964. *Organic Photochemistry. Part III.*[1] *The Effect of Light on some Diels–Alder Systems* *

By J. A. BARLTROP and B. HESP

Excitation of the $n \longrightarrow \pi^*$ transition of *p*-benzoquinone in the presence of butadiene, isoprene, and 2,3-dimethylbutadiene affords the spiro-pyrans (I) as main products; butadiene gives additionally the macrocyclic 2 : 1-adduct (V). Some properties of these systems are described and the mechanisms for their formation are discussed.

SEVERAL photochemical transformations of simple *p*-benzoquinones have been observed. The photodimerisation of *p*-benzoquinone and its simple alkyl derivatives has been shown to give cyclobutanes[2] or spiro-oxetans,[3] and recently photochemical additions of olefins[4] and diphenylacetylene[5] to a carbonyl group of *p*-benzoquinone have been reported. This Paper is concerned with the photochemical addition of simple conjugated olefins to *p*-benzoquinone.

The ultraviolet absorption spectrum of benzoquinone has been described elsewhere.[6] It is sufficient here to draw attention to the weak absorption of solutions of benzoquinone in cyclohexane in the regions 390—510 and 540 mμ. The former corresponds to a forbidden singlet $n \longrightarrow \pi^*$ transition typical of carbonyl compounds, whilst the latter is probably the corresponding $n \longrightarrow \pi^*$ triplet. Solutions of *p*-benzoquinone in 2,3-dimethylbuta-1,3-diene exhibit a broad band ($\lambda_{\text{max.}}$ 297 mμ) not found in the spectrum of either component in cyclohexane. We attribute this band to the presence of a charge-transfer complex.

Earlier work in our laboratory[7] showed that illumination of charge-transfer complexes frequently promotes chemical bonding between the component molecules of the complex and with this end in view we illuminated solutions of *p*-benzoquinone in various conjugated dienes. The formation of the thermal Diels–Alder adduct was inhibited by conducting the illumination at or below 0°.

In the first experiment a deoxygenated solution of *p*-benzoquinone in 2,3-dimethylbuta-1,3-diene was illuminated with light of wavelength greater than 300 mμ. Preparative vapour-phase chromatography (v.p.c.) of the product yielded crystals of a 1 : 1-adduct, to which is ascribed the spiro-pyran structure (Ia) on spectroscopic evidence. The nuclear magnetic resonance (n.m.r.) spectrum showed absorption at τ 3·10, 3·88 ($J = 10{\cdot}2$ c./sec.), 5·92, 7·90, and 8·32 with relative peak areas 4 : 2 : 2 : 6 assigned to the protons on positions

---

* Cf. J. A. Barltrop and B. Hesp, *Proc. Chem. Soc.*, 1964, 195.

[1] Part II, J. A. Barltrop and P. Schofield, *J.*, 1965, 4758.

[2] R. C. Cookson, D. A. Cox, and J. Hudec, *J.*, 1961, 4499; W. Flaig, J. C. Salfeld, and A. Llanos, *Angew. Chem.*, 1960, **72**, 110; D. Bryce-Smith and A. Gilbert, *J.*, 1964, 2428.

[3] R. C. Cookson, J. J. Frankel, and J. Hudec, *Chem. Comm.*, 1965, 16.

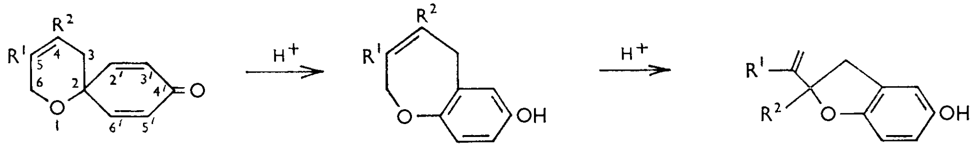
[4] D. Bryce-Smith and A. Gilbert, *Proc. Chem. Soc.*, 1964, 87.

[5] H. E. Zimmerman and L. Craft, *Tetrahedron Letters*, 1964, **31**, 2131; D. Bryce-Smith and A. Gilbert, *ibid.*, p. 2137.

[6] J. C. D. Brand and T. H. Goodwin, *Trans. Faraday Soc.*, 1957, **53**, 295; J. W. Sidman, *J. Amer. Chem. Soc.*, 1956, **78**, 2363; A. Kuboyama, *Bull. Chem. Soc. Japan*, 1962, **35**, 295; A. Julg, J. C. Bery, and M. Bonnet, *Tetrahedron*, 1964, **20**, 2237.

[7] R. Robson, P. W. Grubb, and J. A. Barltrop, *J.*, 1964, 2153.

(2′, 3′, 5′, 6′), 6, 3, and on the methyl groups, respectively. In addition, the ultraviolet (u.v.) spectrum of the adduct in cyclohexane showed strong absorption, $\lambda_{\text{max.}}$ 225 mμ (ε, 13,500), consistent with the presence of the dienone chromophore. The infrared (i.r.) spectrum of the adduct exhibited, *inter alia,* maxima at 1675, 1090, and 1075 cm.$^{-1}$, characteristic of dienone and allyl ether systems.



(Ia: $R^1 = R^2 =$ Me)
(Ib: $R^1 =$ H, $R^2 =$ Me)
(Ic: $R^1 =$ Me, $R^2 =$ H)
(Id: $R^1 = R^2 =$ H)

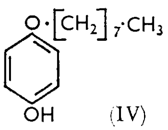
(IIa: $R^1 = R^2 =$ Me)
(IIb: $R^1 = R^2 =$ H)

(IIIa: $R^1 = R^2 =$ Me)
(IIIb: $R^1 = R^2 =$ H)

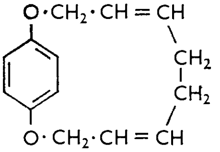
This experiment provided little evidence from which the mechanism of the reaction could be elucidated, since excitation occurred both of the quinone–diene charge-transfer complex and of the $n \longrightarrow \pi^*$ transition of the quinone. In order to define more precisely the electronic transition responsible for spiro-pyran formation, solutions of *p*-benzoquinone in 2,3-dimethylbuta-1,3-diene were illuminated with light of wavelength greater than 400 mμ. In these experiments only the $n \longrightarrow \pi^*$ transition of the quinone was directly excited and a cleaner product ensued, from which (Ia) was isolated after silica-gel chromatography in an overall yield of 33%.

Illumination of a deoxygenated solution of *p*-benzoquinone in isoprene under similar conditions produced a yellow oil, which could not be crystallised after extensive chromatography. The n.m.r., u.v., and i.r. spectra of the oil again confirmed the presence of the dienone and dihydropyran systems, and we conclude that the product was a mixture of the two possible spiro-pyrans (Ib) and (Ic).

Solutions of *p*-benzoquinone in liquid butadiene were also illuminated with light of wavelength longer than 400 mμ. Owing to technical difficulties the reaction mixture was not deoxygenated before irradiation. In addition to the spiro-pyran (Id), a second compound was isolated from the reaction mixture. This compound, a 2 : 1-adduct of butadiene and benzoquinone, exhibited neither carbonyl nor hydroxyl absorption in the infrared but showed strong absorption at 850 cm.$^{-1}$ characteristic of a *para*-substituted aromatic system. The n.m.r. spectrum showed four distinct regions of absorption of equal areas centred at τ 3·19 (sharp singlet), 4·92 (complex), 5·57 (doublet), and 7·99 (broad). Hydrogenation of the compound over Adams catalyst produced the known phenol (IV). We deduce that the adduct is the macrocyclic ether (V).



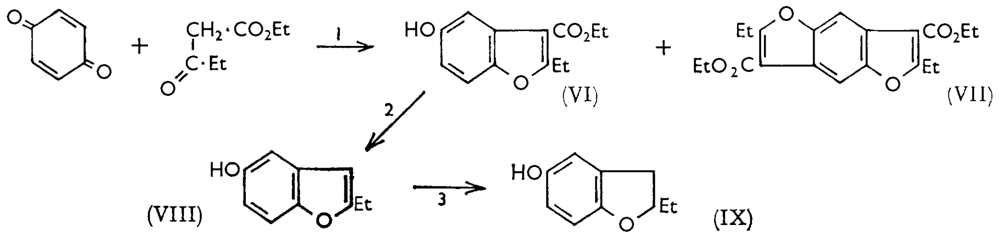
(IV)



(V)

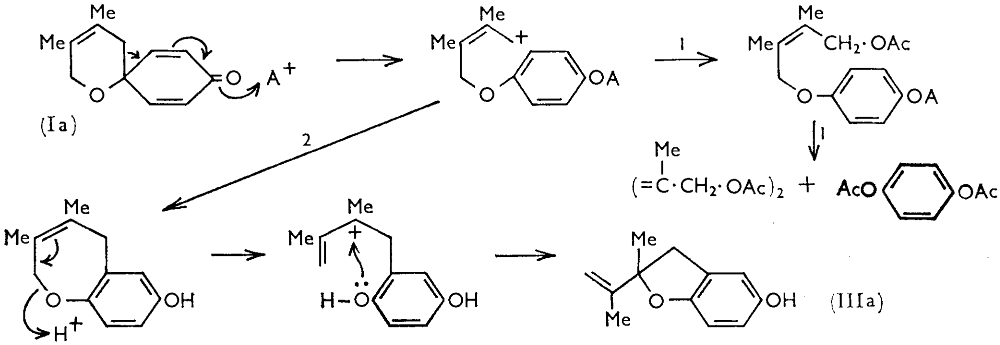
The geometry of the olefinic systems in the macrocycle is uncertain, but the infrared spectrum gave evidence of the presence of both *cis*- and *trans*-double bonds (ν, 708 and 960 cm.$^{-1}$, respectively). The vinyl proton absorption in the n.m.r. spectrum centred at τ 4·92 is too complex to be of diagnostic value.

Treatment of the spiro-pyran (Id) with perchloric acid in acetic acid at 100° resulted in a rapid increase in the absorption at 300 mμ in the spectrum of the mixture, together with the formation of the benzofuran derivative (IIIb). Rearrangement of the spiro-pyran at room temperature was accompanied by an increase in absorption at 280 mμ together with a slow increase at 300 mμ. After 24 hr. the 280-mμ absorption had completely decayed, with concurrent increase in absorption at 300 mμ. The initial 280-mμ absorption is probably due to the formation of the acid-labile intermediate (IIb). Catalytic reduction of the benzofuran (IIIb) gave 2-ethyl-2,3-dihydro-5-hydroxy-benzofuran (IX), identical in every respect with a sample synthesised as outlined.



Reagents: 1, $ZnCl_2$; 2, OH′, $-CO_2$; 3, H_2–Pd.

Treatment of the spiro-pyran (Ia) with hot perchloric–acetic acid resulted in extensive decomposition, but the dienone–phenol rearrangement occurred smoothly and rapidly at room temperature to give the benzofuran derivative (IIIa). With acetic anhydride containing boron trifluoride the pyran (Ia) rapidly produced quinol diacetate and 2,3-dimethylbut-2-enylenediacetate. This reaction did not proceed *via* the acetate of the benzofuran (IIIa), since a solution of the latter in acetic anhydride containing boron trifluoride did not generate quinol diacetate. It is known [8] that the products of dienone–phenol rearrangements are dependent upon the reaction medium.



(A^+ = Lewis acid; BF_3, Ac^+ or H^+).
Reagents: 1, BF_3–Ac_2O; 2, H^+–AcOH.

A possible mechanism accounting for the products derived from the spiro-pyran (Ia) is annexed.

Discussion

In these experiments, the photoadditions are a consequence of exclusive excitation of the $n \longrightarrow \pi^*$ transition of the benzoquinone. Since the $n \longrightarrow \pi^*$ absorption band of benzoquinone lies in the range 390—510 mμ, and the long-wave singlet transitions of butadiene and of its methylated derivatives lie near 220 mμ, there can be no question of transfer of singlet excitation from the quinone to the dienes. Equally, the triplet $n \longrightarrow \pi^*$ level of benzoquinone [9] lies at lower energies (50 kcal.) than the *cis*- and *trans*-triplet levels of butadiene [10] (53·5 and 59·6 kcal., respectively), so that energy transfer from benzoquinone to the dienes at the triplet level is also impossible unless triplet transfer to a low-lying phantom triplet [9] is invoked.

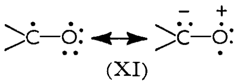
---

[8] See, *e.g.*, W. Metlesics, F. Wessely, and H. Budzikiewicz, *Tetrahedron*, 1959, **6**, 345; A. I. Scott, P. A. Dodson, F. McCapra, and M. B. Meyers, *J. Amer. Chem. Soc.*, 1963, **85**, 3702.

[9] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 1964, **86**, 3197.

[10] D. F. Evans, *J.*, 1960, 1735; G. S. Hammond and R. S. Liu, *J. Amer. Chem. Soc.*, 1963, **85**, 477.

In terms of valence-bond theory, the excited state resulting from the $n \longrightarrow \pi^*$ transition of a carbonyl group can be represented approximately as a resonance hybrid (XI), the lone non-bonding electron(s) conferring an intense chemical reactivity similar to that of free alkoxy-radicals.[11]



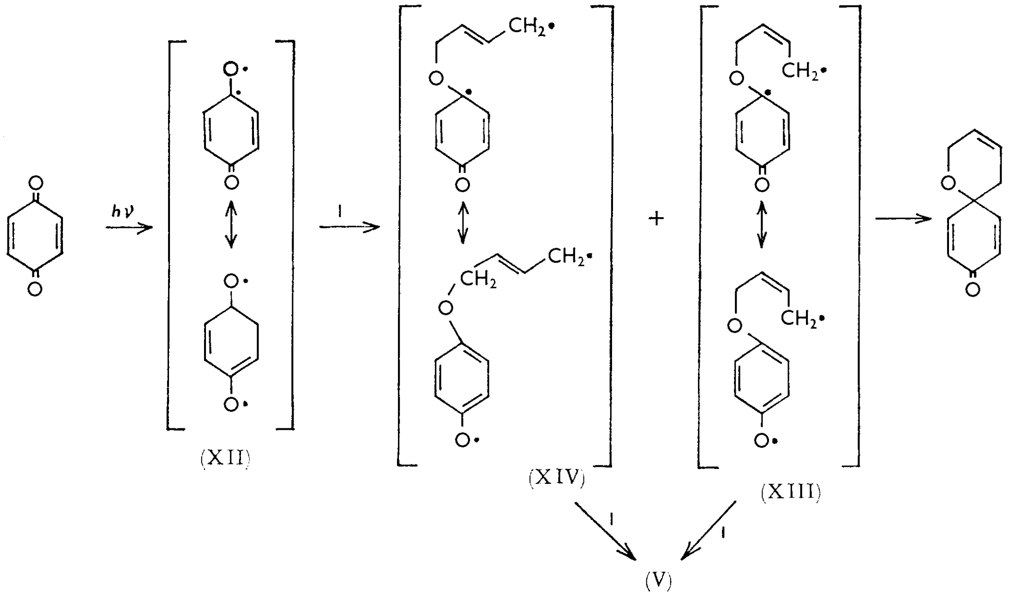
(XI)

For the excited state of benzoquinone, more extensive delocalisation is possible (XII), and this is reflected in the lower energy of the $n \longrightarrow \pi^*$ transition compared with that of saturated ketones.

The production of the photo-adducts may therefore be formulated as shown.

The 1,4-addition of radicals to butadiene gives a mixture of *cis*- and *trans*-adducts. It is tempting to suppose that the *cis*-adduct (XIII) collapses to the spiro-pyran and that it is the *trans*-adduct (XIV) which, since it cannot so stabilise itself, reacts with a further molecule of butadiene to give the macrocyclic ether (V). Such an argument would be valid only if the benzoquinone were reacting in its singlet state, since in this state spin inversion would not be required for collapse to the spiro-pyran, and formation of the latter from the *cis*-diradical (XIII) would be extremely rapid.

However, it is known [12] that intersystem crossing from the $n \longrightarrow \pi^*$ singlet states of ketones to the corresponding triplet states often occurs with high efficiency. If a similar process occurs with benzoquinone, then the diradical (XIII) will also be a triplet, and



Reagent: I, Buta-1,3-diene.

collapse to the spiro-pyran would be slow as a result of the spin conservation rule. The diradical (XIII) might then exist for long enough for it to react with a second molecule of butadiene to give the macrocycle (V). A knowledge of the geometry of the double bonds in the macrocycle might help to resolve this question, but this is, at present, uncertain.

A macrocycle may also be present in the product from the benzoquinone–2,3-dimethylbuta-1,3-diene illumination. The product from this reaction was considerably more complex, and consequently more difficult to resolve, than that from the illumination of

---

[11] P. de Mayo, *Adv. Org. Chem.*, 1960, **2**, 372.

[12] M. Kasha, *Radiation Res. Suppl.*, 1960, **2**, 243.

benzoquinone and butadiene, since the latter product was free from Diels–Alder adduct and from secondary products resulting from the illumination thereof.

EXPERIMENTAL

"Silica gel" refers to Whatman Chromedia, SG31. Petroleum refers to the fraction of b. p. 60—80° unless otherwise stated. Melting points were recorded on a Kofler hot-stage apparatus, and are corrected.

Irradiation Apparatus.—Irradiations were conducted with a 500-w Hanovia medium-pressure mercury lamp coaxial with a quartz annular vessel of 80 ml. surrounding a quartz annulus containing the filter solution. The filter solution, which also acted as coolant, was circulated through a heat exchanger consisting of an aluminium spiral immersed in an ethanol–carbon dioxide bath. Deoxygenation of the diene was achieved by a stream of nitrogen which then displaced air from the reactor. The diene was transferred by nitrogen pressure to a flask containing benzoquinone, and then likewise to the reactor.

Filter Solutions.—Filter A consisted of an 0·6-cm. layer of an aqueous solution containing potassium hydrogen phthalate (5 g./l.) and ethanediol (200 ml./l.). It transmitted less than 10^{-4}% of the light of wavelength <295 mμ and was transparent above 305 mμ.

Filter B was as above but contained, in addition, saturated sodium nitrite solution (250 ml./l.) and was stabilised by bringing to pH 11 with sodium hydroxide. The filter, transparent to wavelengths >410 mμ, transmitted less than 10^{-4}% of the light below 395 mμ, but slowly became more opaque during illumination.

Gas Chromatography.—For preparative work, the column was 5% polypropene adipate on Embacel (300 cm. × 9·5 mm.), operated at 140° and 10 lb./sq. in. The machine incorporated a bypass to a flame ionisation detector; an electrostatic precipitator and cold-trap were used to collect the material leaving the column.

Illumination of p-*Benzoquinone in* 2,3-*Dimethylbuta*-1,3-*diene.*—(*a*) *p*-Benzoquinone (1·2 g.) and 2,3-dimethylbuta-1,3-diene (75 ml.) were deoxygenated separately, mixed, and illuminated at 0° for 1·5 hr. with light transmitted by filter A. The decrease in quinone concentration, followed by the decrease in the intensity of the charge-transfer band at 300 mμ, was approximately 75%. After removal of the excess of diene by distillation, and of quinone by sublimation, the dark brown product was distilled to give a pale yellow oil (0·758 g.), b. p. 90—110° (bath)/0·1 mm. A sample separated by v.p.c. gave, after distillation, Δ^4-*dihydro*-4,5-*dimethylpyran*-2-*spirocyclohexa*-2′,5′-*dien*-4′-*one* (Ia) as pale yellow crystals, m. p. 43—44° (Found: C, 75·9; H, 7·6. $C_{12}H_{14}O_2$ requires C, 75·75; H, 7·4%); $\nu_{max.}$ (CS_2) 3050w, 1675s, 1090s, 1075s, 687s cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 225 mμ (ε 13,500).

(*b*) The illumination was conducted as above, but using light transmitted by filter B. Distillation gave a yellow oil (1·1 g.), b. p. 90—140° (bath)/0·1 mm. The oil, when dissolved in petroleum (10 ml.) and kept at 0° for 12 hr., deposited 4a,5,8,8a-tetrahydro-6,7-dimethyl-1,4-naphthaquinone (0·12 g.) as yellow crystals, m. p. 114—115° (lit.,[13] 116°). The filtrate was chromatographed on silica gel (200 ml.). Benzene–ether (9 : 1) eluted a fraction which on distillation gave the spiro-pyran (0·69 g., 33%) (Ia).

Illumination of p-*Benzoquinone in Isoprene.*—Illumination of *p*-benzoquinone (1·2 g.) in isoprene (75 ml.) using filter B, gave a pale yellow oil (1·03 g.), b. p. 100—130° (bath)/0·05 mm., which was essentially a mixture of Δ^4-*dihydromethylpyran*-2-*spirocyclohexa*-2′,5′-*dien*-4′-*one* (Ib) and its isomer (Ic), (Found: C, 75·05; H, 7·05. $C_{11}H_{12}O_2$ requires C, 74·95; H, 6·85%); $\nu_{max.}$ (CS_2) 3045w, 687m (–CH=CH-*cis*), 1680s (C=C–CO–C=C), 1118s, 1090s, 1080s cm.$^{-1}$; $\lambda_{max.}$ (ethanol) 223 mμ (ε 12,000). The n.m.r. spectrum of the oil in $CDCl_3$ showed absorption at τ 2·97 and 3·77 (AB quartet, J_{AB} 10·2 c./sec.), 4·40, 5·68 (complex), 7·87, and 8·24, with relative peak areas 2 : 2 : 1 : 2 : 2 : 3. Repeated chromatography on silica gel removed minor impurities from the product, but the oil could not be induced to crystallise.

Illumination of p-*Benzoquinone in Butadiene.*—Liquid butadiene (75 ml.) was added directly to *p*-benzoquinone (1·5g.) in the reactor and illuminated (filter B) for 1·5 hr. at −15°. The products from four illuminations were combined and distilled to give a yellow oil (2·75 g.), b. p. 70—120° (bath)/0·05 mm., which, on treatment with petroleum, yielded a brown oil and a yellow solution. The oil, on treatment with benzene, gave quinol (0·125 g.), m. p. and mixed m. p. 172—174°. The solution was chromatographed on silica gel (400 ml.).

[13] L. Tamayo and J. L. Leon, *J.*, 1948, 1499.

Benzene–ether (25 : 1) eluted brown crystals (0·176 g.) which after three recrystallisations from petroleum (b. p. 40—60°) yielded 1,8-(1,4-*phenylenedioxy*)*octa*-2,6-*diene* (V) as needles, m. p. 95—99° (Found: C, 78·25; H, 7·5. $C_{14}H_{16}O_2$ requires C, 77·75; H, 7·45%); parent peak in mass spectrum at *m*/*e* 216, $^{13}C/^{12}C$ isotope ratio 15·42 (Calc. for $C_{14}H_{16}O_2$: *m*/*e* 216, isotope ratio 15·46); $\nu_{max.}$ (KCl) 3065w, 3040w, 2938m, 2880m, 1504s, 1210s, 1188s, 1175s, 958s, 949s, 854s, 708s cm.$^{-1}$; $\lambda_{max.}$ (ethanol) 227 (ε 3680) and 279 mμ (ε 992).

Benzene–ether (9 : 1) eluted a second fraction which, after distillation, gave a pale yellow oil (1·6 g.), b. p. 90—110° (bath)/0·01 mm., which solidified. Three recrystallisations from petroleum gave Δ^4-*dihydropyran*-2-*spirocyclohexa*-2′,5′-*dien*-4′-*one* (Id) as needles, m. p. 50·5—52·5° (Found: C, 74·3, H, 6·25. $C_{10}H_{10}O_2$ requires C, 74·05; H, 6·2%); $\nu_{max.}$ (CS_2) 3035m, 2920m, 2885m, 2825m, 1676s (C=C–CO–C=C), 1087s, 1078m, 678w cm.$^{-1}$; $\lambda_{max.}$ (ethanol) 223 mμ (ε 11,700). The n.m.r. spectrum of (Id) in $CDCl_3$ showed absorption centred at τ 3·01 and 3·81 (AB quartet, J_{AB} = 10·2 c./sec.), 4·13 (singlet), 5·70 (complex), and 7·75 (complex), with relative peak areas 1 : 1 : 1 : 1 : 1.

Hydrogenation of the Macrocycle (V).—The compound (60 mg.) in ethanol (50 ml.) was hydrogenated at room temperature and atmospheric pressure using Adams catalyst. The product, a gum, was purified by preparative thin-layer chromatography on baked Kieselgel G. The eluent was benzene–ether (4 : 1). The plate showed one main band on exposure to iodine. Elution of this band, and two recrystallisations of the product from petroleum, gave *p*-hydroxyphenyl n-octyl ether (IV) (22 mg.), m. p. 60·5—61·5° (lit.,[14] 60—61°); $\nu_{max.}$ (CS_2) 3595s (–OH), 1170s (aryl ether), 820s cm.$^{-1}$ (*p*-substituted aromatic). The n.m.r. spectrum of the phenol in $CDCl_3$ showed absorption centred at τ 3·21 (singlet), 5·23 (singlet, removable by exchange with D_2O), 6·09 (triplet, *J* = 5 c./sec.), 8·69, and 9·12, with relative areas 4 : 1 : 2 : 12 : 3.

Rearrangement of the Spiro-pyran (Id).—The spiro-pyran (300 mg.), in glacial acetic acid (20 ml.) containing 72% perchloric acid (0·25 ml.), was kept at 100° for 10 min., cooled, and brought to pH 5 with sodium hydroxide solution. The solution was concentrated to an oil *in vacuo*, water (20 ml.) was added, and the product was extracted with ether, and chromatographed on silica gel (60 ml.). Benzene–ether (9 : 1) eluted 2,3-*dihydro*-5-*hydroxy*-2-*vinylbenzofuran* as needles (92 mg.), which after two recrystallisations from petroleum had m. p. 78—78·5° (Found: C, 73·6; H, 6·45. $C_{10}H_{10}O_2$ requires C, 74·05; H, 6·2%); $\nu_{max.}$ (CS_2) 3080w, 976s, 925s ($-CH=CH_2$), 3615s (–OH), 795s, 750m cm.$^{-1}$ (1 : 2 : 4 aromatic subs.); $\lambda_{max.}$ (EtOH) 228 (ε 4750) and 302 mμ (ε 4000).

Rearrangement of the Dimethylspiro-pyran (Ia).—The spiro-pyran (300 mg.) in glacial acetic acid (20 ml.) containing 72% perchloric acid (0·25 ml.), was kept for 24 hr. at 20°. The mixture was separated as above to give 2,3-*dihydro*-5-*hydroxy*-2-*isopropenyl*-2-*methylbenzofuran* (157 mg., 52%) as an oil, b. p. 105—120° (bath)/0·03 mm. (Found: C, 75·70; H, 7·55. $C_{12}H_{14}O_2$ requires C, 75·75; H, 7·4%); $\nu_{max.}$ (CS_2) 3600s (–OH), 1245vs (=C–O–), 908s ($-C=CH_2$), 810s, 798s, 780m, 738m cm.$^{-1}$; $\lambda_{max.}$ (EtOH) 228 (ε 4850) and 303 mμ (ε 4000). The n.m.r. spectrum of the product in $CDCl_3$ showed absorption centred at τ 3·29 (complex), 4·22 (singlet), 4·83 (singlet), 5·09 (complex), 6·88 (AB quartet, τ_A 6·77, τ_B 7·02; J_{AB} = 16 c./sec.), 8·16 (singlet), 8·45 (singlet), with relative peak areas 3 : 1 : 1 : 1 : 2 : 3 : 3.

Ethyl 2-*Ethyl*-5-*hydroxybenzofuran*-3-*carboxylate* (VI).—This synthesis was based on the method of Grinev *et al.*[15] for the preparation of the 2-methyl analogue.

p-Benzoquinone (4 g.) was placed in the upper chamber of a Soxhlet extractor without a syphon. The lower flask contained ethyl propioacetate [16] (10·7 g.), anhydrous zinc chloride (5·2 g.), absolute ethanol (8 ml.), and ether (20 ml.), and was kept for 72 hr. in a water-bath at 80—90°. In this way the quinone was added extremely slowly to the ester. The mixture solidified on cooling and the precipitate (7·76 g.) was collected, washed with a little benzene, and dried (P_2O_5 *in vacuo*). Treatment of the solid with cold ether (75 ml.) gave a solution A and a precipitate B.

Solution A yielded *ethyl* 2-*ethyl*-5-*hydroxybenzofuran*-3-*carboxylate* (6·3 g.), which after three recrystallisations from benzene had m. p. 123·5—124° (Found: C, 66·4; H, 6·1. $C_{13}H_{14}O_4$ requires C, 66·65; H, 6·0%); $\nu_{max.}$ (Nujol) 3340s (–OH), 1680s ($-CO_2Et$), 1380m (–Me), 1270s, 1220s, 1050s. The n.m.r. spectrum of the compound in $CDCl_3$ showed absorption centred at

---

[14] R. Nodzu, H. Watanabe, S. Kuwata, C. Nagaishi, and T. Teramatsu, *J. Pharm. Soc. Japan*, 1954, **74**, 875.

[15] A. N. Grinev, Bon-Khvar Pan, and A. P. Terent'ev, *Zhur. obshchei Khim.*, 1957, **27**, 1087.

[16] R. Willstätter and C. H. Clarke, *Ber.*, 1914, **47**, 298.

τ 2·4—3·3 (complex), 3·66 (singlet), 5·60 (quartet, J = 7·3 c./sec.), 6·85 (quartet, J = 7·3 c./sec.), 8·60 (triplet, J = 7·3 c./sec.), and 8·68 (triplet, J = 7·3 c./sec.).

Solid B, recrystallised from acetic acid, gave *diethyl* 2,6-*dimethylbenzo*[1,2-b : 4,5-b′]*difuran*-3,7-*dicarboxylate* (1·03 g.) as needles, m. p. 160—161° (Found: C, 67·45; H, 6·3. $C_{20}H_{22}O_6$ requires C, 67·0; H, 6·2%); $\nu_{max.}$ (CS_2) 2965s, 2898m ($-CH_3$), 2930m, 2870m (CH_2), 1715vs ($-CO_2Et$), 1225s, 1175s, 1090s, 1040s cm.$^{-1}$. The n.m.r. spectrum of the adduct in $CDCl_3$ showed absorption centred at τ 2·02 (sharp singlet), 5·54 (quartet, J = 7·3 c./sec.), 6·75 (quartet, J = 7·3 c./sec.), 8·54 (triplet, J = 7·3 c./sec.), and 8·63 (triplet, J = 7·3 c./sec.).

2-*Ethyl*-5-*hydroxybenzofuran* (VIII).—A solution of the above ester (3·0 g.) in water (30 ml.) containing sodium hydroxide (2·4 g.) was boiled under reflux under nitrogen for 3·5 hr. After cooling, the solution was filtered, acidified with concentrated hydrochloric acid, and stored at 0° for 3 hr. Filtration gave an acid (2·37 g.), m. p. 211—214°. The acid (1 g.) was intimately mixed with calcium oxide (1·5 g.) and placed in the bulb of a small distillation apparatus. The mixture was kept for 1 hr., at 300°/0·1 mm. The solid distillate was dissolved in ether (10 ml.), shaken with sodium hydrogen carbonate solution (4 × 10 ml.), washed with water (10 ml.), then dried and concentrated to give a white solid. Distillation at 110—125°(bath)/0·1 mm. gave 2-*ethyl*-5-*hydroxybenzofuran* (0·28 g., 36%) as needles, m. p. 76—77° (Found: C, 74·2; H, 6·1. $C_{10}H_{10}O_2$ requires C, 74·05; H, 6·2%); $\nu_{max.}$ (CS_2) 3595s, 3025w, 1270s, 1175vs, 1160vs, 973m, 949s, 930vs, 835vs, 800s, 798vs, 770s, 733m cm.$^{-1}$. The n.m.r. spectrum of the compound in $CDCl_3$ showed absorption centred at τ 2·6—3·5 (8 lines), 3·75 (singlet), 4·84 (singlet, exchangeable with D_2O), 7·25 (quartet, J = 7·4 c./sec.), and 8·72 (triplet, J = 7·4 c./sec.).

2-*Ethyl*-2,3-*dihydro*-5-*hydroxybenzofuran* (IX).—(*a*) 2-Ethyl-5-hydroxybenzofuran (151 mg.) in ethanol (50 ml.) was hydrogenated for 24 hr. at room temperature and pressure over 5% palladium–charcoal (20 mg.). The oily product was chromatographed on a column of silica gel (100 ml.). Benzene–ether (9 : 1) eluted a fraction which, on distillation, gave 2-*ethyl*-2,3-*dihydro*-5-*hydroxybenzofuran* (80 mg.) as a pale yellow oil, b. p. 110—115°(bath)/0·01 mm., (Found: C, 72·95; H, 7·5. $C_{10}H_{12}O_2$ requires C, 73·15; H, 7·35%); parent peak in mass spectrum at m/e 164·0838 (Calc. for $C_{10}H_{12}O_2$: m/e 164·0837); $\nu_{max.}$ (CS_2) 3595s, 1230s, 1200s, 1165s, 1125s, 930s, 805s, 795s, 745s cm.$^{-1}$. The n.m.r. spectrum of the compound in $CDCl_3$ showed absorption at τ 3·3—3·5 (complex), 4·30 (broad singlet), 5·30 (complex), 7·01 (octet), 8·24 (complex), and 9·01 (triplet), with relative peak areas 3 : 1 : 1 : 2 : 2 : 3.

(*b*) 5-Hydroxy-2-vinyl-2,3-dihydrobenzofuran (IIIb) (121 mg.) in ethanol (50 ml.) was hydrogenated for 2 hr. at room temperature and pressure, over 5% palladium–charcoal (20 mg.). The oily product was separated from unchanged starting material by preparative thin-layer chromatography (adsorbent of unbaked Kieselgel H, eluent benzene–ether 20 : 1). Distillation of the product gave an oil, b. p. 110—115° (bath)/0·01 mm., the infrared and n.m.r. spectra of which were identical with those of the 2-ethyl-2,3-dihydro-5-hydroxybenzofuran prepared above.

trans-2,3-*Dimethylbut*-2-*enylene diacetate*, prepared by the method of Sweeting and Johnson,[17] had m. p. 37°. The n.m.r. spectrum of the ester exhibited sharp maxima at τ 5·36, 7·92, and 8·20.

Reaction of the Spiro-pyran (Ia) *with Boron Trifluoride and Acetic Anhydride*.—The spiro-pyran (126 mg.) in acetic anhydride (2 ml.) containing boron trifluoride etherate (3 drops) was kept for 2 hr. at room temperature, then washed with sodium hydrogen carbonate solution and extracted with ether (4 × 20 ml.). The ethereal extracts were dried and distilled to give a liquid A (25 mg.), b. p. 40—70° (bath)/0·001 mm., and a semi-crystalline mass (102 mg.), b. p. 80—125° (bath)/0·001 mm., which, after recrystallisation from ether–petroleum, gave quinol diacetate (52 mg.) as needles, m. p. and mixed m. p. 120—122°.

Liquid A showed infrared absorption at 1745, 1370, 1365, 1220, 1018, and 965 cm.$^{-1}$, in common with *trans*-2,3-dimethylbut-2-enylene diacetate. The n.m.r. spectrum of A showed maximum absorption at τ 5·37, 7·93, and 8·20, consistent with the presence of the *trans*-diacetate, together with additional absorption maxima at τ 5·39 and 8·22, possibly ascribable to small amounts of the *cis*-diacetate. That the product was a mixture of the *trans*-diacetate and a second component was confirmed by thin-layer chromatography.

We are indebted to Mr. J. D. Eland for measurements of mass spectra and to the D.S.I.R. and Brasenose College, Oxford, for a Research Studentship.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, March* 30*th*, 1965.]

---

[17] O. J. Sweeting and J. R. Johnson, *J. Amer. Chem. Soc.*, 1946, **68**, 1057.