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A PROTON TRANSFER FROM TRIMETHYLPYRYLIUM CATION TO PYRIDINE

D. FĂRCAŞIU and EUGENIA GÂRD
Institute for Atomic Physics, P.O. Box 35, Bucharest, Rumania

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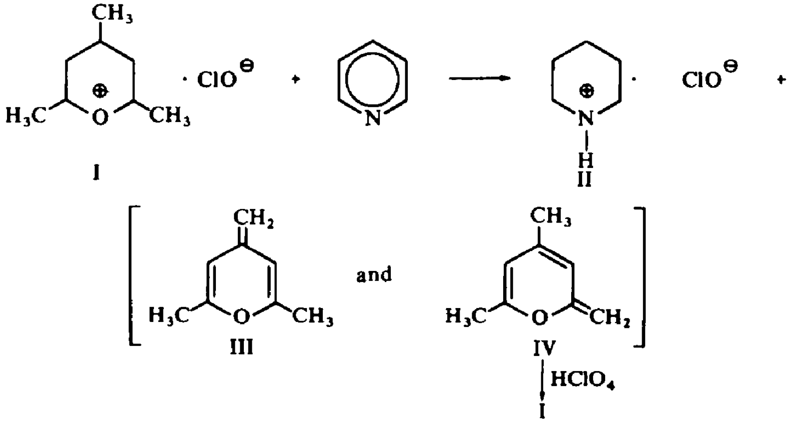
Abstract—The reaction of trimethylpyrylium perchlorate (I) with pyridine is described. It was found that, at variance with the behaviour of other bases, pyridine does not act towards the trimethylpyrilium cation as a nucleophile, but produces a proton transfer, giving the pyridinium perchlorate. Starting from Me-deuterated I, it was proved that the proton is abstracted from both α- and γ-Me groups. The anhydrobases thus formed from I are not isolable, but I is reformed by treatment with acid.

RECENTLY,[1] the formation of a paramagnetic species (donor–acceptor complex) from 2,4,6-triphenylpyrilium perchlorate and anhydrous pyridine was described.

Starting from the 2,4,6-trimethylpyrylium perchlorate (I), we obtained no such complex. The perchlorate I dissolved exothermically in anhydrous pyridine, but by treating with ether the blood-red solution (which is not paramagnetic) thus formed, one obtained the pyridinium perchlorate (II), which precipitated in quantitative yield.

The proton abstracted by pyridine originates, of course, in the trimethylpyrylium cation, the most probably in the methyl groups. Indeed, starting from 2,4,6-tri(methyl-d_3)pyrylium perchlorate (I-d_9),[2] the pyridine perchlorate thus formed, exhibited N-D stretching bands in the IR spectrum, at the same frequencies (2390 and 2445 cm^{-1}, see reference[3]) as an authentic sample of pyridinium-N-d-perchlorate, obtained from pyridine and $DClO_4$. Also, the perchlorate II obtained from a selectively deuterated material (I-α-d or I-γ-d)[2] contained in each case deuterium (bonded to nitrogen).

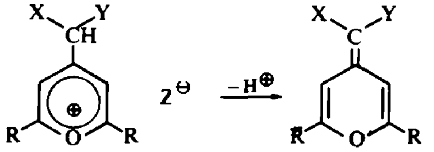
Consequently, as it was expected according to the isotopic exchange data,[2] the proton is transferred from both the α- and γ-Me groups of I, and the reaction could be formulated as follows:



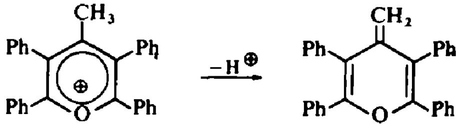
The methylenepyranes III and IV could not be isolated, but they revert to the trimethylpyrylium cation, in acidic medium. So, by treating the ethereal solution—after the filtration of II—with acid, then with ammonia, we obtained a mixture of pyridine (from the excess of reactant) with 2,4,6-trimethylpyridine. The yield of the last compound was very small (0·8 %). The perchlorate I being ether insoluble (as proved in a separate experiment) this small yield of trimethylpyridine could not arise from some initial I which did not react with pyridine, but it was formed from anhydrobases III and IV, *via* I. Moreover, when all operations were conducted at lower temperatures, this yield raised to 5·5 % (at −5°) and 20 % at −35° (determined by GLC).

An assessment of the relative reactivity of α- and γ-Me hydrogens, based on the extent of deuterium incorporation into II in the experiments with selectively deuterated trimethylpyrylium perchlorates (I-α-d and I-γ-d) was not possible because (i) the deuterium bonded to the nitrogen in II could exchange with the hydrogen from traces of water (which may hardly be avoided) during the working up,* and (ii) in the I-α-d and I-γ-d, the Me groups contained also protium, and it is known that proton transfers generally exhibit large and variable isotope effects.[4]

The activity of the pyrylium Me hydrogens was evidenced by the isotopic exchange,[2] or (for compounds with at least one aryl substituent in the pyrylium ring) in condensation reactions.[5] Proton transfers as expressed above, are encountered for the pyrylium salts of the type V, in which one of the substituents X and Y (most frequently the both) are electron-withdrawing groups which can stabilize the resulting methylenepyranes VI[6] (see also [5e]). An exceptional case is the 4-methyl-2,3,5,6-tetraphenylpyrylium cation (VII) the anhydrobase (VIII) of which is unusually stable.[7]

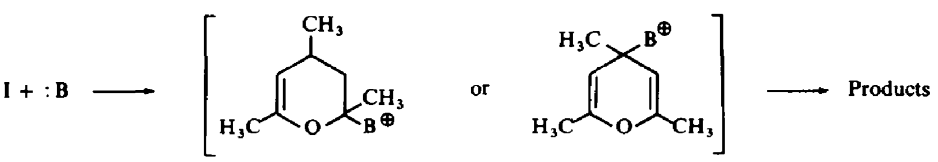


V VI



VII VIII

As concerns the trimethyl-derivative I, bases act usually towards it as nucleophiles, and attack the α or γ carbons of the ring, giving at first adducts IX which undergo further transformation into other cyclic or acyclic products.[8]



The pyridine seems to be the only base as yet known (but other tertiary amines could also be) which does not act as nucleophile towards the trimethylpyrylium perchlorate (I), but produces proton transfer.

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* Even in the case of tri-(methyl-d_3)-pyrylium perchlorate (I-d_9) the II obtained contained some protium bonded to nitrogen. The lability of the hydrogen bonded to the nitrogen in II was also evidenced by the increase of the intensity of the N-H bands (together with the diminution of the intensity of the N-D bands) in the IR spectrum after washing II-N-d (obtained from pyridine and $DClO_4$) with ordinary (undried) ether.

EXPERIMENTAL

Pyridine (a commercial, C. P., material) was dried several days with KOH, then with CaH_2 till the use (at least 2 weeks).

2,4,6-*Trimethylpyrylium perchlorate* (I) obtained as indicated by Balaban and Nenitzescu[9] was recrystallized twice from water, then from alcohol and stored over P_2O_5.

2,4,6-*Tri(methyl-d*$_3$*)pyrylium perchlorate* (I-d_9) was obtained from I by refluxing for 76 hr in D_2O.[2] Its NMR spectrum exhibits no Me proton signal.

2,4,6-*Trimethylpyrylium-α-d* (I-α-d) was prepared from the above material, by dedeuteration in boiling water for 1 hr. NMR analysis showed a protium content of $\leqslant 4{\cdot}3$ and $\geqslant 2{\cdot}7$ atoms ($\pm 10\%$) for α- and γ-Me respectively.

2,4,6-*Trimethylpyrylium-γ-d* (I-γ-d) was obtained from the pure nondeuterated material, by boiling in D_2O for 110 sec. The protium content in the α and γ Me's is $\geqslant 5{\cdot}7$ and $\leqslant 1{\cdot}2$ ($\pm 10\%$) respectively (as determined by NMR).

The reaction of I *with pyridine.* In a typical experiment I (1 g) was added with stirring to anhyd pyridine (5–7 ml). The perchlorate dissolves exothermically. After 5 min* anhyd ether (100 ml) was added to the blood-red soln and the pyridine perchlorate was filtered and washed thoroughly with anhyd ether. The filtrate and washings were catched into 15 ml perchloric acid and 30–40 ml ether, cooled at −40°.

The first ppt (0·8 g, 99%) was purified by dissolving into acetone and precipitating with ether a white powder, m.p. about 285° (lit.[3] m.p. 280–283°). (Found: C, 33·64; H, 3·70; N, 7·85; Calc. for $C_5H_6NClO_4$. C. 33·44; H, 3·36; N, 7·80%). The IR spectrum is identical with that of an authentic sample (obtained from pyridine and $HClO_4$) and in good agreement with the literature data.[3]

From the ethereal soln when filtered into the acid, a white solid precipitated. After filtration and washing with ether it was suspended in 70–80 ml ether and treated with gaseous ammonia for 3 hr. The mixture was treated with water, the ethereal layer was washed with water and dried with solid KOH. After the evaporation of the ether, the mixture of pyridine with trimethylpyridine was analysed by GLC.

The same procedure was applied in the runs at lower temp and also in the runs with deuterated I, but in the last case the experiment was carried out in a dry-box.

Pyridine perchlorate-N-*d* (II-N-d). 21·5 ml soln of anhyd $HClO_4$ in CH_2Cl_2[10] (containing 2 g $HClO_4$) was treated with 0·8 ml D_2O (99·8% atoms D), with external cooling in a dry-box, then shaken for 10 min. The organic layer was discarded and the aqueous soln (calculated as 71% $DClO_4$ with 80% atoms D) was used to prepare I-N-d, by dropping into the cooled anhyd pyridine. The solid was filtered off and washed with anhyd ether. Its IR spectrum is in good agreement with the Cook's data.[3]

Analyses. IR spectra were recorded in KBr disks, with a double beam Jena UR-10 spectrophotometer. NMR analyses for deuterium were run as described,[2] on a Varian A-60-A apparatus. GLC analyses were carried out on a GCHF-18 (Willy Giede) apparatus with a catharometer detector, in the conditions described previously.[11]

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* In the experiment at −35°, 1 hr.

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