Chemistry of Heterocyclic Compounds, Vol. 43, No. 10, 2007

LETTERS TO THE EDITOR

FORMATION OF ADDUCTS OF PYRILIUM CATIONS WITH TRIETHYL PHOSPHITE

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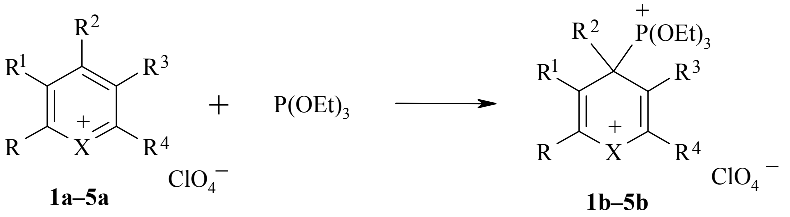
Keywords: pyrilium salts, triethyl phosphite, electron-acceptors, nucleophilic addition, UV, ^{1}H and ^{31}P NMR spectroscopy.

The physicochemical properties of σ-adducts of aromatic heterocyclic cations hold interest since study of the reversible rupture and formation of a σ-bond between a heteroelement and carbon is possible for these compounds [1]. In turn, such behavior is extremely important for understanding the mechanism of the Arbuzov rearrangement, in which $(R^1O)_3P^+{-}R^2$ salts are intermediates [2].

UV, ^{1}H NMR, and ^{31}P NMR spectroscopy in acetonitrile was used to study the reaction of a pyrilium or thiapyrilium salt with triethyl phosphite ($P(OEt)_3$).



1a–5a

1b–5b

1 $R = R^4 = Ph, R^1 = R^2 = R^3 = H$; **2** $R = R^4 = Ph, R^1 = R^2 = R^3 = H$; **3** $R = R^4 = Ph$,
$R^1 = R^3 = H, R^2 = Me$; **4** $R+R^1 = –CH=CH–CH=CH–, R^2 = R^3 = H, R^4 = Ph$;
5 $R+R^1 = –CH=CH–CH=CH–, R^2 = H, R^3+R^4 = –CH=CH–CH=CH–$; **1**,**4**,**5** X = O, **2**,**3** X = S

Pyrilium salts **1a-5a** are yellow-green in acetonitrile. Decoloration is noted upon the introduction of $P(OEt)_3$ to the pyrilium salt solutions studied, while the intensity of the absorption band with λ_{max} 395 nm decreases with increasing reagent concentration.

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The pyrilium-pyran transition to give a triethoxyphosphonium species was detected by ^{1}H and ^{31}P NMR spectroscopy. An sp^3-hybridized carbon atom appears upon the formation of the pyran adduct and there is a shift of the protons of the pyrilium or thiapyrilium ring from low field to high field. Spin-spin coupling is noted with the phosphorus atom, which indicates transition of the pyrilium salt to pyran with formation of a tetracoordinated phosphorus atom. The finding of an upfield shift for H-8 proton and coupling of this proton with ^{31}P unequivocally demonstrates the existence of pyran form **5b** rather than pyrilium salt form **5a**.

The ^{1}H and ^{31}P NMR spectra were taken on a Varian Unity-300 spectrometer at 300 and 121.5 MHz, respectively, in deuteroacetonitrile with TMS and triphenyl phosphate as the internal standards. The spectra were obtained by adding a twofold excess of reagent ($c = 2\cdot10^{-2}$ M) to a solution of the starting salt ($c = 10^{-2}$ M).

(2,6-Diphenyl-4H-pyran-4-yl)triethoxyphosphonium Perchlorate (1b). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.78-7.82 (4H, m, *o*-C_6H_5); 7.49-7.52 (6H, m, *m,p*-C_6H_5); 5.54 (2H, dd, $J_{H\text{-}P} = 3.9$, $J_{H\text{-}H} = 4.8$, H-β); 4.44 (1H, dt, $J_{H\text{-}P} = 21.7$, $J_{H\text{-}H} = 4.8$, H-γ); 4.58 (6H, m, CH_2); 1.45 (9H, m, CH_3). ^{31}P NMR spectrum, δ, ppm: 33,43 (m).

(2,6-Diphenyl-4H-thiapyran-4-yl)triethoxyphosphonium Perchlorate (2b). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.59-7.69 (4H, m, *o*-C_6H_5); 7.42-7.52 (6H, m, *m,p*-C_6H_5); 5.92 (2H, dd, $J_{H\text{-}H} = 6.4$, $J_{H\text{-}P} = 4.9$, H-β); 4.89 (1H, dt, $J_{H\text{-}H} = 6.4$, $J_{H\text{-}P} = 27.8$, H-γ); 4.60 (6H, m, CH_2); 1.47 (9H, m, CH_3). ^{31}P NMR spectrum, δ, ppm: 32.77 ppm (m).

(4-Methyl-2,6-diphenyl-4H-pyran)triethoxyphosphonium Perchlorate (3b). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.40-8.40 (10H, m, C_6H_5); 5.45 (2H, d, $J_{H\text{-}P} = 3.6$, H-β); 2.83 (3H, s, CH_3); 4.57 (6H, m, CH_2), 1.43 (9H, m, CH_3). ^{31}P NMR spectrum, δ, ppm: 34.34 (m).

(4H-Flaven-4-yl)triethoxyphosphonium Perchlorate (4b). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.20-7.90 (9H, m, Ar); 5.62 (1H, t, $J = 5.6$, H-β); 4.94 (1H, dd, $J_{H\text{-}P} = 5.6$, $J_{H\text{-}P} = 22.1$, H-γ); 4.47 (6H, m, CH_2); 1.38 (9H, m, CH_3). ^{31}P NMR spectrum, δ, ppm: 33.63 (m).

Only **5b** of all the systems studied could be isolated as a solid.

(9H-Xanthen-9-yl)triethoxyphosphonium Perchlorate (5b). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.2-7.6 (8H, m, Ar); 5.4 (1H, d, $J = 22.8$, H-γ); 4.31 (6H, m, CH_2); 1.27 (9H, m, CH_3). ^{31}P NMR spectrum, δ, ppm: 34.07 (m).

REFERENCES

1. A. A. Bumber, L. I. Kisarova, E. A. Arzumanyants, V. T. Abaev, and G. A. Palui, *Khim. Geterotsikl. Soedin.*, 1042 (1989). [*Chem. Heterocycl. Comp.,* **25**, 868 (1989)].
2. B. A. Arbuzov, *Z. Chem.*, **14**, No. 2, 41 (1974).