REACTION OF PYRYLIUM SALTS WITH NUCLEOPHILES. PART 24. SPECTRAL STUDY OF PYRIDINIUM SALTS WITH A LONG LINEAR (*PARA*-n-ALKYL)-PHENYL GROUP

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Abstract. 2,4,6-Trimethylpyrylium tetrafluoroborate 1 reacts with *para*-n-alkylanilines with long linear chains (2A-E. n = 7-15) affording pyridinium salts 3A-E. characterized by their IR, ^{1}H- and ^{13}C-NMR spectra. Their surfactant properties are discussed.
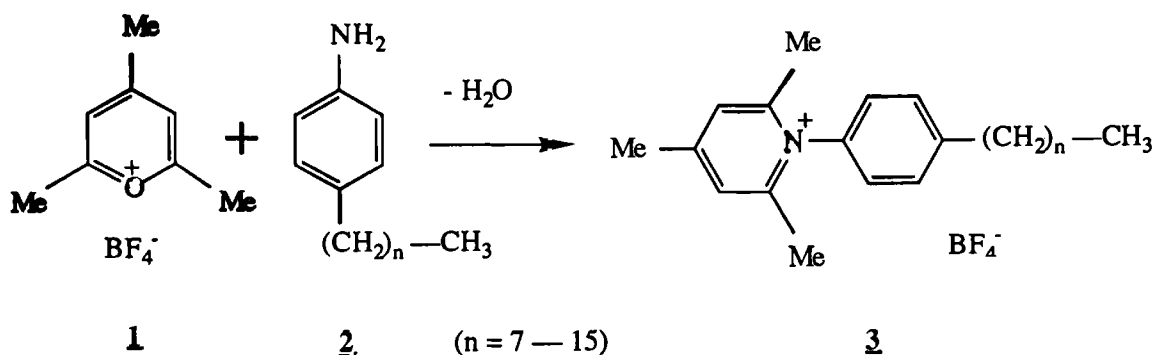
Introduction

Pyridinium salts with long n-alkyl substituents can be obtained either (i) by the Menshutkin quaternization reaction of pyridines with n-alkyl halides, or (ii) from primary n-alkylamines and pyrylium salts (1). In the former case (i), the pyridine may or may not have substituents, but it is known that substitution in the α- (2- or 6-) positions lowers the rate of quaternization owing to steric hindrance. In the latter case (ii), on the contrary, α-substituents are required for a good yield of the reaction (2, 3). These substituents can be alkyl or aryl groups ; only 2,6-di-t-butyl substituents prevent the reaction.

On the other hand, N-arylpyridinium salts cannot be synthesized from pyridines but are formed in good yield from primary aromatic amines and pyrylium salts. Such N-arylpyridinium salts have almost orthogonal rings due to steric hindrance and this fact is apparent from NMR spectra (4, 5), X-ray crystallographic data (6), and the existence of either enantiomerism (7) or diastereomerism (8, 9), according to the substitution pattern.

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It was shown (10, 11) that the reaction of the pyrylium salts with compounds having a primary amino group linked to a primary or an aromatic carbon affords mainly pyridinium salts. Side-products are aniline derivatives when the pyrylium salts have α-methyl(ene) groups (when the primary amino groups are bonded to a secondary or tertiary aliphatic carbon atom, such derivatives may became the main products). Finally 2,6-diisopropylpyrylium salts afford with isopropylamine non-aromatic 2,4-cyclohexadienylidene-1-imino derivatives, along with pyridinium salts (12, 13).

In the present paper we report the spectral study of 2,4,6-trimethyl-1-(*para*-alkylphenyl)-pyridinium tetrafluoroborates 3A-E prepared from 2,4,6-trimethyl-pyrylium tetrafluoroborate 1 and *para*-n-alkylanilines 2A-E with the n-alkyl group having 8 to 16 carbon atoms . These compounds were described in a patent, and were mentioned to be anticorrosive agents (14).

1   2.   (n = 7 — 15)   3

Such pyridinium salts are also expected to have surfactant and bacteriostatic properties, similar to those of n-alkyl-trimethyl-ammonium or 1-n-alkyl-pyridinium salts (10, 15). Unlike these salts, however, compounds 3 are expected to have higher stability since any Ar—N bond-breaking reactions via Hofmann or related degradations are impossible.

Experimental part

The amines 2A-E were purchased from the Aldrich Chemical Company Incorporated. 2,4,6-Trimethylpyrylium tetrafluoroborate was prepared as specified in Org. Synth. Coll. Vol. 5 (16), and ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a 300 MHz Varian VXR-300 instrument in $CDCl_3$ solution with tetramethylsilane as internal standard. Infrared absorption spectra were recorded with a Mattson FT-IR Galaxy 4020 instrument.

Synthetic procedure for 3A-C. The pyrylium salt 1, (1.2 g, 6 mmol) and the amine 2 (5 mmol) were refluxed for 20 minutes in 20 mL ethanol or methanol. After cooling, 1 ml aqueous ammonia and 20 mL water were added. The solution was extracted with 50 ml diethyl ether, the upper layer was washed with 1 % hydrochloric acid, then with water, dried, and evaporated almost to dryness. The resulting crystals were purified by recrystallization from a small amount of aqueous methanol. Yields were 80-90%.

Synthetic procedure for 3D-E. Proceeding as above, the products separated as crystals on diluting the reaction mixture with water or ethyl ether ; they were filtered off, and washed on the filter with small amounts of 1% hydrochloric acid and ethyl ether for removing the unreacted amine as well as the 2,4,6-trimethylpyridine resulted from ammonia and unreacted excess pyrylium salt. Yields were 85-95%.

All compounds 3A-E crystallize as colorless silky needles.

Results and Discussion

The synthesis of pyridinium salts 3 was straightforward and afforded crystalline pyridinium fluoroborates in yields higher than 80%. The reaction was performed by brief refluxing of almost equimolar amounts of the reactants in ethanol or methanol. A slight excess of pyrylium salt was converted, after the reaction, by treatment with ammonia, into sym-collidine which remained in solution. For the lower terms of the series (3A-C), the mixture was treated with water, aqueous ammonia and diethyl ether. The pyridinium salt was extracted in the ethereal layer (this solubility in ether is surprising for a salt, and is due to the long lipophilic substituent) and was left practically pure after the evaporation of the solvent. In the preparation of the higher members of the series (3D-E), the reaction product crystallized on addition of aqueous ammonia and water, and was filtered off. In all cases, the pyridinium salts could be purified by recrystallization from methanol or aqueous methanol. The previously reported synthesis (14) had used a different solvent for the synthesis, namely 1,2-dichloroethane, and no spectral data were provided.

Compounds 3A-E are soluble in acetic acid, the lower alcohols, chloroform, and dichloromethane ; their solubility in diethyl ether is high for the lower members of the series and decreases for the higher members.

Melting points are presented in Table 1. It is remarkable that the melting point of the second and last few fluoroborates of the series 3A-E are higher than for

the middle term ; in some cases, liquid crystalline behaviour may be possible, but further study is needed for this problem.

Table 1. Data for compounds **3A-E**

Comp.	n	Side chain	Formula	M.p. °C
3A	7	C_8	$C_{16}H_{28}N^+ BF_4^-$	72-74
3B	9	C_{10}	$C_{18}H_{32}N^+ BF_4^-$	86-88
3C	11	C_{12}	$C_{20}H_{36}N^+ BF_4^-$	74-76
3D	13	C_{14}	$C_{22}H_{40}N^+ BF_4^-$	103-105
3E	15	C_{16}	$C_{24}H_{44}N^+ BF_4^-$	88-90

Spectroscopic data

The NMR spectra (in $CDCl_3$) confirmed the structure of compounds _3A-E_.

^{1}H-NMR Spectra. First we shall present peaks common to all compounds 3A-E. The pyridinium 3- and 5- protons appear as the lowest-field singlet signal at 7.66 ppm. and the pyridinium 2,6-dimethyl and 4-methyl peaks are singlets at 2.36 and 2.61 ppm, respectively. The ring current effects in orthogonal rings are responsible for the marked shielding and slight deshielding, respectively, of these protons. The AA'BB' phenyl protons give rise to a pair of doublets centered at 7.46 and 7.29 ppm ; the former doublet is due to protons *ortho* to the nitrogen atom, and the latter doublet is assigned to protons *ortho* to the alkyl group. The alkyl protons give rise to a few signals which are fairly constant throughout the series : the N-methylene protons appear as a triplet at 2.71 ppm, the next two methylene groups as quintets at 1.67 and 1.33 ppm, and the terminal methyl protons as another triplet at 0.89 ppm. All remaining methylene groups give rise to a broader peak at 1.28 ppm

^{13}C-NMR Spectra. Again, we shall present first the assignments of aromatic carbon resonances common throughout the series. The highest field signal, at 159.8 ppm, is assigned to the 4-pyridinium carbon atom, and the next signal, at 154.9 ppm having double intensity, to the 2- and 6-pyridinium carbon atoms. The quaternary phenyl carbon atoms bonded to the nitrogen heteroatom and the alkyl group resonate at 146.5 and 135.0 ppm. respectively. The CH phenyl carbon atoms *ortho* to the nitrogen atom give rise to a peak at 130.9 ppm, whereas the adjacent CH carbon atoms *ortho* to the alkyl group resonate at 125.3 ppm ; the 3,5-CH carbon atoms in the pyridinium ring resonate at 127.8 ppm. The pyridinium 4-methyl carbon gives rise to a peak at 21.8 ppm, whereas the 2- and 6-methyl carbons resonate at 21.9 ppm.

The n-alkyl carbon resonances are also fairly constant in the series 3A-E : starting from the nitrogen heteroatom, the methylene resonances appear at 35.6, 31.1, and 31.9 ppm. From the other end, the methyl and the adjacent methylene group resonate at 14.1 and 22.7 ppm, respectively. All intermediate methylene groups appear as distinct peaks (for 3A-C) or partially overlapped peaks (for 3D-E) at 29.3-29.7 ppm.

Assignments in the ^{1}H- and ^{13}C-NMR spectra were substantiated by decoupling and by 2D-NMR experiments, e. g. for the CH aromatic peaks.

Infrared absorption spectra (solids in KBr, using the diffuse reflectance attachment) showed strong bands due to the BF_4^- anion at 1059 cm^{-1}, and to the aliphatic CH vibrations at 2851 and 2918 cm^{-1}, as well as to the pyridinium ring vibrations at 1640 cm^{-1}.

Surfactant properties. Surface tension measurements were performed at 24° C for various concentrations of 3D in deionized water using a Krüss-12 tensiometer. Because of the low solubility, clear solutions were obtained only for concentrations up to 250 mg/ml. The critical micelle concentration (CMC) was reached at 26 mg/ml ; at higher concentrations, the surface tension remained constant at about 40 mN/m.

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