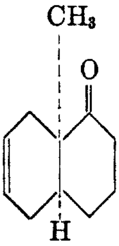
[CONTRIBUTION FROM THE BUREAU OF ANIMAL INDUSTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE SYNTHESIS OF CONDENSED RING COMPOUNDS. XIII. THE PREPARATION OF 5- AND 6-CARBALKOXY-1,4-TOLUQUINONES. ADDITION OF 5-CARBOMETHOXY-1,4-TOLUQUINONE AND 6-CARBOMETHOXY-1,4-TOLUQUINONE TO BUTADIENE[1]

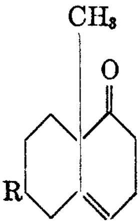
WALTER NUDENBERG, ADAM M. GADDIS, AND LEWIS W. BUTZ

Received July 3, 1943

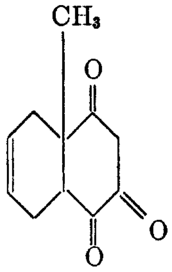
cis-10-Methyl-7-naphthiten-1-one (I) is now available from butadiene and 1-methylcyclohexen-6-one (1), but the trans isomer and 7-substituted-10-methyl-4-naphthiten-1-ones (II) cannot be made so directly by a Diels-Alder synthesis. For these, the addition of 5- and 6-substituted-1,4-toluquinones to butadienes promises to be a fertile general procedure. The preparation of a methylnaphthitenetrione enol (III) and a methylmethoxynaphthitadienedione (IV) in practical yield may make available 10-methyl-1-ketones, of both the cis and the trans series, substituted in the ketonic ring (2). If compounds lacking the substituent at carbon-3 are desired, these two intermediates may not be immediately useful, since they belong to classes of compounds whose reactions are unfamiliar. The addition of carbalkoxytoluquinones to butadiene might yield V and VI, and these could perhaps without too much difficulty be converted to VII.



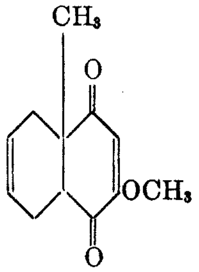
I



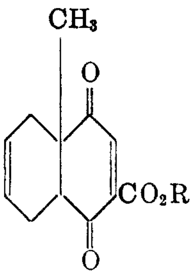
II



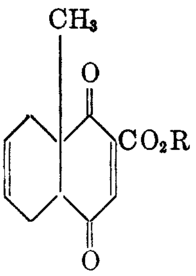
III



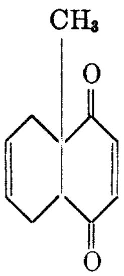
IV



V



VI



VII

---

[1] This work was supported by an allotment from the Special Research Fund (Bankhead-Jones Act of June 29, 1935). Not subject to copyright.

Although carbalkoxy-*p*-benzoquinones are very sensitive compounds, Brunner (3) was able to prepare carbomethoxy-*p*-benzoquinone and carbethoxy-*p*-benzoquinone. By employing his procedure for oxidation of the corresponding quinols we have prepared 5-carbomethoxy-1,4-toluquinone and 6-carbomethoxy-1,4-toluquinone in crystalline form. The individual reactions utilized are shown in Charts 1 and 2.

Butadiene combined with 5-carbomethoxy-1,4-toluquinone and with 6-carbomethoxy-1,4-toluquinone in dry benzene at 100°. The products, which were light yellow viscous liquids boiling at 137–139° (0.5 mm.) and 155–157° (1–2 mm.) respectively, had the expected composition, $C_{13}H_{14}O_4$. They were, however, not angle methyl compounds of the kind (V and VI) that we sought to prepare, for with aqueous methanolic potassium hydroxide they gave the known compound, 2-methyl-5,8-dihydronaphthalene-1,4-diol, XIV (4), with the methyl group at a peripheral position. The adducts must therefore consist, at least in part, of the angle carboxylates, XV and XVI. The liquid from 5-carbomethoxytoluquinone yielded 87% of the diphenol, XIV; and, since there is evidence that some of this angle carboxylate underwent scission of the enedione ring during the alkaline hydrolysis and decarboxylation, the amount of any angle methyl isomer in the adduct must have been very small. The liquid from 6-carbomethoxytoluquinone gave only 66% of XIV, but no evidence of the presence of angle methyl isomers was obtained. The yields of distilled analytically pure adducts from the two quinones were 77% and 78%. Hence butadiene added to the carbomethoxylated double bond to an extent of well over 80% of the quinone taken.

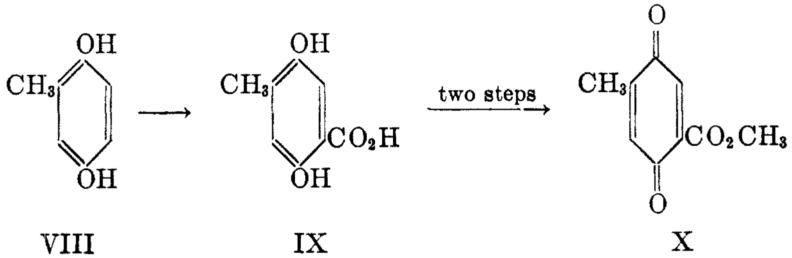


CHART 1

THE PREPARATION OF 5-CARBOMETHOXY-1,4-TOLUQUINONE FROM *p*-TOLUQUINOL

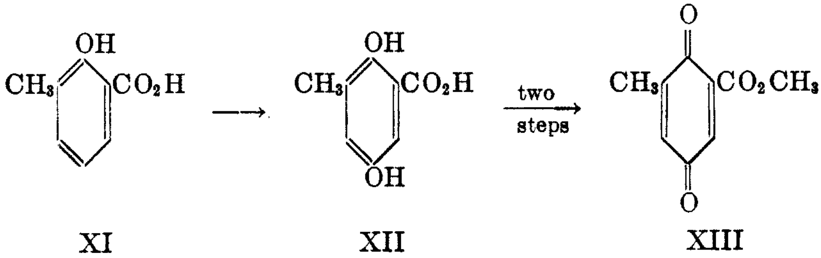
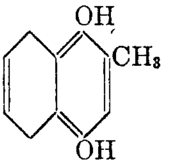


CHART 2

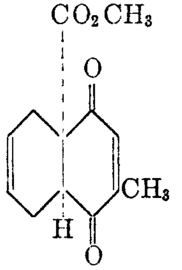
THE PREPARATION OF 6-CARBOMETHOXY-1,4-TOLUQUINONE FROM *o*-CRESOTIC ACID

The fact that the adducts were liquids suggests that they may be mixtures of the two diastereoisomers. It is possible that partial conversion of XV to the trans isomer, XVII and of XVI to its trans isomer, XVIII occurred under the conditions of formation of XV and XVI.

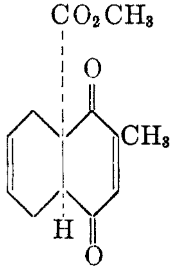
Catalytic hydrogenation of the methyl 1,4-diketo-2-methyl-2,7-naphthitadiene-10-carboxylate (XVI–XVIII) resulted in an uptake of three moles.



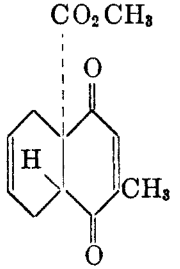
XIV



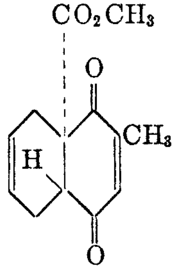
XV



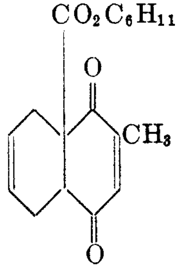
XVI



XVII



XVIII



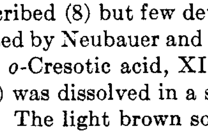
XIX

6-Carbomethoxy-1,4-toluquinone and butadiene were next heated together in methanol in order to determine whether the relative rate of addition of the methylated double bond of the quinone to the diene would be increased in a hydroxylic solvent. A yellow liquid boiling at 151–155° under one mm. was obtained in 68% yield. This contained a large proportion of XVI–XVIII as shown by the isolation of XIV in 62% yield after treatment with potassium hydroxide. The chief product of the reaction in methanol, as in benzene, is the angle carboxylate, XVI. 3-Methylgentisic acid, XII, was also found with the products of the alkaline decomposition of the adduct prepared in methanol. Methyl 3-methylgentisate may have been a contaminant of the distilled adduct.

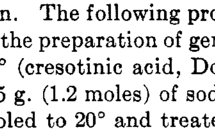
Under the experimental conditions usually employed for the addition of toluquinones to dienes, then, 5-carbomethoxy-1,4-toluquinone reacts almost exclusively at its carbomethoxyethene link with butadiene, and 6-carbomethoxy-1,4-toluquinone reacts at least principally at this link. The selectivity in the formation of structural isomers exhibited by these reactants supports the generalization of Alder and Stein (5) and its extension to the prediction of the chief structural isomers, as recently proposed (6).

Still, it seemed possible that the size and shape of the substituent groups might be important factors in determining the relative rates of addition at the two olefin links of such bifunctional dienophiles. It was thought that the rate of addition at the carbalkoxylated double bond might be reduced by increasing the size of the alkyl part of the ester group. Accordingly cyclohexyl 3-methylgentisate was prepared and oxidized to the quinone, which was used in benzene solution without isolation. Heating with butadiene at 100° gave 77% of a yellow viscous liquid boiling at 165–170° (0.6 mm.). This ester appeared to be more resistant to alkaline decomposition than the methyl esters. It did give the diphenol, XIV, as well as the corresponding quinone, and is therefore to be represented by XIX. Again no evidence was obtained that an angle methyl isomer had been formed, although a quantitative study of the product mixture was not undertaken.

From the acidic fraction of the products of alkaline decomposition of the adducts from 5-carbomethoxy-1,4-toluquinone and 6-carbocyclohexoxy-1,4-toluquinone there was isolated a few milligrams of a yellow solid, $C_{11}H_{10}O_3$, m.p. 171–173°. A very small quantity of material, m.p. 165–168°, was similarly obtained from the adduct from 6-carbomethoxy-1,4-toluquionone. This was the same compound, as indicated by a mixed melting point with the purer specimen. The substance in ethanol exhibited three maxima in the ultraviolet as follows:[2] Maxima: 2505 Å, ϵ 17000; 2770 Å, ϵ 18000; 3310 Å, ϵ 2600. Minima: 2610 Å, ϵ 11000; 3050 Å, ϵ 1350. Unfortunately not enough material was obtained to establish the structure of the compound. The few tests made (experimental part) were inconclusive. The compound probably was formed by hydrolytic splitting of the diketone ring (7) in the adducts, followed by decarboxylation and dehydrogenation. It is difficult to see how a compound with the properties observed could have been formed from the angle methyl compounds V and VI. If this guess is correct, the yellow compound may be *o*-pyruvylacetophenone, XX, or possibly the aldehyde, XXI. This hypothesis accords with the fact that all three adducts, regardless of the relative positions of the ester group and methyl group, gave the same product.



XX



XXI

EXPERIMENTAL[3]

3-Methylgentisic acid (XII). The preparation of this hydroquinone carboxylic acid has already been described (8) but few details were given. The following procedure is a modification of that used by Neubauer and Flatow (9) for the preparation of gentisaldehyde from salicylaldehyde. *o*-Cresotic acid, XI, m.p. 165–166° (cresotinic acid, Dow Chemical Co.) (78.3 g., 0.5 mole) was dissolved in a solution of 55.5 g. (1.2 moles) of sodium hydroxide in 400 cc. of water. The light brown solution was cooled to 20° and treated, while stirring, with 20-cc. portions of 40% sodium hydroxide and 150-cc. portions of 10% potassium per-

---

[2] Our thanks are due to Mr. Harry Bastron for these observations.

[3] All melting points are corrected. Analyses by Dr. Carl Tiedcke.

sulfate solution, beginning with the hydroxide, at such a rate that a temperature of 30–35° was maintained and until ten portions of each had been added. In some runs additional amounts (150–500 cc.) of 10% potassium persulfate were added. This raised the yield 5–10%, but gave a product melting over a larger range. After the addition was completed, stirring was continued for one hour, the mixture was allowed to stand at room temperature for 16–20 hours, and concentrated hydrochloric acid was then added until blue to Congo. Unchanged cresotic acid separated at this point and was filtered. The filtrate was extracted with ether several times to recover the remainder of the cresotic acid. In all, 43–49 g. was recovered. The aqueous solution was now treated with 450–500 cc. of concentrated hydrochloric acid and then heated on a steam-bath to decompose the monosulfate of the 3-methylgentisic acid. The warm solution was allowed to cool to room temperature and the almost black crystalline solid which had come out was filtered, washed with water, and dried. This crude 3-methylgentisic acid (11–15 g.) by sublimation at one mm. and 140–160°, using a dry ice condenser on the sublimator, gave 7.3–11.3 g. of white 3-methylgentisic acid, m.p. 221–223°. By extraction of the aqueous filtrate from the precipitated acid with ether, there was obtained 13–25 g. more of crude brown product, which was leached with a small amount of water and then, on careful sublimation, gave 9–13 g. of acid, m.p. 219–222°. The total yield varied from 18 to 28 g., 58–70% based on the cresotic acid actually consumed. 3-Methylgentisic acid is reported to melt at 215° (8, 10).

Methyl 3-methylgentisate. Ten grams of sublimed 3-methylgentisic acid was dissolved in 125 cc. of absolute methanol, the solution was saturated with dry hydrogen chloride, refluxed for 7 hours, and cooled. The solution was again saturated with hydrogen chloride and refluxing was continued for 18 hours. The methanol, water, and hydrogen chloride were removed at reduced pressure. The practically white crystalline residue was washed with 150–175 cc. of ice-water and filtered. The acid-free crystals were then crystallized from 800–1000 cc. of water containing a few drops of methanol; 9.5 g. (89%), long white needles, m.p. 106.2–108.2°. A sample recrystallized first from water containing a drop of methanol, then from ether-petroleum ether, and finally from water-methanol, m.p. 106.6–108.2°, was taken for analysis.

Anal. Calc'd for $C_9H_{10}O_4$: C, 59.3; H, 5.5.
Found: C, 59.3; H, 5.6.

6-Carbomethoxy-1,4-toluquinone (XIII). Dry silver oxide was prepared by precipitating a solution of silver nitrate with sodium hydroxide, filtering, washing exhaustively with water, acetone, and ether, and drying in a vacuum over phosphorus pentoxide. Methyl 3-methylgentisate (2.5 g.) was completely dissolved in 126 cc. of dry benzene in an amber bottle by gently warming, 2.5 g. of anhydrous sodium carbonate and 7.5 g. of dry silver oxide were added, and the mixture was maintained at 40–50° with shaking for 20 minutes. After settling, the contents of five such bottles were poured through a sintered glass plate and the solids were washed with warm dry benzene. The yellow-orange benzene solution was allowed to stand over anhydrous sodium carbonate in the dark for 3 hours. The benzene was then removed in a vacuum (bath 40°), the last traces with an oil-pump. The residue crystallized on cooling to 0°. Recrystallization from carbon disulfide (dried over P_2O_5) under anhydrous conditions, with rejection of a small quantity of insoluble syrup, gave, after cooling in the dark in ice-salt mixture, long yellow crystals, m.p. 49.8–51°, 10.45 g. (84.2%). A portion was sublimed at 40–50° and one mm. for analysis; m.p. 50.2–51.4°. The compound was kept in nitrogen over phosphorus pentoxide in the dark.

Anal. Calc'd for $C_9H_8O_4$: C, 59.9; H, 4.5.
Found: C, 59.9; H, 4.7.

4-Methylgentisic acid (*IX*). *p*-Toluquinone (Eastman Kodak), without purification, was hydrogenated to *p*-toluquinol in ethanol with Adams catalyst in batches of 20 g.; yield, 91%. The *p*-toluquinol was carboxylated according to Brunner (11) with potassium bicarbonate and potassium sulfite in a sealed tube. The 4-methylgentisic acid, 40–60% based on the *p*-toluquinol consumed, melted at 203–204°.

Methyl 4-methylgentisate. 4-Methylgentisic acid, m.p. 201–208°, 7.7 g., was esterified with 100 cc. of methanolic hydrogen chloride in exactly the same way as the 3-methylgentisic acid. The red oily residue which remained after removal of the methanol at reduced pressure crystallized on being scratched and cooled. Crystallization from 1200 cc. of water containing a few drops of methanol yielded crystals which appeared not to be homogeneous, since they melted from 79–109°. Fractional crystallization from water containing a little methanol finally gave 2.6 g. (34%) of material, m.p. 119–122°, which was taken to be methyl 4-methylgentisate. A small quantity of crystals which seemed to be homogeneous and melted at 79–81° was also obtained. These were not investigated. The ethyl ester was also prepared. Fractional crystallization gave, in poor yield, some material which corresponds to that reported by Brunner (11), m.p. 96–98°.

5-Carbomethoxy-1,4-toluquinone (*X*). The procedure used was the same as that used for the preparation of the 6-carbomethoxytoluquinone. The methyl 4-methylgentisate (2.4 g., m.p. 119–122°) was dissolved in 60 cc. of dry benzene and treated with 2.5 g. anhydrous sodium carbonate and 7.5 g. silver oxide. Yield, 1.5 g. (60%) of crude quinone, some of which was reddish and some yellow, melting at 35–39.4°, from dry carbon disulfide. A portion was sublimed in a vacuum for analysis; m.p. 38.4–39.4°.

Anal. Calc'd for $C_9H_8O_4$: C, 59.9; H, 4.5.
Found: C, 59.95; H, 4.4.

Methyl 1,4-diketo-2-methyl-2,7-naphthitadiene-5-carboxylate (*XV–XVII*). Methyl 4-methylgentisate, 2.5 g., was oxidized as just described, the benzene solution of the quinone was concentrated to 10 cc., and transferred to a Pyrex tube. Three grams of butadiene was added under anhydrous conditions. The tube was sealed and heated at 100° for 16 hours. Removal of the benzene at reduced pressure and distillation of the residue gave 2.48 g., 77%, of light yellow oil, b.p. (0.5 mm.) 137–139°.

Anal. Calc'd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.0.
Found: C, 65.8; H, 6.5.[4]

There was a higher-boiling residue of 0.25 g.

Reaction of XV–XVII with potassium hydroxide. A solution of 2 cc. of methanol and 20 cc. of 10% aqueous potassium hydroxide was added to 2.44 g. of XV–XVII in an atmosphere of nitrogen, and the mixture was shaken for 2 hours. The resulting purple solution was extracted five times with ether and the ether solution was washed with saturated sodium chloride and dried with sodium sulfate. Removal of the ether gave 1.6 g. of purple solid, 87% when calculated as 2-methyl-5,8-dihydronaphthalene-1,4-diol (XIV). Sublimation showed that this consisted entirely of XIV and its oxidation products. At one mm. and 130°, 100–150 mg. of it gave three fractions: A, 60 mg., yellow-brown, impure quinone, melting at 65–76° (2-methyl-5,8-dihydro-1,4-naphthoquinone, m. 86–87°)(4b); B, 20 mg., purple, m. 73–96°; and C, 50 mg., nearly white, m.p. 168–171°. Crystallization of C from benzene-petroleum ether and reduction of A in ether with sodium hydrosulfite, each gave XIV, m.p. 173–174°, identified by mixed m.p. with a specimen prepared according to the literature (4). Reduction of B gave an impure product, m.p. 163–165° alone, mixed with authentic XIV, m.p. 165–167°. The aqueous alkaline solution remaining after ether extraction of the products of decomposition of XV–XVII was acidified with hydrochloric acid, extracted with ether, the ether extract washed and dried, and the ether evaporated. This gave 260 mg. of greenish-yellow solid which darkened on standing, m. 110–135°. This was examined as described in the following section.

A product of ring cleavage of XV–XVII by hydrolysis, possibly o-*pyruvylacetophenone* (*XX*). The 260 mg. of material, m. 110–135°, just noted was dissolved in ether and treated with sodium hydrosulfite. The ether solution was dried and the ether evaporated to give a dark brown material containing yellow crystals. Repeated extraction of this with warm petroleum ether gave 25 mg., yellow, m.p. 167.8–170.6°; mixed melting point with XIV (m.p. 173–174°), 130–132.2°. This material from the acidic products of the alkaline de-

---

[4] Further purification was not attempted since the material gave a high yield of XIV with alkali.

composition of XV–XVII was therefore not XIV. Sublimation at 60–80° and 0.07–0.15 mm. gave 17 mg. of yellow sublimate, which softened at 169.8° and melted at 171.4–172°. This sublimate was analyzed. It did not decompose at the melting temperature, but formed fine yellow needles which upon reheating softened at 168.4° and melted at 171–171.4°.

Anal. Calc'd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30.
Found: C, 69.42; H, 5.05.

A mixed melting point of this compound with another specimen obtained by a similar series of operations from the cyclohexyl 1,4-diketo-2-methyl-2,7-naphthitadiene-10-carboxylate, XIX, was found to be 171.8–173°. XVI–XVIII (made in methanol) gave a very small quantity of what was very probably the same substance; m. 165–168°, mixed m.p. 167–170°.

Addition of one drop of 0.1 *N* sodium hydroxide to the yellow solution of the compound in aqueous methanol changed the color to cherry-red; hydrochloric acid restores the yellow color. Addition of hydrogen peroxide to the red alkaline solution of 6 mg. in methanol and warming gave a colorless solution from which no pure product could be isolated. The yellow compound gave a deep red color with ethanolic ferric chloride and metallic silver with Tollens' reagent. The absorption in the ultraviolet was measured with solutions in ethanol, 0.00003 to 0.003 *M* assuming the compound to be monomeric $C_{11}H_{10}O_3$.

Methyl 1,4-diketo-2-methyl-2,7-naphthitadiene-10-carboxylate (XVI–XVIII). Five grams of 6-carbomethoxy-1,4-toluquinone, XIII, m.p. 49.8–51° in 10 cc. of dry benzene was mixed with 3 g. (2 moles) of butadiene under anhydrous conditions. The mixture was heated in a sealed tube for 66 hours at 100°. After removal of the benzene at reduced pressure a light clear yellow oil remained which could not be crystallized. Distillation gave 5.1 g., 78%, slightly yellow oil, b. 155–157° at 1–2 mm., $n_D^{20.6}$ 1.5270. A small higher-boiling residue remained in the distilling flask. A portion of the adduct was redistilled and a middle cut, b. 184° at 4–5 mm. was taken for analysis.

Anal. Calc'd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.0.
Found: C, 66.4; H, 6.2.

When 139.3 mg. of the adduct ester (0.595 millimole) in ethanol was hydrogenated in the presence of 20 mg. of Adams catalyst, 43 ml. of hydrogen was absorbed in 25 minutes and 46.1 ml. in 3 hours. The calculated volume corresponding to 3 moles plus the volume required for the catalyst is 46.5 ml.

Reaction of XVI–XVIII with potassium hydroxide. Five and one-tenth grams of the adduct was shaken in an atmosphere of nitrogen with 35 cc. of 10% aqueous potassium hydroxide and 2 cc. of methanol. The shaking was done at 25° and continued for 3.75 hours. A light, fluffy precipitate came out. The alkaline mixture was extracted four times with ether. Some of the fluffy solid appeared to go into the ether. Washing the ether extract with saturated sodium chloride, drying with sodium sulfate, and concentration on a steam-bath precipitated a purple solid which was filtered; 2.51 g., 66% as XIV. When 70 mg. of this purple solid was heated at 3 mm. practically all of it (65 mg.) sublimed at 130°. Crystallization of the sublimate from benzene-petroleum ether gave fine white needles, m.p. 174–175.4° with darkening; mixed melting point with authentic XIV of m.p. 173–174°, 172.8–174°. Confirmation of the identity of this product with 2-methyl-5,8-dihydronaphthalene-1,4-diol was afforded by oxidizing it with silver oxide to 2-methyl-5,8-dihydro-1,4-naphthoquinone (4b), m.p. 86–87°, in quantitative yield. Also oxidation in glacial acetic acid with chromic acid gave 2-methyl-1,4-naphthoquinone.

The aqueous alkaline solution from the ether extraction was acidified with hydrochloric acid and extracted with ether; working up the extract gave 1.57 g. of oil. Distillation of a portion of this oil at very low pressure gave some solid, m.p. 148–151°, which did not readily crystallize from petroleum ether. This material was discarded before the yellow substance of m.p. 171–172°, provisionally assigned the structure of *o*-pyruvylacetophenone, had been isolated from similar fractions of the related reactions. It is probable that this same compound could have been isolated in this instance.

Reaction of 6-carbomethoxy-1,4-toluquinone (XIII) with butadiene in methanol. Six and one-tenth grams of quinone (0.034 mole) in 22 g. of absolute methanol was mixed under anhydrous conditions with 3 g. (0.055 mole) of butadiene, and the containing vessel was sealed off in a vacuum. The tube was heated at 75° for 88 hours. A small quantity (50–75 mg.) of solid was filtered out. This melted above 340° and was not further investigated. The methanol was removed and the residue which failed to crystallize was distilled. The fraction which distilled at 151–155° and one mm. was collected, 5.21 g. (68%). The higher-boiling residue was not investigated. Two and three-tenths grams of the distillate was shaken with 17.5 cc. of 10% potassium hydroxide and 4 cc. of methanol under the conditions described for the other preparations. The yield of purple solid from the neutral ether extract was 1.06 g. (62% as XIV). Sublimation gave two fractions which were shown to consist of XIV and the corresponding quinone.

The acidic ether extract gave an oily solid from which 210 mg. of solid, m. 204–210°, was obtained by treatment with warm benzene. This was shown to be 3-methylgentisic acid, XII, by conversion to the methyl ester, m.p. 106.8–108.2° (from water), by hydrogen chloride in methanol. Mixing with an authentic sample of methyl 3-methylgentisate did not depress the melting point.

Cyclohexyl 3-methylgentisate by ester interchange. To 75 cc. of cyclohexanol which had reacted with 200 mg. of potassium was added 18 g. of methyl 3-methylgentisate. The mixture was sealed off in a tube and heated 15 hours at 190°. The cyclohexanol was removed at 11 mm. and the residue was extracted with hot benzene. Concentration and cooling the benzene extract gave 4.2 g. of unchanged methyl ester. Distillation of the residue from the benzene mother liquors gave 4.2 g. more unchanged methyl ester, b. 140–150° (0.5 mm.) and then 4.4 g. (33.4% based on the methyl 3-methylgentisate converted) of cyclohexyl 3-methylgentisate, b. 179–182° (0.8 mm.). A portion of this was redistilled for analysis at 170–174° and 0.25 mm.

Anal. Calc'd for $C_{14}H_{18}O_4$: C, 67.2; H, 7.3.
Found: C, 66.9; H, 7.9.

Cyclohexyl 1,4-diketo-2-methyl-2,7-naphthitadiene-10-carboxylate (XIX). To 4.4 g. of cyclohexyl 3-methylgentisate in 175 cc. of dry benzene in an amber bottle were added 3.2 g. of anhydrous sodium carbonate and 9.6 g. of silver oxide. The mixture was warmed to 50°, shaken for 10 minutes, again warmed to 50°, and shaken for 10 minutes more. The solids were then removed by pouring through a sintered glass funnel and most of the benzene was distilled from the filtrate. The concentrated quinone solution so obtained was mixed with 2 g. of butadiene, sealed in a tube, and the mixture heated at 100° for 44 hours. The product was a yellow viscous material, b. 165–170° (0.6 mm.), 4.26 g., 77%. A cut, b. 160–161° (0.28 mm.), obtained on redistillation, was taken for analysis.

Anal. Calc'd for $C_{18}H_{22}O_4$: C, 71.5; H, 7.3.
Found: C, 71.4; H, 8.3 (?).

Reaction of XIX with potassium hydroxide. Two grams of XIX when treated with 13 cc. of 10% potassium hydroxide and 5 cc. of methanol under the conditions employed for the decomposition of the other adducts was not completely hydrolyzed. About 0.77 g. of oil remained unchanged. The aqueous methanolic alkaline solution was decanted from this oil, extracted with ether, the ethereal extract washed and dried, and the ether evaporated. Both XIV and the corresponding quinone were obtained from the residue by procedures already described. Extraction of the acidified aqueous layer with ether yielded 510 mg. of a red gum which was dissolved in ether and shaken with freshly prepared sodium hydrosulfite solution. Washing with saturated sodium chloride, drying, and evaporating gave 250 mg. of material which was sublimed at 60–80° and 0.07 mm. The semisolid yellow sublimate was crystallized from petroleum ether; 5 mg. of yellow needles, m.p. 170.8–173°, identical with the compound from methyl 1,4-diketo-2-methyl-2,7-naphthitadiene-5-carboxylate which may be *o*-pyruvylacetophenone.

SUMMARY

Under the experimental conditions employed, butadiene reacted only at the double bond with the ester group in 5-carbomethoxy-1,4-toluquinone and 6-carbomethoxy-1,4-toluquinone. The products, methyl 1,4-diketo-2-methyl-2,7-naphthitadiene-5-carboxylate and methyl 1,4-diketo-2-methyl-2,7-naphthitadiene-10-carboxylate, were obtained as high-boiling liquids which possibly are mixtures of the cis and trans isomerides.

These angle esters were converted by aqueous methanolic potassium hydroxide at room temperature into a mixture of products from which were isolated 2-methyl-5,8-dihydronaphthalene-1,4-diol, 2-methyl-5,8-dihydro-1,4-naphthoquinone, and a yellow crystalline compound which may be *o*-pyruvylacetophenone.

The same three products of alkaline decomposition were obtained from a reaction product of butadiene and 6-carbocyclohexoxy-1,4-toluquinone, but the conversion was much smaller. Hence the presence of some angle methyl adduct in the high-boiling liquid obtained is possible, although no positive evidence for it was found.

In addition to the foregoing, the following new compounds were prepared in the course of this work: Methyl 3-methylgentisate, cyclohexyl 3-methylgentisate, methyl 4-methylgentisate, 5-carbomethoxy-1,4-toluquinone, and 6-carbomethoxy-1,4-toluquinone.

BELTSVILLE, MD.

REFERENCES

(1) NUDENBERG AND BUTZ, *J. Am. Chem. Soc.*, **65**, 1436 (1943).

(2) (a) BUTZ AND BUTZ, *J. Org. Chem.*, **8**, 497 (1943); (b) ORCHIN AND BUTZ, *J. Org. Chem.*, **8**, 509 (1943).

(3) BRUNNER, *Monatsh.*, **34**, 913 (1913).

(4) (a) CHUANG AND HAN, *Ber.*, **68**, 876 (1935); (b) FIESER AND CHANG, *J. Am. Chem. Soc.*, **64**, 2043 (1942).

(5) ALDER AND STEIN, *Angew. Chem.*, **50**, 510 (1937).

(6) BUTZ AND BUTZ, *J. Org. Chem.*, **7**, 212 (1942).

(7) MEYER, *Helv. Chim. Acta*, **18**, 461 (1935).

(8) SCHERING, *Jahresber.*, 1851 (1895); SCHERING, Ger. pat. 81297, Friedländer Fortschr. Theerfarbenfabrikation, **4**, 127.

(9) NEUBAUER AND FLATOW, *Z. physiol. Chem.*, **52**, 382 (1907).

(10) LESPAGNOL AND BAR, *Bull. soc. chim.*, (5) **3**, 1107 (1936).

(11) BRUNNER, *Monatsh.*, **2**, 458 (1881).