of white solid, m.p. 94.5–95.5°. It was insoluble in aqueous base and gave a precipitate with 2,4-dinitrophenylhydrazine reagent.[19] Oxidation by the method used on the above dimer gave terephthalic acid in 50% yield. The molecular weight by the benzene freezing point method was found to be 520; calculated for the trimer VI is 564.

Anal. Calcd. for $C_{39}H_{48}O_3$: C, 82.93; H, 8.57. Found: C, 82.78; H, 8.94.

A higher-dilution technique, similar to that of Hedden and Brown,[6] gave an extremely low yield of carbon disulfide soluble material. The main product was a paper-like material, which burned with a smoky flame and left a residue.

High-dilution Friedel–Crafts Reaction of 8-Phenyloctanoyl Chloride.—By the general procedure, 4.5 g. of 8-phenyloctanoyl chloride in 500 ml. of carbon disulfide was added in four days to 6 g. of aluminum chloride in 200 ml. of carbon disulfide. After decomposition of the reaction mixture, only a very small amount of a solid was recovered from the organic layer, m.p. 92–116°. After one recrystallization, a few mg., m.p. 125–130°, was obtained. No further characterization was made.

High-dilution Friedel–Crafts Reaction of 10-Phenyldecanoyl Chloride; VII and VIII.—The same general procedure was used, except that the acid chloride was not distilled because of extensive decomposition during distillation. A solution of crude 10-phenyldecanoyl chloride (made from the reaction of thionyl chloride with 49 g. of 10-phenyldecanoic acid) in 3 liters of carbon disulfide was added in 14 days to 50 g. of aluminum chloride in one liter of carbon disulfide. Three-fourths of the carbon disulfide was removed by distillation and the residual mixture decomposed with 2.5 liters of dilute hydrochloric acid. The organic layer, after separation from the water layer and from a large amount of light brown solid, was distilled to remove carbon disulfide. The liquid residue (6.4 g.) was distilled in a modified Claisen flask. The distillate, b.p. 158–163° (3 mm.), was a heavy oil which soon solidified in the receiver, yield 1.23 g. (3.1%). After several recrystallizations from methanol–hexanol, plates, m.p. 91–92°, were obtained. The compound was insoluble in base and gave an orange precipitate with 2,4-dinitrophenylhydrazine reagent.[19]

Using the procedure outlined for the oxidation of V, 100 mg. of the ketone yielded 50 mg. (70% yield) of terephthalic acid, identified by its infrared spectrum. The mol. wt. of VII by freezing point depression of benzene was 225; calculated for a monomeric ring closure product is 230.

Anal. Calcd. for $C_{16}H_{20}O$: C, 83.42; H, 9.63. Found: C, 83.27, 83.82; H, 9.22, 9.39.

The residue from the above distillation was extracted with methanol to give 290 mg. (0.7% yield) of a material which on repeated recrystallization from methanol melted at 83–83.5°. It was insoluble in aqueous sodium hydroxide and formed an orange precipitate with 2,4-dinitrophenylhydrazine reagent.[19] The mol. wt. by the benzene freezing point method was 491; calculated for dimeric diketone is 460. Oxidation with basic permanganate, as performed on compound V, gave a 50% yield of terephthalic acid, identified by its infrared spectrum.

Anal. Calcd. for $C_{32}H_{44}O_2$: C, 83.42; H, 9.63. Found: C, 83.72; H, 10.00.

Beckmann Rearrangement of 1,2-Benzocycloöctene-1-one-3.—A solution of the oxime (86 mg.) in 10 ml. of 85% sulfuric acid was kept at 40° for 12 days. The solution was diluted with water and extracted with ether. The ether extract yielded only a trace of acidic material and 48 mg. (55%) of neutral product, m.p. 116–120°. After two recrystallizations from aqueous alcohol it melted at 132–134°; yield 35 mg. The infrared spectrum corresponded to that of a lactam. The compound was hydrolyzed by refluxing in 20% hydrochloric acid (5 ml.) and alcohol (2 ml.). There was obtained an amphoteric product which was diazotized with hydrochloric acid and sodium nitrite at 0°. A portion of the clear solution obtained gave off a gas and deposited a precipitate when warmed to room temperature. Another portion gave an immediate red-orange precipitate with a solution of β-naphthol in 10% sodium hydroxide.

The *l*-Menthydrazone of 1,2-Benzocycloöctene-1-one-3.—By the general method of Woodward, Kohman and Harris,[25] 2,3-benzocycloöctene-2-one-1 (10.6 g.) and *l*-menthydrazide (13 g.) yielded an oil which solidified in two days, m.p. 60–90°. No definite separation of diastereoisomers could be discerned after several recrystallizations from ligroin (b.p. 70–90°) and 80% isopropyl alcohol. The melting points of crystals obtained varied from 75 to 125° with most melting between 115 and 117°. Several such fractions, which gave C and H analyses that checked approximately for the menthydrazone, varied in $[\alpha]^{25}D$ from −31.5° for the lowest melting fraction (75–80°) to −38.7° for the highest melting fraction (120–125°).

In a mutarotation experiment, a sample of the 120–125° melting fraction (0.25 g.) was heated to reflux in 10 ml. of ligroin (b.p. 70–90°) for 48 hours. The product recovered by evaporation of the solvent was dried in a Fischer drying pistol over paraffin and phosphorus pentoxide. It was discolored (indicating possible decomposition) and melted at 110–112°, $[\alpha]^{25}D$ −28.9°.

(25) R. B. Woodward, T. P. Kohman and G. C. Harris, This JOURNAL, **63**, 120 (1941).

SEATTLE, WASHINGTON

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

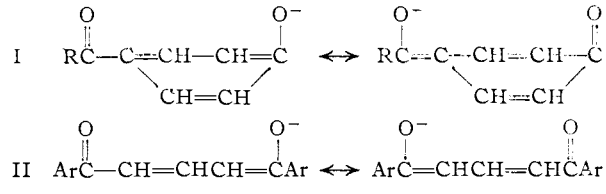
Reactions of Grignard Reagents with *p*-Duroylphenol

BY REYNOLD C. FUSON, WILLIAM D. EMMONS[1] AND GEORGE W. PARSHALL[2]

RECEIVED JUNE 11, 1954

p-Duroylphenol condenses readily with *t*-butylmagnesium chloride to give a product which can be isolated in either of the two tautomeric forms IV and V (in text) by the correct choice of solvent for recrystallization. A similar product, isolated in the keto form, is obtained when the *t*-amyl reagent is employed. Under the influence of the *t*-alkyl reagents the methyl ethers of the enol forms of these compounds undergo displacement of the methoxyl group by the hydrocarbon radical of the reagent.

The phenoxide ions I derived from *p*-acylphenols are vinylogs of the corresponding carboxylate ions and, except that they involve aromatic rings, are closely analogous to the 1,5-diarylpentadienolonates (II).[3] The analogy implies that the phenoxide ions I are vulnerable to nucleophilic attack at a position *ortho* to the keto substituent. We have been able to verify this prediction experimentally by treating *p*-duroylphenol (III) with Grignard reagents.



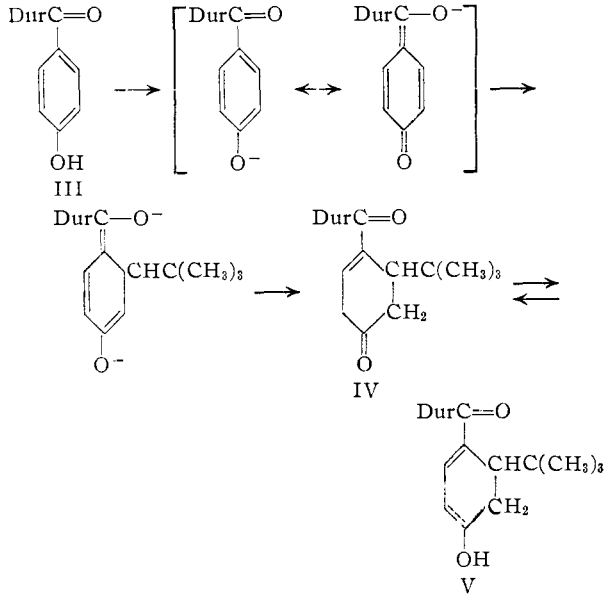
This hydroxy ketone reacts with *t*-butylmagne-

(1) Rohm and Haas Fellow, 1949–1950; Socony–Vacuum Oil Company Fellow, 1950–1951.

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

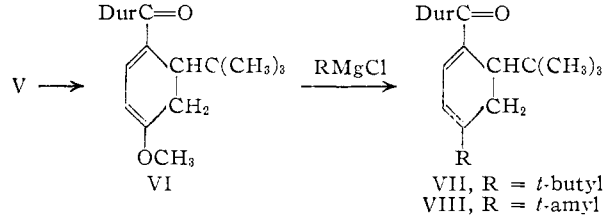
(3) R. C. Fuson and L. R. Melby, This JOURNAL, **75**, 5402 (1953).

sium chloride to give 6-*t*-butyl-4-keto-1-cyclohexenyl duryl ketone (IV) in a yield of 75%.



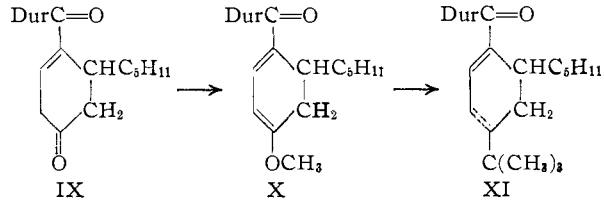
The diketone, recrystallized from high-boiling petroleum ether, is colorless and melts at 158.5–159°. However, when the recrystallization solvent is methanol or ethanol, the enolic tautomer, 2-*t*-butyl-4-hydroxy-2,3-dihydrophenyl duryl ketone (V) (m.p. 173–173.5°), is produced. These tautomers are stable in the solid state and are readily interconvertible. The enol, obtained by recrystallizing the diketone from polar solvents, can be reconverted to the diketone simply by recrystallization from non-polar solvents such as benzene or petroleum ether. Prolonged boiling with the non-polar solvent is necessary since the enol appears to be only slightly soluble in such media. This observation is similar to that of Russell on the β-ketonitriles.[4] As would be expected, either form will serve in the preparation of derivatives such as the oxime of the diketone and the acetate of the enol. This example of tautomerism is remarkable, especially because the enol cannot be chelated.

It is interesting that, whereas esterification of duroic acid is not effected by the Victor Meyer method, its vinylog, the enol V, undergoes etherification under these conditions. Heating with methanol in the presence of hydrogen chloride suffices to convert the enol to its methyl ether VI, which in turn is a vinylog of an ester. The enol ether is saponified by aqueous sodium hydroxide, the salt of the enol being formed.



The *t*-butyl Grignard reagent reacts with this ether VI to give a product in which the methoxyl group has been replaced by the alkyl radical of the reagent. This reaction establishes the structures of the compounds involved since the product, 2,4-di-*t*-butyl-2,3-dihydrophenyl duryl ketone (VII) was previously prepared by the addition of *t*-butylmagnesium chloride to *p*-*t*-butylphenyl duryl ketone.[5] The replacement of the methoxyl group by *t*-amylmagnesium chloride gives 4-*t*-amyl-2-*t*-butyl-2,3-dihydrophenyl duryl ketone (VIII).

t-Amylmagnesium chloride reacts with *p*-duroylphenol in much the same manner as the *t*-butyl reagent to give 6-*t*-amyl-4-keto-1-cyclohexenyl duryl ketone (IX). Like the *t*-butyl analog, this ketone gives a methyl enol ether X when treated with methanol and hydrogen chloride. Displacement of the methoxyl group by *t*-butylmagnesium chloride gives 2-*t*-amyl-4-*t*-butyl-2,3-dihydrophenyl duryl ketone (XI).



Reactions involving the condensation of a Grignard reagent with a vinylog of a carboxylate ion have been reported several times previously. In the earliest example, Zelinsky noted that only one mole of methylmagnesium iodide condenses with acetylacetone whereas two moles combine with biacetyl or acetonylacetone.[6] Most of the later examples also deal with the action of Grignard reagents on enolic 1,3-diketones. The reaction of Grignard reagents with dibenzoylmethane was studied by Smedley,[7] by Vorländer, Osterburg and Meye[8] as well as by Kohler and Erickson.[9] The investigation of the reaction of methylmagnesium iodide with benzoylmesitylene was carried out by Kohler and Barnes.[10] The enolic cyclic diketones, dimedone and dihydroresorcinol, have been shown to react with Grignard reagents in a manner completely analogous to that observed with carboxylic acids.[11,12] The 1,4-addition of phenylmagnesium bromide to 4,7-dihydroxy-2,3-diphenylindone[13] may also be interpreted as a reaction of a Grignard reagent with a vinylog of a carboxylate ion, and is the only previous case in which the effect has been observed in an aromatic system.

Experimental[14]

p-Duroylphenol.—A solution of 85.3 g. of anisoyl chloride and 67.0 g. of durene in 300 ml. of carbon disulfide was stirred vigorously while 73.0 g. of anhydrous aluminum chloride was added at a rate sufficient to produce gentle refluxing. The mixture was stirred at room temperature for

(4) P. B. Russell, THIS JOURNAL, **74**, 2654 (1952).

(5) R. C. Fuson, W. S. Friedlander and G. W. Parshall, *ibid.*, **76**, 5119 (1954).

(6) N. Zelinsky, *Ber.*, **35**, 2138 (1902).

(7) I. Smedley, *J. Chem. Soc.*, **97**, 1493 (1910).

(8) D. Vorländer, J. Osterburg and O. Meye, *Ber.*, **56**, 1136 (1923).

(9) E. P. Kohler and J. L. E. Erickson, THIS JOURNAL, **53**, 2301 (1931).

(10) E. P. Kohler and C. E. Barnes, *ibid.*, **55**, 690 (1933).

(11) G. F. Woods, *ibid.*, **69**, 2549 (1947).

(12) G. F. Woods and I. W. Tucker, *ibid.*, **70**, 2174 (1948).

(13) C. F. Koelsch and E. J. Prill, *ibid.*, **67**, 1299 (1945).

(14) All melting points are corrected.

one hour after the completion of the addition and poured into 1.5 l. of water, with vigorous stirring. A large amount of solid product was collected by filtration. The organic layer of the filtrate was removed, dried over sodium sulfate and freed of solvent by evaporation. The residue was combined with the crude anisyl duryl ketone. Recrystallization from benzene gave white cubical crystals, m.p. 143–144°, yield 122 g. (90%).

A solution of the anisyl duryl ketone in a mixture of 400 ml. of glacial acetic acid and 240 ml. of 48% hydrobromic acid was boiled under reflux for 18 hours and poured into cold water. The *p*-duroylphenol crystallized from benzene in white needles; m.p. 200–202°,[15] yield 87 g. (80%).

The Addition of *t*-Butylmagnesium Chloride to *p*-Duroylphenol.—The Grignard reagent was prepared from 6.0 g. (0.25 gram-atom) of magnesium and 28.0 g. (0.30 mole) of *t*-butyl chloride in 75 ml. of ether. When a solution of 12.8 g. (0.05 mole) of *p*-duroylphenol in 125 ml. of hot benzene was added, the reaction mixture became deep red. After being heated with stirring for one hour, the solution was poured into cold dilute hydrochloric acid. The organic layer was dried over sodium sulfate and freed of solvent by evaporation. Crystallization of the residual red oil was induced by addition of high-boiling petroleum ether. After two recrystallizations from this solvent, the 6-*t*-butyl-4-keto-1-cyclohexenyl duryl ketone (IV) was colorless, m.p. 158.5–159°, yield 11.7 g. (75%).

Anal.[16] Calcd. for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.89; H, 8.97.

The infrared spectrum[17] of this compound contains absorption bands assignable to a hindered conjugated carbonyl group (1661 cm.$^{-1}$), to a cyclic ketone (1718 cm.$^{-1}$) and to a conjugated ethylenic double bond (1631 cm.$^{-1}$).

Reactions of the Diketone (IV). (a) Enolization.—Recrystallization of the diketone from aqueous ethanol converted it quantitatively to the corresponding enol, 2-*t*-butyl-4-hydroxy-2,3-dihydrophenyl duryl ketone (V), which precipitated as light yellow crystals; m.p. 173–173.5°. The infrared spectrum of the enol contains bands assignable to a hindered conjugated carbonyl group (1654 cm.$^{-1}$), to a hydroxyl group (3238 cm.$^{-1}$) and to conjugated ethylenic double bonds (1610 cm.$^{-1}$).

Anal. Calcd. for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.87; H, 9.01.

Prolonged boiling was required to dissolve the enol in high-boiling petroleum ether, but when this solution was cooled, white crystals of the diketone precipitated. The melting point and the infrared spectrum of this specimen were identical with those of the original diketone.

(b) Enol Acetate Formation.—A solution of 0.5 g. of the diketone (or the enol) in 2 ml. of acetic anhydride and 5 ml. of pyridine was heated for 10 minutes and poured into cold water. The enol acetate, which separated as a red oil, crystallized from aqueous methanol in light yellow needles, m.p. 115.5–116.5°.

Anal. Calcd. for $C_{23}H_{30}O_3$: C, 77.93; H, 8.53. Found: C, 78.17; H, 8.60.

(c) Oxime Formation.—A solution of 0.3 g. of the diketone (or the enol) and 0.3 g. of hydroxylamine hydrochloride in 2 ml. of ethanol and 2 ml. of pyridine was heated under reflux for 2 hours. The solvents were distilled, and the residue was washed with water and recrystallized from a mixture of benzene and high-boiling petroleum ether. Although the solution was green, the crystals which formed were colorless and melted sharply at 205.5–206°.

Anal. Calcd. for $C_{21}H_{29}NO_2$: C, 77.02; H, 8.93; N, 4.28. Found: C, 77.29; H, 9.14; N, 4.25.

The infrared spectrum of the oxime contains bands assignable to a hindered conjugated carbonyl group (1660 cm.$^{-1}$), to a cyclic ketoxime (1630, 3269 cm.$^{-1}$) and to a conjugated ethylenic double bond (1606 cm.$^{-1}$).

(d) Enol Ether Formation.—A solution of 19.0 g. of the diketone in 500 ml. of 2% methanolic hydrogen chloride was boiled under reflux for 2 hours. Water was then added and the solution was cooled until a solid precipitated. The 2-*t*-butyl-4-methoxy-2,3-dihydrophenyl duryl ketone (VI) crystallized from aqueous methanol in light yellow crystals; m.p. 160–161°, yield 16 g. (80%).

Anal. Calcd. for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26. Found: C, 81.10; H, 9.23.

The infrared spectrum contained absorption bands assignable to a hindered conjugated carbonyl group (1624 cm.$^{-1}$) and to a system of conjugated ethylenic double bonds (1551 cm.$^{-1}$).

Saponification of the Enol Ether.—A solution of 0.5 g. of 2-*t*-butyl-4-methoxy-2,3-dihydrophenyl duryl ketone in 25 ml. of ether was vigorously shaken with 25 ml. of 10% aqueous sodium hydroxide for 10 minutes. The aqueous layer, which became intensely yellow, was acidified with concentrated hydrochloric acid and extracted with ether. Evaporation of the ether extract left a yellowish-orange residue which was recrystallized from methanol that had been freed of oxygen by prolonged boiling. The yellow crystals of the enol melted at 172.5–173.5°.

The Addition of *t*-Amylmagnesium Chloride to *p*-Duroylphenol.—A solution of 25.6 g. (0.1 mole) of *p*-duroylphenol in 200 ml. of benzene was added rapidly to a Grignard reagent prepared from 12.0 g. (0.5 gram-atom) of magnesium and 75 ml. (0.6 mole) of *t*-amyl chloride in 150 ml. of ether. The resulting deep red solution was heated, with stirring, for 30 minutes and poured into cold dilute hydrochloric acid. The organic layer was dried over sodium sulfate, and the solvent evaporated. The crude 4-keto-6-*t*-amyl-1-cyclohexenyl duryl ketone (IX), when recrystallized repeatedly from high-boiling petroleum ether, formed small white needles, m.p. 123–125°, yield 16.0 g. (50%).

Anal. Calcd. for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26. Found: C, 80.69; H, 9.24.

The infrared spectrum of this compound contains bands assignable to a hindered conjugated carbonyl group (1656 cm.$^{-1}$) to a cyclic ketone (1708 cm.$^{-1}$) and to a conjugated ethylenic double bond (1630 cm.$^{-1}$).

2-*t*-Amyl-4-methoxy-2,3-dihydrophenyl Duryl Ketone (X).—A solution of 4.0 g. of the *t*-amyl adduct in 125 ml. of 10% methanolic hydrogen chloride was boiled under reflux for 2 hours and poured into cold water. The mixture was stirred thoroughly and extracted with ether. The crude 2-*t*-amyl-4-methoxy-2,3-dihydrophenyl duryl ketone, obtained by evaporation of the solvent, crystallized from acetone in transparent cubes; m.p. 120.5–121°, yield 3.5 g. (80%).

Anal. Calcd. for $C_{23}H_{32}O_2$: C, 81.13; H, 9.47. Found: C, 81.28; H, 9.35.

The infrared spectrum of the enol ether contains bands assignable to a hindered conjugated carbonyl group (1625 cm.$^{-1}$) and to a system of conjugated ethylenic double bonds (1548 cm.$^{-1}$).

The Reaction of Grignard Reagents with the Enol Ethers of the Adducts. (a) 4-*t*-Amyl-2-*t*-butyl-2,3-dihydrophenyl Duryl Ketone.—The *t*-amylmagnesium chloride reagent was prepared from 0.48 g. of magnesium and 2.7 g. of *t*-amyl chloride in 15 ml. of ether. A solution of 1.6 g. of the enol ether of the *t*-butyl adduct in 15 ml. of benzene was added rapidly. The bright red solution was stirred at room temperature for 45 minutes and poured into cold dilute hydrochloric acid. The organic layer was washed with water, dried over sodium sulfate and freed of solvent by evaporation. The red oil thus obtained was fractionally crystallized from aqueous methanol. The first fraction was a red viscous material which distilled at 190° (0.5 mm.) to give a yellow glassy solid, insoluble in organic solvents. The second fraction was 4-*t*-amyl-2-*t*-butyl-2,3-dihydrophenyl duryl ketone; it crystallized from aqueous methanol in colorless needles, m.p. 143–144°, yield 0.9 g.

Anal. Calcd. for $C_{26}H_{38}O$: C, 85.19; H, 10.45. Found: C, 85.36; H, 10.50.

The infrared spectrum of this compound contains bands assignable to a hindered conjugated carbonyl group (1639 cm.$^{-1}$) and to a system of conjugated ethylenic double bonds (1560 cm.$^{-1}$).

(b) 2-*t*-Amyl-4-*t*-butyl-2,3-dihydrophenyl Duryl Ketone (XI).—To the *t*-butylmagnesium chloride reagent, prepared from 0.48 g. of magnesium and 2.3 g. of *t*-butyl chloride in 15 ml. of ether, was added a solution of 1.7 g. of the enol methyl ether of the *t*-amyl adduct in 15 ml. of benzene. The

(15) R. C. Fuson and W. D. Emmons, THIS JOURNAL, **73**, 5175 (1951).

(16) The microanalyses were performed by Miss Emily Davis, Mrs. Esther Fett, Mrs. Katherine Pih and Mr. Joseph Nemeth.

(17) The infrared spectra were observed and interpreted by Miss Helen Miklas.

reaction was then carried out exactly like that with the enol ether of the *t*-butyl adduct. As in that experiment, the second fraction obtained in the crystallization from aqueous methanol was a solid which took the form of colorless needles after repeated recrystallization from methanol. Further purification was effected by sublimation at 165° (0.3 mm.). The melting point of the pure 2-*t*-amyl-4-*t*-butyl-2,3-dihydrophenyl duryl ketone is 115–116°, yield 0.5 g. (23%).

Anal. Calcd. for $C_{26}H_{38}O$: C, 85.19; H, 10.45. Found: C, 85.05; H, 10.48.

The infrared spectrum of this compound contains bands assignable to a hindered conjugated carbonyl group (1642 cm.$^{-1}$) and to a system of conjugated ethylenic double bonds (1567 cm.$^{-1}$).

(c) **2,4-Di-*t*-butyl-2,3-dihydrophenyl Duryl Ketone.**—To a *t*-butylmagnesium chloride reagent, prepared from 0.72 g. of magnesium and 4.0 ml. of *t*-butyl chloride in 25 ml. of ether, was added a solution of 3.25 g. of the enol methyl ether of the *t*-butyl adduct in 40 ml. of benzene. After being stirred for 3 minutes, the reaction mixture was decomposed with cold dilute hydrochloric acid. The organic layer was dried over magnesium sulfate and the solvents were evaporated. The residue was fractionally crystallized from aqueous methanol. The initial fractions consisted of unchanged starting material and a red oil, but 1.2 g. of yellow solid precipitated in the following fractions. After sublimation at 130–140° (0.04 mm.), the 2,4-di-*t*-butyl-2,3-dihydrophenyl duryl ketone crystallized from methanol as fine colorless needles which melted at 129.5–130.5°, yield 0.8 g. (22%). A mixed melting point with an authentic sample, prepared by adding *t*-butylmagnesium chloride to *p*-*t*-butylphenyl duryl ketone, was not depressed.

Anal. Calcd. for $C_{25}H_{36}O$: C, 85.17; H, 10.29. Found: C, 85.31; H, 10.49.

The infrared spectrum contains bands at 1645 and 1574 cm.$^{-1}$ assignable to a hindered conjugated carbonyl group and a system of conjugated ethylenic double bonds, respectively.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORY, DOMINION RUBBER CO., LTD.]

t-Butyl as a Blocking Group in the Synthesis of *o*-Hydroxybenzophenones

BY MARSHALL KULKA

RECEIVED MAY 28, 1954

A method has been developed for the synthesis of *o*-hydroxybenzophenones (VIII) utilizing *t*-butyl as a blocking group. *p*-*t*-Butylanisole was condensed with various aroyl chlorides to yield a series of 2-methoxy-5-*t*-butylbenzophenones (VI). These were then simultaneously de-*t*-butylated and demethylated to VIII in high yields by prolonged heating in benzene solution with four moles of aluminum chloride. Milder conditions, which preferentially de-*t*-butylated *p*-*t*-butylphenoxyethanol (I) to phenoxyethanol (II), caused only the demethylation of VI to 2-hydroxy-5-*t*-butylbenzophenones (VII).

The migration of the alkyl and especially the *t*-butyl group is a well-known phenomenon. Poly-*t*-butylbenzenes are dealkylated to *t*-butylbenzene when heated in benzene solution with aluminum chloride.[1] The Friedel–Crafts reaction between *p*-di-*t*-butylbenzene and acetyl chloride occurs after partial dealkylation to form *p*-*t*-butylacetophenone in 72% yield.[2] Smith has reported that heating under reflux a benzene solution of one mole of *p*-*t*-butylphenol with two-thirds of a mole of aluminum chloride resulted in a mixture of phenol and *t*-butylbenzene.[3] A similar migration of the *t*-butyl group to a foreign nucleus occurs with *p*-*t*-butylphenoxyethanol (I) which under conditions similar to those used by Smith gives phenoxyethanol (II) in 78% yield and *t*-butylbenzene (III) in 50% yield (see Experimental). *p*-*t*-Butylanisole can be converted to anisole with aluminum chloride and directly to phenol with hydriodic acid.[4]

$$\underset{\text{I}}{p\text{-}(CH_3)_3CC_6H_4OCH_2CH_2OH} + C_6H_6 \longrightarrow C_6H_5OCH_2CH_2OH + (CH_3)_3CC_6H_5$$

II III

The ease of elimination of the *t*-butyl group from an aromatic nucleus suggested its use as a blocking group in substitution reactions. In the Friedel–Crafts reaction with aroyl chlorides, anisole is attacked at the *ortho* and *para* positions to form a mixture of *o*- and *p*-hydroxybenzophenone with the latter predominating. In order to prepare exclusively *o*-hydroxybenzophenone, it would be necessary to suppress the formation of the *para* isomer by first introducing a blocking group into the *para* position of anisole and then removing it after the Friedel–Crafts reaction. The purpose of this investigation was to evaluate the *t*-butyl as a blocking group in the synthesis of *o*-hydroxybenzophenones.

A series of 2-methoxy-5-*t*-butylbenzophenones (VI) (Table I) was first prepared by heating *p*-*t*-butylanisole (IV) with the appropriate acid chloride V in *sym*-tetrachloroethane as solvent and a trace of zinc chloride. Then VI was treated with aluminum chloride under the conditions which sufficed for the conversion of I to II and III but no de-*t*-butylation occurred. Demethylation of VI to VII was the only reaction as evidenced by the fact that the resulting product was difficultly alkali-soluble and yielded the starting material VI on methylation with dimethyl sulfate. No de-*t*-butylation could be effected in boiling benzene nor boiling toluene. Simultaneous de-*t*-butylation and demethylation to VIII was achieved finally by heating VI with four moles of aluminum chloride in benzene solution at 65–70° for 45 hours. Under the same conditions VII yielded VIII.

The fate of the *t*-butyl group has not been established definitely. In contrast to the formation of *t*-butylbenzene (III) during the de-*t*-butylation of I under the milder conditions, the formation of an alkali-insoluble higher-boiling liquid mixture accompanies the de-*t*-butylation of VI and VII to VIII under the prolonged treatment. It must be presumed that this higher-boiling by-product is

(1) E. Boedtker and O. M. Halse, *Bull. soc. chim.*, **19**, 444 (1916); *C. A.*, **11**, 938 (1917).

(2) G. F. Hennion and S. F. deC. McLeese, THIS JOURNAL, **64**, 2421 (1942).

(3) R. A. Smith, *ibid.*, **59**, 899 (1937).

(4) B. M. Dubinin, *Zhur. Obshchei Khim.*, **18**, 2145 (1948); *C. A.* **43**, 3804 (1949).