

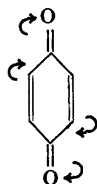
The Reaction between Acetylacetone and *p*-BenzoquinoneIII. $\omega, \omega, \omega', \omega'$ -Tetraacetyl-*p*-xyloquinone

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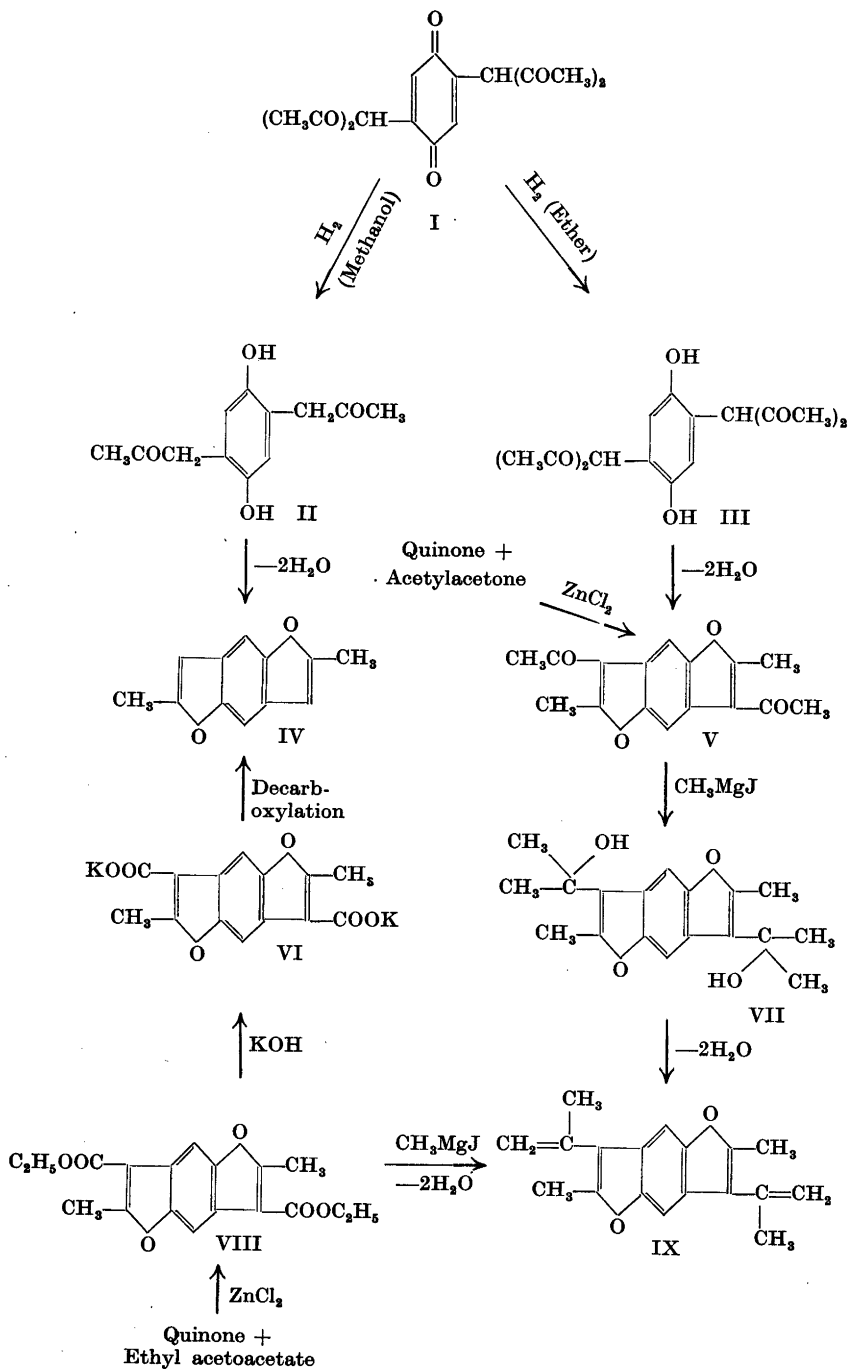
As previously communicated¹ a quinone $C_{16}H_{16}O_6$ was formed in a base-catalyzed reaction between acetylacetone and *p*-benzoquinone where apparently one mole of the quinone and two moles of the diketone participated.

In *p*-benzoquinone the mesomeric (and in reaction electromeric) shifts indicated on the figure are supposed to take place leaving small negative charges on the oxygen atoms and corresponding positive charges on the carbon atoms in the 2- and 5-positions. In *p*-benzoquinone are thus 2,5-substitutions with nucleophilic reagents very common. We were therefore led to the assumption that the acetylacetone anion could have reacted with the quinone in this way which would result in a product $C_{16}H_{16}O_6$ with the structure I.



As is always the case in nucleophilic substitutions an oxidizing agent must be present, in our case *p*-benzoquinone itself. In the present paper evidence shall be furnished for the correctness of this assumption.

Being a quinone $C_{16}H_{16}O_6$ was easily reduced by the action of catalytically activated hydrogen. Though always consuming about one mole of hydrogen the reaction took different courses in different solvents. In absolute ethyl ether a product $C_{16}H_{18}O_6$ (III) could be obtained, obviously the hydroquinone corresponding to I. III could easily be oxidized back to I if treated with *p*-benzoquinone in ethanol. When hydrogenated in absolute methanol, however, $C_{16}H_{16}O_6$ yielded a substance $C_{12}H_{14}O_4$ (II). II and III gave a positive iodoform reaction, could be acetylated to give the diacetates and reacted with 2,4-dinitrophenylhydrazine but yielded no defined hydrazones. The substances gave strong colour when dissolved in dilute alkali, II gave a deep red and III a violet colour both of which became brown when the solutions were kept for a while. On distilling the methanol from the hydrogenation mixture a small quantity of acetaldehyde could be found in the distillate, probably arising from the acetyl groups split off during the hydrogenation. On the other hand II when boiled with 2 *N* hydrochloric acid yielded acetone, other fragments of the molecule could not be isolated. Boiled with undiluted acetyl chloride II



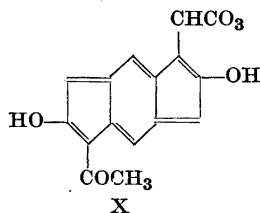
split off two molecules of water giving a compound $C_{12}H_{10}O_2$ from which no simple functional derivatives could be prepared. The substance was very stable, *e.g.* distilling unchanged at ordinary pressure. It is assumed to result from a ring closure with elimination of water from the tautomeric form of II, hence the formula IV is ascribed to it. A similar dehydration and ring closure could be effected with III by the action of cold concentrated sulphuric acid. The resulting product had the composition $C_{16}H_{14}O_4$ (V) and gave a *bis*-2,4-dinitrophenylhydrazone. The iodoform reaction, however, was doubtful and attempts to oxidize $C_{16}H_{14}O_4$ to its corresponding dibasic acid were not successful.

We have previously reported ² that acetylacetone and *p*-benzoquinone react in presence of anhydrous zinc chloride to give a mixture of two substances. One of these substances was soluble in alkali and identified as 2-methyl-3-acetyl-5-hydroxybenzofuran. The other substance has now been found to be identical with $C_{16}H_{14}O_4$ (V).

In order to connect IV and V with a known substance and with each other we repeated Pechmann's ³ and Ikuta's ⁴ synthesis consisting in the condensation of ethyl acetoacetate with quinone in presence of anhydrous zinc chloride. One of the products of this condensation is the benzodifuran derivative VIII which has the same ring skeleton as our compounds IV and V. The corresponding potassium salt VI was prepared by treating VIII with alcoholic potassium hydroxide. This salt was easily decarboxylated to give a compound $C_{12}H_{10}O_2$ identical with IV.

Further the diketone $C_{16}H_{14}O_4$ (V) reacted easily with methyl magnesium iodide to give the corresponding tertiary alcohol $C_{18}H_{22}O_4$ (VII). By heating to 100° *in vacuo* this alcohol as expected lost two moles of water, the product having the composition $C_{18}H_{18}O_2$ and to which we ascribed the structure IX. The same compound could be prepared by reacting Pechmann's ester VIII with an excess of methyl magnesium iodide in xylene. We were not able to isolate the intermediate tertiary alcohol in this case.

Ionescu ⁵ who also studied the reaction between acetylacetone and *p*-benzoquinone isolated a substance $C_{16}H_{12}O_4$ to which he assigned the structure X. This substance should according to Ionescu result from a ring closure of I thus breaking the C = O double bond of the quinone. He did not, however, isolate I but assumed it to be an intermediate in the reaction. We have not so far been able to effect a ring closure with elimination of water from I leading to X.



EXPERIMENTAL

(Melting points not corrected)

ω,ω',ω'-Tetraacetyl-*p*-xyloquinone (I)

To a solution of *p*-benzoquinone (2 g) in very pure acetylacetone (20 ml) was added dry pyridine (about 20 drops). The reaction mixture was left for 4 hours, the separated red product was filtered off and washed with cold ethanol. Yield *ca.* 0.25 g. If the size of the

batches was increased the yield invariably was relatively lower. Recrystallized from ethanol the substance had m.p. 212–213° dec.

$C_{16}H_{16}O_6$	Calc.	C 63.16	H 5.29
	Found	» 63.15	» 5.30

Hydrogenation of I in ethyl ether

I (1.0 g) was suspended in dry ethyl ether (100 ml) to which platinum oxide (0.1 g) was added. Due to the variations in vapour pressure of the ether with the differences in temperature the amount of hydrogen used was difficult to determine but is estimated to 300 ml (1 200 mm Hg) in 8 hours; calc. for one mole of hydrogen 263 ml. The hydrogenation vessel was filled with nitrogen and the platinum oxide filtered off under flushing with nitrogen. The ether was removed in a vacuum desiccator with concentrated sulphuric acid. The solid white residue (0.88 g) was recrystallized twice from acetone-water and had m.p. 199°. It consisted of fine, colourless needles and gave a strong violet colour with aqueous ferric chloride.

$C_{16}H_{16}O_6$	Calc.	C 62.73	H 5.93
	Found	» 62.70	» 6.10

Reoxidation to I: $C_{16}H_{16}O_6$ (0.2 g) was dissolved in ethanol and boiled for a few minutes with an excess of *p*-benzoquinone. The reaction mixture was evaporated to dryness. The red residue was washed with ethanol and recrystallized from the same solvent, m.p. 210°, mixed m.p. with I showed no depression.

$C_{16}H_{16}O_6$	Calc.	C 63.16	H 5.29
	Found	» 62.87	» 5.51

Acetylation: $C_{16}H_{16}O_6$ (0.1 g) was dissolved in acetyl chloride (10 ml) and refluxed for 45 minutes. The reaction mixture was poured into cold water the separated solid substance being filtered off and recrystallized twice from methanol. Small plates of m.p. 220–221°.

$C_{20}H_{20}O_6$	Calc.	C 61.53	H 5.69
	Found	» 61.50	» 5.92

Hydrogenation of I in methanol

A suspension of I (5.0 g) in dry methanol (100 ml) to which platinum oxide (0.5 g) had been added took up 337 ml hydrogen (1 200 mm Hg) in 35 minutes; calc. for one mole of hydrogen 263 ml. After filtering the methanol was evaporated *in vacuo* above calcium chloride. The residue which consisted of a yellow oil and a white crystalline substance weighed 4.35 g. The oil was removed by washing with ethyl acetate and the solid substance (2.2 g) was recrystallized from dilute ethanol and sublimated *in vacuo*. M.p. 193–195°.

$C_{13}H_{14}O_4$	Calc.	C 64.80	H 6.35
	Found	» 64.49	» 6.48

Methoxyl content nil.

In an experiment similar to that above the methanol was distilled off through a Vigreux column. The residue consisted chiefly of $C_{13}H_{14}O_4$. To a part of the distillate was added a solution of 2,4-dinitrophenylhydrazine in dilute hydrochloric acid. Immediately a hydrazone separated which after recrystallization from glacial acetic acid had m.p. 165°.

$C_9H_9N_4O_4$	Calc.	C 42.86	H 3.58	N 25.02
	Found	» 43.22	» 3.69	» 25.80

Mixed melting point with the 2,4-dinitrophenylhydrazone of acetaldehyde showed no depression.

Acetylation: To a solution of acetyl chloride in toluene (10 ml *ca.* 1.5 molar) was added dry pyridine (2 ml) and $C_{16}H_{16}O_6$ (0.18 g). The mixture was heated on a water bath for 20 minutes and the excess of acetyl chloride was removed by shaking with water. The toluene layer was dried with calcium chloride and evaporated to dryness. The residue (0.20 g) was recrystallized from dilute alcohol and had m.p. 126°.

$C_{16}H_{16}O_6$	Calc.	C 62.73	H 5.93
	Found	» 62.65	» 5.92

Treatment with HCl: $C_{12}H_{14}O_4$ (0.1 g) was heated with a solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid on a water bath for 30 minutes. A light yellow substance had separated which after recrystallization from alcohol had m.p. 126°.

$C_9H_{10}N_4O_4$	Calc.	N	23.53
	Found	»	23.59

Mixed melting point with 2,4-dinitrophenylhydrazone of acetone showed no depression.

Ring closure of the hydrogenated product II

II (1.2 g) was dissolved in acetyl chloride (28 ml) and refluxed for one hour. After cooling to room temperature the reaction mixture was poured on ice and the separated product recrystallized twice from dilute methanol. M.p. 112–113°.

$C_{12}H_{10}O_2$	Calc.	C	77.38	H	5.43	M	186.2
	Found	»	77.50	»	5.33	»	182

Ring closure of the hydrogenated product III

III (0.24 g) was dissolved in cold concentrated sulphuric acid (30 ml) and the solution after a few minutes poured into cold water. The white amorphous precipitate (0.18 g) was recrystallized twice from alcohol. M.p. 247–248°.

$C_{14}H_{14}O_4$	Calc.	C	71.08	H	5.23
	Found	»	70.82	»	5.23

Dinitrophenylhydrazone: The derivative was prepared in the usual way by heating the carbonyl compound with 2,4-dinitrophenylhydrazine dissolved in 2 *N* hydrochloric acid. Recrystallized from nitrobenzene it had m.p. 250° (dec.)

$C_{28}H_{22}N_8O_{10}$	Calc.	C	53.45	H	3.49	N	17.78
	Found	»	54.09	»	3.61	»	17.24

Acetylacetone and *p*-benzoquinone in presence of anhydrous zinc chloride

The reaction was carried out as described by Bernatek². The alkali-insoluble part of the reaction mixture was recrystallized twice from glacial acetic acid. M.p. 248°. Mixed melting point with $C_{12}H_{14}O_4$ from the above experiment showed no depression.

Ethylacetoacetate and *p*-benzoquinone in presence of anhydrous zinc chloride

The reaction was carried out as described by v. Pechmann³ and Ikuta⁴. The slightly soluble benzodifuran derivative (VIII) was isolated from the reaction mixture and treated with dilute aqueous sodium hydroxide in order to remove any hydroxybenzofuran. The reaction product which was a diester was hydrolysed by refluxing for two hours with alcoholic potassium hydroxide (10 %), the separated potassium salt being collected and dried.

Decarboxylation: The dry potassium salt was heated in a wide test tube over a luminous flame. The decomposition took readily place and a substance distilled off, condensed and crystallized in the upper part of the test tube. Recrystallized from dilute methanol and treated with charcoal this substance had m.p. 113°.

$C_{12}H_{10}O_2$	Calc.	C	77.38	H	5.43
	Found	»	77.29	»	5.43

Mixed melting point with $C_{12}H_{10}O_2$ (obtained from the ring closure of II) showed no depression.

The methyl ketone V and methyl magnesium iodide

To a solution of methyl magnesium iodide (from 0.2 g of magnesium) in dry ether was added the methyl ketone (1.1 g). After the vigorous reaction had subsided the reaction mixture was refluxed for 15 minutes and decomposed by ice and dilute hydrochloric acid. The ethereal layer was dried and evaporated the residue weighing 1.0 g. Recrystallized several times from dilute methanol, treated with charcoal and finally recrystallized twice from carbon tetrachloride it had m.p. 138–139° (dec.)

$C_{18}H_{22}O_4$	Calc.	C	71.48	H	7.28
	Found	»	71.17	»	7.27

The tertiary alcohol VII thus formed was sublimated *in vacuo* at 100° (bath temperature). It evidently split off water and the sublimated product had m.p. 110–111°. Mixed melting point with the reaction product from the next experiment showed no depression.

v. Pechmanns ester and methyl magnesium iodide

To a solution of methyl magnesium iodide (from 0.2 g of magnesium) in dry ether (10 ml) was added a suspension of the ester (0.6 g) in dry toluene (10 ml). The mixture was refluxed for 30 minutes and decomposed and worked up as usual. The reaction product was sublimated *in vacuo* and recrystallized several times from acetone-water. M.p. 112°.

$C_{18}H_{18}O_2$	Calc.	C	81.20	H	6.76
	Found	»	81.02	»	6.89

SUMMARY

$\omega, \omega, \omega', \omega'$ -Tetraacetyl-*p*-xyloquinone has been found to result from a base-catalyzed reaction between acetylacetone and *p*-benzoquinone. Dependent upon the working conditions the quinone could be hydrogenated with or without loss of acetyl groups. The corresponding hydroquinones easily lost two molecules of water obviously undergoing a ring closure thus being transformed into benzodifuran derivatives. These benzodifuranes have been connected with substances of known structure.

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