

992. Pyrone Series. Part VI.¹ Structure of the Supposed 6-Benzyl-4,5-diphenyl-2-pyrone.

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The condensation product of dibenzyl ketone with ethyl phenylpropionate, described in literature as 6-benzyl-4,5-diphenyl-2-pyrone, has been shown to be 2,4,5-triphenylresorcinol. It has been characterised as mono- and diacetate and mono- and di-methyl ether, and by oxidation to a *para*- and an *ortho*-quinone.

TRAVERSO² considered the compound C₂₄H₁₈O₂ obtained by the action of sodium ethoxide on dibenzyl ketone and ethyl phenylpropionate to be 6-benzyl-4,5-diphenyl-2-pyrone (Ia). El-Kholy, Rafla, and Soliman,³ however, failed to obtain the acid (II) expected from fission of such a pyrone. In this paper, we report that the products "a" and "b" previously obtained³ by methylation of this compound in alkaline medium have the formulæ C₂₄H₁₇O·OMe and C₂₄H₁₆(OMe)₂, respectively. Evidently, they cannot be derivatives of an acid such as (II) or the fission product of the 4-pyrone (Ib) which might be the outcome of Claisen condensation of the original reactants.

Since the two methylene groups in dibenzyl ketone are equally reactive towards ethyl phenylpropionate, Michael addition and Claisen condensation are liable to proceed simultaneously, leading to the formation of 2,4,5-triphenylresorcinol (Ic; R = R' = H). This compound, with diazomethane gave a dimethyl ether (Ic; R = R' = Me), identical with the product "b," and a diacetate which could be partially deacetylated to the monophenol (Ic; R = Ac, R' = H). Methylation of the latter and subsequent deacetylation led to the monoether (Ic; R = H, R' = Me) which is identical with the product "a."

The oily residue left after separation of 2,4,5-triphenylresorcinol contained 6-benzyl-4,5-diphenyl-2-pyrone (Ia) which failed to give the corresponding δ -keto-acid (II) on treatment with methanolic potassium hydroxide (cf. refs. 3 and 4). The isomeric condensation products (Ia and c) are clearly differentiated by their infrared spectra (Table), which show the hydroxyl band^{5a} in one and the 2-pyrone carbonyl band⁴ in the other.

Like 2-alkyl- and 2-aryl-naphthalene-1,3-diols,⁶ the resorcinol (Ic; R = R' = H) undergoes autoxidation in presence of alkali, giving a mixture of 2-hydroxy-3,5,6-triphenyl-1,4-benzoquinone (III) and 4-hydroxy-3,5,6-triphenyl-1,2-benzoquinone (IV). The yellow *para*-isomer was separated from the red *ortho*-isomer by its solubility in sodium hydrogen carbonate. In this respect, the former behaves like the polyphoric acids,⁷ as a vinylogue of a carboxylic acid, having the hydroxyl group activated by the adjacent carbonyl group.

The 1,4-benzoquinone (III) has been characterised by reductive acetylation to the diacetate (Ic; R = R' = Ac), and as its methyl ether (V), which failed to condense with *o*-phenylenediamine. The *ortho*-quinone (IV), however, gave 1,2,4-triacetoxy-3,5,6-triphenylbenzene on reductive acetylation; and methylation led to 4-methoxy-3,5,6-triphenyl-1,2-benzoquinone (VI) which was also prepared by oxidation of 3-methoxy-2,4,5-triphenylphenol (Ic; R = H, R' = Me). This established the position of the

¹ Part V, *J.*, 1962, 1857.

² Traverso, *Boll. sci. Fac. Chim. ind. Bologna*, 1955, **13**, 53.

³ El-Kholy, Rafla, and Soliman, *J.*, 1959, 2588.

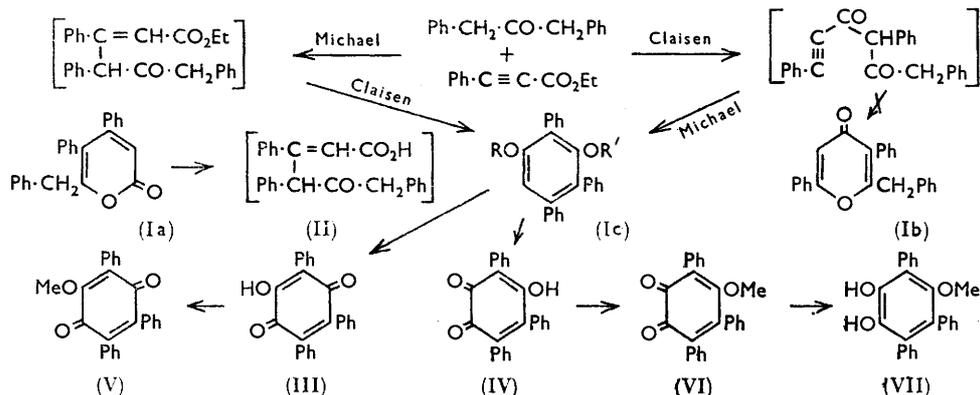
⁴ El-Kholy, Rafla, and Soliman, *J.*, 1961, 4490.

⁵ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1959, pp. (a) 96, (b) 150-151, (c) 179.

⁶ Soliman and Latif, *J.*, 1944, 56.

⁷ Thomson, "Naturally Occurring Quinones," Butterworths Scientific Publns., London, 1957, p. 26.

methoxyl group in the latter compound, as well as that of the acetyl group in the monoacetate (Ic; R = Ac, R' = H). However, the *ortho*-quinone ether (VI) failed to give the expected phenazine with *o*-phenylenediamine, but, instead, afforded 4-methoxy-3,5,6-triphenylcatechol (VII) (cf. Table). The diacetate of this catechol has also been prepared by reductive acetylation of the *ortho*-quinone ether.



Infrared spectra (cm^{-1}) were measured on Perkin-Elmer 137 spectrophotometer for a KBr disc.

No.	Compound		OH Stretch		C=O ^a	C=O	C=O
	R	R'			Acetate	2-Pyrone	Quinone
1	Ia		—	—	—	1742s	—
2	Ic	H	3546m	3448s	—	—	—
3	Ic	H	3534s	—	—	—	—
4	Ic	Ac	—	—	1761s	—	—
5	Ic	Ac	3534s	—	1761s	—	—
6	III		3226mb	—	—	—	1639s
7	III*		3497m	—	—	—	1639s
8	IV		3289mb	—	—	—	1650s
9	IV†		3448m	—	—	—	1656s
10	V		—	—	—	—	1642s
11	VI		—	—	—	—	1656s
12	VII		3534s	—	—	—	—

Ultraviolet absorption bands ($\text{m}\mu$) of ethanol solutions.

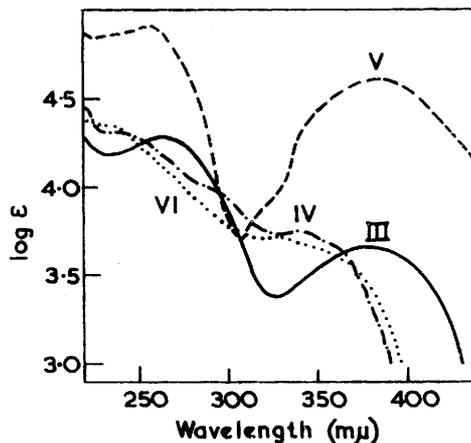
Compound No.	Min.		Max.		Min.		Max.	
	λ	$\log \epsilon$						
2	235	4.34	251	4.40	—	—	—	—
6	232	4.19	265	4.30	327	3.37	383	3.67
8	—	—	—	—	327	3.74	340	3.75
10	227	4.85	257	4.91	308	3.70	385	4.61
11	—	—	—	—	323	3.71	327	3.72

* In CHCl_3 . † In CCl_4 .

These *para*- and *ortho*-benzoquinone derivatives can be distinguished by their ultraviolet absorption curves (see Figure) in which compounds (III) and (V) show two of the three *p*-benzoquinone bands designated A, B, and C by Braude.⁸ However, their infrared spectra (Table) do not show an appreciable difference in the carbonyl absorption, though the *ortho*-quinones absorb at slightly higher frequencies.^{5b,9}

⁸ Braude, *J.*, 1945, 490.

⁹ Otting and Staiger, *Chem. Ber.*, 1955, **88**, 828.

Ultraviolet absorption spectra
of compounds (III)—(VI).

EXPERIMENTAL

Light petroleum used had b. p. 50—70°.

2,4,5-Triphenylresorcinol.—Dibenzyl ketone (6 g., 1 mol.) and ethyl phenylpropiolate (5 g., 1 mol.) were added to sodium ethoxide (1.95 g., 1 mol.) suspended in dry ether. The mixture was kept at 0° for 2 days and then poured into water. The alkaline layer was shaken with ether, the ethereal solution added to the original ethereal layer, and the mixture washed, dried, and distilled. The residue (7.4 g.) yielded the resorcinol (2.7 g.) on treatment with cold methanol; it crystallised from ethanol in needles, m. p. 208—209° (Found: C, 85.1; H, 5.45. Calc. for $C_{24}H_{18}O_2$: C, 85.2; H, 5.4%). The alkaline solution was acidified and extracted with ether, and the ethereal solution shaken with sodium hydrogen carbonate and then with sodium carbonate. An additional 0.9 g. of the resorcinol was recovered from the ethereal solution; phenylpropionic acid (0.6 g.) and a dark oily residue (0.5 g.) were obtained by acidification of the sodium hydrogen carbonate and sodium carbonate extracts.

6-Benzyl-4,5-diphenyl-2-pyrone (Ia).—The neutral oily residues left after separation of the resorcinol were distilled in a vacuum and the fraction of b. p. 240—280°/2 mm. was collected and mixed with cold methanol. The solution gradually deposited the pyrone which crystallised from methanol in needles, m. p. 135—136° (Found: C, 85.4; H, 5.4. $C_{24}H_{18}O_3$ requires C, 85.2; H, 5.4%); it was recovered unchanged after being heated with acetic anhydride and pyridine.

A solution of the pyrone (0.1 g.) in 1% methanolic potassium hydroxide (10 ml.) was warmed for 30 min., then diluted with water and extracted with ether. 2,4,5-Triphenylresorcinol was recovered from the ethereal solution and from the alkaline solution after acidification.

1,3-Dimethoxy-2,4,5-triphenylbenzene (Ic; R = R' = Me).—This ether was prepared when a solution of the resorcinol (0.7 g.) in ether-methanol (100 ml.) was kept with ethereal diazomethane (about 2 g.) at room temperature for 4 days. After decomposition of the excess of diazomethane, the dimethyl ether was recovered and crystallised from ethanol in needles, m. p. and mixed m. p. 153° (cf. ref. 3) (Found: C, 85.2; H, 6.05; OMe, 16.3. Calc. for $C_{26}H_{22}O_2$: C, 85.2; H, 6.05; 2OMe, 16.9%).

1,3-Diacetoxy-2,4,5-triphenylbenzene (Ic, R = R' = Ac).—A solution of the resorcinol (2 g.) in pyridine (20 ml.) and acetic anhydride (20 ml.) was heated on the water-bath for 2 hr. The diacetate crystallised from methanol in needles, m. p. 160—161° (Found: C, 79.5; H, 5.4. $C_{28}H_{22}O_4$ requires C, 79.6; H, 5.25%). Hydrolysis of it (0.25 g.) with 5% ethanolic potassium hydroxide (10 ml.) led to the resorcinol on acidification.

3-Acetoxy-2,5,6-triphenylphenol (Ic; R = Ac, R' = H).—The diacetate (1 g.) was refluxed in ethanol (50 ml.) containing water (3 ml.) and 10 drops of concentrated hydrochloric acid for 3 hr. The monoacetate, m. p. 222—225°, was obtained by dilution and crystallised from

methanol in needles, m. p. 226—227° (Found: C, 81.6; H, 5.4. $C_{26}H_{20}O_3$ requires C, 82.1; H, 5.3%). It gave the diacetate, m. p. 161°, when heated with pyridine-acetic anhydride.

1-Acetoxy-3-methoxy-2,4,5-triphenylbenzene (Ic, R = Ac, R' = Me).—This ether-ester was prepared by the action of diazomethane on the monoacetate in ether-methanol and crystallised from methanol in needles, m. p. 170° (Found: C, 82.2; H, 5.65; OMe, 8.0. $C_{27}H_{22}O_3$ requires C, 82.2; H, 5.6; OMe, 7.9%). Heating it (0.2 g.) in 5% ethanolic potassium hydroxide (10 ml.) for 1 hr. gave 3-methoxy-2,4,5-triphenylphenol which crystallised from benzene-light petroleum in needles, m. p. 207—208°, identical with the monomethyl ether prepared by means of dimethyl sulphate³ (Found: C, 85.1; H, 5.7; OMe, 8.1. Calc. for $C_{25}H_{20}O_2$: C, 85.2; H, 5.7; OMe, 8.8%). It gave 1,3-dimethoxy-2,4,5-triphenylbenzene with diazomethane.

2-Hydroxy-3,5,6-triphenyl-1,4-benzoquinone (III).—A solution of the resorcinol (1 g.) in 5% ethanolic potassium hydroxide (30 ml.) was exposed to air at room temperature for 4 days, during which most of the alcohol evaporated. When an aqueous solution of the dark violet residue from 4 identical experiments was acidified, a yellowish-brown precipitate (2.8 g.) separated. This was dissolved in ether and extracted with aqueous sodium hydrogen carbonate and then with aqueous sodium carbonate. Acidification of the sodium hydrogen carbonate solution afforded most of the *para*-quinone (III) (1.8 g.) which was purified by crystallisation from benzene containing traces of methanol. It recrystallised from dilute methanol in yellow cubes, m. p. 209° (decomp.), which did not give a characteristic colour with ethanolic potassium hydroxide or ferric chloride (Found: C, 81.8; H, 4.9. $C_{24}H_{16}O_3$ requires C, 81.8; H, 4.6%). When this quinone (0.3 g.) was refluxed with zinc dust (0.5 g.) in acetic anhydride (5 ml.) and acetic acid (5 ml.) for 30 min., 1,3-diacetoxy-2,4,5-triphenylbenzene, m. p. and mixed m. p. 160°, had been obtained.

2-Methoxy-3,5,6-triphenyl-1,4-benzoquinone (V) was prepared when the foregoing quinone (0.3 g.) was refluxed with anhydrous potassium carbonate (0.7 g.) and methyl iodide (5 ml.) in acetone (15 ml.) for 5 hr. It crystallised from methanol and recrystallised from ethyl acetate-light petroleum in yellowish-orange prisms, m. p. 189° (Found: C, 81.5; H, 5.35; OMe, 8.4. $C_{25}H_{18}O_3$ requires C, 81.9; H, 4.95; OMe, 8.5%). It was recovered unchanged after being heated with *o*-phenylene diamine in ethanol or acetic acid.

4-Hydroxy-3,5,6-triphenyl-1,2-benzoquinone (IV).—This quinone was obtained as a reddish-brown precipitate (1 g.) by acidification of the sodium carbonate extract of the above oxidation product. Its solution in benzene was heated with charcoal and from the filtrate on cooling, traces of the *para*-isomer separated. The mother-liquor was then evaporated to dryness and the residue treated with cold ethyl acetate; the solution gradually deposited the *ortho*-quinone (0.4 g.), m. p. 150—160°. It crystallised from dilute methanol and recrystallised from benzene-light petroleum in red needles, m. p. 164° (Found: C, 81.8; H, 4.65%). It gave a violet colour with ethanolic potassium hydroxide and a greenish-violet colour with ferric chloride.

1,2,4-Triacetoxy-3,5,6-triphenylbenzene was prepared when the foregoing quinone (0.3 g.) was refluxed with zinc dust, acetic acid, and acetic anhydride for 30 min. It crystallised from dilute methanol in needles, m. p. 197—198° (Found: C, 75.5; H, 4.95; Ac, 26.55. $C_{30}H_{24}O_6$ requires C, 75.0; H, 5.0; 3Ac, 26.9%).

4-Methoxy-3,5,6-triphenyl-1,2-benzoquinone (VI).—This quinone was prepared when 3-methoxy-2,4,5-triphenylphenol (0.7 g.) in acetic acid (70 ml.) was treated (dropwise) with chromium trioxide (1 g.) in 4 ml. of water and 20 ml. of acetic acid. The mixture was kept overnight at room temperature, then diluted with water, and the precipitate was extracted with ether and washed with aqueous sodium hydrogen carbonate. The orange residue (0.3 g.) recovered from the ethereal solution crystallised from methanol in reddish-orange prisms, m. p. 160°, which gave a red colour with ethanolic potassium hydroxide (Found: C, 81.5; H, 4.9; OMe, 8.6. $C_{25}H_{18}O_3$ requires C, 81.9; H, 4.95; OMe, 8.5%). This ether was also prepared when the foregoing *ortho*-quinone was refluxed with methyl iodide and potassium carbonate as for the *para*-isomer.

3,5,6-Triphenyl-4-methoxycatechol (VII) was obtained when a solution of 4-methoxy-3,5,6-triphenyl-1,2-benzoquinone (0.3 g.) and *o*-phenylenediamine (0.15 g.) in glacial acetic acid (8 ml.) was refluxed for 1 hr. After dilution of the mixture with water, the product (0.25 g.) was recovered. It crystallised from benzene-light petroleum in prisms, m. p. 167°, which gave a dark violet colour with ethanolic potassium hydroxide (Found: C, 80.9; H, 5.5. $C_{25}H_{20}O_3$ requires C, 81.5; H, 5.5%). Its diacetate was prepared by heating it with acetic anhydride and pyridine for 2 hr. and crystallised from ethanol in needles, m. p. 205° (Found: C, 76.8;

H, 5.4; OMe, 6.8. $C_{29}H_{24}O_5$ requires C, 77.0; H, 5.35; OMe, 6.85%). This acetate was also prepared when 4-methoxy-3,5,6-triphenyl-1,2-benzoquinone (0.2 g.) was refluxed with zinc dust (0.5 g.), acetic acid (8 ml.), and acetic anhydride (7 ml.) for 2 hr.

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