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Reactions of Alkylidenephosphoranes with Symmetrically Substituted *p*-Quinones

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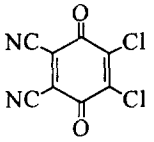
Abstract: The reaction of *p*-quinone **1** with ylides **2a** and **2b** afforded the corresponding phosphonium salts **8a,b**, *p*-quinone-dimethanides **4a,b(*Z*)** and **5a,b(*E*)**; substituted phenols **7a,b(*Z* and *E*)** and coumarin-derivative **11** (only with **2a**). The reaction of **1** with ylide **2c** gave, besides **4c, 5c** and **8c**, hydroquinone[1]cyclobutene **16** and the Diels-Alder product **17**. Reactions of **1** with **2d** and **3** (salts) in the presence of sodium alkoxide yielded through preferred attack on the nitrile function, azo-**22** and bisimino-**24** compounds, respectively. © 1997 Published by Elsevier Science Ltd.

INTRODUCTION

Although an abundance of studies[1-3] dealing with the application of Wittig reagents on *o*-quinones have been performed whereas they take remarkable interesting courses, little is known about *p*-quinones.[4,5] In the area of substituted *p*-quinones, only one study preludes to this approach. This concerns the chemical behaviour of 2-anilino-1,4-naphthoquinone and 2,3,5,6-tetrachlorobenzoquinone toward stabilized phosphorus ylides.[5] The results showed that there is no effect for the ring-site substituents (e.g., Cl) on the reaction products.[5]

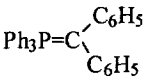


1

$Ph_3P{=}CHCOR$

2

a, R = OCH_3
b, R = OC_2H_5
c, R = C_6H_5
d, R = H



3

What we report here is the interaction of symmetrically substituted *p*-quinone: 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, **1**) and several different alkylidenephosphoranes **2a-d** and **3**. The study was under-

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taken to focus on the factors important in determining the course of our Wittig reaction such as: (1) the nature of the carbanion substituents, (2) the nature of the ring substituents, and (3) the reaction conditions, the knowledge of which should prove useful in interpreting mechanisms of nucleophilic displacement reaction of substituted *p*-quinones.

RESULTS AND DISCUSSION

Reaction of **1** *and phosphorus ylides* **2a,b**.

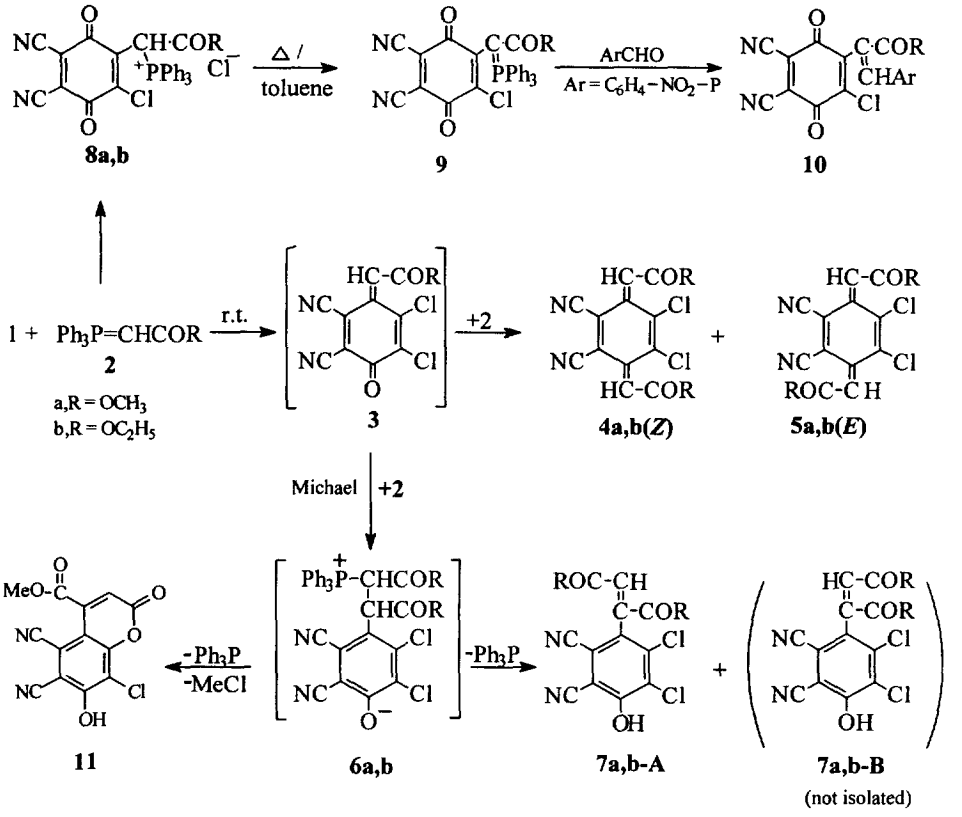
Treatment of the readily available *p*-quinone (DDQ, **1**) with methoxycarbonylmethylenetriphenylphosphorane **2a** (2.3 mol equiv.) in toluene at room temperature for ~18 h gave, the corresponding phosphonium salt **8a** (20%), the dimethanides **4a** (*Z*, 16%), **5a** (*E*, 9%) and the coumarin derivative **11** (12%) along with the substituted phenols **7a** (*Z&E*; 21%). An interesting feature of the reaction is the development of a deep red colour which fades to pale yellow on standing.

The structure of the isolated products **4a**, **5a**, **7a**, **8a** and **11** were in accord with the elemental analyses, molecular weight measurements (MS) and the spectral data. The suggested *cis*- and *trans*- configurations for the isolated diolefins **4a** (*Z*) and **5a** (*E*) although not established with certainty, are supported by the recorded ^{1}H-NMR chemical shifts and melting point measurements. The determined chemical shifts of methoxyl groups and olefinic protons in the recorded ^{1}H-NMR spectra are 3.56, 3.59 and 6.2 ppm for **4a**, mp 268 °C; 3.45, 3.5 and 6.18 ppm for compound **5a**, mp 248 °C. In all cases the higher down field of the two chemical shifts and the higher melting point observed for the isomer suggested as *cis* isomer is greater than those of the corresponding isomer, suggested as *trans*, in agreement with literature.[6]

Likewise, the yellow crystalline product of the substituted phenols **7a** was found to be a mixture of (*E*)- and (*Z*)- configurations. The two isomers were supported by the recorded ^{1}H-NMR spectrum of the isomeric mixture. The major component of the two isomers was considered as **7aA** and the minor **7aB** which were found in the ratio 2:1. The appearance of the chemical shift signals of methoxyl groups and vinyl proton of **7aB** (3.99(br.), 7.58 ppm) at a down field higher than those of **7aA** (3.92(br.), 7.38 ppm). Dimethyl (2,3-dichloro-5,6-dicyano-4-hydroxyphenyl) fumarate **7aA** (11%) is the only isomer (*E*) isolated in a pure form by fractional crystallization from methylene dichloride.

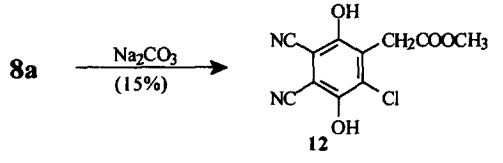
Next, coumarin structure **11** was attested by the following evidence: its IR spectrum revealed the presence of two strong absorption bands at 1740 and 1765 cm^{-1} denoting the presence of carbonyl-ester and a coumarin-carbonyl having C-H grouping.[7a] These two C=O groups were also attested by signals at δ 174.7 and 168.4 ppm in its ^{13}C-NMR[7] spectrum. Meanwhile, the presence of C(O)O**CH$_3$** group in **11** was supported by a singlet at δ_H 3.32 (3H) as well as by a singlet at δ_C 51.82 ppm in its NMR spectrum.

The structure of the phosphonium salt **8** is elucidated by ^{1}H- and ^{31}P-NMR spectroscopy. Its ^{31}P-NMR spectrum shows a chemical shift δ 13.3 ppm which indicates a high contribution of the zwitterionic form[8]. On



Scheme 1

the other hand, the exocyclic methine proton appeared at δ 8.15 ppm and showed a P-H coupling constant $^{2}J_{HP}$ = 18.3 Hz. The phosphonium salt **8a** was converted readily into the parallel ylide **9** upon heating under reflux in toluene for 15 h. On treating **9** with *p*-nitrobenzaldehyde, the normal Wittig product **10** was obtained. On the other hand, treating **8a** with Na_2CO_3 (15%), yielded the expected alkylated hydroquinone **12** (eqn. 1).

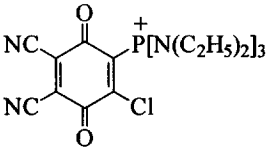


(1)

By a similar treatment of **1** with ethoxycarbonylmethylenetriphenylphosphorane **2b** the corresponding phosphonium salt **8b**, the dimethanides **4b** (*Z*) and **5b** (*E*) were obtained accompanied with the substituted phenols **7b**. Likewise with **2a**, diethyl fumarate derivative **7bA** is the only isomer isolated in a pure form. Moreover, the parallel coumarin-derivative has not hitherto been observed. The identification of the products was proved by combusion analysis, mass and NMR spectroscopy as well as by analogy with **4a**, **5a**,**7a**, and **8a**.

The results of the above reaction (1+**2a,b**) allow interesting conclusions to be drawn. Thus, considering the earlier report,[5] we were able to isolate products **7a,b** analogous with those of Bestmann and Lang, but with **4**, **5**, **8** and **11** we have isolated different condensed products.

A possible mechanism for the formation of the isolated products **4**, **5**, **7**, **8a,b** and **11** from the reaction of DDQ **1** and phosphorus ylides **2a,b** can be assumed to follow the series of reactions shown in Scheme 1 which implies that two positions in **1** are susceptible to nucleophilic attack: the aryl carbonyls and the ring-site chlorine. The initial nucleophilic attack by the carbanion center in **2a** on the aryl carbonyl in **1** yields the *p*-quinonemethanide **3a**, which further reacts with a second ylide **2a** in two different ways affording finally compounds **4a**, **5a**, **7a**, and **11**. Wittig reaction of aryl-carbonyl of **3a** with **2a** gives the dimethanide products **4a** (*Z*) and **5a** (*E*). Trapping of **3a** in Michael type addition of **2a** yields the phenoxy intermediate **6a**. Intramolecular hydrogen transylidation to the electron-rich center of the molecule affords **7a** (*E* & *Z*), 1:6 addition, by triphenylphosphine elemination. Meanwhile, stabilization of **6a** by expulsion of TPP and a molecule of methyl chloride leads to the formation of the coumarin-product **11**. On the other hand, it is evident that the phosphonium salt **8** was formed by a direct nucleophilic replacement of the chlorine atom of DDQ **1** by the carbanion center of **2a**. A similar chlorine replacement in DDQ **1** by tris(diethylamino)phosphine to give **13** was previously reported by Denney and Pendse.[9]



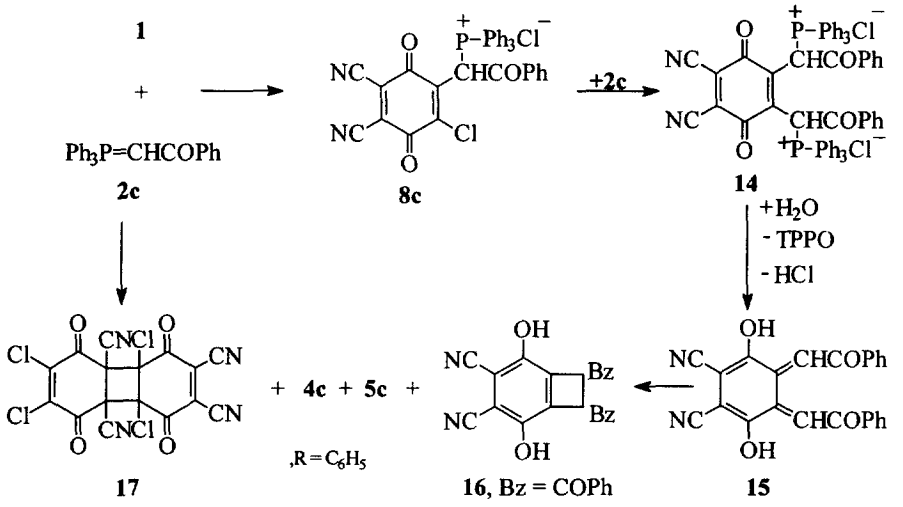
13

The problem posed by the appearance of deep red colours in the early stages of the reaction of **1** with **2** is an interesting one. It is established[10] that the benzene or toluene solutions exhibit strong paramagnetic resonance absorption. These phenomena are probably related to the formation of charge-transfere complexes [(A,D) $\longleftrightarrow$ (A^- ...$^+$D)] between the electron-acceptor quinone (A) and the donor (D).

Reaction of p-Quinone **1** *with Phosphorus Ylide* **2c**.

When the quinone **1** was added portionwise to a stirred toluene solution containing excess (up to 2.6 mol equiv.) of benzoylmethylenetriphenylphosphorane **2c** and the reaction mixture was stirred for further 24 h at room temperature and then subjected to column chromatography, the corresponding phosphonium salt **8c** (26 %), *p*-quinonedimethanides **4c** (9%) and **5c** (8%), along with hydroquinone[1]cyclobutene **16** (14%), and the coupling product **17** (17%) were, irrespectively (Scheme 2), obtained. Structures **8c**, **4c** and **5c** were confirmed by analogy with **4a,b**, **5a,b** and **8a,b** whilst the structure of **16** is proved by its infrared absorptions for hydroxyl, nitrile and carbonyl groups at 3430, 2220 and 1678 cm^{-1}, respectively; its ^{1}H-NMR absorptions at δ_H 4.35, 4.51 (2d, 2H, benzyl-**H**), 7.2-7.64 (m, 10H, aryl-**H**), 8.5 ppm (br., 2H, O**H**), and its ^{13}C-NMR data are in accord with the proposal structure. Likewise, the coupling product **17** was confirmed by MS and ^{13}C-NMR data.

Scheme 2



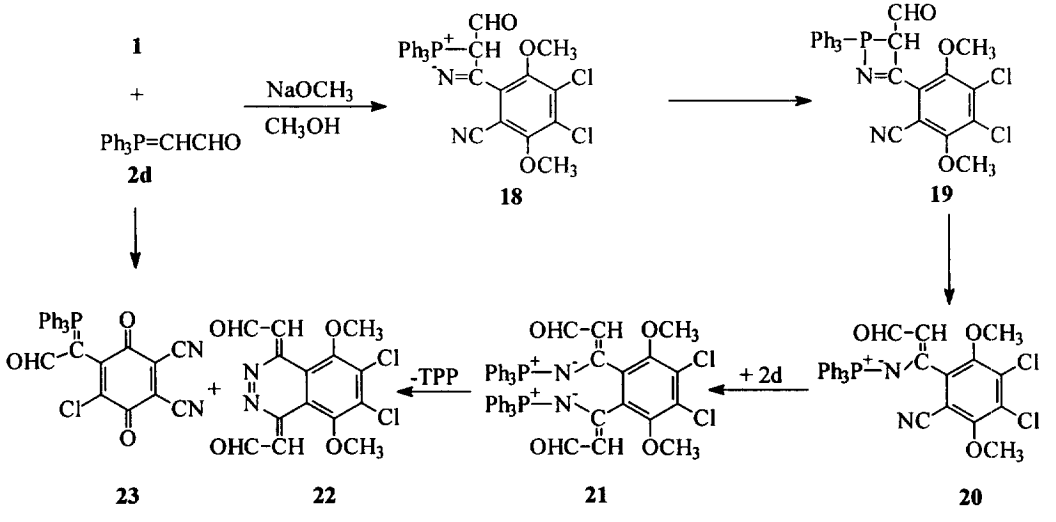
The formation of hydroquinone[1]cyclobutene **16** can be envisaged as proceeding through further nucleophilic attack by the carbanion center in **2c** on the second chlorine atom of the phosphonium salt **8c**, initially formed, to give the intermediate like **14** *via* displacement at halogen. Addition of elements of water (adventitious-moisture) to **14** affords the intermediate **15** accompanied by elemination of TPPO and hydrogen chloride. **16** then probably results from intermolecular cyclization of the crowded intermediate hydroquinone dimethane **15**. Formation of quinone[1]cyclobutenes by the action of Wittig reagents on *o*-quinones has previously been reported.[4,11] Moreover, generation of the intermediates **14** and **15** is not surprising since it is reported that 2,3-dichloro-*p*-benzoquinone reacts readily with nucleophilic reagents to give, exclusively, 2,3-disubstituted products.[12]

In view of the latter observations (**1+2c**), in contrast with **2a,b** it is evident that in the formation of the isolated products, **4c**, **5c**, **8c**, and **16** a preference for a displacement of a ring-chlorine took place to produce **8c** and **16** (40%) rather than the olefination processes to produce **4c** and **5c** (17%).

Formation of the dimeric product **17** is in accordance with the Woodward-Hoffmann rules.[10] Thus the cyclization of the quinone dimer takes place intermoleculary by [2+2[cycloaddition through electron donor-acceptor interaction between C(Cl) in **1** with C(CN) of another molecule of the same quinone.

Reaction of p-Quinone **1** *with Ylide* **2d**.

Treatment of **1** with formylmethylenetriphenylphosphorane **2d,** prepared in *situ* from its chloride salt in the presence of $NaOCH_3$ in methyl alcohol gave the corresponding phosphorane **23** (23%) and the unexpected azo-derivative **22** (36%). No olefination product was observed. The structure **22** was deduced from correct elemental and mass spectral analyses, and its ^{1}H-NMR spectrum which revealed the presence of two singlets at δ 6.6 and 6.77 corresponding to the ethylenes =CH protons; two singlet at 3.41 and 3.88 assigned for the methoxyl groups while the aldehydic protons appeared at 8.85 and 9.18 ppm, and its IR spectrum showed the absence of CN absorption band and, instead, it showed new bands at 1576 and 850 cm^{-1} attributed[7a] to –N=N– and –C–N absorption, respectively. Although two isomers (*E* & *Z*), which can differ in the arrangement of the substituents on the carbon-carbon double bonds, could be assigned for **22**, the data available do not allow a choice of which of these isomers has been isolated.



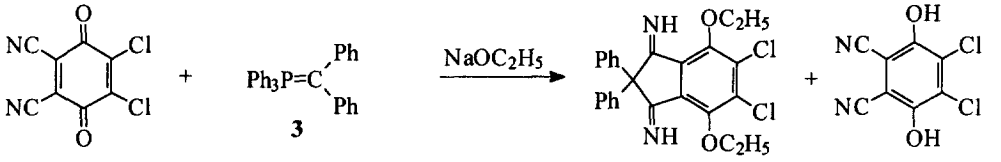
Scheme 3

Obviously, the β-ketoalkylidenetriphenylphosphorane **2d** which is less nucleophile comparatively to **2a-c**

failed to undergo the olefination process, but instead it leads to the formation of phosphorus-nitrogen bond (Scheme 3). The mechanism of condensation of dinitrile **1** with **2d** probably involves initial formation of an adduct such as **18** followed by ring closure to the dihydrophosphazete **19**. Opening of the four-membered ring yields the iminophosphorane **20**. Subsequent (or concurrent) transformations for the second nitrile group in an identical way, affords bis(iminophosphorane) **21**. Compound **22** results through the extrusion of TPP and the ring closure of the crowded intermediate **21**, as in the former case (see Scheme 2). However, O-alkylation processes, due to the methanolic medium,[13] compete with these transformations. Such a mechanism was previously reported for the reaction of activated acetylenes[14] and activated nitriles[15-17] with some phosphorus ylides. Moreover, this result is compatible with the assumption that the presence of the metal (Na) ion complexes with the nitrile increases the electrophilic reactivity of the carbon atom of the cyano group in the condensation reaction under consideration.[15]

Reaction of p-Quinone **1** *with Ylide* **3**.

The reaction of ylide **3** with DDQ **1** was studied in ethyl alcohol solution containing $NaOC_2H_5$ and the products obtained are depicted in Scheme 4. When *p*-quinone **1** was treated with diphenylmethylenetriphenylphosphorane **3** (2.5 mol equiv.) prepared in *situ* from its bromide salt in the presence of $NaOC_2H_5$ in ethyl alcohol, the reaction afforded the corresponding hydroquinone **25** (18%) and the bisimino-adduct **24** (48%). The structure of **24** is assignable from its analysis and spectral properties.The latter type of interaction between dinitrile derivative **1** and **3** and formation of bisimino-adduct **24** parallels the reaction course of phthalonitrile



1 **3** **24** **25**

Scheme 4

derivative and nucleophilic reagents (e.g. NH_3) in the presence of a base.[18] Moreover, it is of interest to notice that the behaviour of ylide **3** in the present study is remincent of its reaction with some *o*-quinones, whereby 1,3-dioxoles are likewise formed.[19,20]

CONCLUSION

In conclusion, reactions of phosphorus ylides with substituted *p*-quinones provide an easy route for the preparation not only of the previously reported Wittig products,[4,5] but also of different adducts depending

on the nature of the ylide used and the reaction conditions. In addition, some concluding remarks should be cited: a) Wittig olefination has found preference with alkoxyalkylidenephosphoranes **2a,b** while with β-ketoalkylidenephosphoranes **2c,d** or methylenephosphoylide **3** afforded products in which site-ring attack has predominated, b) the findings, also support the assumption that the basic medium stimulate the course of the reaction at the N-functions (CN, NH, NO, NOH....);[15,17,21] c) finally the results offer a fertile area for future research in which Wittig reagents may be tailored to produce the desired outcome.

EXPERIMENTAL

Melting points are uncorrected. The IR spectra were recorded with a Perkin Elmer spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ or d_6-DMSO as solvents on a Joel-270 MHz spectrometer, with $SiMe_4$ as internal standard. The ^{31}P-NMR spectra were taken with a Varian CFT-20 (*vs*-external 85% H_3PO_4). Mass spectra were performed at 70 eV on a Shimadzu GCS-QP 1000 EX spectrometer provided with a data system. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, **1**) was purchased from Aldrich Company.

Reaction of DDQ **1** *and Phosphorus Ylides* **2a**. To a stirred solution of methoxycarbonylmethylene-triphenylphosphorane **2a**[22] (2.3 g, 7 mmol) in 30 ml dry toluene was added dropwise, within 30 minutes, a solution of quinone **1** (0.7 g, 3 mmol) in 20 ml toluene. The deeply red coloured reaction mixture was further stirred at room temperature for 18 h (TLC). The brown material that precipitated was collected, recrystallized from ethyl alcohol and identified as *Z*-dimethyl(2,3-dichloro-5,6-dicyano-1,4-dihydrobenzylidene) diacetate **4a** (166 mg, 16 %), mp 265 °C. IR (KBr): 2235 (CN), 1735 (C=O, ester) 1622 cm^{-1} (=CH). NMR (DMSO): δ_H 3.56, 3.59 (2s, 6H, 2C**H**$_3$), 6.2 ppm (s, 2H, =C**H**); δ_C 58.23, 60.72 (2 O**C**H$_3$), 116.9, 119.8 (2**C**N), 137.9, 138.4 (2 =**C**H) and 159.8, 161.8 ppm (2 **C**=O, ester). MS: *m/z* (%) = 339 (22) [M$^+$].

$C_{14}H_8Cl_2N_2O_4$ (339.148) Calcd. C 49.58 H 2.37 Cl 20.91 N 8.26
Found: C 49.52 H 2.33 Cl 20.85 N 8.15

The filterate was separated by column chromatography on silica gel. Elution with hexane-ethyl acetate (8:2 → 3:6) and further with pure ethyl acetate afforded four fractions. The first fraction gave yellow crystals of 3-chloro-5,6-dicyano-1,4-benzoquinone-2-methoxycarbonylmethylenetriphenylphosphonium chloride **8a** (300 mg, 20 %), mp 248 °C (chloroform). IR (KBr): 2233 (CN), 1740 (C=O, ester), 1700, 1685 (C=O, aryl ketone), 1455, 980 (P-C, phenyl). NMR ($CDCl_3$): δ_H 3.2 (s, 3H, OC**H**$_3$), 8.15 (d, $^2J_{HP}$ = 18.3 Hz, 1H, -C**H**), 7.4 -7.85 ppm (m, 15H, aryl-**H**); δ_P 13.3 ppm. MS: *m/z* (%) = 561 (100) [M$^+$] .

$C_{29}H_{19}Cl_2N_2O_4P$ (561.381) Calcd. C 62.04 H 3.41 Cl 12.63 N 4.99 P 5.52
Found: C 61.96 H 3.37 Cl 12.61 N 4.88 P 5.48

The second fraction gave straw yellow crystals of methyl(5,6-dicyano-7-hydroxy-8-chloro-2-oxo-2H-chromene-4yl) carboxylate **11** (112 mg, 12%) mp 148 °C (chloroform/hexane, 1:1 v/v). IR (KBr): 3445 (OH), 2233 (CN), 1765 (C=O, lactone) and 1740 (C=O, ester). NMR ($CDCl_3$): δ_H 3.38 (s, 3H, OCH_3), 7.52 (s, 1H, =CH) 8.7(br., 1H, OH); δ_C: 51.82 (OCH_3), 118.2, 120.1 (2CN), 151.4 (C-OH), 168.4 (C=O,ester), 174.7 ppm (C=O, lactone). MS: *m/z* (%) = 304 (100 %) [M^+].

$C_{13}H_5ClN_2O_5$ (304.656) Calcd. C 51.25 H 1.65 Cl 11.64 N 9.2

Found: C 51.21 H 1.59 Cl 11.58 N 9.15

The third fraction afforded the mixture of isomers **7a** (230 mg, 21 %). The proportion **7aA** : **7aB** and the ^{1}H-NMR data of the isolated mixture were previously described. The mixture of the isomers was redissolved in CH_2Cl_2 and kept at -10 °C for 2 days. The solvent was decanted and the procedure was repeated with fresh CH_2Cl_2. Crystals that separated out were collected and proved to be the major isomer **7aA** (119 mg, 11 %), mp 165 °C . IR (KBr): 3450 (OH), 2235 (CN), 1734, 1725 (2-C=O, esters), 1635 cm^{-1} (-C=CH). NMR ($CDCl_3$): δ_H: 3.85, 3.94 (2s, 6H, $2OCH_3$), 7.38 (s, 1H, =CH), 8.65 ppm (OH). MS: *m/z* (%) = 355 (10) [M^+].

$C_{14}H_8Cl_2N_2O_5$ (355.148): Calcd. C 47.34 H 2.27 Cl 19.96 N 7.89

Found: C 47.26 H 2.21 Cl 19.87 N 7.78

The fourth fraction yielded brown crystal of *E*-dimethyl(2,3-dichloro-5,6-dicyano-1,4-dihydrobenzylidene) diacetate **5a** (93 mg, 9%) mp 248 °C ($CHCl_3$). IR (KBr): 2233 (CN); 1728, 1738 (C=O, ester), 1620 (=CH). ^{1}HNMR (DMSO): δ 3.45, 3.5 (2s, 6H, 2 OCH_3), 6.18 ppm (s, 2H, 2 =CH). MS: *m/z* (%) = 339 (30) [M^+].

$C_{14}H_8Cl_2N_2O_4$ (339.148) Calcd. C 49.58 H 2.37 Cl 20.91 N 18.87

Found: C 49.53 H 2.34 Cl 20.86 N 18.82

Reaction of DDQ **1** *and Phosphorus Ylide* **2b**. The reaction between quinone **1** (0.7 g, 3 mmol) and ethoxycarbonylmethylenetriphenylphosphorane **2b** (2.4 g, 7 mmol) in dry toluene (50 ml) was carried out and the reaction mixture was worked up according to the above described procedure for ylide **2a**. No precipitate was observed in the product mixture. After removal of the solvent, the residue was chromatographed on silica gel with hexane-$CHCl_3$ (7:3→0:10 v/v) and further with pure ethyl acetate and at last with acetone to give four fractions. The first fraction afforded the mixture of diastereomers **7b A&B** (318 mg, 27 %). (*E*)- and (*Z*)- configurations shown only by ^{1}H-NMR whereby they present in ratio 3:2. Likewise with **7a**, fractional crystallization from CH_2Cl_2 afforded a pure sample of the major isomer **7bA** as yellow crystals (118, 10 %), mp 152 °C. IR (KBr): 3440 (OH), 2227 (CN), 1678 cm^{-1} (C=O, ester). ^{1}H-NMR ($CDCl_3$): δ_H 1.42, 1.55 (2t, J_{HH}=4 Hz, 6H, $2CH_3$); 4.3, 4.46 (2q, J_{HH}=4 Hz, 4H, $2CH_2$); 5.35 (s, 1H, = CH), 9.8 ppm (s, 1H, OH). MS: *m/z* (%) = 383(24) [M^+].

$C_{16}H_{12}Cl_2N_2O_5$ (383.2) Calcd. C 50.15 H 3.15 Cl 18.5 N 7.31

Found: C 49.93 H 3.08 Cl 18.33 N 7.26

The minor isomer diethyl (2,3-dichloro-5,6-dicyano-4-hydroxy-phenyl-1yl) maleate **7bB** could not be isolated in a pure form. Its ^{1}H-NMR (shown in the spectrum of the isomeric mixture), δ_H 1.48, 1.67 (2t, 6H, 2C**H**$_3$); 4.6, 4.68 (2q, 4H, 2C**H**$_2$); 5.66 (s, 1H, =C**H**), 9.8 ppm (s, 1H, O**H**).

The second fraction gave a yellow crystals of 3-chloro-5,6-dicyano-1,4-benzoquinone-2-ethoxycarbonyl-methylenetriphenylphosphonium chloride **8b** (319 mg, 18%), mp 240 °C (ethyl alcohol). IR (KBr): 2232 (CN); 1735 (C=O, ester), 1690 (C=O, aryl ketone), 1440 cm^{-1} (P-C, phenyl). NMR (DMSO): δ_H 0.8 (t, J_{HH}=4 Hz, 3H, C**H**$_3$), 3.64 (q, J_{HH}=4 Hz, 2H, C**H**$_2$), 7.24-7.8 ppm (m, 16H, aryl-**H** & C**H**); δ_C 14.38 (**C**H$_3$), 59.66 (O**C**H$_2$),68.5 (d, J_{CP}=104 HZ, **C**-P), 117.3, 119.5 (2**C**N), 163.5 (**C**=O, ester) , 176.4 ppm (**C**=O,aryl-ketone). MS: *m/z*(%) = 575 (100) [M$^+$].

$C_{30}H_{21}Cl_2N_2O_4P$ (575.41) Calcd. C 62.62 H 3.68 Cl 12.32 N 4.87 P 5.38
Found: C 62.55 H 3.69 Cl 12.19 N 4.73 P 5.46

The third fraction (ethyl acetate) yielded brown crystals of *E*-diethyl(2,3-dichloro-5,6-dicyano-1,4-dihydrobenzylidene) diacetate **5b** (147 mg, 13 %), mp 258 °C (benzene). IR (KBr): 2220 (CN), 1680, 1695 (2C=O, ester), 1628 cm^{-1} (br., =CH); NMR (DMSO): δ_H 1.24 (t, J_{HH}=3.6 Hz, 6H, 2C**H**$_3$),4.24 (q, J_{HH}=3.6 Hz, 4H, 2C**H**$_2$), 5.38 ppm (s, 2H, =C**H**). MS: *m/z* (%) = 367 (25) [M$^+$].

$C_{16}H_{12}Cl_2N_2O_4$ (367.202) Calcd. C 52.33 H 3.3 Cl 19.31 N 7.63
Found: C 52.28 H 3.24 Cl 19.18 N 7.54

The fourth fraction (acetone) gave brown crystals of *Z*-diethyl (2,3-dichloro-5,6-dicyano-1,4-dihydrobenzylidene) diacetate **4b** (158 mg, 14%), mp 280 °C (benzene). IR (KBr): 2225 (CN), 1685, 1710 (2C=O, esters), 1625 (= CH); ^{1}H-NMR (DMSO): δ_H 1.28 (t, J_{HH}=3.6 HZ, 6H, 2C**H**$_3$), 4.28 (q, J_{HH}=3.6 Hz, 4H, C**H**$_2$), 6.94 ppm (s, 2H, =C**H**). MS: *m/z* (%) = (367) (22) [M$^+$].

$C_{16}H_{12}Cl_2N_2O_4$ (367.202) Calcd. C 52.33 H 3.3 Cl 19.31 N 7.63
Found: C 52.2 H 3.25 Cl 19.27 N 7.58

Alkaline Treatment of the Phosphonium Salt **8a**. A mixture of **8a** (0.5 g) and 25 ml Na_2CO_3 (15 % aq.) was heated under reflux for 10 h. The mixture was cooled, diluted with water (5 ml) and extracted with $CHCl_3$. The residue obtained on removal of $CHCl_3$ was boiled with light petroleum to afford on concentration 0.13 gm, mp 155 °C, shown to be TPPO. The insoluble portion (0.62 g, 75%) was recrystallized to give the substituted hydroquinone **12** as yellow crystals, mp 193 °C (chloroform). IR (KBr): 3435 (br., OH), 1710 cm^{-1} (C=O, ester). ^{1}H-NMR (DMSO): δ 2.83 (s, 2H, C**H**$_2$), 3.84 (s, 3H, OC**H**$_3$), 9.35 (br., 2H, 2O**H**). MS: *m/z* (%) = 266 (33) [M$^+$]

$C_{11}H_7ClN_2O_4$ (266.65) Calcd. C 49.55 H 2.64 Cl 13.29 N 10.51
Found: C 49.49 H 2.57 Cl 13.16 N 10.38

Thermal Decomposition of Phosphonium Salt **8a**. Compound **8a** (0.7 g) was heated under reflux for 15 h in toluene solution (30 ml). The material that precipitated after concentration and cooling was filtered off and proved to be the new ylide **9** (0.55 g, 85%), mp 185 °C (benzene). IR (KBr): 2235 (CN), 1735 (C=O, ester), 1685 (C=O, aryl-ketone), 1550 cm^{-1} (C=P). ^{1}H-NMR ($CDCl_3$): δ_H 3.35 (s, 3H, C**H**$_3$), 7.35-7.82 ppm (m, 15H, aryl-**H**). MS: *m/z* (%) = 524 (100) [M^+].

$C_{29}H_{18}ClN_2O_4P$ (524.92) Calcd.. C 66.35 H 3.45 Cl 6.75 N 5.34 P 5.9
Found: C 66.23 H 3.37 Cl 6.67 N 5.28 P 5.77

Wittig Reaction of the Produced Ylide **9**. To a solution of **9** (0.5 g, 0.9 mmol) in ethyl acetate (30 ml) containing triethylamine (1.3 mmol), *p*-nitrobenzaldehyde (0.19 g, 1.3 mmol) was added. The reaction mixture was refluxed for 15 h. The solvent evaporated. Extraction of the residual substance with hot petroleum gave on cooling TPPO, mp 155 °C. Crystallization of the residue from acetone yielded the exocyclic olefin **10** (0.2 g, 62%), mp 220 °C ($CHCl_3$-Et_2O). IR (KBr): 2233 (CN), 1725 (C=O,ester), 1685 (C=O,aryl ketone), 1618 cm^{-1} (=CH). ^{1}H-NMR ($CHCl_3$): δ 3.76 (s, 3H, C**H**$_3$), 5.85 (s, 1H, =C**H**), 7.45-7.82 (m, 4H, aryl-**H**). MS: *m/z* (%) = 397 (24) [M^+].

$C_{18}H_8ClN_3O_6$ (397.742) Calcd. C 54.35 H 2.03 Cl 8.91 N 10.56
Found: C 54.24 H 1.95 Cl 8.83 N 10.5

Reaction of DDQ **1** *and Phosphorus Ylide* **2c**. To a stirred suspension of benzoylmethylenetriphenylphosphorane **2c**[23] (3 g, 7.9 mmol) in toluene (50 ml), was added portionwise quinone **1** (0.7 g, 3 mmol) and the reaction mixture was left at r.t. under stirring for 24 h. Working up the product mixture as described with **2b** afforded **17**, **8c**, **16**, **5c** and **4c**, respectively.

The coupling product **17** was eluted with hexane/chloroform (8:2 v/v) as yellow crystals (126 mg, 17 %), mp 228 °C (CH_2Cl_2). IR (KBr): 2233 (CN), 1685 cm^{-1} (C=O). ^{13}C-NMR (DMSO): δ_C 42.77 44.76, 49.32, 51.85 (cyclobutene-**C**), 117.32, 119.55 (CN); 171.35, (**C**=O, aryl-ketones). MS: *m/z* (%) = 454 (100) [M^+].

$C_{16}Cl_4N_4O_4$ (454.136) Calcd. C 42.32 Cl 31.23 N 12.34
Found: C 42.30 Cl 31.21 N 12.29

The phosphonium salt **8c** was eluted with hexane/$CHCl_3$ (6:4 v/v) as yellow crystals (486 mg, 26 %), mp 287 °C (toluene). IR (KBr): 2218 (CN), 1745, 1690 (C=O), 1440 cm^{-1} (P-C, phenyl). NMR (DMSO): δ_H 7.25-7.85 ppm (m,16H, aryl-**H**, C-**H**), δ_P 15.6 ppm. MS: *m/z* (%) = 607 (100) [M^+].

$C_{34}H_{21}Cl_2N_2O_3P$ (607.45) Calcd. C 67.23 H 3.38 Cl 11.67 N 4.61 P 5.1
Found: C 67.18 H 3.34 Cl 11.52 N 4.54 P 5.14

The hydroquinone[1]cyclobutene **16** was eluted with hexane/$CHCl_3$ (2:8 v/v) as yellow crystals (169 mg, 14 %), mp 185 °C (CH_2Cl_2/Et_2O 1:2 v/v). IR (KBr): 3430 (OH, br.), 2220 (CN), 1678 cm^{-1} (C=O). NMR

(DMSO): δ_H 4.35, 4.51 (2d, J_{HH}=4.5 Hz, C**H**-C**H**), 7.2-7.64 (m, 10 H, aryl-**H**); 8.5 ppm (br., 2H, 2OH); δ_C: 47.55, 49.84 (2C-COR); 184.4, 188.5 ppm (2C=O). MS: *m/z* (%) = 394 (100) [M^+].

$C_{24}H_{14}N_2O_4$ (394.39)	Calcd.	C 73.09	H 3.58	N 7.1
	Found:	C 72.96	H 3.46	N 7.05

E-1,4-Quinodimethane **5c** was eluted with chloroform as brown crystals (106 mg, 8 %), mp 292 °C (ethyl alcohol). IR (KBr): 2233 (CN), 1680 cm^{-1} (br., COPh). ^{1}H-NMR (DMSO): δ_H 7.25-8.23 ppm (m, aryl-**H** & =C**H**). MS: *m/z* (%) = 431 (45) [M^+].

$C_{24}H_{12}Cl_2N_2O_2$ (431.29)	Calcd.	C 66.84	H 2.8	Cl 16.44	N 6.49
	Found:	C 66.78	H 2.73	Cl 16.37	N 6.36

Z-1,4-Quinodimethane **4c** was eluted with $CHCl_3$ / AcOEt as brown crystals (119 mg, 9 %), mp 305°C (ethyl alcohol). IR (KBr): 2235 (CN), 1685 cm^{-1} (br., C=O). ^{1}H-NMR (DMSO): δ 7.36-8.28 ppm (m, aryl-**H** & =C**H**). MS: *m/z* (%) = 431 (48) [M^+].

$C_{24}H_{12}Cl_2N_2O_2$ (431.29)	Calcd.	C 66.84	H 2.8	Cl 16.44	N 6.49
	Found:	C 66.76	H 2.7	Cl 16.33	N 6.31

Reaction of DDQ **1** *and Phosphorus Ylides* **2d**. Into a well dried three necked flask containing 0.3 g sodium metal dissolved in 50 ml absolute methyl alcohol, formylmethylenetriphenylphosphonium chloride[24] (2.7 g, 8 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 1 h followed by addition of **1** (0.7 g, 3mmol) portionwise within 30 min. then kept under stirring for 24 h. The product mixture was concentrated to 20 ml, diluted with 20 ml distd. water, acidified with conc HCl and then extracted with two-100 portions of $CHCl_3$. The chloroform extracts were combined, backwashed with 100 ml of H_2O, dried over anhydrous $MgSO_4$, and evaporated *in vacuo* under reduced pressure. The residue was chromatographed on silica gel with hexane-chloroform (7:3→1:9 v/v) to give compounds **23** and **22**, respectively.

The phosphorane **23** was eluted first as yellow crystals (345 mg, 23 %), mp 165 °C (CH_3CN). IR (KBr): 2233 (CN), 1707 (C=O, CHO), 1690 (C=O, aryl-ketone), 1555 cm^{-1} (C=P). NMR (DMSO): δ_H 7.4-7.88 (m, 15H, aryl-**H**), 8.83 ppm (d, $^3J_{HP}$ = 8.5 Hz, 1H, C**H**O); δ_P = 18.7 ppm. MS: *m/z* (%) = 494 (13) [M^+].

$C_{28}H_{16}ClN_2O_3P$ (494.89)	Calcd.	C 67.95	H 3.26	Cl7.16	N 5.66	P 6.26
	Found:	C 67.84	H 3.22	Cl 7.3	N 5.5	P 6.34

The azo-product **22** was obtained as orange crystals (375 mg, 36 %), mp 135 °C (cyclohexane). IR (KBr): 1715 (C=O), 1576 (N=N), 850 cm^{-1} (C–N). ^{1}H-NMR ($CDCl_3$): δ_H 3.41, 3.88 (2s, 6H, OC**H**$_3$), 6.6, 6.77 (2d, J_{HH} = 4 Hz, 2H, =C**H**); 8.85, 9.18 ppm (2d, J_{HH} = 4 Hz, 2H, C**H**O). MS: *m/z* (%) = 341 (20) [M^+].

$C_{14}H_{19}Cl_2N_2O_4$ (341.16)	Calcd.	C 49.29	H 2.95	Cl 20.78	N 8.21
	Found:	C 49.25	H 2.78	Cl 20.66	N 8.1

Reaction of DDQ **1** *and Phosphorus Ylide* **3**. A mixture of **1** and diphenylmethylenephosphonium bromide[25] in ethyl alcohol containing sodium metal whereas the procedure and the working up are the same (with **2d**), using the same amounts. The product residue was chromatographed with hexane-ethyl acetate whereby elution with pure ethyl acetate afforded two fractions.

The first fraction gave hydroquinone **25** (127 mg, 18 %) mp 262-264 °C (dil. ethanol) (lit.[22] 265 °C).

The second fraction yielded brown crystals of **24** (650 mg, 48 %), mp 272 °C (toluene). IR (KBr): 1330 (NH, weak), 1622 cm^{-1} (C=NH). ^{1}H-NMR ($CDCl_3$/DMSO): δ_H 0.78, 1.55 (2t, J_{HH} = 4.5 Hz, 6H, 2-C**H**$_3$); 3.4, 3.62 (2q, J_{HH} = 4.5 Hz, 4H, 2OC**H**$_2$), 7.2-7.75 ppm (m, 12H, aryl-**H** & 2N**H**). MS: *m/z* (%) = 441 (8) [M^+].

$C_{24}H_{22}Cl_2N_2O_2$ (441.37)	Calcd.	C 61.31	H 5.02	Cl 16.06	N 7.25
	Found:	C 61.25	H 4.97	Cl 15.93	N 7.1

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