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The first experimental evidence of the formation of betaines in the Wittig reaction

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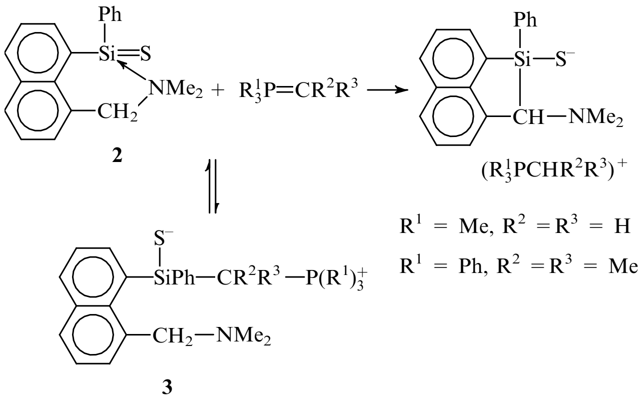
Direct experimental evidence has been obtained for the formation of betaines $R^1_3P^+–CR^2_2–CR^3_2–S^-$ in the reactions of phosphorus ylides with Michler ketone.

Reactions of compounds containing polar multiple C=X bonds (X = O, S, NR, and others) with phosphorus ylides (Wittig reaction) are fundamental reactions in organic chemistry. Many works have been devoted to studying the mechanism of this reaction (see reviews 1 and 2). The nature of the intermediates formed is the subject of continuous attention and extensive discussions in this area. The first data[3] suggesting that they are betaines $R^1_3P^+–CR^2R^3–CR^4R^5–X^-$ **1** were not confirmed.[1,2] Recent quantum-chemical calculations[4,5] indicating the possibility of formation of betaines **1** again evoked interest in this problem.[6] However, no experimental data to confirm the existence of this class of zwitterionic compounds were found in the literature.

We have recently shown that stable monomeric silanethione **2** reacts with phosphorus ylides to form intermediate betaine **3**[7] (Scheme 1).



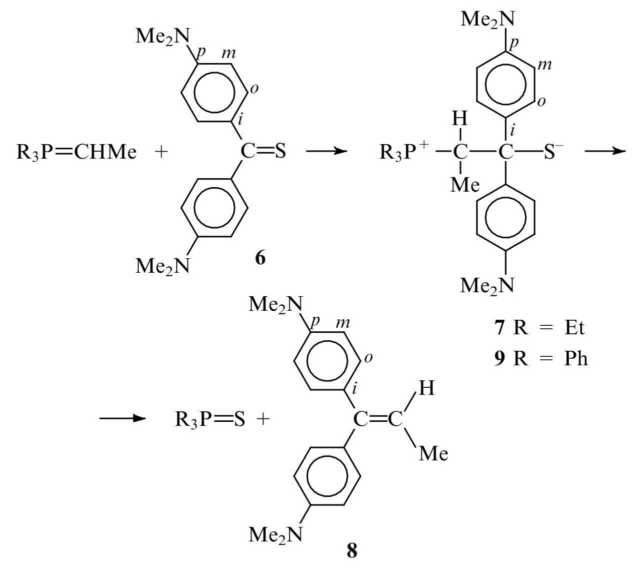
Scheme 1

Silicon organophosphorus betaines **4** analogous to betaines **1** (X = S) were obtained in the reactions of silanethione oligomers **5** with phosphorus ylides[8] (Scheme 2).

$$nR^1_3P{=}CR^2R^3 + \underset{\mathbf{5}}{(R^4R^5SiS)_n} \longrightarrow \underset{\mathbf{4}}{nR^1_3P^+{-}CR^2R^3{-}SiR^4R^5{-}S^-}$$

Scheme 2

Betaines **4** are rather stable, which allowed us to unambiguously solve their structure by direct X-ray diffraction analysis and to develop reliable methods for their identification in solution by multinuclear NMR spectroscopy data.[9] The results obtained made it possible to study in detail the reactions of thiocarbonyl compounds with phosphorus ylides (Scheme 3) and to obtain experimental evidence for the formation of betaines **7** and **9** as intermediates.



Scheme 3

The reaction of Michler thioketone **6**[†] (obtained according to ref. 10) with triethylethylidenephosphorane is carried out in a totally sealed vacuum system by the procedure described previously[11,12] at a residual pressure of 10^{-3} mmHg. When a solution of compound **6** (0.52 g, 1.83 mmol) in 20 ml of THF is mixed with $Et_3P{=}CHMe$ (0.26 g, 1.83 mmol), a violet-red solution changes its colour to red-green, and a finely crystalline red-brown precipitate is formed in *ca.* 3 min. In *ca.* 30 min the precipitate is filtered off and washed with THF on the filter, and the solvent is removed *in vacuo*. [$^2H_5$]Pyridine (1.2 ml) condenses on the precipitate, and the red-green solution formed is placed in an NMR tube, which is sealed off. According to the ^{1}H, ^{13}C and ^{31}P NMR spectral data the solution contains betaine **7**[†] (68%) and products of its decomposition (32%), $Et_3P{=}S$ and ethylene **8**.[†]

The specific feature of the NMR spectra of compound **7** is the fact that carbon atoms and protons of two aromatic rings are diastereotopic, which is caused by the presence of the chiral centre in the molecule, due to which the ^{1}H NMR spectra contain two Me_2N group singlets and two AA′XX′ systems from the benzene ring protons. The ^{13}C NMR spectra contain two *ipso*-carbon atom signals from the aromatic rings at 140.66 ppm and 143.78 ppm. The first signal exhibits distinct splitting at the ^{31}P nucleus equal to 13 Hz, and the second signal is only slightly broadened, because the corresponding spin-spin coupling constant with the ^{13}C nucleus is low.

The spectrum of stable organosilicon betaine Et_3P^+–CHMe–$SiPh_2$–S^- in this range has a similar form.[9] It also exhibits ^{13}C–^{31}P spin-spin coupling for only one of the *ipso*-carbon atoms of the phenyl rings, equal to 5.1 Hz. These data leave no doubts concerning the structure of compound **7**.

After measuring the NMR spectra, a solution of compound **7** in [$^2H_5$]pyridine was heated at 125 °C for 4 h, resulting in its complete decolorization. According to the NMR spectroscopic data, compound **7** completely transforms to a mixture of $Et_3P{=}S$ and compound **8**. Both of these compounds can be isolated in a quantitative yield calculated per initial compound consumed in the reaction.

Triphenylethylidenephosphorane $Ph_3P{=}CHMe$ slowly reacts with Michler ketone, but betaine **9** formed upon this reaction decomposes to final products $Ph_3P{=}S$ and **8** more rapidly than betaine **7**. Therefore, for the reaction of $Ph_3P{=}CHMe$ with Michler thioketone under conditions similar to those described above, we succeeded in observing only traces of compound **9** with a typical signal of chemical shift 27.33 ppm in the ^{31}P NMR spectrum. In *ca.* 3 h after the preparation of a solution in [$^2H_5$]pyridine the content of **9** in the reaction mixture was 9.4%.

Upon slight heating, compound **9** completely decomposes to $Ph_3P{=}S$ and **8**. The reactions of $Ph_3P{=}CH_2$ with thiobenzophenone and $Ph_3P{=}CHMe$ with Michler ketone occur more readily. In the latter case, when a solution of phosphorane in ether is added to a solution of ketone, a typical orange colour appears immediately, which can likely testify to the formation of betaine of the R_3P^+–CH_2–CR_2–O^- type. However, it very rapidly disappears, and only signals of olefin **8** and $Ph_3P{=}O$ can be observed in the spectra.

Unlike oligomeric thioaldehydes,[13] the trimer of thioacetone $(Me_2CS)_3$, according to our data, does not react even with such an active phosphorane as $Et_3P{=}CHMe$ at room

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[†] ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AM360 spectrometer ($SiMe_4$ was used as an internal standard for ^{1}H and ^{13}C NMR spectra and 85% H_3PO_4 in D_2O was used as an external standard for ^{31}P, δ (ppm), [$^2H_5$]pyridine).

6: ^{1}H NMR (C_6D_6): 2.44 (s, 12H, Me_2N), 6.44 (m, 4H, H_m), 8.22 (m, 4H, H_o); ^{13}C NMR (C_6D_6): 39.46 (Me_2N), 110.68 (C_m), 133.03 (C_o), 137.66 (C_i), 152.90 (C_p–N), 229.56 (C=S).

7: ^{1}H NMR: 1.02 (d.t, 9H, Me, $^3J_{HH}$ = 7.7 Hz, $^3J_{PH}$ = 16.8 Hz), 1.59 (dd, 3H, Me, $^3J_{HH}$ = 7.7, $^3J_{PH}$ = 19.2), 2.20 (dq, 1H, CH—P$^+$, $^3J_{HH}$ = 7.7, $^2J_{PH}$ = 12.3), 2.43–2.67 (m, 6H, CH_2–P$^+$, complicated multiplet, AB-part of $ABMX_3$ spectrum), 2.69, 2.73 (both s, each 6H, Me_2N), 6.70 (m, 2H, H_m), 8.34 (m, 2H, H_o), 8.55 (m, 2H, H_o); ^{13}C NMR: 7.73 (d, $Me_{Et_3P^+}$, $^2J_{PC}$ = 5.4), 14.65 (d, Me_{P^+CHMe}, $^2J_{PC}$ = 3.9), 17.13 (d, CH_2P^+, $^1J_{PC}$ = 51.6), 40.53, 40.70 (both s, Me_2N), 49.01 (d, CH$^+$, $^1J_{PC}$ = 67.6), 57.14 (s, Ar_2C–S^-, $^2J_{PC}$ = 0), 111.98, 111.99 (both s, C_m), 129.68, 130.65 (both s, C_o), 140.66 (d, C_i–P$^+$, $^3J_{PC}$ = 13), 143.78 (s, C_i, $^3J_{PC}$ = 0), 148.33, 148.47 (both s, C_p–N), ^{31}P NMR: +25.52 (s).

8: ^{1}H NMR: 1.85 (d, 3H, $^3J_{HH}$ = 7.0), 2.77, 2.81 (both s, each 6H, Me_2N), 6.09 (q, $^3J_{HH}$ 7.0, =CH), 6.74, 6.82 (both m, each 2H, H_m), 7.22, 7.38 (both m, each 2H, H_o), ^{13}C NMR: 15.95 ($Me_{MeCH=}$), 40.32, 40.33 (Me_2N), 112.58, 112.65 (C_m), 119.62 (CH=), 128.67, 131.31 (C_o), 128.82, 132.75 (C_i), 143.0 (C=), 149.90, 150.11 (C_p–N).

temperature in [$^2H_5$]pyridine and on heating to 100 °C (in an evacuated sealed tube).

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