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Reaction of Phosphonium Ylides with 4-Triphenylmethyl-1,2-benzoquinone

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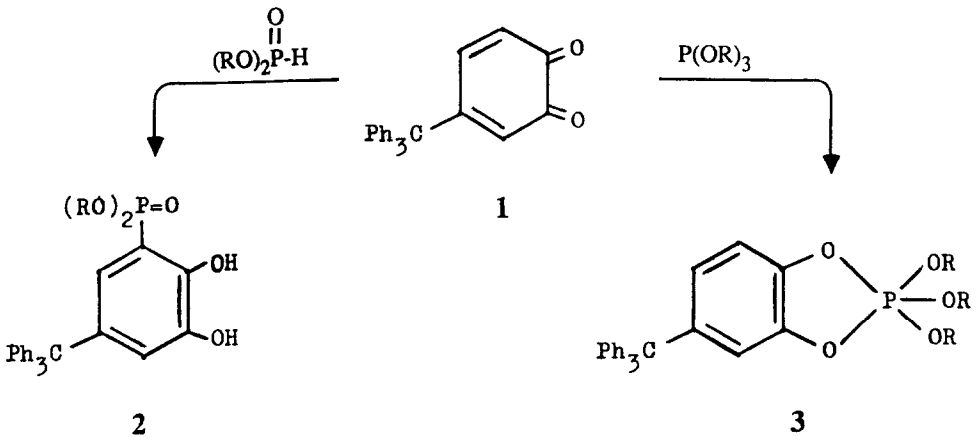
Abstract: The reaction of alkoxycarbonylmethylene(triphenyl)phosphoranes (**4**) with 4-triphenylmethyl-1,2-benzoquinone (**1**) in dry benzene at room temperature for 3 h led to the formation of a novel type of compounds **7** along with triphenylphosphine oxide. When compounds **7** were allowed to reflux in boiling toluene for 5 h, a mixture of 4-alkoxycarbonyl-6-triphenylmethyl-2H-1-benzopyran-2-ones (**11**), 5-triphenylmethyl-3-alkoxycarbonylmethylene-benzo[b]furan-2(3H)-ones (**12**) and triphenylphosphine were obtained. The double bond moiety of the pyrone ring in **11** was reduced with zinc dust in boiling acetic acid to form 4-alkoxycarbonyl-6-triphenylmethyl-3,4-dihydro-2H-1-benzopyran-2-ones (**13**) in quantitative yields. Carrying out the reduction of **11** in presence of methanol yields the succinate derivatives **14**, which upon methylation with methyl iodide in dry acetone and anhydrous potassium carbonate gave the corresponding methyl ethers **15**. The reaction mechanisms are considered and the structural assignments of the new compounds are based on chemical and spectroscopic evidence.

Introduction

In earlier paper,[1] we have reported our studies on the behaviour of 4-triphenylmethyl-1,2-benzoquinone (**1**) as unsymmetrical *o*-quinone towards alkyl phosphites. The dihydroxyaryl phosphonates (**2**) were formed by treatment of the quinone **1** with dialkyl phosphites, however, it reacted with trialkyl phosphites yielding the unsaturated cyclic pentaoxyphosphoranes (**3**). These remarkable results led us to investigate the present work which describes the reaction of quinone **1** with phosphonium ylides **4**. It involves a novel type of compound not previously observed with other *o*-quinones and α-diketones.[2-11]

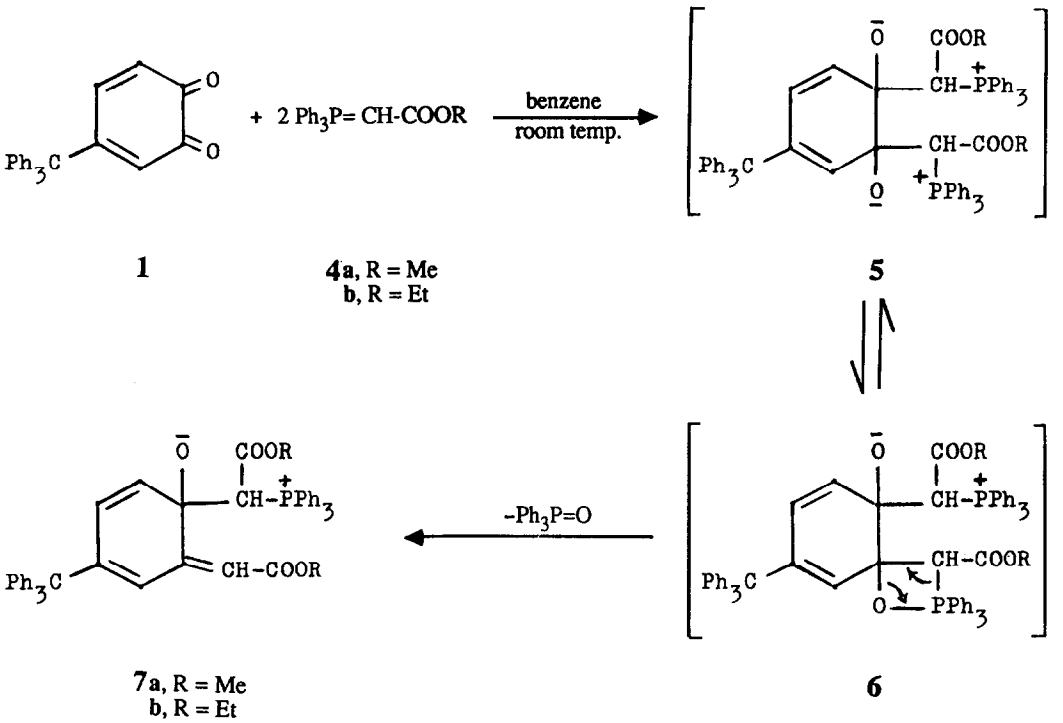


Results and Discussion

We have found that 4-triphenylmethyl-1,2-benzoquinone (**1**) reacted with two molar amounts of stabilized methylenephosphoranes (**4**), in dry benzene at room temperature for 3 h to give colourless crystalline products **7** in fairly good yields (Scheme 1). When the reaction was carried out using one mole amount of the ylide phosphoranes (**4**) instead of two, the adducts **7** were obtained, along with unchanged quinone **1**.

Compounds **7** are quite stable at room temperature. Their assigned structures were established from elemental analyses and spectral properties which are consistent with expectation. The ^{31}P NMR spectrum of **7a**, taken as an example, showed a positive chemical shift δ = 24.7 ppm (vs. 85% H_3PO_4) which indicates a high contribution of the zwitterionic phosphorus betaine structure.[12,13] Its ^1H NMR (in $CDCl_3$) revealed the presence of two singlets at δ 3.07 and 3.69 ppm, due to the two methoxyl groups in the esters. It also shows a doublet centered at δ 3.33 ppm with a P-H coupling constant of $^2J_{P-H}$ = 18 Hz, ascribed to proton at the asymmetrical carbon attached to the phosphorous atom ($\overset{+}{P}$-$\dot{C}$H-) and a singlet at δ 6.17 ppm denoting the exocyclic vinyl proton (=CH-). The aromatic protons appear as multiplets in the region δ 6.80-7.70 ppm which integrates to 33 protons. The IR spectrum of **7a**, in KBr, exhibits absorption bands at 1733 cm^{-1} (C=O, ester); 1614, 1594 cm^{-1} (C=C). The P-phenyl gives rise to strong bands at 1436, 751 and 700 cm^{-1} due to the phenyl ring attached to phosphorus [14] and also, another strong band occurs at 1105 cm^{-1} due to an aromatic vibration involving some P-C stretching.[14]

The reaction mechanism of the Wittig reagents with carbonyl compounds [15] is commonly expressed in terms of two steps: the first is nucleophilic addition of phosphorus ylide to the carbo

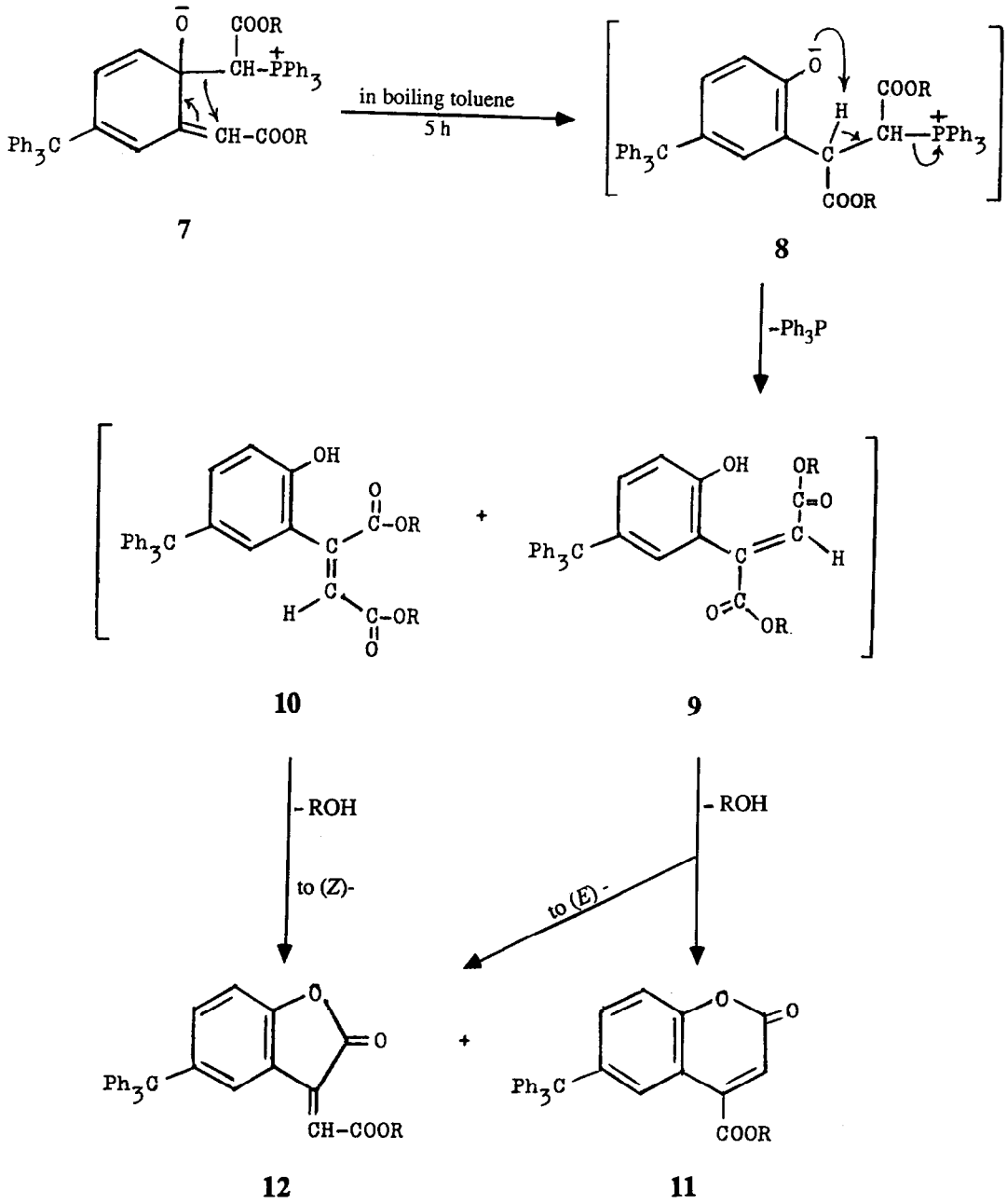


1 **4a**, R = Me, **b**, R = Et **5** **7a**, R = Me, **b**, R = Et **6**

Scheme 1

nyl compound to give a betaine species and the second is irreversible decomposition of the betaine to give alkene and phosphine oxide. The 1,2-oxaphosphetane was considered to be a transition state between the betaine and final products. Accordingly, the possible explanation for the formation of the adducts **7** as shown in the Scheme 1 is suggested by initial nucleophilic attack by the carbanion center in the ylides **4** on the two carbonyl-carbon of the quinone **1** to give the intermediate *bis*-betaine structures **5**. Subsequent decomposition then occurs at only one ß-oxido phosphonium ion group *meta* directing to the C-trityl group of **5** by the way of a four-centered cyclic intermediates **6** which eliminate triphenylphosphine oxide to form the *mono*-alkene derivatives **7**.

Compounds **7** are unstable above 60°C and upon heating in dry toluene for about 5 h followed by column chromatography gave triphenylphosphine in quantitative yield, colourless crystals of 4-alkoxycarbonyl-6-triphenylmethyl-2H-1-benzopyran-2-one (**11**) and a yellow crystalline product 5-triphenylmethyl-3- alkoxycarbonylmethylenebenzo[b]furan-2(3H)-one (**12**).



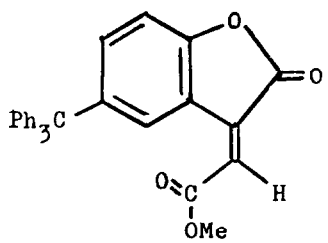
7 **8** **10** **9** **12** **11**

a, R = Me
b, R = Et

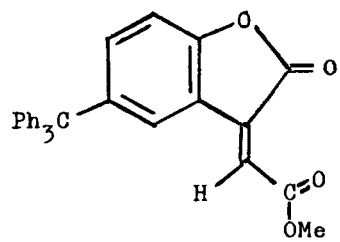
Scheme 2

The identity of compounds **11** and **12** was supported by correct elemental analyses and molecular weight determinations (MS) as well as the IR and ^{1}H NMR spectra which were compatible with the assigned structures. The IR spectra of **11** disclosed the presence of very strong absorption band around 1730 cm^{-1}, due to the carbonyl of the ester group together with the lactonic carbonyl coumarin ring system,[16] while in case of compounds **12**, two strong absorption bands appeared at 1720 and 1800 cm^{-1}, corresponding to the carbonyl-ester and the carbonyl of the five-membered ring γ-lactone,[16] respectively. Moreover, the ^{1}H NMR spectrum of **11a**, taken as an example, showed a singlet at δ 3.98 ppm attributable to the methoxyl group and a singlet at δ 6.92 ppm due to the exocyclic vinyl proton. The multiplet in the region δ 7.10-8.20 ppm corresponds to 18 aromatic protons.

The yellow crystalline product of the 5-triphenylmethyl-3-methoxycarbonylmethylenebenzo[b]furan-2(3H)-one (**12a**) was found to be a mixture of (*E*)- and (*Z*)- configurations. These 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 **12a$_I$** and the minor **12a$_{II}$** which were found in



12a$_I$



12a$_{II}$

ratio 3:2. The appearance of the chemical shift signals of vinyl proton and methoxyl group of **12a$_{II}$** (δ 6.84, 3.60 ppm) at a field higher than those of **12a$_I$** (δ 6.87, 3.86 ppm) is presumably attributed to the deshielding effect of the carbonyl group in the methoxy carbonyl moiety. (*E*)-5-Triphenylmethyl-3-methoxycarbonylmethylenebenzo[b]furan-2(3H)-one (**12a$_I$**) is the only isomer isolated in the pure form by fractional crystallization from petroleum ether (bp 60-80°C).

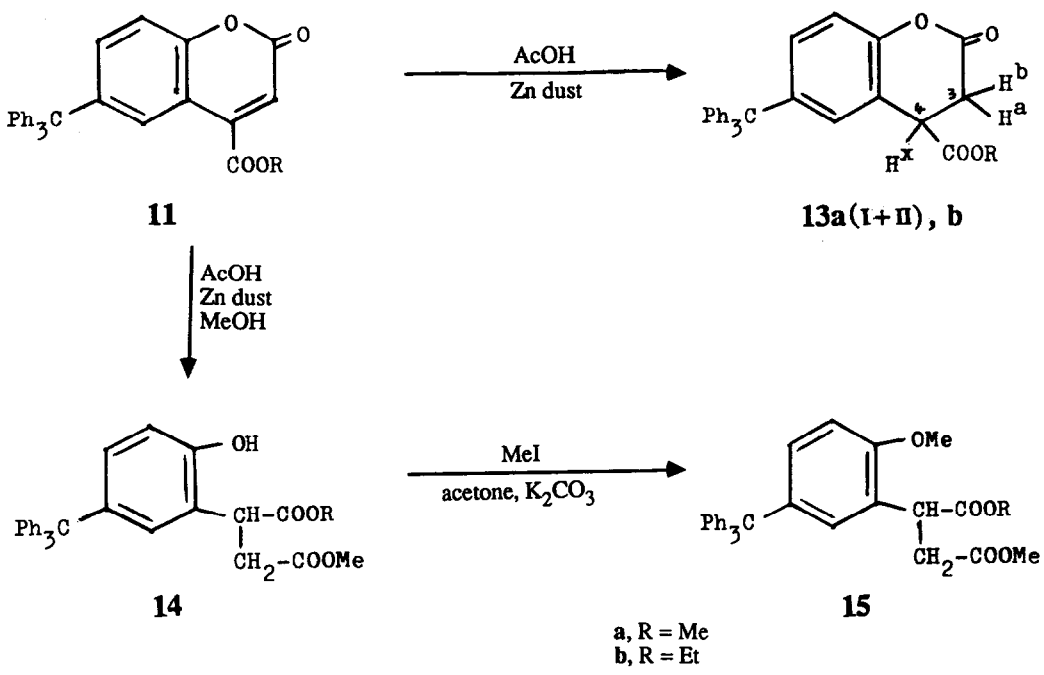
The yellow product 5-triphenylmethyl-3-ethoxycarbonylmethylenebenzo[b]furan-2(3H)-one (**12b**) obtained from heating **7b** in boiling toluene was isolated as only one isomer as proven by its ^{1}H NMR spectrum (Experimental).

A mechanism proposed for the formation of compounds **11** and **12** is shown in Scheme 2. The rearrangement of phosphonium species **7** gives rise to the betaine intermediates **8** which

following by Hofmann elimination of triphenylphosphine through an intramolecular abstraction of the hydrogen atom at β-carbon of the phosphonium group by the phenoxy anion afford the intermediates α,β-unsaturated esters in the form of (*E*)- (**9**) and (*Z*)- (**10**) isomers. The alkyl fumarate derivatives (**9**) undergo cyclization with the formation of coumarin derivatives (**11**) and (*E*)- ϒ -lactones (**12**), whereas the cyclization of alkyl maleate derivatives (**10**) can lead to produce (*Z*)- ϒ -lactones (**12**) together with the coumarin derivatives (**11**).

The double bond moiety of the pyrone ring in 4-alkoxycarbonyl-6-triphenylmethyl-2H-1-benzopyran-2-one (**11**) were reduced with zinc dust in boiling acetic acid to form 4-alkoxycarbonyl-6-triphenylmethyl-3,4-dihydro-2H-1-benzopyran-2-one (**13**) in quantitative yield (Scheme 3).

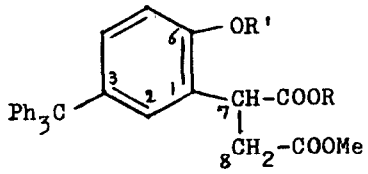
4-Methoxycarbonyl-6-triphenylmethyl-3,4-dihydro-2H-1-benzopyran-2-one (**13a**) was found to be a 3:1 mixture of two stereo-isomers on the basis of the ^{1}H NMR spectrum. The major isomer was considered as $\mathbf{13a_I}$ and the minor $\mathbf{13a_{II}}$. The isomer $\mathbf{13a_I}$ was isolated by fractional crystallization of the isomeric mixture from acetic acid but the other one $\mathbf{13a_{II}}$ could not be isolated in the pure form. In case of 4-ethoxycarbonyl-6-triphenylmethyl-3,4-dihydro-2H-1-benzopyran-2-one (**13b**) appeared by proton NMR spectrum to be in only one isomer. In the ^{1}H NMR spectra of **13a** and **13b** an ABX system pertaining to the methylene protons adjacent to an asymmetric grouping as in CHRR'-CH_2X. [17] Then the methylene protons H^a and H^b are magnetically non-equivalent and so have different chemical shifts. These two protons appeared as two AB-type doublets of doublets, at which the chemical shift at higher field can be assigned to the proton H^a. Each proton is split by the other ($J_{H^aH^b}$ = 16.3 Hz) and unequally by the vicinal proton H^x ($J_{H^aH^x}$ = 6.3 Hz and $J_{H^bH^x}$ = 3.8 Hz). The coupling constant values ($J_{H^aH^x}$ is greater than $J_{H^bH^x}$) confirm that the proton H^a is in a position *trans* to the ester group. The proton H^x appeared as a doublet of doublets and its chemical shift is located at lower field. The ethyl ester function in **13b** appeared as a triplet at δ 1.14 ppm, corresponding to the methyl moiety whereas the methylene protons of the ester are magnetically non-equivalent and located in the region δ 4.00-4.16 ppm. The two methylene protons are mutually coupled to give rise to an AB system and also with the adjacent methyl protons to form multiplet signals. Such non-equivalence of an ester CH_2 group is often observed when an asymmetric carbon is present at the $-\overset{O}{\overset{\|}{C}}-O-$ bond.[17] By comparison of the ^{1}H NMR spectra of the two isomers $\mathbf{13a_I}$ and $\mathbf{13a_{II}}$,the chemical shifts of both methyl ester protons and H^x in $\mathbf{13a_I}$ (δ 3.640, 3.839 ppm) show an upfield shift of 0.11 ppm from that of $\mathbf{13a_{II}}$ (δ 3.752, 3.949 ppm). This is attributed to the aryl group shielding effect . On the other hand, the chemical shift for H^b in $\mathbf{13a_I}$ (δ 3.130 ppm) is slightyl downfield shift about 0.007 ppm from that of $\mathbf{13a_{II}}$(δ 3.123 ppm). This observation is correlated to the deshielding effect of the carbonyl group of the ester on the adjacent proton H^b.



Scheme 3

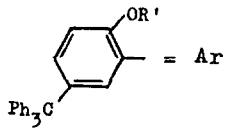
4-Alkoxycarbonyl-6-triphenylmethyl-2H-1-benzopyran-2-one (**11a,b**) undergo ring opening upon treatment with zinc dust in boiling acetic acid and methyl alcohol to give dimethyl (6-hydroxy-α,α,α-triphenyl-*m*-tolyl)succinate (**14a**) and (6-hydroxy-α,α,α-triphenyl-*m*-tolyl)succinic acid 1-ethyl ester 4-methyl ester (**14b**), respectively. Reaction of compounds **14a,b** with methyl iodide in presence of acetone and anhydrous potassium carbonate give the corresponding methyl ethers **15a,b** as shown in Scheme 3. The structure of compounds **14** and **15** was elucidated by correct elemental analyses, molecular weight determination (MS) and compatible spectroscopic results. These compounds contain a methylene group with a porton on the adjacent asymmetric carbon atom. The nature of these compounds make the proton NMR study particularly interesting due to the non-equivalence of the methylene protons which could throw some light on the conformational behaviour of this kind of compounds. In the ^1H NMR spectra of **14** and **15**, the three proton system $-CH_2-\dot{C}H-$ gives rise to an ABX pattern. Then, the methylene protons are non-equivalent. They are coupled to one another and to the vicinal proton to form two doublets of doublets with different chemical shifts. The proton on the asymmetric carbon appeared as doublet of doublets at down field shift. In terms of the Newman projection formulas the staggered confor-

mation of these compounds around the C-7-C-8 single bond is more adequate to represent the molecules as shown in Figure 1 since the coupling constant values $J_{H^a\,H^x}$ are less than $J_{H^b H^x}$. The methylene protons of ethyl ester -CH-$COOCH_2CH_3$ in both compounds **14b** and **15b** give a pattern



14 a, R = Me ; R' = H
b, R = Et ; R' = H

15 a, R = Me ; R' = Me
b, R = Et ; R' = Me



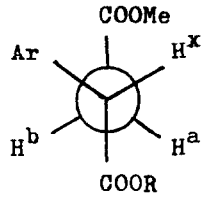


FIGURE 1 Staggered conformation of compounds **14** and **15**

similar to compound **13b**. The ^{1}H NMR spectral data are given in the experimental section. Moreover, the phenyl protons at C-2, C-4 and C-5 in compounds **14** and **15** give an ABC spectra in the δ 6.50 - 7.15 ppm region. The proton at C-2 shows a *meta* doublet with coupling constant J_{HH} = 2.4 Hz and the resonance of proton at C-4 is split into doublet of doublets with J_{HH} = 8.7 Hz and 2.4 Hz. The third proton at C-5 appears as an *ortho* doublet with coupling constant J_{HH} = 8.7 Hz. These coupling constants are in agreement with the expected values for aromatic protons of 1,2,4-trisubstituted benzenes. [18]

The methoxy protons in the *para* pointing to the C-trityl group in compounds **15a** and **15b** appeared in the ^{1}H NMR spectra as a sharp singlet at δ 3.80 ppm. This value is nearly compatible with the methoxyl protons at the same situation in 3,4-dimethoxyltetraphenylmethane[1] and 3-hydroxy-4-methoxytetraphenylmethane.[1] This observation is a good evidence for support of the subsequent decomposition of the *bis*-betaine **5** is occur at the β-oxido phosphonium ion group *meta* to the C-trityl group to form the *mono*-alkene product **7**.

Conclusion

From the present study the reaction of stabilized alkoxycarbonylmethylene(triphenyl)-phosphoranes (**4**) with 4-triphenylmethyl-1,2-benzoquinone (**1**) give rise to a novel type of compounds **7**, not previously observed with other *o*-quinones. Also, this reaction provides a pathway for the preparation of the reported coumarins **11** and ϒ-lactones **12**.

Experimental

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. The benzene (thiophene-free) and petroleum ether were dried over sodium. All reactions were carried out under nitrogen atmosphere. The IR spectra were recorded in KBr disks, on a Philips infracord spectrophotometer Model PU 9712. The NMR spectra were measured in $CDCl_3$, on a Bruker WM 250 or a Varian Gemini 200 spectrometers. Tetramethylsilane for ^1H NMR was used as an internal reference. For ^{31}P NMR shifts, 85% H_3PO_4 was used as an external reference. The mass spectra (MS) were determined at 70 eV on a Shimadzu GCMS-QP1000 EX spectrometer.

Reaction of 4-Triphenylmethyl-1,2-benzoquinone (1) with Methoxycarbonylmethylene (triphenyl)phosphorane (4a)

A mixture of quinone **1**[19] (1.40 g, 4.0 mmol) and ylide **4a**[20] (2.82 g, 8.4 mmol) in dry benzene (40 ml) was stirred at room temperature for 3 h under nitrogen atmosphere. During this time the red quinone run in solution with the formation of colourless precipitate. It was filtered off, washed with petroleum ether (bp 40-60°C) and crystallized from chloroform-petroleum ether (bp 40-60°C) without heating to give **7a** as colourless crystals, mp 175-176°C (2.44 g, 83% yield). Anal. Calcd. for $C_{49}H_{41}O_5P$: C, 79.44; H, 5.58; P, 4.18. Found: C, 79.39; H, 5.46; P, 4.20%. IR cm^{-1}: 1733 (C=O, ester); 1614, 1594 (C=C); 1436, 1105, 751, 700 (P-Phenyl);[14] ^{31}P NMR: signal at δ 24.72 ppm. ^1H NMR (200 MHz): δ 3.07 (s, 3H, ester CH_3); 3.33 (d, J_{PH} = 18 Hz, 1H, $\gtrless\overset{+}{P}\text{-}\overset{|}{C}H$-); 3.69 (s,3H, ester CH_3); 6.17 (s, 1H, exocyclic vinyl proton =CH-); 6.80-7.70 (m, 33H, ArH). MS : m/z (relative intensity) 446 (M^+ - Ph_3P, MeOH, 22%), 369 (75), 262 (100, $=Ph_3P$), 183 (67) and 108 (31).

The benzene filtrate, afforded upon concentration and addition of petroleum ether (bp 40-60°C), a colourless precipitate. Recrystallization from benzene/n-hexane gave triphenylphosphine oxide, mp and mixed mp 151°C (1 g, 90%).

When the reaction was performed using equimolar amounts from the ylide **4a** and the quinone **1**, compound **7a** and triphenylphosphine oxide together with some unchanged quinone **1**.

Reaction of 4-Triphenylmethyl-1,2-benzoquinone (1) with Ethoxycarbonylmethylene (triphenyl)phosphorane (4b)

A mixture of quinone **1** (1.40 g, 4.0 mmol) and ylide **4b**[20] (2.9 g, 8.4 mmol) in dry benzene (50 ml) was stirred at room temperature under nitrogen atmosphere. After 4 h, the colourless precipitate, thus formed, was filtered off and washed with petroleum ether (bp 40-60°C). It was crystallized from chloroform-petroleum ether (bp 40-60°C) without heating to give colourless crystals of **7b**, mp 155-157°C (1.9 g, 61% yield). Anal. Calcd. for $C_{51}H_{45}O_5P$: C, 79.67; H, 5.90; P, 4.03. Found: C, 79.81; H, 5.76; P, 3.92%. IR cm^{-1} : 1727 (C=O, ester); 1611, 1592 (C=C); 1437, 1105, 749,

696 (P-Phenyl).[14] ^{31}P NMR : signal at δ + 24.55 ppm. ^{1}H NMR (200 MHz) : δ 0.35 (t, J_{HH} =7 Hz, 3H, ester CH_3); 1.22 (t, J_{HH} =7 Hz, 3H, ester CH_3); 3.32 (d, J_{PH} = 18Hz, IH, $\overset{+}{P}$-$\overset{1}{C}$H-); 3.52-3.81 (m, 2H, ester CH_2); 4.04-4.28 (m. 2H, ester CH_2); 6.08 (s, 1H, exocyclic vinyl proton =CH-); 6.80-7.70 (m, 33H, ArH). MS : m/z (relative intensity) 460 (M^+-Ph_3P, EtOH, 38%), 383 (58), 262 (100, =Ph_3P); 183 (59) and 108 (29).

The filtrate was concentrated followed by addition of petroleum ether (bp 40-60°C) to form solid product which upon crystallization from benzene/n-hexane gave a quantitative yield of triphenylphosphine oxide (mp and mixed mp).

Action of Heat on 7a. Formation of Compounds 11a and 12a

Compound **7a** (2.22 g, 3.0 mmol) was heated under reflux in boiling toluene (50 ml). After 5 h, the yellow clear solution was evaporated under reduced pressure. The residue, thus obtained, was chromatographed on silica gel. The column was developed with petroleum ether (bp 60-80°C) containing increasing amounts of ethyl acetate. The first fraction (100% petroleum ether) gave colourless crystals (0.62 g, 78% yield), mp 80°C which proved to be triphenylphosphine by comparison with an authentic sample. The second fraction (95% petroleum ether) provided a yellow substance of **12a** (0.24 g, 18% yield) which contained a mixture of a (*E*)- and (*Z*)-configurations (shown only by ^{1}H NMR).

Fractional recrystallization from petroleum ether (bp 60-80°C) afforded a pure sample of the major isomer (*E*)-5-triphenylmethyl-3-methoxycarbonylmethylenebenzo[b]furan-2(3H)-one (**12a$_I$**) as yellow crystals, mp 180-181°C. Anal. Calcd. for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97. Found : C, 80.51; H, 4.82%. IR cm^{-1} : 1803 (C=O, five-membered ring γ-lactone), 1722 (C=O, ester). ^{1}H NMR (250 MHz) : δ 3.86 (s, 3H, ester CH_3); 6.87 (s, 1H, exocyclic vinyl proton =CH-); 7.022 (d, J_{HH}= 8.5 Hz, 1H, ArH at C-7); 7.082 (d, J_{HH} = 1.8 Hz, 1H, ArH at C-4); 7.123(dd, J_{HH}= 8.4 and 1.8 Hz, 1H, ArH at C-6); 7.16-8.50(m, 15H, C-trityl). MS : m/z (relative intensity) 446 (M^+, 25%), 369(100), 243(12) and 165(20).The minor isomer (*Z*)-5-triphenylmethyl-3- methoxycarbonylmethylenebenzo[b]furan-2 (3H) one (**12a$_{II}$**) could not be isolated in the pure form . Its ^{1}H NMR (shown in the spectrum of the isomeric mixture): δ 3.60 (s, 3H ester CH_3); 6.84 (s, 1H, exocyclic vinyl proton = CH-); 7.020 (d, J_{HH} = 8.5 Hz, 1H, ArH at C-7); 7.081 (d, J_{HH} = 1.8Hz, 1H, ArH at C-4); 7.123 (dd, J_{HH} = 8.4 and 1.8 Hz, 1H, ArH at C-6); 7.16- 8.50 (m, 15H, C-trityl). The third fraction (90% petroleum ether) gave colourless crystalline product of 4-methoxycarbonyl-6-triphenylmethyl-2H-1-benzopyran-2-one (**11a**) (0.71 g, 53% yield), recrystallized from acetone, mp 171-172°C. Anal. Calcd. for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97. Found: C, 80.55; H, 4.79% IR cm^{-1}: 1737 (C=O, coumarin and C=O, ester). ^{1}H NMR (250 MHz): δ 3.98 (s, 3H, ester CH_3); 6.92 (s, 1H, coumarin-H); 7.10-8.20 (m, 18H, ArH). MS: m/z (relative intensity) 446 (M^+, 50%), 369 (100), 243 (30) and 165 (50).

Action of Heat on 7b. Formation of Compounds 11b and 12b

A suspension of **7b** (1.54 g, 2.0 mmol) in dry toluene (40 ml) was heated under reflux for 6 h. Then the solvent and volatile materials were removed under reduced pressure and the residue was chromatographed on silica gel; using system: petroleum ether (bp 60-80°C), then petroleum ether containing increasing amounts of ethyl acetate. The first fraction (100% petroleum ether) gave colourless crystals (0.46 g, 88% yield), identified as triphenylphosphine by mp and mixed mp. The second fraction (95% petroleum ether) afforded yellow crystalline product of only one isomer (*E*)-5-triphenylmethyl-3-ethoxycarbonylmethylenebenzo[b]furan-2(3H)-one (**12b**) (0.11 g, 12% yield), recrystallized from benzene-petroleum ether (bp 40-60°C), mp 145-146°C. Anal. Calcd. for $C_{31}H_{24}O_4$: C, 80.85; H, 5.25. Found: C, 80.97; H, 5.11%. IR cm^{-1}: 1797(C=O, five-membered ring γ-lactone). 1714 (C=O, ester). ^1H NMR (250 MHz) : δ 1.17 (t, J_{HH} = 7.1 Hz, 3H, ester CH_3); 4.10 (q, J_{HH} = 7.1 Hz, 2H, ester CH_2); 6.85 (s, 1H, exocyclic vinyl proton =CH-); 7.02 (d, J_{HH} = 8.6 Hz, 1H, ArH at C-7); 7.10-8.50 (m, 17H, ArH). MS: m/z (relative intensity) 460 (M^+, 18%), 383 (100), 243 (12) and 165 (22). The third fraction (90% petroleum ether) gave colouress crystalline product of 4-ethoxycarbonyl-6-triphenylmethyl-2H-1-benzopyran-2-one (**11b**) (0.56 g, 61% yield), recrystallized from acetone, mp 216-217°C. Anal. Calcd. for $C_{31}H_{24}O_4$: C, 80.85; H, 5.25. Found : C, 80.71; H, 5.11%. IR cm^{-1} : 1730 (C=O, coumarin and C=O, ester). ^1H NMR (250 MHz): δ 1.21 (t, J_{HH} = 7.1 Hz, 3H, ester CH_3); 2.26 (q, J_{HH} =7.1 Hz, 2H, ester CH_2); 6.88 (s,1H, coumarin-H) ; 7.00-8.18 (m, 18H, ArH). MS: m/z (relative intensity) 460 (M^+, 14%), 383 (100), 243 (15) and 165 (34).

4-Methoxycarbonyl-6-triphenylmethyl-3,4-dihydro-2H-1-benzopyran-2-one (13a).

To a solution of **11a** (0.22 g, 0.5 mmol) in acetic acid (7 ml), zinc dust (0.2 g) was added in small portions over a period of 30 minutes at reflux temperature. Heating was continued for 2 h and then filtered off to remove the inorganic residue. The solution was concentrated under reduced pressure, followed by the addition of small portion of water. The solid product, thus formed, was filtered off to give colourless crystals of **13a** (0.19 g, 86% yield) containing a mixture of two isomeric forms in ratio 3:1 (from the ^1H NMR spectrum of the mixture). The major isomer $\mathbf{13a_I}$ was isolated in the pure form by dissolving the isomeric mixture in hot acetic acid which upon cooling gave colourless crystalline product of $\mathbf{13a_I}$, mp 215-216°C. Anal. Calcd. for $C_{30}H_{24}O_4$: C, 80.34; H 5.39. Found: C, 80.45; H, 5.28%. IR cm^{-1}: 1767 (C=O, lactone); 1728 (C=O, ester). ^1H NMR (250 MHz): δ 2.831 (dd, J_{HH} = 16.3 and 6.3 Hz, 1H, H at C-3); 3.125 (dd, J_{HH} = 16.3 and 3.8 Hz, 1H, H at C-3); 3.640 (s, 3H, ester CH_3); 3.836 (dd, J_{HH} = 6.3 and 3.8 Hz, 1H, H at C-4); 6.90-7.35 (m, 18H, ArH). MS : m/z (relative intensity) 448 (M^+, 20%), 371 (100), 311 (25), 243 (13) and 165 (43).

The minor isomer $\mathbf{13a_{II}}$ could not be obtained in an isolable form. Its ^1H NMR characteristics (shown from the spectrum of the isomeric mixture) (250 MHz): δ 2.831 (dd, J_{HH} = 16.3 and 6.3

Hz, 1H, H at C-3); 3.119 (dd, J_{HH} = 16.2 and 3.7 Hz, 1H, H at C-3); 3.750 (s, 3H, ester CH_3); 3.946 (dd, J_{HH} = 6.3 and 3.8 Hz, 1H, H at C-4); 6.90- 7.35 (m, 18H, ArH).

Similarly, compound **13b** was obtained as a colourless crystalline product in only one isomer by the reduction of **11b** with zinc dust in acetic acid.

4-Ethoxycarbonyl-6-triphenylmethyl-3,4-dihydro-2H-1-benzopyran-2-one (13b) (94% yield), crystallized from acetic acid, mp 204-205°C, Anal. Calcd. for $C_{31}H_{26}O_4$: C, 80.50; H, 5.67. Found: C, 80,61; H, 5.58%. IR cm^{-1} : 1780 (C=O, lactone); 1725 (C=O, ester). ^1H NMR (250 MHz): δ 1.14 (t, J_{HH} = 7.1 Hz, 3H, ester CH_3); 2.82 (dd, J_{HH} = 16.3 and 6.3 Hz, 1H, H at C-3); 3.12 (dd, J_{HH} = 16.3 and 3.8 Hz, 1H, H at C-3); 3.81 (dd, J_{HH} = 6.3 and 3.8 Hz,1H, H at C-4); 4.00-4.16 (m, 2H, ester CH_2); 6.90-7.35 (m, 18H, ArH). MS: m/z (relative intensity) 462 (M^+, 31%), 385 (100), 311 (13), 243 (9) and 165 (11).

Dimethyl (6-hydroxy-α,α,α-triphenyl-*m*-tolyl)succinate (14a)

A solution of **11a** (0.22 g, 0.5 mmol) in acetic acid (5 ml) and methanol (5 ml) was heated under reflux. Then zinc dust (0.2 g) was added in small portions over a period of 1 h and the mixture was heated for 5 h,. After removal of the inorganic residue by filtration, the solution was concentrated under reduced pressure followed by the addition of small portions of water. The solid material, so obtained, was filtered off, crystallized from benzene-petroleum ether (bp 40-60°C) to give **14a** as colourless crystals (0.19 g, 79% yield), mp 174-175°C. Anal. Calcd. for $C_{31}H_{28}O_5$: C, 77.49; H, 5.87. Found : C, 77.64; H, 5.71%. IR cm^{-1}: 3450 (OH); 1732 and 1701 (C=O, 2 esters). ^1H NMR (250 MHz) : δ 2.73 (dd, J_{HH} = 17.2 and 5.6 Hz, 1H, H at C-8); 3.28 (dd, J_{HH} = 17. 2 and 9.6 Hz, 1H, H at C-8); 3.67 (s, 3H, -CH_2- COO**CH$_3$**); 3.74 (s, 3H, -CH-**COOCH$_3$**); 4.25(dd, J_{HH} = 9.6and 5.6 Hz, 1H, H at C-7); 6.72 (dd, J_{HH} = 8.2 and 1.9 Hz, 1H, ArH at C-4); 6.79 (d, J_{HH} = 1.9 Hz, 1H, ArH at C-2); 6.95 (d, J_{HH} = 8.2 Hz, 1H, ArH at C-5); 7.10-7.35 (m, 16H, C-trityl and OH). MS : m/z (relative intensity) 480 (M^+ - MeOH, 70%), 388 (44), 371 (65), 311 (100), 243 (40), 205 (11) and 165 (55).

In a similar manner, compound **14b** was obtained as colourless crystals by the addition of zinc dust to a solution of **11a** in acetic acid and methanol.

(6-Hydroxy-α,α,α-triphenyl-*m*-tolyl) succinic Acid 1-Ethyl Ester 4-Methyl Ester (14b) (86% yield), crystallized from benzene-petroleum ether (bp 40-60°C), mp 146-147°C, Anal. Calcd. for $C_{32}H_{30}O_5$: C, 77.71; H, 6.11. Found:C, 77.89; H, 6.24%. IR cm^{-1} : 3420 (OH); 1722 (C=O, ester). ^1H NMR (250 MHz) : δ 1.16 (dt, J_{HH} = 7.1 Hz, 3H, ester CH_3); 2.64 (dd, J_{HH} =17.1 and 6.4 Hz 1H, H at C-8); 3.13 (dd, J_{HH} =17.1 and 8.9 Hz, 1H, H at C-8); 3.63 (s, 3H, -CH_2-**COOCH$_3$**);

3.99-4.17 (m, 2H, ester CH_2); 4.16 (dd, J_{HH} = 8.9 and 6.4 Hz, 1H, H at C-7); 6.75 (d, J_{HH} = 8.5 Hz, 1H, ArH at C-5); 6.92 (d, J_{HH} = 2.4 Hz, 1H, ArH at C-2); 6.99 (dd, J_{HH} = 8.5 and 2.4 Hz, 1H, ArH at C-4); 7.10-7.35 (m, 16H, C-trityl and OH. MS: m/z (relative intensity) 494 (M^+, 16%), 462 (14), 371 (100), 311 (78), 243 (31) and 165 (79).

Dimethyl (6-methoxy-α,α,α-triphenyl-*m*-tolyl)succinate (15a)

A mixture of **14a** (0.72 g, 1.5 mmol) and anhydrous powdered potassium carbonate (2 g) in dry acetone (50 ml) was stirred at room temperature for about 1 h. Then freshly distilled methyl iodide (0.25 g, 1.8 mmol) was added dropwise and the mixture was gently heated under reflux for 10 h. After removal of the inorganic residue, the solution was evaporated under reduced pressure to give colourless crystalline product of **15a** (0.66 g, 89% yield), recrystallized from benzene-petroleum ether (bp 40-60°C), mp 154-155°C. Anal. Calcd. for $C_{32}H_{30}O_5$: C, 77.71; H, 6.11. Found : C, 77.65; H, 6.01%. IR cm^{-1}: 1733 (C=O, ester). ^1H NMR (200 MHz): δ 2.54 (dd, J_{HH} = 16.6 and 5.2 Hz, 1H, H at C-8); 2.95 (dd, J_{HH} = 16.6 and 9.7 Hz, 1H, H at C-8); 3.53 (s, 3H, -CH_2-COO**CH_3**); 3.62 (s, 3H, -CH-COO**CH_3**); 3.80 (s, 3H, OCH_3 at C-6); 4.34 (dd, J_{HH} = 5.2 and 9.7 Hz, 1H, H at C-7); 6.25 (d, J_{HH} = 8.7 Hz, 1H, ArH at C-5); 6.92 (d, J_{HH} = 2.4 Hz, 1H, ArH at C-2); 7.10 (dd, J_{HH} = 8.7 and 2.4 Hz, 1H, ArH at C-4); 7.15-7.35 (m, 15H, C-trityl). MS: m/z (relative intensity) 494 (M^+, 16%), 417 (100), 243 (11), 165 (33) and 59 (24).

Similarly, compound **15b** was produced as colourless crystals from the reaction of **14b** with methyl iodide.

(6-Methoxy-α,α,α-triphenyl-*m*-tolyl)succinic Acid 1-Ethyl Ester 4-Methyl Ester (15b) (92% yield), crystallized from benzene-petroleum ether (bp 40-60°C). mp 167-168°C, Anal. Calcd. for $C_{33}H_{32}O_5$: C, 77.93; H, 6.34. Found: C, 78.02; H, 6.21%. IR cm^{-1} : 1731 (C=O, ester). ^1H NMR (250 MHz): δ 1.09 (dt, J_{HH} = 7.1 Hz, 3H ester CH_3), 2.54 (dd, J_{HH} = 16.6 and 5.2 Hz, 1H, H at C-8); 2.95 (dd, J_{HH} = 16.6 and 9.7 Hz, 1H, H at C-8); 3.62 (s, 3H, -CH_2- COO**CH_3**); 3.80 (s, 3H, OCH_3 at C-6); 3.92-4.10 (m, 2H, ester CH_2); 4.32 (dd, J_{HH} = 5.2 and 9.7 Hz, 1H, H at C-7); 6.74 (d, J_{HH} = 8.8 Hz, 1H, ArH at C-5); 6.95 (d, J_{HH} = 2.3 Hz, 1H, ArH at C-2); 7.07 (dd, J_{HH} = 8.7 and 2.4 Hz, 1H, ArH at C-4); 7.13- 7.30 (m, 15H, C-trityl). MS: m/z (relative intensity) 508 (M^+, 17%), 431 (100), 299 (11), and 165 (22).

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