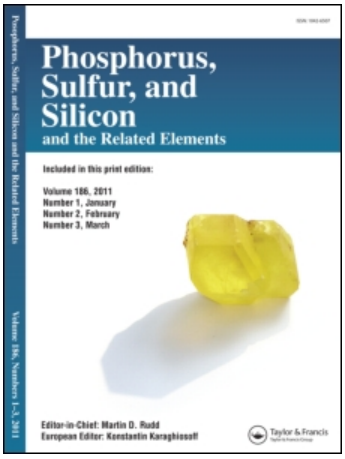


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# THE BEHAVIOR OF 4-TRIPHENYLMETHYL-1,2-BENZOQUINONE TOWARDS ALKOXY CARBONYLMETHYLENE(TRIPHENYL)-PHOSPHORANES AND TRIPHENYLPHOSPHINE IN ACETIC ANHYDRIDE

Fayez H. Osman[a]; Fatma A. El-samahy[a]
[a] Department of Pesticide Chemistry, National Research Center, Dokki, Cairo, Egypt

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# THE BEHAVIOR OF 4-TRIPHENYLMETHYL-1,2-BENZOQUINONE TOWARDS ALKOXYCARBONYLMETHYLENE(TRIPHENYL)-PHOSPHORANES AND TRIPHENYLPHOSPHINE IN ACETIC ANHYDRIDE

FAYEZ H. OSMAN* and FATMA A. EL-SAMAHY
*Department of Pesticide Chemistry, National Research Center, Dokki, Cairo 12622, Egypt*

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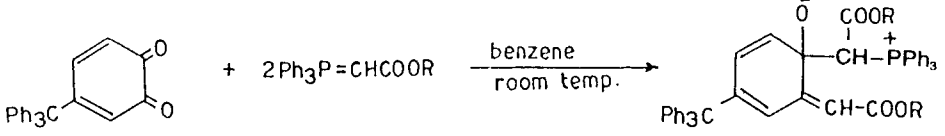
The reaction of alkoxycarbonylmethylene(triphenyl)phosphoranes (**2**) with 4-triphenylmethyl-1,2-benzoquinone (**1**) in acetic anhydride at room temperature for 7 h led to the formation of alkyl (6-acetoxy-$\alpha,\alpha,\alpha$-triphenyl-*m*-tolyl)fumarates (**7**), alkyl (6-acetoxy-$\alpha,\alpha,\alpha$-triphenyl-*m*-tolyl)maleates (**8**), benzofuran derivatives (**13** and **14**), 3,4-diacetoxytetraphenylmethane (**18**) along with triphenylphosphine and triphenylphosphine oxide. The action of alcoholic HCl on the fumarates **7** give the coumarin derivatives (**19**) whereas the maleates **8** yielded **19** and two additional products, alkyl (6-hydroxy-$\alpha,\alpha,\alpha$-triphenyl-*m*-tolyl)maleates (**6**) and (*E*)-5-triphenylmethyl-3-alkoxycarbonylmethylenebenzo[b]furan-2(3H)-ones (**20**). Methylation of the products **6** with methyl iodide in dry acetone and anhydrous potassium carbonate gave the corresponding methyl ethers **21**. When the maleates **6** were heated in boiling toluene for about 30 h, a mixture of the coumarin derivatives **19** and (*Z*)-isomer of **20** was obtained. Triphenylphosphine reacted with quinone **1** in acetic anhydride to give quantitative yield of **18** with triphenylphosphine oxide. Possible reaction mechanisms are considered.

*Key words:* Phosphoranes, NMR spectra, reaction mechanisms.



## INTRODUCTION

In a previous paper,[1] we have found that alkoxycarbonylmethylene(triphenyl)-phosphoranes (**2**) reacted with 4-triphenylmethyl-1,2-benzoquinone (**1**) in dry benzene at room temperature to give 2:1 adducts proved to possess structure **3**. Continuing this work, it appeared interesting to study the behavior of the quinone **1** towards the Wittig reagents **2**, using acetic anhydride as a solvent.




**1** **2** a, R = Me; b, R = Et **3**

## RESULTS AND DISCUSSIONS

When 4-triphenylmethyl-1,2-benzoquinone (**1**) was treated with two equivalents of alkoxycarbonylmethylene(triphenyl)phosphoranes (**2**) in acetic anhydride at room

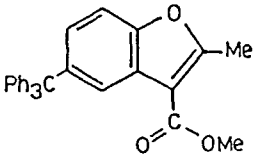
temperature for 7 h, a mixture of products was obtained consisting of mainly compounds **7** and **8** together with other amounts of unexpected products **13**, **14** and **18** (Scheme I). These compounds were separated by column chromatography on silica gel. Triphenylphosphine and triphenylphosphine oxide were also isolated and identified.

Alkyl (6-acetoxy-$\alpha,\alpha,\alpha$-triphenyl-*m*-tolyl)fumarates (**7**) and alkyl (6-acetoxy-$\alpha,\alpha,\alpha$-triphenyl-*m*-tolyl)maleates (**8**) are the two isomeric forms of (*E*)- and (*Z*)-isomers of $\alpha,\beta$-unsaturated esters. They were separated as colorless crystals and their assigned structures were established from the elemental analyses, IR, $^1$H NMR and mass spectra. The IR spectra of these adducts **7** and **8** exhibited a strong absorption bands around 1770 $cm^{-1}$ and 1725 $cm^{-1}$ corresponding to C=O, acetyl[2] and C=O, esters,[2] respectively. The $^1$H NMR spectra of **7** and **8** gave good evidence supporting their structures. The chemical shift of the olefinic proton in the alkyl fumarates **7** was deshielded by 0.88 ppm compared with the corresponding alkyl maleates **8**. This difference observed is due to the anisotropic effect of the ester carbonyl group at $\alpha$-carbon.[3]

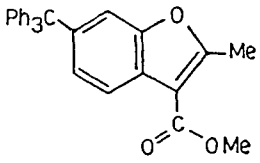
In another experiment, compounds **7** and **8** were obtained in much better yields by stirring a suspension of compounds **3** in acetic anhydride at room temperature for 15 h.

The proposed mechanism for the formation of **7** and **8** illustrated in Scheme I shows the phosphonium species **3** initially undergo a rearrangement to account for the formation of the phenoxy anion intermediate **4** which was followed by intramolecular Hofmann elimination of triphenylphosphine to give the non-isolated alkyl (*o*-hydroxyaryl)fumarates (**5**) and alkyl (*o*-hydroxyaryl)maleates (**6**). The presence of acylating agents led to the intermediates **5** and **6** to form the corresponding acetoxy derivatives **7** and **8**.

The colorless crystalline products of benzofuran derivatives **13** and **14** were isolated in the pure forms and their assigned structures were established from elemental analyses and spectral properties which were consistent with expectation. The suggested configurations of compounds **13** and **14** were supported by the recorded $^1$H

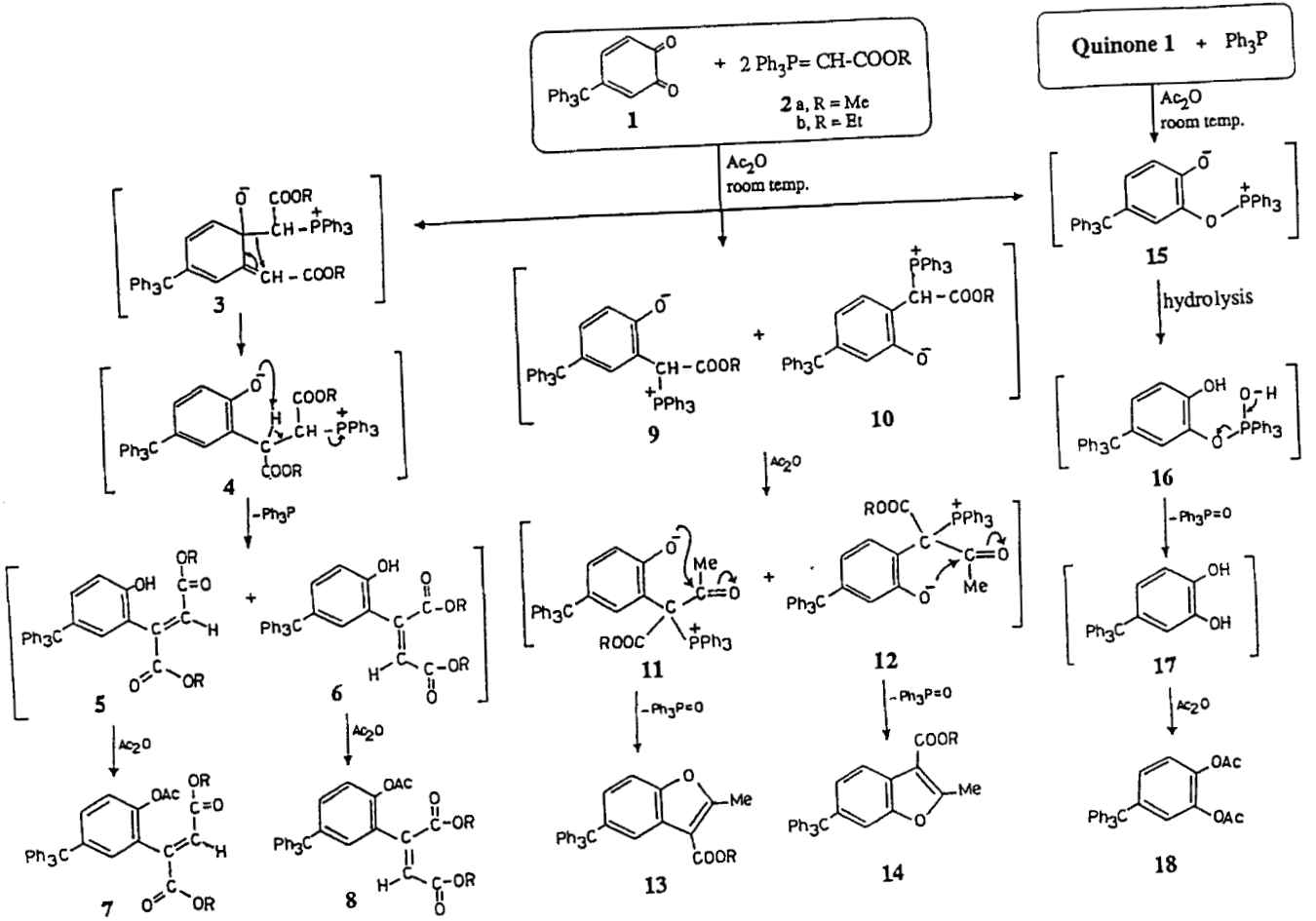



**13a**




**14a**

NMR chemical shifts and coupling constants of three protons in the benzofuran ring which gave rise to an ABX pattern.[4] The $^1$H NMR spectrum of **13a** showed a *meta* doublet at $\delta$ 7.85 ppm with $J_{H4H6}$ = 2.2 Hz for the proton at C-4 and *ortho*/*meta* doublet of doublets at $\delta$ 7.05 ppm with coupling constant $J_{H6H7}$ = 8.8 Hz and $J_{H4H6}$ = 2.2 Hz for the proton at C-6. The *ortho* doublet of the proton at C-7 is hidden under the multiplets of C-trityl protons in the region $\delta$ 7.14–7.31 ppm. On the other hand, the $^1$H NMR spectrum of **14a** showed the proton at C-4 as an *ortho* doublet at $\delta$ 7.77 ppm with $J_{H4H5}$ = 8.8 Hz and the proton at C-5 exhibited a characteristic *ortho*/*meta* doublet of doublets at $\delta$ 7.11 ppm with $J_{H4H5}$ = 8.8 Hz and $J_{H5H7}$ = 2.2 Hz. The third proton at C-7 appeared as a *meta* doublet at $\delta$ 7.34 ppm with $J_{H5H7}$ =




SCHEME I

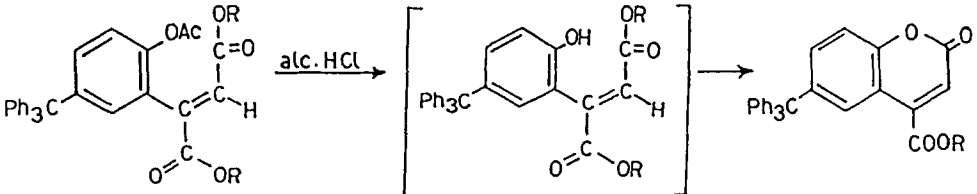
2.2 Hz. On the basis of the above $^1$H NMR data, it should be noted that the chemical shift of the proton at C-7 with characteristic coupling constant in both compounds **13a** and **14a** appeared at a higher field than that of the proton at C-4. This observation is correlated with the deshielding effect of the carbonyl group in the methoxy carbonyl moiety.

A possible mechanism for the formation of the products **13** and **14** is suggested in Scheme I. The phosphonium intermediates **9** and **10** which could be formed from the reaction of quinone **1** with ylides **2** go on acetylation by acetic anhydride to afford the corresponding phenoxy anion intermediates **11** and **12**, followed by ring closure after elimination of triphenylphosphine oxide to give the benzofuran derivatives **13** and **14**.

3,4-Diacetoxytetraphenylmethane (**18**) obtained from the reaction of quinone **1** with phosphonium ylides **2** in acetic anhydride was isolated as colorless crystals and its structure was elucidated by correct elemental analyses, molecular weight determination (MS) and compatible spectroscopic results. The IR spectrum disclosed the presence of sharp absorption band at 1768 cm$^{-1}$, corresponding to the carbonyl of the acetyl groups. The $^1$H NMR spectrum of **18** showed two singlets at $\delta$ 2.16 and 2.25 ppm, attributable to the methyl protons of the two acetyl groups.

Compound **18** was also obtained in quantitative yield from the reaction of quinone **1** with triphenylphosphine in acetic anhydride at room temperature for 5 h.

The formation of diacetoxytetraphenylmethane (**18**) can be explained as shown in Scheme 1. This involves initial nucleophilic attack by phosphorus on the carbonyl oxygen atom to form the phosphonium species (**15**) like other *o*-quinones,[5,6] which is easily hydrolyzed to give the transient intermediate **16**. The latter ejects rapidly and spontaneously triphenylphosphine oxide is formed 3,4-dihydroxytetraphenylmethane (**17**), followed by acylation to give the final product **18**.

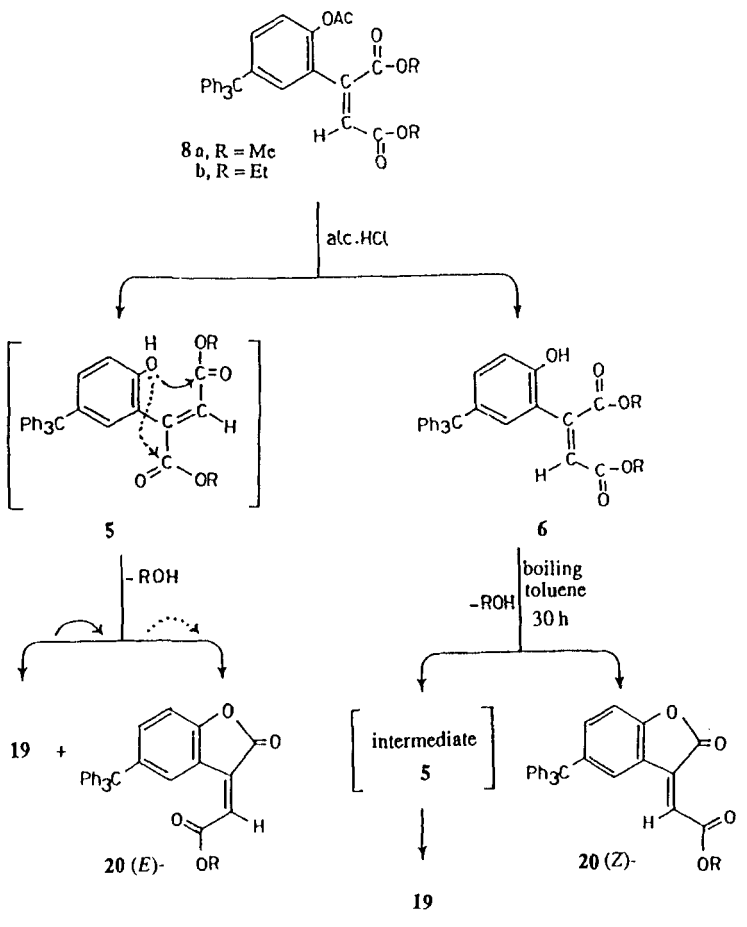



**7a**, R = Me
**b**, R = Et

**5**

**19**

When the acetoxy fumarates (**7**) were heated in alcoholic solution containing hydrochloric acid at 70°C for about 4 h, the coumarin derivatives (**19**)[1] were obtained quantitatively. On the other hand, treatment of the acetoxy maleates (**8**) with alcoholic hydrochloric acid solution under the same experimental conditions gave alkyl (*o*-hydroxyaryl)maleates (**6**) as the major products, along with the coumarin derivatives (**19**)[1] and the (*E*)-isomer of 3-alkoxycarbonylmethylene-$\gamma$-lactones (**20**).[1] The formation of the coumarin derivatives (**19**) and (*E*)-$\gamma$-lactones (20) was accomplished via the rapid lactonization of the non-isolated alkyl (*o*-hydroxyaryl)fumarates (**5**) as shown in Scheme II. The reaction products were separated by column chromatography and their assigned structures were established from elemental analyses and spectral properties.



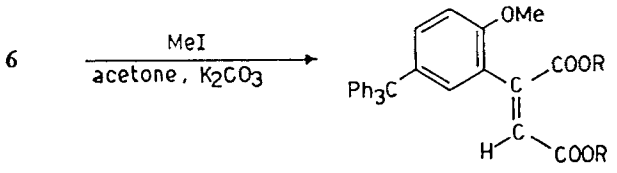

SCHEME II

When alkyl (*o*-hydroxyaryl)maleates (**6**) were heated in boiling toluene for about 30 h followed by column chromatography, they gave a yellow crystalline products of (*Z*)-isomer of 3-alkoxycarbonylmethylene-γ-lactones (**20**) and colourless crystals of the coumarin derivatives (**19**). A possible explanation for the formation of (*Z*)-γ-lactones (**20**) and the coumarin derivatives (**19**) from alkyl (*o*-hydroxyaryl)maleates (**6**) is presented in Scheme II. The lactonization of **6** led to the formation of (*Z*)-γ-lactones (**20**) whereas the coumarin derivatives (**19**) were obtained via the formation of alkyl (*o*-hydroxyaryl)fumarate intermediates (**5**).

From the above results, it could be noted that the lactonization of alkyl (*o*-hydroxyaryl)fumarates (**5**) led to the formation of the coumarins (**19**) and/or to the formation of the (*E*)-γ-lactones (**20**) whereas the lactonization of alkyl (*o*-hydroxyaryl)maleates (**6**) led only to the formation of the (Z)-γ-lactones (**20**). This rule is in agreement with that reported by Nicolaides *et al.*[5,7] in other similar reactions.

Methylation of alkyl (*o*-hydroxyaryl)maleates (**6a,b**) with methyl iodide in the presence of acetone and anhydrous potassium carbonate led to the formation of the corresponding methyl ethers (**21a,b**). The structure of these compounds was verified

by correct elemental analyses, molecular weight determinations (MS) and compatible spectroscopic results. The IR spectra of compounds **21** revealed the absence of the absorption bands around 3200 $cm^{-1}$ characteristic of the hydroxy group of the parent compounds **6**. Moreover, the $^1H$ NMR spectra of **21** showed a singlet at $\delta$ 3.80 ppm, attributable to the methoxy protons in the *para* directing to the C-trityl group.[1,8,9]




**21** a, R = Me
b, R = Et

## CONCLUSION

From the present study, it was found that the reaction of 4-triphenylmethyl-1,2-benzoquinone (**1**) with alkoxycarbonylmethylene(triphenyl)phosphoranes (**2**) using acetic anhydride as a solvent gave new products of acetoxy fumarates **7**, acetoxy maleates **8**, benzofuran derivatives **13**, **14** and 3,4-diacetoxytetraphenylmethane (**18**) whereas this reaction in benzene solution under the same experimental conditions previously reported[1] led to the formation of compounds **3**. Furthermore, the fumarates **7** and maleates **8** were also obtained from the reaction of compounds **3** with acetic anhydride.



## EXPERIMENTAL

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. The IR spectra were recorded in KBr disks, on a Phillips infracord spectrophotometer Model PU 9712. The $^1H$ NMR spectra were measured in $CDCl_3$, on a Jeol EX-270 MHz spectrometer, using tetramethylsilane as an internal reference. The mass spectra (MS) were determined at 70 eV on a Shimadzu GCMS-QP1000 EX or Finnigan MAT 95 spectrometers.

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

A mixture of quinone **1**[10] (0.70 g, 2.0 mmol) and ylide **2a**[11] (1.40 g, 4.2 mmol) in acetic anhydride (15 ml) was stirred at room temperature for 7 h (examined by TLC). Then, the clear solution of the reaction mixture was added into water (20 ml) and extracted with chloroform (4 × 30 ml). The extract solution dried over anhydrous sodium sulfate and evaporated to dryness in the presence of silica gel. The mixture was subjected to column chromatography on silica gel with *n*-hexane. The column was developed with *n*-hexane followed by *n*-hexane containing increasing amounts of ethyl acetate. The first fraction (100% *n*-hexane) gave colorless crystals (34 mg), proved to be triphenylphosphine (mp and mixed mp 80°C). The second fraction (99–96% *n*-hexane) gave colorless crystals (73 mg, 8% yield) containing a mixture of benzofuran derivatives **13a** and **14a** in ratio 3:2 (shown only by $^1H$ NMR spectrum). For separation of these two isomers **13a** and **14a** in the pure forms, this fraction was subjected to another column chromatography using petroleum ether (bp 60–80°C)-ethyl acetate (100:0 → 98:2) as eluant. The minor isomer methyl 2-methyl-6-triphenylmethylbenzofuran-3-carboxylate (**14a**) (20 mg) was eluted first, recrystallized from benzene-petroleum ether (bp 40–60°C), mp 202–203°C. Anal. Calcd. for $C_{30}H_{24}O_3$: C, 83.31; H, 5.59. Found: C, 83.25; H, 5.53%. IR $cm^{-1}$: 1719 (C=O, ester), 1595 (C=C). $^1H$ NMR:

δ 2.71 (s, 3H, $CH_3$), 3.89 (s, 3H, ester $CH_3$), 7.11 (dd, $J_{HH}$ = 8.8 and 2.2 Hz, 1H, ArH at C-5), 7.14–7.31 (m, 15H, C-trityl), 7.34 (d, $J_{HH}$ = 2.2 Hz, 1H, ArH at C-7), 7.77 (d, $J_{HH}$ = 8.8 Hz, 1H, ArH at C-4). MS: m/z (relative intensity) 432 ($M^+$, 21%), 355 (100) and 165 (20). The major isomer methyl 2-methyl-5-triphenylmethylbenzofuran-3-carboxylate (**13a**) (32 mg) was eluted next, recrystallized from benzene-petroleum ether (bp 40–60°C), mp 234–235°C. Anal. Calcd. for $C_{30}H_{24}O_3$: C, 83.31; H, 5.59. Found: C, 83.22; H, 5.51%. IR $cm^{-1}$: 1725 (C=O, ester), 1603 (C=C). $^1H$ NMR: δ 2.72 (s, 3H, $CH_3$), 3.74 (s, 3H, ester $CH_3$), 7.05 (dd, $J_{HH}$ = 8.8 and 2.2 Hz, 1H, ArH at C-6), 7.14–7.40 (m, 16H, C-trityl and ArH at C-7), 7.85 (d, $J_{HH}$ = 2.2 Hz, 1H, ArH at C-4). MS: m/z (relative intensity) 432 ($M^+$, 20%), 355 (100) and 165 (34). The third fraction (95–93% *n*-hexane) gave colorless crystals of 3,4-diacetoxytetraphenylmethane (**18**) (0.10 g, 11% yield), recrystallized from benzene/*n*-hexane, m.p. 196–197°C. Anal. Calcd. for $C_{29}H_{24}O_4$: C, 79.80; H, 5.54. Found: C, 79.91; H, 5.48%. IR $cm^{-1}$: 1768 (C=O, acetyl). $^1H$ NMR: δ 2.16 (s, 3H, $CH_3$), 2.25 (s, 3H, $CH_3$), 7.00–7.60 (m, 18H, ArH). MS: m/z (relative intensity) 437 ($M^+$ + 1, 11%), 394 (21), 352 (64), 317 (11), 275 (36), 243 (12), 165 (22) and 43 (100). The fourth fraction (92–90% *n*-hexane) afforded colorless crystals of dimethyl (6-acetoxy-α,α,α-triphenyl-*m*-tolyl)fumarate (**7a**) (0.15 g, 14% yield), recrystallized from benzene-petroleum ether (bp 40–60°C), mp 168–169°C. Anal. Calcd. for $C_{33}H_{28}O_6$: C, 76.14: H, 5.42. Found: C, 76.03; H, 5.37%. IR $cm^{-1}$: 1773 (C=O, acetyl), 1723 (C=O, ester). $^1H$ NMR: δ 2.15 (s, 3H, acetyl), 3.50 (s, 3H, ester $CH_3$), 3.70 (s, 3H, ester $CH_3$), 6.94 (s, 1H, =CH—), 6.95–7.35 (m, 18H, ArH). MS: m/z (relative intensity) 520 ($M^+$, 27%), 478 (79), 401 (100), 369 (81), 341 (16), 281 (11), 252 (16), 165 (34), 69 (11), 57 (16) and 43 (11). The fifth fraction (90–85% *n*-hexane) gave colorless crystals of dimethyl (6-acetoxy-α,α,α-triphenyl-*m*-tolyl)maleate (**8a**) (0.19 g, 18% yield), recrystallized from benzene-petroleum ether (bp 40–60°C), mp 178–179°C. Anal. Calcd. for $C_{33}H_{28}O_6$: C, 76.14; H, 5.42. Found: C, 76.25; H, 5.34%. IR $cm^{-1}$: 1767 (C=O, acetyl), 1739 (C=O, ester). $^1H$ NMR: δ 2.25 (s, 3H, acetyl), 3.73 (s, 3H, ester $CH_3$), 3.78 (s, 3H, ester $CH_3$), 6.05 (s, 1H, =CH—), 6.92–7.41 (m, 18H, ArH). MS: m/z (relative intensity) 520 ($M^+$, 7%), 478 (53), 446 (24), 401 (28), 369 (100), 341 (12), 281 (7), 252 (11), 165 (24), 97 (3), 57 (5) and 43 (5). The last fraction (80–65% *n*-hexane) yielded colorless crystalline product of triphenylphosphine oxide (0.46 g) (mp and mixed mp 155°C).

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

The reaction of quinone **1** (0.70 g, 2.0 mmol) with ylide **2b**[11] (1.46 g, 4.2 mmol) in acetic anhydride (15 ml) was carried out for 5 h and the reaction mixture was worked up according to the above described procedure for ylide **2a**. Triphenylphosphine was eluted first (30 mg). The second fraction gave colorless crystalline product (61 mg, 7% yield) contained a mixture of benzofuran derivatives **13b** and **14b** with relative ratio 5:1 (shown only by $^1H$ NMR spectrum). the major isomer, ethyl 2-methyl-5-triphenylmethylbenzofuran-3-carboxylate (**13b**) was isolated in the pure from by fractional recrystallization from benzene-petroleum ether (bp 40–60°C), mp 183–184°C. Anal. Calcd. for $C_{31}H_{26}O_3$: C, 83.38; H, 5.87. Found: C, 83.45; H, 5.79%. IR $cm^{-1}$: 1717 (C=O, ester), 1595 (C=C). $^1H$ NMR: δ 1.20 (t, $J_{HH}$ = 7 Hz, 3H, ester $CH_3$), 2.78 (s, 3H, $CH_3$), 4.24 (q, $J_{HH}$ = 7 Hz, 2H, ester $CH_2$), 7.09 (dd, $J_{HH}$ = 8.6 and 2.2 Hz, 1H, ArH at C-6), 7.20–7.35 (m, 16H, C-trityl and ArH at C-7), 7.88 (d, $J_{HH}$ = 2.2 Hz, 1H, ArH at C-4). MS: m/z (relative intensity) 446 ($M^+$, 26%), 369 (100), 277 (19) and 165 (22). The other isomer ethyl 2-methyl-6-triphenylmethylbenzofuran-3-carboxylate (**14b**) could not be isolated in the pure form. Its $^1H$ NMR (from the spectrum of the isomeric mixture): δ 1.41 (t, $J_{HH}$ = 7 Hz, 3H, ester $CH_3$), 2.78 (s, 3H, $CH_3$), 4.37 (q, $J_{HH}$ = 7 Hz, ester $CH_2$), 7.15 (dd, $J_{HH}$ = 8.6 and 2.2 Hz, 1H, ArH at C-5), 7.20–7.35 (m, 15H, C-trityl), 7.39 (d, $J_{HH}$ = 2.2 Hz, 1H, ArH at C-7), 7.82 (d, $J_{HH}$ = 8.6 Hz, 1H, ArH at C-4). The third fraction yielded a crystalline product of 3,4-diacetoxytetraphenylmethane (**18**) (0.11 g, 12% yield) (mp, mixed mp and comparative IR spectra) (*vide supra*). The fourth fraction gave colorless crystals of diethyl (6-acetoxy-α,α,α-triphenyl-*m*-tolyl)fumarate (**7b**) (0.18 g, 16% yield), recrystallized from benzene-petroleum ether (bp 40–60°C), mp 130–131°C. Anal. Calcd. for $C_{35}H_{32}O_6$: C, 76.62; H, 5.88. Found: C, 76.69; H, 5.81%. IR $cm^{-1}$: 1766 (C=O, acetyl), 1714 (C=O, ester). $^1H$ NMR: δ 1.04 (t, $J_{HH}$ = 7.3 Hz, 3H, ester $CH_3$), 1.19 (t, $J_{HH}$ = 7.3 Hz, 3H, ester $CH_3$), 2.19 (s, 3H, acetyl), 3.99 (q, $J_{HH}$ = 7.3 Hz, 2H, ester $CH_2$), 4.18 (q, $J_{HH}$ = 7.3 Hz, 2H, ester $CH_2$), 6.96 (s, 1H, =CH—), 7.00–7.45 (m, 18H, ArH). MS: m/z (relative intensity) 548 ($M^+$, 26%), 506 (80), 429 (84), 383 (100), 355 (26), 252 (9), 243 (17), 165 (32), 69 (18), 57 (26) and 43 (18). The fifth fraction gave diethyl (6-acetoxy-α,α,α-triphenyl-*m*-tolyl)maleate (**8b**) (0.21 g, 19% yield) as colorless crystals, recrystallized from benzene-petroleum ether (bp 40–60°C), mp 175–176°C. Anal. Calcd. for $C_{35}H_{32}O_6$: C, 76.62; H, 5.88. Found: C, 76.78; H, 5.94%. IR $cm^{-1}$: 1767 (C=O, acetyl), 1727 (C=O, ester). $^1H$ NMR: δ 1.218, 1.244 (2t, overlap, $J_{HH}$ = 7.2 Hz, 6H, 2 ester $CH_3$), 2.25 (s, 3H, acetyl), 4.166, 4.192 (2q overlap, $J_{HH}$ = 7.2 Hz, 4H, 2 ester $CH_2$), 6.15 (s, 1H, =CH—), 6.93–7.33 (m, 18H, ArH). MS: m/z (relative intensity) 548 ($M^+$, 6%), 506 (48), 460 (29), 429 (21), 383 (100), 355 (19), 252 (6), 243 (12), 165 (21), 97 (4), 57 (8) and 43 (6). The last fraction afforded colorless crystals of triphenylphosphine oxide (0.39 g) (mp and mixed mp).

*Conversion of Compound* **3a** *into Compounds* **7a** *and* **8a**

A suspension of **3a**[1] (0.90 g, 1.2 mmol) in acetic anhydride (20 ml) was stirred at room temperature. After about 15 h, the solid material run in solution. Then, the reaction mixture was added into water (20 ml) and extracted with chloroform (4 × 30 ml). The extract was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was chromatographed on silica gel, using system: *n*-hexane followed by *n*-hexane contains increasing amounts of ethyl acetate. The first fraction (100% *n*-hexane) gave colorless crystalline product of triphenylphosphine (0.14 g, 45% yield). The second fraction (95–91% *n*-hexane) gave **7a** (0.20 g, 32% yield). The third fraction (90–85% *n*-hexane) afforded **8a** (0.24 g, 38% yield).

In a similar manner, compounds **7b** (29% yield) and **8b** (32% yield) along with triphenylphosphine (42% yield) were obtained by stirring a suspension of **3b**[1] in acetic anhydride for 15 h at room temperature.

*Reaction of Quinone* **1** *with Triphenylphosphine*

To a suspension of quinone **1** (0.35 g, 1.0 mmol) in acetic anhydride (10 ml), triphenylphosphine (0.29 g, 1.1 mmol) was added. The reaction mixture was stirred at room temperature for 5 h and then allowed to stand overnight. The white precipitate, thus formed, was filtered off and crystallized from benzene-petroleum ether (bp. 40–60°C) to give colorless crystals (0.26 g, 60% yield), proved to be 3,4-diactoxytetraphenylmethane (**18**) (mp, mixed mp, comparative IR and $^1$H NMR spectra) (*vide supra*). The acetic anhydride filtrate was added into water (10 ml) and extracted with chloroform (4 × 15 ml). The extract was dried over anhydrous sodium sulfate, the solvent removed under reduced pressure and the residue was chromatographed on silica gel. Elution with ethyl acetate-petroleum ether (bp 60–80°C) afforded two fractions. The first fraction (90–95% petroleum ether) gave an additional amount of the diacetate **18** (50 mg). The second fraction (75–65% petroleum ether) yielded triphenylphosphine oxide (0.12 g, 43% yield).

*Action of Alcoholic Hydrochloric Acid on the Fumarate* **7a**: *Formation of Compound* **19a**

A mixture of **7a** (100 mg, 0.19 mmol) in ethyl alcohol (10 ml) and hydrochloric acid (sp. gr. 1.16, 1 ml) was heated under reflux (bath temperature 70°C) for 4 h. After cooling, the solid material was filtered off (90 mg, 100% yield), crystallized from acetone and proved to be 4-methoxy-carbonyl-6-triphenylmethyl-2H-1-benzopyran-2-one (**19a**) (mp and mixed mp 171–172°C).[1]

Similarly, 4-ethoxycarbonyl-6-triphenylmethyl-2H-1-benzopyran-2-one (**19b**)[1] (98% yield) was obtained by allowing the above described procedure using **7b**.

*Action of Alcoholic Hydrochloric Acid on the Maleate* **8a**: *Formation of Compounds* **6a**, **19a** *and* **20a**

A mixture of **8a** (100 mg, 0.19 mmol) in ethyl alcohol (10 ml) and hydrochloric acid (sp. gr. 1.16, 1 ml) was heated under reflux at 70°C for 6 h. Then, the solution was added into water (10 ml) and extracted with chloroform (3 × 40 ml). The extract was dried over anhydrous sodium sulfate and evaporated to dryness. Chromatography on silica gel with ethyl acetate-petroleum ether (bp 40–60°C) as eluent gave three fractions. The first fraction (95% petroleum ether) yielded a yellow crystalline product, identified as (*E*)-5-triphenylmethyl-3-methoxycarbonylmethylenebenzo[b]furan-2(3H)-one (**20a**)[1] (4 mg, 5% yield). The second fraction (90% petroleum ether) gave colorless crystals of compound **19a**[1] (9 mg, 10% yield). The third fraction (85–80% petroleum ether) provided colorless crystals of dimethyl (6-hydroxy-α,α,α-triphenyl-*m*-tolyl)maleate (**6a**) (48 mg, 52% yield), recrystallized from ethyl acetate/*n*-hexane mp 190–191°C. Anal. Calcd. for $C_{31}H_{26}O_5$: C, 77.81; H, 5.48. Found: C, 77.85; H, 5.41%. IR cm$^{-1}$: 3228 (OH), 1716, 1694 (C=O, esters). $^1$H NMR: δ 3.78 (s, 3H, ester $CH_3$), 3.79 (s, 3H, ester $CH_3$), 6.45 (s, 1H, =CH—), 6.83–7.37 (m, 18H, ArH), 8.55 (s, 1H, OH). MS: m/z (relative intensity) 478 ($M^+$, 5%), 446 (17), 369 (100), 252 (24) and 165 (37).

*Action of Alcoholic Hydrochloric Acid on the Maleate* **8b**: *Formation of Compounds* **6b**, **19b** *and* **20b**

Carrying out the same experimental procedure as described for **8a** gave also three fractions. (*E*)-5-triphenylmethyl-3-ethoxycarbonylmethylenebenzo[b]furan-2(3H)-one (**20b**)[1] (6% yield) was eluted first. The second fraction gave colorless crystals of **19b**[1] (9% yield). The third fraction afforded a colorless crystalline product of diethyl (6-hydroxy-α,α,α-triphenyl-*m*-tolyl)maleate (**6b**) (57% yield), recrystallized from ethyl acetate/*n*-hexane, mp 197–198°C. Anal. Calcd. for $C_{33}H_{30}O_5$: C, 78.24; H, 5.97. Found: C, 78.10; H, 5.92%. IR cm$^{-1}$: 3198 (OH), 1712, 1690 (C=O, esters). $^1$H NMR: δ 1.25 (t, $J_{HH}$ = 7.1 Hz, 3H, ester $CH_3$), 1.29 (t, $J_{HH}$ = 7.1 Hz, 3H, ester $CH_3$), 4.200, 4.226 (2q overlap, $J_{HH}$ = 7.1 Hz, 4H, ester $CH_2$), 6.28 (s, 1H, =CH—), 6.78–7.41 (m, 18H, ArH), 8.25 (s, 1H, OH). MS: m/z (relative intensity) 506 ($M^+$, 2%), 460 (21), 383 (100), 252 (16) and 165 (28).

*Action of Heat on Compound* **6a**: *Formation of Compounds* **19a** *and* **20a**

Compound **6a** (48 mg, 0.1 mmol) in dry toluene (5 ml) was heated under reflux. After 25 h, the solution was evaporated under reduced pressure and the residue 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 (95% petroleum ether) gave a yellow crystalline product of (*Z*)-5-triphenylmethyl-3-methoxycarbonylmethylenebenzo[b]furan-2(3H)-one (**20a**) (18 mg, 40% yield), recrystallized from petroleum ether (bp 60–80°C), mp 175–176°C. Anal. Calcd. for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97. Found: C, 80.79; H, 4.92%. IR $cm^{-1}$: 1801 (C=O, five membered ring γ-lactone), 1721 (C=O, ester). $^1H$ NMR: δ 3.60 (s, 3H, ester $CH_3$); 6.84 (s, 1H, exocyclic vinyl proton =CH—); 7.01(d, $J_{HH}$ = 8.5 Hz, 1H, ArH at C-7); 7.10–8.50 (m, 17H, ArH). MS: m/z (relative intensity) 446 ($M^+$, 18%), 369 (100), 243 (18), 165 (33). The second fraction (90% petroleum ether) afforded colorless crystalline product (15 mg, 33% yield) proved to be 4-methoxycarbonyl-6-triphenylmethyl-2H-1-benzopyran-2-one (**19a**) (mp and mixed mp with an authentic sample).[1]

*Action of Heat on Compound* **6b**: *Formation of Compounds* **19b** *and* **20b**

A solution of **6b** (50 mg, 0.1 mmol) in dry toluene (5 ml) was heated under reflux for 30 h. Then, the solution was evaporated under reduced pressure and the residue was chromatographed on silica gel using petroleum ether (bp 60–80°C) and ethyl acetate. The first fraction (95% petroleum ether) gave yellow crystalline product of (*Z*)-5-triphenylmethyl-3-ethoxycarbonylmethylenebenzo[b]furan-2(3H)-one (**20b**) (15 mg, 32% yield), recrystallized from petroleum ether (bp 60–80°C), mp 180–181°C. Anal. Calcd. for $C_{31}H_{24}O_4$: C, 80.85; H, 5.25. Found: C, 80.68; H, 5.13%. IR $cm^{-1}$: 1801 (C=O, five membered ring γ-lactone), 1720 (C=O, ester). $^1H$ NMR: δ 1.14 (t, $J_{HH}$ = 7 Hz, 3H, ester $CH_3$), 4.07 (q, $J_{HH}$) = 7 Hz, 2H, ester $CH_2$), 6.81 (s, 1H, exocyclic vinyl proton =CH—), 7.00 (d, $J_{HH}$ = 8.6 Hz, 1H, ArH at C-7), 7.14–8.50 (m, 17H, ArH). MS: m/z (relative intensity) 460 ($M^+$, 22%), 383 (100), 252 (14) and 165 (26). The second fraction (90–85% petroleum ether) yielded colorless crystalline product (23 mg, 50% yield), identified as 4-ethoxycarbonyl-6-triphenylmethyl-2H-1-benzopyran-2-one (**19b**) by comparison with an authentic sample.[1]

*Dimethyl (6-methoxy-α,α,α,-triphenyl-m-tolyl)maleate* (**21a**)

A mixture of **6a** (50 mg, 0.1 mmol), freshly distilled methyl iodide (20 mg, 0.15 mmol) and anhydrous powdered potassium carbonate (0.2 g) in dry acetone (5 ml) was gently heated under reflux for 6 h. After removal of the inorganic residue and volatile materials, the solid product, thus obtained (42 mg, 81% yield), was crystallized from benzene-petroleum ether (bp 40–60°C) to give **21a** as colorless crystals, mp. 176–177°C. Anal. Calcd. for $C_{32}H_{28}O_5$: C, 78.03; H, 5.73. Found: C, 78.18; H, 5.64%. IR $cm^{-1}$: 1726 (C=O, ester). $^1H$ NMR: δ 3.70 (s, 3H, ester $CH_3$), 3.72 (s, 3H, ester $CH_3$), 3.80 (s, 3H, $OCH_3$), 6.35 (s, 1H, =CH—), 6.75–7.35 (m, 18H, ArH). MS: m/z (relative intensity) 492 ($M^+$, 18%), 415 (100), 355 (13), 252 (14) and 165 (32).

Compound **21b** was also obtained when **6b** reacted with methyl iodide under the same experimental conditions described above.

*Diethyl (6-methoxy-α,α,α-triphenyl-m-tolyl)maleate* (**21b**) (84% yield), crystallized from benzene-petroleum ether (bp 40–60°C), m.p. 175–176°C. Anal. Calcd. for $C_{34}H_{32}O_5$: C, 78.44; H, 6.20. Found: C, 78.57; H, 6.12%. IR $cm^{-1}$: 1736, 1711 (C=O, esters). $^1H$ NMR; δ 1.20, 1.25 (2t overlap, $J_{HH}$ = 7.0 Hz, 6H, esters $CH_3$), 3.80 (s, 3H, $OCH_3$), 4.15, 4.16 (2q overlap, $J_{HH}$ = 7.0 Hz, 4H, esters $CH_2$), 6.32 (s, 1H, =CH—), 6.75–7.37 (m, 18H, ArH). MS: m/z (relative intensity 520 ($M^+$, 29%), 443 (100), 369 (12), 297 (11), 252 (16) and 165 (41).

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