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# Synthesis, Thermolysis and Photolysis of Trimethylammonium-*N*-diphenylphosphinylimine

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**Synopsis.** Ammonim-*N*-phosphinylimine was prepared from the corresponding hydrazinium salt. The ylid gave phosphinylnitrenes on thermolysis, predominantly in the singlet state. On photolysis, the ylid also gave a singlet product.

A number of aminimides have been studied extensively and reviewed.[1] Higher homologues of trialkylammonium-*N*-alkanoylimine and sulfonylimine have also been reported,[2,3] however, a similar type of nitrogen ylid with a phosphinyl group has received far less attention.

It is well known that the thermal decomposition of the aminimides gives corresponding isocyanates. In a previous paper,[3] the present authors have indicated that the photolysis of trialkylammonium-*N*-alkanoylimine was hindered by the introduction of a hydroxyl group into the 2-position of the alkyl chain attached to the positive nitrogen atom in the aminimide. Robson and Speakman[4] have found that trimethylammonium-*N*-dodecanoylimine afforded only an amide upon photolysis, and that a similar sulfonylimine underwent no photolysis, but instead thermally decomposed producing both singlet and triplet nitrenes.

This paper deals with the synthesis of a nitrogen ylid trimethylammonium-*N*-diphenylphosphinylimine (I), and the generation of phosphinylnitrene by the thermolysis and photolysis of I.

The nitrogen ylid I was synthesized from 1,1,1-trimethyl-2-diphenylphosphinylhydrazinium iodide (II), which was prepared from 1,1-dimethyl-2-diphenylphosphinylhydrazine (III) and methyl iodide.

The IR absorption frequencies assigned to the phosphinyl group of I are lower than those of II and III. A similar shift is known for a carbonyl group in aminimides and attributed to a delocalization of the negative charge on the imine nitrogen.[1] The shift was also found for a sulfonyl group in ammonium-*N*-sulfonylimines.[2] The base peak of the mass spectrum of I, due to the elimination of a methyl group, is a characteristic pattern for aliphatic amines. Three main peaks in the low mass region suggest that I decomposes to form phosphinylnitrene and trimethylamine. The differential thermal and thermogravimetric analysis data show that I has one mole of water of crystallization and decomposes producing trimethylamine at a temperature higher than its mp by about 60 °C. This decomposition temperature is higher than those for ammonium-*N*-acylimine and sulfonylimine.[2]

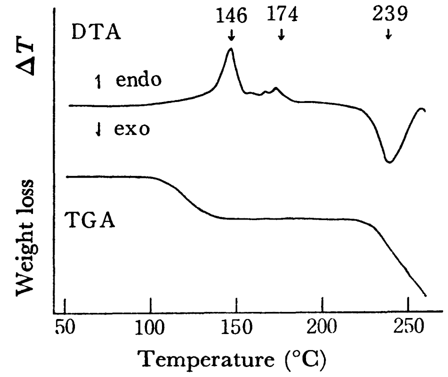

Fig. 1. DTA and TGA curves for $(CH_3)_3N^+N^-PO(Ph)_2$. α-Alumina standard; heating, 2.5 °C/min in air.

The aqueous solution of I was neutral, had a low electric conductivity and was titratable with an HCl aqueous solution at room temperature. When this acidic aqueous solution was boiled for a couple of minutes, I decomposed to give trimethylhydrazinium salt and diphenylphosphinic acid quantitatively.

Thermally, I was decomposed in DMSO and gave diphenylphosphinamide (IV) and *N*-diphenylphosphinyldimethylsulfoximine (V) with some unknown prod-

Table 1. Thermolysis of $(CH_3)_3N^+N^-{-}X$ (5 h)

| X | Solvent | Temp (°C) | Recovery (%) | Sulfoximine (mol %) | Amide (mol %) | Others (mol %) | Unknown (wt %) |
|---|---|---|---|---|---|---|---|
| $POPh_2$ | DMSO | 180 | — | 29 | — | — | — |
| $POPh_2$ | DMSO | 150 | 50 | 19 | 11 | — | 2 |
| $POPh_2$ | DMSO | 120 | 100 | — | — | — | — |
| $POPh_2$ | $C_{12}H_{25}OH$ | 180 | 13 | — | 22 | 29[a] | 17 |
| $POPh_2$ | $C_{12}H_{25}OH$ | 150 | 46 | — | 13 | 18[a] | 4 |
| $POPh_2$ | $C_{12}H_{25}OH$ | 120 | 100 | — | — | — | — |
| COPh | DMSO | 170 | 17 | — | — | 49[b] | — |
| COPh | DMSO | 140 | 100 | — | — | — | — |
| COR[c] | DMSO | 170 | — | — | — | 21[b] | — |
| $SO_2R$[d] | DMSO | 170 | — | 65 | 41 | — | — |

a) $(C_6H_5)_2POOC_{12}H_{25}$, b) *N,N'*-dialkylurea, c) R: $C_{11}H_{23}$, Ref. 4, d) R: $C_{12}H_{25}$, Ref. 4.

ucts. In 1-dodecanol, I gave IV and dodecyl diphenylphosphinate (VI). These results are shown in Table 1.

It can be assumed that diphenylphosphinylnitrene, produced in the singlet state, immediately reacts with DMSO to form V, on the other hand, in the presence of a poor singlet trap, the nitrene produces the triplet product IV by way of an intersystem crossing. The molar ratio of the singlet to triplet products was somewhat larger than that for the sulfonylimine. Moreover, I gave only V at 180 °C in DMSO. An almost identical proportion of I was decomposed in both DMSO and 1-dodecanol at a temperature lower than the mp of I.

Table 2. Photolysis of $(CH_3)_3N^+N^-$–X

| X | Solvent | Time (h) | Recovery (%) | Sulfoximine (mol %) | Amide (mol %) | Unknown (wt %) |
|---|---|---|---|---|---|---|
| $POPh_2$ | DMSO | 12 | 22 | 29 | 51 | 13 |
| $POPh_2$ | amine[a)] | 12 | 46 | — | 37 | — |
| COPh | DMSO | 14 | 100 | — | — | — |
| COPh | DMSO | 57 | 56 | — | 35 | 8 |
| COPh | amine[a)] | 14 | 100 | — | — | — |
| $COC_{11}H_{23}$ | amine[b)] | 33 | 67 | — | 6 | 9 |

a) $(CH_3)_2NCH_2CH_2OH$. b) $(CH_3)_2NCH_2CH_2OH+$ cyclohexane.

As in the case of thermolysis, the photolysis of I resulted in the smooth production of the singlet nitrene as shown in Table 2. In the presence of 2-(dimethylamino)ethanol, I transferred no additional products of the nitrene to the amine.

## Experimental

All the melting points are uncorrected. The IR spectra were obtained using a Hitachi EPI-G3 infrared spectrometer. The NMR spectra were recorded on a Varian A-60D spectrometer in $CDCl_3$ at 60 MHz, using tetramethylsilane as an internal standard. The mass spectra were measured using a Nihon Denki JMS07 mass spectrometer operating at 25 eV. Differential thermal and thermogravimetric analyses were carried out using a Rigaku Denki Thermoflex DG-CIH.

*Preparation of Trimethylammonium-*N*-diphenylphosphinylimine (I).* Diphenylphosphinic chloride, prepared from chlorodiphenylphosphine in the usual way,[5)] was added to a benzene solution of two moles of 1,1-dimethylhydrazine at room temperature. The precipitated white crystal was washed thoroughly with water, and gave 1,1-dimethyl-2-diphenylphosphinylhydrazine (III) in a 40% yield, mp 178.2—178.5 °C (167—168 °C)[6)]; IR 1110, 1123, 1190, 1205 $cm^{-1}$. In ethanol, III was refluxed with an excess of methyl iodide to give 1,1,1-trimethyl-2-diphenylphosphinylhydrazinium iodide (II) in a 90% yield; IR 1103, 1122, 1200 $cm^{-1}$. At room tempera- ture II was treated with a 10% NaOH aq. solution. From the alkaline solution, I was extracted with chloroform in a 69% yield, mp 178.3—178.5 °C (from acetone); IR 1027, 1048, 1110, 1150 $cm^{-1}$; NMR $\delta$ 3.0—3.1 (s, *ca.* 2H, $H_2O$), 3.31 (s, 9H, $CH_3$), 7.2—8.2 (m, 10H, phenyl); mass spectrum (peaks more than 30% of the base peak) *m/e* (%) 58 (78), 59(59), 216 (33), 259 (100), 273 (50), 274 (47, $M^+$). The DTA and TGA curves are shown in Fig. 1. Found C, 61.36; H, 7.15; N, 9.42; P, 9.9%. Calcd for $C_{15}H_{19}N_2OP \cdot H_2O$: C, 61.63; H, 7.24; N, 9.58; P, 10.6%.

*Thermolysis.* In a stream of nitrogen, an approximately 7% solution of I in DMSO was heated. After 5 h, the solvent was distilled off at reduced pressure. Two products, diphenylphosphinamide (IV) and *N*-diphenylphosphinyldimethylsulfoximine (V) were isolated from the reaction mixture by recrystallization and/or by column chromatography. In addition, two or three unknown products were detected by TLC in the residue. In the same way as described above, I was decomposed in 1-dodecanol, and gave IV and dodecyl diphenylphosphinate (VI). These products, IV and VI, were confirmed by direct comparisons with authentic samples. On the basis of elemental analysis, IR and NMR spectra, V (mp 168.0—168.5 °C (from acetone)) was identified. Trimethylammonium-*N*-benzoylimine was also decomposed in DMSO and gave *N*,*N′*-diphenylurea.

*Photolysis.* Solutions of I and other aminimides (about 1 g) in 250 ml of DMSO or 2-(dimethylamino)ethanol were irradiated using a 10W low-pressure mercury arc lamp at room temperature. The products were isolated and identified in the same way as described for thermolysis.

## References

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