Tetraphenylphosphonium Nitrites

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Three different forms of tetraphenylphosphonium nitrite have been found to exist: an ionic nitrite, a co-ordinated nitrite, and a molecular species.

During investigations into the KF/$Ph_4P^+Br^-$ fluorination system,[1] it was found that the phosphonium catalyst can normally be recovered quantitatively, with no loss in catalytic activity. However, we have since found that for higher temperature (130—150 °C) fluorodenitration reactions, a new phosphorus species can be obtained, which has only slight catalytic activity. We present here evidence that this compound (**1**) is an isomer of tetraphenylphosphonium nitrite, in which the P^+ centre is co-ordinated to one of the oxygen atoms of the nitrite ion.

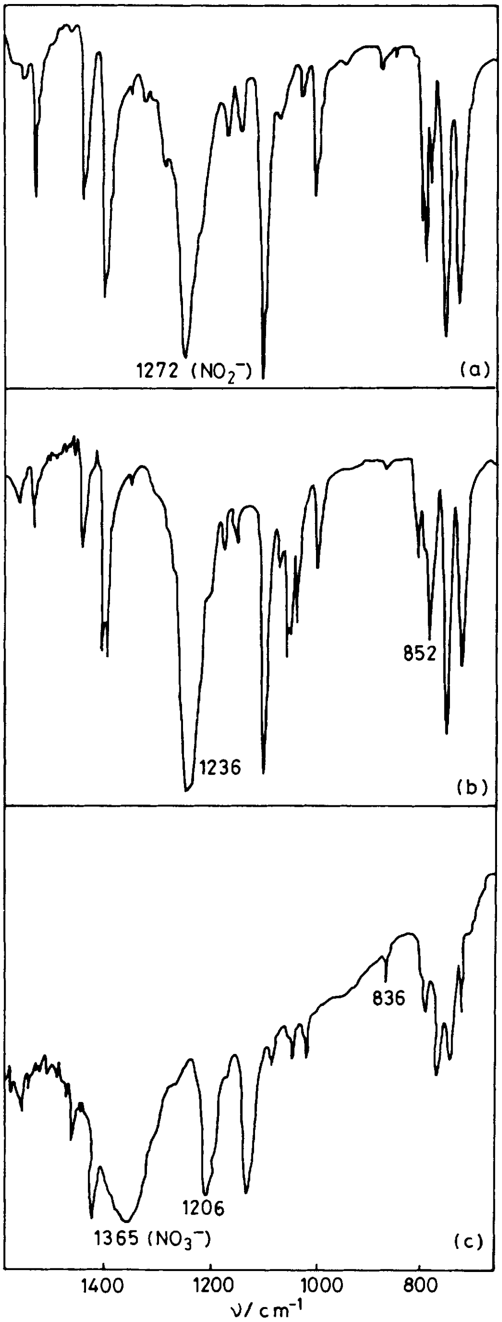


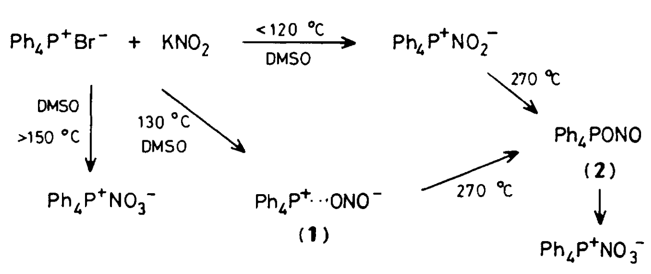
Figure 1. I.r. spectra (1600—625 cm^{-1}) of (a) $Ph_4P^+NO_2^-$, (b) $Ph_4P^+ \cdots ONO$, and (c) Ph_4PONO.

In a typical reaction, a mixture of 4-chloro-3-nitro-α,α,α-trifluorotoluene and $Ph_4P^+Br^-$ (molar ratio 1 : 1) was heated to 130 °C in dimethyl sulphoxide (DMSO) in the presence of KF (2 mol. equiv.) After completion of the reaction, the potassium and phosphonium salts were precipitated by the addition of acetone and ether. The phosphorus species was then recrystallised from chloroform to give (**1**), m.p. 296—297 °C, in yields of up to 98%. Compound (**1**) can also be prepared from KNO_2 and $Ph_4P^+Br^-$ in DMSO at 130—150 °C. Higher temperatures give only $Ph_4P^+NO_3^-$, whereas lower temperatures gave $Ph_4P^+NO_2^-$ containing a normal ionic NO_2^- ion. The latter can also be prepared by ion exchange of $Ph_4P^+Cl^-$ with aqueous $NaNO_2$ (recrystallised from $CHCl_3$–ether, m.p. 224.5—225 °C). Determination of nitrite in (**1**) or $Ph_4P^+NO_2^-$ by titration[2] gave 96 and 98% of the expected values, respectively. The ^{13}C and ^{31}P n.m.r. spectra of the two materials are very similar (see Table 1),† the most interesting data being obtained from their i.r. spectra (Figure 1). The i.r. spectrum of $Ph_4P^+NO_2^-$ (Figure 1a)

Table 1. ^{13}C and ^{31}P N.m.r. chemical shifts and coupling constants.[a]

Compound	$\delta(^{13}C), J_{CP}$/Hz	$\delta(^{31}P)^b$
Ph_4PONO	117.48, 89.1; 130.89, 12.2; 134.41, 9.8; 135.90, 3.7.	23.15 22.41^c
$Ph_4P^+NO_2^-$	117.31, 89.1; 130.67, 12.2; 134.24, 9.8; 135.70, 2.4.	22.95 22.24^c

[a] Spectra were run in $CDCl_3$ solution unless stated otherwise. [b] P.p.m. with respect to 85% H_3PO_4. [c] CD_3CN solution.



Scheme 1

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† ^{31}P N.m.r. chemical shifts of phosphonium cations are normally quite insensitive to the type of and interaction with the anion (*e.g.* the $\delta(^{31}P)$ range for the compounds $Ph_4P^+Br^-$, $Ph_4P^+HF_2^-$, and $Ph_4P^+ \cdots F^-$ is only 0—8 p.p.m.[5]). It should also be noted that both forms of the compound can be recovered unchanged from solution, suggesting that they maintain their individual structures in the homogeneous phase.

consists of the spectra of the NO_2^- anion and the tetrahedral Ph_4P^+ cation.[3] In the i.r. spectrum of (**1**) (Figure 1b), the NO_2^- bands are not observed, but bands appear at 1236 and 852 cm^{-1}, which we believe to arise from co-ordination of the NO_2^- ion to the cation. Additional bands are also present at *ca.* 1050 cm^{-1}, which are consistent with distortion of the cation[3,4] caused by interaction with NO_2^-. Similar bands were found in $Ph_4P^+ \cdots F^-$,[5] which contains a strong $P^+ \cdots F^-$ interaction, resulting in distortion of the tetrahedral geometry around the phosphorus.

Compound (**1**) and $Ph_4P^+NO_2^-$ give rise to the same gas phase species when heated to 270 °C in the presence of air, presumably tetraphenylnitritophosphorane (**2**). In the i.r. spectrum of this material (Figure 1c) the bands at 1270 and 848 cm^{-1} ($Ph_4P^+NO_2^-$), or at 1236 and 852 cm^{-1} (**1**), are replaced by bands at 1206 and 836 cm^{-1}. The peak at 1365 cm^{-1} is due to $Ph_4P^+NO_3^-$ which formed on the windows of the cell, and was found to be identical to an authentic sample. No Ph_3PO was observed.

The reactions of (**1**) with primary alkyl halides were also investigated and compared to the reactions of $AgNO_2$[6] which contains an $Ag \cdots O$ interaction. Under heterogeneous conditions $AgNO_2$ reacts with 1-iodobutane to give a 6:1 mixture of 1-nitrobutane and n-butyl nitrite. Compound (**1**) gives a similar mixture, ratio 5:1, whereas $Ph_4P^+NO_2^-$ gives an approximately 1:1 mixture. Similar results were obtained using 1-bromobutane and 1-iodoheptane.

In summary, we have shown that tetraphenylphosphonium nitrite can exist in three forms: as a simple ion pair, as an ionic form which contains a significant $P^+ \cdots ONO^-$ interaction, both of which give rise to the covalent phosphorane, a reactive species giving rise to tetraphenylphosphonium nitrate on condensation in the presence of air. These reactions are summarised in Scheme 1.

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