained after slow recrystallization of (4a) from abs. ethanol. The elemental analysis agreed with $C_{25}H_{21}NO\cdot EtOH$, m.p. 195-198°C.
2. All intensity measurements for (9), (12a) and (3) were carried out using a P$\bar{1}$ diffractometer and Zr-filtered Mo$K\alpha$ radiation to a limit of 45°. Only reflections with $I > 2\sigma(I)$ were considered reliable and were used in the analysis. All three structures were all solved using MULTAN-78[3] and refined by least-square methods. The R value is defined as $R = \Sigma|Fo-Fc|/\Sigma|Fo|$. The final parameters for all three compounds have been deposited with the Cambridge Crystallographic Data Center. Further structural details will be forthcoming.
3. P. Main 'MULTAN 78', University of York, York, England, 1978.

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