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SYNTHESES OF PYRYLIUM SALTS BY HYDRIDE TRANSFER FROM 1,5-DIKETONES TO TRIPHENYLMETHYL HEXACHLOROANTIMONATE GENERATED *IN SITU*

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Abstract—Pyrylium chloroantimonates were conveniently synthesized at the ordinary temperature, from 1,5-diketones by hydride-ion transfer to triphenylmethyl chloroantimonate generated *in situ*, from triphenylchloromethane and antimony pentachloride.

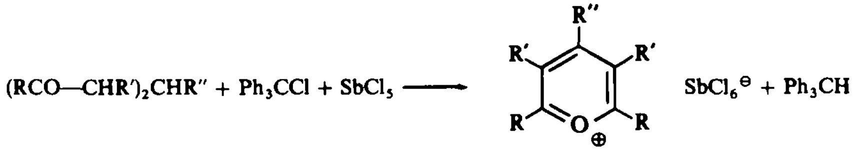
THE use of triphenylmethyl cation (I) as hydride-ion acceptor, in the synthesis of pyrylium salts, is well known.[1] (other acceptors used for the same purpose are the t-butyl cation,[2a] and the conjugate acid of chalcone[2b]). However, the triphenylmethyl perchlorate (Ia), presents a serious problem in that both the reactant (Ia) and the products (pyrylium salts) are explosive.[3] This problem can be avoided, if triphenylmethyl fluoborate (Ib) is used instead of Ia[4] as hydride-ion acceptor.

$$(C_6H_5)_3C^{\oplus}\cdot X^{\ominus} \qquad \begin{array}{l} a: X = ClO_4 \\ b: X = BF_4 \\ c: X = SbCl_6 \end{array}$$

I

In the present work an attempt has been made to obtain pyrylium salts (II) from 1,5-diketones (III) and triphenylmethyl chloroantimonate (Ic). This salt can be obtained easily from the triphenylchloromethane (IV),[5] or triphenylmethane,[5b] and $SbCl_5$; its ability to accept hydride ions is well established.[5b, 6]

In the reaction with 1,5-diketones (III), Ic was not isolated, the pyrylium salts being prepared by treating solutions containing the 1,5-diketones and triphenylchloromethane (IV), with antimony pentachloride:



III IV II

a: R = R' = R" = Ph
b: R = Ph; R' = R" = H
c: R = R" = Me; R' = H

Acetic acid, indicated[7] as the best solvent for hydride transfers with Ia, could not be used, as it does not dissolve Ic, even when heated under reflux. Instead, acetic anhydride or 1,2-dichloroethane were used as solvents and the reaction with 1,5-diketones (III) (40–45 hr at the room temperature) gave good yields of pyrylium hexachloroantimonates (II). Nitromethane was also tried as a solvent (it dissolves Ic, when heated under reflux) but the yield of II was smaller. The results are presented in the following Table.

TABLE 1. PYRYLIUM HEXACHLOROANTIMONATES OBTAINED BY HYDRIDE TRANSFER WITH Ic (40–45 HRS, ORDINARY TEMP)

No.	Diketone Formula	I Mmoles	IV Mmoles	$SbCl_5$ Mmoles	Solvent (ml)	II		
						Yield %	M.p.[a]	Lit. m.p.
1	IIa	2·5	3·0	2·8	Ac_2O (30)–dioxane (15)	21[b]	256°	—[c]
2	IIa	2·5	3·0	2·8	Ac_2O (30)–dioxane (15)	33	253°	
3	IIa	2·5	3·0	2·8	Ac_2O (15)–dioxane (7·5)	38	256°	
4	IIa	2·5	6·0	5·5	Ac_2O (15)–dioxane (7·5)	60	255°	
5	IIa	2·5	3·0	2·8	$MeNO_2$ (12·5)–Ac_2O (2·5)	17[d,e]	217°	
6	IIb	2·5	6·0	5·5	Ac_2O (15)–dioxane (4)	95	220 … … 230°	245°[8]
7	IIb	2·5	3·2	3·0	Ac_2O (13·5)	66	240°	
8	IIb	2·5	3·2	3·0	Dichloroethane (15)	91	237°	
9	IIb	2·5	3·2	3·0	Dichloroethane (15)	10[e]	239°	
10	IIc	2·5	6·0	5·5	Ac_2O (15)	74	163°	174°[9]

[a] Crude product (all m.ps are not corrected).

[b] Reaction time 20 hr.

[c] Analytically pure product melted at 267° (dec) (Experimental).

[d] Under reflux.

[e] Reaction time 40 min.

As Table 1 shows, if acetic anhydride is used as a solvent, excess of Ic is necessary. The dioxan added in some runs to help dissolve the diketones, resulted in less pure products. (The dioxan, like other ethers,[10] reacts with Ic, giving hydride transfer, and then polymerization). The hydride transfer from III to Ic at ordinary temperature is slow compared with the hydride transfer from cycloheptatriene to Ic.[5b] This is not unexpected, since in the latter case the aromatic tropylium system is formed directly, while in the former, the hydride transfer gives an acyclic carbonium ion which cyclizes to the pyrylium cation.

As indicated previously,[7] the volume of solvent influences the yield, but it is not a critical factor.

EXPERIMENTAL

Starting materials. The triphenylmethyl chloride and antimony chloride used were pure, commercial products. The diketones were prepared by known methods.

Pyrylium salta. The experiments were conducted in the proportions given in the Table. The antimony chloride was added dropwise with external cooling into the mixture of the other reactants. Ic precipitated instantaneously. The flask was stoppered and left for 40–45 hr at the room temp. The product partly crystallized. The crystallization was completed by adding ether and pet ether, and the pyrylium salt II, was filtered off and washed with ether. The moisture in the ether decomposed the unreacted I (or excess of I was decomposed with alcohol before filtration).

Pentaphenylpyrylium chloroantimonate, m.p. 267–269° (dec) from acetone–pet-ether. (Found: C, 53·14; H, 3·38; Cl, 27·37. $C_{35}H_{25}Cl_6OSb$ requires: C, 52·80; H, 3·17; Cl, 26·72%).

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