910. *Properties and Reactions of Free Alkyl Radicals in Solution. Part V.* A Study of the Reactions of the 2-Cyano-2-propyl Radical with Quinones.*

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The products of the decomposition of αα′-azo*iso*butyronitrile in toluene solutions of a series of quinones have been investigated. It has been shown that in the main the reactivity of quinones, at their oxygen atoms, towards the 2-cyano-2-propyl free radical follows the order of their oxidation–reduction potentials; quinones of lower potential than +0·45 v do not react. There are, however, significant differences in the order of reactivity which are ascribed to the steric hindrance of vicinal nuclear substituents.

There is also some correlation between the ratio % of quinol monoether : % of quinol diether and the critical oxidation potentials of the corresponding phenols, as given by Fieser (*J. Amer. Chem. Soc.*, 1930, **52**, 5204).

Direct nuclear substitution by the cyanopropyl group has been detected only with 1 : 4-naphthaquinone, but in two instances it has been found that the second cyanopropyl group must attack a nuclear position since lactones formed thereby have been isolated. This effect is ascribed to mesomerism of the initial aryloxy-radical, and as would be predicted, a dilactone is one of the reaction products of a mixture of *p*-xyloquinone and the corresponding quinol.

In Part I (*J.*, 1950, 1764) Bickel and Waters showed that 2-cyano- and 2-carbomethoxy-2-propyl radicals reacted with *p*-benzoquinone and with chloranil to yield both the mono- and di-ethers of quinol and of tetrachloroquinol. They pointed out that their results had a direct bearing on the elucidation of the inhibiting powers of quinones in vinyl polymerisation processes. More recently, Dunn, Waters, and Wickham-Jones (*J.*, 1952, 2427), and Moore and Waters (*ibid.*, p. 2432) have shown that a similar addition of radicals to the oxygen atoms of 3 : 5 : 3′ : 5′-tetrachloro-4 : 4′-diphenoquinone provides an explanation of quinone inhibition of benzaldehyde autoxidation. The relative reactivities of a series of quinones towards a typical free radical are thus a subject directly relevant to at least two aspects of free-radical chemistry which have far-reaching technical applications. We have therefore extended the scope of Part I in a more detailed study of the actions on a series of quinones of 2-cyano-2-propyl radicals generated by the thermal decomposition of αα′-azo*iso*butyronitrile in toluene solution.

$$2R^{\cdot} \longrightarrow R{-}R \text{ (tetramethylsuccinonitrile)} \quad (1)$$

$$R^{\cdot} + Q \longrightarrow R{-}Q^{\cdot} \text{ (an aryloxy-radical)} \quad (2)$$

$$R^{\cdot} + R{-}Q^{\cdot} \longrightarrow R{-}Q{-}R \text{ (a quinol diether)} \quad (3)$$

$$R^{\cdot} + R{-}Q^{\cdot} \longrightarrow R{-}Q{-}H \text{ (a quinol monoether)} + (?) \text{ olefin } [CH_3{\cdot}C(CN){:}CH_2] \quad (4)$$

It was shown by Bickel and Waters (*Rec. Trav. chim.*, 1950, **69**, 1490) that 2-cyano-2-propyl radicals do not react with toluene. When generated in this solvent they combine, to the extent of 84%, to give the dimer, tetramethylsuccinonitrile, and only to a slight degree interact by disproportionation. In the presence of a quinone, Q, these reactions [chiefly (1)] compete with the concurrent combination (2), and with succeeding rapid reactions, such as (3) and (4), which lead to the formation of stable addition and substitution products.

In principle, when minor side reactions are neglected, the relative reactivities of different quinones, Q, and aryloxy-radicals, R–Q·, can be assessed by determination of the percentage yields of the reaction products of types R–R, R–Q–R, and R–Q–H; *e.g.*, a low yield of dimer R–R indicates the presence of a quinone of high reactivity towards 2-cyano-2-propyl radicals. Though the experimental difficulties encountered in the separation and purification of the various compounds resulting from quinone–radical interactions (3) and

* Part IV, *J.*, 1952, 3108.

(4) are such that only "crude percentage yields" are worth consideration, it is fortunate that tetramethylsuccinonitrile can be separated effectively from all reaction mixtures on account of its volatility in steam and its insolubility in cold aqueous alkali and alkaline reducing agents. Thus a general procedure of first washing each initial reaction product with cold alkali to remove phenols, R–Q–H, produced by reaction (4), then distilling the product in steam, collecting the distillate, and removing quinones with alkaline sodium dithionite, leads to a nearly quantitative separation of the product, R–R, produced by reaction (1): the final involatile residue can be regarded mainly as material of type R–Q–R derived by reaction (3).

TABLE 1. *Yields, %, of the products of the reactions of 2-cyano-2-propyl radicals with quinones.*

Quinone	Monoether, R–Q–H crude	Monoether, R–Q–H pure	Diether, R–Q–R crude	Diether, R–Q–R pure	Dimer, R–R pure	Redox potential of quinone, v
1 : 4-*Benzoquinones.*						
Chloranil [a]	17	—	67	47·0	44·1	0·703
2 : 5-Diacetoxybenzoquinone	23	—	32	6·0	18·0	—
Benzoquinone [a]	56	40·5	—	10·0	25·7	0·711
Toluquinone	31	7·3	46	14·0	26·0	0·653
2 : 6-Dimethylbenzoquinone	8·6	—	41	18·5	37·6	0·600
2 : 5-Dimethylbenzoquinone [c]	5·9	1·7	35	4·0	47·5	0·597
Thymoquinone	1·0	—	32	—	49·2	0·589
2 : 5-Diethoxybenzoquinone	2·3	0·6	26	9·3	57·8	0·480
2 : 5-Di-*tert.*-butylbenzoquinone	all quinone recovered unchanged					0·554
Duroquinone	93% recovery of quinone				67·0	0·466
1 : 4-*Naphthaquinones.*						
2 : 3-Dichloronaphthaquinone	—	—	9·0	1·1	66·8	0·499
Naphthaquinone [b]	—	—	19	1·3	47·0	0·492
2-Methylnaphthaquinone [a]	—	0	—	0	—	0·422
Phenanthraquinone	—	0	20	17·7	49·0	0·471
Anthraquinone	98% recovery of quinone				78·6	0·150

[a] Bickel and Waters (Part I). [b] 2·7% Yield of 2-substituted naphthaquinone. [c] 3·8% Yield of lactone, indicative of nuclear substitution.

From our experimental results, summarised in Table 1, we suggest that the quinones investigated decrease in reactivity [reaction (2)] towards 2-cyano-2-propyl radicals in the order given, since this is the order of ascending yield of the dimer R–R. Variations in relative yield of neutral and alkali-soluble products indicate, much less accurately, the relative velocities of processes (3) and (4). Both sets of observations may be considered in relation to the structures of the quinones concerned.

From Table 1, columns 6 and 7, it can be seen that there is a partial correlation between the oxidation–reduction potential of a quinone, measured in aqueous ethanol containing N-hydrochloric acid, and the extent of its overall reaction with 2-cyano-2-propyl radicals. Though these redox potentials, which we have measured when necessary, do not exactly measure the redox potentials of the quinones in the toluene solutions used for their free-radical reactions, they should certainly give a good indication of their relative ease of hydrogen-atom uptake, particularly since Kvalnes (*J. Amer. Chem. Soc.*, 1934, **56**, 667, 670, 2487; Hunter and Kvalnes, *ibid.*, 1932, **54**, 2869) has shown that redox potentials of quinones in aqueous ethanol constitute a very good guide to the values of the equilibrium constants for quinone–quinol interactions in benzene solution.

The irreversible reaction (5) and the equilibrium (6) are similar in that they are both additions to the oxygen atom of the quinone, and both involve energy changes from the quinonoid to the benzenoid resonance systems (cf. Evans and De Heer, *Quart. Reviews*, 1950, **5**, 94).

$$Q + 2R\cdot \longrightarrow R\text{–}Q\text{–}R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$Q + 2e + 2H^+ \rightleftharpoons H_2Q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It would be expected therefore that quinones of high redox potential would most easily combine with 2-cyano-2-propyl radicals. In general this seems to be the case; quinones of lower redox potential than +0·45 v appear not to react. There are, however, significant

exceptions amongst quinones of higher redox potential. Thus 2 : 5-di-*tert.*-butyl-1 : 4-benzoquinone (+0·554 v) does not react whilst phenanthraquinone (+0·471 v) and 2 : 5-diethoxy-1 : 4-benzoquinone (+0·480 v) give good yields of reaction products. Again 2 : 3-dichloro-1 : 4-naphthaquinone (+0·499 v) was attacked much less than the unsubstituted naphthaquinone (0·492 v). We suggest that this lack of correlation between redox potential and quinone reactivity at the oxygen atoms towards free radicals is due to steric hindrance by the bulky groups vicinal to the oxygen atoms at which combination occurs. Effective collision rates can affect the speeds of irreversible processes such as (5), but cannot affect the equilibrium constants of reversible processes such as (6). In this connection it is significant that, when measuring the redox potentials of the sterically hindered quinones, such as 2 : 5-di-*tert.*-butyl-1 : 4-benzoquinone by the standard method with titanous chloride as the reducing agent, we noticed that after each addition of reducing agent the time required for attainment of electrochemical equilibrium was much longer than when unhindered quinones were used. Conant and Fieser (*J. Amer. Chem. Soc.*, 1923, **45**, 2194; 1924, **46**, 1858) have commented on the similar slow reductions of duroquinone and anthraquinone, but have ascribed this to their low redox potentials. With the di-*tert.*-butyl-quinone, however, the redox potential is higher than in many other cases in which electrochemical equilibrium is soon attained.

Such steric influences may well be important in determining the chain-stopping efficiencies of quinones in autoxidations or polymerisations. Effective chain-stopping reactions have very low activation energies, and so their velocities may be more dependent on collision frequencies than on energy factors.

Only tentative conclusions can be reached about the relative yields of mono- and di-ethers, R–Q–H and R–Q–R, formed from different quinones, since the true yields of pure reaction products are not known. However, as Table 2 shows, there appears to be some relation between the ratio, crude monoether : crude diether, and the critical oxidation potential of the corresponding monohydric phenol, as given by Fieser (*J. Amer. Chem. Soc.*, 1930, **52**, 5204; 1934, **54**, 1565).

TABLE 2. *The relation between yields of 2-cyano-2-propyl addition products to quinones and the critical oxidation potentials of related phenols.*

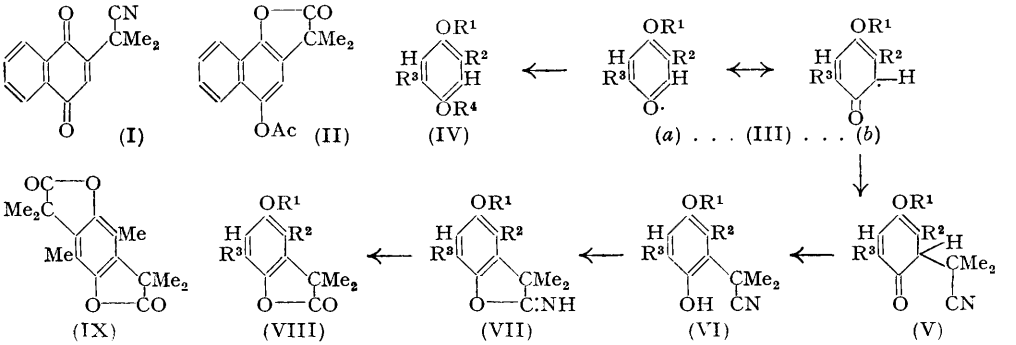
Quinone	Ratio, monoether/diether	Critical oxidation potential, v
p-Benzoquinone (pure yields)	4·0	1·089 (phenol)
Toluquinone (crude yields)	0·7	1·037 (1 Me)
2 : 6-Dimethylbenzoquinone (crude yields)	0·21	0·985 (2 Me)
2 : 5-Dimethylbenzoquinone ,,	0·17	0·985 (2 Me)
2 : 5-Diethoxybenzoquinone ,,	0·088	[0·619 (2 OMe)]
Chloranil (crude yields)	0·25	1·104

It is reasonable to suppose that the critical oxidation potential of a phenol, as defined by Fieser, is a measure of the stability of the corresponding aryloxy-radical, $R{\cdot}C_6H_4{\cdot}O{\cdot}$; when this radical is very stable, as in the case of the radical reduction product of 9 : 10-phenanthraquinone (cf. Goldschmidt and Schmidt, *Ber.*, 1922, **55**, 3197) the monoether does not appear to be formed in any appreciable quantity. Conversely it may be that active radicals $R{\cdot}C_6H_4{\cdot}O{\cdot}$ form monoethers in significant yield because they can easily pick up hydrogen atoms either from the solvent or, more probably, from the 2-cyano-2-propyl radicals. The stability of the semiquinone radicals of the phenanthrene series seems to be enhanced by the presence of vicinal groups, and a steric effect of this nature may perhaps explain the low yield of monoether from chloranil.

From 1 : 4-naphthaquinone, alone amongst the quinones which we have examined, there was isolated in 2·7% yield the nuclear-substituted product 2-(2-cyano-2-propyl)-1 : 4-naphthaquinone (I). The structure (I) was established by comparison of its ultra-violet spectrum with that of 1 : 4-naphthaquinone and by reductive acetylation to the lactone (II). The infra-red spectrum of (II) showed a characteristic absorption maximum at 1805 cm.$^{-1}$, indicative of a $\beta\gamma$-unsaturated five-membered lactone ring (cf. Grove, *J.*, 1951, 884), as well as absorptions at 1764 and 1208 cm.$^{-1}$ indicative of an acetyl group and at 1400 and 1370 cm.$^{-1}$ indicative of the *iso*propyl group. Again, oxidation of (I) gave phthalic acid, showing that the nuclear substitution had occurred in the quinonoid ring.

The isolation of (I) is of interest in relation to the work of Fieser and Oxford (*J. Amer. Chem. Soc.*, 1942, **64**, 2060) and of Fieser and Chang (*ibid.*, p. 2043) who have shown that 2-methylnaphthaquinone, and a few substituted *p*-benzoquinones, undergo nuclear alkylation when treated with diacyl peroxides or lead tetra-acetate. The lack of initial nuclear attack on the substituted *p*-benzoquinones may perhaps be due to the steric hindrance of the vicinal substituent groups, but unless one concludes that the much higher redox potential of *p*-benzoquinone than of 1 : 4-naphthaquinone renders it more prone to radical attack on oxygen rather than on carbon it is difficult to see why there should be, in our investigation, this difference in reactivity between the two.

There is, however, clear evidence in the *p*-benzoquinone series of secondary attack [reaction (3) above] on carbon as well as on oxygen. For instance, in addition to the quinol mono- and di-ethers, there were isolated from the reactions with *p*-xyloquinone and thymoquinone the lactones (VIII; $R^1 = CMe_2{\cdot}CN$, R^2, R^3 = Alkyl), the infra-red spectra of which had absorption maxima at 1800 cm.$^{-1}$ indicative of the lactone ring.



The first attack, at an oxygen atom, of a 2-cyano-2-propyl radical on a *p*-xyloquinone molecule would produce the aryloxy-radical (III; $R^1 = CMe_2{\cdot}CN$, $R^2 = R^3 = Me$) which is a mesomeric hybrid of benzenoid (III*a*) and ketonic (III*b*) forms. The addition of a second cyanopropyl radical can therefore yield both the quinol diether (IV; $R^1 = R^4 = CMe_2{\cdot}CN$, $R^2 = R^3 = Me$) and the cyclic unsaturated ketone (V; $R^1 = CMe_2{\cdot}CN$, $R^2 = R^3 = Me$) which would tend to tautomerise to the nuclear-substituted phenol (VI). On account of the vicinity of the nitrile and hydroxyl groups, this could easily pass, *via* (VII), to the lactone (VIII) under the conditions used for the isolation of the individual reaction products [compare, for instance, Haworth and Hirst's synthesis of ascorbic acid (*J. Soc. Chem. Ind.*, 1933, **52**, 645; *J.*, 1933, 1420) in which the hydroxy-nitrile immediately cyclised and hydrolysed]. We have already suggested (see also Part I) that quinol monoethers are formed from reactions of aryloxy-radicals (III) with available hydrogen-containing solutes. Now the reaction of 2-cyano-2-propyl radicals with *p*-xyloquinone gives only a small percentage of the quinol monoether, but if a mixture of *p*-xyloquinone with *p*-xyloquinol is taken then the yield of the quinol monoether (IV; $R^1 = CMe_2{\cdot}CN$, $R^2 = R^3 = Me$, $R^4 = H$) is greatly increased, as would be expected if (III; $R^1 = CMe_2{\cdot}CN$, $R^2 = R^3 = Me$) attacked the quinol.

Alternatively, however, this same monoether could possibly be formed by the direct attack of 2-cyano-2-propyl radicals on the semiquinone of *p*-xyloquinone itself (*i.e.*, III; $R^2 = R^3 = Me$, $R^1 = H$) or perhaps on its corresponding quinhydrone dimer. This semiquinone (III; $R^1 = H$) being a mesomeric hybrid might be expected to give some nuclear-substituted product, *via* (III*b*). In fact there has been isolated from this reaction mixture not (IV; $R^1 = R^4 = CMe_2{\cdot}CN$) but the lactone (VIII; $R^1 = CMe_2{\cdot}CN$, $R^2 = R^3 = Me$) together with the dilactone (IX) which could be derived from (III; $R^1 = H$, $R^2 = R^3 = Me$) by repeated attack in the manner suggested above.

It may be concluded therefore that the structural characteristics of aryloxy-radicals (III) play an important part in determining the natures and the extent of combination reactions between free radicals and quinones.

Experimental

Reaction of αα′-Azoisobutyronitrile with Toluquinone.—The azo-compound (Bickel and Waters, *Rec. Trav. chim., loc. cit.*) (16·4 g.) and the quinone (Chattaway and Parkes, *J.*, 1925, 1309) (12·2 g.) were refluxed in dry toluene (100 c.c.) for 30 minutes. After cooling, the red solution was extracted with an aqueous solution of potassium hydroxide (11 g.) and then with a similar solution containing sodium sulphite (4 g.) also. Toluene and tetramethylsuccinonitrile were removed by steam-distillation and the latter (26%; m. p. 166—167°) was separated by fractional distillation. The residue from the steam-distillation (46%) was extracted with ether, dried (Na_2SO_4), and distilled in a vacuum. It gave an oil which slowly crystallised (14%), b. p. 128—130°/0·15 mm. Crystallisation from aqueous ethanol gave prismatic needles of *2-methylquinol di-(2′-cyano-2′-propyl) ether*, m. p. 51—52° (Found: C, 69·8; H, 7·0; N, 10·7. $C_{15}H_{18}O_2N_2$ requires C, 69·7; H, 7·0; N, 10·8%). The infra-red spectrum exhibited the following bands: 2230 cm.$^{-1}$ (weak), C≡N group; 1610 and 1505 cm.$^{-1}$, aromatic C=C; 1390 and 1375 cm.$^{-1}$, CMe_2; 860 and 826 cm.$^{-1}$, unsymmetrical trisubstituted benzene ring.

Alkaline hydrolysis followed by acidification yielded the corresponding dibasic *acid*, which crystallised from aqueous ethanol in rhombs, m. p. 121—122° (Found: C, 61·0; H, 6·8. $C_{15}H_{20}O_6$ requires C, 60·8; H, 6·8%).

The first aqueous alkaline extract was treated with sodium sulphite and then acidified; the resulting oil (11 g.) was distilled at 126—130°/0·3 mm. Oxidation of the crystalline portion (2·6 g.) of the product with an excess of ferric chloride at 100° gave toluquinone, m. p. and mixed m. p. 67°. Benzoylation yielded the *monobenzoate* of a 2-methylquinol 2′-cyano-2′-propyl ether; this ester crystallised from methanol in prisms, m. p. 83—84° (Found: C, 72·8; H, 6·0; N, 4·7. $C_{18}H_{17}O_3N$ requires C, 73·1; H, 5·8; N, 4·7%). Reaction of the solid with anhydrous ethanol and hydrogen chloride in dry dioxan at 0° yielded the corresponding *imino-ether hydrochloride* which after precipitation by dry ether and crystallisation from glacial acetic acid–ether had m. p. 124—125° (Found: C, 57·1; H, 7·3; N, 5·5. $C_{13}H_{19}O_3N$,HCl requires C, 57·0; H, 7·4; N, 5·1%). When heated above its m. p. this gave a *2-methylquinol 2′-carbamyl-2′-propyl ether* which after crystallisation from dilute methanol had m. p. 146—147° (Found: N, 6·8. $C_{11}H_{15}O_3N$ requires N, 6·7%).

When the crude oil was benzoylated *2-methylquinol dibenzoate*, m. p. 124°, was isolated (Found: C, 75·7; H, 4·8. $C_{21}H_{16}O_4$ requires C, 75·9; H, 4·8%).

Reaction of αα′-Azoisobutyronitrile with 2 : 6-Dimethyl-1 : 4-benzoquinone.—Reaction (as above) of the quinone (Cosgrove and Waters, *J.*, 1951, 1726) (5·1 g.) and the azo-compound (6·15 g.) gave tetramethylsuccinonitrile (38%). Acidification of the alkaline extract gave a dark oil (8·6%), presumably the monoether. The neutral residue, after steam-distillation, was extracted with ether and yielded an oil (41%) which after chromatography on active alumina, benzene being used as eluent, yielded *2 : 6-dimethylquinol di-(2′-cyano-2′-propyl) ether*, prisms (from MeOH), m. p. 59° (Found: C, 70·6; H, 7·5; N, 10·3. $C_{16}H_{20}O_2N_2$ requires C, 70·6; H, 7·4; N, 10·3%). Alkaline hydrolysis yielded the corresponding dibasic acid as an oil which eventually solidified; its *S*-benzylthiuronium salt had m. p. 175—179°.

Reaction of αα′-Azoisobutyronitrile with 2 : 5-Dimethyl-1 : 4-benzoquinone.—The azo-compound (23 g.) and the quinone (19 g.) (Kehrmann and Stiller, *Ber.*, 1912, **45**, 3348) were refluxed in dry toluene (140 c.c.) for 30 minutes. After cooling, part of the excess of quinone crystallised and was collected. The solution that remained was distilled in steam; the distillate gave tetramethylsuccinonitrile (47·2%). The residue gave a neutral fraction (34·6%) which was chromatographed on activated alumina (500 g.), benzene–light petroleum (40—60°) (3 : 7) being used. From the first 2·5 l. of eluant a solid (2·8 g.) was obtained which, when crystallised from light petroleum (40—60°), gave needles, m. p. 84°, of *2 : 5-dimethylquinol di-(2′-cyano-2′-propyl) ether* (Found: C, 70·9; H, 7·5; N, 10·4. $C_{16}H_{20}O_2N_2$ requires C, 70·6; H, 7·4; N, 10·3%). The infra-red spectrum showed the following bands: 2235 cm.$^{-1}$, C≡N group; 1513 cm.$^{-1}$, aromatic C=C; 1400, 1390, and 1375 cm.$^{-1}$, CMe_2 group; 1200, 1160, and 1120 cm.$^{-1}$, C–O group in ether; 875 cm.$^{-1}$, 1 : 2 : 4 : 5-tetrasubstituted benzene nucleus. Hydrolysis with alcoholic potassium hydroxide gave the corresponding dibasic acid, m. p. 145—146°, identical with a specimen prepared by hydrolysis of the authentic diethyl ester (see below). Reaction with dry ethanol and hydrogen chloride in anhydrous dioxan at 0° yielded the corresponding *di-imino-ether hydrochloride* which was precipitated by ether and after crystallisation from acetic acid–ether had m. p. 252—254° (decomp.) (Found: C, 54·4; H, 7·8; N, 8·1. $C_{20}H_{32}O_4N_2$,2HCl requires C, 54·9; H, 7·8; N, 6·4%). Heating of this hydrochloride in alcohol for 30 minutes gave *2 : 5-dimethylquinol di-(2′-carbethoxy-2′-propyl) ether*, prisms (from MeOH),

m. p. 69—70° not depressed after admixture with an authentic specimen prepared as described below.

A second fraction (2·7 l.) from the chromatogram gave a mixture (1·5 g.) of needles and short crystals, whilst the last 3·7 l. (with an increased proportion of benzene) gave short rhombic crystals (from light petroleum) of the *lactone* (1·04 g.) of 2-(2-carboxy-2-propyl)-4-(2-cyano-2-propoxy)-3 : 6-dimethylphenol; this had m. p. 105—106° (Found: C, 70·5; H, 7·2; N, 5·0%; *M*, 249. $C_{16}H_{19}O_3N$ requires C, 70·3; H, 7·0; N, 5·1%; *M*, 273). The infra-red spectrum showed the following bands: 1800 cm.$^{-1}$, five-membered βγ-unsaturated lactone ring; 1406, 1390, and 1370 cm.$^{-1}$, CMe_2 group; 1100 cm.$^{-1}$, C–O group; 870 cm.$^{-1}$, H–C of penta-substituted benzene ring. This lactone could also be separated from the di-ether by slow crystallisation from light petroleum whereby large crystals were obtained which could be hand-picked.

The alkaline solution from the original reaction mixture, after acidification with dilute sulphuric acid, gave an oil (1·7 g., 5·9%) which was collected in ether; this gave plates (from 50% ethanol), m. p. 111°, of 4-(2′-*cyano*-2′-*propoxy*)-2 : 5-*dimethylphenol* (Found: C, 70·0; H, 7·1; N, 6·4. $C_{12}H_{15}O_2N$ requires C, 70·2; H, 7·3; N, 6·8%). Its *benzoate* crystallised from ethanol in fine needles, m. p. 64° (Found: C, 73·6; H, 6·4; N, 4·8. $C_{19}H_{19}O_3N$ requires C, 73·8; H, 6·2; N, 4·5%).

On oxidation with ferric chloride at 100° the hydroxy-compound gave *p*-xyloquinone, m. p. and mixed m. p. 126°. The corresponding *imino-ether hydrochloride*, when crystallised from acetic acid–ether, had m. p. 117—118° (decomp.) (Found: C, 58·5; H, 7·8; N, 5·0. $C_{14}H_{21}O_3N$,HCl requires C, 58·4; H, 7·7; N, 4·9%). Its infra-red spectrum showed the following bands: 3200 cm.$^{-1}$, O–H or N–H; 1660 cm.$^{-1}$, C=N; 1600 and 1525 cm.$^{-1}$, aromatic C=O; 1410, 1390, and 1365 cm.$^{-1}$, CMe_2 group. When heated this compound gave the corresponding *amide*, m. p. 172° (from ethanol) (Found: C, 64·6; H, 7·5; N, 6·4. $C_{12}H_{17}O_3N$ requires C, 64·5; H, 7·6; N, 6·3%).

Synthesis of 2 : 5-*Dimethylquinol Di*-(2′-*carbethoxy*-2′-*propyl*) *Ether*.—A solution of sodium ethoxide [from sodium (0·81 g.) and ethanol (20 ml.)] was treated successively with 2-methylquinol (2·5 g.) and ethyl α-bromo*iso*butyrate (7·0 g.) and refluxed until it was neutral (phenolphthalein) (1 hour). After removal of the alcohol, the product was extracted with ether, the extract dried, the ether removed, and the residue crystallised from dilute ethanol; it formed prisms, m. p. 70° (Found: C, 65·8; H, 8·3. $C_{20}H_{30}O_6$ requires C, 65·6; H, 8·2%). Its infra-red spectrum showed the following bands; 1730 cm.$^{-1}$, C=O in ester; 1410, 1385, and 1370 cm.$^{-1}$, CMe_2 group; 1515 and 860 cm.$^{-1}$, aromatic ring; 1212, 1180, 1150, and 1100 cm.$^{-1}$, C–O in ester. Alkaline hydrolysis yielded the corresponding *dibasic acid*, in short prisms (from aqueous ethanol), m. p. 146° (see above) (Found: C, 62·1; H, 7·3. $C_{16}H_{22}O_6$ requires C, 61·9; H, 7·1%).

*Reaction of αα′-Azo*iso*butyrate with Thymoquinone*.—A solution of the azo-compound (32·7 g.) and thymoquinone (32·8 g.) (Kremers and Wakeman, *Zentr.*, 1910, I, 24) in dry toluene (200 c.c.) was refluxed for 30 minutes. Tetramethylsuccinonitrile (49·2%) was separated by distillation in steam; the residue after being washed with alkaline dithionite and extracted with ether gave a reddish oil (32%) which was chromatographed through activated alumina (150 g.) with light petroleum (60—80°). A colourless oil was obtained which solidified when rubbed and gave rhombic crystals (from aqueous MeOH), m. p. 50°, of 2-*methyl*-5-iso*propylquinol di*-(2′-*cyano*-2′-*propyl*) *ether* (Found: C, 71·9; H, 8·2; N, 9·5. $C_{18}H_{24}O_2N_2$ requires C, 71·9; H, 8·1; N, 9·3%), together with the *lactone* of 2-(2-carboxy-2-propyl)-4-(2-cyano-2-propoxy)-3(6)-methyl-6(3)-*iso*propylphenol as prismatic needles, m. p. 64° (Found: C, 71·9; H, 7·7; N, 4·6. $C_{18}H_{23}O_3N$ requires C, 71·7; H, 7·7; N, 4·6%). The infra-red spectrum of this compound showed the following bands: 1800 cm.$^{-1}$, C=O of five-membered βγ-unsaturated lactone; 1630 and 1490 cm.$^{-1}$, aromatic C=C; 1400, 1385, and 1370 cm.$^{-1}$, CMe_2 group; 1225 and 1105 cm.$^{-1}$, C–O. No attempt was made to discriminate between the alternative positions of nuclear substitution. The original alkaline extract on acidification gave a crude oil (1%) in amount too small for isolation of the pure quinol monoether.

*Reaction of αα′-Azo*iso*butyronitrile with* 2 : 5-*Diacetoxy*-1 : 4-*benzoquinone*.—The diacetoxyquinone [prepared from 2 : 5-dihydroxy-1 : 4-benzoquinone as described by Kehrmann and Sterchi (*Helv. Chim. Acta*, 1926, **9**, 859)] (4·36 g.), m. p. 150—152°, was treated with an equimolar proportion of the azo-compound in the usual way and on cooling unchanged quinone (0·42 g.) separated. The toluene solution was extracted with 5% aqueous potassium hydroxide (50 ml.) and then with a similar solution containing also sodium sulphite (0·5 g.). Toluene and tetramethylsuccinonitrile (18%) were removed by steam distillation, and the residue (32% calc. as diether) was crystallised from ethanol, giving small prisms (6%), m. p. 146—147° of 2 : 5-*di*-

acetoxyquinol di-(2′-cyano-2′-propyl) ether (Found: C, 59·9; H, 5·8; N, 7·7. $C_{18}H_{20}O_6N_2$ requires C, 60·0; H, 5·6; N, 7·7%).

The alkaline solutions were acidified and the oil which separated was extracted with ether and dried (Na_2SO_4). Removal of the ether left a solid (23% calc. for mono-ether) which decomposed in the air.

Reaction of αα′-Azoisobutyronitrile with 2 : 5-Diethoxy-1 : 4-benzoquinone.—The quinone (Knoevenagel and Bückel, *Ber.*, 1901, **34**, 3994) was purified by chromatography on alumina, chloroform being used as solvent, and then crystallised from methanol; it had m. p. 183°. The reaction was carried out, with 0·03 mole of each reagent, in the normal manner. The excess of quinone crystallised from the cooled toluene solution, and more (total recovery, 59%) was obtained by concentrating the solution, which was then washed successively with cold alkali and cold alkaline dithionite. Tetramethylsuccinonitrile (58%) was separated, and the neutral residue (26%) was chromatographed on activated alumina, benzene being used. Crystallisation of the product from ethanol gave plates, m. p. 108°, of *2 : 5-diethoxyquinol di-(2′-cyano-2′-propyl) ether* (Found: C, 65·3; H, 7·4; N, 8·5. $C_{18}H_{24}O_4N_2$ requires C, 65·0; H, 7·3; N, 8·4%). Alkaline hydrolysis in aqueous ethanol yielded the corresponding *dibasic acid*, needles (from ethanol), m. p. 143° (Found: C, 58·4; H, 7·3. $C_{18}H_{26}O_8$ requires C, 58·4; H, 7·1%). When the ether was heated for 3 hours at 200—220° with acetylpyridinium chloride a white product, m. p. 205—208°, was obtained; this was probably 1 : 2 : 4 : 5-tetra-acetoxybenzene (m. p. 217°). Reaction of the dinitrile with anhydrous ethanol and hydrogen chloride in dry dioxan at 0° for 4 days gave the corresponding *di-imino-ether hydrochloride*, m. p. 204—206° after crystallistion from acetic acid–ether (Found: C, 52·9; H, 7·8; N, 5·6; Cl, 14·8. $C_{22}H_{36}O_6N_2,2HCl$ requires C, 53·1; H, 7·7; N, 5·6; Cl, 14·3%).

The original alkaline extract was treated with sodium sulphite and then acidified. The product which separated (2·3%) was extracted with ether, dried, and crystallised from light petroleum (40—60°), whereupon *2 : 5-diethoxyquinol mono-(2′-cyano-2′-propyl ether)* separated in two interconvertible crystalline forms, (i) prismatic needles, m. p. 72—73°, and (ii) short prisms, m. p. 83—84°, which when kept under petroleum in the presence of the needles changed to (i) (Found: C, 63·4; H, 7·3; N, 5·5. $C_{14}H_{19}O_4N$ requires C, 63·4; H, 7·2; N, 5·3%). The infra-red spectrum showed the following bands: 3400 cm.$^{-1}$, O–H group; 1600 and 1515 cm.$^{-1}$, aromatic C=C; 1390 and 1370 cm.$^{-1}$, CMe_2 group; 1220, 1175, 1155, and 1110, C–O; 855 cm.$^{-1}$, *para* C–H groups of benzene ring. The characteristic band of the C≡N group was absent (cf. Kitson and Griffith, *Anal. Chem.*, 1952, **24**, 334). The *benzoate* formed rhombic prisms, m. p. 66°, after crystallisation from alcohol (Found: C, 68·3; H, 6·3; N, 3·3. $C_{21}H_{23}O_5N$ requires C, 68·2; H, 6·3; N, 3·7%).

In another experiment, in which quinone which had been purified only by crystallisation from alcohol was used, the yields were: tetramethylsuccinonitrile 55·6%, crude diether, 7·2%, phenolic compound 22·9%, and recovered quinone 44%. This change in relative yields of mono- and di-ethers is indicative of the use of a quinone–quinol mixture.

Attempted Reactions with Duroquinone and with 2 : 5-Di-tert.-butyl-1 : 4-benzoquinone.—The duroquinone, prepared *via* durene (*Org. Synth.*, Coll. Vol. 2, p. 248), was purified by steam-distillation to m. p. 109—110°. The di-*tert.*-butyl-quinone was prepared by oxidising the quinol with ferric chloride in alcoholic hydrochloric acid; the product (sublimed in a vacuum and crystallised from ethanol) had m. p. 153° (Found: C, 76·2; H, 9·2. Calc. for $C_{14}H_{20}O_2$: C, 76·3; H, 9·1%).

From the reaction of duroquinone with the azo-compound 67% of tetramethylsuccinonitrile was recovered and 93% of the quinone, together with 6·6% of 2 : 3 : 5-trimethyl-2 : 3 : 5-tricyanohexane (cf. Bickel and Waters, *Rec. Trav. chim., loc. cit.*). 99% of the di-*tert.*-butyl-quinone was recovered after the corresponding reaction with this substance.

Reaction of αα′-Azoisobutyronitrile with 1 : 4-Naphthaquinone.—The azo-compound (28·7 g.) and the quinone (27·7 g.) were refluxed in toluene (200 c.c.) for 30 minutes and the cooled solution was extracted successively with aqueous potassium hydroxide (400 ml.; 5%) and with a similar alkaline solution containing sodium sulphite (4 g.). The toluene and tetramethyl-succinonitrile (47%) were removed with steam, and the residue (18%) was chromatographed through activated alumina, with benzene, yielding 1 : 4-di-(2-cyano-2-propoxy)naphthalene (1·3%), m. p. 108°, needles (from ethanol) or prisms (from methanol) (Found: C, 73·3; H, 6·4; N, 9·5. $C_{18}H_{18}O_2N_2$ requires C, 73·4; H, 6·2; N, 9·5%). In another experiment using 0·10 mole of each reactant, the crude neutral fraction (18·5%) was distilled, giving an oil, b. p. 165—175°/0·3 mm., which crystallised and yielded yellow plates (from methanol) of *2-(2-cyano-2-propyl)-1 : 4-naphthaquinone* (2·7%), m. p. 105—106° (Found: C, 74·5; H, 5·0;

N, 6·1. $C_{14}H_{11}O_2N$ requires C, 74·6; H, 4·9; N, 6·2%). Comparative measurements of ultra-violet absorption spectra substantiate the structure given above :

Quinone	Maxima, Å	log ϵ_{molar}
1 : 4-Naphthaquinone	2480, 3300	4·23, 3·46
2-Methyl-1 : 4-naphthaquinone	2500, 3310	4·21, 3·41
2-(2-Cyano-2-propyl)-1 : 4-naphthaquinone	2520, 3340	4·24, 3·42

From the mother liquor a small amount of 1 : 4-di-(2-cyano-2-propoxy)naphthalene, m. p. 107—108°, was also separated. 2-(2-Cyano-2-propyl)naphthaquinone (0·18 g.), zinc dust (0·18 g.), and a drop of triethylamine were heated in acetic anhydride (1·2 c.c.) until decoloration occurred, and then for a further 90 seconds. The mixture was fractionally extracted with hot glacial acetic acid (4 c.c.) and filtered, and the boiling solution then treated cautiously with water (9 c.c.) and allowed to cool whereupon needles (0·15 g.) separated of the *lactone* of 4-acetoxy-2-(2-carboxy-2-propyl)-1-naphthol, m. p. 133° (from ethanol) (Found : C, 71·3; H, 5·0. $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2%). Its infra-red spectrum showed the following bands : 1805 cm.$^{-1}$, C=O of $\beta\gamma$-unsaturated five-membered lactone ring; 1765 cm.$^{-1}$, C=O of AcO; 1600 cm.$^{-1}$, aromatic C=C; 1400 and 1370 cm.$^{-1}$, CMe_2 group; 1208 and 1085 cm.$^{-1}$, C–O in ester; and 859 and 763 cm.$^{-1}$, H–C bonds in naphthalene nucleus.

A suspension of the substituted naphthaquinone in dilute sulphuric acid was oxidised at 40° with an excess of potassium permanganate. Ether extraction of the cooled solution gave phthalic anhydride, m. p. 129—130° (after sublimation) (positive fluorescein test).

Reaction of αα'-Azoisobutyronitrile with 2 : 3-Dichloro-1 : 4-naphthaquinone.—The quinone (16·7 g.; m. p. 193°) Ullmann and Ettisch, *Ber.*, 1911, **54**, 262) and the azo-compound (12 g.) were refluxed for 30 minutes in toluene; on cooling unchanged quinone (75%) separated. The toluene solution was washed twice with potassium hydroxide solution (5%; 160 c.c.), then with a solution of stannous chloride in dilute hydrochloric acid, and again with potassium hydroxide solution. Toluene and tetramethylsuccinonitrile (67%) were removed by steam-distillation, and the residue (9% calc. as di-ether) was separated by ether extraction. Purification through activated alumina, with benzene, gave a little unchanged 2 : 3-dichloronaphthaquinone and then 2 : 3-*dichloro*-1 : 4-*di*-(2-*cyano*-2-*propoxy*)*naphthalene* (1·1%), m. p. 134° (after crystallisation from ethanol and dilute acetic acid) (Found : C, 59·4; H, 4·5; N, 7·4. $C_{18}H_{16}O_2N_2Cl_2$ requires C, 59·5; H, 4·4; N, 7·7%). No phenolic product separated on acidification of the alkaline extract.

Reaction of αα'-Azoisobutyronitrile with 9 : 10-Phenanthraquinone.—After completion of the usual reaction between the quinone (20·8 g.) and the azo-compound much of the excess of quinone crystallised on cooling. The toluene solution was washed thrice with 2·5% potassium hydroxide solution (total 250 c.c.), then water, and finally was heated with saturated aqueous sodium hydrogen sulphite (100 c.c.). By steam-distillation tetramethylsuccinonitrile (49%) was separated. The residue, which solidified, was crystallised from ethanol, giving 9 : 10-*di*-(2-*cyano*-2-*propoxy*)*phenanthrene* (17·7%), m. p. 147—148° after further purification through activated alumina and crystallisation from methanol (Found : C, 76·9; H, 6·0; N, 7·7. $C_{22}H_{20}O_2N_2$ requires C, 76·7; H, 5·8; N, 8·1%). The infra-red spectrum showed the following bands : 1613 cm.$^{-1}$, aromatic C=C or C=N; 1490 cm.$^{-1}$, aromatic C=C; 1205 and 1110 cm.$^{-1}$, C–O. The characteristic (weakish) absorption band of the nitrile group was not observed. Alkaline hydrolysis in aqueous ethanol gave a rather insoluble *monoamide* which crystallised from ethanol in needles, m. p. 306—310° (decomp.) after being vacuum-dried at 150° (Found : C, 73·1; H, 6·3; N, 7·7. $C_{22}H_{22}O_3N_2$ requires C, 72·9; H, 6·1; N, 7·7%). The corresponding *mono-imino-ether hydrochloride* crystallised from glacial acetic acid–ether in prisms, m. p. 143—145° (decomp.) (Found : C, 67·8; H, 6·6; N, 6·7. $C_{24}H_{26}O_3N_2$,HCl requires C, 67·5; H, 6·4; N, 6·6%). When this salt was heated at 150° until decomposition was complete, the preceding mono-amide, m. p. and mixed m. p. 307—310° (decomp.), was obtained, together with a *product*, rhombs (from ethanol), m. p. 214—216° (Found : C, 77·5; H, 5·4; N, 5·4. $C_{18}H_{15}O_2N$ requires C, 77·9; H, 5·4; N, 5·1%). The infra-red spectrum of this product showed the following bands; 3220 cm.$^{-1}$, bonded O–H or N–H; 1690 cm.$^{-1}$ (strong), C=N in imino-ether; 1650 cm.$^{-1}$, C=N; 1615 and 1515 cm.$^{-1}$, aromatic C=C; 1380 and 1360 cm.$^{-1}$, CMe_2 group; 1225 and 1125 cm.$^{-1}$, C–O. It may possibly be a cyclic imide formed from the phenanthraquinol diether by the loss of methylacrylonitrile, but the amount isolated was too small for further investigation. It may be noted that phenanthraquinone is the only 1 : 2-quinone which we have examined, and cyclisation of its reaction products may be possible.

Attempted Reaction with Anthraquinone.—Because of the low solubility of the quinone a solution of 0·05 mole of quinone in 500 ml. of toluene had to be used. Most of the quinone

separated unchanged when the reaction mixture was cooled, and, after concentration, the total recovery was 98%. A 79% yield of tetramethylsuccinonitrile was also obtained and no phenolic product could be detected.

The Reaction of αα'-Azoisobutyronitrile with a Mixture of p-Xyloquinone and the Corresponding Quinol.—A mixture of the azo-compound (14·3 g.), the quinone (9·4 g.) and the quinol (2·05 g.) was heated in toluene (85 ml.) for 30 minutes. Toluene, tetramethylsuccinonitrile (46%), and unchanged quinone were removed by steam-distillation, and the residue was extracted with ether and washed first with 5% aqueous potassium hydroxide and then with a similar solution containing sodium dithionite. After removal of the solvent the reddish residue (3·95 g.) was chromatographed on activated alumina (70 g.) with benzene. The first 200 c.c. of solution gave short prisms [from light petroleum (b. p. 40—60°)], m. p. 224° (0·36 g.), of the *dilactone* of 3 : 6-di-(2-carboxy-2-propyl)-2 : 5-dimethylquinol (Found: C, 70·0; H, 6·7%; *M*, 249. $C_{16}H_{18}O_4$ requires C, 70·0; H, 6·6%; *M*, 274). The infra-red spectrum showed the following bands: 1800 cm.$^{-1}$, C=O in βγ-unsaturated five-membered lactone ring; 1505 cm.$^{-1}$, aromatic C=C; 1390 and 1370 cm.$^{-1}$, CMe_2 group; 1215 cm.$^{-1}$, C–O in lactone. The characteristic absorption band at 3030—3070 cm.$^{-1}$, indicative of an aromatic C–H group, was absent from the spectrum in CCl_4, showing that the benzene ring was fully substituted. Again the band at 1110 cm.$^{-1}$, indicative of O–C, when the carbon is fully saturated as in ether, was absent.

From the mother liquor and the succeeding fractions of the eluate there was isolated 2-(2-carboxy-2-propyl)-4-(2-cyano-2-propoxy)-3 : 6-dimethylphenol lactone, m. p. and mixed m. p. 105—106°. The alkaline extract on acidification yielded an oil (4·55 g.) from which, by crystallisation from 50% ethanol, there was separated 4-(2-cyano-2-propoxy)-2 : 5-dimethylphenol, m. p. and mixed m. p. 110—111°.

The Determinations of Oxidation–Reduction Potentials.—The measurements were made with a Tinsley D.C. potentiometer, type 3184. The cell was a 400-c.c. deep Pyrex beaker immersed in a thermostat at 25° ± 0·1°. It was fitted with a waxed cork through which passed (i) a bright and a platinised platinum electrode, (ii) a salt bridge leading to a saturated calomel electrode, (iii) the tip of a burette containing 1% titanous chloride in N-hydrochloric acid, (iv) a mercury-sealed stirrer, and (v) inlet and exit tubes for oxygen-free nitrogen which had previously been

TABLE 3. *Oxidation–reduction potentials in 80% ethanol containing N-hydrogen chloride.*

Quinone	Differences, mv. 20% redn.	80% redn.	E_0, v.	E_0, average, v.
2 : 5-Di-*tert.*-butyl-1 : 4-benzoquinone...	14	23	+0·553	+0·5535
	17	23	0·554	
2 : 6-Dimethyl-1 : 4-benzoquinone	17	19	+0·600	+0·600
	17	19	0·600	
2-Methyl-1 : 4-naphthaquinone	15	17	+0·4225	+0·4225
	23	19	0·4225	

passed through a similar solvent to that contained in the cell. All the measurements were made in carefully purified 80% ethanol containing N-hydrogen chloride, and by using a hydrogen electrode to determine the potentials of each solvent it was possible to correct all oxidation–reduction potentials to the standard scale. For example, check measurements with *p*-benzoquinone and 2 : 5-diethoxy-1 : 4-benzoquinone gave 0·712 and 0·4735 v, respectively [Conant and Fieser (*J. Amer. Chem. Soc.*, 1922, **44**, 2480; 1924, **46**, 1858) give 0·712 and 0·474 v].

Solutions (0·001—0·003M) of freshly purified quinones in buffer (200 ml.) were used, and after each addition of the reducing agent the system was left until both the bright and the platinised platinum electrode gave the same potential value (5—10 minutes). The normal potentials were calculated by interpolation of the titration curves for 50% reduction. As an indication of the gradients of these curves Table 3 gives the potential differences at 20% and 80% reduction. Difficulties arising from slow reduction have already been noted (p. 4668). The other potentials given in Table 1 are those by Conant and Fieser (*J. Amer. Chem. Soc.*, 1923, **45**, 2208; 1924, **46**, 858). The redox potential of 2-methyl-1 : 4-naphthaquinone had not previously been determined in this solvent.

Microanalyses are by Drs. Weiler and Strauss.

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