Base-induced Rearrangement of Tetraalkyl(diphenylphosphinoyl)hydrazinium Salts to Phosphinoyl Aminals; Possible Relevance to the Photochemical Rearrangement of Trialkylammonio(diphenylphosphinoyl)imides

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The phosphinoylhydrazinium salt $Ph_2P(O)N(Me)\overset{+}{N}Me_3\ \bar{I}$ **8** has been prepared by methylation of $Ph_2P(O)\bar{N}\text{–}\overset{+}{N}Me_3$ **1**. It readily forms the phosphinoyl aminal $Ph_2P(O)N(Me)CH_2NMe_2$ **10** on treatment with Bu^{t}OK at room temperature, presumably by [1,2] sigmatropic rearrangement of the ylide $Ph_2P(O)N(Me)\overset{+}{N}(\bar{C}H_2)Me_2$ **9**. Replacing just one or two Me groups by Et at the ammonium centre of **8** has a rather small effect; the principal product is still a methylene aminal, although a small amount of the ethylidene aminal is also formed. The possible relevance of this [1,2] sigmatropic rearrangement to the mechanism of the photochemical rearrangement of trialkylammonio-*N*-diphenylphosphinoylimides (phosphinic aminimides) is considered.

Photolysis of the phosphinic aminimide **1**[1] in methanol affords largely the phosphinic amide **3** (>90%).[2,3] Given the formation of a nitrene adduct, albeit in modest yield, when the aminimide is photolysed in dimethyl sulphoxide[1,3] or dimethyl sulphide,[4] it would be easy to assume that the amide is also nitrene derived. A recent study found, however, that most of the amide is not derived directly from **1** *via* the nitrene; rather is it a secondary product, resulting from decomposition of the phosphinoyl aminal **2** formed from aminimide **1** by an unexpected photochemical rearrangement.[3] Several mechanisms were considered for the reaction, one of the most straightforward being a [1,2] sigmatropic rearrangement of the ylide **4** derived from the aminimide by a photochemical tautomerisation. Experiments intended to clarify the picture did not provide unambiguous evidence.[3] We have therefore tried to generate a model of **4**, the tautomeric form of the aminimide, to see if it does undergo ready rearrangement.[5]

$Ph_2P(O)\bar{N}\text{–}\overset{+}{N}Me_3$ **1**

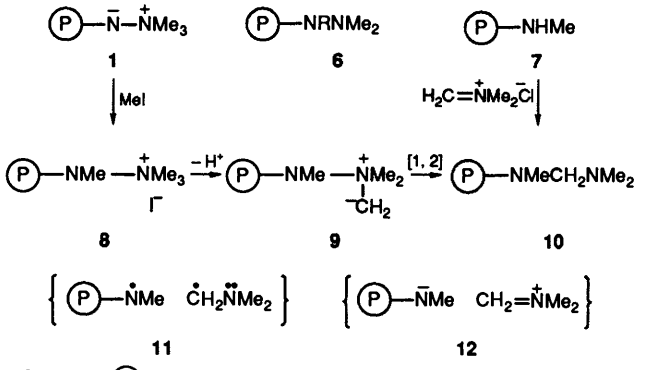
$Ph_2P(O)NHCH_2NMe_2$ **2** $\qquad$ $Ph_2P(O)NH_2$ **3**

$Ph_2P(O)NH\text{–}\overset{+}{N}Me_2$ ($\bar{C}H_2$) **4** $\qquad$ $Ph_2P(O)NH\text{–}\overset{+}{N}Me_2$ (CH_3) **5**

Results and Discussion

In principle, the ylide **4** could be formed from the salt **5**, by removal of a proton from a Me group, but in practise deprotonation will occur at the amide NH, giving just the aminimide **1**; no significant amount of ylide **4** will be formed. The most one can realistically aim for is a reasonable model for ylide **4**. An attempt was therefore made to prepare the tetramethylhydrazinium salt **8**, with a view to generating ylide **9**, the *N*-methyl analogue of **4**.

The trimethylhydrazide **6** (R = Me) was prepared from the dimethyl compound **6** (R = H) using NaH and MeI, but even under forcing conditions it could not be quaternised with methyl iodide. The aminimide **1**, however, did react slowly with MeI (4 mol equiv., no solvent) on heating (70 °C, 17 h), and gave



Scheme 1. [(P) = $Ph_2P(O)$].

the required hydrazinium salt **8**. The trimethylhydrazide **6** (R = Me) was a by-product, presumably as a result of demethylation of the hydrazinium salt **8** by iodide ion. That being so, it is not surprising that our attempts to quaternise **6** (R = Me) proved unsuccessful.

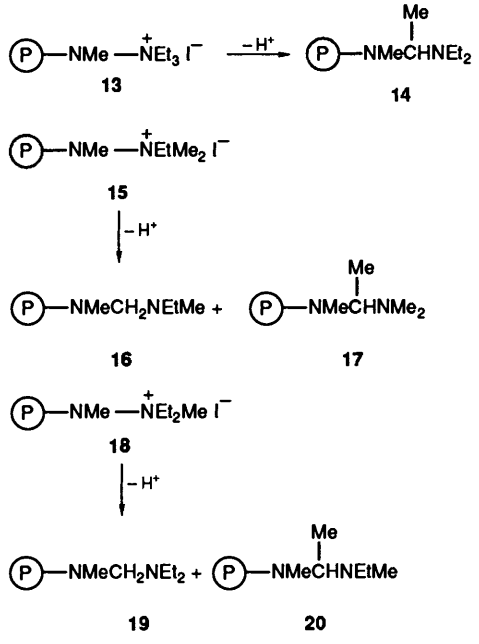
The hydrazinium salt **8** reacted rapidly (2 min at room temperature) with NaOMe in MeOH, but not by rearrangement: the product was the phosphinate $Ph_2P(O)OMe$ [δ_P(MeOH) 34.5], resulting from nucleophilic attack of methoxide at phosphorus and cleavage of the P–N bond. Phosphinic amides are known to be very susceptible to acid-catalysed solvolysis,[6] but it is unusual for them to react readily in the absence of acid. In the case of salt **8** the displaced group will be an aminimine ($Me\bar{N}\text{–}\overset{+}{N}Me_3$) rather than a simple amine anion ($Me\bar{N}R$), and the negative charge will be stabilised. This, it seems, is enough to make the P–N bond labile, even without acid to protonate the N atom.

To minimise nucleophilic attack by the base, the hydrazinium salt was stirred with tetrahydrofuran (THF) and the suspension was treated with potassium t-butoxide (2 mol equiv.). The salt dissolved and reacted over 0.5 h, and the product was now formed without cleavage of the P–N bond [δ_P(THF) 26.0]. Although of rather limited stability, the product was isolated in an analytically pure state and was found to have spectroscopic characteristics indicative of the group $MeNCH_2NMe_2$ attached to a phosphinoyl centre, *viz.* $\delta_H(CDCl_3)$ 3.50 (2 H, d, J_{PH} 7 Hz), 2.67 (3 H, d, J_{PH} 10.5 Hz) and 2.17 (6 H, s); *m/z* (EI) 288 (M^+, 2%), 87 ($Me\overset{+}{N}CH_2NMe_2$, 85) and 58 ($CH_2=\overset{+}{N}Me_2$, 100); *m/z*

(FAB) 289 ($M^+ + 1$, 46%) and 244 ($M^+ - NMe_2$, 100). This evidence clearly points to the phosphinoyl aminal structure **10**. For confirmation, an authentic sample of compound **10** was prepared by alkylation of the phosphinic amide **7** with $H_2C{=}\overset{+}{N}Me_2\ \bar{Cl}$; this was found to be identical with the product formed by the hydrazinium salt.

As regards the mechanism of reaction, the phosphinoyl aminal is formally derived from the hydrazinium salt by [1,2] sigmatropic rearrangement of the ylide **9**. Such a rearrangement is not expected to be concerted;[7] a stepwise mechanism is likely, with either a radical pair **11** or an ion pair **12** as the reaction intermediate. For the Stevens rearrangement,[8] which differs only in the nature of the group that migrates from nitrogen to carbon, an ion-pair mechanism was at one time favoured.[9] However, with the observation of CIDNP signals in many cases,[10] a radical pair[11] has now become generally accepted.[10] No CIDNP signals were seen when the rearrangement of the phosphinoylhydrazinium salt was examined by ^1H NMR spectroscopy, and it could be that the stability of a phosphinamide anion makes formation of the ion-pair intermediate **12** particularly favourable in this case.

To learn more about the rearrangement of the hydrazinium salt, the investigation was extended to homologues of **8** containing one, two or three Et groups in place of Me groups. The salts **13**, **15** and **18** were prepared from the corresponding aminimides,[3] by heating with MeI, and their reactions with Bu^{t}OK were examined in THF.

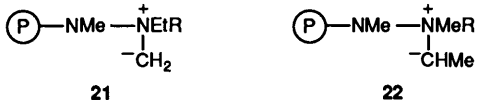


Scheme 2. [Ⓟ = $Ph_2P(O)$].

The triethylammonium compound **13** gave a single product [δ_P(THF) 25.4] which was isolated and found to have a ^1H NMR spectrum consistent with the ethylidene aminal structure **14**, in particular $\delta_H(CDCl_3)$ 4.22 (1 H, dq, $J_{PH} \sim J_{HH} \sim 6.5$ Hz) and 1.35 (3 H, d, J_{HH} 6.5 Hz) for the ethylidene group and 2.51 (3 H, d, J_{PH} 10.5 Hz) for the amide Me group. The product could not be further characterised because of the ease with which it was degraded to the phosphinic amide **7**. That an ethylidene aminal like **14** should be less stable than a methylene aminal like **10** is not really surprising (*cf.* discussion in ref. 3).

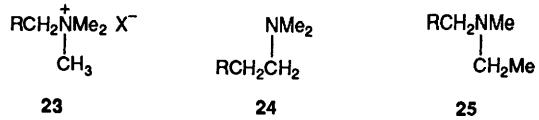
The 'mixed' hydrazinium salts **15** and **18** can in principle form two products, a methylene aminal **16** or **19** and an ethylidene aminal **17** or **20**, depending on whether a Me or an Et group participates in the rearrangement. In both cases the isolated product was found to be an unequal mixture of two compounds having similar ^{31}P NMR chemical shifts, $\delta_P(CDCl_3)$ 29.6 (major) and 28.4 (minor). The ^1H NMR spectra (300 MHz) of the product mixtures were inevitably quite complex, but by comparison with the spectra of the aminals **10** and **14** it was possible to assign all the important peaks to one or other of the possible rearrangement products (Table 1). In each case the methylene aminal was seen to be much more abundant than the ethylidene aminal, the measured ratio being 10:1 for substrate **15**, 9:1 for **18**. Provided the spectra were recorded as soon as the products were dissolved in $CDCl_3$, decomposition [to $Ph_2P(O)NHMe$] was not extensive (<3% with substrate **15**; ~7% with **18**). This decomposition will, however, cause a disproportionate loss of the more unstable ethylidene aminal, which in any case is substantially the minor product. The measured ratios almost certainly understate the proportion of the ethylidene aminal actually formed, and product ratios of *ca.* 8:1 for **15** and 6:1 for **18** seem likely.

A preference for methylene aminal formation with the 'mixed' hydrazinium salts is not what would be expected based solely on the relative stabilities of the alternative radical-pair (or ion-pair) intermediates; alkylation of the electron deficient centre should enhance the stability of $MeCHNMeR^{\bullet(+)}$ relative to $CH_2NEtR^{\bullet(+)}$ (R = Me or Et) and so assist the formation of the ethylidene aminal. However, the ethylidene aminal can only be formed when the species that undergoes rearrangement is the ethylidene ylide. If ylide formation is fast and reversible, the final product ratio will depend on the equilibrium between the alternative ylides as well as the rates at which they rearrange. Alkylation will destabilise the ethylidene ylide **22** relative to the methylene ylide **21** (R = Me or Et). Our results suggest that this outweighs



the beneficial effect of alkylation on ylide rearrangement, so that the ethylidene aminal is formed less readily than the methylene aminal and is only a minor product.* Why the proportions of the ethylidene aminal in the product should be quite similar for the two 'mixed' hydrazinium salts, in spite of the fact that the ethyl (CH_2):methyl proton ratio is 4/3 in substrate **18** but only 1/3 in **15**, is not clear.

Comparison of the hydrazinium salt reactions with the Stevens rearrangement is hampered by the fact that most ammonium salts containing only simple alkyl groups undergo Hofmann elimination with base rather than rearrangement. Generalisations are difficult, as illustrated by the behaviour of the salts **23**. When R = Bu^t the major product is amine **24**, derived from the more stable (less substituted) methylene ylide, with migration of the more substituted alkyl group.[8a] When R = Ph_3C the major product is again compound **24**,[12] even though in this case the methylene ylide must surely be the less stable [alternative ylide stabilised by Ph_3C group (−I effect)].



* If ylide formation were rate limiting (or fast but irreversible) then, of course, the final outcome of the reaction would be determined only by the relative ease of formation of the ethylidene and methylene ylides.

Table 1. Selected ^{1}H NMR data ($CDCl_3$) for rearrangement products.

	δ(PNCH_2N, 2 H, d, J_{PH} 7 Hz)	δ(PNCHMeN, 1 H, dq, $J_{PH} \sim J_{HH} \sim$ 6.5 Hz and 3 H, d, J_{HH} 6.5 Hz)	δ(PNMe, 3 H, d, J_{PH} 10.5 Hz)[a]	δ(NMe_2 or NMeEt, 6 H or 3 H, s)
Ⓟ N(Me)CH_2NMe_2 **10**	3.50	—	2.67	2.17 (6 H)
Ⓟ N(Me)CH_2NMeEt **16**	3.62	—	2.69	2.20 (3 H)
Ⓟ N(Me)CH(Me)NMe_2 **17**	—	3.69 and 1.35	2.56	2.26 (6 H)
Ⓟ N(Me)CH_2NEt_2 **19**	3.70	—	2.67	—
Ⓟ N(Me)CH(Me)NMeEt **20**	—	3.97 and 1.35	2.54	2.25 (3 H)
Ⓟ N(Me)CH(Me)NEt_2 **14**	—	4.22 and 1.35	2.51	—

[a] In the decomposition product $Ph_2P(O)NHMe$: 2.67 (3 H, dd, J_{PH} 12.5 and J_{HH} 6 Hz).

Finally, when R = menthyl, the major product is amine **25**, formed *via* the more stable (less substituted) ylide, but with migration of the less substituted alkyl group.[13]

A common feature of these Stevens rearrangements is the need for a very strong base (BuLi, KNH_2) or a high temperature (170 °C with aqueous NaOH).[8a,12,13] The phosphinoylhydrazinium salts rearrange much more easily. They have no particular advantage in ylide formation, so it must be that the ylide rearrangement is unusually favourable – presumably because the phosphinamide radical or anion in the intermediate is unusually stable. The facility of the ylide rearrangement is important; were it otherwise, the sigmatropic pathway for the aminimide photochemical rearrangement would not be tenable.

From the relative amounts of methylene and ethylidene aminal formed in the reactions of the 'mixed' hydrazinium salts **15** and **18** it is clear that there is a fairly strong preference for the involvement of Me rather than Et in the rearrangement. As a consequence, replacing just one or two Me groups by Et has a rather small effect on the outcome of reaction. Corresponding changes to the substrate in the aminimide photochemical reactions had a relatively dramatic effect, reducing the yield of the methylene aminal from 70% for the $\overset{+}{N}Me_3$ compound to 35% for $\overset{+}{N}Me_2Et$ and just 13% for $\overset{+}{N}MeEt_2$.[3,*] That being so, it might seem that the two rearrangements cannot be mechanistically related. However, if the aminimides are to form the aminal products by a [1,2] sigmatropic rearrangement, there must first be a photochemical proton transfer to generate the tautomeric ylide. We do not know how this would occur, or what discrimination it would show between Me and Et as the source of the proton, but it will inevitably influence the course of the reaction and the relative yields of the methylene and ethylidene aminals. The observed differences between the rearrangements of the 'mixed' aminimides and the hydrazinium salts might well arise in the initial stage of the reaction and not in the rearrangement step itself.

Experimental

Most instrumentation was as previously described.[3] ^{1}H NMR spectra were recorded with a Varian EM 390 (90 MHz) or Bruker AM-300 (300 MHz) spectrometer, and ^{31}P NMR spectra with a JEOL JNM-FX60 (24.3 MHz) or Bruker AM-300 (121.5 MHz) (positive chemical shifts downfield from external 85% H_3PO_4). Tetrahydrofuran (THF) was dried by distillation from $LiAlH_4$ and potassium t-butoxide was purified by vacuum sublimation. Ether refers to diethyl ether. Trialkylammonio-*N*-diphenylphosphinoylimides (aminimides) were as previously described.[3] *N*-Methyldiphenylphosphinic amide was prepared from diphenylphosphinic chloride and anhydrous methylamine in CH_2Cl_2 (95% yield), m.p. 116–117.5 °C (from CH_2Cl_2–ether) (lit.,[6b] 112–114 °C); *m/z* 231 (M^+, 45%).

1,1,2-*Trimethyl*-2-*diphenylphosphinoylhydrazine* **6** (R = Me).—Sodium hydride (0.55 g, 23 mmol) was added to a stirred solution of 1,1-dimethyl-2-diphenylphosphinoylhydrazine[1] (2.0 g, 7.7 mmol) in CH_2Cl_2 (10 ml). After 5 min, MeI (3.3 g, 23 mmol) was added, and stirring was continued overnight. Insoluble matter was removed by filtration and volatile material by evaporation. Extraction of the residue with ether gave the hydrazine **6** (R = Me) (0.77 g, 36%) contaminated with some of the aminimide **1**. A further ether extraction afforded spectroscopically pure **6** (R = Me), m.p. 156–158 °C (lit.,[14] 165–165.5 °C); *m/z* 274 (M^+, 4%) and 231 (100); $\delta_P(CH_2Cl_2)$ 27.6; δ($CDCl_3$) 8.0–7.2 (10 H, m), 2.57 (3 H, d, J_{PH} 10 Hz) and 2.40 (6 H, s). This compound was largely unchanged after heating with methyl iodide (4 mol equiv.) at 72 °C (sealed tube) for 24 h; none of the hydrazinium salt **8** was formed (^{1}H and ^{31}P NMR).

1,1,1,2-*Tetramethyl*-2-*diphenylphosphinoylhydrazinium Iodide* **8**.—A mixture of trimethylammonio-*N*-diphenylphosphinoylimide **1**[1] (2.02 g, 7.4 mmol) and MeI (4.2 g, 29.5 mmol) was heated in a sealed tube at 70 °C for 17 h. Addition of a little CH_2Cl_2 dissolved the by-products, leaving the *tetramethylhydrazinium salt* **8** (1.56 g, 51%); recrystallised from CH_2Cl_2–ether, m.p. 149–151 °C; δ_P(MeOH) 39.1, δ(CD_3OD) 8.0–7.5 (10 H, m), 3.78 (9 H, s) and 3.02 (3 H, d, J_{PH} 10 Hz) (Found: C, 46.1; H, 5.25; N, 6.6. $C_{16}H_{22}IN_2OP$ requires C, 46.2; H, 5.3; N, 6.7%). The principal by-products were the trimethylhydrazide **6** (R = Me) (spectra as above) and the hydrazinium salt **1**·HI (protonated starting material).[3,†]

1-*Ethyl*-1,1,2-*trimethyl*-2-*diphenylphosphinoylhydrazinium Iodide* **15**.—A mixture of ethyldimethylammonio-*N*-diphenylphosphinoylimide[3] (1.8 g, 6.25 mmol) and MeI (3.6 g, 25 mmol) was heated at 70 °C for 1 h. Volatile material was evaporated and the residue was crystallised from CH_2Cl_2–ether to give the *ethyltrimethylhydrazinium salt* **15** (0.94 g, 35%), m.p. 121–122.5 °C, $\delta_P(CH_2Cl_2)$ 37.1; δ($CDCl_3$) 7.95–7.4 (10 H, m), 4.46 (2 H, q, J_{HH} 7 Hz), 3.92 (6 H, s), 3.08 (3 H, d, J_{PH} 10 Hz) and

* In these photochemical reactions, and that of the $\overset{+}{N}Et_3$ compound, no ethylidene aminal was actually detected but that, we believe, was due to its instability under the conditions of the reactions rather than because it was not formed. In any case, it is clear that Et groups in the substrate divert reaction away from the formation of methylene aminal to a greater extent in the photochemical reactions of the aminimides than in the base-induced reactions of the hydrazinium salts.

† The acid that protonates the aminimide starting material is probably HI liberated by hydrolysis of MeI. It was not possible to exclude moisture completely because the aminimide could only be prepared as a partial hydrate.[3]

1.44 (3 H, t, J_{HH} 7 Hz) (Found: C, 47.4; H, 5.6; N, 6.5. $C_{17}H_{24}IN_2OP$ requires C, 47.45; H, 5.6; N, 6.5%).

Concentration of the mother liquor gave the by-product *1-ethyl-1,2-dimethyl-2-diphenylphosphinoylhydrazine* (0.65 g, 36%), purified by washing with water and crystallisation from ether–light petroleum (b.p. 40–60 °C), m.p. 101–103 °C, *m/z* 288 (M^+, 4%) and 231 (100); $\delta_P(CH_2Cl_2)$ 28.0; $\delta(CDCl_3)$ 8.0–7.2 (10 H, m), 2.7–2.5 [5 H, m, including 2.57 (3 H, d, J_{PH} 9 Hz)], 2.43 (3 H, s) and 0.81 (3 H, t, J_{HH} 7 Hz) (Found: C, 66.7; H, 7.4; N, 9.7. $C_{16}H_{21}N_2OP$ requires C, 66.65; H, 7.3; N, 9.7%).

1,1-Diethyl-1,2-dimethyl-2-diphenylphosphinoylhydrazinium Iodide **18**.—A mixture of diethylmethylammonio-*N*-diphenylphosphinoylimide[3] (0.136 g, 0.45 mmol) and MeI (0.64 g, 4.5 mmol) was heated at 45 °C for 16 h. Volatile material was evaporated and the residue was partitioned between CH_2Cl_2 (5 ml) and aqueous K_2CO_3. The organic layer was dried ($MgSO_4$) and diluted with ether. The oil that separated was washed thoroughly with ether to give the *diethyldimethylhydrazinium salt* **18** (0.063 g, 32%), $\delta_P(CH_2Cl_2)$ 37.1; $\delta(CDCl_3$; 300 MHz) 7.9–7.5 (10 H, m), 4.49 (2 H, dq, J_{gem} 13, J_{HH} 7 Hz), 4.28 (2 H, dq, J_{gem} 13, J_{HH} 7 Hz), 3.77 (3 H, s), 3.14 (3 H, d, J_{PH} 9 Hz) and 1.48 (6 H, t, J_{HH} 7 Hz). Further purification was achieved by adding ethyl acetate to a solution of the oil in CH_2Cl_2; a complex, m.p. 79–81.5 °C, precipitated. The pure salt **18**, free of ethyl acetate, was obtained as a foam on evaporation of a solution of the complex in CH_2Cl_2.

1,1,1-Triethyl-2-methyl-2-diphenylphosphinoylhydrazinium Iodide **13**.—A mixture of triethylammonio-*N*-diphenylphosphinoylimide[3] (7.0 g, 22 mmol) and MeI (15.5 g, 110 mmol) was heated at 48 °C for 24 h. The excess MeI was evaporated and the residue was dissolved in methanol. The ^{31}P NMR spectrum indicated a mixture of the required salt **13** (δ_P 37.9, 60%) and partially-protonated starting material (δ_P 22.4, 30%).† To facilitate isolation of the product, sodium methoxide (6.3 mmol) was carefully added until the partially-protonated starting material was almost completely neutralised (δ_P 18.3). [Use of more methoxide caused breakdown of the product to $Ph_2P(O)OMe$ (δ_P 33.3) and 2-methyl-1,1,1-triethylhydrazinium iodide, m.p. 190–192.5 °C (from CH_2Cl_2–ether), ν_{max}/cm^{-1} (Nujol) 3220 (NH); $\delta(CDCl_3)$ 6.13 (1 H, q, J_{HH} 6 Hz, NH), 3.53 (6 H, q, J_{HH} 7 Hz), 2.60 (3 H, d, J_{HH} 6 Hz) and 1.38 (9 H, t, J_{HH} 7 Hz)]. The methanol solution was evaporated and the residue was dissolved in CH_2Cl_2 (30 ml). Addition of ethyl acetate precipitated the *methyltriethylhydrazinium salt* **13** as a complex with ethyl acetate (4.6 g, 38%), m.p. 73–75 °C, ν_{max}/cm^{-1} (KBr) 1730 (EtOAc); $\delta_P(CDCl_3)$ 37.5; $\delta(CDCl_3)$ 7.95–7.35 (10 H, m), 4.22 (6 H, q, J_{HH} 7 Hz), 3.23 (3 H, d, J_{PH} 9 Hz), 1.39 (9 H, t, J_{HH} 7 Hz) and signals for EtOAc [4.05 (2 H, q, J_{HH} 7 Hz), 1.98 (3 H, s) and 1.21 (3 H, t, J_{HH} 7 Hz)] (Found: C, 50.0; H, 6.6; N, 5.3. $C_{19}H_{28}IN_2OP$·EtOAc requires C, 50.05; H, 6.6; N, 5.1%). The ethyl acetate could not be removed by heating the solid complex *in vacuo* at 50 °C, and use of a higher temperature resulted in deethylation to $Ph_2P(O)N(Me)NEt_2$. The pure salt **13** was obtained as a foam, free of ethyl acetate, on evaporation of a solution of the complex in CH_2Cl_2.

Reactions of Phosphinoylhydrazinium Salts.—(*a*) The tetramethylhydrazinium iodide **8** (0.238 g, 0.57 mmol) was stirred in THF (5 ml) and potassium t-butoxide (0.128 g, 1.14 mmol) was added. Within 0.5 h the salt had dissolved (reacted), giving a product, δ_P(THF) 26.0. The solvent was evaporated (no heat) and ether was added. Insoluble matter (KI) was removed by filtration. Concentration of the filtrate afforded N-(*dimethylaminomethyl*)-N-*methyldiphenylphosphinic amide* **10** (0.107 g, 65%), recrystallised from ether–toluene, m.p. 97–102 °C (decomp.), *m/z* (EI) 288 (M^+, 2%), 87 ($Me\overset{+}{N}CH_2NMe_2$, 85) and 58 ($CH_2=\overset{+}{N}Me_2$, 100); *m/z* (FAB; glycerol matrix) 289 ($M^+ + 1$, 46%), 287 ($M^+ - 1$, 7), 244 ($M^+ - NMe_2$, 100) and 201 (50); ν_{max}/cm^{-1} (Nujol) 1195 and 1175 (P=O); $\delta_P(CH_2Cl_2)$ 29.4; $\delta(CDCl_3)$ 7.95–7.30 (10 H, m), 3.50 (2 H, d, J_{PH} 7 Hz; simplifies to s when P irradiated), 2.67 (3 H, d, J_{PH} 10.5 Hz; simplifies to s when P irradiated) and 2.17 (6 H, s) (Found: C, 66.6; H, 7.4; N, 9.4. $C_{16}H_{21}N_2OP$ requires C, 66.65; H, 7.3; N, 9.7%). The identity of this product was confirmed by comparison with an authentic sample of compound **10** prepared by alkylation of *N*-methyldiphenylphosphinic amide **7** [$\delta_P(CH_2Cl_2)$ 24.0] with *N,N*-dimethylmethyleneammonium chloride[3] in CH_2Cl_2 and neutralisation of the resulting salt [**10**·HCl; $\delta_P(CH_2Cl_2)$ 33.7] with anhydrous K_2CO_3.

(*b*) The ethyltrimethylhydrazinium iodide **15** with potassium t-butoxide (1.5 mol equiv.) gave, in a similar experiment (time 10 min), a mixture of two isomeric aminals, m.p. 47–52 °C, *m/z* 302 (M^+, 6%), 101 ($Me\overset{+}{N}CH_2NMeEt$, 45) and 72 ($CH_2=\overset{+}{N}MeEt$, 100); ν_{max}/cm^{-1} (Nujol) 1195 and 1170 (P=O) (Found: C, 67.3; H, 7.65; N, 9.1. $C_{17}H_{23}N_2OP$ requires C, 67.5; H, 7.7; N, 9.3%). The aminals in the mixture were identified as *N*-(ethylmethylaminomethyl)-*N*-methyldiphenylphosphinic amide **16** (major), $\delta_P(CDCl_3)$ 29.6, $\delta(CDCl_3$, 300 MHz) 7.9–7.4 (10 H, m), 3.62 (2 H, d, J_{PH} 7 Hz; simplies to s when P irradiated), 2.69 (3 H, d, J_{PH} 10.5 Hz; simplifies to s when P irradiated), 2.43 (2 H, q, J_{HH} 7 Hz), 2.20 (3 H, s) and 0.98 (3 H, t, J_{HH} 7 Hz), and *N*-[1-(dimethylamino)ethyl]-*N*-methyldiphenylphosphinic amide **17** (minor), $\delta_P(CDCl_3)$ 28.4, $\delta(CDCl_3$; 300 MHz) 7.9–7.4 (10 H, m), 3.69 (1 H, dq, $J_{PH} \sim J_{HH} \sim 6.5$ Hz), 2.56 (3 H, d, J_{PH} 10.5 Hz), 2.26 (6 H, s) and 1.35 (3 H, d, J_{HH} 6.5 Hz) in a ratio of 10:1.

(*c*) The diethyldimethylhydrazinium iodide **18** with potassium t-butoxide (2.0 mol equiv.) gave, in a similar experiment (time 10 min), a mixture (oil) of two isomeric aminals identified as *N*-(diethylaminomethyl)-*N*-methyldiphenylphosphinic amide **19** (major) $\delta(CDCl_3$; 300 MHz) 7.9–7.4 (10 H, m), 3.70 (2 H, d, J_{PH} 7 Hz), 2.67 (3 H, d, J_{PH} 10.5 Hz), 2.56 (4 H, q, J_{HH} 7 Hz) and 0.90 (6 H, t, J_{HH} 7 Hz), and *N*-[1-(ethylmethylamino)ethyl]-*N*-methyldiphenylphosphinic amide **20** (minor) $\delta(CDCl_3$; 300 MHz) 7.9–7.4 (10 H, m), 3.97 (1 H, dq, $J_{PH} \sim J_{HH} \sim 6.5$ Hz), 2.54 (3 H, d, J_{PH} 10.5 Hz), 2.25 (3 H, s), 1.35 (3 H, d, J_{HH} 6.5 Hz) and 0.96 (3 H, t, J_{HH} 7 Hz) (signal for CH_2 of *N*-ethyl group concealed by signals from the major isomer) in a ratio of 9:1. The ^1H NMR spectrum was recorded as soon as the product had been dissolved in $CDCl_3$ but nonetheless showed some decomposition (~7%) to *N*-methyldiphenylphosphinic amide (δ 2.67, dd, J_{PH} 12.5, J_{HH} 6 Hz). The ^{31}P NMR spectrum, recorded 0.5 h later, showed quite extensive decomposition to the amide (δ_P 25.0; ~25%); the aminals, δ_P 29.6 (major) and 28.4 (minor), were then present in a ratio of 17:1.

(*d*) The methyltriethylhydrazinium iodide **13** with potassium t-butoxide (1.5 mol equiv.) gave, in a similar experiment (time 15 min), an oil identified as *N*-[1-(diethylamino)ethyl]-*N*-methyldiphenylphosphinic amide **14** (90%), δ_P(THF) 25.4, ν_{max}/cm^{-1} (film) 1195 (P=O), $\delta(CDCl_3$; 300 MHz) 7.9–7.35 (10 H, m), 4.22 (1 H, dq, $J_{PH} \sim J_{HH} \sim 6.5$ Hz), 2.80 and 2.64 (both 2 H, dq, J_{gem} 14, J_{HH} 7 Hz), 2.51 (3 H, d, J_{PH} 10.5 Hz), 1.35 (3 H, d, J_{HH} 6.5 Hz) and 0.90 (6 H, t, J_{HH} 7 Hz).

(*e*) Potassium t-butoxide (5 mol equiv.) was added to a solution of the tetramethylhydrazinium iodide **8** (21 mg) in $(CD_3)_2SO$ (0.4 ml) contained in an NMR tube. The spectrum was immediately recorded. It indicated complete conversion of the salt into the aminal **10**, $\delta[(CD_3)_2SO]$ 8.05–7.7 (Ph), 3.54 (d, J_{PH} 9 Hz, CH_2), 2.60 (d, J_{PH} 10 Hz, NMe) and 2.12 (s, NMe_2), and no CIDNP signals were apparent.

(*f*) Sodium methoxide (2 mol equiv.) was added to a solution of the tetramethylhydrazinium iodide **8** (26 mg) in methanol (1.5 ml). The salt was consumed within 2 min, giving a product

δ_P(MeOH) 34.5. The product was isolated and identified as methyl diphenylphosphinate,[2] *m/z* 232 (M^+, 95%) and 231 (100), ν_{max}/cm^{-1} (CH_2Cl_2) 1225 (P=O), δ($CDCl_3$) 7.95–7.15 (10 H, m) and 3.72 (3 H, d, J_{PH} 11 Hz).

Acknowledgements

We thank the SERC for a Research Studentship and for access to the SERC Mass Spectrometry service.

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Paper 0/02961K
Received 2nd *July* 1990
Accepted 17th *July* 1990