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THE REACTION OF WITTIG-HORNER REAGENTS AND PHOSPHACUMULENES WITH NITROSONAPHTHOL

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Wittig-Horner reagent **1a** reacts with 2-nitroso-1-naphthol **3** to give the olefinic adduct **5**, the alkylated product **4** and the dimeric compound **6**. When 2-nitroso-1-naphthol **3** reacts with Wittig-Horner reagents **1b,c**, the corresponding phosphonate adducts **8a,b** together with compounds **4** and **6** were obtained. Oxovinylidenetriphenylphosphorane **2** reacts with **3** to give the corresponding phosphoranylidene cyclobutylidene adduct **10** and triphenylphosphine oxide. The structural assignments of the new products are based on compatible analytical and spectroscopic results.

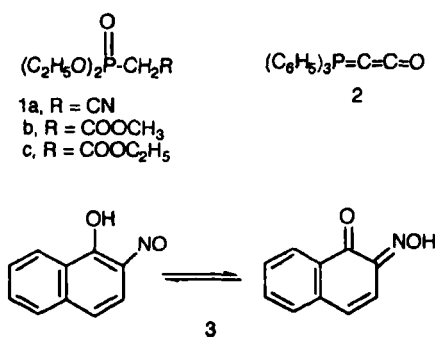
Keywords: Wittig-Horner reagents (**1a–c**); phosphacumulene (**2**); 2-nitroso-1-naphthol **3**; The alkylated product **4**; the olefinic adducts **5**; the dimeric product **6**; the phosphonate adducts **8a, b** and the phosphoranylidene cyclobutylidene adduct **10**

INTRODUCTION

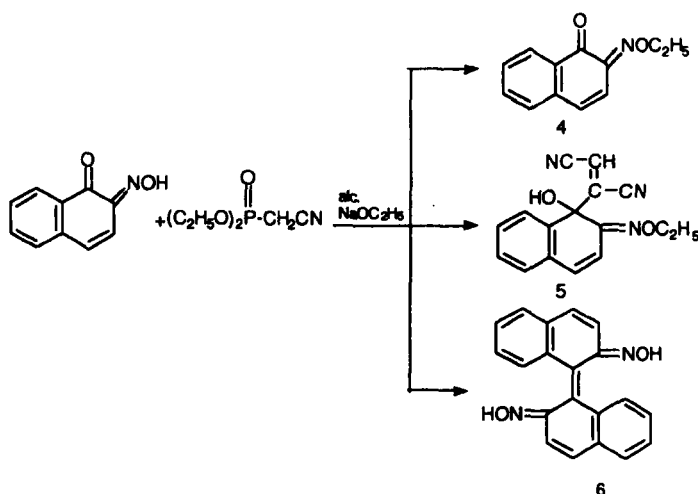
In previous publications we examined the action of Wittig-Horner reagents on o-, and p-quinones.^{1,2} Recently we reported³ that o-quinone diimines react with the same reagents to give the respective phosphonate adducts and the alkylated product.

The present work is an extension on the behavior of Wittig-Horner reagents **1** and phosphacumulene **2** toward 2-nitroso-1-naphthol **3** (Scheme 1). This was done to establish whether the nitroso-, or the carbonyl function would be preferentially attacked by the reagents.

*Corresponding author.



SCHEME 1



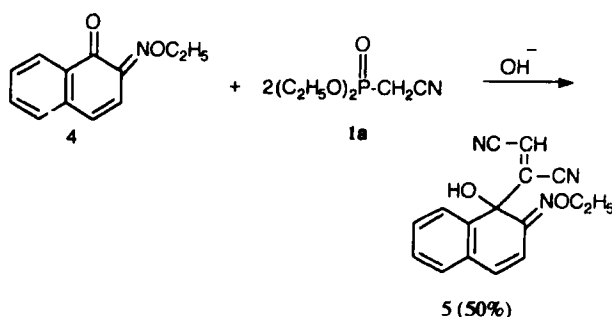
SCHEME 2

RESULTS AND DISCUSSION

We have found that the reaction of 2-nitroso-1-naphthol **3** with one mol equivalent of diethyl (cyanomethyl)phosphonate **1a**, in the presence of alcoholic sodium ethoxide solution, proceeds at reflux temperature to give chromatographically pure adducts formulated as **4** (35%), **5** (30%), and **6** (25%) (Scheme 2).

The structure of compound **4** is deduced from its analysis, IR, ^1H -NMR and mass spectral data.

It gave correct elementary ($\text{C}_{12}\text{H}_{11}\text{NO}_2$) and mass (MS) spectroscopic analyses. The IR spectrum of **4**, in KBr, revealed the presence of strong absorption bands at 1670 cm^{-1} ($\text{C}=\text{O}$), 1575 cm^{-1} ($\text{C}=\text{N}$) and at 941 cm^{-1} ($\text{N}-\text{O}$). The ^1H -NMR spectrum of **4** in CDCl_3 disclosed the presence of a triplet centered at



SCHEME 3

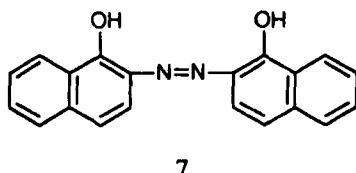
1.2 ppm (3H, t, OCH_2CH_3) and a quartet at 4.55 ppm (2H, q, OCH_2CH_3) due to the OEt group attached to the N atom. A multiplet appeared at 6.8–8.25 ppm corresponding to the 6 protons of the naphthyl ring. Compound **4** was established to be the alkylated^{3,4} known 1,2-naphthoquinone-2-oxime ethylether⁵.

Structure **5** was indicated by the following evidence: (a) Elemental analysis for compound **5** correspond to an empirical formula of $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_2$. The IR spectrum of adduct **5** (in KBr) revealed the presence of strong absorption bands at 3205 cm^{-1} (OH), 2202 cm^{-1} (C–N). Compound **5** gives negative color reaction with 1% alcoholic FeCl_3 . The $^1\text{H-NMR}$ spectrum of compound **5** disclosed the presence of signals at $\delta = 1.40$ (t, 3H, OCH_2CH_3), 4.5 (q, 2H, OCH_2CH_3), 4.3 (s, 1H, $=\text{CHCN}$). The -OH proton showed a singlet (exchangeable with D_2O) at 9.8 ppm. The mass spectrum of adduct **5** yielded a prominent ion peak for M^+ at m/e 279 (100%).

When 1,2-naphthoquinone-2-oxime-ethylether **4** was allowed to react with 2 mol equivalents of **1a**, in the presence of alcoholic sodium ethoxide, adduct **5** was isolated in 50% yield (mixed m.p. and comparative IR, $^1\text{H-NMR}$ and MS spectra) (Scheme 3).

Structure elucidation of the dimeric compound **6** is assignable from its analysis, IR, $^1\text{H-NMR}$ and mass spectral data. Compound **6** gave correct elemental analyses and molecular weight determination (MS). The violet crystals of compound **6** does not dissolve in 10% aqueous NaOH and gives a negative color reaction with 1% alcoholic FeCl_3 which indicates the absence of the phenolic -OH group. The -N=N- absorption band characteristic for azo-compound⁶ (at 1570 cm^{-1}) was absent in the IR spectrum of **6**. Besides, the absorption band due to the carbonyl function which was observed in the IR spectrum of **4** at 1670 cm^{-1} , was absent in the spectrum of **6**. Moreover, the IR spectrum of compound **6** exhibited bands at 3322 cm^{-1} ($=\text{N-OH}$) and at 941 cm^{-1} ($>\text{N-O-}$). The $^1\text{H-NMR}$ spectrum of **6** (in CDCl_3) showed only a multiplet in the region δ 8.2–6.6 due to the (12H) protons on sp^2 C atoms. The -OH protons appeared as $\text{D}_2\text{O-}$ ex-

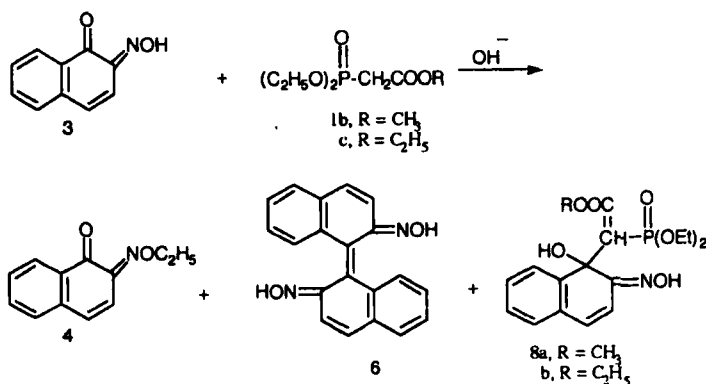
changeable singlet at 12.1 ppm. The mass spectrum of **6** showed the molecular ion peak at 314 (M^+ , $C_{20}H_{14}N_2O_2$, 40%). Loss of 2H radicals from M^+ , which is frequently observed in the behaviour of condensed aromatics under electron impact⁷, yielded the radical cation at m/z 312 (base peak). Based upon these arguments, an alternative structure⁸ like **7** can be disregarded.



A possible explanation for the course of the reaction of Wittig-Horner reagent **1a** with 2-nitroso-1-naphthol **3** is shown in Scheme 3. Wittig-Horner reagent **1a** reacts with 2-nitroso-1-naphthol **3** to give the alkylated^{3,4} product **4**, adduct **5** (possibly through alkylation followed by 1,2-addition of 2 mols of **1a**) and adduct **6** (possibly via intermediate formation of carbene followed by dimerization).

The reaction of 2-nitroso-1-naphthol **3** with methyl diethylphosphono-acetate **1b** was also investigated. When nitrosonaphthol **3** was treated with one equivalent of **1b**, in the presence of alcoholic sodium ethoxide solution for 3 hr, products **4** (25%), **6** (20%), and **8a** (40%) were isolated (Scheme 4). The structure of compounds **4** and **6** were established from comparative m.p., IR, ¹H-NMR and Mass spectroscopic data with authentic samples.

The structure of the phosphonate adduct **8a** is deduced from its IR, ¹H-NMR and mass spectral data. It gave correct elementary analyses and molecular



SCHEME 4

weight determination (MS). Its IR spectrum, in KBr, revealed the presence of strong absorption bands at 3200 cm^{-1} (C-OH), 1230 cm^{-1} (P=O, bonded)⁹, 1088 cm^{-1} (P-O-C₂H₅), >C=N at 1575 cm^{-1} , >N-O at 941 cm^{-1} , N-OH at 3322 cm^{-1} and at 1717 cm^{-1} (C=O, ester). The ¹H-NMR spectrum of **8a** disclosed the presence of signals at $\delta = 1.31$ (6H, CH₃, t) and at 4.22 (4H, CH₂, q, ³J_{CP} = 12.05 Hz) corresponding to the two ethoxy groups attached to the phosphorus atom. Moreover, the ¹H-NMR spectrum of the phosphonate adduct **8a** showed signals centered at 3 ppm (d with ²J_{HP} = 21 Hz) corresponding to the methine proton attached to the phosphorus, and at 4.5 ppm (3H, CH₃, s) corresponding to the methoxy group. The exchangeable D₂O protons (C-OH) and (N-OH) appeared as singlets at 8.9 ppm and 12.2 ppm, respectively. Compound **8a** exhibits negative color reaction with alcoholic FeCl₃ solution and does not dissolve in dilute aqueous alkali which indicates the absence of a phenolic -OH group. The mass spectrum of compound **8a** showed the molecular ion peak at m/e 383.

Similarly, when 2-nitroso-1-naphthol **3** was treated with one equivalent of triethylphosphonoacetate **1c** in the presence of alcoholic sodium ethoxide solution at 60–70° for 3 hrs, the phosphonate adduct **8b** (main product 50%), the alkylated product **4** (20%) and the dimeric compound **6** (15%) were isolated.

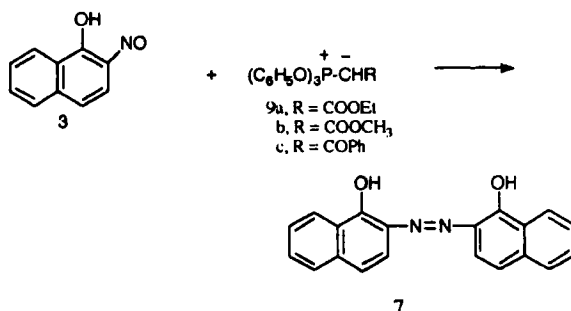
Compounds **4** and **6** are established from mixed melting points and comparative IR, ¹H-NMR and mass spectral data with authentic samples.

Compound **8b** is chromatographically pure and possesses sharp melting points. The structure assigned for compound **8b** was based on the ³¹P-NMR shift (+19.75 ppm) which corresponds to the phosphonate structure.^{10–12} The structure of compound **8b** was also deduced from its IR, ¹H-NMR and mass spectral data (cf. Experimental).

Although 2-nitroso-1-naphthol **3** has been reported⁸ to react with ylid-phosphoranes **9a–c** yielding in each case the same dimeric compound **7** (Scheme 5), a different behaviour is observed in this work in the reaction of Wittig-Horner reagents **1a–c** with the same naphthol where an addition reaction products takes place to form a new type of the phosphonate derivatives **8a,b** together with the alkylated product **4**, the olefinic compound **5** and the dimeric product **6**.

This study has been extended to include the reaction of phosphacumulene **2** with the same naphthol **3**. We have found that 2-nitroso-1-naphthol **3** reacts with two mol equivalents of 2-oxovinylidene-triphenylphosphorane **2** in tetrahydrofuran at reflux temperature to give brown crystalline product assigned structure **10** (Scheme 6). Triphenylphosphine oxide was also isolated and identified.

Compound **10** was confirmed by the following evidence: (a) Elementary analyses for compound **10** corresponded to an empirical formula of C₃₂H₂₂NO₃P. Its IR spectrum, in KBr, revealed the presence of signals at 1720,



SCHEME 5

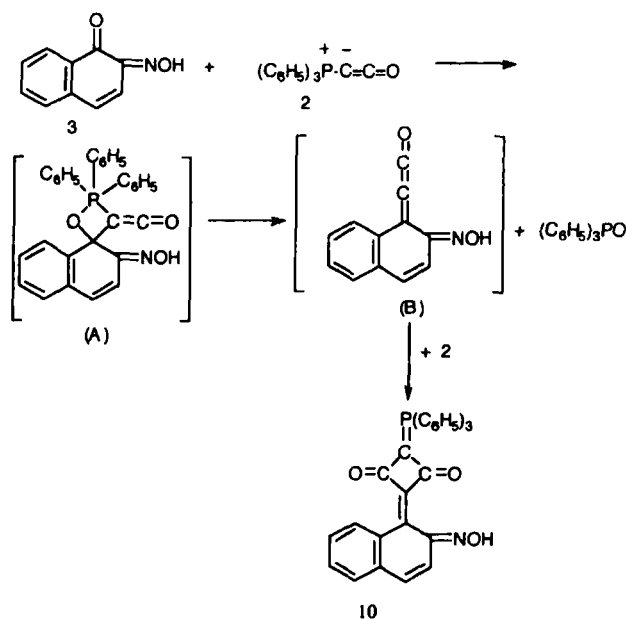
1700 (C=O), 1615 (C=P) and 1455 cm^{-1} (p-phenyl). Moreover, the PNMR spectrum of compound **10** in (CDCl_3) showed a multiplet in the region 7.4–8.6 ppm and a singlet at 8.9 ppm (exchangeable with D_2O , N-OH). The mass spectrum of compound **10** yielded a prominent ion peak at m/e 499 which is in accord with structure **10**.

Formation of phosphoranylidene-cyclobutylidene **10** occurs by the [2 + 2] cycloaddition of one carbonyl group in the quinone-oxime **3** to the ylidic C-P of the phosphacumulene **2** to give the oxaphosphetane (A) as intermediate^{13–15}. Triphenyl phosphine oxide is eliminated with the formation of the unstable ketene (B)¹⁶, which add a second molecule of the active ylide **2** by a [2 + 2]-cycloaddition to give the phosphoranylidene-cyclobutylidene **10** (Scheme 6).

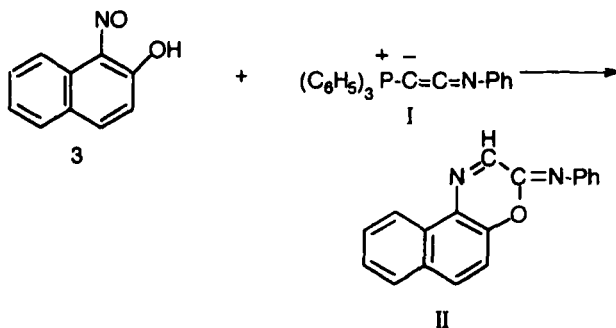
Although nitrosonaphthol has been reported¹⁷ to react with iminovinylidenetriphenylphosphorane **I** yielding adduct **II**, a different behavior is observed in this work in the reaction of 2-oxovinylidenephosphorane **2** with nitrosonaphthol **3** where [2 + 2] cycloaddition takes place to form the phosphoranylidene-cyclobutylidene **10** (Scheme 6,7).

CONCLUSION

The present study shows that 2-nitroso-1-naphthol **3** reacts with Wittig-Horner reagents **1** and phosphacumulene **2** exclusively in the quinone-oxime structure and not in the tautomeric benzenoid nitroso- form at least under the prevailing experimental conditions. Moreover, the behavior of **3** towards Wittig-Horner reagents **1** and phosphacumulenes **2** leading to phosphonates **8a,b**, alkylated product **4**, the dimeric adduct **6** and the phosphoranylidene-cyclobutylidene adduct **10** presents a new finding and supplements the wide aspects of utilization of Wittig-Horner and phosphacumulenes in preparative purposes^{18,19}.



SCHEME 6



SCHEME 7

EXPERIMENTAL

All melting points are uncorrected. Diethyl(cyanomethyl)phosphonate, methyl diethylphosphonoacetate, triethylphosphonoacetate and phosphacumulene were prepared by means of Michaelis Arbuzov reaction^{20,21,22}. IR spectra were measured in KBr with a Perkin Elmer Infracord Spectrophotometer Model 157, Grating. The ¹H-NMR spectra were run on a Varian Spectrophotometer at 270 MHz, using TMS as internal reference. The ³¹P-NMR spectra were recorded in

CDCl_3 (vs, H_3PO_4 as external standard) with a JNM-PS100 Fa Spectrometer. The mass spectra were run at 70 eV with Kratos MS equipment and/or a Varian MAT 311 A Spectrometer.

Reaction of Diethyl (Cyanomethyl) Phosphonate (1a) with 2-nitroso-1-naphthol (3)

A solution of 1 molar of sodium ethoxide in absolute ethanol was treated with an equimolar amount of the phosphonate (1a), (0.17 g, 0.001 mol), after 5 min 1 mol of 2-nitroso-1-naphthol (3) (0.17 g, 0.001 mol) was added and the resulting reaction mixture was refluxed for 4 hrs. The reaction mixture was allowed to cool to room temperature. Then poured on a small amount of water, extracted with ethyl acetate, dried and the extracts were evaporated under reduced pressure. The residue was subjected to silica gel column chromatography using the eluent state below. The melting points and yields are also given.

Compound 4, eluent: petroleum ether/benzene (90:10 v:v), as yellowish green crystals, yield (35%), m.p. 101–102°C. Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{NO}_2$ (201.207), C, 71.63; H, 5.51; N, 6.96. Found: C, 71.60; H, 5.58; N, 6.98%. (MS): 201.

Compound 5, eluent: petroleum ether/benzene (70:30, v:v), as yellow crystals, yield (30%), m.p. 133°C. Anal. Calcd. for $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_2$ (279.281), C, 68.81; H, 4.69; N, 15.04. Found: C, 68.78; H, 4.67; N, 15.01%. (MS): 279. Compound 6, eluent: petroleum ether/benzene (50:50, v:v), as a violet crystals, yield (25%), m.p. 260°C. Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2$ (314.33), C, 76.42; H, 4.49; N, 8.91. Found: C, 76.40; H, 4.47; N, 8.90. (MS): 314.

Reaction of Methyl Diethylphosphonoacetate (1b) with 2-nitroso-1-naphthol (3)

A solution of 1 molar of sodium ethoxide in absolute ethanol was treated with an equimolar amount of the phosphonate (1b), (0.21 g, 0.001 mol) after 1 mol of 2-nitroso-1-naphthol (3) (0.17 g, 0.001 mol) was added and the resulting reaction mixture was refluxed for 5 hrs. Then poured on a small amount of water, extracted with ethyl acetate, dried and the extracts were evaporated under reduced pressure. The residue was applied to silica gel column using petroleum ether: benzene (75:25, v:v) eluent to give compound (8a) as brown crystals, yield (40%), m.p. 240–241°C. Anal. Calcd. for $\text{C}_{17}\text{H}_{22}\text{NO}_7\text{P}$ (383.27), C, 53.27; H, 5.79; N, 3.65; P, 8.08. Found: C, 53.25; H, 5.76; N, 3.63; P, 8.07%. (MS): 383. Compounds 4, 6 were also isolated and identified by m.p. and mixed m.p.

Similarly triethylphosphonoacetate (**1c**) (0.22 g, 0.001 mol) reacted with 2-nitroso-1-naphthol (**3**) (0.17 g, 0.001 mol) to give **8b**, eluent benzene: petroleum ether (95:5, v:v), yield (50%), m.p. 250°C. Anal. Calcd. for $C_{18}H_{24}NO_7P$ (397.297), C, 54.42; H, 6.09; N, 3.53; P, 7.79. Found: C, 54.40; H, 6.12; N, 3.50; P, 7.76%. (MS) = 397. IR: 3202 cm^{-1} (C-OH), 1230 cm^{-1} (P=O, bonded), 1090 cm^{-1} (P-O-C₂H₅), 1570 cm^{-1} (CN), 940 cm^{-1} (N-O-), 3320 cm^{-1} (N-OH) and 1717 cm^{-1} (C=O, ester). ¹H-NMR: signals at 1.31 (t, 6H, P(OCH₂CH₃)₂), 4.2 ppm (q, 4H, P(OCH₂CH₃)₂), ³J_{HP} = 12.05 Hz), 1.40 ppm (t, 3H, COOCH₂CH₃), 4.3 (q, 2H, COOCH₂CH₃), 3.2 ppm (d, 1H, CH—P—, ²J_{HP} = 21 Hz), 8.97 ppm (s, 1H, C-OH, exchangeable with D₂O) and 12.25 ppm (s, 1H, N-OH, exchangeable with D₂O). ³¹P-NMR: δ = +19.75 ppm. Also compounds **4**, **6** were isolated and identified by m.p. and mixed m.p.

Reaction of Phosphacumulenes with 2-nitroso-1-naphthol (**3**)

To a solution of 2-nitroso-1-naphthol (**3**) (0.17 g, 0.001 mol) in dry tetrahydrofuran (30 ml) was added phosphacumulene (**2**) (0.60 g, 0.002 mol). The mixture was refluxed for 10 hrs. After evaporation of the volatile materials, in vacuum, the residual product was evaporated under reduced pressure. The residue washed with petroleum ether and cyclohexane to give adduct **10** as brown crystals, m.p. 270°C (from benzene-cyclohexane), yield (30%).

Anal. Calcd. for $C_{32}H_{22}NO_3P$ (499.48), C, 76.95; H, 4.44; N, 2.80; P, 6.20. Found: C, 76.93; H, 4.42; N, 2.78; P, 6.18%. (MS) = 499. IR: $1720, 1700\text{ cm}^{-1}$ (C=O), 1615 cm^{-1} (C=P) and 1445 cm^{-1} (P-phenyl). Triphenylphosphine oxide was also isolated and identified (mixed m.p.).

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