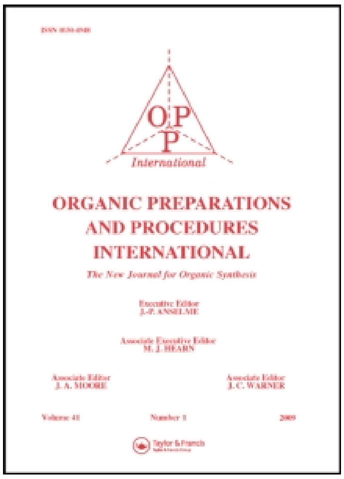

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POLYARYLPYRYLIUM HEXA CHLOROANTIM ONATES

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POLYARYLPYRYLIUM HEXACHLOROANTIMONATES

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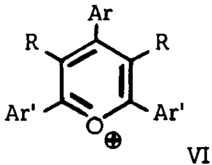
In connection with one-electron transfer studies,[2] we were interested in preparing several arylsubstituted pyrylium hexachloroantimonates (VI). These compounds were prepared from the corresponding 1,5--pentanediones (III) which were obtained by the condensation of aromatic aldehydes (I) with acetophenone or a derivative of it (II).[3] Two of the diones III were new compounds and are described in Table 1. Treatment of III with triphenylchloromethane (IV) and antimony pentachloride (V) gave the pyrylium hexachloroantimonates (VI), by a hydride transfer.[4]

$$\underset{\mathrm{I}}{\mathrm{ArCHO}} + \underset{\mathrm{II}}{2\mathrm{Ar'COCH_2R}} \longrightarrow \underset{\mathrm{III}}{\mathrm{ArCH(CHR\text{-}COAr')_2}}$$

$$\mathrm{III} + \underset{\mathrm{IV}}{\mathrm{Ph_3CCl}} + \underset{\mathrm{V}}{\mathrm{SbCl_5}} \longrightarrow$$



$\mathrm{SbCl_6}^{\ominus}$

VI

a. Ar = Ar' = Ph; R = H

b. Ar = Ar' = R = Ph

c. Ar = R = Ph; Ar' = p-MeC_6H_4

d. Ar = p-MeC_6H_4; Ar' = R = Ph

e. Ar = p-ClC_6H_4 ; Ar' = R = Ph

f. Ar = p-$MeOC_6H_4$; Ar' = R = Ph

g. Ar = m-$O_2NC_6H_4$; Ar' = R = Ph

For the hydride transfer, ethylene dichloride was the best solvent ; in two cases, acetic anhydride was added to dissolve the diketone (a larger amount of IV and V had to be used in these experiments). The reaction was completed in several days (Table 2).

The pyrylium cations of VIc and VId were also synthesized as their perchlorates (VII and VIII, respectively) . For this purpose, the hydride transfer from IIIc and IIId was attempted with phosphorus pentachloride,[5] chalcone and perchloric acid,[6] and triphenylmethyl perchlorate.[7] The first two methods gave good yields, but the products were usually dark-colored and could not be separated from the impurities causing the darkening; the third method gave pure (yellow) products, but the yield for VII was unexpectedly low (cf last two entries of Table 2) .

Table 1. 1,5-Diketones (new compounds).[8]

Formula	Yield %	Mp.[9]	Analysis[10] Calculated C %	H %	Found C %	H %
IIIc	80	210-1°	87.36	6.34	87.30	6.12
IIIe	97	232-5°	82.44	5.05	82.31	5.37

Table 2. Pyrylium Salts.[8]

Formula	Starting materials (mmoles)			Ethylene chloride (ml)	Reaction time (days)	Yield %	Mp.[9]	Analysis[10]			
								Calculated		Found	
	III	IV	V					C %	H %	C %	H %
VIa	5.0	6.4	6.0	20	3	88	318-9[a]				
VIb	2.5	3.2	3.1	40	5[b]	76	267-9				
VIc	2.5	6.4	6.0	15[c]	5	73	264-5	53.92	3.55	53.74	3.72
VId	2.5	4.8	4.5	15[d]	4	79	250-1	53.37	3.36	53.68	3.17
VIe	2.5	3.2	3.1	35	5	75	225-9	50.61	2.92	50.87	2.90
VIf	2.5	3.2	3.1	35	4	76	222-4	52.34	3.29	52.89	3.48
VIg	2.5	3.2	3.1	35	7	67	261-4	49.98	2.88	50.16	2.91
VII	2.5					20	291-3	75.44	4.96	75.69	4.69
VIII	2.5					76	318-9	75.19	4.73	74.89	5.06

[a] Lit.[11] mp. 320° (prepared in about 50% yield).

[b] After 40 hrs the yield was only 60% (mp. 267-9°).[4]

[c] Acetic anhydride (20 ml) was added.

[d] Acetic anhydride (10 ml) was added.

EXPERIMENTAL

Pentanediones (III). The procedure of Japp and Klingemann[3] was followed as such. For the starting ketones (II) which were insoluble in alcohol, the heterogeneous mixture was kept for 4 - 5 days at room temperature. The products (III) were then filtered, washed 5 - 6 times with alcohol and 3 - 4 times with water. For analysis they were recrystallized from alcohol or benzene.

Pyrylium hexachloroantimonates (VI). The quantities of reagents are given in Table 2. The diketone III and triphenylchloromethane (IV) were dissolved in ethylene dichloride containing 0.5 - 1 ml acetyl chloride, and V was dropped into this solution, at room temperature. Some diones (IIIc, IIId) started to crystallize at this point; the mixture was then heated at 50 - 60° for 5 - 10 min, until the solid redissolved. The solution was kept in a stoppered flask for the indicated interval of time at room temperature and the product (VI) then precipitated with ether and light petroleum (b.p. 30 - 60°) (1 : 2 v/v), filtered and washed with moist[4] ether. The mp. of crude VI was only slightly lower than that of the analytically pure products, obtained after crystallization from acetone : ether or from ethylene dichloride : pet. ether.

Pyrylium perchlorates VII and VIII. The literature procedure[7] gave analytically pure products directly.

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8. The IR spectra for all the compounds were in good agreement with the structures.
9. Mps. are not corrected; all pyrylium salts melt with decomposition.
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