Pergamon

Tetrahedron, Vol. 53, No. 10, pp. 3649-3658, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00088-4

Studies on Phosphonium Ylides XXI[1]. Reactions of Wittig Reagents with Substituted 2-Amino-1,4-Naphthoquinones

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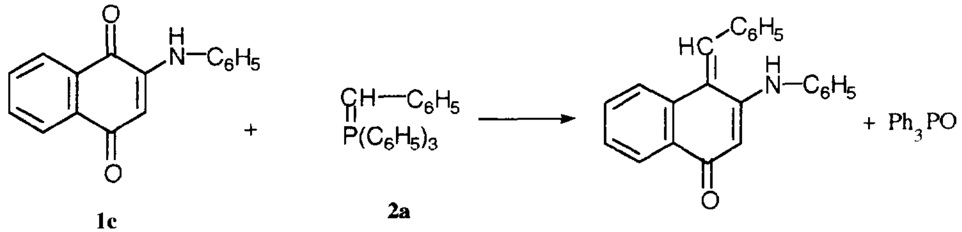
Abstract : The reaction of methoxycarbonylmethylene **2b**- and ethoxycarbonylmethylene **2c**-triphenylphosphoranes with substituted 2-amino-1,4-naphthoquinones **1a-c** afforded the new pyrroline-ylidphosphoranes **3b-3g** via 1,2- and 1,4-addition reactions. On the other hand, 2-dimethylamino-1,4-naphthoquinone **1d** reacts with cyanomethylenetriphenylphosphorane **2d** to give adduct **4**. Mechanisms accounting for the formation of the new products are discussed.

INTRODUCTION

It has been reported [2] that 2-anilino-1,4-naphthoquinone **1c** reacts with benzylidene-triphenylphosphorane **2a** yielding the respective quinonemethide **3a** and triphenylphosphine oxide (Scheme 1).



1c **2a** **3a**

Scheme 1

Our continuing interest in the reaction of phosphonium ylides for the production of novel, synthetically useful ylides and new heterocyclic systems,[1,3-11] led us to examine the behaviour of substituted 2-amino-1,4-naphthoquinones **1a-d** toward some phosphonium ylides **2b-2d**.

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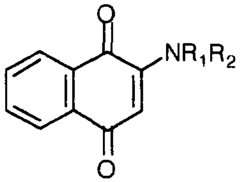
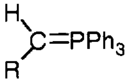


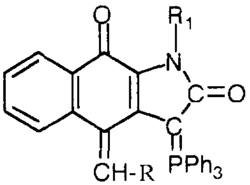
1a, R_1=H; R_2=CH_3
b, R_1=H; R_2=C_2H_5
c, R_1=H; R_2=C_6H_5
d, R_1=R_2=CH_3



2b, R=$COOCH_3$
c, R=$COOC_2H_5$
d, R=CN

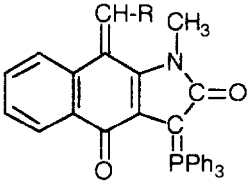
RESULTS AND DISCUSSION

When 2-methylamino-1,4-naphthoquinone **1a** was treated with one equivalent of methoxycarbonylmethylenetriphenylphosphorane **2b** in boiling benzene for 4 hrs, adduct **3b**, triphenylphosphine oxide, and the starting quinone **1a** were isolated. Carrying out the reaction using two moles of the phosphonium ylide **2b** instead of one, led to the formation of the phosphorane adduct **3b** in good yield along with triphenylphosphine oxide.



3b, R=$COOCH_3$; R_1=CH_3
c, R=$COOC_2H_5$; R_1=CH_3
d, R= $COOCH_3$; R_1=C_2H_5
e, R=$COOC_2H_5$; R_1=C_2H_5
f, R=$COOCH_3$; R_1=C_6H_5
g, R=$COOC_2H_5$; R_1=C_6H_5

Compound **3b** is chromatographically pure pink crystals and possesses a sharp melting point. Structure elucidation of the new phosphorus ylide **3b** is based on the following evidence : The IR spectrum of **3b** disclosed the presence of strong absorption bands at 1635 cm^{-1} (C=O, amide), 1670 (C=O, quinone), 1709 (C=O, ester), 1549 (C=P)[12] and at 1417 cm^{-1} (P-C(phenyl)).[13] Moreover, the IR spectrum of **3b** lacks both the C=O and -NH absorption bands appearing in the spectrum of **1a** at 1640 cm^{-1} and 3230 cm^{-1}, respectively. Adduct **3b** exhibits a positive phosphorus shift at δ 21.14 ppm (vs 85% H_3PO_4).[14] The ^1H-NMR spectrum (400 MHz) of compound **3b** shows signals centered at δ 2.89 (3H, s, N-$\underline{CH_3}$), 3.39 (3H, s, COO$\underline{CH_3}$), 6.04 (1H, s, =$\underline{CH}$COOCH$_3$), 7.35-8.23 (19H, m, Ar). Through Nuclear Overhauser Effect (NOE) techniques it has been found that irradiation of the methyl group protons of **3b** afforded no recognizable enhancement of the olefinic methine proton as well as the methyl ester protons which confirm the isomer **3b** and exclude completely the other possible isomeric form **3b**'.

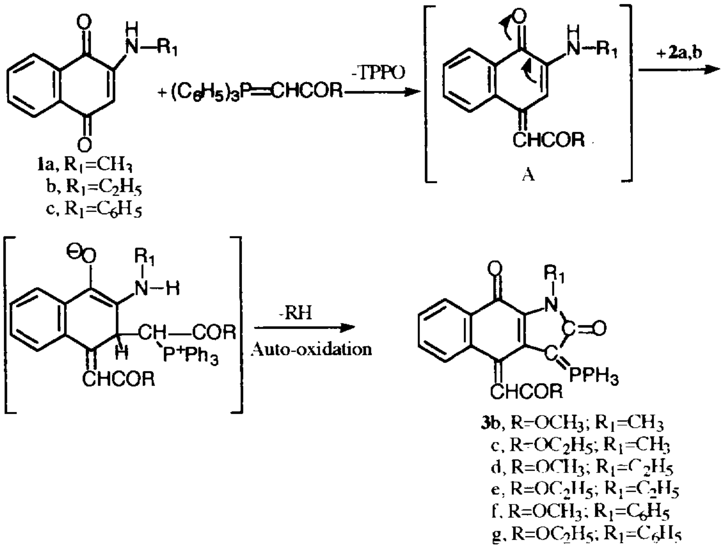


3b'

Actually, the structure assigned for compound **3b** was based on the ^{13}C-NMR which indicates the presence of three carbonyl groups at 184.8 ppm (corresponding to the C=O of the quinone), 170.2 (C=O, ester) and at 167.3 ppm (allocated to the C=O, amide), respectively. Moreover, the ^{13}C-NMR spectrum of compound **3b** reveals the presence of a doublet at 50.1 ppm ($\geq$P=C, J=125Hz).[15] The mass spectrum of 3b provided strong evidence in support of the ylid-phosphorane adduct **3b**. The mass spectrum of **3b** showed the ion peak at m/z = 543 [M$^+$].

Worthy to mention that compounds **3** are stable towards alkali and acid hydrolysis (cf. Experimental).

A possible explanation for the formation of product **3b** is illustrated in Scheme 2. Quinone **1a** reacts with 1 mol of ylide **2b** to give triphenylphosphine oxide (TPPO) and the reactive olefinic intermediate (A) via a 1,2-addition, which reacts with another molecule of ylide **2b** to afford the cyclic phosphorane adduct **3b**, through loss of a suitable moiety (i.e RH, R=OCH$_3$) followed by auto-oxidation to attain the aromaticity (due to the driving force).



Scheme 2.

2-Methylamino-1,4-naphthoquinone **1a** reacts with two equivalents of ethoxycarbonylmethylenetriphenylphosphorane **2c** in refluxing benzene to give a crystalline product that was assigned the structure **3c**. Triphenylphosphine oxide was also isolated from the reaction mixture and identified (cf. Scheme 4). On the basis of IR, ^1H, ^{13}C-NMR, MS and elemental analysis, the structure of compound **3c** was deduced. Elemental analysis and molecular weight determination (MS) of **3c** support the molecular formula $C_{35}H_{28}NO_4P$ (557.58). It showed an infrared absorption bands at 1630 cm^{-1} (C=O, amide), 1660 (C=O, quinone) and at 1710 cm^{-1} (C=O, ester). The ^1H-NMR spectrum of **3c** exhibited signals at δ 0.7 (3H, t, $COOCH_2\underline{CH_3}$), 3.87 (2H, q, $COO\underline{CH_2}CH_3$), 2.8 (3H, s, N-$\underline{CH_3}$), 5.92 (1H, s, =$\underline{CH}COOC_2H_5$), 7.35-8.22 (19H, m, Ar.). ^{13}C-NMR had signals at δ 185 ppm (C=O, quinone), 172.2 (C=O, ester), 168.3 (C=O, amide), 51.1 ppm (C=P, d, J=125 Hz).

We have found that the reaction products of 2-ethylamino-1,4-naphthoquinone **1c** with phosphonium ylides **2b,c** were assigned analogous structures **3d** and **3e**, respectively, on the basis of comparable spectroscopic arguments (IR, ^1H, ^{13}P, ^{13}C-NMR and MS, cf. Experimental).

Furthermore, this study has been extended to include the reaction of 2-anilino-1,4-naphthoquinone **1c** with the same phosphonium ylide reagents to establish whether it would behave in a similar mannar.

When 2-anilino-1,4-naphthoquinone **1c** was allowed to react with methoxycarbonylmethylenetriphenylphosphorane **2b**, in 1 : 2 molar ratio, in boiling benzene for 6 hrs, adduct **3f** was isolated in 80% yield. Triphenylphosphine oxide was also isolated from the reaction mixture and identified (cf. Scheme 2 and Experimental). The structure of the isolated compound **3f** is deduced from its analysis, ^{1}H, ^{31}P, ^{13}C-NMR and mass spectral data. Elemental and mass spectroscopic analyses for compound **3f** corresponding to an empirical formula $C_{39}H_{28}NO_4P$. Its IR spectrum (in KBr) revealed the presence of absorption bands at 1630 cm^{-1} (C=O, amide), 1670 cm^{-1}(C=O, quinone), 1712 (C=O, ester), 1496 (C=P), 1415 (P-C-(Phenyl). Moreover, its IR spectrum lacked the carbonyl absorption band appearing in the spectrum of **1c** at 1642 cm^{-1} (allocated for the C=O at 4-position).[2] The ^{1}H-NMR of **3f** exhibited signals centered at 3.4 (3H, s, $COO\underline{C}\underline{H}_3$), 5.8 (1H, s, $\underline{CH}COOCH_3$) and at δ 6.9-8.3 (m, 24H, Ar). Adduct **3f** possesses an ylide-phosphorane structure, since it exhibits a positive shift in its ^{31}P-NMR (δ =+21.34 vs 85% H_3PO_4 spectrum). Actually, the structure assigned for compound **3f** was based on the ^{13}C-NMR (400 M Hz) which indicates the presence of three carbonyl groups at δ 187 (C=O, quinone), 172 (C=O, ester) and 170 (C=O, amide). Moreover, the ^{13}C-NMR spectrum of **3f** showed signals at 28.67 ($COO\underline{C}H_3$), and 52.2 (d, P=C, J_{CP}=125 Hz).

Proton decoupled ^{13}C-NMR of compound **3f** showed 20 signals in the sp^2-C-range (103-153.6) consistent with the number of sp^2 carbon in the proposed structure taking into consideration the fact that each of the phenyl P groups appears as doublet due to splitting ($^1J_{PC}$, $^2J_{PC}$, $^3J_{PC}$ and $^4J_{PC}$, respectively). These values are in full accord with structure 3f.[15] The mass spectrum of **3f** yielded a prominent ion peak for M$^+$ at m/z 605.

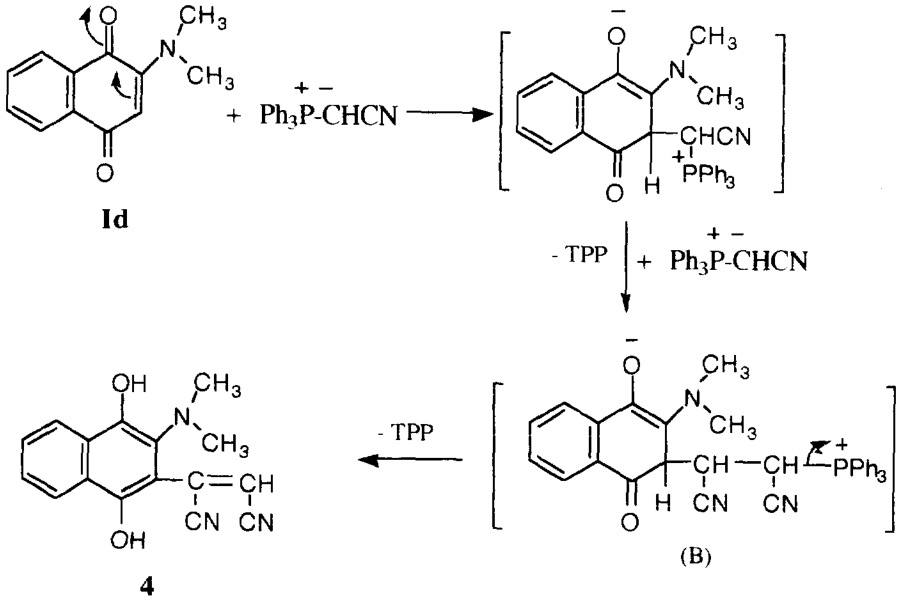
Similarly, 2-anilino-1,4-naphthoquinone **1c** reacts with two equivalents of ethoxycarbonylmethylenetriphenylphosphorane **2c** in refluxing benzene to give a pink crystalline product that was assigned the structure **3g**. Triphenylphosphine oxide was also isolated (cf. Scheme 2 and Experimental). The identity of the ylide-phosphorane adduct **3g** was deduced from its elemental analysis, IR, ^{1}H, ^{31}P, ^{13}C-NMR and mass spectral data (cf. Experimental).

From the above results, it is evident that 2-anilino-1,4-naphthoquinone **1c** behaves toward phosphonium ylides **2b,c** in a manner quite similar to that described for 2-amino-1,4-naphthoquinones **1a,b** where the pyrroline-phosphonium ylide derivatives is the sole reaction product.

The reaction of 2-dimethylamino-1,4-naphthoquinone **1d** with cyanomethylene-triphenylphosphorane **2d** was also investigated.

We have found that the reaction of 2-dimethylamino-1,4-naphthoquinone **1d** with two mol equivalents of **2d** in toluene proceeds at reflux temperature for 12 hrs. The reaction mixture was separated by column chromatography on silica gel, whereby, triphenylphosphine (TPP) as well as crystalline product **4** were isolated (Scheme 3). The structure of adduct **4** (colourless crystalline compound, m.p. 196 °C, yield 65%) was deduced from its elemental analysis and high resolution MS to possess the composition $C_{16}H_{13}N_3O_2$ (279.29, m/z=279, M^+, 75%). Its IR spectrum exhibited absorption bands at 3125 cm^{-1} (OH), 3100 (OH), 2254 cm^{-1} (CN). The ^{1}H-NMR spectrum of compound **4** shows signals at δ 5.25 (1H, =CHCN, s), 3.25 ppm (6H, $N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$, s), 7.45-8.1 (4H, m, Ar.). The two -OH protons gave two singlets (exchangeable with D_2O) at 8.08, 8.2 ppm.

A possible explanation for the course of the reaction of cyanomethylene-triphenylphosphorane **2d** with 2-dimethylamino-1,4-naphthoquinone **1d** is shown in Scheme 3. Adduct **4** can be obtained via 1,4-addition of two moles of ylide **2d** to the starting quinone **1d** yielding adduct **4**, possibly through an internal elimination of triphenylphosphine from the betaine (B).



Scheme 3.

Significantly, the reaction of Wittig reagents here are indicative of the broad reaction spectrum of which ylides are capable in addition to the usual olefin-forming reactions. Moreover, the present study clearly shows that alkylidene phosphoranes react with substituted 2-amino-1,4-naphthoquinones **4a-c** in a manner rather different from that already known.[2] Also, this finding, which represents a novel route to **3** is a supplement to the expanded utility of reagents **2** for the production of new pyrroline-phosphonium ylide derivatives **3b-3g**.

EXPERIMENTAL SECTION

All melting points are uncorrected. Benzene, toluene and petroleum ether (boiling range 60-80 °C) were dried over sodium. Methoxycarbonylmethylene-, ethoxycarbonylmethylene-[16], and cyano-methylene-triphenylphosphoranes[17] were prepared according to established procedure. The IR spectra were measured in KBr pellets on a Perkin-Elmer Infrarcord Spectrophotometer Model 157 (Grating). The ^{1}H-NMR spectra were recorded in $CDCl_3$ on a JNM-GX-400 Fa JEOL (Tokyo). The ^{31}P-NMR spectra were recorded in $CDCl_3$ (vs. H_3PO_4 as external standard) on JNM-PS-100 Fa Spectrometer. ^{13}C-NMR spectra were taken in $CDCl_3$ on Varian Spectrometer at 200 M Hz. The mass spectra were run at 70 ev on a Kratos MS instrument and/or a Varian MAT 311 Spectrometer.

Reaction of methoxycarbonylmethylenetriphenylphosphorane 2b with 2-methylamino-1,4-naphthoquinone 1a :

A mixture of 1,4-naphthoquinone **1a** (0.18 g, 0.001 mol), ylide **2b** (0.66 g, 0.002 mol), and dry benzene (30 ml) were refluxed for 4 hrs. The volatile materials were evaporated under reduced pressure, the residual substance was purified by silica gel column chromatography using diethyl ether / petroleum ether (60 : 40 , v : v) as eluent to give **3b** as pink crystals; m.p. 202 °C (yield 68%). Anal. Calcd. for $C_{34}H_{26}NO_4P$ (543.55) : C, 75.13; H, 4.82; N, 2.57; P, 5.69. Found : C, 75.22; H, 4.9, N; 2.5, P; 5.73. IR (KBr) : 1635, 1670, 1709, 1549, 1417 cm^{-1}. ^{1}H-NMR ($CDCl_3$) : signals at 2.89 ppm (s, 3H, N-$\underline{CH_3}$), 3.39 (s, 3H, COO$\underline{CH_3}$), 6.04 (s, 1H, =$CHCOOCH_3$), 7.35-8.23 (19H. m). ^{31}P-NMR : δ=+21.14. ^{13}C-NMR ($CDCl_3$) : 184.5 (C=O. quinone), 170.2 (C=O, ester), 167.3 (C=O. amide), 50.1 ppm (P=C, J=125 Hz). MS : m/z (%) 543 (75) [M^+].

Similarly, 2-methylamino-1,4-naphthoquinone **1a** (0.18 g, 0.001 mol) was reacted with ylide **2c** (0.69 g, 0.002 mol) in 30 ml of dry benzene to give compound **3c** (eluent, diethyl ether / petroleum ether (40 : 60 V : v), m.p. 198 °C (yield 70%). Anal. Calc. for $C_{35}H_{28}NO_4P$ (557.58) : C, 75.39; H, 5.06; N, 2.51; P, 5.55. Found : C, 75.30; H, 5.13; N, 2.55; P, 5.60. IR (KBr) : 1630, 1675, 1710, 1544, 1417 cm^{-1}. ^1H-NMR ($CDCl_3$) : signals at 0.07 (t, 3H, $COOCH_2\underline{CH_3}$), 3.87 (q, 2H, $COO\underline{CH_2}CH_3$), 2.8 (s, 3H, N-$\underline{CH_3}$). 5.92 (s, 1H, =$\underline{CH}COOC_2H_5$), and at 7.35-8.22 ppm (19H, m). ^{31}P-NMR : δ =+ 21.04. ^{13}C-NMR ($CDCl_3$) : δ 185 (C=O, quinone), 172.2 (C=O, ester), 168.3 (C=O, amide) and at 51.1 ppm (C=P, J=125 Hz). MS : m/z (%) 557 (80) [M^+].

Reaction of methoxycarbonylmethylenetriphenylphosphorane 2b with 2-ethylamino-1,4-naphthoquinone 1b :

A mixture of **1b** (0.20 g, 0.001 mol), ylide **2b** (0.66 g, 0.002 mol) and dry benzene (30 ml) were refluxed for 4 hrs. The volatile materials were evaporated in vacuo and the residual substances was chromatographed on a silica gel column using diethyl ether / petroleum ether (50 : 50, v :v) as eluent to give **3d** as pink crystals, m.p. 197 °C (yield 73%). Anal. Calcd. for $C_{35}H_{28}NO_4P$ (557.58) : C, 75.39; H, 5.06; N, 2.51; P, 5.55. Found : C, 75.43; H, 5.12; N, 2.48; P, 5.50. IR in (KBr) : 1635, 1660, 1719, 1535 cm^{-1}. ^1H-NMR ($CDCl_3$) : δ = 3.4 (s, 3H, $COO\underline{CH_3}$), 0.75 (t, 3H, N-$CH_2\underline{CH_3}$), 3.3 (q, 2H, N-$\underline{CH_2}CH_3$), 5.8 (s, 1H, =$\underline{CH}COOCH_3$) and at 7.2-8.2 ppm (19H, m, Ar). ^{31}P-NMR : δ = + 20.2. ^{13}C-NMR ($CDCl_3$) : δ 185 (C=O, quinone), 170 (C=O, ester), 168.3 (C=O, amide) and at 48.7 ppm (P=C, J=125 Hz). MS : m/z (%) 557 (70) [M^+].

Similarly, 2-ethylamino-1,4-naphthoquinone **1b** (0.20 g, 0.001 mol) was reacted with ylide **2c** (0.69 g, 0.002 mol) in 30 ml dry benzene to give **3e** as pink crystals, m.p. 220 °C, yield (75%). Anal. Calcd. for $C_{36}H_{30}NO_4P$ (571.61) : C, 75.64; H, 5.29; N, 2.45; P, 5.42. Found : C, 75.73; H, 5.34; N, 2.40; P, 5.50. IR (KBr) : 1635, 1662, 1706, 1544 cm^{-1}. ^1H-NMR : δ =0.8 (t, 3H, $COOCH_2\underline{CH_3}$), 3.85 (q, 2H, $COO\underline{CH_2}CH_3$), 0.7 (t, 3H, N-$CH_2\underline{CH_3}$), 3.3 (q, 2H, N-$\underline{CH_2}CH_3$), 5.3 (s, 1H, =$\underline{CH}COOC2H5$) and at 7.35-8.2 (19H, m, Ar.). ^{31}P-NMR : δ = + 20.45. ^{13}C-NMR : δ 185.5 (C=O, quinone), 170.3 (C=O, ester), 167.4 (C=O, amide) and at 50.7 ppm (P=C, J=125 Hz). MS : m/z (%) 571 (80) [M^+].

Reaction of methoxycarbonylmethylenetriphenylphosphorane 2b with 2-anilino-1,4-naphthoquinone 1c :

A mixture of **1c** (0.24 g, 0.001 mol), ylide **2b** (0.66 g, 0.002 mol) and dry benzene were refluxed for 6 hrs. The volatile material was evaporated in vacuo and the residual substance was chromatographed on a silica gel column using ethyl acetate / petroleum ether (25 : 75, v : v) as eluent to give **3f** as violet crystalline product, m.p. 195-196 °C (yield 82%). Anal. Calcd. for $C_{39}H_{28}NO_4P$ (605.63) : C, 77.35; H, 4.66; N, 2.31; P, 5.11. Found : C 77.43; H, 4.70; N, 2.30; P 5.06. IR (KBr) : 1630, 1670, 1712, 1496, 1415 cm^{-1}. ^1H-NMR ($CDCl_3$) : δ =3.4 (3H, s, $COO\underline{CH_3}$), 5.8 (1H, s, $\underline{CH}COOCH_3$) and at 6.9-8.3 (24 H, m, Ar.). ^{31}P-NMR: δ = + 21.34. ^{13}C-NMR : δ 187 (C=O, quinone), 172 (C=O, ester), 170 (C=O, amide), 28.67 ($COO\underline{C}H_3$) and at 52.2 (P=C, J=125 Hz). MS : m/z (%) 605 (100%) [M^+].

Similarly, **3g** was obtained as pink crystals, m.p. 218-220 °C (yield 80%). Anal. Calcd. for $C_{40}H_{30}NO_4P$ (619.65) : C, 77.53; H, 4.88; N, 2.26; P, 4.99. Found : C, 77.60; H, 4.93; N, 2.21; P, 4.87. IR (KBr) : 1630, 1660, 1719, 1498, 1417 cm^{-1}. ^1H-NMR : δ =0.65 (t, 3H, $COOCH_2\underline{CH_3}$), 3.85 (q, 2H, $COO\underline{CH_2}CH_3$), 5.8 (s, 1H, $=\underline{CH}COOC_2H_5$) and at 6.9-8.3 (24H, m, Ar.).^{31}P-NMR : δ =+ 21.14. ^{13}C-NMR : δ 184.4 (C=O, quinone), 170.2 (C=O, ester), 167.3 (C=O, amide), 48.1 (d, P=C, J=125 Hz) and at 14.4, 58.9 (OEt). MS : m/z (%) 619 (100%) [M^+].

Alkali and acid hydrolysis of compound 3b :

Compound **3b** (0.05 g) was added to 20 ml of 10% NaOH solution and the reaction mixture was refluxed for 10 hours. The precipitated material was filtered off, washed with n-hexane to give pink crystals of **3b** (m.p. and mixed m.p.). Similarly, acid hydrolysis was carried out using 10% HCl to give unchanged **3b** (m.p. and mixed m.p.).

Reaction of cyanomethylenetriphenylphosphorane 2d with 2-dimethyl-amino-1,4-naphthoquinone 1d :

A mixture of **1d** (0.20 g, 0.001 mol), ylide **2d** (0.60 g, 0.002 mol) and dry toluene were refluxed for 12 hrs. The volatile material was evaporated in vacuo and the residual substance was chromatographed on a silica gel column using acetone / petroleum ether (25 : 75, v : v) as eluents to give **4** as colourless crystals, m.p. 196 °C (yield 60%). Anal. Calcd. for $C_{16}H_{13}N_3O_2$ (279.29) : C, 68.80; H, 4.69; N, 15.05. Found : C, 68.82; H, 4.66; N, 15.1. IR (KBr) : 3125, 3100, 2245 cm^{-1}. ^1H-NMR : 3.25 (s, 6H, $N(CH_3)_2$), 5.25 (s, 1H, =CHCN), 6.45-8.10 (4H, m, Ar.), and at 8.08, 8.2 (s, 2(OH) exchangeable with D_2O. MS : m/z (%) 279 (75%) [M^+]. Colourless crystals were also isolated and proved to be triphenyl phosphine.

References and Notes

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(*Received in UK* 6 *September* 1996; *revised* 21 *January* 1997; *accepted* 23 *January* 1997)