228. *Quinones. Part II. The Addition of Mercapto-acids to Benzoquinones and* 1 : 4-*Naphthaquinone.*

By A. Blackhall and R. H. Thomson.

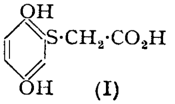
The reaction of thioglycollic acid with equimolecular amounts of benzoquinone, toluquinone, *m*- and *p*-xyloquinone, and 1 : 4-naphthaquinone in aqueous suspension has been studied. In all cases, except possibly toluquinone, all the reactive positions are attacked. β-Mercaptopropionic acid is equally reactive, yielding the quinol (II; $n = 2$) with benzoquinone, and the quinones (IV; $R = -S\cdot[CH_2]_2\cdot CO_2H$, $R' = H$, and $R = R' = -S\cdot[CH_2]_2\cdot CO_2H$) with 1 : 4-naphthaquinone. γ-Mercaptobutyric acid formed only a di-addition product with benzoquinone under the same conditions, as did propane-1-thiol. Thiophenol gave a mixture of mono- and di-phenylthiobenzoquinone.

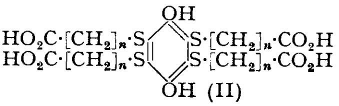
In connection with other work, we recently attempted to prepare 2-carboxymethylthioquinol (I), by condensing 2-chlorobenzoquinone with thioglycollic (mercaptoacetic) acid. Reaction in alcohol containing pyridine gave a mixture, but in aqueous suspension at room temperature a small amount of a colourless compound, m. p. 276° (decomp.), was obtained. However this substance, which we also obtained by interaction of equimolecular amounts of benzoquinone and thioglycollic acid under the same conditions, was not (I) but 2 : 3 : 5 : 6-tetra(carboxymethylthio)quinol (II; $n = 1$), previously obtained by Schubert (*J. Amer. Chem. Soc.*, 1947, **69**, 712), who established its structure by its preparation from chloranil and thioglycollic acid. This tetra-addition product is formed rapidly in aqueous suspension at room temperature, and *ca.* 18% of the thioglycollic acid is converted into it even when added slowly to the quinone. The reaction is not inhibited by the presence of picric acid. Although the addition of thiols to quinones appears to proceed by a radical mechanism in certain cases (Thomson, *J. Org. Chem.*, 1951, **16**, 1082, and Part III, in preparation) the addition of thioglycollic acid to benzoquinone is almost certainly an ionic reaction, and proceeds by alternate addition and oxidation, four molecules of benzoquinone being required to produce one molecule of (II; $n = 1$) (Schubert, *loc. cit.*, isolated 63% of quinol).

The addition of thioglycollic acid to equimolecular quantities of toluquinone, *m*- and *p*-xyloquinones, and 1 : 4-naphthaquinone in aqueous suspension is very similar. In all cases, except possibly toluquinone, the thioglycollic acid attacks all the free reactive positions giving the corresponding quinols. Both mono- and di-addition products were isolated from the reaction with naphthaquinone. This has not been observed before in the naphthaquinone series except in the addition of methane- and ethane-thiol (Miyaki, Ikeda, and Mizuno, *J. Pharm. Soc. Jap.*, 1951, **71**, 643), where a large excess of thiol was used.

In the addition of thioglycollic acid to toluquinone the products were obtained as an oil, and attempts to obtain solid derivatives under mild conditions failed. By heating at

190°/1 mm. toluquinol was removed, and a solid residue obtained which yielded two compounds. The failure of these compounds to react with diazomethane and acetyl chloride, and their desulphurisation with Raney nickel to toluquinol diacetate, established the structures of the two substances as the isomeric dilactones (VI). Failure to isolate a tri-addition product from the reaction mixture does not exclude its formation, since it was formed by interaction of trichlorotoluquinone and thioglycollic acid, and was found to be extremely soluble in water and very difficult to extract with ether. It was necessary to make the aqueous solution strongly acid, and ether extraction then afforded the monolactone. We were not able to isolate the tricarboxylic acid. The addition of thioglycollic acid to toluquinone in benzene solution gave a dark red oil, which could not be purified.


(I)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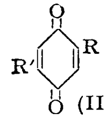
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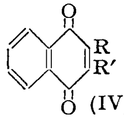
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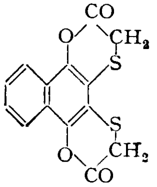
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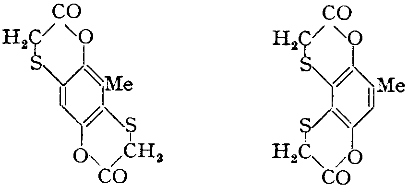
(VI)

The crude product arising from reaction of thioglycollic acid with 1 : 4-naphthaquinone could not be purified, because of its sensitivity to aerial oxidation, but oxidation with chromic acid yielded a mixture of quinones, from which only 2-carboxymethylthio-1 : 4-naphthaquinone (IV; R = $S{\cdot}CH_2{\cdot}CO_2H$, R′ = H) could be isolated. Its structure was established by replacement of the carboxymethylthio-group by aniline, to give 2-anilino-1 : 4-naphthaquinone. With acetic anhydride the crude quinol mixture afforded the dilactone (V), which was also prepared from the quinol obtained by reaction of 2 : 3-dibromo-1 : 4-naphthaquinone and thioglycollic acid.

The remarkable reactivity of thioglycollic acid has been noted previously by Fieser and Turner (*J. Amer. Chem. Soc.*, 1947, **69**, 2335) who found that, in contrast to most other addition reagents, it reacted readily with 2-methyl-1 : 4-naphthaquinone. In the case of 2-*tert.*-butyl-1 : 4-naphthaquinone, however, steric hindrance is too great and we could detect no reaction after 12 hours' refluxing in alcohol or 28 days' storage at room temperature. Attempts to add thioglycollic acid to dibenzylideneacetone also failed.

The reaction of thioglycollic acid with benzoquinone is not unique. Under the same conditions (*i.e.*, using equimolecular amounts) β-mercaptopropionic acid also gives rise to a tetra-addition product (II; $n = 2$), and with 1 : 4-naphthaquinone mono- and di-addition products were again obtained. Oxidation of the last two gave (IV; R = $S{\cdot}[CH_2]_2{\cdot}CO_2H$, R′ = H, and R = R′ = $S{\cdot}[CH_2]_2{\cdot}CO_2H$ respectively). Addition of γ-mercaptobutyric acid to benzoquinone however yielded only a 2 : 5(?)-disubstituted quinone (III; R = R′ = $S{\cdot}[CH_2]_3{\cdot}CO_2H$), and 2 : 3 : 5 : 6-tetra-(3-carboxypropylthio)-quinol (II; $n = 3$) (prepared from chloranil) was not found. (III; R = R′ = $S{\cdot}[CH_2]_3{\cdot}CO_2H$) could not be obtained from 2 : 5-dichlorobenzoquinone and γ-mercaptobutyric acid, mixtures resulting, but the other quinone acids mentioned above were readily prepared by this method (see Experimental).

For comparison with the mercapto-acids the addition of thiophenol and propane-1-thiol (in equimolecular amounts) to benzoquinone was examined. Reaction was rapid at room temperature in aqueous suspension, thiophenol giving a mixture of 2 : 5- (13·5%) and 2 : 6-diphenylthiobenzoquinone (1%) and 2-phenylthiobenzoquinone (19%). Neither the tri- nor the tetra-substituted quinone was detected. Under different conditions (3 moles of quinone to two of thiophenol, in hot acetic acid) Dimroth, Kraft, and Aichinger (*Annalen*, 1940, **545**, 124) obtained mono-, di-, and tri-phenylthiobenzoquinones. Propane-1-thiol afforded only 2 : 5-dipropylthiobenzoquinone (III; R = R′ = SPr^n). This was also obtained by reaction of 2 : 5-dichloroquinone with the potassium derivative of the thiol but we failed to obtain tetrapropylthiobenzoquinone by this method (cf. Tjepkema, *Rec. Trav. chim.*, 1952, **71**, 853).

Cunneen (*J.*, 1947, 36, 134) has shown that the ease of addition of thiols to olefins is roughly parallel to their acidities; in particular he found thioglycollic acid to be more reactive than thiophenol. Our results confirm this general trend. The SH acidity of the mercapto-acids should diminish with increasing separation of the polar groups, and electrostatic interaction is probably negligible in γ-mercaptobutyric acid. In the reactions with benzoquinone γ-mercaptobutyric acid is less reactive than β-mercaptopropionic and thioglycollic acids and is comparable to propane-1-thiol. Thiophenol is slightly more reactive than γ-mercaptobutyric acid. These reactions are also affected by the nature of the solvent. This was observed by Dimroth *et al.* (*loc. cit.*) in the addition of thiophenol to benzoquinone, and in the case of thioglycollic acid reaction in chloroform gives two isomeric di-addition products (Gebauer-Fuelnegg and Jarsch, *J. Amer. Chem. Soc.*, 1930, **52**, 2451), whereas Snell and Weissberger (*ibid.*, 1939, **61**, 450) could only isolate a mono-addition product from the reaction in 95% alcohol.

EXPERIMENTAL

2 : 3 : 5 : 6-*Tetra(carboxymethylthio)quinol*.—To finely powdered 2-chlorobenzoquinone (1 g.) suspended in water (60 c.c.), thioglycollic acid (0·483 c.c.) was added during 5 minutes with stirring. Stirring was continued till dissolution was complete and the solution was then ether extracted (twice), and the extract dried ($MgSO_4$) and evaporated, yielding a dark oily residue. Repeated crystallisation from water gave needles, m. p. 276° (decomp.) (Found : C, 35·9; H, 3·2; S, 27·3. Calc. for $C_{14}H_{14}O_{10}S_4$: C, 35·8; H, 3·0; S, 27·2%). Schubert (*loc. cit.*) reported m. p. 288° (decomp.).

3 : 6- *and* 5 : 6-*Di(carboxymethylthio)toluquinol Dilactones* (VI).—A suspension of finely powdered toluquinone (10 g.) in water (200 c.c.) was treated with thioglycollic acid (5·7 c.c.), and stirred till a red solution was obtained. The solution became colourless overnight, and was then extracted twice with ether. The extracts were dried ($MgSO_4$) and evaporated. The residual yellow oil was heated at 190°/1 mm. to remove toluquinol (21% recovered). Fractional crystallisation of the solid residue from acetone yielded two *dilactones*, (*a*) m. p. 205—206° (placed in bath at 200°), and (*b*) less soluble, m. p. 235—236°, in approximately equal amounts (total yield 24%) [Found : (*a*) C, 48·8; H, 3·4; S, 23·7; (*b*) C, 48·8; H, 3·0; S, 23·6. $C_{11}H_8O_4S_2$ requires C, 49·3; H, 3·0; S, 23·9%).

Desulphurisation. The dilactone (0·3 g.) was refluxed in dioxan (15 c.c.) for 45 minutes with Raney nickel (3 g.). The mixture was filtered, the residue was extracted with boiling dioxan (2 × 10 c.c.), and the combined filtrates were evaporated to dryness. Vacuum-distillation of the oily residue gave a liquid which solidified overnight at 0° and had m. p. 43—44° [26% from (*a*), 39% from (*b*)]. A mixed m. p. with authentic toluquinol diacetate (m. p. 44°) was 43—44° (Schmid, *Monatsh.*, 1911, **32**, 437, reports m. p. 49°).

3 : 5 : 6-*Tri(carboxymethylthio)toluquinol Monolactone*.—A mixture of 3 : 5 : 6-trichlorotoluquinone (1·57 g.), water (100 c.c.), pyridine (0·5 c.c.), and thioglycollic acid (2·94 c.c.) was refluxed till a colourless solution was obtained. The solution was cooled, made alkaline with solid sodium carbonate, and extracted twice with ether. The solution was then acidified with concentrated hydrochloric acid (100 c.c.), and extracted with ether (twice). The extract was dried ($MgSO_4$) and evaporated, yielding a colourless oily residue, which solidified during 24 hours in a vacuum-desiccator. Recrystallisation from ethyl acetate–light petroleum (b. p. 100—120°) gave crystals, m. p. 164° (29%) (Found : C, 41·4; H, 3·4; S, 25·5. $C_{13}H_{12}O_7S_3$ requires C, 41·5; H, 3·2; S, 25·5%).

3 : 6-*Di(carboxymethylthio)*-2 : 5-*dimethylquinol*.—Thioglycollic acid (0·345 c.c.) was added to a suspension of *p*-xyloquinone (0·68 g.) in water (10 c.c.) at 60—70°, and this temperature was maintained with continuous stirring till dissolution was complete. The orange solution, on cooling, deposited a little dark oil (separated by decantation) and a white solid. After 1 hour at 0°, the latter was filtered off and washed with a little cold water. Recrystallisation from water yielded the *quinol* as crystals, softening 150—155°, m. p. 290—294 (decomp.) (50%). If placed in a bath at 160°, the acid melted immediately (Found : C, 45·3; H, 4·4; S, 20·1. $C_{12}H_{14}O_6S_2$ requires C, 45·2; H, 4·4; S, 20·1%).

3 : 6-*Di*(*carboxymethylthio*)-2 : 5-*dimethylbenzoquinone*.—The above quinol (0·15 g.) was dissolved in hot water (30 c.c.), and the solution was cooled to 35° and treated with a solution of potassium dichromate (0·5 g.) in water (1·5 c.c.) and concentrated sulphuric acid (0·5 c.c.). The mixture was cooled immediately in a freezing mixture; after 1 hour the orange precipitate was collected, washed with cold water, and recrystallised from water. The *quinone* separated as orange-red needles, m. p. 183° (75%) (Found: C, 45·4; H, 3·9; S, 20·0. $C_{12}H_{12}O_6S_2$ requires C, 45·6; H, 3·8; S, 20·25%).

m-*Xyloquinone*.—This was prepared (yield, 16%) from 2 : 6-dimethylphenol by the method of Smith, Opie, Wawzonek, and Prichard (*J. Org. Chem.*, 1939, **4**, 318) who used 3 : 5-dimethylphenol.

3 : 5-*Di*(*carboxymethylthio*)-2 : 6-*dimethylquinol*.—Thioglycollic acid (0·173 c.c.) was added to a suspension of finely powdered *m*-xyloquinone (0·34 g.) in water (5 c.c.). The mixture was stirred for 30 minutes, a small quantity of black material filtered off, and the red filtrate acidified with concentrated hydrochloric acid (1 c.c.) and kept overnight at 0°. The precipitate of *quinol* which formed was crystallised from 2N-hydrochloric acid, then having m. p. 154° (38%) (Found: C, 45·2; H, 4·6; S, 20·3. $C_{12}H_{14}O_6S_2$ requires C, 45·2; H, 4·4; S, 20·1%).

3 : 5-*Di*(*carboxymethylthio*)-2 : 6-*dimethylbenzoquinone*.—To the quinol (0·15 g.) dissolved in water (12 c.c.) at 20—25° was added with stirring a solution of potassium dichromate (0·5 g.) in water (1·5 c.c.), containing concentrated sulphuric acid (0·5 c.c.). The red precipitate which formed was filtered off after being kept at 0° overnight. Recrystallisation from water yielded the *quinone* as red needles, m. p. 174° (66%) (Found: C, 45·9; H, 3·8; S, 19·8. $C_{12}H_{12}O_6S_2$ requires C, 45·6; H, 3·8; S, 20·25%).

2-*Carboxymethylthio*-1 : 4-*naphthaquinone*.—To a stirred suspension of finely powdered 1 : 4-naphthaquinone (0·79 g.) in water (20 c.c.) at 40—50° thioglycollic acid (0·35 c.c.) was added, and the mixture was stirred at 40—50° for 15 minutes, heated to 70°, and decanted from a black tar. The precipitate (0·21 g.) which formed on cooling was collected after 3 hours, dissolved in water (50 c.c.), and oxidised by the addition of potassium dichromate (2 g.) in water (6 c.c.) containing concentrated sulphuric acid (2 c.c.). The *quinone* appeared immediately and was collected after chilling for 1 hour. Repeated crystallisation from water yielded yellow crystals, m. p. 172° (Found: C, 57·9; H, 3·5; S, 12·9. $C_{12}H_8O_4S$ requires C, 58·1; H, 3·2; S, 12·9%).

2-*Anilino*-1 : 4-*naphthaquinone*.—A mixture of 2-carboxymethylthio-1 : 4-naphthaquinone (0·12 g.), alcohol (5 c.c.), and aniline (0·05 c.c.) was refluxed for 1 hour. After being kept overnight at 0°, the product was filtered off and crystallised from aqueous alcohol, to give red needles, m. p. and mixed m. p. with 2-anilino-1 : 4-naphthaquinone 190—191° (42%).

2 : 3-*Di*(*carboxymethylthio*)-1 : 4-*naphthaquinol Dilactone* (V).—(*a*) The crude 1 : 4-naphthaquinone–thioglycollic acid addition product (0·84 g.) obtained as above was dissolved in pyridine (4 c.c.), and acetic anhydride (2 c.c.) added. A precipitate formed almost immediately and was collected after 1 hour. Recrystallisation from benzene yielded the dilactone in needles, m. p. 271—275° (decomp.) (11%).

(*b*) A mixture of 2 : 3-dibromo-1 : 4-naphthaquinone (0·15 g.) in water (5 c.c.), pyridine (0·05 c.c.), and thioglycollic acid (0·14 c.c.) was refluxed for 1 hour and the mixture filtered hot. The filtrate was chilled overnight, and the crude quinol which was deposited was washed with ice-cold water, dried, and dissolved in pyridine (0·5 c.c.). On addition of acetic anhydride (0·25 c.c.) crystals of the *dilactone* separated almost immediately. Recrystallisation from benzene afforded needles, m. p. 271—275° (decomp.) (47%), indistinguishable from those recorded in (*a*) (Found: C, 55·2; H, 2·6; S, 21·1. $C_{14}H_8O_4S_2$ requires C, 55·3; H, 2·6; S, 21·05%).

2 : 3 : 5 : 6-*Tetra*-(2-*carboxyethylthio*)*quinol*.—(*a*) β-Mercaptopropionic acid (0·434 c.c.) was added dropwise to a stirred suspension of finely powdered benzoquinone (0·54 g.) in water (15 c.c.). A bright red suspension was formed almost immediately. After 30 minutes' stirring the pale red suspension was filtered off, washed with water, and recrystallised first from glacial acetic acid and then from water (containing a trace of sodium dithionite), to yield the *quinol* in needles, m. p. 205—206° (12%). Addition of sodium hydrogen carbonate to the filtrate, and extraction with ether gave quinol, m. p. and mixed m. p. 172° (42%).

(*b*) A suspension of chloranil (0·246 g.) in a mixture of ethanol (15 c.c.), pyridine (1 c.c.), and β-mercaptopropionic acid (0·434 c.c.) was refluxed for 30 minutes and then evaporated to dryness. The residue crystallised from water in needles, m. p. 205—206° (53%) (Found: C, 41·2; H, 4·2; S, 24·4. $C_{18}H_{22}O_{10}S_4$ requires C, 41·1; H, 4·2; S, 24·3%).

2 : 3 : 5 : 6-*Tetra*-(2-*carboxyethylthio*)*benzoquinone*.—To 2 : 3 : 5 : 6-(tetra-2-carboxyethylthio)-quinol (0·15 g.) in water (30 c.c.) at 95° was added concentrated nitric acid (3 c.c.), and the

intense red solution immediately cooled to room temperature. After being kept overnight at 0°, the *quinone* was collected, washed with water, and crystallised from water in reddish-brown crystals, m. p. 194° (73%) (Found : C, 41·35; H, 4·0; S, 24·35. $C_{18}H_{20}O_{10}S_4$ requires C, 41·2; H, 3·8; S, 24·4%).

*2-2′-Carboxyethylthio-*1 : 4-*naphthaquinone.*—(*a*) Finely powdered 1 : 4-naphthaquinone (0·79 g.) was stirred in water (30 c.c.) at 50—55° and β-mercaptopropionic acid (0·434 c.c.) added dropwise. Stirring was continued for 30 minutes at 50—55°. The mixture was then heated rapidly to 85°, and filtered from a black tar, the filtrate depositing a mixture of quinols (0·4 g.) on cooling, which was collected next morning and washed with water (see below). The black tarry residue was dried and stirred with a little ether, and the insoluble material crystallised from methanol in golden-yellow needles, m. p. 188° (13%). (*b*) A mixture of 2-bromo-1 : 4-naphthaquinone (0·35 g.), pyridine (0·5 c.c.), and β-mercaptopropionic acid (0·13 c.c.) in ethanol (8 c.c.) was refluxed for 30 minutes. The *quinone* separated on cooling, and crystallised from methanol in golden-yellow needles, m. p. 188° (43·5%), identical with those reported in (*a*) (Found : C, 59·2; H, 3·9; S, 12·3. $C_{13}H_{10}O_4S$ requires C, 59·5; H, 3·8; S, 12·2%).

2 : 3-*Di*-(2-*carboxyethylthio*)-1 : 4-*naphthaquinone.*—(*a*) The crude quinol mixture (0·4 g.) from the naphthaquinone–β-mercaptopropionic acid reaction (above) was dissolved in boiling water (30 c.c.). Concentrated nitric acid (5 c.c.) was added at 95°, a dark red solution resulting, which was immediately cooled in ice-water. The orange solid precipitated was crystallised from excess of ethanol, to give golden-yellow needles of 2-2′-carboxyethylthio-1 : 4-naphthaquinone (6·3%). The mother-liquor was evaporated to dryness and the residue recrystallised from ethanol. From the heterogeneous crystalline product obtained, the red crystals were mechanically separated and recrystallised from ethanol, to yield a small quantity of 2 : 3-*di*-(2-*carboxyethylthio*)-1 : 4-*naphthaquinone* as brick-red crystals, m. p. 204°. (*b*) 2 : 3-Dibromo-1 : 4-naphthaquinone (0·316 g.) was refluxed for 30 minutes in ethyl alcohol (5 c.c.) containing pyridine (0·5 c.c.) and β-mercaptopropionic acid (0·174 c.c.). A dark red solid formed on cooling, and crystallised from ethanol affording brick-red crystals, m. p. 204° (79%) (Found : C, 52·3; H, 3·9; S, 17·4. $C_{16}H_{14}O_6S_2$ requires C, 52·45; H, 3·8; S, 17·5%).

γ-Mercaptobutyric Acid.—This was prepared (52% yield) by the method of Holmberg and Schjånberg (*Arkiv Kemi, Mineral., Geol.*, 1940, **14**, *A*, No. 7) and had b. p. 102—103°/2·5 mm.

2 : 5(?)-*Di*-(3-*carboxypropylthio*)*benzoquinone.*—γ-Mercaptobutyric acid (1·545 c.c.) was added during 2 minutes to a stirred suspension of benzoquinone (1·62 g.) in water (60 c.c.). Stirring was continued for 30 minutes, and the product then filtered off, dried, and extracted with boiling chloroform (30 c.c.). The residue was crystallised from 50% aqueous alcohol, to yield red needles, m. p. 201—203° (12·4%) (Found : C, 48·6; H, 5·0; S, 18·6. $C_{14}H_{16}O_6S_2$ requires C, 48·8; H, 4·65; S, 18·6%). The filtrate was made alkaline with solid sodium carbonate and extracted with ether (twice), from which quinol, m. p. 172° (37%), was obtained.

2 : 3 : 5 : 6-*Tetra*-(3-*carboxypropylthio*)*benzoquinone.*—A mixture of chloranil (0·246 g.), pyridine (1 c.c.), and γ-mercaptobutyric acid (0·618 c.c.) in water (20 c.c.) was refluxed until an almost colourless solution was formed (*ca.* 15 minutes). Concentrated nitric acid (3 c.c.) was then added to the solution at 95°, and the whole immediately cooled to room temperature. The red precipitate formed was filtered off, and crystallised from aqueous acetic acid. The *quinone* formed reddish-brown crystals, m. p. 140° (50%) (Found : C, 45·8; H, 5·0; S, 22·3. $C_{22}H_{28}O_{10}S_4$ requires C, 45·5; H, 4·8; S, 22·1%).

Addition of Thiophenol to Benzoquinone.—To finely powdered benzoquinone (4·32 g.) suspended in water (140 c.c.), thiophenol (4·08 c.c.) was added during 5 minutes with stirring. A dark sticky solid was immediately formed. The suspension was stirred for 30 minutes, then extracted twice with ether. Evaporation of the extract to small bulk gave an orange solid. One crystallisation from glacial acetic acid yielded pure 2 : 5-diphenylthiobenzoquinone in orange-red leaflets, m. p. and mixed m. p. with an authentic specimen (Dimroth, Kraft, and Aichinger, *loc. cit.*) 256—258° (8%). 2 : 6-Diphenylthiobenzoquinone was isolated from the mother-liquor by dilution with water, and recrystallised from glacial acetic acid, to give brick-red crystals, m. p. and mixed m. p. 206° (1%).

The ethereal filtrate above was dried ($MgSO_4$) and evaporated, leaving a dark oily residue, which crystallised from benzene to give quinol, m. p. 172° (16%). Evaporation of the benzene mother-liquor to dryness again yielded a dark oil. Reductive acetylation of this with acetic anhydride (10 c.c.), zinc dust (1 g.), and pyridine (1 c.c.) gave, after fractional crystallisation from alcohol, two compounds : (*a*) less soluble, needles, m. p. 170° (5·5%), and (*b*) more soluble, needles, m. p. 84—85° (19%) (from aqueous alcohol). Mixed m. p. determinations showed that (*a*) was 2 : 5-*diphenylthioquinol diacetate* and (*b*) 2-phenylthioquinol diacetate. (*a*) was also obtained by reductive acetylation of 2 : 5-diphenylthiobenzoquinone as above in needles, m. p. 170° (87%) (Found: C, 64·15; H, 4·4; S, 15·9. $C_{22}H_{18}O_4S_2$ requires C, 64·4; H, 4·4; S, 15·6%).

2 : 3 : 5 : 6-*Tetraphenylthiobenzoquinone.*—This was prepared from chloranil and potassium thiophenoxide according to Tjepkema (*loc. cit.*). It crystallised from glacial acetic acid in reddish-brown crystals, m. p. 176—177° (96%) (Found: C, 66·6; H, 3·75; S, 23·9. $C_{30}H_{20}O_2S_4$ requires C, 66·7; H, 3·7; S, 23·7%).

2 : 5-*Dipropylthiobenzoquinone.*—(*a*) Propane-1-thiol (0·91 c.c.) was added during 2 minutes to a stirred suspension of benzoquinone (1·08 g.) in water (35 c.c.), and stirring continued for 30 minutes. The dark red oily mixture obtained was extracted with ether, the extract evaporated to small bulk and the orange precipitate collected. Recrystallisation from ethanol yielded orange-red leaflets, m. p. 163° (10%). The ethereal filtrate was dried ($MgSO_4$) and evaporated, leaving a black residue which was crystallised from benzene giving almost pure quinol (40%).

(*b*) The potassium salt of propane-1-thiol (0·912 g.), dissolved in 50% aqueous alcohol, was added to 2 : 5-dichlorobenzoquinone (0·7 g.) suspended in ethyl alcohol (30 c.c.). The mixture was shaken for 3 hours, and the product precipitated from the dark red solution by dilution with water (50 c.c.). Crystallisation from ethanol afforded the *quinone* as orange-red leaflets, m. p. 163° (19%) (Found: C, 56·1; H, 6·2; S, 25·1. $C_{12}H_{16}O_2S_2$ requires C, 56·25; H, 6·25; S, 25·0%).

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