sorption peak in carbon tetrachloride at 11.2 μ was used for quantitative analysis.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.82. Found: C, 75.52; H, 8.78.

To an identical metalation mixture which had stood for 18 days to allow the amylsodium to decompose, was added 10 ml. of 2,6-diisopropylanisole. Carbonation of the mixture after one week gave 0.1 g. of distilled acids whose infrared spectrum showed no trace of an absorption peak at 9.9 μ.

Metalation of 2,6-Diisopropylanisole.—To each of two bottles containing 4.80 g. (0.025 mole) of 2,6-diisopropylanisole was added a 100-ml. aliquot of the amylsodium preparation. Carbonation of a bottle after one week and short-path distillation of the acids gave 0.23 g. (4.0%) of product, m.p. 160.0–161.5° after two crystallizations from 50% aqueous ethanol. The material did not depress the melting point of 3,5-diisopropyl-4-methoxybenzoic acid. After 18 days, the other bottle was treated with 10 ml. of 1,3-diisopropylbenzene. The contents were carbonated one week later. Infrared examination of the 0.41 g. of distilled acids disclosed no peak at 11.2 μ.

A 100-ml. aliquot of amylsodium was added to a bottle containing 4.80 g. (0.025 mole) of 2,6-diisopropylanisole and 4.05 g. (0.025 mole) of 1,3-diisopropylbenzene. Carbonation after one week and distillation of the acids gave 0.30 g. of mixed acids which was found from the infrared spectrum to consist of 72% of 3,5-diisopropylbenzoic acid and 28% of 3,5-diisopropyl-4-methoxybenzoic acid. The same method of analysis applied to a known mixture of the two acids showed the probable error to be ±2%.

Acknowledgment.—The author is indebted to Dr. S. M. Nagy of this Laboratory, and to his staff, for all analyses and infrared spectra.

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

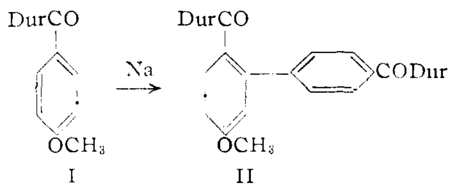
Conjugate Bimolecular Reduction of Hindered Ketones Involving Replacement of Methoxyl Groups. III[1]

BY REYNOLD C. FUSON, GEORGE W. PARSHALL[2] AND EARL H. HESS[3]

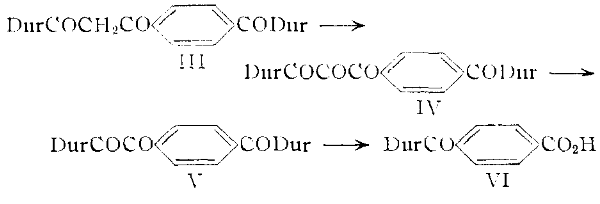
RECEIVED FEBRUARY 3, 1955

A number of hindered methoxy ketones have been shown to undergo bimolecular reduction with methoxyl group elimination when treated with sodium. Anisyl duryl ketone thus was converted to 2,4′-diduroyl-5-methoxy-3,4-dihydrobiphenyl (II, in text). Anisyl mesityl ketone reacted similarly. Structure proof of the reduction products was based primarily on the results of an alkaline permanganate oxidation. The two oxidation products which were isolated have been identified by comparison with authentic samples. Duryl *o*-methoxyphenyl ketone and mesityl *o*-methoxyphenyl ketone also underwent reduction to yield products analogous to those from the anisyl ketones.

Conjugate bimolecular reduction of duryl *o*-methoxyphenyl ketone with the binary mixture, Mg + MgI_2,[4] has been shown to proceed with loss of methoxyl groups.[5] We now have found that similar results can be obtained with metallic sodium. When anisyl duryl ketone (I) was treated with sodium in an ether–benzene solution, a product, which proved to be 2,4′-diduroyl-5-methoxy-3,4-dihydrobiphenyl (II), was obtained in 54% yield. Chromatographic adsorption yielded the reduction product in a state of high purity as well as a small amount of a high-melting by-product, the structure of which has not been investigated.



Treatment of the hydroaromatic diketone II with a palladium-on-charcoal catalyst converted it to the corresponding fully aromatic compound, which could be cleaved to a phenol; an attempted cleavage before aromatization gave a red resin. The hydroaromatic compound reacted with maleic anhydride to form a Diels–Alder adduct and also absorbed two moles of hydrogen under mild conditions to produce the corresponding diketone containing a fully saturated ring. Alkaline permanganate oxidation of the dihydroaromatic compound gave *p*-duroylphenyl duryl diketone (V) and *p*-duroylbenzoic acid (VI), the structures of which have been proved by independent syntheses. It is assumed that destruction of the non-aromatic ring takes place and that the resulting tetraketone IV undergoes decarbonylation. Cleavage of the triketone V might be expected to yield *p*-duroylbenzoic acid (VI). The *p*-duroylbenzoic acid was obtained from the corresponding ethyl ester, prepared in turn either by condensation of *p*-carbethoxybenzoyl chloride with durene or by ethanolysis of duryl *p*-cyanophenyl ketone.



The tetraketone was synthesized by condensing *p*-duroylbenzoyl chloride with the bromomagnesium enolate of acetodurene and oxidizing the resulting triketone III with selenium dioxide. Because of its extreme sensitivity to heat and to alkali, the tetraketone could not be isolated in pure form. However, when treated with base, it did break down into the same mixture of products V and VI that was obtained by the permanganate degradation of the dihydroaromatic compound.

---

(1) This investigation was supported in part by a grant from the Office of Ordnance Research (Contract No. DA-11-022-ORD-874).

(2) National Science Foundation Fellow, 1952–1953; Allied Chemical and Dye Corp. Fellow, 1953–1954.

(3) Socony–Vacuum Oil Co. Fellow, 1954–1955.

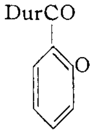
(4) M. Gomberg and W. E. Bachmann, THIS JOURNAL, **49**, 236 (1927).

(5) R. C. Fuson and R. O. Kerr, *J. Org. Chem.*, **19**, 373 (1954).

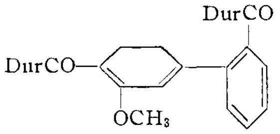
Prolonged treatment of the dihydroaromatic compound with ozone produced small amounts of a di- or triketo ester in addition to a water-insoluble acid. These compounds were not obtained in amounts sufficient for identification. When the dihydroaromatic compound was allowed to react with *t*-butylmagnesium chloride, displacement of the methoxyl group and aromatization took place. It has been demonstrated that in order for displacement to occur the methoxyl group must be attached at a conjugate position. The aromatization may well have proceeded by way of a disproportionation process; a trace amount of a second product was isolated in which saturation of the dihydroaromatic ring apparently had occurred. Of the two possible structures that can be written in which the methoxyl group is in conjugation with the carbonyl function, II is considered more likely because of its conjugation with the adjoining ring.

When anisyl mesityl ketone was treated with sodium, a yellow-brown oil was obtained. Adsorption chromatography permitted the isolation of a yellow reduction product ($C_{33}H_{34}O_3$) in 18% yield having an infrared spectrum very similar to that of the reduction product II of the duryl ketone. On this basis it has been assumed to be the mesityl analog of the duryl compound II.

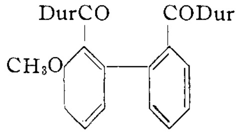
Duryl *o*-methoxyphenyl ketone and its mesityl analog reacted with sodium to give products which, although not all have been identified, are clearly bimolecular and serve to show that this type of reaction is general for hindered *o*- and *p*-methoxy ketones. The skeletal structure of the product from the duryl ketone VII must be either VIII or IX.



VII

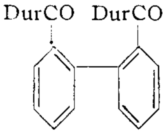


VIII

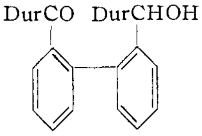


IX

Two additional products X and XI were isolated, the structures of which have been proved by comparison with authentic samples.

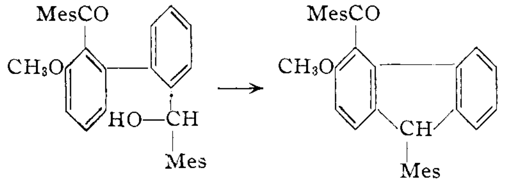


X



XI

Sodium reduction of mesityl *o*-methoxyphenyl ketone led to a complex mixture of products. A hydroaromatic compound was obtained which was considered to be the mesityl analog of the hydroaromatic product VIII (or IX). Another compound was shown to be *o*-(*o*-mesitoylphenyl)-phenylmesitylcarbinol by comparison with a known sample. A third product was assigned structure XII. In the presence of sulfuric acid it underwent dehydration to give a product that is probably the fluorene derivative XIII.



XII XIII

Since these methoxy ketones are vinylogs of esters, it seems probable that the theories which have been developed to account for the acyloin reaction[6] are applicable here. The violet or blue color of the reaction mixtures could be due to the presence of free radicals.

Experimental[7]

Anisyl Duryl Ketone and Anisyl Mesityl Ketone.—These ketones were synthesized by Friedel–Crafts reactions as described earlier.[8] In order to obtain pure anisyl mesityl ketone, however, distillation at reduced pressure was necessary, b.p. 150–155° at 0.1–0.5 mm. It was recrystallized from 95% ethanol, m.p. 77–78° (reported[9] 78°).

Sodium Reduction of the *p*-Methoxy Ketones.—A solution of 0.04 mole of the ketone in 100 ml. of anhydrous benzene was added over a 30-minute interval to 2.0 g. (0.09 g. atom) of freshly powdered sodium in 100 ml. of anhydrous ether. The sodium had been powdered by violent shaking of the molten metal under xylene. When the first portion of the ketone was added, the surface of the sodium became red. This color soon began to diffuse into the solution and the whole reaction mixture turned deep red. In some experiments this color change did not occur immediately, and it was necessary to wait until the red color did appear before the main portion of the ketone was added. Otherwise the reaction took an entirely different course, anisic acid being one of the products. This solution was heated under reflux, with stirring, for 2 hours after the addition was complete. The flask was then placed in an ice-bath, and 50 ml. of cold 10% sulfuric acid was added *cautiously* to the reaction mixture. The organic layer was removed, washed with water and dried over sodium sulfate. The solvent then was distilled at diminished pressure.

The reduction product from anisyl duryl ketone could be induced to crystallize by trituration with methanol. After several washings with methanol, the yellow crystalline solid melted at 213–215° and weighed 5.5 g. (54%). Repeated recrystallization of the compound from methanol raised the melting point to 216–217°.

Anal.[10] Calcd. for $C_{35}H_{38}O_3$: C, 82.97; H, 7.56. Found: C, 82.88; H, 7.53.

The infrared spectrum[11] of this compound contains a band assignable to a hindered conjugated ketone (1662 cm.$^{-1}$) and bands assignable to the ether linkage (1041, 1264 cm.$^{-1}$). There is also an extremely intense absorption band at 1544 cm.$^{-1}$, probably assignable to the highly conjugated olefinic system of the hydroaromatic ring.

The high-melting by-product, obtained from the reaction mixture by chromatographic separation, was present in only trace amounts. When recrystallized from a mixture of benzene and high-boiling petroleum ether it melted at 294–298° (uncor.).

The corresponding hydroaromatic reduction product of anisyl mesityl ketone was obtained by eluting a column containing 120 g. of activated alumina with successively more polar mixtures of cyclohexane and ether. From half

---

[6] S. M. McElvain, "Organic Reactions," Vol. 4, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 256.

[7] All melting points are corrected unless stated otherwise.

[8] R. C. Fuson, W. D. Emmons and G. W. Parshall, THIS JOURNAL, **76**, 5466 (1954).

[9] R. C. Fuson and R. Gaertner, *J. Org. Chem.*, **13**, 496 (1948).

[10] The microanalyses were performed by Mr. Joseph Nemeth, Mrs. Esther Fett, Mr. Katherine Pih and Mrs. Lucy Chang.

[11] The infrared spectra were determined and interpreted by Miss Helen Miklas and Mr. James Brader.

of the crude reaction mixture described above (about 5.0 g.), 0.85 g. (18%) of the hydroaromatic compound was obtained during the elution with 10:1 cyclohexane–ether, m.p. 157.5–159°. Recrystallization of the compound from methanol raised the melting point to 159–160°.

Anal. Calcd. for $C_{33}H_{34}O_3$: C, 82.81; H, 7.16. Found: C, 82.56; H, 7.25.

The infrared spectrum is identical to that of its duryl analog except for the slight differences between mesityl and duryl absorption.

Aromatization of the Reduction Product from Anisyl Duryl Ketone.—Two grams of the hydroaromatic compound was mixed well with 0.2 g. of a 10% palladium-on-charcoal catalyst and the mixture was held at 300° for one hour in a cold finger sublimation apparatus. During this period evolution of a gas was observed. The aromatized product then was distilled under diminished pressure onto the cold finger. It formed a light yellow glass, b.p. 280–300° at 0.1–0.15 mm., which was crystallized readily from a mixture of ether and low-boiling petroleum ether. It weighed 1.25 g. (62.5%), m.p. 178–182°. Two further crystallizations of the compound from the same solvent pair raised the melting point to 185–186°.

Anal. Calcd. for $C_{35}H_{36}O_3$: C, 83.30; H, 7.19. Found: C, 83.01; H, 7.34.

The intense infrared absorption band previously observed at 1544 cm.$^{-1}$ is absent in the spectrum of this compound, indicating the loss of the highly conjugated hydroaromatic system.

Cleavage of the Methoxyl Group of the Aromatized Compound.—A mixture of 1.0 g. of the aromatized product, 2 ml. of 48% hydrobromic acid and 10 ml. of glacial acetic acid was heated under reflux for 16 hours and poured into 150 ml. of ice-water. The solid which separated was collected on a filter and dissolved in hot 5% sodium hydroxide solution. When allowed to cool, the solution deposited the sodium salt as a colorless precipitate; it was recrystallized twice from water and treated with hydrochloric acid to free the phenol. The phenol was collected on a filter, washed with water, dried and recrystallized from a mixture of benzene and high-boiling petroleum ether; yield 0.43 g. (43.5%), m.p. 183–185°. Two further recrystallizations from the same solvent pair, followed by another from aqueous ethanol, yielded pure white needles melting at 184.5–185°.

Anal. Calcd. for $C_{34}H_{34}O_3$: C, 83.23; H, 6.99. Found: C, 83.49; H, 7.16.

Significant in the infrared spectrum of this compound is a band assignable to a phenolic hydroxyl group (3390 cm.$^{-1}$).

When the hydroaromatic compound II was subjected to these same ether-cleavage conditions, a red amorphous powder was obtained which decomposed above 200°. Chromatographic separation yielded a cardinal-red resin which likewise did not have a melting point.

Hydrogenation of the Sodium Reduction Product from Anisyl Duryl Ketone.—A solution of 9.5 g. of the sodium reduction product from anisyl duryl ketone in 100 ml. of purified dioxane[12] was treated with hydrogen over 1 g. of platinum oxide catalyst for 8 hours (60 p.s.i. at 25°). To the reaction mixture was added an additional gram of platinum oxide catalyst, and the treatment at 60 p.s.i. was continued for 15 hours. During the process, a fine, white solid precipitated from the dioxane solution. It was removed together with the catalyst by filtration. Distillation of the filtrate at reduced pressure left only a small amount of a pale yellow gum. The solid material was separated from the catalyst by dissolving it in a mixture of benzene and high-boiling petroleum ether, from which it was recrystallized. It weighed 4.9 g. (51.5%) and melted at 237–238°. Three recrystallizations of the compound from dioxane did not change its melting point.

Anal. Calcd. for $C_{35}H_{42}O_3$: C, 82.31; H, 8.29. Found: C, 82.28; H, 7.99.

Saturation of the hydroaromatic ring of the sodium reduction product caused the expected changes in the infrared spectrum. The absorption band indicative of the presence of the hydroaromatic double bonds (1544 cm.$^{-1}$) was missing as was one of the absorption bands assignable to a highly conjugated ketone (1630 cm.$^{-1}$). A new absorption band assignable to a hindered, unconjugated ketone (1683 cm.$^{-1}$) was present.

In preliminary experiments it was found that the product from the hydrogenation reaction was very difficult to obtain in a pure form when a shorter reaction time was used or when a second batch of catalyst was not added.

Formation of a Diels–Alder Adduct.—To 1.5 g. of the hydroaromatic compound was added a solution of 0.4 g. of maleic anhydride in 10 ml. of xylene. This mixture was heated under reflux for 8 hours. A few glassy, light yellow crystals formed when the solution was allowed to stand overnight. These were washed with low-boiling petroleum ether, m.p. 243–248°. In an attempt to recrystallize the substance from a mixture of benzene and high-boiling petroleum ether, only starting material was isolated. Since the melting point of the product was 25° above that of the starting material, it is reasonable to assume that an adduct was formed which dissociated during the recrystallization.

Permanganate Oxidation of the Hydroaromatic Compound.—A solution of 1.5 g. of the hydroaromatic compound, 5 ml. of pyridine and 2 ml. of water was stirred at 40° while 3.9 g. of solid potassium permanganate was added over a 30-minute interval. The reaction mixture was stirred for one hour after the addition was complete. It was then diluted to 20 ml., the manganese dioxide removed by filtration, and the filtrate poured into 25 ml. of dilute hydrochloric acid. After the permanganate color was discharged, a nearly white solid remained. It was dissolved in ether, and the ether solution was extracted with 5% sodium hydroxide solution. Acidification and subsequent cooling of the solution produced a white, flocculent precipitate. After three crystallizations from aqueous ethanol, the acid melted at 218–221° and weighed 0.5 g. (52.5%). Three vacuum sublimations of this material raised the melting point to 224–225°. A mixed melting point determination and comparison of infrared spectra showed this acid to be identical to a sample of *p*-duroylbenzoic acid which was synthesized independently.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.63; H, 6.38.

The manganese dioxide was collected on a filter, dried thoroughly and then extracted several times with ether. Evaporation of the ether left a small quantity of a yellow solid which, after two recrystallizations from aqueous methanol, melted at 201–204°. A mixed melting point determination and a comparison of infrared spectra showed it to be identical to a sample of *p*-duroylphenyl duryl diketone obtained by independent synthesis.

Independent Synthesis of *p*-Duroylbenzoic Acid.—The preparation of *p*-carbethoxybenzoyl chloride beginning with terephthalic acid was essentially the same as that described earlier by Cohen and Pennington.[13] One important change made in this procedure was in the purification of ethyl hydrogen terephthalate, which could be separated from terephthalic acid quite satisfactorily by a multiple extraction with chloroform in which terephthalic acid is nearly insoluble.

***p*-Duroylbenzoic Acid.**[14,15]—To a solution of 91 g. of *p*-carbethoxybenzoyl chloride in 200 ml. of anhydrous *sym*-tetrachloroethane, cooled to 0°, was added 115 g. of anhydrous aluminum chloride. While the solution was kept at 0°, 57.5 g. of durene in 275 ml. of anhydrous *sym*-tetrachloroethane was added, with stirring, over a 45-minute interval. The reaction mixture was stirred at 0° for 3 hours after which it was allowed to come to room temperature and stirred for an additional 7 hours. The complex was hydrolyzed by adding 200 ml. of ice-water through the dropping funnel. The solvent was removed by steam distillation. When allowed to stand overnight the residue from the steam distillation solidified. A small portion was removed; after four crystallizations from aqueous ethanol the ethyl *p*-duroylbenzoate melted at 78.5–79°.

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.15; H, 7.20.

A mixed melting point determination and comparison of infrared absorption spectra showed it to be identical to a sample of ethyl *p*-duroylbenzoate prepared by a second method.

---

[12] The dioxane was purified by heating under reflux for six hours over sodium followed by distillation of the pure solvent.

[13] J. B. Cohen and H. Smith de Pennington, *J. Chem. Soc.*, **113**, 62 (1918).

[14] M. E. Smith, THIS JOURNAL, **43**, 1920 (1921).

[15] D. Papa, E. Schwenk and H. Hankin, *ibid.*, **69**, 3018 (1947).

The main portion of the residue from the steam distillation was melted and added to a solution of 30 g. of sodium hydroxide in 300 ml. of ethanol and 100 ml. of water. This mixture was heated under reflux for 2.5 hours, then diluted with 1000 ml. of water. The solution was filtered, and the filtrate was acidified with dilute hydrochloric acid. The precipitate which formed was washed with water and dried in an oven at 120°. When crystallized from methanol it melted at 240–243° and weighed 88 g. (73.3%). Two further crystallizations from methanol followed by two recrystallizations from benzene *lowered* the melting point to 224–225°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.64; H, 6.66.

The infrared absorption spectrum of this compound showed absorption bands assignable to a bonded carboxylic acid (3040, 2650, 2540, 1688 cm.$^{-1}$) and to a hindered conjugated ketone (1674 cm.$^{-1}$).

Alternate Synthesis of Ethyl *p*-Duroylbenzoate.[16]—Dry hydrogen chloride was passed rapidly into a suspension of 15 g. of duryl *p*-cyanophenyl ketone[17] in one l. of absolute ethanol for 5 hours. This process caused the reaction mixture to become warm. The mixture was boiled under reflux for 7 hours while a slow stream of hydrogen chloride was passed in. The clear solution was allowed to stand overnight, the temperature being held at about 70°. The alcohol was removed under reduced pressure and the residue was shaken with 200 ml. of water. The mixture was extracted with ether, the ether layer washed twice with a 5% potassium carbonate solution and then with water. Drying of the ether solution followed by evaporation of the solvent left 16.8 g. (95%) of ethyl *p*-duroylbenzoate; m.p. 75–76.5°. Recrystallization from aqueous ethanol raised the melting point to 77–77.5°.

Anal. Calcd. for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.65; H, 7.36.

Independent Synthesis of *p*-Duroylphenyl Duryl Diketone. (a) ***p*-Duroylbenzoyl Chloride.**—A mixture of 88 g. of *p*-duroylbenzoic acid and 130 g. of thionyl chloride was heated under reflux for 8 hours. When the excess thionyl chloride was distilled at reduced pressure, a brown solid crystallized. After two recrystallizations from high-boiling petroleum ether, the yellow acid chloride weighed 67 g. (71.6%). The acid chloride retained its yellow color after two further recrystallizations from the same solvent; m.p. 114.5–115.5°.

Anal. Calcd. for $C_{18}H_{17}ClO_2$: C, 71.87; H, 5.70; Cl, 11.79. Found: C, 71.97; H, 5.97; Cl, 11.62.

The infrared absorption spectrum of this compound showed bands assignable to an aromatic acid chloride (1775, 1740, 880 cm.$^{-1}$) and to a hindered conjugated ketone (1677 cm.$^{-1}$).

(b) **1-(*p*-Duroylphenyl)-3-duryl-1,3-propandione.**[18]—Ethylmagnesium bromide was prepared from 26.6 g. of ethyl bromide and 5.9 g. of magnesium in 125 ml. of anhydrous ether. To this reaction mixture there was added, with vigorous stirring, a solution of 40 g. of acetodurene in 125 ml. of anhydrous ether over a 40-minute interval. Immediately after the addition was begun, a white precipitate formed. After the addition was complete, the reaction mixture was heated under reflux for 45 minutes.

The flask was cooled in an ice–salt-bath, and to it was added, with stirring, a solution of 34.2 g. of *p*-duroylbenzoyl chloride in 100 ml. of anhydrous ether and 50 ml. of anhydrous benzene. During this process the white precipitate disappeared and a yellow-green sludge replaced it. The addition required 40 minutes after which it was stirred for 45 minutes longer at ice–salt-bath temperature. The reaction mixture was hydrolyzed with 100 ml. of an ice-cold mixture of 1:1 concentrated hydrochloric acid and water. A white precipitate, formed during the hydrolysis, dissolved when 2000 ml. of benzene was added. The organic layer was washed with 300 ml. of 10% sodium carbonate solution, and then with an equal volume of water. The volume of the benzene solution was reduced to about 200 ml. by distillation at diminished pressure, after which it was steam distilled. Twenty grams (50%) of acetodurene was recovered from the distillate. The residue from the steam distillation solidified when allowed to cool. When recrystallized from benzene it weighed 29 g. (58%), m.p. 243–245°. After two further recrystallizations from benzene it melted at 244–245°.

Anal. Calcd. for $C_{30}H_{32}O_3$: C, 81.78; H, 7.32. Found: C, 81.78; H, 7.27.

The infrared absorption spectrum of this compound showed an absorption band assignable to a hindered conjugated ketone (1674 cm.$^{-1}$) and a broad band centering at 1605 cm.$^{-1}$ assignable to a chelated ketone.

(c) **Attempted Preparation of *p*-Duroylphenyl Duryl Triketone.**[19]—To a hot solution of 8 g. of selenium dioxide in 100 ml. of dioxane, was added 10 g. of 1-(*p*-duroylphenyl)-3-duryl-1,3-propandione. The mixture was heated under reflux for 20 hours. This caused the precipitation of a quantity of black selenium which was removed by filtration. The filtrate was distilled under reduced pressure until about 15 ml. of a bright orange oil remained. The oil was decanted from the unchanged selenium dioxide which precipitated during the removal of the solvent. Trituration of this oil with a little low-boiling petroleum ether caused the precipitation of an orange solid. Repeated washings with low-boiling petroleum ether removed most of the orange color, thus leaving a bright yellow amorphous solid weighing 4.3 g., m.p. 158–166°. Three crystallizations of this material from absolute ethanol brought it to a constant melting point of 207–208°, but with very poor recovery.

Anal. Calcd. for $C_{30}H_{30}O_4$: C, 79.27; H, 6.65. Found: C, 81.00; H, 7.06.

The infrared absorption spectrum of this material showed only one very intense absorption band in the carbonyl region (1685 cm.$^{-1}$). This was likely a combination of several carbonyl absorptions.

One gram of this material from a second oxidation reaction mixture was subjected to chromatographic separation after a single crystallization from absolute ethanol. Elution of a Florisil column (2.5 × 45 cm.) with 15:1 cyclohexane–ether yielded 0.31 g. of a bright yellow crystalline material melting at 209–210°.

Anal. Found: C, 81.16; H, 7.01.

(d) ***p*-Duroylphenyl Duryl Diketone.**—A mixture of 1.3 g. of the selenium dioxide oxidation product, 5 ml. of pyridine, 2 ml. of water and 0.4 g. of sodium hydroxide was stirred and held at 40° for one hour. The basic solution was diluted with water to a volume of 25 ml. after which it was extracted with ether. Evaporation of the ether left a yellow solid, m.p. 201–204°.

The infrared absorption spectrum of this compound was quite different from that of the starting material. This spectrum showed a resolution of the carbonyl absorption into two bands, an intense band (1676 cm.$^{-1}$) assignable to two hindered conjugated carbonyl groups and a second band (1695 cm.$^{-1}$) of approximately half the intensity assignable to a hindered ketone, conjugated to a lesser degree. Vacuum sublimation raised its melting point to 206.5–207.5°.

Anal. Calcd. for $C_{29}H_{30}O_3$: C, 81.66; H, 7.09. Found: C, 81.73; H, 7.05.

Acidification of the basic solution from the reaction mixture caused a white, fluffy precipitate to form. It was collected on a filter, washed and crystallized three times from aqueous ethanol; m.p. 219–222°. Comparison of the infrared absorption spectrum with that of the known *p*-duroylbenzoic acid showed them to be identical. A mixture with pure *p*-duroylbenzoic acid (m.p. 224–225°) melted at 218–222°.

Ozonolysis of the Hydroaromatic Compound.—A solution of 5 g. of the sodium reduction product of anisyl duryl ketone in 50 ml. of methylene chloride was treated with ozone for 2 hours. The solvent was then removed under reduced pressure and the residue was added to 35 ml. of glacial acetic acid. The resulting solution was added, with stirring, to a mixture of 50 ml. of water, 30 g. of 30% hydrogen peroxide and 1.5 ml. of concentrated sulfuric acid. After the addition the mixture was heated under reflux, with stirring, for 3 hours. The mixture was cooled and the insoluble gum which remained was extracted with ether. This

---

[16] This experiment was performed by R. J. Tull.

[17] R. C. Fuson, W. D. Emmons and R. J. Tull, *J. Org. Chem.*, **16**, 648 (1951).

[18] R. C. Fuson, W. O. Fugate and C. H. Fisher, THIS JOURNAL, **61**, 2362 (1939).

[19] R. C. Fuson, H. H. Weinstock and G. E. Ullyot, *ibid.*, **57**, 1803 (1935).

operation caused the precipitation of a small amount of a nearly white solid, which was collected on a filter and recrystallized from a mixture of benzene and high-boiling petroleum ether; m.p. 190.5–191.5°. The infrared spectrum of this compound has absorption bands assignable to an ester (1732 cm.$^{-1}$) and a very strong band (1676 cm.$^{-1}$) indicating two or more conjugated keto-carbonyl groups.

The water-insoluble, acidic fraction of the ozonolysis mixture contained a small amount of material that could not be induced to crystallize.

Reaction of *t*-Butylmagnesium Chloride with the Hydroaromatic Compound.[8]—*t*-Butylmagnesium chloride was prepared from 2.0 g. of *t*-butyl chloride and 0.48 g. of magnesium in 25 ml. of ether. Rapid addition of 3.0 g. of the hydroaromatic compound produced a deep red-brown color. The reaction mixture was stirred for 45 minutes at room temperature and then was hydrolyzed with dilute hydrochloric acid. The organic layer was washed with water and dried over sodium sulfate. Removal of the solvent at reduced pressure left a yellow-orange oil which could not be induced to crystallize from any of the common solvents. Chromatographic separation on a column containing 120 g. of activated alumina, the column being developed with a cyclohexane–ether solvent pair, gave two products. The first, eluted with 3:1 cyclohexane–ether, weighed 0.35 g. (11%) and melted at 234–237°. Recrystallization of the compound from aqueous ethanol raised the melting point to 238°.

Anal. Calcd. for $C_{38}H_{42}O_2$: C, 85.99; H, 7.98. Found: C, 85.93; H, 8.10.

The infrared absorption spectrum of this compound showed an unsymmetrical band assignable to two hindered conjugated ketone functions (1670, 1675 cm.$^{-1}$). The absence of the absorption band typical of the conjugated hydroaromatic system (1544 cm.$^{-1}$) was also significant as in the case of the aromatization reaction.

Elution of the column with 100% ether yielded a small amount of a white solid, m.p. 207–208°. Its infrared spectrum showed two significant absorption bands, one assignable to a hindered conjugated ketone group (1680 cm.$^{-1}$) and the other to a less highly conjugated ketone group (1701 cm.$^{-1}$).

Duryl *o*-Methoxyphenyl Ketone and Mesityl *o*-Methoxyphenyl Ketone.—These ketones were prepared in 82 and 64% yields, respectively, by a method previously reported.[5,20]

Sodium Reduction of Duryl *o*-Methoxyphenyl Ketone.—The sodium reduction of this ketone was carried out in a similar manner to those already described. The color changes observed were also similar with the exception that the deep red color which formed when the first portion of the ketone was added, gradually changed to an inky blue.

Chromatographic separation of one-third (3 g.) of the crude duryl *o*-methoxyphenyl ketone mixture yielded 0.45 g. (13%) of a yellow compound when the column was eluted with 5:1 cyclohexane–ether; m.p. 168.5–171.5°. Two recrystallizations of the compound from methanol raised the melting point to 173.5–174.5°.

Anal. Calcd. for $C_{35}H_{38}O_3$: C, 82.97; H, 7.56. Found: 83.23; H, 7.56.

The infrared spectrum of this compound was similar to those of the other hydroaromatic compounds. The intense absorption band at 1544 cm.$^{-1}$, however, was not present.

Elution of the column with 3:1 cyclohexane–ether produced 0.1 g. (3%) of a white compound which, after four recrystallizations from a mixture of benzene and high-boiling petroleum ether, melted at 263–264°. A mixed melting point determination with an authentic sample of *o*-(*o*-duroylphenyl)-phenyldurylcarbinol[21] showed no depression. The infrared spectrum of this compound was identical to that of the authentic sample.

On one occasion a trace of a third product was isolated from this reaction mixture. It was eluted from the column preceding the keto alcohol described above. When recrystallized from a mixture of benzene and high-boiling petroleum ether it melted at 255–256°. A mixed melting point determined with an authentic sample of 2,2′-diduroylbiphenyl[5] showed no depression. Comparison of the infrared absorption spectrum with that of the authentic sample also showed them to be identical.

Sodium Reduction of Mesityl *o*-Methoxyphenyl Ketone.—This reduction proceeded in a manner analogous to that of duryl *o*-methoxyphenyl ketone. Because of the complexity of the product, it was separated on a larger scale than that of the chromatographic separations previously described. The entire reaction mixture (about 10 g. of brown oil) was added to a column containing one pound of activated alumina. The column then was eluted with successively more polar mixtures of cyclohexane and ether as described below.

Elution of the column with 10:1 cyclohexane–ether yielded 0.2 g. (2%) of a compound melting at 114–115.5°. A mixed melting point determination showed it to be unchanged starting material.

A 3:1 cyclohexane–ether mixture produced 0.69 g. (7%) of a yellow compound, m.p. 159–161.5°. Three recrystallizations of the compound from methanol narrowed the melting range to 160–161°.

Anal. Calcd. for $C_{33}H_{34}O_3$: C, 82.81; H, 7.16. Found: C, 83.02; H, 6.90.

The infrared absorption spectrum of this compound was similar to those of the other hydroaromatic reduction products.

Immediately following the yellow product a trace amount of a white compound was eluted with the same solvent pair; m.p. 228–231.5°. Recrystallized from ethyl acetate it melted at 237–238°.

The infrared spectrum of this compound showed absorption bands assignable to a hydroxyl group (3370 cm.$^{-1}$) a hindered conjugated ketone (1637 cm.$^{-1}$) and an ether linkage (1253, 1018 cm.$^{-1}$).

Elution of the column with 1:1 cyclohexane–ether yielded a trace amount of a compound melting at 239–240°. A mixed melting point determination and a comparison of infrared spectra showed it to be identical to an authentic sample of *o*-(*o*-mesitoylphenyl)-phenylmesitylcarbinol.[21]

One hundred per cent. ether eluted 0.51 g. (5.2%) of another white compound, m.p. 189.5–190.5°. Three recrystallizations of the compound from a mixture of benzene and high-boiling petroleum ether raised the melting point to 190.5–191°.

Anal. Calcd. for $C_{33}H_{34}O_3$: C, 82.81; H, 7.16. Found: C, 82.52; H, 7.13.

Absorption bands indicative of the presence of a hydroxyl group (3525 cm.$^{-1}$), a hindered, conjugated ketone (1642 cm.$^{-1}$) and an ether linkage (1250, 1050 cm.$^{-1}$) were present in its infrared spectrum. In one case the reaction proceeded abnormally. Practically none of the compounds described above were isolated. Elution of the column with 1:1 ether–methanol yielded 0.45 g. of a white compound, m.p. 138–139°. Two recrystallizations of the compound from a mixture of benzene and high-boiling petroleum ether did not change its melting point.

Its infrared spectrum showed absorption bands assignable to a hindered, conjugated ketone (1663 cm.$^{-1}$) and an ether linkage (1100 cm.$^{-1}$).

Attempted Oxidation of Keto-alcohol.[21]—A solution of 0.91 g. of the keto alcohol (m.p. 190.5–191°), obtained from the reduction of mesityl *o*-methoxyphenyl ketone, in 25 ml. of benzene and 12.5 ml. of glacial acetic acid, was added slowly, with stirring, to a mixture of 1.7 g. of sodium dichromate, 2.25 ml. of concentrated sulfuric acid, 1.25 ml. of glacial acetic acid and 7.5 ml. of water. The reaction mixture was stirred overnight at room temperature. The organic layer was washed with 5% sodium hydroxide solution and then with water. The solution was dried over sodium sulfate, and the benzene was distilled at reduced pressure. Trituration of the residue caused the precipitation of a pink solid, m.p. 200–202°. Four crystallizations from 95% ethanol yielded a white solid melting at 203–203.5°.

Anal. Calcd. for $C_{33}H_{32}O_2$: C, 86.05; H, 7.00. Found: C, 85.98; H, 6.89.

The infrared spectrum of this compound showed a single absorption band assignable to a hindered, conjugated ketone (1646 cm.$^{-1}$). It also showed bands indicative of the presence of an ether linkage (1245, 1050 cm.$^{-1}$).

URBANA, ILLINOIS

---

(20) R. C. Fuson and W. C. Hammann, THIS JOURNAL, **73**, 1851 (1951).

(21) R. C. Fuson and C. S. Hornberger, *J. Org. Chem.*, **16**, 631 (1951).