

## SYNTHESIS AND REACTIVITY OF 2,6-DIMETHYLPYRYLIUM SALTS

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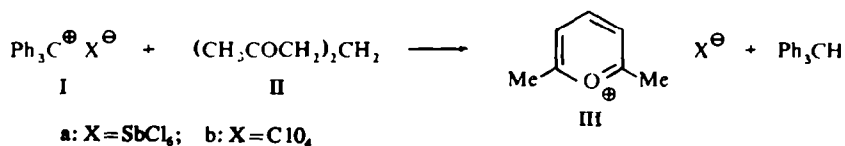
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**Abstract**—A convenient method for preparing 2,6-dimethylpyrylium hexachloroantimonate (IIIa) and the first synthesis of the corresponding perchlorate (IIIb) are reported. The chloroantimonate (IIIa) undergoes H–D exchange in deuterioacetic acid. The reactivity sequence is, as in other cases  $\alpha$ -methyls >  $\beta$ -hydrogens ( $\gamma$ -hydrogens do not exchange); however, the reactivity difference is smaller than in other cases. A mechanism involving the nucleophilic solvent attack on the  $\gamma$ -position is suggested for the exchange of  $\beta$ -hydrogens. The salt IIIa abstracts a hydride ion from phenyl-substituted 1,5-diketones, to give phenyl-substituted pyrylium salts. This reaction also takes place with pyrylium salts other than III, thus enabling to compare the relative stabilities of these compounds.

THE 2,6-dialkylsubstituted pyrylium salts were previously obtained in very small yields by diacylation of propene.<sup>2</sup> More recently, a simple method for preparing pyrylium hexachloroantimonates from 1,5-diketones, by hydride transfer to triphenylmethyl hexachloroantimonate (Ia) generated *in situ* was described.<sup>3</sup> We have found now that this reaction can be applied to 2,6-heptanedione (II) to give 2,6-dimethylpyrylium hexachloroantimonate (IIIa) in 53–64% yield. (At variance with the synthesis of aryl-substituted pyrylium salts,<sup>4</sup> much better yields of IIIa were obtained in acetic anhydride rather than dichloroethane as solvent.) Since the starting material (II) can be conveniently synthesized,<sup>5</sup> and the product IIIa is virtually pure, the 2,6-dimethylpyrylium system becomes readily available.

At the same time we tried to obtain the yet unknown 2,6-dimethylpyrylium perchlorate (IIIb) which had resisted our previous attempts by other methods.<sup>2</sup> Present attempts to synthesize this compound from the diketone II in boiling acetic acid,<sup>6</sup> or in acetonitrile at 40° failed, but in the last solvent at room temperature, IIIb could be prepared in 25% yield. It was identified by its IR spectrum which exhibits the characteristic perchlorate bands, being for the remainder identical with that of IIIa.<sup>7</sup>



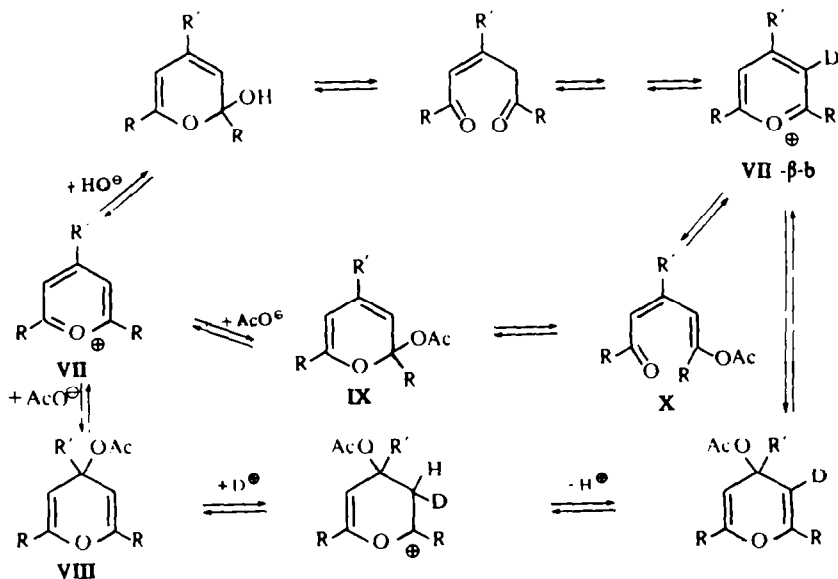
A comparison between the properties of IIIa and IIIb revealed the beneficial effect of the chloroantimonate anion on the stability of III. Thus, IIIb did not resist heating in solvents even for a short time (*cf* the unsuccessful attempts to prepare it at higher temperatures which gave untractable tars), while IIIa was only partly decomposed after 70 hr in acetic acid at about 80°. The perchlorate IIIb could not even be obtained analytically pure. On standing, both IIIa and IIIb darken, becoming red to reddish-brown, but the second much faster than the first.

The reactivity of H atoms in III toward isotopic exchange was studied by heating IIIa in deuterioacetic acid, at 70–90°, and analyzing the recovered salt by NMR spectroscopy.<sup>8</sup> Both  $\alpha$ -Me hydrogens and ring  $\beta$ -hydrogens underwent the exchange. The reaction was slow, as expected for an exchange in acetic acid,<sup>9</sup> and was slowed down more by the relatively low temperature used, due to the thermal instability of IIIa. No deuterium was evidenced (by NMR) in the  $\gamma$ -position after 72 hr under these conditions. This observation agrees with the findings for the 2,3,5,6-tetramethylpyrylium perchlorate (IV),<sup>8b</sup> and shows that a sterically unhindered  $\gamma$ -position, as in III, also does not exchange its hydrogen under these conditions.

Amongst the reactive positions, the  $\alpha$ -Me hydrogens in III are exchanged faster than the ring  $\beta$ -hydrogens (half-lives about 10 hr and 170 hr respectively). The difference in reactivity (measured by the ratio of half-lives—about 17) is noticeably smaller than for other pyrylium cations, like the 2,4,6-trimethyl (V)<sup>8a</sup> ( $T_{1/2\alpha\text{-Me}}:T_{1/2\beta\text{-H}}$ —about 90),

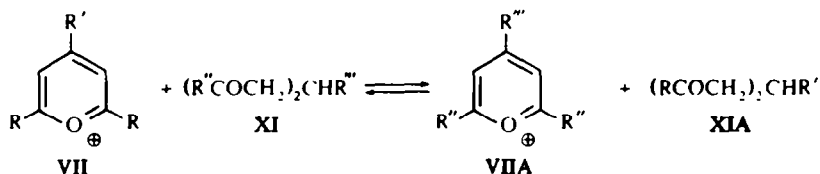


or 2,3,6-trimethyl-4-phenyl-derivative (VI)<sup>8b</sup> ( $T_{1/2\alpha\text{-Me}}:T_{1/2\beta\text{-H}}$ —about 200). This fact suggests the existence of another mechanism for the exchange of hydrogen from  $\beta$ -position of pyrylium ring in acetic acid, besides those discussed previously. The first step of this mechanism consists in a nucleophilic attack of the  $\gamma$ -positive in the pyrylium ring (VII) by the solvent acetic acid (or by the acetate anion). The protonation–deprotonation of the 4[*H*]-pyran thus formed (VIII) results in deuterium incorporation (VII- $\beta$ -d). (Protonation–deprotonation sequences also give VII- $\beta$ -d from the corresponding  $\alpha$ -pyran, IX, or its valence isomer X):



While the formation of VIII from 4-substituted pyrylium salts (VII, R' = alkyl, aryl) is unimportant, in the 4-unsubstituted derivatives (VII, R' = H), e.g. III, the  $\gamma$ -position is very reactive toward nucleophiles, and the sequence VIII  $\rightarrow$  VIII  $\rightarrow$  VII- $\beta$ -d may become important.

The increased reactivity of III over other pyrylium salts, was evidenced by the reaction of hydride transfer from 1,5-diketones (XI) to pyrylium cations (VII):



a: R'' = R''' = Ph; b: R'' = Ph, R''' = H

The hydride abstraction from 1,5-diones to give pyrylium salts is well established and was used in the synthesis of III described above. On the other hand, pyrylium cations combine with hydride ions from sodium borohydride,<sup>9</sup> and a hydride exchange between the pyrylium cation and 4[*H*]-thiapyran or benzo-4[*H*]-pyran has also been described,<sup>10</sup> We found that a hydride ion can be transferred from a (less stable) pyrylium cation to a 1,5-dione, to give the more stable pyrylium salt. Thus, heating IIIa with an equivalent of 1,3,5-triphenyl-1,5-pentanedione (XIa) in acetic anhydride at 70° for 1 hr gave 2,4,6-triphenylpyrylium hexachloroantimonate (VIIAa), with an IR spectrum identical with an authentic specimen.<sup>4</sup> Similarly, the reaction of IIIa with 1,5-diphenyl-1,5-pentanedione (XIb) gave (after 2.5 hr) the 2,6-diphenylpyrylium chloroantimonate (VIIAb)<sup>2</sup> containing only traces of IIIa (as determined by IR). This indicates the greater stabilizing effect on the pyrylium system of the Ph groups in VIIAb than of the Me groups in III.

The introduction of a third Me group in the  $\gamma$ -position (as in V) diminishes noticeably the propensity for hydride abstraction of the pyrylium ring. Thus, from 2,4,6-trimethylpyrylium perchlorate (V<sup>⊕</sup>C 10<sup>⊖</sup>), heated with the triphenyl-pentanedione XIa for 4 hr at 100–120° in acetic anhydride, a mixture of perchlorates V and VIIAa in comparable proportions was isolated. Using acetic acid instead of acetic anhydride as a solvent for the treatment of V with XIa resulted in a much slower reaction. Nevertheless, after 74 hr of boiling in this solvent, the mixture of pyrylium salts in solution consisted of about 62% moles of V and 38% moles of VIIAa (*c*/Experimental). At the same time, an acetic acid solution of XIa heated for the same period gave no VIIAa on treatment with ether. By UV spectroscopy<sup>11</sup> it was established that less than 0.1% of XIa was converted into VIIAa in these conditions; consequently, the hydride acceptor in the previous case was indeed the trimethylpyrylium cation V.

The hydride transfer described here should be considered as a reversible process. The position of the equilibrium is determined by the relative stability of the two pyrylium salts; however the possibility of an equilibrium shift due to the irreversible disappearance of one of the two ketones (XI and XIa) in a secondary reaction<sup>13</sup> must be taken into account.

## EXPERIMENTAL

The triphenylchloromethane and antimony pentachloride used for the synthesis of IIIa were commercial, pure products. The other pyrylium salts, and the diketones used, were prepared using standard literature procedures. IR spectra were recorded in KBr disks; NMR analyses were run at 60 MHz.

**2,6-Dimethylpyrylium hexachloroantimonate (IIIa).** To a mixture of II (0.5 g; 4 mmoles),<sup>5</sup> triphenylchloromethane (2.2 g, 8 mmoles) and  $\text{Ac}_2\text{O}$  (20 ml) cooled at  $0^\circ$ ,  $\text{SbCl}_5$  (1.25 ml 8 mmoles) was added slowly, with gentle swirling, to avoid local heating. Compound Ia partly precipitated. The mixture was allowed to react in the stoppered flask for 30 min in the cooling bath, then for about 42 hr at room temp. The product was precipitated with ether and light petroleum (1:2 by volumes), filtered off and thoroughly washed with moist<sup>3</sup> ether, affording a straw-yellow powder, m.p.  $153\text{--}156^\circ$  (dec), yield 53–64%. Purification from EtOAc light petroleum or/and acetone ether, raised the m.p. to  $163^\circ$  (dec). When ethylene dichloride was used as solvent instead of  $\text{Ac}_2\text{O}$ , the yield was noticeably smaller.

**2,6-Dimethylpyrylium perchlorate (IIIb):** II (0.5 g, 4 mmoles) was treated with Ib (1.5 g, 4.4 mmoles) in freshly distilled MeCN (40 ml) and  $\text{Ac}_2\text{O}$  (0.5 ml) for 41 hr at room temp. The product was isolated as above and purified from acetone-ether and acetonitrile-light petroleum, white crystals, m.p.  $124\text{--}126^\circ$  (dec); IR spectrum: 625 vs, 695 w, 712 w, 812 s, 927 m, 940 m, 1031s, 1100 vs (broad), 1190 s, 1255 w, 1278 w, 1372 ms, 1450 m, 1482 m, 1510 vs, 1561 s, 1642 vs, 2025 w, 2942 mw, 3023 w, 3090 m, and 3146 vw  $\text{cm}^{-1}$  (cf IR spectrum of IIIa,<sup>7</sup> which does not contain the italicized bands due to  $\text{C } 10_4$ <sup>⊖</sup>).

**Isotopic exchange with IIIa.** The salt IIIa was heated in a large excess of deuterioacetic acid (ca 150 moles) for periods of 25 and 72 hr, at  $80^\circ$ . Most of the solvent was evaporated in vacuum at room temp, then ether was added and IIIa was isolated in the usual manner; m.p.  $140\text{--}145^\circ$ . The deuterium content was determined by NMR, using tetramethylammonium bromide as integration standard, according to the procedure described previously.<sup>5a</sup>

**Hydride transfer from 1,5-diketones to IIIa.** IIIa (1mmole) and diketone XI (1 mmole) were heated in acetic anhydride (10 ml) at  $65\text{--}70^\circ$  for the indicated length of time. After cooling, ether was added, then the solid was filtered off and washed with ether:

2,4,6-Triphenylpyrylium chloroantimonate ( $\text{VIIAa}^{\oplus}\text{SbCl}_4^{\ominus}$ ) (from IIIa and XIa), yield 40%, m.p.  $289^\circ$ ; the IR spectrum was identical with that of an authentic specimen.<sup>4</sup>

2,6-Diphenylpyrylium chloroantimonate ( $\text{VIIAb}^{\oplus}\text{SbCl}_4^{\ominus}$ ) (from IIIa and XIb), yield 60%, m.p.  $170^\circ$ . Comparison of IR spectrum with that of authentic specimens<sup>2,7</sup> showed the product is VIIAb containing traces of IIIa.

**Hydride transfer from XIa to V in acetic anhydride.** Three mmoles each of  $\text{V}^{13}\text{C } 10_4^{\oplus}$  and XIa with  $\text{AC}_2\text{O}$  (20 ml) and 1–2 drops of 72% perchloric acid were heated at  $100\text{--}120^\circ$  for 4hr. After cooling and diluting with ether, the product precipitated (0.52 g), m.p.  $210^\circ$ . The IR analysis<sup>7</sup> showed the presence of V and VIIa (as perchlorates) in comparable amounts.

**Hydride transfer from XIa to V in acetic acid.** The same quantities and concentrations of reagents were used as in the previous experiment, but no perchloric acid was added. The product precipitated with ether at different reaction times was analyzed by NMR in  $\text{SOCl}_2$  with external TMS (s denotes singlet, m multiplet):

V:  $\tau$  2.06 (s, 2H,  $\beta\text{--H}$ ), 6.83 (s, 6H,  $\alpha\text{--CH}_3$ ), 6.99 (s, 9H,  $\gamma\text{--Me}$ );

VIIAa:  $\tau$  1.15 (s, 2H,  $\beta\text{--H}$ ), 1.32–1.57 (m, 6H, phenyl-oH), 1.91–2.04 (m, 9H, phenyl-m + p-H); (cf. ref.<sup>12</sup> for the NMR spectra in  $\text{SO}_2$  solon).

The ratio of the two pyrylium salts in the ppt was different from that existing in the solon before the precipitation with ether. In order to calculate the relative concentrations of the two salts in solon from the composition of the ppt, acetic acid solutions of pure V and VIIAa (perchlorates) in various proportions were prepared, and the composition of the pyrylium salts mixture precipitated with ether from each solon was determined by NMR.

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