BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 563—564 (1971)

Diels-Alder Reactions of Benzoquinone. I. Reactions of Methoxybenzoquinone with Styrene and *o*-Methylstyrene[1]

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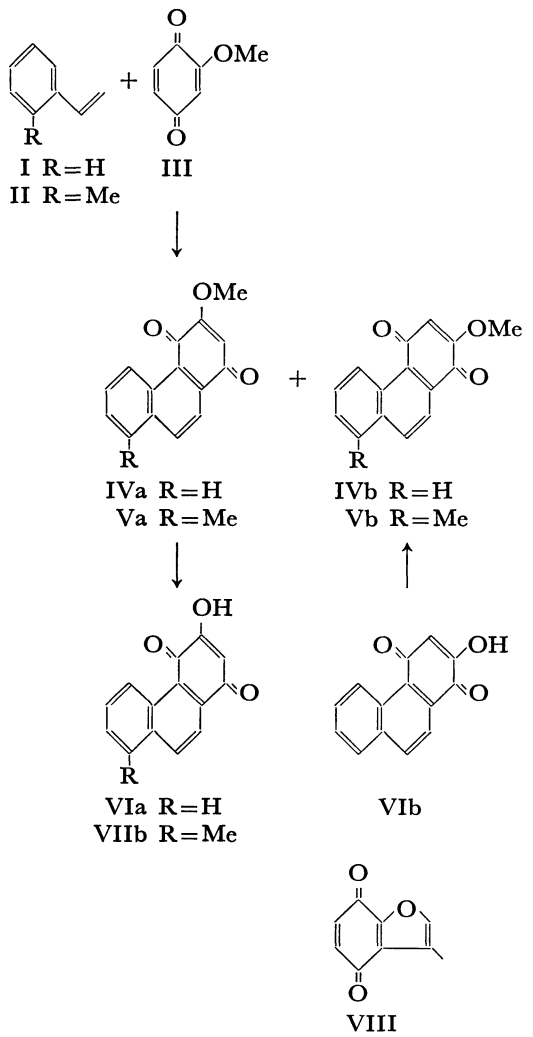
(Received July 9, 1970)

The Diels-Alder reactions of substituted benzoquinones with vinyl aromatics were mainly examined by Lora-Tamayo.[2] The characteristic features of substituted benzoquinones when compared with those of aliphatic dienes[3,4] are as follows: i) the addition occurs only at the non-substituted ethylene linkage of benzoquinone, and no addition occurs if subtituents are present on both ethylene linkages such as in *p*-xyloquinone and 4-methoxytoluquinone[5]; ii) the reaction generally accompanies tetradehydrogenation[2] to give a phenanthrenequinone derivative. The orientation of the quinone is not clarified except the reaction between styrene (I) and methoxybenzoquinone (III) to afford 2-methoxyphenanthrene-1,4-quinone (IVb) exclusively.[2]



During the course of our studies on the Diels-Alder reaction of 3-methylbenzofuran-4,7-quinone (VIII),[4] we found that the orientation (namely of the oxygen function) of VIII to the aliphatic diene was identical with that of methoxybenzoquinone (III), and that the reaction of VIII with *o*-methylstyrene (II) gave 3,7-dimethylphenanthro[3,2-*b*]furan-4,11-quinone as a main product.

These results throw doubt upon Lora-Tamayo's experiments.[2] Firstly we examined the Diels-Alder reaction between *o*-methylstyrene (II) and methoxybenzoquinone (III) to clarify the difference between III and VIII in the behavior to vinyl aromatics.

The mixture of II and III was heated at 100—110°C for 10 hr and the phenanthrenequinone parts were isolated through silicic acid column in 42% yield. Recrystallization from benzene afforded a pure quinone Va (or Vb), $C_{16}H_{12}O_3$, mp 243—245°C (dec), although the melting point was slightly lower than that of the reported, mp 253°C (dec).[2] The quinone Va (or Vb) was hydrolyzed with ethanolic potassium hydroxide to the corresponding hydroxyquinone VIIa (or VIIb), $C_{15}H_{10}O_3$, mp 219—224°C (dec), which was identified as 3-hydroxy-8-methylphenanthrene-1,4-quinone (VIIa) by mixed melting point and by comparison of IR spectra with the authentic sample.[6]

As Lora-Tamayo has not clarified the position of the methoxyl group, the difference in melting points seemed to be due to the positional isomer. However, the isomer VIIb could never be characterized in the present work.

Determination of the methoxyl position in the reaction of *o*-methylstyrene (II) prompted us to reinvestigate the reaction of styrene (I) itself. The reaction between I and III was carried out under the same condition as before. The phenanthrenequinone fractions were obtained in 26% yield, from which pure 3-methoxyphenanthrene-1,4-quinone (IVa),[7] mp 168—169°C was isolated by recrystallization from methanol. Melting point of IVa was similar to but IR spectrum was quite different from that of the authentic isomer IVb[8] (see

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[1] Presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

[2] M. Lora-Tamayo, *Tetrahedron*, **4**, 17 (1958) and references cited therein.

[3] M. F. Ansell, B. W. Nash, and D. A. Wilson, *J. Chem. Soc.*, **1963**, 3012.

[4] a) Y. Inouye and H. Kakisawa, This Bulletin, **42**, 3318 (1969). b) H. Kakisawa and Y. Inouye, *Tetrahedron Lett.*, **1969**, 1929.

[5] C. de Corral, *Rev. real acad. cienc. exact., fis. y nat. Madrid*, **51**, 103 (1597); *Chem. Abstr.*, **52**, 7257b (1958).

[6] A. C. Baillie and R. H. Thomson, *J. Chem. Soc., C*, **1968** 48.

[7] L. F. Fieser, *J. Amer. Chem. Soc.*, **51**, 940 (1929).

[8] L. F. Fieser, *ibid.*, **51**, 1896 (1929).

experimental). By careful chromatographic separation, IVb was isolated in low yield. The ratio of IVa to IVb was 12.

Lora-Tamayo's confidence to 2-methoxyl structure has been based on comparison of the physical properties and the products formed on alkaline hydrolysis with those of the authentic samples,[7,8] although details were not reported. Alkaline hydrolysis of IVa gave 3-hydroxyphenanthrene-1,4-quinone (VIa), $C_{14}H_8O_3$, mp 194—196°C (dec), to which Fieser[7] reported the melting point to be 230°C (dec).

In conclusion, the position of methoxyl group in the main product in the Diels-Alder reaction of methoxybenzoquinone and vinyl aromatics is not at C_2, but at C_3 in contrast to Lora-Tamayo's assignment.[2]

Finally, the influence of the molar ratio of methoxybenzoquinone (III) to styrene (I) on the yield of adducts was investigated and the results are summarized in Table 1. Apparently, the yield depends on the molar ratio when it is below 3, but does not when it is above 3. This might correspond to the fact that two moles of the quinone act as the acceptor of hydrogen from the adduct.

TABLE 1. REACTIONS BETWEEN SYTRENE (I) AND METHOXYBENZOQUINONE (III)

Run	Styrene (I) mg	Quinone (III) mg	Molar ratio of III/I	Solvent m*l*	Reaction time hr	Yield[a)] mg	%
1	65	85	1	—	10	20	13.4
2	58	154	2	—	10	34	26
3	30	120	3	—	10	21	31
4	—	50	0	0.15 benzene	40	b)	
5	65	87	1	0.25	40	18	12.1
6	58	154	2	0.2	40	35	26
7	23	92	3	0.2	40	18	34
8	27	180	5	0.2	40	20	32

a) mixtures of IVa and IVb

b) 100% recovery of the quinone (III)

Experimental

Diels-Alder Reaction between o-*Methylstyrene (II) and Methoxybenzoquinone (III).* a) A mixture of 53 mg of *o*-methylstyrene (II) and 124 mg (two equivalents to the diene) of methoxybenzoquinone (III) in a sealed tube was heated at 100—110°C for 10 hr.[2] The resulting dark red oil was chromatographed on silicic acid (10 g) and phenanthrenequinone fractions (47 mg, 42%) were collected from chloroform eluates. Repeated recrystallization from benzene afforded 3-methoxy-8-methylphenanthrene-1,4-quinone (Va), mp 243—245°C(dec).[9] IR(KBr): 1668, 1643, 1620 cm^{-1}. UV(EtOH): 227(logε=4.62), 287.5(4.36), 320 (3.70), 376 mμ(3.54).

Found: C, 76.06; H, 4.93%. Calcd for $C_{16}H_{12}O_3$; C, 76.18; H, 4.80%.

b) A suspension of 55 mg of II and 129 mg of III in 0.2 m*l* of benzene was heated at 100—110°C in a sealed tube for 40 hr. Working up as in a) afforded 50 mg (42%) of phenanthrenequinones.

Hydrolysis of 3-Methoxy-8-methylphenanthrene-1,4-quinone (Va). To a suspension of 30 mg of Va in 3 m*l* of ethanol was added *ca.* 200 mg of powdered potassium hydroxide. After standing overnight, water was added and the solution was acidified with 6 N hydrochloric acid. Precipitates were collected and purified through silicic acid column. Recrystallization from benzene gave 3-hydroxy-8-methylphenanthrene-1,4-quinone (VIIa), mp 219—224°C (dec). IR (KBr): 3320, 1653, 1632, 1587 cm^{-1}. UV (EtOH): 225, 290, 331, 380 mμ. Mass: *m/e* 238 (M^+), 210 (M^+-CO). Found: C, 75.25; H, 4.12%. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23%.

The IR spectrum of VIIa was identical with that of Thomson's[6] and mixed melting point was 217—220°C (dec) although the original Thomson's sample had somewhat different melting point (~213°C (dec)).

2-Hydroxyphenanthrene-1,4-quinone (VIb). Following the known procedure,[6,10] 2-hydroxyphenanthrene[11] was converted into 2-hydroxyphenanthrene-1,4-quinone *via* 1,2-phenanthrenequinone. Pure VIb, mp 184—185°C (dec) (from benzene). (Lit,[8] mp 190°C (dec)). IR (KBr): 3370, 1660sh, 1647, 1640sh cm^{-1}.

2-Methoxyphenanthrene-1,4-quinone (IVb). To a solution of 25 mg of 2-hydroxyphenanthrene-1,4-quinone (VIb) in 3 m*l* of ether was added 10 m*l* of ethereal diazomethane (prepared from 300 mg of nitrosomethylurea) and the mixture was left for 30 min. The ether solution was washed with dilute alkali, dried through anhydrous sodium sulfate layer and was evaporated to give solid (25 mg). Recrystallization from methanol afforded pure 2-methoxyphenanthrene-1,4-quinone (IVb), mp 168—169°C. (Lit,[8] mp 172.5°C). IR (KBr): 1675, 1640, 1620 cm^{-1}. UV (EtOH): 223 (4.59), 282 (4.38), 374 mμ (3.31).

Found: C, 75.28; H, 4.17%. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23%.

Diels-Alder Reaction between Styrene (I) and Methoxybenzoquinone (III). a) The reaction was carried out with or without benzene as in the case of *o*-methylstyrene and the phenanthrenequinone was obtained in 26% yield in both reactions. Recrystallization from methanol gave 3-methoxyphenanthrene-1,4-quinone (IVa), mp 168—169°C. (Lit,[7] mp 170°C). IR (KBr): 1670, 1648, 1623 cm^{-1}. UV (EtOH): 226 (4.58), 282.5 (4.33), 316 (3.82), 371 mμ (3.51). Mass: *m/e* 238 (M^+), 223.

Found: C, 75.14;H, 4.12%. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23%.

The crude mixture (69 mg) was recrystallized from methanol to give 48 mg of IVa and the residue was chromatographed on silicic acid (10 g) to afford further 10 mg of IVa and 5 mg IVb. The latter, purified by recrystallization from methanol, melted at 169°C and showed identical IR spectrum with that of the authentic sample.

b) A mixture of styrene and methoxybenzoquinone in a different molar ratio was heated at 100—110°C in a sealed tube. The results are summarized in Table 1.

Hydrolysis of 3-Methoxyphenanthrene-1,4-quinone (IVa). As in the case of Va, IVa was hydrolyzed in ethanolic potassium hydroxide to afford 3-hydroxyphenanthrene-1,4-quinone (VIa) in 93% yield. Recrystallization from benzene gave the pure sample, mp 194—196°C (dec). (Lit,[7] mp 230°C (dec)). IR(KBr): 3200, 1650, 1627 cm^{-1}.

Found: C, 74.90; H, 3.60%. Calcd for $C_{14}H_8O_3$: C, 74.99; H, 3.60%.

We are deeply indebted to Professor Thomson for a gift of 3-hydroxy-8-methylphenanthrene-1,4-quinone.

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9) Lora-Tamayo[2] reported the melting point of the adduct to be 253°C (dec), though the position of methoxyl group has not been clarified.

10) L.F. Fieser, "Organic Syntheses," Coll. Vol. II, p. 35, 430 (1943).

11) This substance was derived from 7-methoxy-4-oxo-1,2,3,4-tetrahydrophenanthrene[12] by successive reactions: sodium borohydride reduction, hydrogenolysis, DDQ oxidation and hydrolysis.

12) M. Ghosal, *J. Org. Chem.*, **25**, 1856 (1960).