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PYRANYLTRIPHENYLPHOSPHONIUM SALTS

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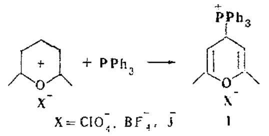
The reaction of pyrylium salts having a free α or γ position with triphenylphosphine has given pyranylphosphonium salts. 2, 4, 6-Trisubstituted pyrylium salts do not react with triphenylphosphine. The properties and IR spectra of the compounds synthesized are discussed.

The phosphonium salts that are finding wide use in the Wittig reaction are readily obtained by the reaction of alkyl halides, α-halogenoacids, or ketones having terminal halogen atoms with triphenylphosphine [1]. In a study of pyrylium salts with a free α or γ position we have found that the latter also react with triphenylphosphine giving high yields of pyranylphosphonium salts I according to the scheme:



The reaction takes place when a mixture of the reactants in a polar solvent (for example, nitromethane) is heated for a short time. When ethyl acetate is added to the hot reaction mixture, the crystalline final product separates out on cooling. The elementary analysis and the IR spectra and the frequently almost quantitative yields of the substances formed permit the statement with full certainty that the compounds obtained are the pyranylphosphonium salts I. They are colorless or faintly colored crystalline products which melt, as a rule, lower than the initial pyrylium salts and which have properties (solubility, stability, etc.) similar to those of ordinary phosphonium salts. Boiling in acetic acid does not change the phosphonium salts, nor does their prolonged boiling in ethanol with an aldehyde.

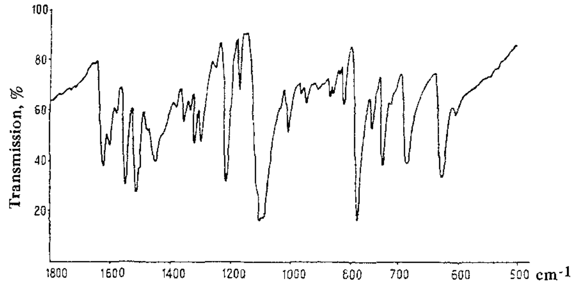
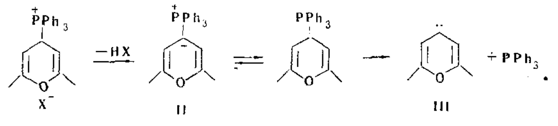


Fig. 1. IR spectrum of 2, 6-diphenylpyrylium perchlorate.

When bases are added to suspensions of the compounds under consideration in ether, a dark color appears which immediately disappears again. Treating a suspension of a phosphonium perchlorate in ether or in ethanol with an equimolecular amount of sodium ethoxide leads to the separation of triphenylphosphine from the mixture. It is likely that the normal product of the Wittig reaction—the colored phosphorane II—formed in this process decomposes under the usual conditions into triphenylphosphine and the carbene III by the reaction:



Since trisubstituted pyrylium salts do not form phosphonium salts, this method can be used to establish the presence of a free α or γ position in a pyrylium salt.

Characteristics of the Phosphonium Salts Obtained

Compound	Mp, °C	Empirical formula	Found, %				Calculated, %				Yield, %
			C	H	Cl	P	C	H	Cl	P	
Ia	163.5	$C_{35}H_{27}ClO_5P$	69.93	4.86	5.61	4.90	70.82	4.55	5.92	5.23	99
Ib	152.0	$C_{35}H_{27}BF_4OP$	72.65	4.80	—	—	72.41	4.66	—	—	98
Ic	152.5	$C_{35}H_{27}OPI$	68.01	4.51	—	—	67.63	4.34	—	—	80
IV	140—142	$C_{35}H_{27}ClO_4PS$	68.25	4.92	5.52	4.99	68.74	4.58	5.81	5.23	98
V	190	$C_{33}H_{25}ClO_5P$	70.46	4.93	7.36	5.10	69.84	4.41	6.20	5.46	95
VI	206—208	$C_{33}H_{25}ClO_5P$	70.57	4.82	7.72	5.56	69.84	4.41	6.20	5.46	81
VII	234—235	$C_{31}H_{24}ClO_5P$	68.20	4,58	6.31	—	68.48	4.43	6.55	—	85
VIII	181—182	$C_{38}H_{31}ClO_6P$	69.80	4.52	6.02	—	70.27	4.77	5.47	—	80

The phosphonium salts obtained from thiapyrylium, benzopyrylium, and xanthylium perchlorates, IV–VIII, are similar in their method of preparation and properties.

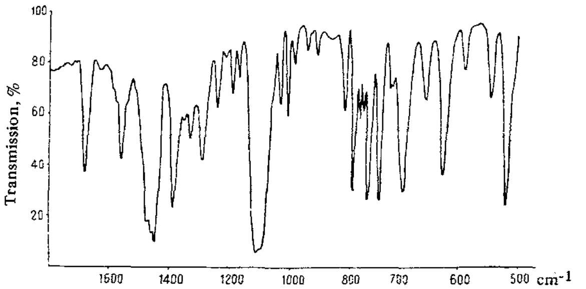
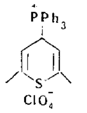
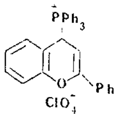


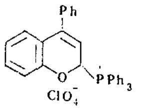
Fig. 2. IR spectrum of the phosphonium salt Ia.



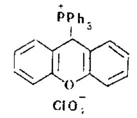
IV



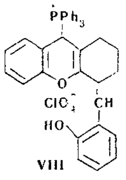
V



VI

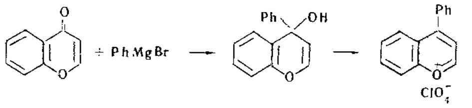


VII



VIII

The 2, 6-diphenylpyrylium salts were obtained by a known method [2], 2, 6-diphenylthiapyrylium perchlorate by Wizinger's method from dibenzylideneacetone and H_2S [3], 2-phenylbenzopyrylium perchlorate from salicylaldehyde and acetophenone, and the salt VIII from salicylaldehyde and cyclohexanone, as described by Ridgway and Robinson [4]. Xanthylium perchlorate was obtained from xanthydrol and perchloric acid [5]. The 4-phenylbenzopyrylium salt was synthesized in low yield by the following route:



To confirm the structure of the phosphonium salts under consideration, their UV spectra in the form of mulls in paraffin oil were recorded on a UR-10 spectrophotometer. The spectra of the compounds described have a strong band in the 1690–1670 cm^{-1} region which can be ascribed to the vibrations of the pyran ring [6]. At the same time, the bands characteristic for the pyrylium cation [7] have disappeared. Thus, on comparing the spectra of 2, 6-diphenylpyrylium perchlorate and the phosphonium salt obtained from it (Figs. 1, 2), the disappearance of strong bands characteristic for the pyrylium salt (1629, 1540 cm^{-1}) and the appearance of a band at 1680 cm^{-1} can be clearly seen. A more detailed analysis of the IR spectra of the end-products will probably enable the distribution of the electron density in the molecule of the pyranylphosphonium salt to be established.

EXPERIMENTAL

Pyranyltriphenylphosphonium tetrafluoroborate. (Ib). A mixture of 3.2 g (0.01 mole) of 2, 6-diphenylpyrylium fluoroborate and 2.9 g (0.011 mole) of triphenylphosphine in 10 ml of dry nitromethane was carefully heated with stirring until the reactants had dissolved completely, and was then boiled for 0.5–1 min and treated in the hot with 40–50 ml of dry ethyl acetate. After 2–3 hr, the yellow crystalline product that had deposited was filtered off, washed with ether, and dried. Yield 5.7 g (98%), mp 152.0° C (from a mixture of nitromethane and ethyl acetate).

The yields, melting points, and analyses, of the phosphonium salts, including those obtained from thiapyrylium, benzopyrylium, and xanthylium salts are given in the table.

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