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Michael adducts of 2,5-bismethoxycarbonyl-1,4-benzoquinone with several different donor molecules

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Abstract: The synthesis of Michael adducts from 2, 5- bismethoxycarbonyl-1,4-benzoquinone as acceptor and malononitrile, p-cresol and thiophenol as donors, using a number of different bases such as 2-methoxypyridine, 4-dimethyl-aminopyridine, 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 18-crown-6 + potassium fluoride were investigated. From the results obtained in this research for 2,5-bismethoxycarbonyl-1,4-benzoquinone as the Michael acceptor, it is concluded that clean reactions leading to mono-adducts are difficult to achieve, and that better control of mon-adduct formation would be obtained if one ethane linkage of the quinone were protected. In case of thiophenol, it reacted readily with 2,5-bismethoxycarbonyl-1,4-benzoquinone by using 2-methoxypyridine as base. Sublimation of the crude product gave diphenyl disulphide followed by dimethyl 2,5-dihydroxyterephthalate and the desired mono-adduct, dimethyl 2,5-dihydroxy-3-phenylthioterephthalate. The reaction was repeated using DBU, DBN, 4-dimethylaminopyridine, and 18-crown-6 +KF as bases; almost identical results were obtained.

Keywords: Michael adducts, 2,5-bismethoxycarbonyl-1,4-benzoquinone, dimethyl 2,5-dihydroxyterephthalate, dimethyl 2,5-dihydroxy-3-phenylthioterephthalate.

Introduction

2,5-Bismethoxycarbonyl-1,4-benzoquinone (I) is a particularly attractive reactant because it can be readily obtained from dimethyl succinate (Fig. 1). This quinone (I) had previously been obtained by oxidation of dimethyl 2,5-dihydroxyterephthalate (II) using silver oxide[1], but the author found that phenyliodine bistrifluoroacetate[2] (III) was more effective. It is a powerful oxidizing agent which produces phenyl iodide and trifluoroacetic acid together with the quinone, but does not usually interfere in the reaction.

Experimental[3,4]

Nuclear magnetic resonance (n.m.r.) spectra were recorded with Perkin-Elmer R12B (60 MHz), R32 (90 MHz) and R34 (220 MHz) spectrometers, respectively. Tetramethylsilane (TMS) was used as an internal standard and coupling constants (J) are expressed in Hz. Infrared spectra were measured using a Pye Unicam SP3-200 Spectrophotometer. Low resolution Electron Impact (EI) mass spectra were recorded on A.E.I. MS30 and Kratos MS25 instruments; mass measurements (M.M.) were made on the former, and Chemical Ionization (CI) spectra were recorded on the latter using ammonia as the reagent gas. Sublimation and bulb-to-bulb distillation temperature are those of the Buchi Oven (heating bath). All solvents, liquid reagent and starting material were distilled prior to use. Irradiation with visible light was carried out at 15 °C, using tungsten-filament lamps. Analytical and preparative TLC were carried out with Merck silica gel plates (5×10 cm×0.25 mm and 10×20 cm×0.25 mm), type $60F_{254}$.

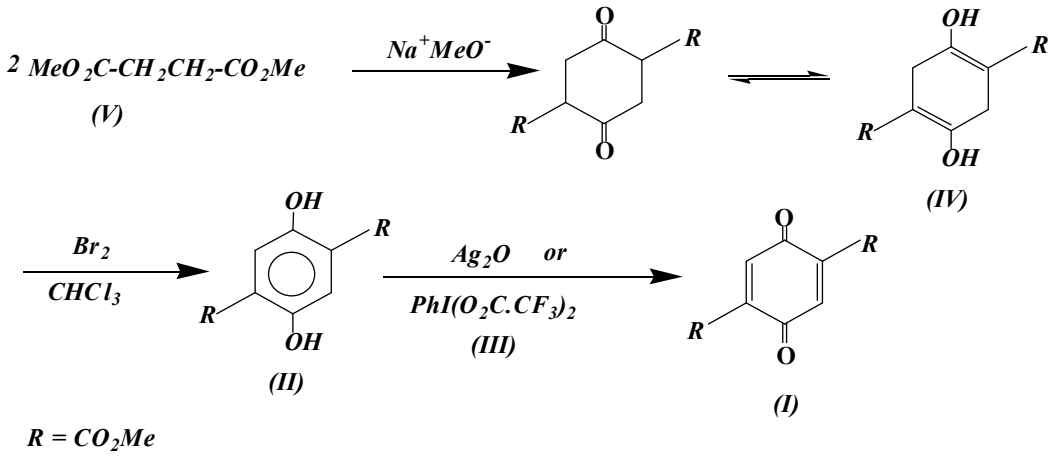


Figure 1

1-Preparation of 1,4-dihydroxy-2,5-bismethoxy carbonyl-1,4-cyclohexadiene (IV)

A solution of sodium methoxide was prepared by adding small pieces of Na (16 g) to absolute methanol (150 mL) in a 500 mL three-necked round-bottomed flask equipped with a mechanical stirrer, reflux condenser with a drying tube packed with calcium chloride, and a stopper. The reaction was completed by heating the mixture under reflux for 0.5 hour (using an oil bath) and adding more absolute methanol (ca. 30 mL). Freshly distilled dimethyl succinate (46 g, 41.26 mL) was added in one portion to the hot solution of sodium methoxide (caution: exothermic reaction) and the mixture was heated under reflux by maintaining the original bath temperature for 5 days while mechanically stirring to prevent bumping of the mixture. Removal of the solvent afforded a thick coloured precipitate. This was added to 10% sulphuric acid (360 mL) in a 1-litre beaker while it was vigorously mechanically stirred (for ca. 2 hrs.). The mixture was filtred with suction and washed with water several times (until the washing became neutral). The air-dried product was a pale-buff powder (28 g, 78%). Crystallization from ethanol gave pale white-green needles (25 g, 70%), m.p. 162-164 °C (lit.[3], 155.5-157 °C). It had δ(4%, $CDCl_3$, 60 MHz) 12.11 (s, 2×OH), 3.78 (s, 2×CO_2Me), 3.16 (s, 2×CH_2); m/z (E.I.) 228 (M^{+}, 84).

2. Preparation of dimethyl 2,5-dihydroxy terephthalate (II)

To a cold (0 °C) solution of 1,4-dihydroxy-2,5-bismethoxycarbonyl-1,4-cyclohexadiene (3.9 g) **(IV)** in chloroform (41.25 mL), a cold solution (0 °C) of bromine (1.78 mL) in chloroform (11.25 mL) was added. The solution was kept at room temperature for 2 hours, then at 40 °C for further 2 hours, washed with 10% sodium thiosulphate solution, then with water, and dried (K_2CO_3). Filtration, followed by removal of the solvent gave dimethyl 2,5-dihydroxterephthalate (3.53 g, 91%), m.p. 179-181 °C. It was sublimed at 110-115°C/0.1 mmHg to give a yellow fluorescent crystalline compound (3.28 g, 84%), m.p. 174-176 °C (lit.[4], 177-179 °C).). It had δ(4%, $CDCl_3$, 60 MHz) 10.03 (s, 2×OH), 7.46 (s, 2×H, ring), 3.95 (s, 2×CO_2Me); m/z (E.I.) 226 (M^{+}, 71), 194 [(M-MeOH)$^{+}$, 100], 162 [(M-2×MeOH)$^{+}$, 87], 134 [(162-CO)$^{+}$, 45].

3. Preparation of 2,5-bismethoxycarbonyl-1,4-benzoquinone (I)

a. Oxidation with silver oxide

In a 25 mL round-bottomed flask, dimethyl-2,5-dihydroxyterephthalate (92 mg, 0.407 mmol), freshly prepared silver oxide (2.30 g, completely dried), anhydrous sodium sulphate (2.30 g, baked at 200 °C for 2 days), and freshly distilled benzene (10 mL) were placed. The mixture was refluxed for ca. 2.5 hours, cooled to room temperature, and quickly filtred through a short plug of Celite and the cake was washed with dry benzene (until no coloured solution passed the cake). Removal of the solvent gave orange-yellow crystals (88 mg, 97%), m.p. 124-128 °C (lit.[1], 124-126°C) (Found: C, 52.5; H, 3.8. Calculated for $C_{10}H_8O_6$: C, 53.6; H, 3.6%). It had δ(5%, $CDCl_3$, 60 MHz) 7.12 (s, H-3 + H-6), 3.95 (s, 2×CO_2Me); δ(7%, C_6 D_6, 60 MHz) 6.42 (s, H-3 + H-6), 3.32 (s, 2×CO_2Me).

b. Oxidation with phenyliodine bistrifluoro acetate

To a solution of dimethyl 2,5-dihydroxyterephthalate (452 mg, 2 mmol) in freshly distilled methylene chloride (10 mL) at 0 °C was added phenyliodine bistrifluoroacetate (1.032 g, 2.4 mmol, 20% excess). A bright red coloured solution was quickly formed and left at 0°C for ca. 5-10 minutes, while stirring. Removal of the solvent at 0 °C, followed by pumping off at 0.1 mmHg at 0 °C, then at room temperature afforded a very nice orange crystalline compound (480 mg, 106%, i.e. some iodobenzene left with the quinone), m.p. 120-122 °C. Recrystallisation of 100 mg of the crude product with petroleum ether (b.p. 60-80 °C) : cyclohexane (ca. 1:2) gave orange crystals (80 mg, overall yield 86%), m.p. 126-128 °C ((lit.[1], 124-126°C). %). It had δ(3%, $CDCl_3$, 60 MHz) 7.18 (s, H-3 + H-6), 3.93 (s, 2×CO_2Me); m/z (E.I.) 226 [($M^{\cdot+}$+2), 38], 224 ($M^{\cdot+}$, 11), 194 [(M+2-MeOH)$^{\cdot+}$, 100], 162 [(M-2×MeOH)$^{\cdot+}$, 91], 134 [(162-CO)$^{\cdot+}$, 40], 106 [(134-CO)$^{\cdot+}$, 9], 78 [(106-CO)$^{\cdot+}$,19], 50 [(78-CO)$^{\cdot+}$, 17]. The reaction was done in benzene at 0-5 °C and almost identical results were obtained.

4. Treatment of 2,5-bismethoxycarbonyl-1,4-benzoquinone with p-cresol

a. Using 2-methoxypyridine as base

2,5-bismethoxycarbonyl-1,4-benzenoquinone (60 mg, 0.268 mmol) in methylene chloride (2 mL) was added to a mixture of p-cresol (28.9 mg, 0.268 mmol) and 2-methoxypyridene (5.8 mg, 0.2 equ.) in methylene chloride (1 mL) during 10 minutes at room temperature and left for 3 hours. A dark red coloured solution was formed. Removal of the solvent gave a dark red oil (91 mg). NMR spectroscopy showed that a mixture of the hydroquinone, p-cresol and a small portion of the addition product had been formed. %). It had δ(6%, $CDCl_3$, 60 MHz) 10.26 (bs, 2× OH), 7.45 (s, H-3 + H-5), 3.95 (s, 2×CO_2Me), 3.75 (s, 2×CO_2Me), 2.32 (as a hump of δ 2.24, Me, of the products), 2.24 (s, Me, p-cresol); m/z (E.I.) 439 [(438+H)$^+$, 4], 350 [(M+18)$^+$, 16], 333 [(M+H)$^+$, 18], 301 [(333-MeOH)$^+$, 9], 244 [(301-HCO - CO)$^{\cdot+}$, 3], 227 [(226+H)$^+$, 26], 110 [(227-H CO_2Me - CO_2Me)$^{\cdot+}$+100], 108 [(Me.C_6 H_4. OH)$^+$, 54], 107 [(108-H)$^{\cdot+}$, 30], for which m/z (438 + 1) indicates the addition of 2 mol of p – cresol to the quinone , m/z (332+1) indicates the addition of 1 mol, and m/z (226+1) indicates the hydroquinone of the starting material; m/z (E.I.) 194 (19), 162 (23), 134 (28), 119 (28), 108 (70), 107 (71), 40 (100).

b. Using 4-dimethyl-aminopyridine /DBU/DBN as base

Reaction (a) was repeated except 4-dimethyl-aminopyridine (0.1 equ.) was used instead of 2-methoxypyridine. NMR showed that a 46:54 mixture of the addition product(s) and the hydroquinone of the starting material were formed.

Reaction was repeated with using DBU or DBN as base and similar results were obtained as in (a).

c. Using 18-crown-6 + KF as base

2,5-bismethoxycarbonyl-1,4-benzenoquinone (75 mg, 0.335 mmol) in methylene chloride (2 mL) was added to a mixture of p-cresol (36.2 mg, 1 equ.) , 18-crown-6 (2.75 mg, 0.03 equ.), and KF (5.83 mg, 0.3 equ.), in methylene chloride (1 mL) over 10 minutes at room temperature and the mixture was stirred for 3 hours. Removal of the solvent gave an orange solid (94 mg). TLC in 10:1 toluene-ethyl acetate showed three spots. Column chromatography through silicic acid using 10:1 toluene-ethyl acetate as solvent gave a fluorescent solution. Removal of the solvent gave a yellow crystalline compound (35 mg), m.p. 246-249 °C. It was partially soluble in d-chloroform. Therefore, a suspension in d-chloroform was passed through cotton wool and the solution collected. The solid fraction on the cotton wool was dissolved in hot chloroform. Removal of the chloroform gave a yellow crystalline compound, m.p. 258-263°C. It had δ(2%, $CDCl_3$, 90 MHz) 11.1 (s, OH), 8.86 (s, H-2), 7.55 (s, H-5), 7.20 (s, 4×H, aromatic), 4.01 (s, 2×CO_2Me), 2.46(s, Me). These chemical shifts suggested that p-cresol had displaced methanol from one of the two methoxycarbonyl groups.

The fraction soluble in d-chloroform had δ(3%, $CDCl_3$, 90 MHz) 11.60 (s, OH), 1108 (s, OH), 8.95 (s, H-2), 7.54 (s, H-5), 7.20 (s, 4×H, aromatic), 4.0 (s, CO_2Me), 3.66 (s, 18-crown-6), 2.45(s, Me);); m/z (E.I.) 302 (1.4), 301 (11.5), 300 (56), 268 [(300-MeOH)$^+$, 100], 240 [(268 - CO)$^{\cdot+}$, 42], 212 [(240-CO)$^{\cdot+}$, 28], 184 [(212- CO)$^{\cdot+}$+45]; (C.I.) 303 (2), 302 (17), 301 [(300+H)$^+$+100], 300 (19), 268 (10), 227 (24), again indicating transesterification by p-cresol.

5. Attempted reaction between 2,5-bismethoxy carbonyl-1,4-benzoquinone and malononitrile

2,5-bismethoxycarbonyl-1,4-benzoquinone (30 mg, 0.134 mmol) in methylene chloride (1 mL) was added to a mixture of malononitrile (8.84 mg, 1 equ.) and 2-methoxypyridene (2.92 mg, 0.2 equ.) in methylene chloride (1 mL) at room temperature and left for 2 hours. Removal of the solvent gave a very dark green oil (ca. 50 mg). NMR spectroscopy showed that the mixture was mostly starting material and a small portion of addition product. It had δ(4%, $CDCl_3$, 60 MHz) 7.84 (s, OH), 7.47 (s,?), 7.22 (s, H-6?), 4.26 (s, $CH(CN)_2$, 4.07 (s, CO_2Me ?), 3.98 (s, 2×CO_2Me, starting material), 3.90 (s, CO_2Me ?).

6. Preparation of dimethyl 2,5-dihydroxy-3-phenylthioterephthalate

a. 2,5-bismethoxycarbonyl-1,4-benzoquinone (500 mg, 2.232 mmol) in methylene chloride (5 mL was added to a solution of thiophenol (245.5 mg, 1 equ.) and 2-methoxypyridine (24.4 mg, 0.1 equ.) in methylene chloride (2 mL) at room temperature. A yellow-brown mixture was obtained. The mixture was left at room temperature for 12 hours. Removal of the solvent gave a red-orange sticky oil (758 mg). NMR spectroscopy showed the product to be a mixture. Fractional sublimation gave:

(i) At 85-90 °C/0.1 mmHg, pale yellow crystals (70 mg), m.p. 57.5-59 °C. It had δ(3%, $CDCl_3$, 220 MHz) 7.55 (m, 4×H, aromatics), 7.30 (m, 6×H, aromatics); δ(4%, C_6 D_6, 220 MHz) 7.46 (dd, J_1=8.5, J_2=2, 4×H, aromatics), 6.95 (m, , 6×H, aromatics);); m/z (E.I.) 217 (46), 109 (PhS^+, 100); (C.I.) 236 [$(218+18)^+$, 46], 219 [$(218+H)^+$, 48], 218 [$(PhSSPh)^+$, 100], 110 [$(PhSH)^+$, 72], 109 [$(PhS)^+$, 72], identical with an authentic sample of diphenyldisulphide, which had m.p. 58-60 °C.

(ii) At 100-110 °C/0.1 mmHg, yellow crystals (42 mg). It had δ(5%, $CDCl_3$, 90 MHz) 9.96 (s, 2×OH), 7.40 (s, 2×H, aromatics), 3.92 (s, 2× CO_2Me); ν $^-(cm^{-1})$ (Nujol), 3270 m, 1680 s, 1200 s; m/z (E.I.) 226 ($M^{\cdot+}$, 99), 194 [$(M-MeOH)^{\cdot+}$, 100], 162 [$(194-MeOH)^{\cdot+}$, 95], 134 [$(164-CO)^{\cdot+}$, 73]; (C.I.) 244[$(M+18)^+$, 52], 227 [$(M+H)^+$, 86], 226 [$M^{\cdot+}$, 87], identical with authentic dimethyl 2,5-dihydroxyterephthalate.

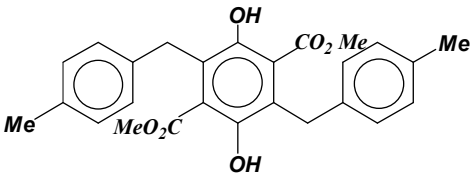
(iii) At 135-140 °C/0.1 mmHg, yellow crystals (260 mg, 35%), m.p.146-148 °C. (Found: C, 56.6; H, 4.2, S, 9.5. Calculated for C_{16} H_{14} O_6 S : C, 57.5; H, 4.2; S, 9.58%). It had δ(10%, $CDCl_3$, 90 MHz) 10.76 (s, OH), 8.25 (bs, OH), 7.45 (s, H-6), 7.14 (bs, 5×H, aromatics), 3.90 (s, CO_2Me), 3.80 (s, CO_2Me); δ(6%, C_6D_6, 90 MHz) 10.94 (s, OH), 8.43 (bs, OH), 7.34 (s, H-6), 7.25 (m, 2×H, aromatics), 6.90 (m, 3×H, aromatics), 3.34 (s, CO_2Me), 3.17 (s, CO_2Me); m/z (E.I.) 334 ($M^{\cdot+}$, 71), 302 [$(M-MeOH)^{\cdot+}$, 49], 270 [$(302-MeOH)^{\cdot+}$, 21], 242 [$(270-CO)^{\cdot+}$, 30], 214 [$(242-CO)^{\cdot+}$, 14], 186 [$(214-CO)^{\cdot+}$, 72], 158 [$(186-CO)^{\cdot+}$, 34], 40 (100); (C.I.) 352[$(M+18)^+$, 40], 335[$(M+H)^+$, 100], 334 [M^+, 66], 303 [$(335-MeOH)^+$, 45]. This is dimethyl 2,5-dihydroxy-3-phenylthioterephthalate **(XIII).**

(b). Reaction **(a)** was repeated with the following bases. Almost identical results were obtained, but with the lower yields:

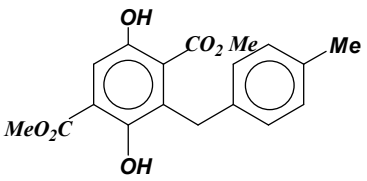
(i) 1,5-Diazabicyclo[5.4.0]undec-5-ene (DBU).
(ii) 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN).
(iii) 4-Dimethyl-aminopyridine
(iv) 1,4,7,10,13,16-Hexaoxacyclo-octadecane (18-crown-6)+KF.

7- Preparation of 2,5-bismethoxycarbonyl-3-phenylthio-1,4-benzoquinone (XIV)

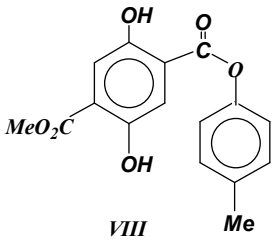
Dimethy-2,5-dihydroxy-3-phenylthioterephthalate (150 mg, 0.499 mmol), silver oxide (4.5 g, 30 equ.) (freshly prepared and dried), anhydrous sodium sulphate (4.5 g) and freshly distilled methylene chloride (25 mL) were shaken together for 12 hours. Filtration through Celite, washing of the cake with methylene chloride and removal of the solvent gave a deep red sticky oil (125 mg, 84%). Crystallization from cyclohexane afforded fine red crystals (80 mg, 54%), m.p. 94-96 °C. (Found: C, 56.6; H, 3.6, S, 11.2. Calculated for C_{16} H_{12} O_6 S : C, 57.8; H, 3.6; S, 9.6%). It had δ(4%, $CDCl_3$, 90 MHz) 7.40 (m, 5×H, aromatics), 7.13 (s, H-6, aromatics), 3.93 (s, CO_2Me), 3.43 (s, CO_2Me); δ(3%, C_6D_6, 90 MHz) 7.38 (m, 2×H, aromatics), 6.93 (m, 3×H, aromatics), 7.49 (s, H-6), 3.34 (s, CO_2Me), 3.19 (s, CO_2Me);); ν $^-(cm^{-1})$ (Nujol), 1730 s, 1673 s, 1645 m, 1625 w, 1565 w; m/z (E.I.) 334 ($MH_2^{\cdot+}$, 45), 332 ($M^{\cdot+}$, 20), 302 [$(MH_2-MeOH)^{\cdot+}$, 35], 300 [$(M-MeOH)^{\cdot+}$, 14], 270 [$(302-MeOH)^{\cdot+}$, 15], 242 [$(270-CO)^{\cdot+}$, 26], 214 [$(242-CO)^{\cdot+}$, 13], 186 [$(214-CO)^{\cdot+}$, 76], 158 [$(186-CO)^{\cdot+}$, 42], 40 (100) , 109 (PhS^+, 36), 77 [$(109-S)^+$, 100] ; (C.I.) 350[$(M+18)^+$, 38], 335[$(MH_2+H)^+$, 90], 333[$(M+H)^+$, 18], 242 [$(MH_2 - CO_2Me - MeOH)^+$, 73], 126[$(PhS+18-H)^+$, 91], 32 (100).



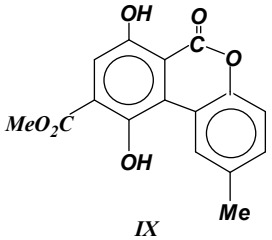
VI



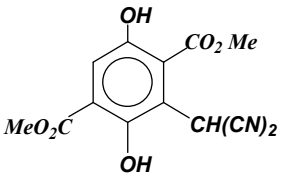
VII



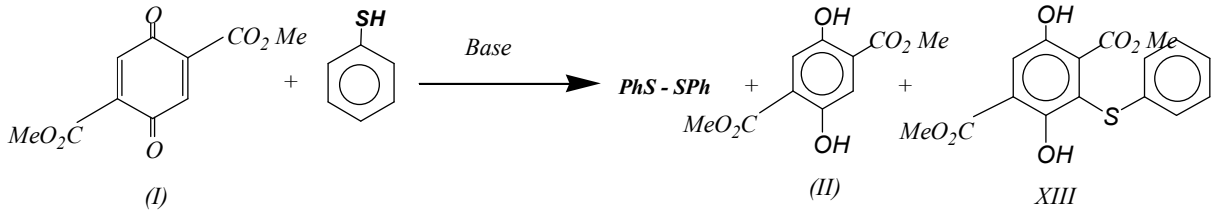
VIII



IX

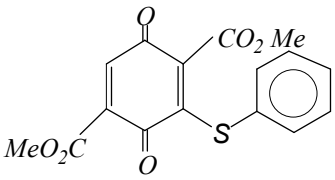


X



(I) *(II)* *XIII*

Figure 2



XIV

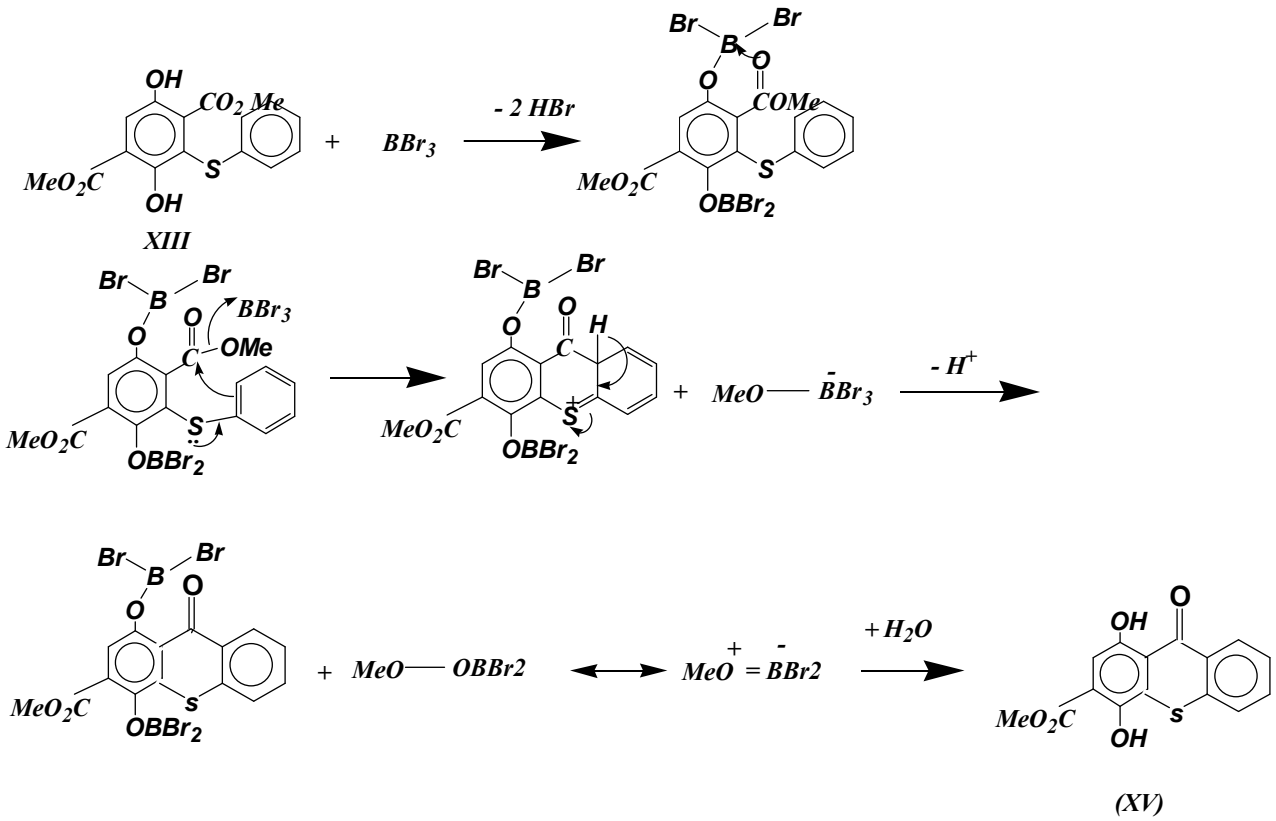


Figure 3

Discussion

Addition of an equimolar solution of 2,5-bismethoxycarbonyl-1,4-benzoquinone in methylene chloride to a mixture of p-cresol and 2-methoxypyridine in methylene chloride gave a red oil. NMR and mass spectra showed the formation of a mixture of the Michael addition product (VII) and the parent hydroquinone (II). Separation was unsuccessful. Other bases such as 4-dimethyl-aminopyridine, DBU, and DBN were tried, similar results were obtained. The reaction was repeated using 18-crown-6 + KF as base. An orange solid material was obtained, which showed three spots on TLC. Column chromatography through silicic acid gave a fluorescent yellow crystalline compound which was recrystallized from chloroform. Its NMR in d-chloroform showed, unexpectedly, that p-cresol had displaced methanol from one of the methoxycarbonyl groups to give compound (VIII). The formation of this product is surprising, because Michael addition would have been expected and as the reaction was carried out in a basic medium, there was little chance of C-C bond formation occurring to give a compound like (IX), analogous to the benzocoumarins obtained by Eugster et al.[5] from the treatment of methoxycarbonyl-1,4-benzoquinone with phenols in the presence of trifluoroacetic acid. In another attempt to obtain Michael adducts from 2,5-bismethoxycarbonyl-1,4-benzoquinone (I) with the other nucleophiles, the reaction was repeated but, malononitrile was used instead of p-cresol. A dark green oil was obtained whose NMR spectrum showed a mixture of mostly the initial quinone and a small portion of the addition product (X). Again separation was unsuccessful. In another attempt, thiophenol was used. It reacted readily with 2,5-bismethoxycarbonyl-1,4-benzoquinone (I) by using 2-methoxypyridine as base. Sublimation of the crude product gave diphenyl disulphide followed by dimethyl 2,5-dihydroxyterephthalate and a yellow crystalline compound whose NMR and mass spectra and microanyalysis were consistent with those expected for the desired mono-adduct, dimethyl 2,5-dihydroxy-3-phenylthioterephthalate (XIII). The reaction was repeated using DBU, DBN, 4-dimethylaminopyridine, and 18-crown-6 +KF as bases; almost identical results were obtained.

Snell et al.[6] reported that the reaction of thiol compounds with 1,4-benzoquinone and substituted 1,4-benzoquinones can yield both disulphides and Michael adducts. The present results are consistent

with Snell's[6] proposition (figure 2). The hydroquinone (XIII) was oxidized to 2,5-bismethoxycarbonyl-3-phenylthio-1,4-benzoquinone (XIV) by treatment with silver oxide. Attempted cyclization of dimethyl 2,5-dihydroxy-3-phenylthioterephthalate (XIII) using boron tribromide resulted in a 2:3 mixture of 1,4-dihydroxy-2-methoxycarbonylthioxanthenone (XV) and the starting material, respectively. A mechanism for this reaction is proposed in figure 3. Cyclization with polyphosphoric acid (PPA) was also attempted, but this gave a mixture which was sparingly soluble in d-chloroform, d_6-benzene, and d_6-acetone, although the soluble part was similar to that from the boron tribromide reaction. The inefficient cyclization reaction is not surprising since free hydroxyl groups are present, and Eugster et al.[7] reported cyclization of the analogous compound (XIII; R=H), from the mono-ester quinone only after methylation of the hydroxyl functions. Separation of the adduct (XIII) and the thioxanthenone (XV) was not attempted.

From these results for bismethoxycarbonyl-1,4-benzoquinone (I) as the Michael acceptor, it is concluded that clean reactions leading to mono-adducts are difficult to achieve, and that better control of mon-adduct formation would be obtained if one ethane linkage of the quinone were protected. In the bismethoxycarbonyl-1,4-benzoquinone (I) there would be no regioselectivity problem in single Diels-Alder reactions because both carbon-carbon double bonds are identical. Therefore, reactions of (I) with different dienes were carried out to obtain mono-adducts for Michael reaction, the results will be published in the coming article.

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