626. *Hydrogen Transfer. Part XIV.*[1] *The Quinone Cyclodehydrogenation of Acids and Alcohols.*

By A. M. Creighton and L. M. Jackman.

The formation of γ- and δ-lactones from suitably substituted carboxylic acids by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone is described. In one example a side reaction leading to a coupled product has been observed. Evidence has been obtained which shows that neighbouring carboxyl groups can provide driving force for the abstraction of hydride ions by quinones.

The formation of cyclic ethers during the reaction of appropriately substituted alcohols with dichlorodicyanobenzoquinone has been observed and the nature of several competing reactions has been established.

Dehydrogenation by quinones has some of the features of a unimolecular β-elimination (E_1) process.[2,3] In previous studies the structures of the substrates have ensured that elimination was the sole reaction. Even so, in the attempted dehydrogenation of 2,2-dimethylindane, a substitution product was encountered.[2] Thus it is to be expected that with certain structures substitution might occur. Such reactions would be analogous to unimolecular nucleophilic substitution (S_N1) in the same way as the dehydrogenation is to the (E_1) process. In particular, it should be possible to effect internal substitution (S_Ni) which could be regarded as a cyclodehydrogenation. Many cyclisations involving conventional leaving groups (halogens, OH_2^+, etc.) are known and amongst the most active and common participating groups are carboxyl, hydroxyl, and amino. The available quinones [2] of high potential likely to prove effective for cyclodehydrogenation all contain fairly labile chlorine and compounds containing amino-groups were avoided in the preliminary study. The initial experiments reported below therefore involved carboxyl and hydroxyl groups and result in the formation of lactones and cyclic ethers respectively.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone [4] was used in the dehydrogenation experiments described below.

8-Diphenylmethyl-1-naphthoic acid reacted slowly with the quinone in benzene at 80°; the reaction required five days for completion, being retarded by the low solubility of the acid in benzene. The product, isolated in 85% yield, was the δ-lactone (I). *o*-Diphenylmethylbenzoic acid was converted in 80% yield into the γ-lactone, 3,3-diphenyl phthalide; the reaction required *ca.* 24 hr. at 80° for completion; after 3 hr. the yield was 35%.

2-Benzylbenzoic acid reacted more slowly, requiring 7 days at 80° for completion. Under these conditions the theoretical quantity of quinol was obtained, but the yield of

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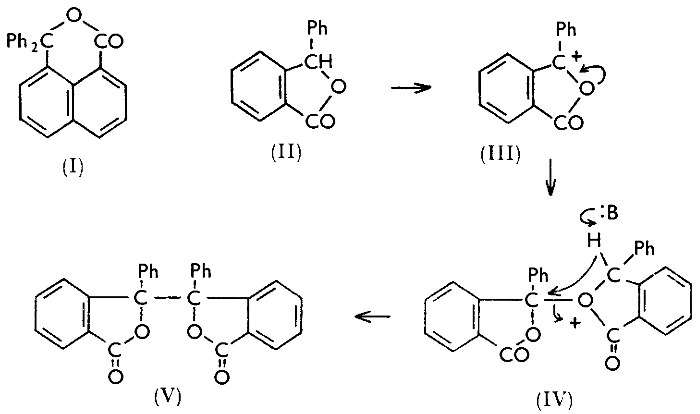
[1] Part XIII, preceding paper.

[2] Barnard and Jackman, *J.*, 3110.

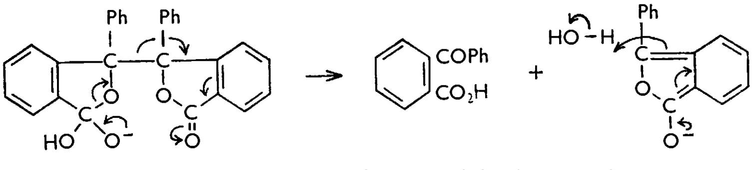
[3] Braude, Jackman, Linstead, and Lowe, *J.*, 3123.

[4] Thiele and Meisenheimer, *Ber.*, 1900, **33**, 675; Allen and Wilson, *J. Amer. Chem. Soc.*, 1941, **63**, 1756; Brook, *J.*, 1952, 5040.

3-phenylphthalide (II) was only 45%. From the other products of this reaction there were isolated two substances whose intense absorption at 1775 cm.$^{-1}$ was characteristic of 3,3-disubstituted phthalides. This fact, together with the high melting points, suggested that the compounds might be the DL- and *meso*-forms of the biphthalidyls (V). A compound, m. p. 265°, purported to have this structure has been recorded.[5] We have repeated one of these reported syntheses, namely, the reductive coupling of 3-phenylphthalide by aluminium powder in concentrated sulphuric acid.[10] In our hands the reaction gave two products, in roughly equal amounts, with infrared spectra identical respectively with those of the two compounds from the dehydrogenation. Melting points were similar but not characteristic. Both compounds were quantitatively degraded by alkali to equimolecular amounts of 3-phenylphthalide and *o*-benzoylbenzoic acid; this reaction was described by Ullmann [5] and probably involves the mechanism shown in the annexed scheme.



(I) (II) (III) (IV) (V)



The formation of the bi-lactones during the cyclodehydrogenation was shown to involve subsequent attack of the phthalide, as the same compound was formed when the phthalide was treated directly with the quinone. It is to be expected that the phthalide would be more susceptible to hydride-ion abstraction than the parent acid, as in the former the α-carbon atom is activated by the $+T$ effect of the oxygen substituent and, being part of a five-membered ring, will more readily lead to an sp^2-configuration coplanar with the aromatic nucleus.[3] Even so, the reaction of phthalide is slow and it is unlikely that a radical-dimerisation mechanism could operate in the formation of the coupled product. The most likely mechanism for the formation of compound (V) appears to involve a Stevens-type rearrangement of the oxonium salt (IV) formed from the carbonium ion (III) and a molecule of phthalide. In the Stevens rearrangement of ammonium, sulphonium, and phosphonium salts much of the driving force is derived from the attacking base.[6] An oxonium salt is inherently less stable and it is conceivable that the rearrangement of compound (IV) is promoted by much weaker bases such as the quinol anion or even another molecule of phthalide. The migration terminus in (IV) is also suitably activated by the *o*-carbonyl group.

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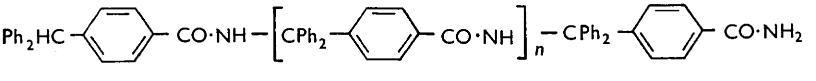
[5] Ullmann, *Annalen*, 1896, **291**, 17; Meyer, *Monatsh.*, 1904, **25**, 1177; Bauer and Endres, *J. prakt. Chem.*, 1913, **87**, 545; Eckert and Pollak, *Monatsh.*, 1917, **38**, 11.

[6] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1957, p. 524; Hine, " Physical Organic Chemistry," McGraw-Hill, New York, 1956, p. 116.

o-Toluic acid reacted very slowly with the quinone, but no identifiable product could be isolated.

When *o*- and *p*-diphenylmethylbenzoic acid were allowed to compete for an insufficiency of the quinone, the two isomers reacted at similar rates. However, it seemed likely that, in the absence of participation by the *o*-carboxyl group, the *o*-substituted acid would react much more slowly than the *para*-isomer, for models indicated that the *ortho*-substituent inhibited the formation of the near-co-planar triphenylmethyl ion. In conformity with this, the *o*-amide did not react with quinone at 80° while the *p*-amide reacted completely in 40 hours to give, apparently, the polyamide (VI) [with concentrated sulphuric acid at 40° this underwent N-alkyl fission to *p*-(α-hydroxydiphenylmethyl)benzamide]. The relative reactivities of the two acids and their amides towards the quinone make it clear that, in the absence of driving force from the neighbouring group, an *ortho*-derivative is less reactive than its *para*-isomer.



(VI)

From the point of view of participation amido- and carboxy-groups are bifunctional. The electron-source may be either the carbonyl-oxygen atom on the one hand or the hydroxyl-oxygen atom or the nitrogen atom on the other. Scott, Glick and Winstein[7] established that carbonyl participation is stronger with amides, at least for substituted amides; this requires that the formation of phthalides occurs by participation of hydroxyl rather than of carbonyl groups, since if the latter were involved the *o*-amide should have cyclised. On this basis a qualitative order of participation may be put forward, *viz.*; acid hydroxyl oxygen $>$ amide carbonyl oxygen $>$ acid carbonyl oxygen, and acid hydroxyl oxygen $>$ amide nitrogen. The second inequality doubtless arises because nitrogen has but one lone pair which is strongly involved in amide resonance whereas with the hydroxyl oxygen only one of its two lone pairs is delocalised, leaving the other free for participation. The present conclusions should not be accepted as general, for it may be that in the fairly rigid systems under investigation the directive properties of the orbitals involved are of importance.

Two examples of cyclic ether formation have been examined. Cyclodehydrogenation of *o*-diphenylmethyltriphenylmethanol (VII) gave, not the expected 1,1,3,3-tetraphenylphthalan (VIII), but 9,10-dihydro-9,9,10-triphenylanthranol (IX), in 70% yield. This can be interpreted as an acid-catalysed rearrangement of the tetraphenylphthalan. The catalyst could well be the quinol, which is quite a strong acid, or possibly traces of hydrogen chloride derived from the quinone. Unfortuntely this reaction does not provide an unambiguous example of hydroxyl participation as the product could also have arisen by cyclodehydration of the alcohol (VII) followed by conversion into the hydroquinolyl ether of (IX) and subsequent hydrolysis during the working up.

An authentic example of hydroxyl participation was provided by the reaction of 2-diphenylmethylbenzyl alcohol with the quinone. The reaction is complex, as both substituents can undergo hydride-ion abstraction and, in addition, one of the primary products may undergo further oxidation. Initial attack of the quinone occurred principally at the triaryl-substituted carbon atom, but a small quantity of *o*-diphenylmethylbenzaldehyde was also formed. The aldehyde was rather difficult to elute from alumina and the fractions containing it smelt strongly of hydrogen cyanide. It is concluded that the aldehyde was present in the crude mixture as its cyanohydrin. Hydrogen cyanide is a hydrolysis product of the quinone. The bulk of the product consisted of a mixture of two compounds and was shown to be 1,1-diphenylphthalan (20%) and a compound considered to have structure (XI) or (XII). For this second component analyses

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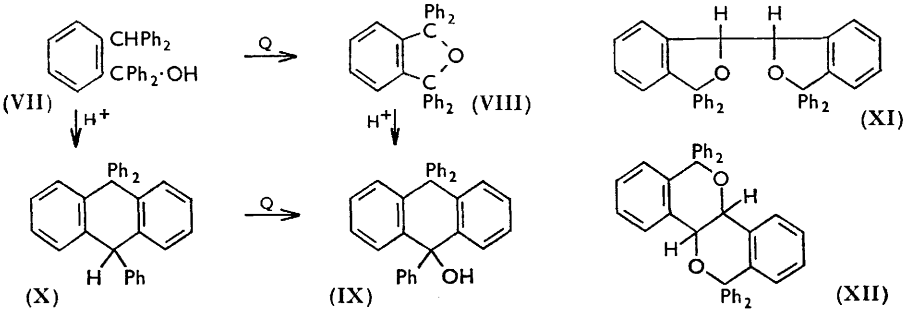
[7] Scott, Glick, and Winstein, *Experientia*, 1957, **13**, 183.

and a molecular-weight determination indicated the bimolecular composition, the ultra-violet spectrum showed only benzenoid absorption, the infrared spectrum was consistent



with that of an ether, and the compound did not react with 2,4-dinitrophenylhydrazine. A biphthalanyl (XI) would be analogous to the biphthalidyl formed from *o*-benzylbenzoic acid (see above). In the presence of acid catalysts the biphthalanyl could have rearranged to the dioxachrysene (XII), and the present evidence is insufficient to distinguish between the two structures.

The ability of oxygen functions to participate and, in the case of the acids at least, to provide a driving force in the reaction with quinones is further evidence of an ionic mechanism. The analogous free-radical mechanism is not expected to support lone-pair participation as the resulting intermediate would necessarily have the unpaired electron in an antibonding orbital.

EXPERIMENTAL

For general comments see Part XII.[3]

2,3-*Dichloro*-5,6-*dicyano*-1,4-*benzoquinone*.—(i) 2,3-Dicyanoquinol was prepared by a modification of the method of Thiele and Meisenheimer [4] suggested by Allen and Wilson.[4]

Concentrated sulphuric acid (25 ml.) in ethanol (100 ml.) was added to a stirred suspension of benzoquinone (20 g.) in ethanol (500 ml.). The temperature was adjusted to 24—28° and maintained in that range during the addition of potassium cyanide (40 g.) in water (100 ml.) during 30—40 min., until the reaction mixture was dark brown with a green fluorescence and was alkaline to litmus. The liquid was then just acidified and the precipitated potassium sulphate was removed by filtration. The filter cake was washed with hot ethanol (100 ml.), and the combined filtrate and washings were evaporated under reduced pressure to a small bulk (150 ml.) without excessive or prolonged heating. On cooling, the solution deposited crude 2,3-dicyanoquinol which recrystallised (charcoal) from water to give the pure compound (9·4 g., 63% based on 2 mol. of quinone). The average yield for a number of batches (20—50 g. of quinone) was 64%.

(ii) *Oxidation and hydrochlorination of* 2,3-*dicyanoquinol*. Liquid oxides of nitrogen (mainly N_2O_4) have been used for the oxidation of cyanoquinols (Brook [4]), and this method is incorporated in the present procedure.

To 2,3-dicyanoquinol (10 g.), suspended in carbon tetrachloride (125 ml.), liquid oxides of nitrogen (3 ml.) were added and the mixture was stirred for 10 min. A rapid stream of dry hydrogen chloride was passed in for 1 hr. A further 3 ml. of the nitrogen oxides were added and the mixture was stirred for 10 min. Further treatment with hydrogen chloride followed by nitrogen oxides afforded crude 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. Crystallisation from benzene–light petroleum (b. p. 60—80°) gave the quinone as bright red crystals containing benzene of crystallisation. The solvent was lost on drying in a vacuum-desiccator, and the quinone was obtained as a bright yellow powder (5·9 g., 42%), m. p. 201—203°. With larger batches it was necessary to cool the reaction mixture during the oxidation.

Cyclodehydrogenation of 8-*Diphenylmethyl*-1-*naphthoic Acid*.—The acid [8] (1·49 g.), dichlorodicyanobenzoquinone (1·0 g.), and benzene (4 ml.) were heated in a sealed tube at 80° for 5 days. The mixture was periodically shaken. The acid gradually dissolved, being replaced by quinol.

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[8] Bachmann and Chu, *J. Amer. Chem. Soc.*, 1936, **58**, 1118.

When the reaction was complete the contents of the tube were extracted with 50 ml. of hot benzene. The insoluble quinol (0·95 g.) was collected and the solution chromatographed over alumina. Evaporation of the benzene eluate and crystallisation of the residue from ethanol yielded 8-(α-hydroxydiphenylmethyl)-1-naphthoic acid δ-lactone (1·26 g., 85%), m. p. 107—108°, undepressed on admixture with an authentic specimen prepared by oxidation of the acid with chromic acid.[9]

Cyclodehydrogenation of 2-*Diphenylmethylbenzoic Acid.*—*o*-Diphenylmethylbenzoic acid [10] (1·00 g.), dichlorodicyanobenzoquinone (1·08 g.), and benzene (10 ml.) were heated in a sealed tube at 80° for 24 hr. Working up as in the previous experiment yielded the quinol (0·92 g.) and 3,3-diphenylphthalide (0·79 g., 80%), m. p. 115—116°, undepressed on admixture with a sample prepared by Brisson's method.[11]

In a similar experiment in which the reaction time was reduced to 3 hr., the amounts of quinol (0·53 g.) and lactone (0·35 g.) recovered indicated incomplete reaction.

Cyclodehydrogenation of 2-*Benzylbenzoic Acid.*—This acid (1·00 g.), dichlorodicyanobenzoquinone (1·47 g.), and benzene (8 ml.), heated in a sealed tube at 80° for 7 days, afforded the quinol (1·40 g.) and 3-phenylphthalide (0·43, 45%), m. p. 115°, undepressed on admixture with a sample prepared from 2-benzoylbenzoic acid by zinc dust in acetic acid.[12] During the chromatography a number of yellow bands appeared which were not eluted by benzene. Elution of these with benzene–ethanol (10 : 1) and crystallisation from benzene gave material, m. p. 265—275°, $\nu_{max.}$ 1775s cm.$^{-1}$ (γ-lactone).

Similar reaction for 70 hr. yielded quinol (1·07 g.) and 2-phenylphthalide (0·15 g.).

Reaction of 3-*Phenylphthalide and Dichlorodicyanobenzoquinone.*—3-Phenylphthalide (1·00 g.), dichlorodicyanobenzoquinone (1·46 g.), and benzene (8 ml.) were heated in a sealed tube at 80° for 138 hr. The solvent was removed and the residue refluxed with xylene (100 ml.) for 1 hr. The solution was filtered and the filtrate evaporated to dryness. The residue, after extraction with cold benzene (2 × 10 ml.) to remove unchanged reactants, had m. p. 260—275° and an infrared spectrum similar to the corresponding product obtained in the previous experiment. This substance (190 mg.) was recrystallised three times from acetic acid, to give transparent rhombs (80 mg.), m. p. 280—284°, which had an infrared spectrum (in Nujol) identical with compound A described in the next experiment. Concentration of the mother-liquors gave white crystals which after several crystallisations from toluene afforded opaque rhombs (70 mg.), m. p. 277—281°, which had an infrared spectrum (in Nujol) identical with that of compound B described in the next experiment.

DL- *and* meso-3,3′-*Diphenylbi*-3-*phthalidyl.*—Aluminium powder (1·0 g.) was added to *o*-benzoylbenzoic acid (5 g.) dissolved in concentrated sulphuric acid (100 ml.). The mixture was stirred for 10 min. at 20° and then warmed to 35°. When an exothermic reaction began (20 min.) the mixture was poured on ice. The solid was removed, the filter cake being extracted with boiling xylene (2 × 200 ml.). On cooling, the xylene solution deposited crystals (2·0 g.) (compound A). The mother-liquor was reduced to a small volume (40 ml.) and, on cooling, a second crop (1·8 g.) (compound B) was obtained.

Compound A (a *biphthalidyl*) recrystallised from acetic acid as transparent rhombs [Found: C, 80·0; H, 4·3%; *M* (ebullioscopic in PhCl), 412. $C_{28}H_{18}O_4$ requires C, 80·5; H, 4·3%; *M*, 418], $\nu_{max.}$ (in Nujol) 1775, 760, 732, 711, and 690 cm.$^{-1}$. The infrared spectrum was unaltered by further crystallisation from acetic acid or xylene. From toluene the compound separated as transparent plates which lost their crystalline form on drying. The dried substance had the same infrared spectrum as the material from acetic acid. It was difficult to obtain consistent m. p.s for this compound. At or near the m. p. the compound is sensitive to alkali and even in Pyrex melting-point tubes there was evidence of decomposition. The best m. p. obtained was 180—184° and the m. p. retaken on the same specimen was 170—180°.

Compound B (a *biphthalidyl*) recrystallised from acetic acid or toluene with a constant infrared spectrum (in Nujol) ($\nu_{max.}$ 1775, 973, 755, 739, 714, 696, and 690 cm.$^{-1}$) [Found: C, 80·2; H, 4·7%; *M* (as above), 425]. This compound showed the same melting behaviour as compound A and there was a small depression (*ca.* 4°) for a mixture of the two.

Alkaline Cleavage of the 3,3′-*Diphenylbi*-3-*phthalidyls.*—The biphthalidyl A (612 mg.) was

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[9] Zsuffa, *Ber.*, 1910, **43**, 2915.

[10] Brown and Jackman, following paper.

[11] Brisson, *Ann. Chim.*, 1952, **7**, 311.

[12] Barnett, Cook, and Nixon, *J.*, 1927, 504.

refluxed with ethanolic sodium ethoxide (110 mg. of sodium in 10 ml. of ethanol) for 4 hr. Dissolution was complete in ½ hr. The ethanol was removed under reduced pressure and the residue taken up in water (30 ml.). Concentrated hydrochloric acid (2 ml.) was added, an oil separating. Sodium carbonate (800 mg.) was added, causing the oil to solidify. The solid was taken up in ether (20 ml.), and the mixture shaken. The ether was then allowed to evaporate and the crystalline solid which separated was removed. This solid (296 mg., 96%) was 3-phenylphthalide, m. p. 113—114°, mixed m. p. 113—115°.

The aqueous filtrate was acidified to Congo Red and continuously extracted with ether for 24 hr. The ether was removed, benzene (20 ml.) added, and the solution evaporated to dryness. The residue (330 mg., 100%) was *o*-benzoylbenzoic acid, m. p. 123—128°, mixed m. p. 125—128°.

A similar result was obtained with compound B.

Reaction of o-*Toluic Acid with Dichlorodicyanobenzoquinone*.—*o*-Toluic acid (0·52 g.), the quinone (1·00 g.), and benzene (8·0 ml.) were heated in a sealed tube at 80° for 48 days. Tar gradually separated but there was no evidence of the formation of the quinol. Working up in the usual way afforded only a trace of material which was readily eluted from alumina.

Relative Rates of Dehydrogenation of o- *and* p-*Diphenylmethylbenzoic Acid*.—Two parallel experiments were carried out in which *o*-diphenylmethylbenzoic acid alone, and with an equimolecular amount of the *para*-isomer, was treated with dichlorodicyanobenzoquinone at 80° for 24 hr. The lactones formed were isolated by chromatography over alumina and elution with benzene. The quantities of reagents and yields of products are given in the annexed Table.

	(i)	(ii)
Quinone (g.)	0·67	0·67
o-Diphenylmethylbenzoic acid (g.)	0·80	0·80
p-Diphenylmethylbenzoic acid (g.)	Nil	0·80
Benzene (ml.)	10	10
Yield of quinol (g.)	0·435	0·63
Yield of lactone (g.)	0·51	0·24

Attempted Reaction of o-*Diphenylmethylbenzamide with Dichlorodicyanobenzoquinone*.—The amide [14] (1·0 g.), the quinone (1·0 g.), and benzene (7 ml.) were heated at 80° in a sealed tube for 7 days. No quinol was precipitated and working up afforded unchanged amide (0·95 g.), m. p. and mixed m. p. 128—130°.

Reaction of p-*Diphenylmethylbenzamide with Dichlorodicyanobenzoquinone*.—The amide [13] (1·0 g.), the quinone (0·90 g.), and benzene (7 ml.) were heated at 80° in a sealed tube for 40 hr., a brown deposit (D) being formed. The liquid was decanted and chromatographed over alumina. The evaporated benzene eluate consisted of a white amorphous solid (A) (0·135 g.) which did not melt below 300°. The brown deposit (D) (1·20 g.) was dissolved in chloroform and shaken with sodium carbonate to remove the quinol. Removal of the chloroform afforded a yellow amorphous solid (0·600 g.) which was partially purified to a buff solid (B) by repeated precipitation by methanol from chloroform solution. This substance did not melt below 300°. The infrared spectra (in $CHCl_3$) of A and B were nearly identical over the range 3700—670 cm.$^{-1}$ and were characterised by bands at 3413 (NH) and 1678 cm.$^{-1}$ (amide C=O).

The solid B (100 mg.) was dissolved in concentrated sulphuric acid (2 ml.) at 40°. After 2 min. the solution was poured into water (50 ml.), and the precipitated solid was collected. Recrystallisation of it from aqueous methanol gave p-(α-*hydroxy-diphenylmethyl*)*benzamide* as prisms, m. p. 188° (Found: C, 79·0; H, 5·7; N, 4·7. $C_{20}H_{17}NO_2$ requires C, 79·2; H, 5·7; N, 4·6%), $\nu_{max.}$ 3497, 3395, and 1681 cm.$^{-1}$.

Reaction of p-*Diphenylmethyltriphenylmethanol with Dichlorodicyanobenzoquinone*.—The alcohol [14] (1·5 g.), the quinone (0·9 g.), and benzene (5 ml.) were heated at 80° in a sealed tube for 20 hr. The quinol (0·76 g.) was removed. Chromatography of the filtrate over alumina yielded a sticky solid. Crystallisation of the solid from benzene (4 ml.)-light petroleum (16 ml.; b. p. 60—80°) gave colourless crystals (1·05 g.), m. p. 196—198·5°. Further crystallisation from propan-1-ol gave pure 9,10-dihydro-9,9,10-triphenylanthranol, m. p. 203—204° (lit.[13] 204°) (Found: C, 90·65; H, 6·0. Calc. for $C_{32}H_{24}O$: C, 90·5; H, 5·7%).

Reaction of o-*Diphenylmethylbenzyl Alcohol with Dichlorodicyanobenzoquinone*.—The alcohol [10] (1·00 g.), the quinone (0·94 g.), and benzene (5 ml.) were heated at 80° in a sealed tube for 3 hr.

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[13] Jones and Root, *J. Amer. Chem. Soc.*, 1926, **48**, 181.

[14] Huller and Guyot, *Compt. rend.*, 1904, **139**, 9.

The quinol (0·77 g.) was removed and the filtrate chromatographed over alumina, with elution by benzene. The eluate was evaporated to a gummy solid (A) (0·853 g.). The column was then eluted with benzene–methanol (10 : 1) and evaporation of the eluate, which smelt strongly of hydrogen cyanide, gave a pale yellow solid (77 mg.). This solid, with Brady's reagent, gave a 2,4-dinitrophenylhydrazone; chromatography over bentonite–keiselguhr, and crystallisation from ethyl acetate–methanol, afforded o-*diphenylmethylbenzaldehyde* 2,4-*dinitrophenylhydrazone*, red needles, m. p. 202—203° (Found: C, 68·8; H, 4·6; N, 12·1. $C_{26}H_{20}O_4N_4$ requires C, 69·0; H, 4·5; N, 12·4%).

The solid (A) was dissolved in hot methanol (80 ml.). On cooling, the solution deposited colourless crystals (360 mg.), m. p. 144—152°. Crystallisation of this material from light petroleum gave opaque clusters of needles, m. p. 132—134°, and translucent rhombs, m. p. 148—152°. If the crystals were allowed to stand under the mother-liquors for several days the lower-melting form was completely transformed into the higher-melting substance. This behaviour was noted in all subsequent crystallisations from light petroleum. The form, m. p. 132—134°, was most readily produced by rapid cooling and the other by slow cooling. After four recrystallisations the high-melting form had m. p. 154—156° (Found: C, 88·2; H, 6·2%). Recrystallisation from ethanol afforded opaque crystals of an *ethanol solvate*, m. p. 132—133° (Found: C, 85·8; H, 6·1. $C_{40}H_{30}O_2,C_2H_6O$ requires C, 85·7; H, 6·2%). Both the ethanol solvate and the form of m. p. 154—156° lost solvent when heated under vacuum above their m. p.s and eventually sublimed to give the *product* (XI) or (XII), m. p. 63° [Found: C, 88·4; H, 6·0%; *M* (Rast), 521. $C_{40}H_{30}O_2$ requires C, 88·5; H, 5·6%; *M*, 542). Recrystallisation of the sublimate from ethanol or light petroleum regenerated the corresponding solvates.

The ethanol solvate (20 mg.) was refluxed for 3 hr. with 2,4-dinitrophenylhydrazine in aqueous-methanolic sulphuric acid. On cooling, the solution deposited unchanged solvate.

The methanol mother-liquors from the initial separation of material (A) were evaporated to dryness and the residue in cyclohexane was run through alumina. Elution with benzene–cyclohexane (1 : 4) afforded diphenylphthalan (200 mg.), m. p. 99—101°. Subsequent elution with benzene–cyclohexane (3 : 2) gave 29 mg. of pure compound (A).

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