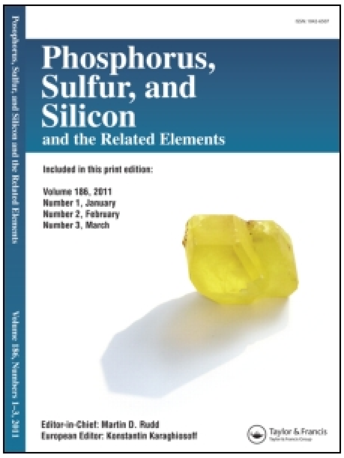


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

NEW CARBON-PHOSPHORUS BOND CONTAINING COMPOUND IN THE REACTION OF 2-ACETYLTHIOPHENE WITH PHOSPHORUS PENTACHLORIDE

Antonio Alivert[a]; Jorge Bujons[a]; Juan-Julio Bonet[a]
[a] Department of Organic Chemistry C.E.T.S., Institut Químic de Sarrià, Barcelona, Spain

To cite this Article Alivert, Antonio , Bujons, Jorge and Bonet, Juan-Julio(1990) 'NEW CARBON-PHOSPHORUS BOND CONTAINING COMPOUND IN THE REACTION OF 2-ACETYLTHIOPHENE WITH PHOSPHORUS PENTACHLORIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 54: 1, 205 — 207
To link to this Article: DOI: 10.1080/10426509008042139
URL: http://dx.doi.org/10.1080/10426509008042139

Phosphorus, Sulfur, and Silicon, 1990, Vol. 54, pp. 205–207
Reprints available directly from the publisher
Photocopying permitted by license only

Communication

NEW CARBON-PHOSPHORUS BOND CONTAINING COMPOUND IN THE REACTION OF 2-ACETYLTHIOPHENE WITH PHOSPHORUS PENTACHLORIDE

ANTONIO ALIVERT, JORGE BUJONS and JUAN-JULIO BONET
Department of Organic Chemistry
C.E.T.S. Institut Químic de Sarrià, 08017-Barcelona, Spain

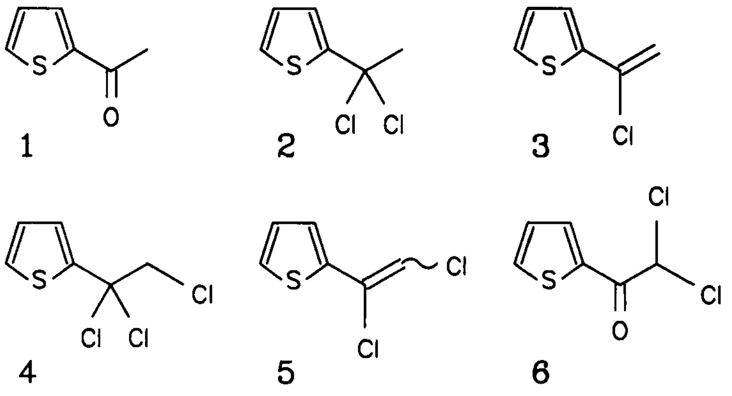
(Received January 19 1990)

The treatment of 2-acetylthiophene with phosphorus pentachloride led, besides other products reported in previous studies, to 2-(2-thienyl)-2-chloroethenephosphonic acid in 16% yield. This compound was transformed, in the course of purification attempts, into 2-(2-thienyl)-2-oxoethanephosphonic acid. Full spectroscopic data for both compounds are provided.

Key words: 2-Acetylthiophene, Carbon-Phosphorus Bond, Phosphonic Acids, Phosphorus Pentachloride, 2-(2-Thienyl)-2-chloroethenephosphonic Acid, 2-(2-Thienyl)-2-oxoethanephosphonic Acid.

RESULTS AND DISCUSSION

The treatment of 2-acetylthiophene (**1**) with phosphorus pentachloride was previously studied by F. F. Nord and co-workers.[1] They assumed that the reaction yields, after distillation of the crude reaction mixture, 1,1-dichloro-1-(2-thienyl)ethane (**2**) and 1-chloro-1-(2-thienyl)ethene (**3**).



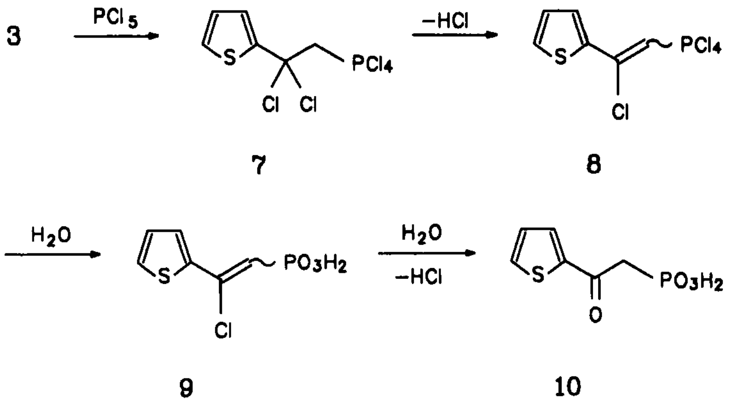
Scheme 1

In 1983, revising the work of Nord, J. Kagan and his team[2] applied this reaction to **1** as well as to acetophenone and other methylketones. In the case of **1**, the main products of the reaction were **2**, **3**, 1-(2-thienyl)-1,1,2-trichloroethane (**4**), E and Z isomers of 1,2-dichloro-1-(2-thienyl)ethene (**5**) and 2-(dichloroacetyl)thiophene (**6**), the *gem*-dihalide **2** being a minor component accounting only for 5% of the mixture. Distillation afforded the major components **3** and **5** (instead of **2**, as in Nord's results). A pathway, based on several chlorination and dehydrochlorination steps, was proposed to explain the formation of the products (e.g., $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5$).

Both papers don't mention the presence of compounds having a carbon-phosphorus bond. As we report now, a product of this kind has been found when, in connection with other work, we repeated the reactions between **1** and PCl_5.

During the aqueous work-up, the formation of 2-(2-thienyl)-2-chloroethenephosphonic acid (**9**) in 16% yield was observed. This compound was transformed, in the course of purification attempts, into 2-(2-thienyl)-2-oxoethanephosphonic acid (**10**). The other products isolated after distillation were essentially the same as those described by Kagan.

It is known that PCl_5 can add to double bonds.[3] As is shown in Scheme 2, an addition of PCl_5 to **3** could be the first step to **9** through a parallel route to the pathway cited above.



Scheme 2

The final hydrolytic step was previously observed by L. Maier[4] in the case of analogous phenyl compounds. In addition, this report provides spectroscopic data consistent with those showed by **9** and **10**.

EXPERIMENTAL

NMR spectra were taken on a Perkin-Elmer R-24 (^{1}H-NMR) and a Varian XL-200 (^{13}C-NMR and ^{31}P-NMR) spectrometers, using TMS or H_3PO_4 as standard. Mass spectra (MS) were recorded on a Hewlett-Packard 5330 A spectrometer. This instrument was connected to a Hewlett-Packard 5995 A chromatograph in the GC/MS experiments. IR and UV spectra were recorded on a Perkin-Elmer 683 and Hewlett-Packard 8450 A spectrophotometers. Elemental analyses were performed by Institut de Química Bio-Orgánica de Catalunya C.S.I.C. (Barcelona, Spain).

Reaction of 2-Acetylthiophene (1) with PCl_5. 90.40 g (0.717 mol) of **1** were added, with stirring, to 199.12 g (0.955 mol) of PCl_5 covered with 120 mL of dry benzene. Within 10 min a vigorous reaction began with evolution of HCl; the temperature rose to 50°C. When the reaction subsided and the temperature began to fall, the mixture was heated to 70°C for 2 h. The resulting clear reddish solution was allowed to cool and poured carefully over a mixture of 600 g of crushed ice and 200 mL of EtOEt.

At this point, the final system showed, besides the organic and aqueous layers, a third green syrupy phase with marked acidic character. The layers were separated and the aqueous one was extracted with EtOEt (3 × 200 mL). The combined ethereal extracts were washed with water and saturated $NaHCO_3$ solution, dried over $MgSO_4$ and concentrated. The resulting residue was distilled (3 torr) and three cuts (18.09 g bp 59–68°C, 13.07 g bp 69–75°C and 32.51 g bp 77–89°C) were obtained. All of them were mixtures of the same components at different rates but no pure products were isolated. The compounds were identified by ^{1}H-NMR ($CDCl_3$) and GC/MS analysis as Z-**5** (20%, ^{1}H-NMR: $\delta = 6.6$ (s, 1H, CH); MS: 182/180/178, $M^{+\cdot}$), E-**5** (11%, ^{1}H-NMR: $\delta = 6.3$ (s, 1H, CH); MS: 182/180/178, $M^{+\cdot}$), **3** (19%, ^{1}H-NMR: $\delta = 5.25$, 5.6 (2d, 2H, CH_2); MS: 146/144, $M^{+\cdot}$), and unreacted starting material **1** (5%).

The third layer separated during the hydrolysis of the crude reaction mixture, solidified after being repeatedly washed with benzene and EtOEt. The resulting deep-green crystalline material was identified as **9** (26.20 g, 16%). Recrystallization attempts from benzene led, with release of acidic vapors and in quantitative yield, to a new solid, yellowish, crystalline, and stable, identified as **10**. An analytical sample was obtained by several crystallizations from acetone.

The not previously reported compounds **9** and **10** showed the following data:

9: mp 100–105°C (dec); ^{1}H-NMR (d_6-acetone) $\delta = 6.45$ (d, 1H, $J_{HCP} = 7$ Hz, C═CH—P), 7.0, 7.5 (2m, 3H, arom), 9.45 (br, 2H, PO_3H_2); ^{31}P-NMR (d_6-DMSO) $\delta = 7.33$ (d, $J_{PCH} = 6.8$ Hz); ^{13}C-NMR (d_6-DMSO) $\delta = 116.99$ (dd, $J_{CP} = 188.8$ Hz, C═CH—P), 128.51, 128.69, 129.90, 136.83 (d, d, d, s, ring), 141.19 (sd, $J_{CCP} = 18.0$ Hz, C═C—P); IR (KBr): 3400–2500, 2400–2000, 1585, 1510, 1420, 1350, 1150, 1010, 940, 770, 725 cm^{-1}; UV (EtOH) λ_{max} (ε) = 204 (11100), 289 (12700); Anal. (quali): positive for S, P and Cl.

10: mp 156–157°C (acetone); ^{1}H-NMR (d_6-acetone) $\delta = 3.65$ (d, 2H, $J_{HCP} = 22$ Hz, CH_2-P), 7.2, 7.9 (2m, 3H, arom); 9.05 (br, 2H, PO_3H_2); ^{31}P-NMR (d_6-DMSO) $\delta = 14.78$ (t, $J_{PCH} = 22.0$ Hz); ^{13}C-NMR (d_6-DMSO) $\delta = 41.82$ (td, $J_{CP} = 122.2$ Hz, CH_2-P), 128.84, 135.14, 135.37, 144.36 (d, d, d, s, ring), 186.23 (sd, $J_{CCP} = 6.1$ Hz, C═O); MS *m/e* (%) = 206 ($M^{+\cdot}$, 7.7), 126 (15.0), 111 (100), 83 (13.2), 81 (13.3); IR (KBr): 3300–2500, 2400–2100, 3120, 3000, 2940, 1660, 1520, 1420, 1360, 1300, 1195, 1130, 1070, 1015, 760, 750 cm^{-1}; UV (EtOH) λ_{max} (ε) = 205 (3600), 263 (9400), 282 (7800) Anal. Calcd. for $C_6H_7O_4PS$: C: 34.96; H: 3.42. Found: C: 35.18; H: 3.40.

REFERENCES

1. a) H. Keskin, R. E. Miller and F. F. Nord, *J. Org. Chem.*, **16**, 199 (1951). b) A. Vaitiekunas and F. F. Nord, *J. Org. Chem.*, **19**, 902 (1954).
2. J. Kagan, S. K. Arora, M. Bryzgis, S. N. Dhawan, K. Reid, S. P. Singh and L. Tow, *J. Org. Chem.*, **48**, 703 (1983).
3. E. Bergmann and A. Bondi, *Chem. Ber.*, **66**, 278 (1933).
4. L. Maier, *Synth. Inorg. Metal-Org. Chem.*, **3**, 329 (1973).