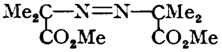
357. *Properties and Reactions of Free Alkyl Radicals in Solution. Part I. Some Reactions of 2-Cyano- and 2-Carbomethoxy-2-propyl Radicals with Quinones.*

By A. F. Bickel and W. A. Waters.

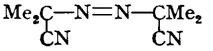
The free radicals $Me_2\dot{C}{\cdot}CO_2Me$ and $Me_2\dot{C}{\cdot}CN$ can be formed by the thermal decomposition of dimethyl αα'-azo*iso*butyrate (I) and αα'-azo*iso*butyronitrile (II) in boiling toluene. Their reactions with quinones have been studied with the object of gaining direct information concerning the natures of the chain-stopping and rate-retarding actions of quinones in olefin polymerization. It is found that *p*-benzoquinone and chloranil react with these tertiary alkyl radicals to give both mono- and di-ethers of quinol and tetrachloroquinol respectively, whilst 2-methyl-1 : 4-naphthaquinone and some αβ-unsaturated aldehydes and ketones do not appear to react. The significance of this work is discussed in connection with the free-radical polymerization of olefins.

The thermal decomposition, in solution, of aliphatic azo-compounds such as dimethyl αα'-azo*iso*butyrate (I) and αα'-azo*iso*butyronitrile (II) yields free tertiary alkyl radicals. These radicals are capable of initiating polymerization and are very similar in structure to the growing radicals which are concerned in the polymerization of vinyl compounds (Bickel and Waters, *Rec. Trav. chim.*, 1950, **69**, 312, in the press). The radical (III; A = H) for instance can be regarded as the end group of a growing poly(methyl methylacrylate) radical, and similarly the radical (IV; A = H) is the prototype of the growing chain of poly(methylacrylonitrile).



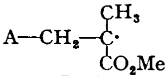
$$Me_2\underset{CO_2Me}{C}{-}N{=}N{-}\underset{CO_2Me}{C}Me_2$$

(I.)



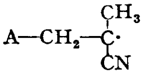
$$Me_2\underset{CN}{C}{-}N{=}N{-}\underset{CN}{C}Me_2$$

(II.)



$$A{-}CH_2{-}\overset{CH_3}{\underset{CO_2Me}{C}}\cdot$$

(III.)



$$A{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}\cdot$$

(IV.)

When polymerization processes themselves are studied the carbon chain, represented by A in (III) and (IV), is so large that the many chemical reactions which may be concerned in chain-terminating processes have, as yet, been investigated only by kinetic methods. This physico-chemical approach is incapable of revealing more than the activation energies and probabilities of occurrence of reactions of different types, *e.g.*, radical combination, disproportionation of two radicals, chain transfer; it can give very little precise information about the structural arrangement at the chain-terminating end of a macromolecule. Information of this character is particularly important in the study of polymerizations which have been controlled deliberately by the addition of " radical inhibitors " or " retarding agents " such as quinones or aromatic nitro-compounds or have been modified by the admixture of chain-transfer agents or co-polymerizing substances. The spectroscopic study of these modified macromolecules gives, at the best, an uncertain impression of the structures of their end groups since the modifying group composes such a small part of the whole molecule that distinctive absorption bands appear only with low intensity. Moreover, it may be impossible to discriminate between isomeric structures, or between mono- and di-substituted products. Again, unless a tedious separation of fractions of different molecular-weight range has previously been carried out, it may well be that some part of the modifying agent remains chemically intact though mechanically entangled in the polymer.

However, if it can be presumed that the simple radicals (III) and (IV), where A = H, will behave in a very similar way to the analogous macromolecular radicals, then the structures of the end groups of macromolecules can be deduced by the exact methods of experimental organic chemistry. We have already shown (Bickel and Waters, *loc. cit.*) that the decomposition of aliphatic azo-compounds in the inert solvents benzene and toluene indicates that the termination of radicals of type (III) proceeds by combination and disproportionation processes in comparable amounts, but that the latter process is much less probable with radicals of type (IV).

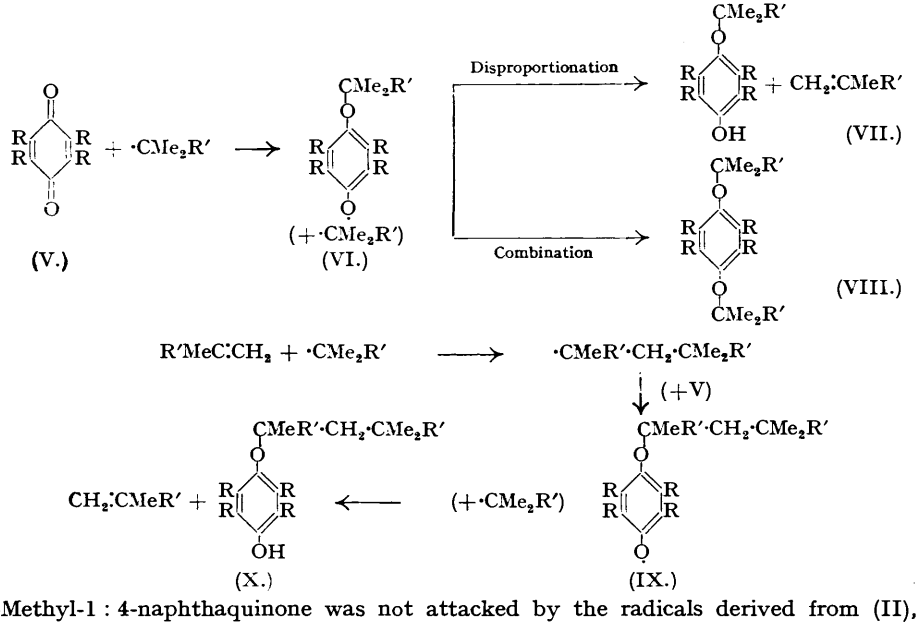
Knowing the products which can be formed by the thermal decompositions of (I) and (II) themselves, we have now proceeded to examine the substances which they yield when decomposed in boiling toluene, in the presence of *p*-benzoquinone and similar compounds, and we have been successful in isolating and characterizing crystalline reaction products which clearly indicate the course of free radical–inhibitor molecule interactions. The success of our method is such that we propose to develop it further for the elucidation of other problems concerning free-radical polymerization processes.

When dimethyl αα′-azo*iso*butyrate (I) is decomposed in boiling toluene with an equimolar proportion of *p*-benzoquinone (V; R = H), quinol mono-(2-carboxymethyl-2-propyl) ether (VII; R = H, R′ = CO_2Me) and quinol di-(2-carboxymethyl-2-propyl) ether (VIII; R = H, R′ = CO_2Me) are formed in yields of 46 and 27% respectively. The di-ether could be isolated as such from the reaction mixture, but extraction of the mono-ether with alkali results in its hydrolysis to the corresponding acid. This compound on methylation with diazomethane yields the methyl ether of (VII; R = H, R′ = CO_2Me), whilst on oxidation with ferric chloride *p*-benzoquinone is formed. These reactions clearly prove the structure of (VII; R = H, R′ = CO_2H) and exclude the possibility of substitution by the radical in the benzene ring.

When αα′-azo*iso*butyronitrile (II) is used, the quinol mono-ether (VII; R = H, R′ = CN) is again obtained in a yield of 40%, but the di-ether is formed in a yield of 10% only. Furthermore the benzoate of a compound, probably (X), could be isolated in a 3% yield.

When (II) is allowed to decompose in boiling toluene containing half an equivalent of chloranil (V; R = Cl), there is no abstraction of chlorine atoms from the latter. Again both the mono- (VII; R = Cl, R′ = CN) and the di-ether (VIII; R = Cl, R′ = CN) of tetrachloroquinol are formed, showing that the radical attack is upon the oxygen atoms only, but in this case the yield of the di-ether (47%) is much larger than that of the mono- (17%).

The formation of all these compounds is satisfactorily explained by assuming the primary production of semiquinone radicals of type (VI) or (IX). These will either combine or disproportionate with the tertiary alkyl radicals of type (III) and (IV). The methyl methylacrylate or methylacrylonitrile formed in the disproportionation reaction is not found as such, but is probably incorporated in neutral material of high molecular weight which is formed to the extent of 20—40% in these reactions.



(V.) (VI.) (VII.) (VIII.) (X.) (IX.)

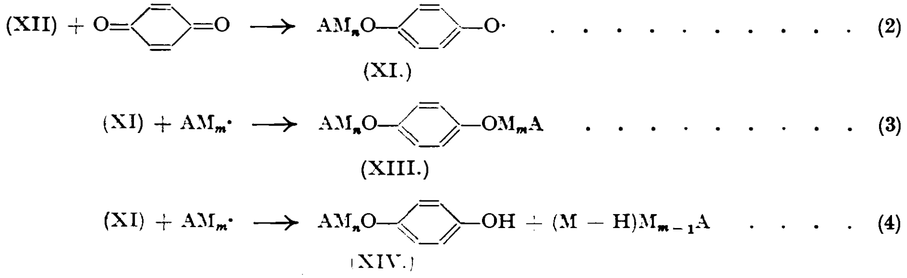
2-Methyl-1 : 4-naphthaquinone was not attacked by the radicals derived from (II), and neither were mesityl oxide and cinnamic aldehyde, both of which contain the reactive catio-enoid system C=C—C=O to which much of the characteristic chemical reactivity of quinones has been ascribed. Finally it was established that the radicals (III; A = H) do not react with quinol.

It is significant therefore that the free radicals (III) and (IV) (A = H) have a sufficient degree of reactivity to attack only highly active quinones. An explanation for the relative inhibiting actions of different quinones can therefore be sought by extending the present work to the examination of the products obtainable from a series of substituted quinones.

Our work does not confirm several of the speculations concerning the modes of action of quinones as inhibitors, retarders, or chain-transfer agents in the chain polymerization of olefins.

The nuclear substitution of quinones, to give quinonoid products, has been proposed by Price (" Reactions at Carbon–Carbon Double Bonds," Interscience, New York, 1946, pp. 85—87), and others, who have based their judgments on the behaviour of such intensely reactive free radicals as methyl and phenyl. Thus benzenediazonium chloride reacts with *p*-benzoquinone to give 2-phenylbenzoquinone (Kvalnes, *J. Amer. Chem. Soc.*, 1934, **56**, 2478), whereas diacyl peroxides of both the aliphatic and the aromatic series react with 2-methyl-1 : 4-naphthaquinone to give 3-substituted products (Fieser and Oxford, *J. Amer. Chem. Soc.*, 1942, **64**, 2060). In contrast to this it has long been known that the resonance-stabilised radical triphenylmethyl combines with *p*-benzoquinone to give the bistriphenylmethyl ether of quinol. Our tertiary radicals (III) and (IV) (A = H), which closely resemble the corresponding macroradicals, behave similarly in yielding quinol mono- and di-ethers. It would appear therefore, that Price's explanation of the manner of retardation by quinones cannot be correct in the case of tertiary macro-radicals. Instead the mechanism must involve semiquinone radicals of type (XI), which may combine or disproportionate with radicals (XII) to yield (XIII) and (XIV).

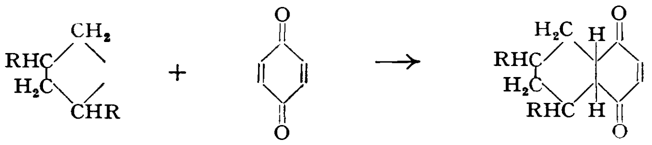
$$AM_n\cdot + M \longrightarrow AM_{n+1}^{\cdot} \quad \text{(XII.)} \qquad (1)$$



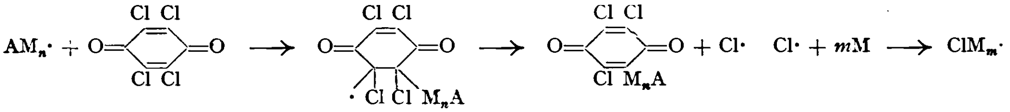
A = initiator fragment. M = monomer.
n and *m* = number of monomer units in chain.

When the reaction (2) between radical and quinone is relatively slow compared to the propagation reaction (1), the quinone may be classed as a retarding agent. In these circumstances the combination mechanism (3) would lead to polymers possessing one di-ether system per chain, whilst the disproportionation reaction would result in half the molecules containing a phenolic hydroxyl group. Reactions (2—4) represent retardation by *p*-benzoquinone of a polymerization involving mono-radicals, *e.g.*, those initiated by radicals produced by decomposition of benzoyl peroxide or azo-compounds. In this kind of polymerization complete inhibition is unknown, in other words the propagation (1) appears to be able to compete more or less effectively with the radical-inhibitor reaction (2).

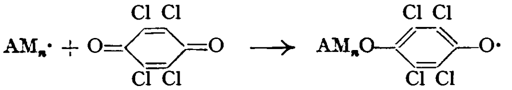
When, as in thermal and photo-polymerizations, a di-radical is the chain carrier, complete inhibition is known to occur in several instances (Foord, *J.*, 1940, 48; Goldfinger, Skeist, and Mark, *J. Physical Chem.*, 1943, **47**, 578; Burnett and Melville, *Proc. Roy. Soc.*, *A*, 1947, **189**, 456; Melville and Watson, *Trans. Faraday Soc.*, 1948, **44**, 886). In these cases, however, it seems probable that the inhibition reaction is of a type different from that outlined in (1—4) above and it may involve a very fast modified Diels–Alder reaction of the quinone with a dimeric di-radical produced by the initiation reaction. The structure of this product, however, has never been established with certainty (Kern and Feuerstein, *J. prakt. Chem.*, 1941, **158**, 186; Melville and Watson, *loc. cit.*). It is surprising that the photo-polymerization of methyl methylacrylate in the presence of *p*-benzoquinone, which has been investigated by Mackay and Melville (*Trans. Faraday Soc.*, 1950, **46**, 63), shows retardation instead of inhibition. This they attributed to an unsuitable configuration of the dimeric di-radical caused by the presence of the methyl groups. Our reactions (2—4) will probably be valid for this retardation process.



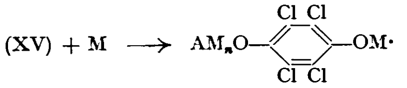
The formation from chloranil of both the mono- and the di-substituted ethers of tetrachloroquinol has an important bearing on polymer chemistry. It is known that the addition of chloranil to a polymerizing system may result in a polymer of considerably lower molecular weight than is normal, though the rate of polymerization is not greatly affected. In other words chloranil acts as a chain-transfer agent and not as an inhibitor. It has been suggested (Price, *loc. cit.*) that in these cases chloranil behaves like carbon tetrachloride by providing chlorine atoms to start new radical chains:



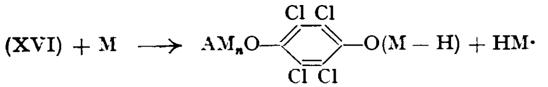
Evidently this mechanism is incorrect, since the radicals (IV; A = H) react with chloranil at the oxygen atoms only, and the reaction process (5) must therefore proceed *via* a semiquinol radical (XV). To explain the chain transfer we suggest that (XV) can add on monomer to give a radical (XVI), which in turn may react with monomer to yield (XVII) and a new initiating radical. This scheme is still mainly hypothetical, but it is supported by the fact that radicals of type (XVI) seem to react rather with unsaturated molecules than with radicals $AM_n\cdot$. This follows from work by Breitenbach *et al.* (*Ber.*, **1943**, **76**, 272, 1088), who have shown that the polymers of low molecular weight, obtained on polymerization of styrene with benzoyl peroxide in the presence of chloranil, have the approximate composition $(C_8H_8 + C_6Cl_4O_2)_n$. This co-polymerization of monomer and inhibitor can be represented as (8—9) below.



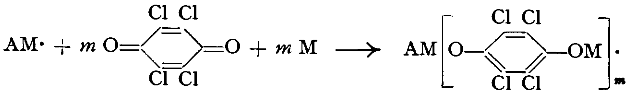
(XV.) . . . (5)



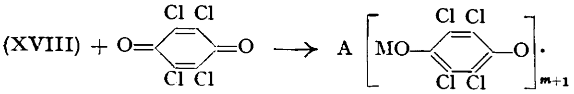
(XVI.) . . . . . . (6)



(XVII.) . . (7)

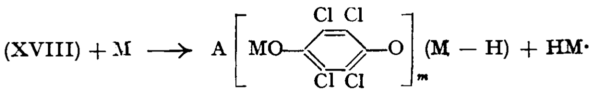


(XVIII.) . (8)



(XIX.) . (9)

The co-polymer chains should then be terminated mainly (*a*) by radicals of type (XVIII) reacting with monomer to yield (according to 10) products of type (XX) together with an initiating radical, and (*b*) to a small extent by radicals of type (XIX) reacting with radicals $AM_n\cdot$ to yield either, by disproportionation, a polymer with a phenolic hydroxyl end group or else a combination product.



(XX.)

. . . . (10)

There are indications that *p*-benzoquinone may also be co-polymerized by some monomers. A reaction of this kind would account for the greatly increased rate of photo-polymerization of butyl acrylate in the presence of *p*-benzoquinone (Melville and Bickel, *Trans. Faraday Soc.*, **1949**, **45**, 1049).

Our observation that quinol, like phenol (Bickel and Waters, *loc. cit.*), did not react with the 2-carbomethoxy-2-propyl radical is in accord with the findings of Breitenbach, Springer, and Horeischy (*Ber.*, **1938**, **71**, **1438**) who stated that quinol does not inhibit the polymerization of styrene in the complete absence of oxygen.

EXPERIMENTAL.

*Reaction of Dimethyl αα′-Azo*iso*butyrate with* p-*Benzoquinone*.—A solution of dimethyl αα′-azo*iso*butyrate (9·2 g.) and *p*-benzoquinone (2·16 g.) in toluene (50 ml.) was heated to about 100° in such a manner as to produce a steady evolution of nitrogen (30 minutes) and then refluxed for 1 hour. To the cold red solution was added an aqueous solution of sodium sulphite (2 g.). Then it was extracted with a solution of sodium hydroxide (2·5 g.) in water.

The toluene layer was subjected to fractional distillation and fractions, b. p. 100—115° and 200—220° (2·5 g.), were collected. The first fraction was hydrolysed and was found to contain 0·5 g. of methyl *iso*butyrate. The second consisted of almost pure dimethyl tetramethylsuccinate. The residue on distillation in a high vacuum gave an orange oil (3·2 g.), b. p. 120—140°/0·1 mm. This product was mixed with potassium hydroxide (2 g.), ethanol (10 ml.), and water (10 ml.), and the resulting solution was refluxed for 16 hours. The ethanol was distilled off, the residue acidified, and the dark brown oil that separated was dissolved in ether. Evaporation of the ether yielded a slowly crystallizing oil. Recrystallization from ethyl acetate gave *quinol di-(2-carboxy-2-propyl) ether* (VIII; R = H, R′ = CO_2H) (1·5 g., 27% calc. on quinone), m. p. 182—186°. Further recrystallization raised the m. p. to 186—188° (Found: C, 59·3; H, 6·4. $C_{14}H_{18}O_6$ requires C, 59·6; H, 6·4%). The derived *di*-p-*nitrobenzyl* ester, recrystallized from 70% ethanol, had m. p. 103—104° (Found: C, 60·9; H, 4·8; N, 5·3. $C_{28}H_{28}O_{10}N_2$ requires C, 60·9; H, 5·1; N, 5·1%).

The aqueous layer was acidified and extracted with ether. Evaporation of the ether gave a brown crystalline residue (1·8 g., 46% calc. on quinone). After recrystallization from ethyl acetate the m. p. of *quinol mono-(2-carboxy-2-propyl) ether* (VII; R = H, R′ = CO_2H) was 161·5—162·5° (Found: C, 61·3; H, 6·2. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·2%). The *amide* of (VII, R = H, R′ = CO_2H), prepared in the usual manner, had m. p. 173—173·5° after recrystallization from water (Found: C, 61·8; H, 7·0; N, 6·8. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·7; N, 7·2%). The compound (VII; R = H, R′ = CO_2H) gave a *dibenzoyl* derivative which was recrystallized 3 times from ethanol and then had m. p. 113—114·5° (Found: C, 70·9; H, 5·2. $C_{24}H_{20}O_6$ requires C, 71·3; H, 5·0%). This product was insoluble in sodium hydroxide solution so that evidently the carboxyl group as well as the phenolic hydroxyl group must have been involved in the reaction. *Quinol methyl (2-carbomethoxy-2-propyl) ether* was obtained by treating (VII; R = H, R′ = CO_2H), suspended in ether, with an excess of ethereal diazomethane solution. The ether was evaporated and the residue distilled in a high vacuum. The almost colourless liquid boiled at 120—124°/0·75 mm. (Found: C, 64·6; H, 7·6; OMe, 28·4. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·2; OMe, 27·7%). Oxidation of (VII; R = H, R′ = CO_2H) with a large excess of ferric chloride at 100° yielded *p*-benzoquinone, which was isolated in 50% yield by steam-distillation and extraction, with ether, of the distillate. The mixed m. p. with pure *p*-benzoquinone showed no depression. The same yield of mono-ether may be obtained by extraction of the reaction mixture with alkali only. It is advisable, however, to reduce a small amount of unreacted *p*-benzoquinone first by adding some sodium sulphite.

The same yields of products were obtained when equimolar quantities of azo-compound and *p*-benzoquinone were used.

*Reaction of αα′-Azo*iso*butyronitrile with* p-*Benzoquinone*.—A solution of αα′-azo*iso*butyronitrile (16·4 g.) and *p*-benzoquinone (10·8 g.) in toluene (100 ml.) was refluxed for 30 minutes. When cold, the dark red solution was extracted with an aqueous solution of potassium hydroxide (11 g.) and sodium sulphite (2 g.).

The toluene solution was distilled with steam and from the distillate 3·5 g. of tetramethylsuccinonitrile were isolated. The residue from the steam-distillation was a brown tarry mass. Recrystallization from ethanol gave *quinol di-(2-cyano-2-propyl) ether* (VIII; R = H, R′ = CN) (2·5 g., 10% calc. on quinone), m. p. 123—126°. Recrystallization from acetone raised the m. p. to 128—129° (Found: C, 68·8; H, 6·6; N, 11·8. $C_{14}H_{16}O_2N_2$ requires C, 68·8; H, 6·6; N, 11·5%). The corresponding acid was obtained by alkaline hydrolysis of the dinitrile and after recrystallization from ethyl acetate had m. p. 186—188°. A mixed m. p. with the di-acid, obtained from the experiment with dimethyl αα′-azo*iso*butyrate showed no depression.

The aqueous extract was acidified with dilute sulphuric acid and the resulting oil (10·0 g., 56·5% calc. on quinone) was extracted with ether. Distillation of this oil in a high vacuum produced *quinol mono-(2-cyano-2-propyl) ether* (VII; R = H, R′ = CN) (7·15 g., 40·5% calc. on quinone), b. p. 129—135°/0·08 mm. When subjected to alkaline hydrolysis this oil gave an acid, m. p. 161·5—162·5° after recrystallization from ethyl acetate. A mixed m. p. with the mono-ether prepared from the experiment with dimethyl αα′-azo*iso*butyrate showed no depression. Benzoylation of the nitrile (VII; R = H, R′ = CN) gave a *monobenzoate*, m. p. 86·5—87·5° after recrystallization from ethanol (Found: C, 72·6; H, 5·5; N, 4·8. $C_{17}H_{15}O_3N$ requires C, 72·6; H, 5·4; N, 5·0%). In another experiment the crude product (10·0 g.) obtained by acidifying the aqueous layer was benzoylated with 20 ml. of benzoyl chloride and 150 ml. of 10% sodium hydroxide. The crude benzoates on recrystallization from ethanol gave the benzoate, m. p. 86·5—87·5° (8·0 g.) (see above). The mother-liquor on concentration yielded the *benzoate*, m. p. 117—121° (1·0 g., 3% calc. on quinone) of (X; R = H, R′ = CN). Further recrystallization from ethanol raised the m. p. to 123—124° (Found: C, 72·3; H, 5·5; N, 7·9. $C_{21}H_{20}O_3N_2$ requires C, 72·4; H, 5·8; N, 8·0%).

*Reaction of αα′-Azo*iso*butyronitrile with Chloranil*.—A solution of αα′-azo*iso*butyronitrile (8·2 g.) and chloranil (6·15 g.; recrystallized from chlorobenzene) in chlorobenzene (150 ml.) was heated at 100° until evolution of nitrogen stopped (30 minutes) and then refluxed for 5 minutes. The cold light-brown solution was extracted with an aqueous solution of sodium hydroxide (2·5 g.) and sodium sulphite (0·5 g.).

The chlorobenzene layer was distilled with steam and yielded tetramethylsuccinonitrile (3·0 g.). The residue was collected by filtration and dried (6·4 g.). Recrystallization from a large volume of ethanol gave *tetrachloroquinol di-(2-cyano-2-propyl) ether* (VIII; R = Cl, R′ = CN), m. p. 162—166° (4·5 g., 47% calc. on quinone), raised to 166—167° by recrystallization from acetone (Found: C, 44·2; H, 3·3; N, 7·2; Cl, 36·2. $C_{14}H_{12}O_2N_2Cl_4$ requires C, 44·0; H, 3·2; N, 7·3; Cl, 37·1%).

After addition of an excess of dilute sulphuric acid the aqueous layer yielded a crystalline precipitate. *Tetrachloroquinol mono-(2-cyano-2-propyl) ether* (VII; R = Cl, R′ = CN) was filtered off and dried (1·35 g., 17% calc. on quinone). After recrystallization from ethanol, the m. p. was 135° (decomp.) (Found: C, 38·3; H, 2·2; N, 4·4; Cl, 45·6. $C_{10}H_7O_2NCl_4$ requires C, 38·1; H, 2·2; N, 4·5; Cl, 45·0%). The *benzoate* (of VII; R = Cl, R′ = CN), recrystallized from ethanol, had m. p. 130·5—131·5° (Found: C, 49·1; H, 2·7; N, 3·0; Cl, 33·3. $C_{17}H_{11}O_3NCl_4$ requires C, 48·7; H, 2·7; N, 3·3; Cl, 33·8%).

*Reaction of Dimethyl αα′-Azo*isobutyrate *with Quinol.*—A solution of dimethyl αα′-azo*iso*butyrate (30·8 g.) and quinol (33·55 g.) in ethanol (120 ml.) was heated under reflux for 6 hours. The solvent was removed by distillation and the residue, dissolved in ether, was extracted with a solution of sodium hydroxide (30 g.) and sodium suphite (5 g.) in water (300 ml.). On fractional distillation the ethereal solution yielded fractions, b. p. 215—230° (13·5 g., 51%), and 180—190°/27 mm. (5·5 g., 21%). Almost the same quantities were obtained when (I) was decomposed in benzene or phenol as solvents (Bickel and Waters, *loc. cit.*). The aqueous solution was acidified and extracted with ether, yielding quinol, m. p. 168—170° (32·48 g., 97%).

One of the authors (A. F. B.) is indebted to the Koninklijke Shell-Laboratorium, Amsterdam, for the opportunity to carry out this investigation.

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[*Received, April 3rd*, 1950.]