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THE PROBLEM OF SYNTHESIZING BISPYRYLIUM SALTS

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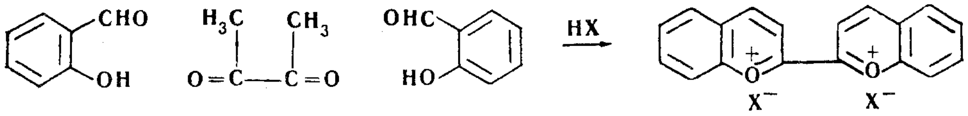
Potentially useful methods of synthesizing bispyrylium salts are reviewed. It is found that alkaline condensation of aromatic dialdehydes with aliphatic-aromatic ketones gives tetraketones, converted into bispyrylium salts by the action of hydride ion acceptors. Contrary to expectation, condensation of 1, 1, 2, 2-tetraacetylethane with resorcinol in acid solution gives a monopyrylium salt. Acetylation of 2, 4-dimethylpentane-2, 4-diol with acetic anhydride in the presence of perchloric acid led to the isolation of 2, 4, 6-trimethylpyrylium perchlorate, in addition to the expected methylenebispyrylium salt. Reaction of 2, 4-diphenyl-6-methylpyrylium perchlorate with terephthaldehyde gives a low yield of the product formed by condensation at both carbonyl groups.

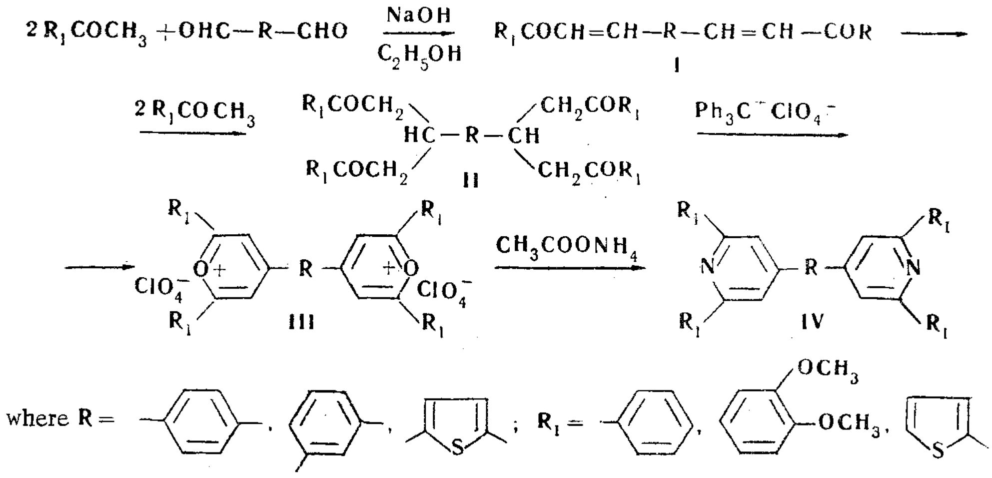
Among the numerous pyrylium, thiopyrylium, benzopyrylium and other salts [1-3], quite an important place must be assigned to bispyrylium salts as a starting point for interesting aromatic and heterocyclic compounds. However, up to the present only isolated cases of the syntheses of such salts have been reported in the literature [4, 5]. In searching for synthetic routes to bispyrylium salts, we have sought to apply some previously known methods for preparing such compounds.

Acid condensation of salicyladehyde and related compounds with ketones is known to give benzopyrylium salts [6]. However, our attempts to synthesize bispyrylium salts according to the equation



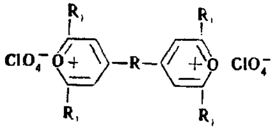
did not lead to the expected results, only resinous materials being obtained.

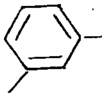
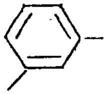
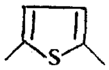
The method of direct acid condensation of aromatic aldehydes with aliphatic-aromatic ketones [7] is quite convenient, and we attempted to apply it to the synthesis of bispyrylium salts by condensing terephthaldehyde with aliphatic-aromatic ketones in the presence of perchloric acid, but the desired compounds were not obtained. It was further found that 1, 4-phenylenebis (1', 5'-diarylpentane-1', 5'-diones) were obtained by the corresponding alkaline condensation. Evidently, this reaction proceeds in two stages. First of all a molecule of dialdehyde condenses with two molecules of ketone to give a bischalcone (I), which then undergoes a Michael reaction, adding a further two molecules of ketone to give the corresponding tetraketone (II). When the latter is boiled with trityl perchlorate in glacial acetic acid, it loses a hydride ion and cyclizes to the phenylenebispyrylium salt III, in almost quantitative yield:



In the present work the condensation of dialdehydes (terephthaldehyde, isophthaldehyde, and thiophene-2, 5-dialdehyde) with aliphatic-aromatic ketones (acetophenone, 2-acetothienone, and 3, 4-dimethoxyacetophenone) was

Table 1



Experiment number	R	R₁	Color of re-action product	IR spectrum, cm⁻¹	Formula	Found, %			Calculated, %			Yield, %
						C	H	Cl	C	H	Cl	
1		C_6H_5	Yellow	1620, 1600 1579, 1506	$C_{40}H_{28}Cl_2O_{10}$	65.36 65.46	4.06 4.03	9.83 9.97	64.95	3.79	9.61	93.7
2		$(CH_3O)_2C_6H_3$	Red	1618, 1600 1518, 1496	$C_{48}H_{44}Cl_2O_{18}$	58.43 57.99	4.63 4.74	6.75 6.95	58.83	4.49	7.25	82.6
3		α-C_4H_3S	Red	1624, 1520 1497	$C_{32}H_{20}Cl_2O_{10}S_4$	51.03 50.83	2.82 2.79	9.63[a] 9.50	50.33	2.62	9.30	98.2
4		C_6H_5	Yellow	1621, 1603 1581, 1504	$C_{40}H_{28}Cl_2O_{10}$	64.65 64.35	4.02 3.95	9.21 9.36	64.95	3.79	9.60	81.0
5		α-C_4H_3S	Orange	1617, 1520 1496	$C_{32}H_{20}Cl_2O_{10}S_4$	49.94 49.25	2.63 2.57	9.50[b] 9.63	50.33	2.62	9.30	77.1
6		C_6H_5	Red	1607, 1578 1515, 1488	$C_{38}H_{26}Cl_2O_{10}S$	60.42 60.59	3.46 4.07	9.73[c] 9.75	61.21	3.49	9.53	80.0
7	Compound XII		Red	1632, 1600 1494	$C_{44}H_{32}Cl_2O_{10}$	65.98 66.28	4.44 4.23	9.45 9.23	66.75	4.04	8.98	Low

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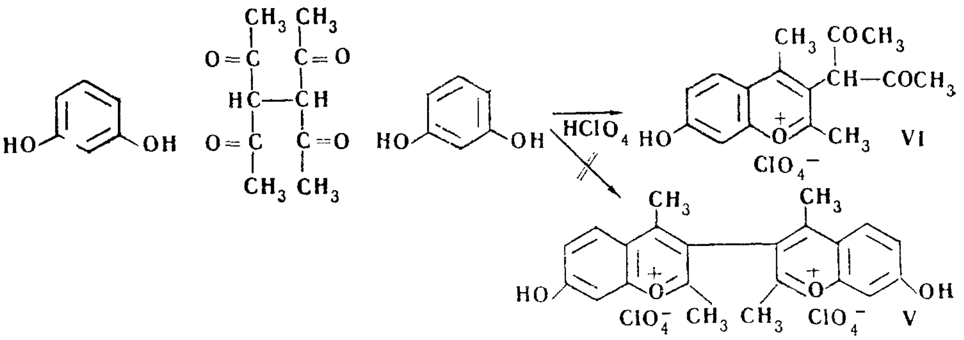
Found: S[a] 15.5; 16.1; [b] 14.33; 14.45; [c] 3.67; 3.97%. Calculated: S[a] 16.77; [b] 16.77; [c] 4.29%.

investigated. Tetraketones could not be prepared from terephthaldehyde, p-methyoxyacetophenone, and 2-acetylfuran. The first of these gave a bischalcone, but without the Michael reaction taking place, while with the second no end reaction product could be isolated, due to marked resinification. Crystalline tetraketones could be isolated only when methyl ketones were condensed with terephthaldehyde. Otherwise the products were non-crystalline tetraketones, which were cyclized to the corresponding pyrylium salts without being purified. These salts were colored and crystalline, and slightly soluble in polar organic solvents. They decomposed without melting above 300° C. As they exploded violently on heating, elementary analysis was effected with samples mixed with cane sugar.

The IR spectra of all the compounds synthesized were determined using an IKS-14 spectrophotometer with the sample mixed with vaseline. They all had the intense bands at 1624–1610 cm^{-1} characteristic of 2, 4, 6-triarylpyrylium salts [8]. The spectra of the pyrylium salts also had intense absorption bands in the 1600 and 1520–1490 cm^{-1} regions, and a medium intensity band (1580–1570 cm^{-1}), ascribable to valence vibrations of C=C bonds of aromatic substituents. It is quite possible that the 1490–1500 cm^{-1} region band of valence vibrations characteristic of the pyrylium cation is not separately visible because of the intense absorption in that region due to aryl groups. Table 1 gives IR spectra, yields and analyses of the salts prepared.

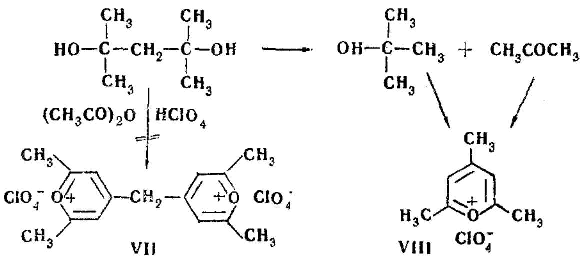
When phenylenebispyrylium salts are boiled with ammonium acetate in glacial acetic acid, they are with difficulty converted into the corresponding 1, 4-phenylenebis (γ, γ-pyridines) (IV), which are also only slightly soluble in the ordinary organic solvents.

It is known [6] that benzopyrylium salts are formed by the facile reaction of β-diketones with phenols in acid solution [6]. It seemed likely that use of 1, 1, 2, 2-tetraacetylethane as the β-diketone in this reaction should give bispyrylium salts (V), the equations being

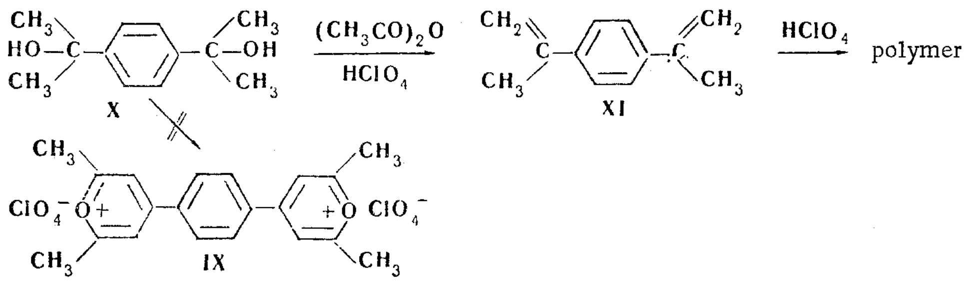


However, when this condensation was attempted with resorcinol in the presence of perchloric acid (1:2.5:1.5) in acetic acid solution, reaction stopped at formation of a mono product containing a β-diketone group (VI), and prolonged heating of the latter with excess resorcinol and perchloric acid led only to isolation of the starting pyrylium perchlorate (VI).

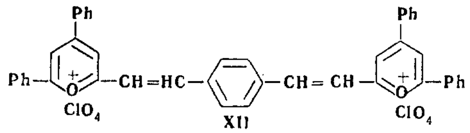
Starting from the fact that acetylation of tertiary alcohols with acetyl perchlorate gives pyrylium salts [8], this type of reaction was carried out with ditertiary alcohols, with a view to preparing bispyrylium salts. However, acetylation of 2, 4-dimethylpentane-2, 4-diol with acetic anhydride in the presence of equimolecular amounts of $HClO_4$ unexpectedly gave, along with the methylenebispyrylium salt VII, a small yield of 2, 4, 6-trimethylpyrylium perchlorate (VIII). It is assumed that the reaction involves decomposition of the pinacone to tert-butanol and acetone, and this is in good accord with the literature [10]. The latter then, under the conditions of the reaction [9, 11], give 2, 4, 6-trimethylpyrylium perchlorate (VIII):



Attempted synthesis of the phenylenebispyrylium salt IX by acetylating 1, 4-phenylenebis (1', 1'-dimethylcarbinol) led to isolation of brown polymer:

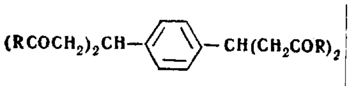
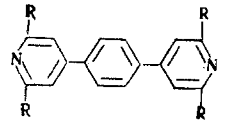


It is known [12] that heating α- and γ-methylpyrylium salts with aldehydes in glacial acetic acid readily gives styryl derivatives of pyrylium salts. Prolonged boiling (8–10 hr) of a mixture of terephthaldehyde and 2,4-diphenyl-6-methylpyrylium perchlorate (1 : 2) in glacial acetic acid gave a low yield of a product formed by condensation at both methyl groups XII, having properties analogous to those of phenylenebispyrylium salts.



To remove unreacted 2,4-diphenyl-6-methylpyrylium perchlorate, the salt formed was boiled with a small quantity of nitromethane, and the undissolved bispyrylium salt filtered off.

Table 2

Experiment number	R	mp, °C	Formula	Found, %		Calculated, %		Yield, %
				C	H	C	H	
								
1	C_6H_5	205— —204	$C_{40}H_{34}O_4$	82.60 82.73	5.98 6.01	83.01	5.88	95.0
2	$(OCH_3)_2C_6H_3$	210	$C_{48}H_{50}O_{12}$	69.51	6.16	70.41	6.11	97.0
3	α-C_4H_3S	202	$C_{32}H_{26}O_4S_4$	63.64	4.40ᵃ	63.78	4.32	86.4
								
1	C_6H_5	274	$C_{40}H_{28}N_2$	89.35 89.23	5.34 5.30	89.55	5.22	
2	$(CH_3O)_2C_6H_3$	decomp.	$C_{48}H_{44}N_2O_8$	74.11 74.25	5.79 5.71	74.22	5.67	
3	α-C_4H_3S	decomp.	$C_{32}H_{20}N_2S_4$	68.85 69.02	4.13b 4.17	68.57	3.57	

Found: S^a 20.90; 21.05; ^{b}20.65; 21.20%. Calculated: S^a 21.26; ^{b}22.85%.

Experimental

Condensation of terephthaldehyde with acetophenone. A solution of 2.7 g terephthdialdehyde, and 14.5 g acetophenone in 35 ml EtOH was vigorously stirred, and a solution of 2.8 g KOH in 3 ml water added, when the mixture became slightly warm. After a few minutes there was copious crystallization, the mixture ultimately solidifying to a mass which could be stirred with difficult. This was refluxed for 10 min on a water bath, when the crystalline chalcone dissolved almost completely, and crystalline tetraketone separated in the course of the reaction. The tetraketone was filtered off from the hot reaction products, washed twice with EtOH (5 ml each time), then dried, yield 10.9 g (95%), mp 205°. As the reaction product was only slightly soluble in the usual organic solvents, it was purified by boiling with a small amount of ethanol and filtering off.

The other tetraketones were prepared similarly from 3,4-dimethoxyacetophenone, α-acetylthiophene, and terephthdialdehyde (Table 2).

In the cases of isophthaldehyde and 2,5-diformylthiophene, the tetraketones could not be isolated crystalline. After boiling with ethanol and vacuum-drying, they were used without further purification.

1,4-Phenylenebis-γ, γ'-(2', 6'-diphenylpyrylium) perchlorate. a) 2.9 g of the tetraketone prepared was boiled for 15 min with 3.75 ml triphenylmethylperchlorate in 40 ml glacial AcOH, the product coming out as crystals as the reaction proceeded. Purification by boiling the crystals with AcOH gave the phenylenebispyrylium perchlorate as yellow crystals, yield 3.6 g (97.3%).

b) 1.5 g tetraketone in 10 ml Ac_2O was stirred, and 1.7 g 70% $HClO_4$ added, when the tetraketone gradually dissolved, and a yellow crystalline product separated. The latter was filtered off, washed with Et_2O, and dried. After purification as described above, the yield of the product in question was 1.76 g (92.0%).

Bispyrylium salts were similarly prepared from the tetraketones obtained by reacting terephthdialdehyde, isophthdialdehyde, and thiophene-2,5-dialdehyde with aliphatic-aromatic ketones, as described (see Table 1).

1,4-Phenylenebis-γ, γ'-(2', 6'-diphenylpyridine). 1 g of the phenylenebispyrylium perchlorate obtained was boiled for 1 hr 30 min with 2.5 g anhydrous ammonium acetate in 25 ml glacial AcOH, and the products then poured into 150 ml water and left for 1 hr in a refrigerator. The precipitate (sometimes lumpy) of product was filtered off, washed with EtOH, and dried, yield 0.46 g (64%). The phenylenebispyridine was recrystallized from nitromethane or a large volume of EtOH, mp 274° C. Table 2 gives the analytical data for the bispyridines.

Condensation of 1,1,2,2-tetraacetylethane with resorcinol. 1 g 1,1,2,2-tetraacetylethane was added to a solution of 2.8 g resorcinol plus 2 ml 70% $HClO_4$ in 5 ml glacial AcOH, and the whole heated on a boiling water bath for 30 min. After cooling the products were diluted with 50 ml Et_2O, and the resultant yellow crystalline precipitate of 2,4-dimethyl-3-(3'-pentane-2', 5'-dione)-7-hydroxypyrylium perchlorate filtered off, washed with ether, and dried. Yield 1.78 g (97%), mp 238°–239° (ex AcOH). IR spectrum, cm^{-1}: 1626 (strong), 1585 (medium), 1495 (medium). Found: C 51.62, 51.69; H 4.60, 4.63; Cl 9.50, 9.53%. Calculated for $C_{16}H_{17}ClO_5$: C 51.54; H 4.56; Cl 9.53%.

2,4,6-Trimethylpyrylium perchlorate from 2,4-dimethylpentane-2,4-diol. 5 g 70% $HClO_4$ was carefully added to 1.32 g 2,4-dimethylpentane-2,4-diol plus 25 ml Ac_2O in 15 ml nitromethane, and the mixture heated for 1 hr on a water-bath. After cooling the crystalline product, weighing 0.24 g, was filtered off. 100 ml Et_2O was added to the filtrate, and the resin which separated was dissolved in a minimum quantity of acetone, the 0.5 g undissolved product filtered off, washed with Et_2O, and dried. Total yield of 2,4,6-trimethylpyrylium perchlorate 0.74 g (33.4%), mp 245° (ex water). The literature [10] gives mp 245°. Undepressed mixed mp with authentic 2,4,6-trimethylpyrylium perchlorate, and in the 1800–700 cm^{-1} region, the IR spectra of the two coincided completely: that they were identical was also confirmed by chromatographing on $CaSO_4$, using a reference spot.

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