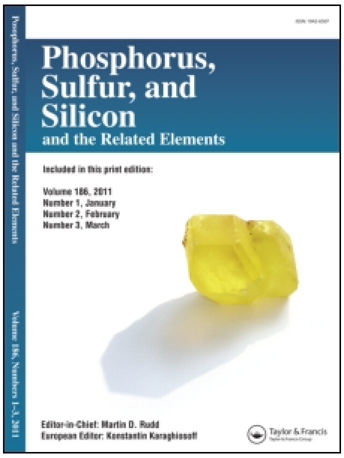

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REACTION OF SOME WITTIG REAGENTS WITH GLYOXYLANILIDE-2-OXIME AND DIACETYLMONOXIME

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REACTION OF SOME WITTIG REAGENTS WITH GLYOXYLANILIDE-2-OXIME AND DIACETYLMONOXIME

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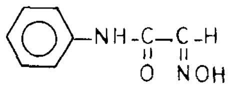
Glyoxylanilide-2-oxime (**I**) reacts with Wittig reagents **IIIa–c** in refluxing dry toluene to give the ylid phosphoranes **Va**, **Vb** and **IVc** respectively. Diacetylmonoxime (**II**) reacts with the same reagents **IIIa–c** to give the ethylenic adducts **VIa–c** respectively. The identity of the new products is established from analytical and spectroscopic evidences.

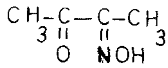
Key words: Wittig reagents, glyoxylanilde-2-oxime, diacetylmonoxime, ylid phosphorancs, ethylenic adducts.

INTRODUCTION

Extending our work[1–3] on the reaction of Wittig reagents with different carbonyl functions, in which we concluded that the results obtained depend on the nature of the ylid used, the structure of the carbonyl compound as well as on the stability of the addition products, we examined the reaction of some Wittig reagents **IIIa–c** with glyoxylanilide-2-oxime (**I**) and diacetylmonoxime (**II**), which bear a carbonyl function adjacent to an oxime moiety.



I

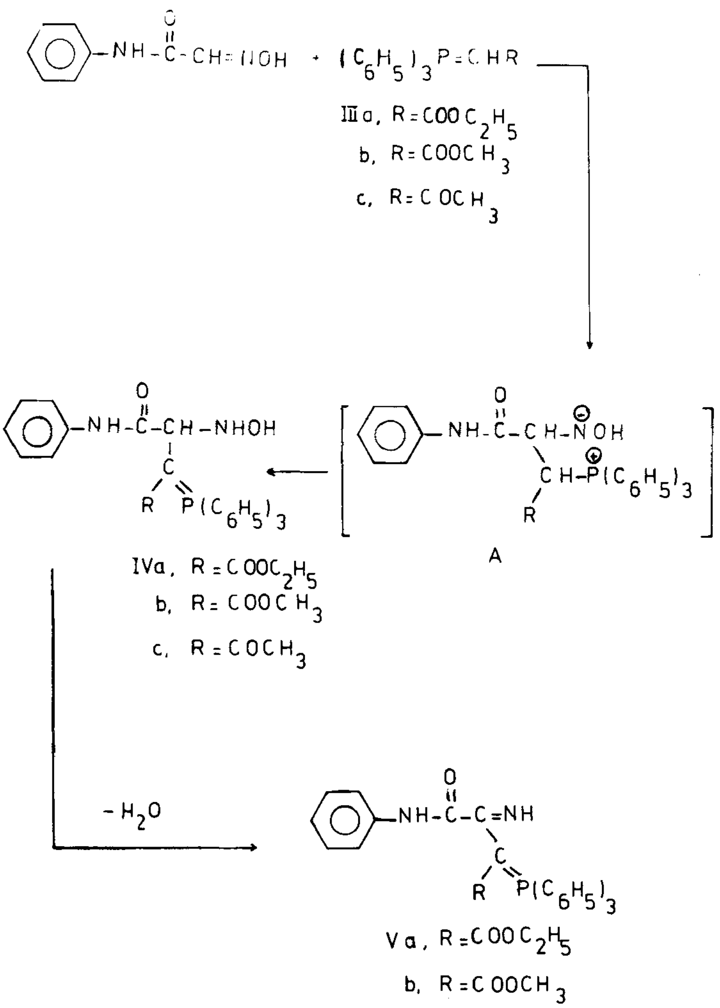


$CH_3-\underset{O}{\underset{\|}{C}}-\underset{NOH}{\underset{\|}{C}}-CH_3$

II

RESULTS AND DISCUSSION

We have found that glyoxylanilide-2-oxime (**I**) reacts with carbethoxymethylene triphenylphosphorane (**IIIa**) in refluxing dry toluene to give colorless crystalline products formulated as **Va**. The ylid phosphorane **Va** is chromatographically pure and posseses sharp melting points and is equally obtained, whether one or two mole equivalents of the Wittig reagent **IIIa** were used with one mole equivalent of compound **I**. *Structure* **Va** *is confirmed by the following evidence:* (a) correct elementary analyses and molecular weight determination by (MS); (b) the IR spectrum of adduct



SCHEME I

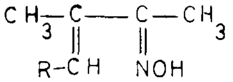
Va, taken as example (in $CDCl_3$, expressed in cm^{-1}) reveals the presence of an absorption band at 1613 characterestic for >C=P group absorption,[4] 1444 for the P—C (phenyl,[5] 1588 for the >C=N,[6] 1645 for the >C=O amide[7] and 3579, 3289 for the two NH groups; (c) the ^1H-NMR spectrum of **Va** (in $CDCl_3$ expressed in δ scale) showes a triplet centered at 0.50 (3H, CH_3 group), a quartet at 3.70 (2H, CH_2 group) a multiplet at 7.00–7.75 (21H, aromatic and the imino proton, exchangeable with D_2O) and a singlet at 10.90 for the NH amide. It lacks the OH absorption which is recorded in the starting material **I** at 12.25; (d) the ^{31}P-NMR measurement supports structure **Va**, it exhibits a sharp signal at $\delta = +19.50$ (vs. H_3PO_4).[8]

In a similar manner compound **I** reacts with carbmethoxymethylene triphenylphosphorane (**IIIb**) to give the ylid phosphorane adduct **Vb** (c.f. Experimental).

The reaction of **I** with acetylmethylenetriphenylphosphorane (**IIIc**) leads to the formation of the ylid phosphorane **IVc**. Structure **IVc** is confirmed from correct elementary analyses, MS, ^{1}H-NMR and ^{31}P-NMR spectra. The ^{1}H-NMR of **IVc** reveals the presence of the OH, NH and CH groups (c.f. Experimental).

Formation of adduct **V** can be explained (Scheme I) in terms of initial nucleophilic attack by the carbanion centre in the Wittig reagent **III** on the carbon attached to the oxime group in **I** to give the dipolar adduct A which collapses to give **IV**. The latter adduct is not stable under the experimental condition and loses a mole of water to give the final product **V**. In the case of the addition of Wittig reagent IIIc on I, the final product is **IVc** which is stable under experimental conditions with no loss of water. Adduct **IVc** is stable when refluxing in toluene for 10 hr.

Oxime **II** reacts with Wittig reagents **IIIa–c** in refluxing toluene to yield the ethylenic adducts **VIa–c**, respectively, with triphenylphosphine oxide.



$$CH_3-\underset{\underset{R-CH}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-CH_3$$

VIa, R = $COOC_2H_5$
b, R = $COOCH_3$
c, R = $COCH_3$

Attempted reaction of **VIa** with another mole of Wittig reagent **IIIa** leads to the isolation of unchanged **VIa**

Structures **VIa–c** are confirmed by correct elemental analyses, MS, IR and ^{1}H-NMR spectra. The IR spectrum of **VI** taken as example (in $CDCl_3$, expressed in cm^{-1}) reveals the absence of the carbonyl absorption of the acetyl group which is recorded in the starting material at 1773. It shows 1575 $\left(>C{=}N\right)$, 941 $\left(>N{-}O\right)$ and 3322 (N—OH). The ^{1}H-NMR of **VIa** (expressed in δ scale) gives two singlets at 2.10 and 2.35 (6H, $2CH_3$ groups), triplet at 1.40 (3H, CH_2—CH_3), a quartet at 4.25 (2H, CH_2—CH_3), a singlet at 6.15 (1H, C=CH) and a singlet at 12.00 (1H, OH)

CONCLUSION

From the present investigation it seems that the two oximes **I** and **II** react differently with stabilized ylids of type **III**, where compound **I** reacts with Wittig reagents **III** according to Michal addition to give ylid phosphorane adducts. Compounds **II** reacts with the same reagents according to Wittig mechanism[9,10] yielding the respective ethylenes and triphenylphosphine oxide. The reaction of oxime **I** with Wittig reagents affords a new type of ylid phosphorane.

EXPERIMENTAL

All melting points are uncorrected. Carbethoxymethylene-,[11] carbmethoxymethylene-,[11] acetylmethylenetriphenylphosphorane,[12,13] glyoxylanilide-2-oxime[14] and diacetylmonoxime[15] were prepared according to established procedures. The IR spectra were measured in $CDCl_3$, on Perkin-Elmer Infracord spectrometer Model 1576. The ^1H-NMR spectra were taken in $CDCl_3$ on a Varian A-60, T-60. The ^{31}P-NMR spectra were recorded in $CDCl_3$ (vs. H_3PO_4 as external standard) on Varian CFT20, 32 MHz spectrometer. The mass spectra were run at 70 ev on a Kratos MS equipment spectrometer.

Reaction of Oximes **I** *and* **II** *with Wittig Reagent*

General procedure: A mixture of **I** or **II** (0.002 mole) and the Wittig reagent (0.0025 mole) in dry toluene, was refluxed, after the reaction was completed (by T.L.C.), the reaction solvent was removed under reduced pressure. The residue was placed on a column of silica-gel and eluted with acetone/petroleum ether (2:8).

Reaction of Oxime **I** *with Reagent* **IIIa**

Refluxing time is 15 hr, colorless crystals from benzene m.p. 180°C in 65% yield. Anal. Calcd. for $C_{30}H_{27}N_2O_3P$ (494.542). C, 72.87; H, 5.46; N, 5.66; P, 6.26 Found: C, 72.70; H, 5.39; N, 5.60; P, 6.34% Mol. wt (MS) = 494.

Reaction of **I** *with Reagent* **IIIb**

Refluxing time 13 hr, yellow crystals from benzene m.p. 190°C in 70% yield Anal. Calcd. for $C_{29}H_{25}N_2O_3P$ (480.515) C, 72.50; H, 5.20; N, 5.83; P, 6.44. found: C, 72.46.; H, 5.27; N, 5.76; P, 6.56% Mol. wt (MS) = 480.

IR, 1609 $\left(>C{=}P\right)$, 1439 (P—C(phenyl), 1587 $\left(>C{=}N\right)$, 1666 $\left(>C{=}O \text{ amide}\right)$, 3655 and 3379 (2NH). ^1H-NMR of **Vb**, singlet at 3.00 (3H, $COO\underline{CH_3}$, a singlet at 10.95 (1H, $CO\underline{NH}$) and multiplet at 6.95–7.72 (21H, aromatic protons and the imino proton, exchangeable with D_2O), ^{31}P-NMR of **Vb** in $CDCl_3$ = +20.75 ppm.

Reaction of **I** *with Reagent* **IIIC**

Refluxing time 17 hr, dark yellow crystals from chloroform m.p. 135°C in 60% yield. Anal. Calcd. for $C_{29}H_{27}N_2O_3P$ (482.551). C, 72.18; H, 5.64; N, 5.80; P, 6.42. Found: C, 71.29; H, 5.42; N, 5.74; P, 6.50% Mol. wt. (MS) = 482.

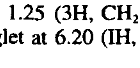
IR of **IVc**, 2854 (CH aliphatic), 1619 $\left(>C{=}P\right)$, 1650 $\left(>C{=}O \text{ amide}\right)$, 3534, 3430 (2NH groups), 1441 (P—C(Phenyl) and 3572 (OH). ^1H-NMR of **IVc**, a singlet at 2.50 (3H, $CO\underline{CH_3}$) a singlet at 6.70 (1H, $\underline{CH}$), a singlet at 12.52 (1H, $\underline{OH}$), a singlet at 10.20 (1H, $\underline{NH}$ amide) and multiplet at 7.00–7.75 (21H aromatics and NH proton, exchangeable with D_2O). ^{31}P-NMR = +19.56.

Stability of Adduct **IVc**

Adduct **IVc** 0.24 gm (0.0005 mole) was refluxed in 20 ml dry toluene for 15 hr. The volatile material was removed under reduced pressure, the residue obtained was crystallized from chloroform to give adduct **IVc** unchanged in 95% yield as dark yellow crystals with the same m. p. mixed m. p. and comparative IR spectra.

Reaction of Oxime **II** *with Reagent* **IIIa**

Refluxing time 20 hr, eluted with a mixture of chloroform/petroleum ether (3:7) colorless crystals from benzene m. p. 70°C in 75% yield. Anal. Calcd. for $C_8H_{13}NO_3$ (171.120). C, 56.14; H, 7.60; N, 8.18, Found: C, 56.20; H, 7.65; N, 8.17% Mol. wt. (MS) = 171.

IR of **VIa**, 3414 (OH), 1722 $\left(>C{=}O\text{, ester}\right)$, 1626 $\left(>C{=}N\right)$ and it lacks the  $-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ absorption which is recorded in the starting material at 1773 The ^1H-NMR of **VIa**, triplet at 1.25 (3H, $CH_2{-}\underline{CH_3}$), quartet at 4.25 (2H, $\underline{CH_2}{-}CH_3$), two singlet at 2.00 and 2.35 (6H, $2\underline{CH_3}$), a singlet at 6.20 (IH, $\underline{CH}$) and a singlet at 12.40 (1H, $\underline{OH}$).

Attempted Reaction of Adduct **VIa** *with Reagent* **IIIa**

A mixture of **VIa** 0.34 gm (0.002 mole) and reagent **IIIa** (0.0025 mole) in dry toluene was refluxed for 20 hr. The volatile materials were removed in vacuo and the residue was placed on a column of silica-gel and eluted with a mixture of chloroform/petroleum either (2:5) to give **VIa** and **IIIa** in 90% yield.

Reaction of **II** *with Reagent* **IIIb**

Refluxing time 15 hr colorless crystals from benzene, m. p. 98°C in 80% yield. Anal. Calcd. for $C_7H_{11}NO_3$ (157.103). C, 53.50; H, 7.00; N, 8.91. Found: C, 53.46; H, 6.95; N, 9.20 Mol. wt. (MS) = 157.

IR of **VIb**, 3426 (OH), 1731 $\left(>C{=}O\ \text{ester}\right)$, 1628 $\left(>C{=}N\right)$. The ^{1}H-NMR of **VIb**, two singlets, at 2.00 and 2.40 (6H, $2\underline{CH_3}$), a singlet at 6.40 (1H, $\underline{CH}$), a singlet at 3.60 (3H, $COO\underline{CH_3}$) and a singlet at 12.40 (1H, $\underline{OH}$).

Reaction of **II** *with Reagent* **IIIC**

Refluxing time 15 hr, colorless crystals form benzene, m. p. 121°C in 60% yield. Anal. Calcd for $C_7H_{11}NO_2$ (141.103). C, 59.57; H, 7.80; N, 9.92. Found; C, 59.44; H, 7.79; N, 10.00.

IR of **VIc**, 3379 (OH), 1630 $\left(>C{=}N\right)$, 1660 $\left(>C{=}O\ \text{acyl}\right)$. The ^{1}H-NMR of **VIc**, two singlets at 2.15 and 2.40 (6H, $2\underline{CH_3}$), a singlet at 2.40 (3H, $\underline{CH_3}$ acyl), A singlet at 6.30 (1H, $\underline{CH}$) and a singlet at 12.35 (1H, $\underline{OH}$).

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