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A NEUTRAL, ISOLABLE COVALENT ADDUCT BETWEEN PIPERIDINE AND A TROPONOIDAL PHOSPHONIUM SALT: A PECULIAR ACYLPHOSPHORANE

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Summary: The phosphonium salt obtained by P-methylation of 2-diphenylphosphinotropone with methyl iodide was found to undergo C-7 addition by piperidine, and loss of hydrogen iodide, to give an acylphosphorane which could be isolated; the regiospecificity of piperidine addition was proven by deuterium labeling at the troponoid ring.

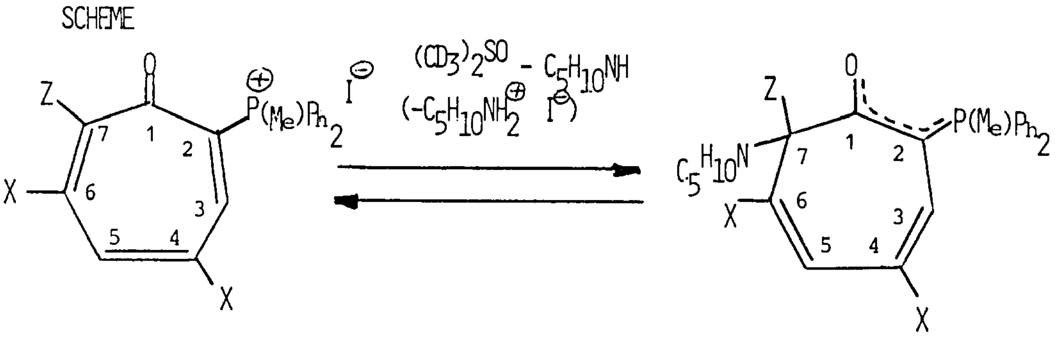
In our search for novel σ-adducts between troponoids and bases,[1] tropones bearing either a quaternary ammonium[2] or a sulphonium[3] substituent at C-2 gave particularly interesting results. We now report on the reaction of a related phosphonium salt with piperidine, leading to a peculiar acylphosphorane.

The reactions of either 2-iodo- or 2-chlorotropone with triphenylphosphine or tri-n-butylphosphine, in a variety of solvents, under nitrogen, only led to untractable tars. However, when 2-diphenylphosphinotropone[4] (0.2 g, 0.7 mmol) in dry ethyl ether (10 ml), under nitrogen, was added of methyl iodide (0.215 g, 1.5 mmol), an orange-brown powder immediately precipitated, which proved to be the desired quaternary phosphonium salt **1a**[†] (0.28 g, 97 %). Mp 98-101°C; uv, $\lambda_{max}^{(CH_3)_2SO}$ 335, 311, 295 nm; ^{1}H nmr, δ[‡] ($(CD_3)_2SO$) 8-7 (15H,m), 3.0 (3H, d, ^2J(PCH) = 13.8 Hz, CH_3); ^{13}C nmr, [§]δ[‡] ($(CD_3)_2SO$) 184.8 (d, ^3J(PCC) = 6.0 Hz, C = O), 120.8 (d, ^1J(PC) = 89.6 Hz, C-2), 8.9 (d, ^1J(PC) = 57.4, CH_3), while the signals for the other carbons were difficult to assign.

1b[†] Was prepared analogously, in a comparable yield, from 2-diphenylphosphino [4,6-$^2H_2$]tropone.[4] ^{1}H nmr, δ[‡] ($(CD_3)_2SO$) 8-7 (13H, m), 3.0 (3H, d, ^2J(PCH) = 13.8 Hz, CH_3).

On addition of a few drops of piperidine to a ca. 0.32 M solution of **1a** in dry $(CD_3)_2SO$,under nitrogen, both the ^{1}H nmr signals and the uv absorption bands due to **1a** immediately disappeared while the colour of the mixture turned to deep-green and the following signals attributable to the acylphosphorane **2a** (Scheme) appeared. Uv, $\lambda_{max}^{(CH_3)_2SO}$ 312 nm; ^{1}H nmr, δ[‡] ($(CD_3)_2SO$) 7.6 (10H, m, phenyl protons), 6.1 (1H, m, $J_{5,6}$ = 9.0 Hz, ^5J(PCCCCH)= 1.5 Hz, H-5), 5.7 (2H, m, in which a doublet with ^3J(PCCH) = 11.7 Hz could be seen, H-3 and H-4), 5.1 (1H, dd, $J_{6,5}$ = 9.0 Hz and $J_{6,7}$ = 6.0 Hz, H-6), 2.6 (3H, d, ^2J(PCH)= 14.0 Hz, CH_3); ^{13}C nmr, [§]δ[‡]($(CD_3)_2SO$) 177.5 (d, ^3J(PCC) = 6.0 Hz, C = O), 133 and 129 (series of signals for o-, m-, and p-C of the phenyl groups), 126.7 (s, C-5), 125.4 (d, ^{1}J(PC) = 15.0 Hz, possibly phenyl C-P), 118.6 (s, C-6), 115.8 (d, ^{3}J(PCCC) = 16.4 Hz, C-4), 77.7 (d, ^{1}J(PC) = 104.5 Hz, C-2), 74.9 (d, ^{2}J(PCC) = 10.4 Hz, C-3), 53.3 (s, C-7), 10.4 (d, ^{1}J(PC) = 62.9, CH_3).

SCHEME



1a X = Z = H

1b X = D (and partial deuteriation at C-7)

2a X = Z = H

2b X = D (and partial deuteriation at C-7)

Addition of piperidine, following the above lines, to a sample of 1b obtained from 2-chloro-[4,6-$^{2}H_2$]tropone, partially (ca. 20%) deuteriated at C-7, ^{4} gave 2b. Consistently with the presence of a deuterium at both C-6 and C-4 in 2b, no ^{1}H nmr signal appeared at δ 5.1 and a simple doublet, with ^{3}J(PCCH) = 11.7 Hz, appeared at δ 5.7, while all other ^{1}H nmr signals were quite similar to those reported for 2a. Furthermore, in accordance with such a deuteriation pattern, the ^{13}C nmr spectrum for 2b revealed only extremely weak, broadened signals at both δ 118.6 and 115.8, whereas all other ^{13}C nmr signals were similar to those reported for 2a.[⌖]

The structural assignement was further confirmed by isolating both 2a and 2b and by running their ^{1}H nmr spectra in hexadeuteriobenzene in the absence of free piperidine in excess. This allowed us to identify the signals for both H-7 and the bound-piperidine protons which were buried by the signals due to the free-piperidine protons in the spectra reported above for 2a and 2b. Thus, always working under nitrogen, a solution of 2a in $(CD_3)_2SO$ was added of chloroform, washed with water, and the green-coloured organic layer was separated, dried over sodium sulphate, and evaporated at reduced pressure. By taking great care of always having free piperidine present in traces (which was ensured by adding piperidine during the work-up), dark-green, solid 2a could be isolated. ^{1}H nmr, δ[‡] (C_6D_6) 7.0 (10H, m, phenyl protons), 6.4 (1H, m, $J_{5,6}$ = 9.3 Hz, ^{5}J(PCCCCH) = 1.5

Hz, H-5), 5.9 (2H, m, in which a doublet with $^{3}J(\mathrm{PCCH})$ = 12.0 Hz could be seen, H-3 and H-4), 5.7 (1H, dd, $J_{6,5}$ = 9.3 Hz and $J_{6,7}$ = 6.0 Hz, H-6), 3.4 (1H, d, $J_{7,6}$ = 6.0 Hz, H-7), 3.0 (4H, m, N-CH_2-), 2.0 (3H, d, $^{2}J(\mathrm{PCH})$ = 13.5 Hz, CH_3), 1.4 (6H, CH_2).

Similar experiments were carried out with **2b**. In comparison with the ^{1}H nmr spectrum of **2a**, the ^{1}H nmr spectrum of **2b** in C_6D_6 lacked the δ 5.77 signal, while the signals at δ 6.4, δ 5.9, and δ 3.4 became, respectively, a doublet with $^{5}J(\mathrm{PCCCCH})$ = 1.5 Hz, a doublet with $^{3}J(\mathrm{PCCH})$ = 12.0 Hz, and a singlet. All other signals were quite similar to those reported above for **2a**. Clearly this is in full accordance with the deuteriation pattern proposed for **2b**.

It is interesting now to consider the peculiar phosphorane **2** in the perpective of the long, continuing debate about the electronic structure of phosphoranes. To this concern, we have found that on going from **1a** to **2a** in $(CD_3)_2SO$ there is a high-field shift of the ^{31}P resonance by 9.6 ppm, which indicates less positive charge at phosphorus with **2a** than with **1a**. This observation, together with the facts that on going from **1a** to **2a** there is both a high-field shift of the ^{13}C-2 resonance and an increase in the P — C-2 coupling constant, point to an extended conjugation from oxygen to phosphorus, as indicated by **2** in the Scheme. This is in qualitative agreement with the conclusions drawn for typical phosphoranes and acylphosphoranes from both spectral data[5a] and calculations.[5b,◇]

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FOOTNOTES

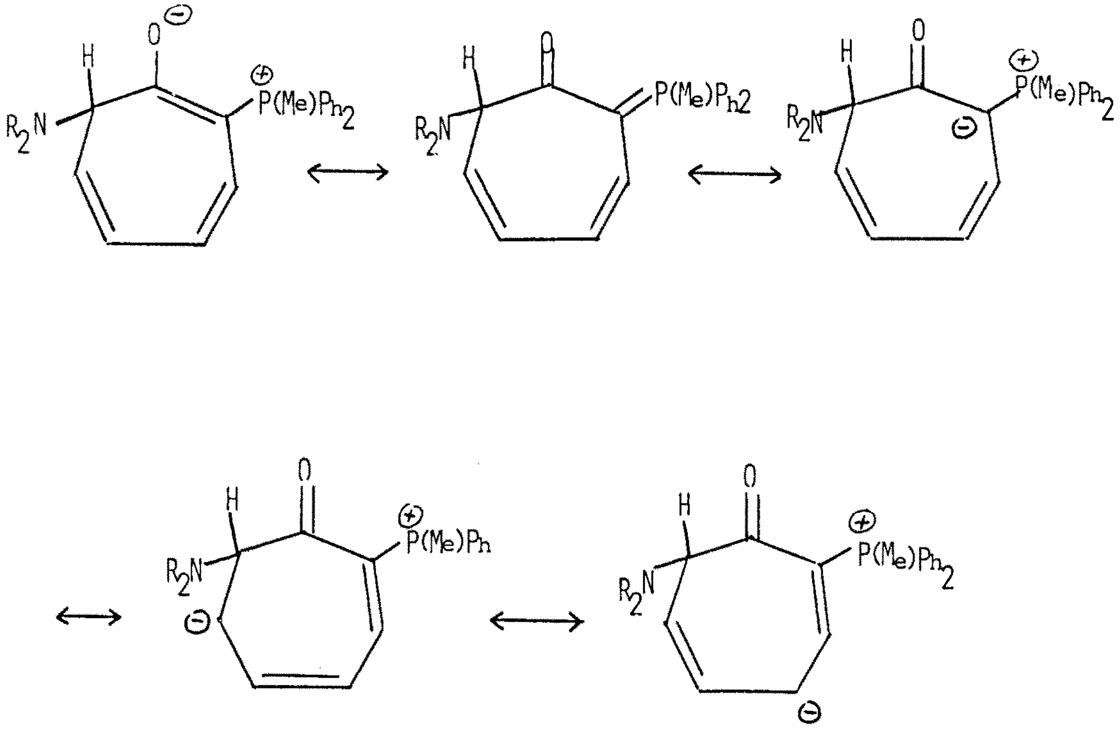
[†] Satisfactory elemental analyses were obtained.

[‡] In ppm, with respect to internal $SiMe_4$ as reference (100 MHz for ^{1}H and 25 MHz for ^{13}C).

[§] Fully proton decoupled spectrum.

[✧] Neither broadening nor weakening of the C-7 signal could be appreciated, which is compatible with the low extent of deuteriation at this carbon (see also the accompanying paper[4]).

[◇] Unfortunately, since with both **1a** and **1b** most nmr signals were superimposed with one another, we do not have indications about the extent of the shielding for corresponding hydrogens and carbons, on going from **1** to **2**. Therefore, we lack informations about the extent of negative charge dispersal on the seven-membered ring with **2**. In view of previous experience with related compounds,[1] it might well be, however, that the entire seven-membered ring enters the conjugation, as is shown by the following canonical forms for **2a**.



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