[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, MARISCHAL COLLEGE, UNIVERSITY OF ABERDEEN]

STUDIES IN THE JUGLONE SERIES. III. ADDITION REACTIONS

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In previous work on the structure of various juglone compounds (1, 2) a number of unexpected reactions came to light, chiefly concerning the halogen derivatives. To obtain further information which might assist in explaining these results a number of addition reactions have now been carried out with juglone and juglone acetate, where the quinonoid ring is free from complicating substituents. The results are summarized in Table I.

Thiols were the most satisfactory reagents, the additions proceeding rapidly at room temperature with some evolution of heat. The formation of 3-phenylthiojuglone by addition of thiophenol to juglone has already been reported (3). The addition of acetic anhydride to juglone, or more correctly, juglone acetate, since acetylation occurs immediately on addition of the catalyst, is not new (2, 4), but the reaction was re-examined. Only one isomer, 1,3,4,5-tetraacetoxynaphthalene, was found. The alternative 1,2,4,5-tetraacetoxynaphthalene was obtained by reductive acetylation of 2-hydroxyjuglone diacetate. Addition reactions with amines were disappointing. As mentioned previously (1) interaction of aniline and juglone under a variety of conditions yields a black amorphous solid, and a similar product has now been obtained with *p*-anisidine and *p*-nitroaniline. The only aminojuglone which has been obtained by direct addition of an amine is 2-dimethylaminojuglone (5). The original conditions have been modified but the yield (34%) is still poor. Moreover the reaction could only be carried out in aqueous suspension and the result is of doubtful value for the present purpose as it is uncertain whether free juglone, an amine salt, or an ion takes part in the reaction. Juglone is unstable under alkaline conditions and no definite product could be obtained from the reaction of juglone and dimethylamine in alcohol solution. No other amines were tried as the parallel additions to juglone acetate failed. Aliphatic amines hydrolyze juglone acetate but the addition of aniline was achieved in moderate yield. Weaker aromatic bases (*e.g.* *p*-nitroaniline and *p*-chloroaniline) did not react. Other reactions which involve alkaline conditions such as the addition of malonic ester and other compounds containing reactive methylene groups were not successful. The addition of halogens to the 2,3-double bond followed by elimination of halogen acid, carried out earlier with juglone (1), was extended to juglone acetate.

The orientation of the new compounds was determined in the following manner. 2- and 3-*p*-tolylthiojuglone were obtained by reaction of *p*-thiocresol with 2- and 3-chlorojuglone respectively, and one of the thioglycolic acid addition products was similarly identified. Reductive acetylation of the *p*-tolylthiojuglones followed by permanganate oxidation yielded the corresponding 1,4,5-triacetoxynaphthyl-2- and 3-*p*-tolylsulfones. The latter compounds were also obtained by reductive acetylation of the *p*-toluenesulfinic acid addition products which were thus identified.

It will be observed [Table I, see also the reactions of 2,3-dihalogenojuglones (1)] that if a given reagent attacks juglone or a derivative in the 3-position it invariably attacks the corresponding acetate in the 2-position, whereas if a 2-substituted juglone is formed the same reagent will generally yield a 3-substituted juglone acetate. In all the addition reactions only one of the two possible products was found. As yields are only moderate in certain cases, exclusive formation of one isomer cannot be claimed but it is clear that (except in the addition of dimethylamine) one isomer predominates in every case. Had chromatographic analysis of the reaction products been possible, the formation of only one isomer could have been established with greater certainty, but this procedure has never been successfully applied to juglone derivatives, although the method is occasionally useful for the partial purification of crude products and removal of hydrojuglone.

TABLE I

THE DERIVATIVES OF JUGLONE AND JUGLONE ACETATE OBTAINED BY VARIOUS ADDITION REACTIONS

REAGENT	POSITION AND YIELD OF SUBSTITUENT	
	Juglone (%)	Juglone acetate (%)
Dimethylamine	2 (34)	—
Aniline	—	3 (56)
Acetic anhydride	—	3 (74)
p-Thiocresol	3 (90)	2 (83.5)
Thioglycolic acid	3 (73)	2 (70)
p-Tolylsulfinic acid	3 (69)	2 (70)
Chlorine[a]	3 (92)	2 (54)
Bromine[a]	3 (82)	2 (60)

[a] Refers to the monochloro (bromo) juglone obtained by addition of chlorine (bromine) followed by elimination of the elements of hydrochloric (hydrobromic) acid.

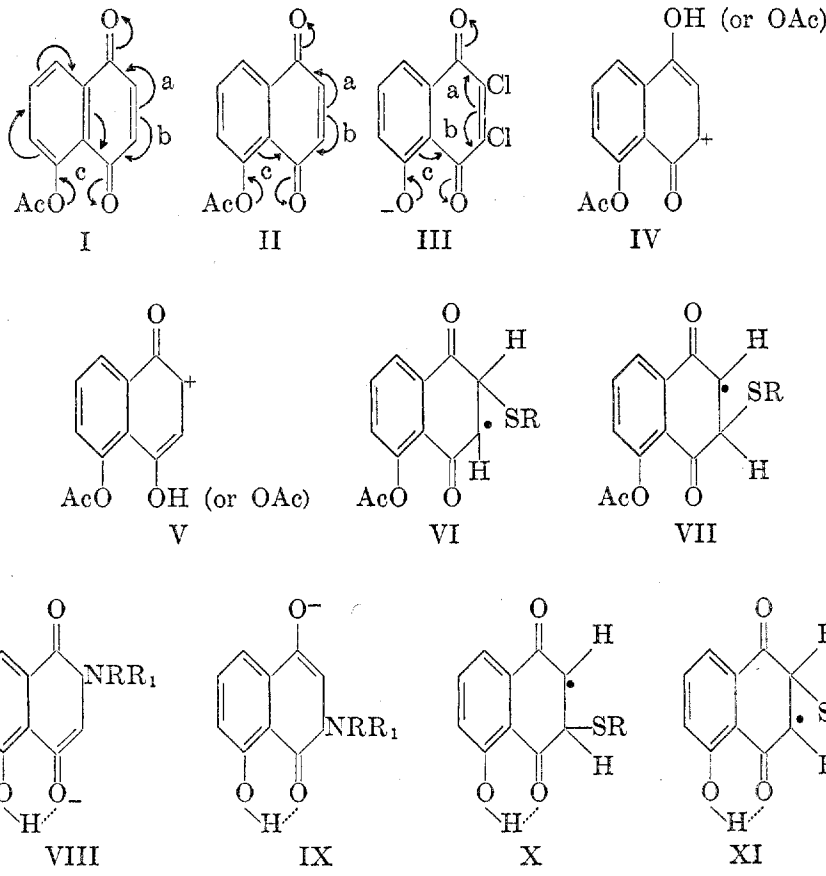
The more complete addition reactions of juglone acetate will be considered first. Since the carbonyl group at C_4 is conjugated with the acetoxy group at C_5 (I and II), the mesomeric shift *b* competes with that culminating in *c* and consequently *b* is weaker than *a*. It follows that C_3 is more positive than C_2 and will therefore be attacked preferentially by nucleophilic reagents. Thus addition of aniline to juglone acetate yields 3-anilinojuglone acetate, and the reaction of aniline with 2-chloro- and 2,3-dichloro-juglone acetate yields 3-anilino-2-chlorojuglone acetate (1). The reactions of halogenated juglones in alkaline solution are similar in character involving anions such as (III), where the shift *b* is further suppressed, leading to nucleophilic attack at C_3. Thus the reaction of 2,3-dichlorojuglone with sodium hydroxide yields exclusively 2-chloro-3-hydroxyjuglone (2).

Addition to the same conjugated system occurs in the Thiele acetylation of juglone acetate. This reaction is catalyzed by strong acids, the initial step being the addition of a proton or acetyl cation[1] to oxygen (6). Of the two possible in-

[1] Burton and Praill (11) have introduced the term acetylium for Ac^+.

termediate ionic structures (IV and V) (and the alternative Kekulé forms), IV is the more probable since the accumulation of positive charge at C_2 in V would be opposed by the +T effect of the acetoxyl group at C_5. Hence the product of the reaction is 1,3,4,5-tetraacetoxynaphthalene.

It has been shown (8) that addition of thiols to double bonds is a chain reaction involving thiol radicals, the addition being "abnormal" under ordinary conditions. This is borne out by the addition of *p*-thiocresol and thioglycolic acid to



juglone acetate, radical addition occurring at C_2 (*cf.* the ionic reagents discussed above). Resonance stabilization of the intermediate radical (VI) is presumably greater than that of the alternative (VII) because the more negative carbonyl group at C_4 is a better electron source than that at C_1. The addition of *p*-toluenesulfinic acid to juglone acetate also takes place at C_2 and is probably a free radical reaction. The mechanism of addition of sulfinic acids to double bonds has apparently not been studied, but it is noteworthy that sulfinic acids are effective catalysts for polymerization (9). The reaction of juglone and its acetate with methyl radicals yields an inseparable mixture of methyljuglones (10), and it is

now found that in the reaction of juglone with somewhat less active carboxyphenyl radicals both isomers are also formed.

The formation of 2-chloro-(and bromo)juglone acetate from the dichloride (and dibromide) was less satisfactory than the parallel reactions with the juglone dihalides, possibly because pure dihalide acetates were not obtained. The elimination of halogen acid probably proceeds by a *beta*-cleavage mechanism [*cf.* (13)], the initial step being the removal of a proton from C_2 by the base, followed by loss of chloride ion from C_3. This orientation would be anticipated as the $-I$ effect of the C_4 carbonyl group will be less than that of the C_1 carbonyl group, and thus C_2 is more positive than C_3 in these dihalide acetates.

Preliminary results of some addition reactions suggest that the behavior of other Bz-substituted-1,4-naphthoquinones is in line with juglone acetate rather than with juglone. The latter is distinguished from the other quinones by the presence of a hydrogen bond, some effects of which have already been observed (12), and the course of the present reactions may be attributed to the same cause. The addition of amines to juglone would involve formation of the intermediate ions VIII or IX. The former would be stabilized by hydrogen bonding to a greater extent than IX so that 2-aminojuglones should result. In practice, such addition reactions met with little success but in the reaction of aniline with 2-halogeno- and 2,3-dihalogeno-juglones 2-anilino derivatives are obtained (1). In the case of thiol additions, the possible intermediate free radicals are X and XI; by analogy with VI and VII, XI should be the more stable. In this case, however, resonance stabilization of XI is offset by consequent weakening of the hydrogen bond so that X is favored, thiol and sulfinic acid additions yielding 3-substituted juglones. It is less obvious why elimination of the elements of halogen acid from juglone dichloride and dibromide affords only the 3-halogenojuglones (1). Yields are high and the initial products are nearly pure. The results indicate that the electron-attracting power of the chelate ring exceeds that of the C_1 carbonyl group, in contrast to the situation found in the juglone acetate dihalides.

Although it is possible to account for most of the experimental results recorded in Table I, it is somewhat surprising that in all cases only one isomer has been detected. Thiele acetylation of 6-chloro-1,4-naphthoquinone yields two products (7) however, and this may occur with other naphthoquinones, or with more active reagents. Work is proceeding in this direction.

In a few instances the normal course of a reaction is affected by the presence of a halogen atom in the quinonoid ring. The reaction of aniline with 3-chlorojuglone yields 3-anilinojuglone (1) and not the expected 2-anilino-3-chlorojuglone, although the yield is only moderate (52%) and the crude product is contaminated with black material similar to that obtained by interaction of aniline and juglone. The failure of these amine addition reactions is possibly connected with the instability of the intermediate hydrojuglones. Both 2- and 3-*p*-tolylthiojuglone may be obtained by reaction of 2- and 3-chlorojuglone with *p*-thiocresol in the presence of pyridine. Presumably these are ionic and not free radical reactions. The yield of 2-*p*-tolylthiojuglone was very poor and a second unidentified product was isolated.

EXPERIMENTAL[2]

Microanalyses are by Mrs. M. A. B. Fyfe. Melting points are uncorrected.

2-Chlorojuglone acetate. Solutions of 0.54 g. of juglone acetate in 5 cc.of glacial acetic acid, and 0.18 g. of chlorine in 5 cc. of glacial acetic acid were mixed at room temperature and allowed to stand for one hour, with occasional shaking. The color faded to pale yellow. After the addition of 0.3 g. of anhydrous sodium acetate the solution was refluxed gently for five minutes, saturated with water at the boil, and allowed to crystallize. The product (0.52 g., m.p. 122–128°) once recrystallized from alcohol formed yellow needles, m.p. 141° (not depressed by authentic material, m.p. 143°); yield, 0.34 g. (54%). The isomer was not detected in the mother liquor.

By chlorinating in chloroform solution and subsequently removing the solvent at room temperature, a colorless oil was obtained, presumably a mixture of geometrical and optical isomers. This formed a glass on cooling but could not be induced to crystallize. Treatment with sodium acetate in glacial acetic acid as before gave 2-chlorojuglone acetate in similar yield.

2-Bromojuglone acetate. This was prepared in the same manner as the chloro compound using 0.86 g. of juglone acetate in 15 cc. of glacial acetic acid, and 0.2 cc. of bromine in 2 cc. of glacial acetic acid. The product (1.02 g., m.p. 138–140°), once recrystallized from alcohol, formed yellow needles, m.p. 156° (not depressed by authentic material, m.p. 158°); yield, 0.7 g. (60%). No isomer was detected in the mother liquor. Attempts to isolate the dibromide by bromination in chloroform yielded an oil which could not be crystallized.

1,3,4,5-Tetraacetoxynaphthalene. Four drops of concentrated sulfuric acid were added to a suspension of 1 g. of juglone in 8 cc. of acetic anhydride. On swirling, juglone acetate was immediately deposited. The suspension was warmed until solution was complete and allowed to stand at room temperature. After 11 days the solution was poured onto ice and the oil stirred until it solidified. The product (1.82 g., m.p. 122–134°) was fractionally crystallized from alcohol to yield 0.2 g. of unchanged juglone acetate and 1.29 g. (74%) of 1,3,4,5-tetraacetoxynaphthalene, m.p. 154°. A trace of some other low-melting material could not be purified.

1,2,4,5-Tetraacetoxynaphthalene. This was obtained by reductive acetylation of 2-hydroxyjuglone diacetate in the usual way using zinc dust, acetic anhydride, and a drop of triethylamine as catalyst. The tetraacetate crystallized from alcohol in colorless micro-crystals, m.p. 174° (it softens and shrinks several degrees below the m.p. like the 1,3,4,5-isomer).

Anal. Calc'd for $C_{18}H_{16}O_8$: C, 60.0; H, 4.5.
Found: C, 59.9; H, 4.3.

2-Dimethylaminojuglone. A suspension of 1 g. of finely divided juglone in 50 cc. of water was stirred vigorously and 2 cc. (excess) of aqueous dimethylamine solution (25% w/v) was added. A transient violet color became red immediately and then dark brown. After one hour the suspended solid was washed and dried. This afforded 0.52 g. of red-brown material, m.p. 143°, which crystallized from alcohol in glistening red plates, m.p. 147°; yield, 0.42 g. (34%). Acetylation with acetic anhydride in boiling pyridine yielded the acetate which crystallized from alcohol in orange-red plates, m.p. 138°.

Anal. Calc'd for $C_{14}H_{13}NO_4$: C, 64.85; H, 5.05; N, 5.4.
Found: C, 65.05; H, 5.2; N, 5.5.

3-Dimethylaminojuglone. A solution of 0.5 g. of 3-chlorojuglone in 35 cc. of alcohol was refluxed for a few minutes with 0.9 cc. of aqueous dimethylamine (25% w/v). After cooling, the red solution was diluted with 100 cc. of water, acidified with glacial acetic acid, and allowed to stand several hours. The precipitate was crystallized first from alcohol, and then from ligroin (b.p. 100–120°). 3-Dimethylaminojuglone separated in red micro-crystals, m.p. 156°, yield 0.4 g. (77%).

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[2] The author is indebted to Imperial Chemical Industries Ltd., Dyes tuffs Division, for further gifts of 1,5-dihydroxynaphthalene.

Anal. Calc'd for $C_{12}H_{11}NO_3$: C, 66.3; H, 5.1; N, 6.45.
Found: C, 66.5; H, 5.2; N, 6.2.

The *acetate* separated from ligroin in orange micro-crystals, m.p. 153°.

Anal. Calc'd for $C_{14}H_{13}NO_4$: C, 64.85; H, 5.05; N, 5.4.
Found: C, 65.1; H, 5.2; N, 5.3.

3-Anilinojuglone acetate. To a warm solution of 0.5 g. of juglone acetate in 25 cc. of alcohol an excess of aniline (0.5 cc.) was added, and the mixture allowed to stand at room temperature for 48 hours. Almost pure 3-anilinojuglone acetate was deposited, and a further small amount was obtained by working up the mother liquor. Recrystallization from alcohol afforded red needles, m.p. 168°; yield, 0.4 g. (56%).

3-p-Tolylthiojuglone. (*a*) To a fine suspension of 0.87 g. of juglone in 40 cc. of alcohol, a solution of 0.3 g. of *p*-thiocresol in 10 cc. of alcohol was added. The juglone rapidly dissolved forming a brown solution, followed almost immediately by a yellow-brown crystalline precipitate. The product was recrystallized first from alcohol (charcoal) and then from aqueous acetic acid. The quinone formed glistening orange-yellow plates, m.p. 171°; yield, 0.62 g. (90%).

(*b*) A solution of 0.31 g. of *p*-thiocresol in 5 cc. of alcohol containing 0.2 cc. of pyridine was added to 0.5 g. of 3-chlorojuglone in 30 cc. of alcohol. The quinone dissolved rapidly with evolution of heat followed by deposition of 3-*p*-tolylthiojuglone. The suspension was raised to the boil and the dark-red solution allowed to cool. The crystals which separated were recrystallized from alcohol forming orange-yellow plates, m.p. 171°; yield 0.45 g. (66%).

Anal. Calc'd for $C_{17}H_{12}O_3S$: C, 68.9; H, 4.05.
Found: C, 68.7; H, 4.0.

The *acetate* separated from alcohol in elongated orange plates or fine yellow needles, m.p. 199°.

Anal. Calc'd for $C_{19}H_{14}O_4S$: C, 67.45; H, 4.15.
Found: C, 67.4; H, 4.1.

Reductive acetylation of the acetate afforded 1,4,5-triacetoxynaphthyl-3-*p*-tolylsulfide which crystallized from aqueous acetic acid in colorless plates, m.p. 149°.

Anal. Calc'd for $C_{23}H_{20}O_6S$: C, 65.1; H, 4.75.
Found: C, 65.0; H, 4.8.

2-p-Tolylthiojuglone acetate. A suspension of 1.74 g. of juglone acetate in 60 cc. of alcohol was mixed with 0.5 g. of *p*-thiocresol in 15 cc. of alcohol. In this and other thiol additions, reaction occurred in the cold but the mixture was raised to the boil to insure completion. The product which separated on cooling was almost pure. Recrystallization from alcohol yielded long yellow needles, m.p. 190°; yield, 1.14 g. (83.5%).

Anal. Calc'd for $C_{19}H_{14}O_4S$: C, 67.45; H, 4.15.
Found: C, 67.4; H, 4.15.

Reductive acetylation gave 1,4,5-triacetoxynaphthyl-2-*p*-tolylsulfide which crystallized from aqueous acetic acid in fine colorless needles, m.p. 162°.

Anal. Calc'd for $C_{23}H_{20}O_6S$: C, 65.1; H, 4.75.
Found: C, 64.9; H, 4.8.

2-p-Tolylthiojuglone. (*a*) The above acetate (0.5 g.) in 60 cc. of alcohol was boiled for five minutes with 25 cc. of concentrated hydrochloric acid. Pure 2-*p*-tolylthiojuglone separated on cooling. It crystallized from alcohol in orange needles, m.p. 174°; yield, 100%.

(*b*) A solution of 0.42 g. of *p*-thiocresol in 5 cc. of alcohol containing 0.3 cc. of pyridine was added to 0.7 g. of 2-chlorojuglone in 20 cc. of alcohol. A dark red solution was formed and crystals began to separate rapidly. The mixture was heated just to the boil and allowed to cool. The crystalline product (0.53 g.) was a mixture of minute dark red crystals and yellow needles. The yellow material was separated by extraction with hot alcohol from which it crystallized in orange-yellow needles, m.p. 174°; yield, 0.12 g. (12%).

Anal. Calc'd for $C_{17}H_{12}O_3S$: C, 68.9; H, 4.05.
Found: C, 68.7; H, 4.2.

The dark red material crystallized from aqueous acetic acid in fine needles, m.p. 194°. It contained sulphur but no chlorine or nitrogen.

Juglone-3-thioglycolic acid. (*a*) A suspension of 0.87 g. of juglone in 25 cc. of alcohol containing 0.17 cc. of thioglycolic acid was warmed until dissolution was complete, and allowed to stand overnight. The crystalline precipitate which separated was washed with a little alcohol and recrystallized from alcohol (charcoal) forming short orange needles, m.p. 218° (dec.); yield, 0.48 g. (73%).

(*b*) A mixture of 0.42 g. of 3-chlorojuglone, 0.14 cc. of thioglycolic acid, and 0.5 cc. of pyridine in 25 cc. of alcohol was warmed until all had dissolved, and allowed to cool. After two hours the crystalline product was recrystallized from alcohol to yield orange needles, m.p. 218° (dec.); yield, 0.21 g. (39.5%).

Anal. Calc'd for $C_{12}H_8O_5S$: C, 54.5; H, 3.05.
Found: C, 54.15; H, 3.1.

The *acetate* crystallized from benzene in yellow micro-crystals, m.p. 174°.

Anal. Calc'd for $C_{14}H_{10}O_6S$: C, 54.9; H, 3.5.
Found: C, 55.0; H, 3.5.

The *ethyl ester* was obtained by boiling a solution of 0.31 g. of the acid in 40 cc. of alcohol for two minutes with 14 cc. of concentrated hydrochloric acid. It crystallized from alcohol in fine orange needles, m.p. 154°.

Anal. Calc'd for $C_{14}H_{12}O_5S$: C, 57.5; H, 4.15.
Found: C, 57.7; H, 4.4.

Juglone-2-thioglycolic acid. A solution of 1.1 g. of juglone acetate and 0.17 cc. of thioglycolic acid in 30 cc. of alcohol was heated just to the boil and allowed to stand overnight. The solution was diluted with 100 cc. of water, acidified with 20 cc. of 2 *N* sulfuric acid, and stirred in an ice-bath until the oil initially precipitated had crystallized. The product was recrystallized from aqueous alcohol forming minute yellow needles of the acetate of juglone-2-thioglycolic acid, m.p. 217–218° (dec.); yield, 0.55 g. (70%).

Anal. Calc'd for $C_{14}H_{10}O_6S$: C, 54.9; H, 3.5.
Found: C, 55.0; H, 3.4.

A solution of 0.3 g. of the above acetate in 10 cc. of glacial acetic acid containing 3 cc. of concentrated hydrochloric acid was boiled for two minutes. Juglone-2-thioglycolic acid separated on cooling. It crystallized from water in minute orange leaflets, m.p. 217–218° (dec.), which did *not* depress the m.p. of the 3-isomer [*cf.* (2)]; yield, 0.15 g. (58%).

Anal. Calc'd for $C_{12}H_8O_5S$: C. 54.5; H, 3.05.
Found: C, 54.2; H, 3.05.

The *ethyl ester* was obtained directly from the acetate (0.3 g.) in 18 cc. of alcohol, by boiling with 6 cc. of concentrated hydrochloric acid for two minutes. The ester, which separated on cooling, crystallized from alcohol in small glistening orange plates, m.p. 158°. (Mixture m.p. with the 3-isomer, 145°.)

Anal. Calc'd for $C_{14}H_{12}O_5S$: C, 57.5; H, 4.15.
Found: C, 57.6; H, 4.3.

Juglone-3-p-tolylsulfone. To 1 g. of juglone in 50 cc. of acetone, 1 g. of *p*-toluenesulfinic acid was added, followed by 25 cc. of water. The mixture was shaken for ten minutes becoming quickly homogeneous, the color fading to a light yellow-brown, and then added to a filtered solution of 5 g. of ferric chloride in 50 cc. of water containing 0.8 cc. of concentrated hydrochloric acid. The suspension obtained was warmed to 45° with stirring, and allowed to cool. The light red solid (1.67 g., m.p. *ca.* 200° (dec.) was crystallized from ethyl acetate. The sulfone formed small orange-red plates, m.p. 206° (dec.); yield, 1.3 g. (69%).

Anal. Calc'd for $C_{17}H_{12}O_5S$: C, 62.2; H, 3.65.
Found: C, 62.2; H, 3.65.

The *acetate* separated from ethyl acetate in fine yellow needles, m.p. 221°.

Anal. Calc'd for $C_{19}H_{14}O_6S$: C, 61.6; H, 3.8.
Found: C, 61.6; H, 4.0.

Reductive acetylation yielded 1,4,5-triacetoxynaphthyl-3-*p*-tolylsulfone which crystallized from aqueous acetic acid in small colorless leaflets, m.p. 239°.

Anal. Calc'd for $C_{23}H_{20}O_8S$: C, 60.5; H, 4.4.
Found: C, 60.5; H, 4.45.

The same compound was obtained by gradually adding a solution of 0.3 g. of potassium permanganate in 10 cc. of water to a warm solution of 0.4 g. of 1,4,5-triacetoxynaphthyl 3-*p*-tolyl sulfide in 12 cc. of glacial acetic acid. After dilution with ice, the crystalline precipitate was recrystallized from aqueous acetic acid forming leaflets, m.p. and mixture m.p. 239°.

Acetyljuglone-2-p-tolylsulfone. To 0.5 g. of juglone acetate in 25 cc. of acetone, 0.4 g. of *p*-toluenesulfinic acid and 15 cc. of water were added and the mixture shaken, quickly becoming almost colorless. After standing for 30 minutes the solution was added to 2.5 g. of ferric chloride dissolved in 25 cc. of water containing 0.4 cc. of concentrated hydrochloric acid. The pale yellow flocculent precipitate obtained was warmed to 40° and allowed to cool. The solid (0.74 g., m.p. 204°) crystallized from glacial acetic acid in clusters of small yellow needles, m.p. 222°, which did *not* depress the m.p. of the 3-isomer [*cf.* (2)]; yield, 0.6 g. (70%). For analysis the compound was recrystallized from ethyl acetate.

Anal. Calc'd for $C_{19}H_{14}O_6S$: C, 61.6; H, 3.8.
Found: C, 61.6; H, 3.8.

Reductive acetylation afforded 1,4,5-triacetoxynaphthyl-2-*p*-tolylsulfone. It formed minute colorless leaflets, m.p. 230° (Mixture m.p. with the isomeric 3-*p*-tolylsulfone, 200°).

Anal. Calc'd for $C_{23}H_{20}O_8S$: C, 60.5; H, 4.4.
Found: C, 60.2; H, 4.4.

The identical sulfone was formed by permanganate oxidation of 1,4,5-triacetoxynaphthyl 2-*p*-tolyl sulfide.

2- and 3-p-Carboxyphenyljuglones. Diazotization of 0.92 g. of *p*-aminobenzoic acid was effected in the usual way. After addition of excess anhydrous sodium acetate the solution was filtered and the filtrate (25 cc. in all) was run slowly into a solution of 1.16 g. of juglone in 100 cc. of acetone stirred at 35–40° Nitrogen was evolved briskly about 15 minutes after addition was complete, and an orange precipitate appeared. After stirring for 45 minutes the suspension was cooled and the solid collected. Recrystallization from a large volume of boiling glacial acetic acid yielded two fractions. The less soluble portion (0.3 g.) formed minute orange-red crystals, m.p. 340° (dec.).

Anal. Calc'd for $C_{17}H_{10}O_5$: C, 69.4; H, 3.4.
Found: C, 69.2; H, 3.7.

The *acetate* crystallized from benzene in fine yellow needles, m.p. 230–231° (turning red).

Anal. Calc'd for $C_{19}H_{12}O_6$: C, 67.85; H, 3.6.
Formed: C, 67.75; H, 3.6.

The more soluble fraction (0.12 g.) crystallized from glacial acetic acid in orange micro crystals, m.p. 292° (dec.).

Anal. Calc'd for $C_{17}H_{10}O_5$: C, 69.4; H, 3.4.
Found: C, 69.1; H, 3.5.

The *acetate* crystallized from aqueous alcohol in orange-yellow micro crystals, m.p. 220° (turning red).

Anal. Calc'd for $C_{19}H_{12}O_6$: C, 67.85; H, 3.6.
Found: C, 67.6; H, 3.75.

SUMMARY

The addition of amines, acetic anhydride, *p*-thiocresol, thioglycolic acid, *p*-toluenesulfinic acid, chlorine, and bromine to juglone and juglone acetate has been studied. Theoretical considerations are put forward to account for these reactions and others described in Parts I and II.

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