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SOME RESULTS OBTAINED IN THE UTILISATION OF QUINONES AS PHILODIENE

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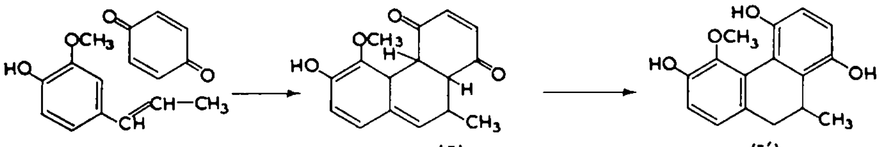
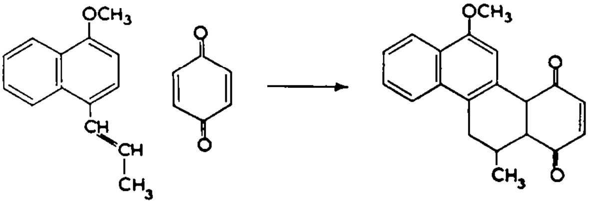
Abstract—In the course of a study of new applications of the Diels–Alder reaction, the addition of *p*-benzoquinone and substituted quinones to ethylene-aromatic dienes and heteroconjugations containing nitrogen, has been investigated.

Ethylene-aromatic conjugations

As the influence of the methoxyl group on the addition of maleic anhydride to ethylene-aromatic conjugations is already known,[1] a study of the behaviour of *p*-benzoquinone with eugenol[2] and 1:4-methoxypropenylnaphthalene[3] was undertaken; derivatives of phenanthrene (I) and chrysene(II) were obtained. In both cases diene and dienophile are added in a 1 : 1 proportion, and in the former the mobility of the hydrogen next to the =CO group is decisive in the isomerisation to the hydroquinone structure (I′). This is shown by the formation of an acetyl derivative.



(I) (I′)



(II)

Results previously obtained in this laboratory with styrene and anethol[4] only led to copolymers when *p*-benzoquinone was employed, but substituted quinones (toluquinone and methoxyquinone), and styrene and its methoxy and methyl derivatives, gave 1 : 1-tetradehydrogenated adducts in which it has been shown that

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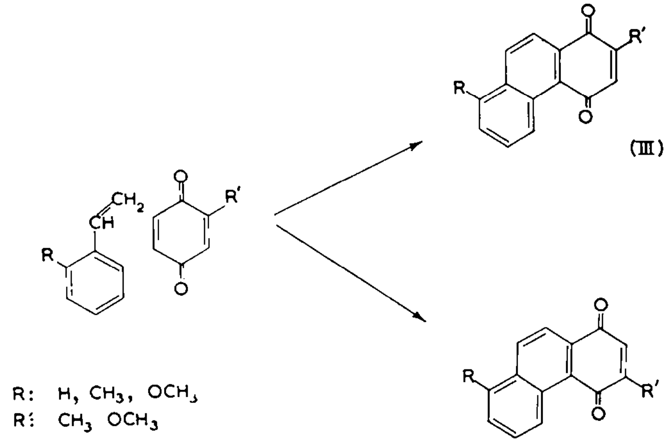
[1] B. J. F. Hudson and R. Robinson, *J. Chem. Soc.* 715 (1941).
[2] M. Lora-Tamayo and D. G. Fernández Martín, *An. Fis. Quim.* **40**, 1178 (1944).
[3] M. Lora-Tamayo and D. G. Fernández Martín, *An. Fis. Quim.* **42**, 1083 (1946).
[4] M. Lora-Tamayo and J. M. Viguera, *An. Fis. Quim.* **38**, 192 (1942).

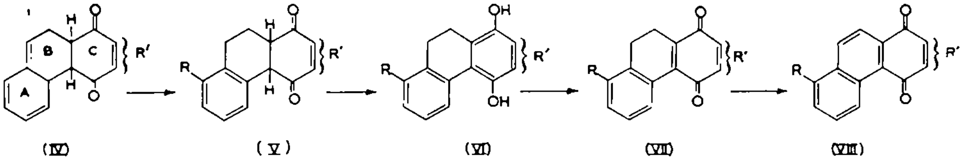
addition has taken place at the non-substituted dienophile double bond [(III) and (III')]:[5]



(III)

(III')

This tetradehydrogenation of the primary adduct is shown in the following scheme (IV) to (VIII):



(IV) (V) (VI) (VII) (VIII)

(V). Aromatisation of ring A, as shown in the adducts of maleic anhydride and with quinone.

(VI). Migration of the angular H atoms to the adjacent =CO groups, yielding a hydroquinone structure. This isomerisation is similar to that observed in the adducts of aliphatic dienes with quinones, and, even though it usually does not take place during addition, it can be achieved by using various reagents, such as acetic anhydride formation of the diacetate of the enolic form, traces of hydrobromic acid, traces of hydrochloric acid and stannous chloride, and by fusion.[6,7,8]

(VII). Oxidation to quinone, produced by toluquinone itself, which is to be found among the reaction products partially reduced to toluhydroquinone.

(VIII). Finally, aromatisation of the B ring by the toluquinone itself, leading to the tetradehydrogenated adduct, which can be isolated (cf. Johnson *et al.*,[9] Adams and Wicks[10] and Weizmann *et al.*[11]).

In support of this interpretation Johnson *et al.*[9] and Adams and Wicks[10] have studied the formation of tetradehydrogenated adducts 2:3-dimethoxybutadiene and from toluquinone or 2:3-dimethyl-*p*-benzoquinone. Similar observations have been made by Weizmann *et al.*[11] and Diels *et al.*[7] The loss of four atoms of hydrogen in the adduct excludes the existence of substituent R' in the angular position, which is inconsistent with the dehydrogenation mechanism, and suggests that the addition has taken place at the non-substituted double bond of the quinone. The quinonoid character of the adduct is indicated by oxime formation and also by reduction to the corresponding hydroquinone. Owing to the ease with which it oxidises, it was found preferable to reduce in presence of an acylating reagent (acetic anhydride,

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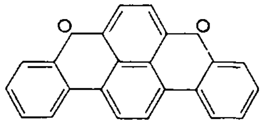
[5] M. Lora-Tamayo, A. Alberola and C. Corral, *An. Fis. Quim.* B **53**, 63 (1957).
[6] K. Okahara and M. Suzuki, *J. Chem. Soc. Japan*, **63**, 1354 (1942). *Chem. Abstr*, **4**, 3088 (1947).
[7] O. Diels, K. Alder and G. Stein, *Ber. Dtsch. Chem. Ges.* **62**, 2337 (1929).
[8] L. F. Fieser and F. C. Chang, *J. Amer. Chem. Soc.* **64**, 2048 (1942).
[9] J. R. Johnson, W. H. Jobling and George W. Bodamer, *J. Amer. Chem. Soc.* **63**, 131 (1941).
[10] R. Adams and Z. W. Wicks, *J. Amer. Chem. Soc.* **66**, 1315 (1944).
[11] C. Weizmann, E. Bergmann and L. Haskelberg, *J. Chem. Soc.* 391 (1939).

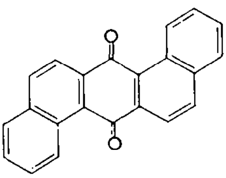
acetic acid and zinc). The diacetates of the corresponding hydroquinones are obtained. The reaction with hydroxylamine hydrochloride agrees with Kehrmann's rule, according to which trisubstituted quinones only form mono-oximes.

Fieser[12] has synthesised 2-methoxy- and 3-methoxy-1:4-phenanthrene(III) and (III'), and the adduct from styrene and 2-methoxy-*p*-benzoquinone corresponds to (III) both in physical properties and in the products formed on alkaline hydrolysis.

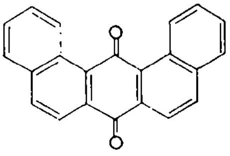
The reaction of styrene with *p*-benzoquinone did not yield a simple adduct. Kern and Feuerstein[13] obtained a compound the analysis of which indicated that it was formed from two molecules of styrene and one of *p*-benzoquinone, and assigned the structure (IX) to their product. The experimental facts adduced by Kern and Feuerstein can be readily explained if their compound is regarded as a styrene-*p*-benzoquinone (2:1) bis-adduct, which has lost eight hydrogen atoms. The compound would then be the result of a double dienic addition of the ethylene-aromatic conjugation of styrene to the two dienophilic unsaturations of *p*-benzoquinone. Of the two possible octadehydrogenated bis-adducts 1:2:5:6-dibenzoanthraquinone (X) and 1:2:7:8-dibenzoanthraquinone (XI), the former has been described[14] and appears to be identical with Kern and Feuerstein's compound.



(IX)

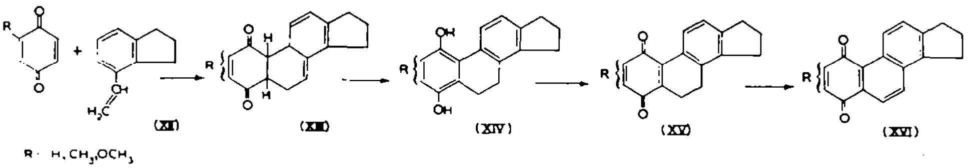


(X)



(XI)

In view of the biological interest of the *cyclo*pentenophenanthrene derivatives it was decided to study the reactions of quinones with 4-vinylindane (XII), and in every case a 1 : 1 adduct is obtained; the adduct from (XII) and *p*-benzoquinone corresponding to (XIII, R = H) decomposes at the m.p. 210°, losing 2H. It yields an acetyl derivative of (XIV),[15] but no oxime. The following scheme summarises the reactions:



R = H, CH_3, OCH_3

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[12] L. F. Fieser, *J. Amer. Chem. Soc.* **51**, 1896 (1929).

[13] W. Kern and J. Feuerstein, *J. Prakt. Chem.* **158**, 186 (1941).

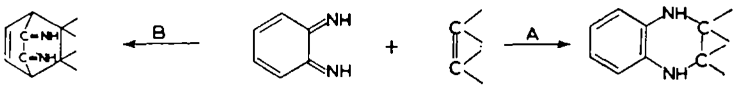
[14] R. Weitzenböck and A. Klinger, *Mh. Chem.* **39**, 315 (1918).

[15] M. Lora-Tamayo and J. Marín, *An. Fis. Quim.* B **48**, 693 (1952).

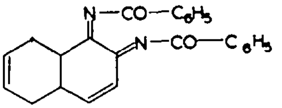
With the object of obtaining compounds with an angular methyl in (XIII), attempts were made to prepare the adduct from 4-vinylindane and 2-methyl-5-methoxy-*p*-benzoquinone (cf. refs. 16–21). After heating for 6–8 days only unchanged quinone could be isolated. This agrees with the interpretation put forward to explain the formation of tetradehydrogenated adducts.

Heteroconjugations containing nitrogen (cf. refs. 22–29)

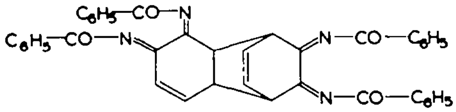
In view of Horner and Sturm's investigation[30] of *o*-quinones as "heterodienes" in the Diels–Alder reaction, it was decided to investigate the behaviour of *o*-quinone-di-imines, which may react with the ethylenic double bond in two ways, by addition to the heteroconjugation $NH{=}C{-}C{=}NH$ (A) or the ethylenic conjugation (B):



Adams and co-workers[31,32] have shown that dienes such as butadiene form (1:1) adducts with *o*-quinonedibenzimide, e.g., (XVII), and also that *o*-quinonedi-imides are good dienophiles, e.g., (XVIII), which is regarded as an *o*-quinonedibenzimide dimer.

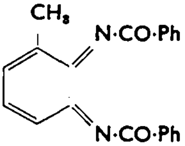


(XVII)



(XVIII)

3-Methyl-*o*-quinonedibenzimide (XIX)[33] was prepared by the method of Adams and Way.[32]



(XIX)

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[16] M. Lora-Tamayo and C. Corral, *An. Fis. Quim.* B **53**, 45 (1957).

[17] L. F. Fieser and A. M. Seligmann, *Ber. Dtsch. Chem. Ges.* **68**, 1748 (1935).

[18] C.-K. Chuang and C.-T. Han, *Ber. Dtsch. Chem. Ges.* **68**, 876 (1935).

[19] A. Alder, *Ark. Kemi Min. Geol.* B **11**, 49 (1949).

[20] M. Orchin and L. W. Butz, *J. Org. Chem.* **8**, 509 (1943).

[21] R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, *J. Amer. Chem. Soc.* **74**, 4223 (1952).

[22] R. Pummerer and H. Fiesselmann, *Liebigs Ann.* **544**, 206 (1940).

[23] M. Lora-Tamayo and F. Fariña, *An. Fis. Quim.* B **48**, 91 (1952).

[24] M. Lora-Tamayo and J. Royo, *An. Fis. Quim.* B **48**, 81 (1952); M. Lora-Tamayo and F. Alvarez, *An. Fis. Quim.* B **48**, 75 (1952); M. Lora-Tamayo, R. Pérez Ossorio and M. Sanz Burata, *An. Fis. Quim.* B **50**, 865 (1954).

[25] F. Bergmann, *J. Amer. Chem. Soc.* **60**, 2811 (1938).

[26] G. La Paralo, *Gazz. Chim. Ital.* **64**, 919 (1934).

[27] G. Carrona, *Gazz. Chim. Ital.* **78**, 38 (1948).

[28] M. Lora-Tamayo and J. Fontán Yanes, *An. Fis. Quim.* **43**, 777 (1947).

[29] M. Lora-Tamayo and J. Fontán Yanes, *An. Fis. Quim.* B **44**, 583 (1948).

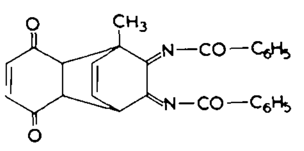
[30] L. Horner and K. Sturm, *Liebigs Ann.* **597**, 1 (1955).

[31] R. Adams and W. P. Samuels, Jr., *J. Amer. Chem. Soc.* **77**, 5357 (1955).

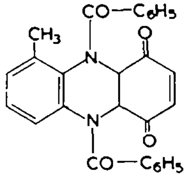
[32] R. Adams and J. W. Way, *J. Amer. Chem. Soc.* **76**, 2763 (1954).

[33] M. Lora-Tamayo and J. L. Soto Cámara, *An. Fis. Quim.* B **53**, 27 (1957).

(XIX) reacts with *p*-benzoquinone to form an adduct for which two structures are possible depending whether the addition takes place at the carbon conjugation (XX) or at the heteroconjugation —N=C—C=N— (XXI). Hydrolysis of the adduct yields benzoic acid, ammonia and a nitrogen-free now-crystalline product, for which the structure (XXII) is suggested, corresponding to (XX). Analysis and infra-red spectrum (see Fig. 1) are in agreement with the suggested structure. A hydroquinone structure is inadmissible, since there are no bands in the spectrum of the adduct corresponding to —OH.



(XX)



(XXI)

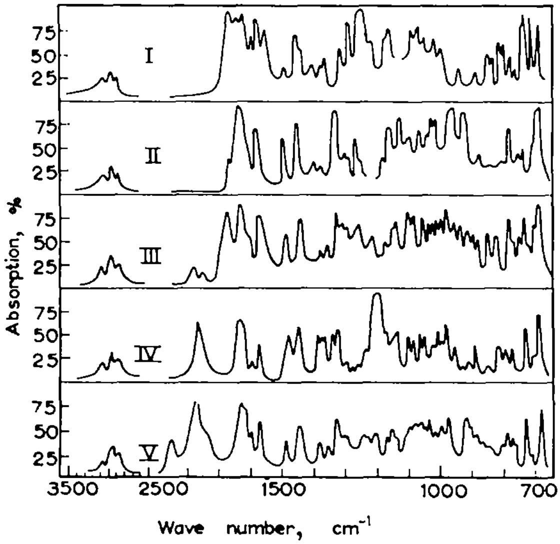
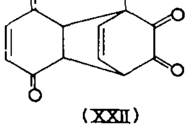
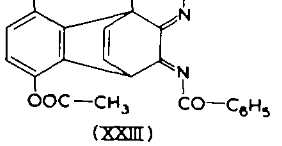


Fig. 1. Infra-red absorption spectra of: (I) 3-methyl-*o*-quinonedibenzimide dimer (red); (II) 3-methyl-*o*-quinonedibenzimide (white); (III) adduct of 3-methyl-*o*-quinonedibenzimide and and *p*-benzoquinone; (IV) acetylated derivative of the former; (V) adduct of 3-methyl-*o*-quinonedibenzimide and maleic anhydride. Determined with a Perkin-Elmer (model 112) spectrograph.

Acetylation of the adduct yields a diacetyl derivative (XXIII), which, as in the case of other quinone adducts, is probably formed after previous isomerisation of the adduct. Its infra-red spectrum also agrees with structure (XX).



(XXII)



(XXIII)

The most important feature of the spectra is the presence of the very intense 1635 cm^{-1} band in all of them, corresponding to an atomic group in every compound. The band is less intense in spectrum I of the dimer, which reveals another very intense band at 1666 cm^{-1}, which almost disappears in the monomer and is not found in the adducts. The 1635 cm^{-1} band is due to the C=O bond in the =C=N—CO—Ph group. The intensity of conjugation of C=O with the aromatic nucleus and the C=N bond explains the lowness of this band. Accordingly the C=O bond in =N—CO—Ph gives a band of a higher frequency, which would correspond to 1666 cm^{-1}. This explains why both bands appear in the red product (dimer), while the absence of the 1666 cm^{-1} band in the adduct spectra is determined by the addition of dienophiles to the carbon conjugation. The C=N groups are preserved and, consequently, the 1635 cm^{-1} band. The faint 1666 cm^{-1} band in the white product (monomer) must be due to traces of impurities in the dimer. A 1677 cm^{-1} band in spectrum III is due to the C=O of the quinone residue. In *p*-benzoquinone this band appears at 1665 cm^{-1} and, when one of the double bonds disappears, frequency increases slightly for conjugation decreases. The bands assigned to the C=O of the maleic anhydride adduct are in their normal position.

In no case do bands characteristic of the O-H and N-H bonds (3200–2500 cm^{-1}) appear, and therefore structures containing these groups can be discarded. The very intense deformation band (1515–1470 cm^{-1}) of the N-H group of the secondary amides does not appear. This supports the elimination of those structures containing the —NH—CO group.

EXPERIMENTAL

Adducts from styrene or 4-vinylindane and quinones. The mixture of diene and quinone in 1 : 2 molar proportions is heated at 100° (2 hr) in a closed tube or heated under reflux in toluene for 6–20 hr. A coloured solid is obtained, which is treated with ethanol to remove soluble impurities, and the residual adduct is purified by crystallisation from acetic acid or by sublimation. Table 1 summarises the adducts obtained.

Acetyl derivatives of the reduction products of adducts. The adduct (1 g), acetic anhydride (10 ml), glacial acetic acid (2·5 ml) and anhydrous sodium acetate (0·25 g) are heated under reflux, and zinc dust (1 g) is added in small portions during 1 hr. The colourless solution is poured into water, and the precipitated white solid and excess of zinc are filtered off, boiled with ethanol or acetic acid and again filtered, the acetyl derivative crystallising from the filtrate on cooling. In the case of the *iso*eugenol adduct, the triacetyl derivative was obtained by the usual method of acetylation without the addition of a reducing agent. Table 2 summarises the results obtained.

3-*Methyl-*o*-quinonedibenzimide* (XIX). This was prepared by oxidising 3-methyl-*o*-quinonedibenzamide with lead tetra-acetate, following the procedure of Adams and Way.[32] The product (7 g from 13·6 g of the dibenzamide) consists of red crystals mixed with a yellow powder, m.p. 126°, softening at 124–125, and is a mixture of monomeric and dimeric forms of the di-imide (Found: C, 76·55, 76·33; H, 4·82, 5·04; N, 8·67, 8·64. $C_{21}H_{16}O_2N_2$ requires C, 76·89; H, 4·88; N, 8·54 per cent. (*a*) M. wt. 345–346 (cryoscopic in benzene), corresponding to 6 per cent of the dimeric form; (*b*) 546 ± 30 (micro. Rast), corresponding to 60–75 per cent of the dimeric form). The determination was done on a red product, which on grinding

TABLE 1. ADDUCTS FORMED

Diene	Philodiene	Adduct			
		M.P. (°C)	Analysis		Formula
			Calculated (per cent)	Found (per cent)	
*iso*Eugenol[a]	*p*-Benzoquinone	215	C, 70·59; H, 5·88; OCH₃, 11·40	C, 70·4; H, 5·86; OCH₃, 11·4	$C_{16}H_{16}O_4$
1-Methoxy-4-propenylnaphthalene[b]	*p*-Benzoquinone	213	—OCH₃, 10·13	—OCH₃, 10·12	$C_{20}H_{18}O_3$
1-Methoxy-4-vinylnaphthalene	*p*-Benzoquinone	227–230	C, 78·2; H, 5·5; OCH₃, 10·6	C, 78·1; H, 5·3; OCH₃, 10·3	$C_{19}H_{16}O_3$
Styrene[c]	1:4-Toluquinone	141–142	C, 81·0; H, 4·54	C, 80·9; H, 4·61	$C_{15}H_{10}O_2$
Styrene[c]	2-Methoxy-*p*-benzoquinone	172	C, 75·6; H, 4·20	C, 57·7; H, 4·25	$C_{15}H_{10}O_3$
o-Methylstyrene[c]	2-Methoxy-*p*-benzoquinone	252 (dec.)	C, 76·1; H, 4·76	C, 76·1; H, 4·76	$C_{16}H_{12}O_3$
o-Methylstyrene[c]	1:4-Toluquinone	211·5	C, 81·3; H, 5·08	C, 81·2; H, 4·95	$C_{16}H_{12}O_2$
o-Methylstyrene	2-Methyl-5-methoxy-*p*-benzoquinone	—	—	—	—
o-Methoxystyrene[d]	1:4-Toluquinone	171–175	C, 76·2; H, 4·72	C, 76·3; H, 4·90	$C_{16}H_{12}O_3$
p-Methoxystyrene[d]	1:4-Toluquinone	218–219	C, 76·2; H, 4·72	C, 76·3; H, 4·96	$C_{16}H_{12}O_3$
m-Methoxystryrene[e]	1:4-Toluquinone	—	—	—	—
4-Vinylindane	*p*-Benzoquinone	210 (dec.)	C, 81·6; H, 5·60	C, 81·8; H, 5·64	$C_{17}H_{14}O_2$
4-Vinylindane[f]	1:4-Toluquinone	169·5–170	C, 82·4; H, 5·34	C, 82·4; H, 5·36	
4-Vinylindane[g]	2-Methoxy-*p*-benzoquinone	269	C, 77·6; H, 5·03	C, 77·5; H, 5·12	$C_{18}H_{14}O_3$
4-Vinylindane	2-Methyl-*p*-benzoquinone	—	—	—	—

[a] Red coloured adduct from diene and deinophile (1 : 1).

[b] Crimson needles from diene and dienophile (1 : 1).

[c] Yellow tetradehydrogenated adduct.

[d] Red needles.

[e] Amorphous product, probably a polymer.

[f] Orange crystals from acetic acid. The adduct corresponds to 2- or 3-methyl-7:8-*cyclo*pentene-1:4-phenanthrenequinone. The adduct is a tetradehydrogenated addition product.

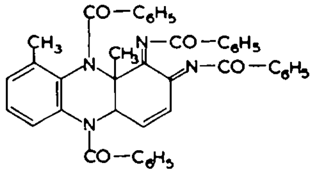
[g] Orange crystals from acetic acid, corresponding to 2-or 3-methoxy-7:8-*cyclo*pentene-1:4-phenanthrenequinone.[16]

TABLE 2. ACETYLATION OF THE REDUCTION PRODUCTS OF ADDUCTS TO GIVE DIACETYL DERIVATIVE

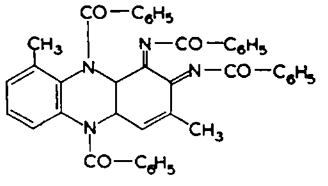
Adduct	Acetylated derivative		
	M.P. (°C)	Analysis	
		Calculated (per cent)	Found (per cent)
*iso*Eugenol-*p*-benzoquinone*	259	C, 66·3; H, 5·52	C, 66·9; H, 5·56
Styrene–1:4-toluquinone	139·5	C, 74·0; H, 5·19	C, 74·5; H, 5·45
Styrene-2-methoxy-*p*-benzoquinone	170	C, 70·3; H, 4·93	C, 70·4; H, 5·11
o-Methylstyrene-3:4-toluquinone	142	C, 74·5; H, 5·59	C, 74·5; H, 5·60
o-Methylstyrene-2-methoxy-*p*-benzoquinone	181	C, 71·0; H, 5·32	C, 70·9; H, 5·11
o-Methoxystyrene–1:4-toluquinone	175–178	C, 71·0; H, 5·32	C, 71·2; H, 5·51
p-Methoxystyrene–1:4-toluquinone	183	C, 71·0; H, 5·32	C, 71·2; H, 5·41
4-Vinylindane–1:4-toluquinone	177	C, 75·8; H, 5·74	C, 75·5; H, 5·81
4-Vinylindane–2-methoxy-*p*-benzoquinone	183	C, 72·5; H, 5·49	C, 72·4; H, 5·33

* Formed triacetyl derivative.

gave an intensely yellow powder. The red product on solution in a polar solvent (such as chloroform, methanol or ethanol) crystallised as a white solid, m.p. 126°, mixed m.p. with the red product 116–120° (Found: C, 76·27; H, 5·11; N, 8·54. $C_{21}H_{16}O_2N_2$ requires C, 76·89; H, 4·88, N, 8·54. M. wt. found 328; required 328). The red product (7 g) is converted to the white form by dissolving in hot ethanol (40 ml), from which it separates as a yellow crystalline mass, which after successive recrystallisations from ethyl acetate gave a white product, m.p. 126°. In solution it is unstable, gradually dimerising to the red form. Colourless solutions in benzene, chloroform or ethanol slowly turn yellow to orange, a change which is accelerated by heat. In the solid state the product is stable. The m.p. of 126° corresponds to the dimer, for it has been observed that 4–5° below this temperature the white product turns orange until 126°, when it begins to melt, the colour increasing in intensity. Evidence shows that (XIX) exists as a white monomer and a red dimer. The interpretation which Willstätter and Müller[34] advanced to explain the existence of white and red forms of the *o*-quinones as an example of structural isomerism between a peroxide (white) and ketonic (coloured) form cannot be applied to the present case. It is suggested that, if the dimer is formed by a Diels–Alder reaction in which one of the di-imide molecules behaves as a diene and another as a dienophile, the resulting adduct would be either (XXIV) or (XXV).



(XXIV)



(XXV)

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[34] R. Willstätter and F. Muller, *Ber. Dtsch. Chem. Ges.* **41**, 2580 (1908).

Adduct (XX) *of 3-methyl-o-quinonedibenzimide and p-benzoquinone. p*-Benzoquinone (6 g) and (XIX) (9 g) in benzene (300 ml) are heated under reflux for 24 hr or left to stand for 30 days at room temperature. After removal of the benzene under reduced pressure, the residue is treated with ethanol to dissolve unreacted material and the adduct remaining (9·5 g, 79 per cent) is crystallised from ethyl acetate to give yellow needles, m.p. 237–238° (dec.). After repeated recrystallisations from ethyl acetate then was no gradual increase in m.p. (Found: C, 73·97; H, 4·36; N, 6·26. $C_{27}H_{20}O_4N_2$ requires C, 74·29; H, 4·61; N, 6·41 per cent). The adduct is soluble in benzene and dioxan, insoluble in ether and light petroleum and slightly soluble in warm ethanol. When the adduct (0·5 g) was heated under reflux with anhydrous sodium acetate (0·25 g) in acetic anhydride (10 ml) for 30 min, and the product was poured into cold water, the *diacetyl derivative* separated in crystalline form, which on repeated crystallisation from ethanol was obtained as colourless prisms, m.p. 196–198° (Found: C, 71·28; H, 5·23; N, 5·36. $C_{31}H_{24}O_6N_2$ (XXIII) requires C, 71·53; H, 4·61; N, 5·38 per cent). The adduct (1 g) was hydrolysed by being heated with concentrated hydrochloric acid (15 ml) and water (10 ml) under reflux for 30 min. The benzoic acid formed sublimed and a brownish red oil separated and solidified on cooling. The solid was washed with warm water to remove benzoic acid, and after drying the brownish red product weighed 0·5 g. After several crystallisations from ethanol the dark-coloured product melted at 145–147°, which is nitrogen-free, and does not react with 2:4-dinitrophenylhydrazine (Found: C, 68·32; H, 4·61. $C_{13}H_{10}O_4$ (XXII) requires C, 67·8; H, 4·16 per cent).