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Studies on Phosphonium Ylides XX. The Behavior of Wittig Reagents toward 1,4-Benzoquinone Monoimines

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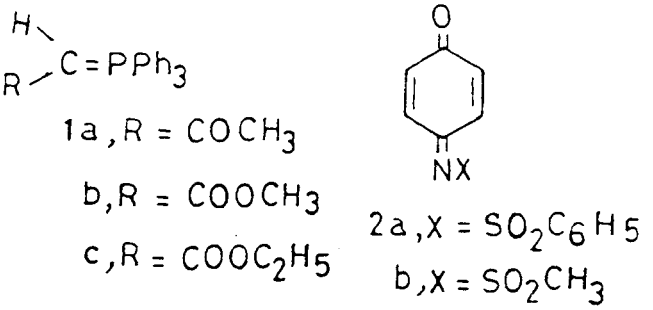
ABSTRACT

*Wittig reagents (**1a–c**) react with N-(phenylsulfonyl)-1,4-benzoquinone monoimine **2a** to give adducts **3a**, **4a**, and **4b**. On the other hand, the reactions of **2b** with the same ylides (**1a–c**) yield the new products **3b**, **6a**, and **6b**, respectively. Mechanisms accounting for the formation of the new products are discussed and the probable structures of the products are presented, based on compatible analytical and spectral data.*

INTRODUCTION

During the course of our studies on the behavior of 1,4-benzoquinone monoimines **2** toward organophosphorus compounds [1–3], we concluded that alkyl phosphites [1,2], the Lawesson reagent, and phosphorus pentasulfide [3] preferentially attack the carbonyl oxygen of p-quinone monoimines **2** rather than the imino groups. Moreover, we have reported [1,2] that *N*-(methylsulfonyl)-1,4-benzoquinone monoimine **2b** behaves toward alkyl phosphites in a different manner than that found for *N*-(phenylsulfonyl)-1,4-benzoquinone monoimine **2a** with the same alkyl phosphites. This prompted us to study the reactivity of the same quinone monoimines **2** toward Wittig reagents **1**.



RESULTS AND DISCUSSION

When *N*-(phenylsulfonyl)-1,4-benzoquinone monoimine (**2a**) was treated with 1 equivalent of acetylmethylenetriphenylphosphorane (**1a**) in benzene at room temperature for 6 hours, adduct **3a** and triphenylphosphine oxide were isolated in good yields (Scheme 1). Compound **3a** is chromatographically pure and possesses a sharp melting point.

The IR spectrum of 2,6-bis-*N*-(phenylsulfonyl)-9,10-diacetylanthracene (**3a**) revealed the presence of strong absorption bands at 3250 (NH), 1740 (C=O, acetyl), 1600 (C=C, Ar), and 1347, 1180 cm^{-1} (SO_2). Moreover, its IR spectrum lacks the carbonyl and C=N absorption bands appearing in the spectrum of **2a** at 1656 and 1586 cm^{-1}, respectively. The ^1H NMR spectrum (400 MHz) of **3a** exhibits signals centered at δ 6.88, 6.92 (dd, 2H with Jab = Ja'b' = 6.6 Hz, Jac = Ja'c' = 2.1 Hz corresponding to H-a and H-a'). The two protons at b, b' appeared as a doublet centered at δ 7.34 with Jba = Jb'a' = 6.6 Hz, Hc, and c' protons appeared as a doublet centered at 7.22 with Jca = Jc'a' = 2.1 Hz. The spectrum shows a singlet at δ 2.5 (s, 6H, $2CO\underline{CH_3}$)

Dedicated to Prof. Dr. Hans Jurgen Bestmann on the occasion of his sixty-ninth birthday.

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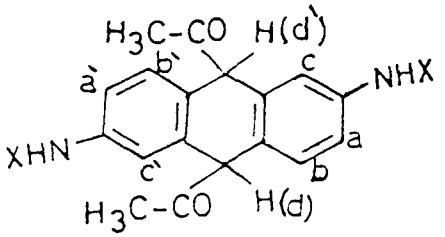


3a, X = $SO_2C_6H_5$

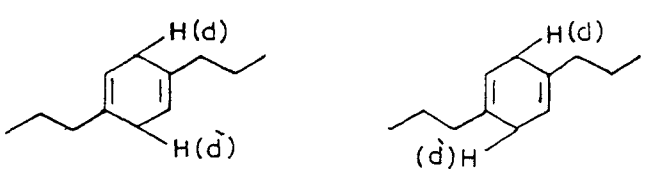
b, X = SO_2CH_3

SCHEME 1

and at 10 (s, 2NH, exchangeable with D_2O). The two methine protons at d, d' appeared as two singlets at δ 6.49 and 6.51. The presence of two delta singlets in the ^1H NMR spectrum of **3a** can positively confirm the presence of the isomer (**A**) rather than the other possible alternative isomer (**B**), which would predict one singlet for the two protons Hd and Hd', respectively (Scheme 2).

Actually, the mass spectrum of compound **3a** by the field ionization method yielded a prominent ion peak M^+ at 574, which supports structure **3a**. Formation of the diacetylanthracene derivative **3a** can be explained in terms of carbonyl olefination of **2a** by the Wittig reagent **1a** to give the reactive intermediate (**D**) with expulsion of triphenylphosphine oxide. Dimerization [4,5] of the unstable reactive intermediate (**D**) resulted in the formation of the unstable dimeric form (**E**). A possible reaction mechanism is suggested to illustrate the transformation of the dimeric form (**E**) to the final product **3a** (via successive 1,2-alkyl shifts in **E** followed by 1,4-H shifts) (Scheme 3).

N-(phenylsulfonyl)-1,4-benzoquinone monoimine (**2a**) reacts with two equivalents of carbomethoxymethylenetriphenylphosphorane **1b** at room temperature to give the product assigned structure **4a** (Scheme 4). Triphenylphosphine was also isolated and identified. The isolated product (85%) was assigned structure **4a**, because its ^{31}P NMR spectrum (in $CDCl_3$) showed a signal at δ = +20.28 that agrees with ylide structure [6]. Moreover, the ^1H NMR spectrum of **4a** (in $CDCl_3$) showed a signal at δ 3.6 (d, ^1H, $^3J_{HP}$ = 10.5 Hz) corresponding to the methine proton. The two methoxy groups appeared as two singlets centered at 3.3 (s, 3H, $COOCH_3$) and 3.4 (s, 3H, $COOCH_3$). The exchangeable (D_2O) protons [(NH) and (OH)] appeared as signals at δ 8.5 and 9.3, respectively. The aromatic protons appeared as a multiplet at δ 6.4–7.9 (23H). The main features of the IR spectrum of **4a** (in KBr, expressed in cm^{-1}) were the presence of absorption bands at 3400 (OH), 3300 (NH), 1730 (C=O, ester), and 1600 (C=C, Ar). The spectrum also revealed the presence of strong bands around 1680 and 1510 cm^{-1}, characteristic of the C=P group absorption [7] and at 1430, 990 cm^{-1} for the p-C(phenyl) absorption. Moreover, the strong absorption bands at 1586 and 1665 cm^{-1} recorded for the C=N and C=O groups in quinone monoimine **2a** are absent in the IR spectrum of **4a**. In the mass spectrum of **4a**, the m/e = 653 (M^+, 75%).



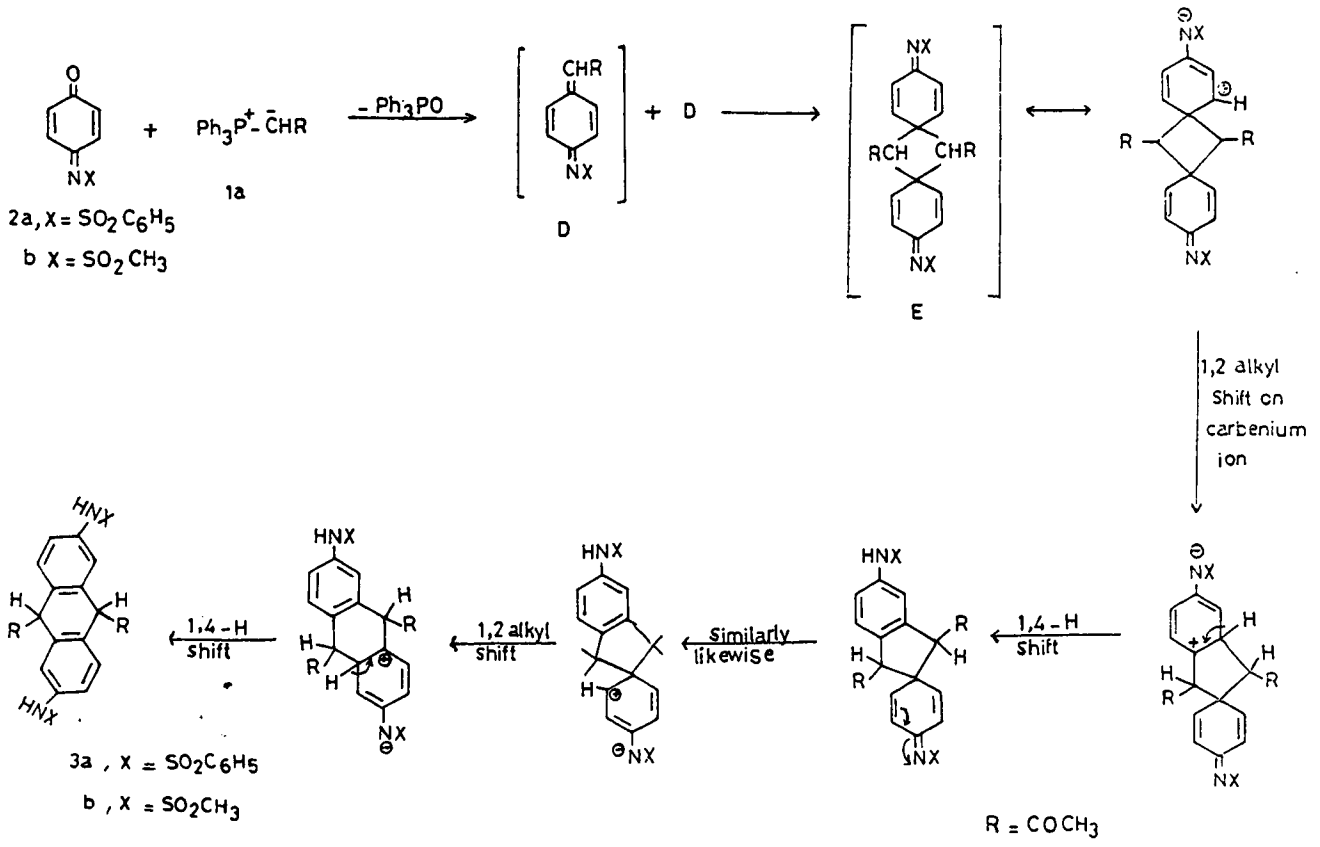
SCHEME 2

Treatment of the ylide-phosphorane adduct **4a** with benzoic acid brought about an elimination reaction [8] that resulted in the formation of the *trans* and *cis* isomeric compounds **5a** and **5b**, respectively [9] (Scheme 4). Melting points and ^1H NMR and mass spectroscopic data of **5a** and **5b** are given (cf. the Experimental section). Alkaline hydrolysis of adduct **4a** gave rise to p-aminophenol (**5c**).

A possible explanation for the course of the reaction of the phosphonium ylide **1b** with quinone monoimine **2a** is shown in Scheme 4. Quinone monoimine **2a** reacts with 1 mol of ylide **1b** to give triphenylphosphine and the reactive intermediate (**A**) via a 1,4-addition, and this reacts with another molecule of ylide **1b** to afford the stable ylide-phosphorane **4a** (Scheme 4) [9].

Similarly, carbethoxymethylenetriphenylphosphorane (**1c**) reacts with *N*-(phenylsulfonyl)-1,4-benzoquinone monoimine (**2a**) in benzene at room temperature for 6 hours to give a colorless crystalline product that was assigned the structure **4b**. Triphenylphosphine was also isolated from the reaction mixture and identified (cf. Scheme 4). On the basis of IR, ^1H NMR, ^{31}P NMR, MS, and elemental analyses, the structure of compound **4b** was deduced.

Adduct **4b** possesses an ylide-phosphorane structure, since it exhibits a positive shift in its ^{31}P NMR (δ = +20.2 vs. 85% H_3PO_4) spectrum in the region characteristic for this class of compounds [6]. The IR spectrum of **4b** exhibited strong absorption bands of 1670 and 1500 cm^{-1} characteristic for the C=P group absorption, 1410 cm^{-1} for the P–C (phenyl) absorption [7], and at 3300 (NH), 1730 (C=O, ester). The ^1H NMR spectrum of adduct **4b** (200 MHz) showed two triplets at δ 0.7 (3H, $COOCH_2\underline{CH_3}$) and 1.22 (3H, $COOCH_2\underline{CH_3}$) and two quintets centered at 3.8 (2H, $COOCH_2CH_3$) and 4.05 (2H, $COOCH_2CH_3$) for the two ethoxyl groups. The methine proton appeared as a doublet centered at



SCHEME 3

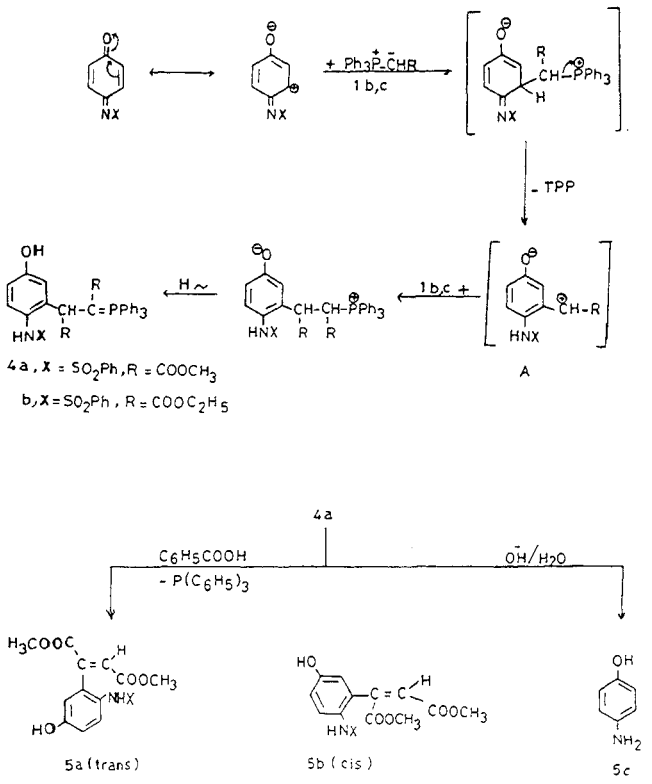
δ 3.4 with $^3J_{HP}$ = 10 Hz. The aromatic protons appeared as a multiplet in the region δ 7–7.9. The exchangeable D_2O proton (NH) appeared as a singlet at 8.7. In the mass spectrum of **4b**, the m/e = 681 (M^+) (field ionization method).

Furthermore, this study has been extended to include the reaction of *N*-(methylsulfonyl)-1,4-benzoquinone monoimine (**2b**) with the same ylide reagents (**1a–c**) to establish whether it would behave in a similar manner.

We have treated *N*-(methylsulfonyl)-1,4,-benzoquinone monoimine (**2b**) with an equimolar amount of acetylmethylenetriphenylphosphorane **1a** in absolute benzene at room temperature for 8 hours. The reaction mixture was separated by column chromatography on silica gel, whereby, triphenylphosphine oxide, as well as two crystalline products **3b** and **6a**, was isolated (Schemes 1 and 5).

The first product was obtained as colorless crystals in 55% yield and was formulated as 2,6-bis-N-(methylsulfonyl)-9,10-diacetylanthracene (**3b**) for the following reasons. (1) Elemental and mass spectroscopic analyses (by the field ionization method) for compound **3b** corresponded to an empirical formula $C_{20}H_{22}N_2O_6S_2$. (2) Its IR spectrum (in KBr) revealed the presence of strong absorption bands at 3314 (NH), 1746 (C=O, acetyl), 1600 (C=C, Ar), and 1347, 1185 cm^{-1} (SO_2). Moreover, its IR spectrum lacked the carbonyl and C=N absorption bands appearing in the spectrum of **2b** at 1656 and 1586 cm^{-1}, respectively. The ^1H NMR spectrum (400 MHz) of compound **3b** exhibited signals centered at δ 7.2 and 7.23 (2H, dd with Jab = Ja'b' = 8.54 Hz, Ja, c = Ha',c' = 2.44 Hz) corresponding to the hydrogen protons in positions a and a', at δ 7.47 (2H, d with Jba = Jb'a' = 8.54 Hz) corresponding to the hydrogen protons at b' and at δ 7.55 (2H, d with Jca = Jc'a' = 2.44 Hz) corresponding to the hydrogen protons at c and c'. The two methine protons (Hd, d') appeared as two singlets at δ 6.48 and 6.47. Moreover, it showed signals at 2.58 (s, 6H, $2COC\underline{H}_3$), 3.15 (s, 6H, $2SO_2C\underline{H}_3$), and 7.9 (s, 2NH exchangeable with D_2O). The ^{13}C NMR spectrum of **3b** in $CDCl_3$ showed signals at δ 113.3 (C-1), 132.2 (C-2), 116.6 (C-3), 120.5 (C-4), 133.2 (C-4'), 136 (C-1'), 104.7 (C-9), 167.5 ($COCH_3$), 15.8 ($CO\underline{C}H_3$), and 40.5 ($SO_2\underline{C}H_3$) (Scheme 5). A possible explanation for the formation of product **3b** is illustrated in Scheme 3.

The structure of the other isolated product **6a** (colorless crystalline compound, mp 146–147°C, yield 15%) was deduced from its elemental analysis and high resolution MS to possess the com-



SCHEME 4

position $C_{13}H_{15}NO_4S$ (281.279, m/z = 281, M^+). Its IR spectrum exhibited absorption bands at 3224 (NH), 1717, 1730 (C=O, acetyl $COCH_3$), 1594 (C=C), and 1610 cm^{-1} (C=CH). In its ^1H NMR spectrum (δ), the aromatic multiplet centered at 7.4 corresponded to four protons (m, 4H, Ar), and the singlet at 6.45 (s, 1H) was attributed to the (C=CH) methine proton. The chemical shift recorded for the methine proton suggested the *cis* form rather than the *trans* one, which would require a downfield chemical shift [9] (cf. the ^1H NMR spectrum of **5a**). The two methyl protons of the acetyl groups appeared as two singlets at 2.42 (s, 3H) and 2.48 (s, 3H). The methyl protons of the methylsulfonyl group appeared as a singlet at 3 (s, 3H). Moreover, the spectrum of product **6a** showed a signal at δ 8 (s, NH, exchangeable with D_2O). It is worth mentioning that, when quinone monoimine **2b** was reacted with 2 mol of the phosphonium ylide **1a**, adducts **3b** (65%) and **6a** (25%) were isolated in good yields.

N-(methylsulfonyl)-1,4-benzoquinone monoimine (**2b**) reacted with 2 equivalents of carbmethoxymethylenetriphenylphosphorane (**1b**) in refluxing benzene for 8 hours to give a colorless crystalline compound that was assigned structure **6b**. Triphenylphosphine was also isolated from the reaction mixture and identified (Scheme 5).

The structure of the new compound **6b** is indicated by its analysis, IR, ^1H NMR, and mass spectral data. The main features of the IR spectrum of **6b** (in KBr) were the presence of absorption bands at 3574 (OH), 3258 (NH), 1736 (C=O, ester), and 1617 cm^{-1} (C=C, Ar). The ^1H NMR spectrum of **6b** (in $CDCl_3$, δ) showed signals at 3.5 (s, 3H, $COOCH_3$), 3.8 (s, 3H, $COO\underline{CH_3}$ for the two methoxy groups), and 3.0 (s, 3H, $SO_2\underline{CH_3}$). Moreover, signals were present at 6.8 (s, 1H, =CH), 8 (s, 1H, NH), and 9 (s, 1H, OH). Shielding leads to a lowering of processional frequency, i.e., to a lower chemical shift value. Hence, the chemical shift at δ 6.8 for the methine proton suggests the *trans* isomeric form (cf. the ^1H NMR spectrum of **5b**). The familiar pattern of the aromatic protons was represented by signals at 7.2–7.6 (m, 3H, Ar). The mass spectrum of **6b** yielded a prominent ion peak for M^+ at m/e 329 (25%).

Similarly, carbethoxymethylenetriphenylphosphorane (**1c**) reacted with **2b** to give adduct **6c** and triphenylphosphine. The structure of **6c** was deduced from its analysis, IR, ^1H NMR, and mass spectral data (cf. the Experimental Section).

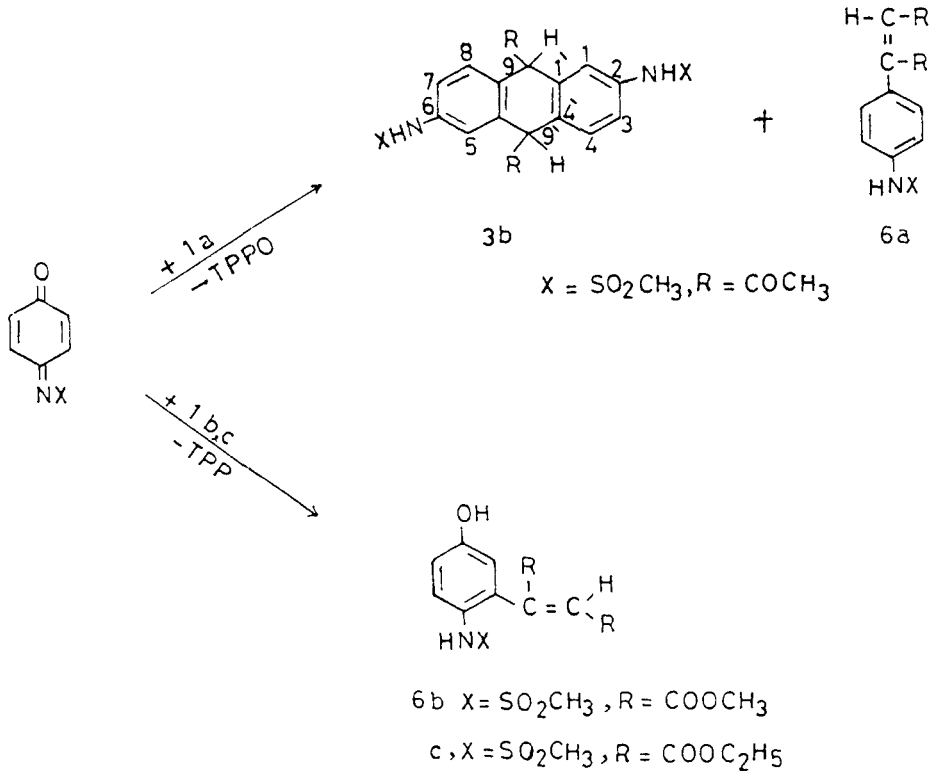
CONCLUSIONS

Although p-quinone diimines **7**, **8** have been reported [10–12] to react with Wittig reagents to give (1:1) adducts **9**, **10**, a different behavior is observed in the reaction of quinone monoimines **2** with the same reagent (Scheme 6)

Based on the results of the present investigation, it could be inferred that Wittig reagents preferentially attack the carbonyl oxygen of p-benzoquinone monoimines **2a,b** to yield mainly the 1:4 and/or 1:6 addition products, depending on the ylide reagents [13,14] as well as on the stability of the reaction products. Moreover, the disparity in the behavior of the two quinone monoimines **2a** and **2b** toward Wittig reagents is in accord with that previously reported [1,2] for the reactions with alkyl phosphites.

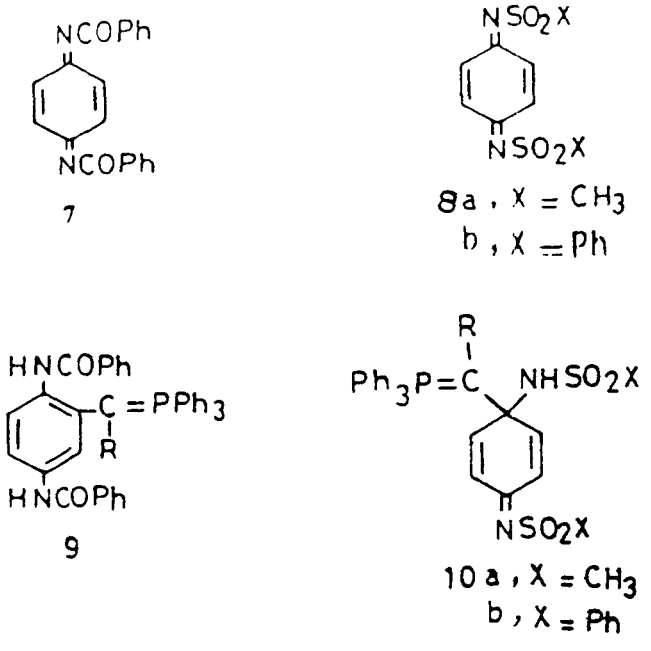
EXPERIMENTAL SECTION

All melting points are uncorrected. Benzene (thiophene-free) and petroleum ether (boiling range, 60–80°C) were dried over sodium. Acetylmethylene-[15,16]carbomethoxymethylene-, and carbethoxymethylenetriphenylphosphoranes [1,2] were prepared according to established procedures. The IR spectra were measured in KBr pellets on a Perkin-Elmer Infracord Spectrophotometer Model 157 (Grating). The ^1H NMR spectra were recorded in $CDCl_3$ on a JNM-GX-400Fa JEOL Spectrometer (Tokyo). The ^{31}P NMR spectra were recorded in $CDCl_3$ (vs. H_3PO_4 as external standard) on a JNM-PS-100Fa Spectrometer. ^{13}C NMR spectra were taken in $CDCl_3$ on a Varian Spectrometer at 200 MHz. The mass spectra were run at 70 eV on a Kratos MS instrument and/or a Varian MAT 311A Spectrometer.



Reaction of Acetylmethylenetriphenylphosphorane (**1a**) *with N-(Phenylsulfonyl)-1,4-benzoquinone Monoimine* (**2a**)

A mixture of **2a** (0.24 g, 0.001 mol), ylide **1a** (0.31 g, 0.001 mol), and dry benzene (30 mL) was stirred for 6 hours. The volatile materials were evaporated under reduced pressure, and the residual substance was chromatographed on a silica gel column using acetone/petroleum ether (40:60 v:v) as eluent to give 2,6-bis-*N*-(phenylsulfonyl)-9,10-diacetylanthracene (**3a**) as colorless crystals, mp 136–138°C (yield 65%). Anal. calcd for $C_{30}H_{26}N_2O_6S_2$ (574.67): C, 62.70; H, 4.56; N, 4.87; S, 11.16. Found: C, 62.68; H, 4.54; N, 4.85; S, 11.15%. MS = 574 IR: 3250 cm^{-1} (NH), 1740 cm^{-1} (C=O, acetyl), 1600 cm^{-1} (C=C, Ar), and 1347, 1180 cm^{-1} (SO_2). ^1H NMR: signals at δ 6.88, 6.92 (dd, 2H, Ja,b = Ja′,b′ = 6.6 Hz; Ja,c = Ja′,c′ = 2.1 Hz Ha,a′), δ 7.34 (d, 1H, Jb,a = Jb′,a′ = 6.6 Hz, H-b,b′), δ 7.22 (d, 1H, Jc,a = Jc′,a′ = 2.1 Hz, H-c,c′), two singlets at δ 6.49 and 6.51 (2H, =CH, H-d,d′), 2.5 (s, 6H, $2COCH_3$), and 10.0 (s, 2NH, exchangeable with D_2O). Triphenylphosphine oxide was also isolated and identified.



SCHEME 6

Reaction of Carbomethoxymethylenetriphenylphosphorane (**1b**) *with N-(Phenylsulfonyl)-1,4-benzoquinone Monoimine* (**2a**)

To a solution of the quinone monoimine **2a** (0.24 g, 0.001 mol) in dry benzene (20 mL) was added a solution of the ylide **1b** (0.66 g, 0.002 mol) in benzene, and the reaction mixture was left at room temperature under stirring for 8 hours. The colorless material that had precipitated was filtered off, washed with benzene and then ethyl acetate,

and recrystallized from tetrahydrofuran-cyclohexane to give compound **4a**, as colorless crystals, mp 201–202°C (yield 85%). Anal. calcd for $C_{36}H_{32}NO_7PS$ (653.689): C, 66.14; H, 4.93; N, 2.14; P, 4.73; S, 4.90. Found: C, 66.12; H, 4.90; N, 2.10; P, 4.70; S, 4.93%. MS = 653 IR: 3400 cm^{-1} (OH), 3300 cm^{-1} (NH), 1730 cm^{-1} (C=O, ester), 1600 cm^{-1} (C=C, Ar), 1680, 1510 cm^{-1} (C=P), and 1430, 990 cm^{-1} [P–C (phenyl)]. ^1H NMR: signals at δ 3.6 (d, 1H, $^3J_{HP}$ = 10.5 Hz, CH–CP), 3.3 (s, 3H, $COOCH_3$), 3.4 (s, 3H, $COOCH_3$), 8.5 (s, 1H, NH, exchangeable with D_2O), 9.3 (s, 1H, OH, exchangeable with D_2O), and 6.4–7.9 (m, 23H, Ar). ^{31}P NMR: δ = +20.28. Triphenylphosphine was also isolated and identified.

Action of Benzoic Acid on **4a**

To a suspension of **4a** (0.2 g) in tetrahydrofuran (30 mL) was added benzoic acid (0.24 g, 0.002 mol), and the reaction mixture was refluxed for 8 hours. The volatile materials were removed under reduced pressure, and the residual substance was applied to silica gel column chromatography using ethyl acetate/petroleum ether as eluent.

Triphenylphosphine was isolated (5:95) and identified (mixed mp and comparison of IR spectra). Benzoic acid was recovered (10:90) and identified.

Adduct **5a** was separated (40:60) as colorless crystals, mp 155°C. Anal. calcd for $C_{18}H_{17}NO_7S$ (391.39): C, 55.24; H, 4.38; N, 3.58, S, 8.19. Found: C, 55.2; H, 4.13; N, 3.45, S, 8.1%. MS = 391 IR: 3430 cm^{-1} (OH) and 3260 cm^{-1} (NH). ^1H NMR: signals at δ 6.82 (s, 1H, =CH), 3.6 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 9.1 (s, 1H, OH), and 8.2 (s, 1H, NH). Adduct **5b** was isolated (50:50) as colorless crystals, mp 165°C (*cis* isomeric form). Anal. calcd for $C_{18}H_{17}NO_7S$ (391.39): C, 55.24; H, 4.38; N, 3.58; S, 8.19. Found: C, 55.15; H, 4.24; N; 3.32; S, 8.12%. MS = 391 IR: 3330 cm^{-1} (NH), 3400 cm^{-1} (OH). ^1H NMR: signals at δ 6.28 (s, 1H, =CH), 3.80 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 8.3 (s, NH), and 9.4 (s, OH).

Alkaline Hydrolysis of **4a**

To a solution of **4a** (0.1 g) in 0.5 mL pyridine a 2N sodium hydroxide solution (0.1 mL) was added with a few drops of distilled water to obtain a homogeneous solution. The reaction mixture was refluxed for 8 hours, then the volatile materials evaporated and the residue diluted by distilled water. The solution was warmed briefly and then cooled. Triphenylphosphine oxide was filtered off and identified. The filtrate was washed with benzene, and the benzene layer was removed. To the filtrate a few drops of sulfuric acid were added until a pH = 2–3 was achieved, and then it was extracted with diethyl ether and left at room temperature for 16 hours. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure, and the residue was crystallized from ethyl acetate-benzene to give p-aminophenol (**5c**), mp 186°C.

Reaction of Carbethoxymethylenetriphenylphosphorane (**1c**) *with N-(Phenylsulfonyl)-1,4-benzoquinone Monoimine* (**2a**)

To a solution of quinone monoimine **2a** (0.24 g, 0.001 mol) in dry benzene (20 mL) was added a solution of ylide **1c** (0.69 g, 0.002 mol) in dry benzene, and the reaction mixture was left at room temperature under stirring for 8 hours. After evaporation of the volatile materials under reduced pressure, the residue was chromatographed on a silica gel column using acetone/petroleum ether (60:40, v:v) as eluent to give compound **4b** as colorless crystals, mp 197–198 °C (yield 70%). Anal. calcd for $C_{38}H_{36}NO_7PS$ (681.74): C, 66.94; H, 5.32; N, 2.05; P, 4.54; S, 4.70. Found: C, 66.90; H, 5.30; N, 2.01; P, 4.52; S, 4.68%. MS = 681 IR: 1670, 1509 cm^{-1} (C=P), 1410 cm^{-1} [P–C(phenyl)], 3400 cm^{-1} (OH), 3300 cm^{-1} (NH), and 1730 cm^{-1} (C=O, ester). ^1H NMR: signals at δ 0.7 (t, 3H, $COOCH_2CH_3$), 1.22 (t, 3H, $COOCH_2CH_3$), 3.8 (q, 2H, $COOCH_2CH_3$), 4.05 (q, 2H, $COOCH_2CH_3$), 3.4 (d, 1H, $^3J_{HP}$ = 10 Hz), 7–7.9 (m, Ar), 8.7 (s, 1H, NH, exchangeable with D_2O), and 9.20 (s, 1H, OH). Triphenylphosphine was also isolated and identified.

Reaction of Acetylmethylenetriphenylphosphorane (**1a**) *with N-(Methylsulfonyl)-p-benzoquinone Monoimine* (**2b**)

A mixture of **2b** (0.36 g, 0.002 mol) [18], ylide **1a** (0.62 g, 0.002 mol), and dry benzene was stirred for 6 hours. The volatile material was evaporated in vacuo and the residual substance was chromatographed on a silica column using the eluent stated subsequently. The melting points and yields are also given.

Compound **3b**: 2,6-bis-*N*-(methylsulfonyl)-9,10-diacetylanthracene: eluent ethyl acetate/petroleum ether (25:75, v:v), colorless crystals, mp 108°C (yield 55%). Anal. calcd for $C_{20}H_{22}N_2O_6S_2$ (450.532): C, 53.32; H, 4.92; N, 6.22; S, 14.23. Found: C, 53.30; H, 4.90; N, 6.21; S, 14.2%. MS = 450 IR: 3314 cm^{-1} (NH), 1746 (C=O, acetyl), 1600 (C=C, Ar), and 1347, 1185 cm^{-1} (SO_2). ^1H NMR: two signals at δ 7.2, 7.23 (dd, 2H, Jab = Ja', b' = 8.54 Hz, Ja, c = Ja',c' = 2.44 Hz, H-a,a'), 7.47 (d, 2H, Jba = Jb'a' = 8.54 Hz, H-b,b'), 7.55 (d, 2H, Jc, a = Jc'a' = 2.44 Hz, H-c,c'), 6.48 (s, 1H), 6.48 (s, 1H), 6.47 (s, 1H) Hd,d', 2.58 (s, 6H, $2COCH_3$), 3.15 (s, 6H, $2SO_2CH_3$) and 7.9 (s, 2NH, exchangeable with D_2O). ^{13}C NMR: signals at δ 113.3 (C-1), 132.2 (s, C-2), 116.6 (C-3), 120.5

(C-4), 133.2 (s, C-4'), 136 (C-1'), 104.7 (C-9), 167.5 ($COCH_3$), 15.8 ($COCH_3$), and 40.5 (SO_2CH_3).

Compound **6a**: eluent: ethyl acetate/petroleum ether (10:90, v:v), mp 146–147°C (yield 15%). Anal. calcd for $C_{13}H_{15}NO_4S$ (281.33): C, 55.50; H, 5.37; N, 7.98; S, 11.40. Found: C, 55.48; H, 5.34; N, 4.96; S, 11.38%. MS = 281, IR 3224 cm^{-1} (NH), 1717, 1730 (C=O, acetyl $COCH_3$), 1594 cm^{-1} (C=C), 1610 cm^{-1} (C=CH). ^1H NMR: signals at δ 7.4 (m, 4H, Ar), 6.45 (s, 1H, C=CH), 2.42 (s, 3H, $COCH_3$), 2.48 (s, 3H, $COCH_3$), 3.0 (s, 3H, SO_2CH_3), and 8.0 (s, NH, exchangeable with D_2O). Triphenylphosphine and triphenylphosphine oxide were also isolated from the reaction mixture and identified [19].

Reaction of Carbomethoxymethylenetriphenylphosphorane (**1b**) *with N-(Methylsulfonyl)-p-benzoquinone Monoimine* (**2b**)

A mixture of **2b** (0.18 g, 0.001 mol), ylide **1b** (0.66 g, 0.002 mol), and dry benzene (30 mL) was refluxed for 8 hours on a water bath. The volatile material was evaporated in vacuo and the residual substance chromatographed on a silica gel column using ethyl acetate/petroleum ether (60:40, v:v) as eluent to give **6b** as colorless crystals, mp 140–141°C (yield 60%). Anal. calcd for $C_{13}H_{15}NO_7S$ (329.33): C, 47.41; H, 4.59; N, 4.25; S, 9.74%. Found: C, 47.40; H, 4.56; N, 4.23; S, 9.70%. MS = 329 IR: 3574 cm^{-1} (OH), 3258 cm^{-1} (NH), 1736 cm^{-1} (C=O, ester), 1740 cm^{-1} (C=O, ester), and 1617 (C=C, Ar). ^1H NMR: signals at δ 3.5 (s, 3H, $COOCH_3$), 3.8 (s, 3H, $COOCH_3$), 3.0 (s, 3H, SO_2CH_3), 6.8 (s, 1H, =CH), 8.0 (s, 1H, NH), 9.0 (s, 1H, OH), and 7.2–7.6 (m, 3H, Ar). Colorless crystals were also isolated (15%) and proved to be triphenylphosphine.

Similarly, *N*-(methylsulfonyl)-1,4-benzoquinone monoimine (**2b**)(0.18 g, 0.001 mol) was reacted with ylide **1c** (0.69 g, 0.002 mol) in 30 nl of dry benzene to give compound **6c** (eluent ethyl acetate/petroleum ether 70:30, v:v), mp 164–165°C (yield 65%). Anal. calcd for $C_{15}H_{19}NO_7S$ (357.38): C, 50.41; H, 5.36; N, 3.92; S, 8.97. Found: C, 50.39; H, 5.33; N, 3.90; S, 8.95%. MS = 357 (55) [M^+], 312 (40) [M^+-OEt], 267 (100) [312-OEt] IR: 3570 cm^{-1} (OH), 3250 cm^{-1} (NH), 1730 cm^{-1} (C=O, ester), 1740 cm^{-1} (C=O, ester), and 1600 cm^{-1} (C=CAr). ^1H NMR: signals at δ 1.2 (t, 3H, ethoxy-CH_3), 3.45 (q, 2H, ethoxy-CH_2), 1.6 (t, 3H, ethoxy-CH_3), 4.15 (q, 2H, ethoxy-CH_2), 6.9 (s, 1H, =CH), and 7.2–7.6 (m, 3H, Ar). Triphenylphosphine was also isolated and identified.

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