saturated ketone, 35 cc. of ethyl acetate and 50 mg. of platinum oxide catalyst was found to absorb one mole of hydrogen over a period of one and one-half hours. The yellow color was discharged during the reaction. The mixture was filtered and the solvent evaporated by use of an air-blast. During the evaporation the solution became yellow. The residue, recrystallized from ethanol, proved to be the unsaturated ketone used as starting material. Reduction, carried out in benzene, chloroform, acetic acid or absolute ethanol, led to the same results.

Hydrogenation in acetic anhydride in the presence of zinc chloride failed to produce an acetate; the starting material was recovered.

The unsaturated ketone was also obtained in an attempt to prepare a peroxide of 2,3-diphenyl-1-duryl-1-propenol (VII) by the method of Kohler.[9]

When the solution of the enol was allowed to stand for forty-eight hours, the hydrogenated ketone was obtained. The α,β-diphenylethyl duryl ketone so prepared crystallized from ethanol in white needles; m. p. 106–107° (cor.). The yield was practically quantitative.

Anal. Calcd. for $C_{26}H_{26}O$: C, 87.72; H, 7.60. Found: C, 87.82; H, 7.71.

The saturated ketone could be obtained, together with the vinyl ketone, by reducing the latter with sodium and ethanol according to the method of Klingemann.[10] It could also be made by hydrogenation of the unsaturated ketone in ethyl acetate and boiling the resulting solution for two hours in a nitrogen atmosphere. This is in accord with Kohler's observation that 1,2,3,3-tetraphenyl-1-propen-1-ol is very sensitive to oxygen and is ketonized rapidly by heat.[9]

The three other unsaturated ketones gave results very

(9) Kohler, *Am. Chem. J.*, **36**, 177 (1906).

(10) Klingemann, *Ann.*, **275**, 65 (1893).

similar to those described for α,β-diphenylvinyl duryl ketone. Each absorbed a mole of hydrogen, but when the mixture was exposed to the air immediately only starting material was found. However, when the solution of the enol was allowed to stand for forty-eight hours it was found to contain the saturated ketone. The three products were crystallized from ethanol.

α,β-Diphenylethyl 2,4,6-triisopropylphenyl ketone; m. p. 143–144° (cor.).

Anal. Calcd. for $C_{30}H_{36}O$: C, 87.38; H, 8.73. Found: C, 87.20; H, 8.92.

Duryl α-phenyl-β-(p-chlorophenyl)-ethyl ketone; m. p. 129–130° (cor.).

Anal. Calcd. for $C_{25}H_{25}OCl$: C, 79.95; H, 6.65. Found: C, 80.01; H, 6.75.

Mesityl α-phenyl-β-(p-chlorophenyl)-ethyl ketone; 148–149° (cor.).

Anal. Calcd. for $C_{24}H_{23}OCl$: C, 79.45; H, 6.35. Found: C, 79.43; H, 6.29.

Summary

Hydrogenation of triarylpropenones of type A, in which Ar is phenyl or p-chlorophenyl and Ar' is mesityl, duryl or 2,4,6-triisopropylphenyl, produces an enol (B) that is oxidized immediately by the air to yield the parent vinyl ketone.
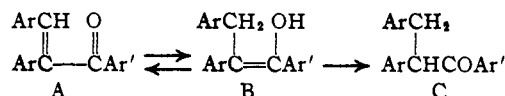
If the solution of the enol is allowed to stand the corresponding ketone (C) is formed.

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

Vinyl Alcohols. VII.[1] Hindrance at the β-Carbon Atom

BY REYNOLD C. FUSON AND QUENTIN F. SOPER

The persistence of enol forms of certain mesityl ketones has been ascribed to the influence of the mesityl radical.[2] The stability of enediols such as 1,2-dimesitylacetylene glycol (I) and vinyl alcohols of the type represented by 1,2-dimesityl-1-propen-1-ol (II) is very much greater than that of the simpler α-mesitylvinyl alcohols. This difference suggests that it is the steric hindrance about the *beta* rather than the *alpha* carbon atom which is chiefly responsible for the stability of the enols illustrated by compounds I and II.

(1) For the preceding communication in this series see Fuson and Foster, THIS JOURNAL, **65**, 913 (1943).

(2) Kohler, Tishler and Potter, *ibid.*, **57**, 2517 (1935); Kohler and Thompson, *ibid.*, **59**, 887 (1937).

According to this viewpoint the stability of compound I requires the presence of both mesityl radicals whereas that of II would be, to a greater extent if not entirely, dependent on the hindrance offered by the β-mesityl radical. To explore this possibility we have prepared a number of enols with a 2,4,6-triisopropylphenyl group in the *alpha* position and a phenyl group in the *beta* position. The triisopropylphenyl group was chosen because experience indicates that it is more effective than mesityl, duryl, etc., in stabilizing enols.

The first compound to be examined was benzyl triisopropylphenyl ketone (III).[3] Although this compound gave a mole of gas in the Grignard machine,[4] decomposition of the reaction mixture to free the enol, yielded only the ketone. As a matter of fact, all unchelated enols so far reported have more than one substituent in the *beta* position. However, the introduction of a methyl
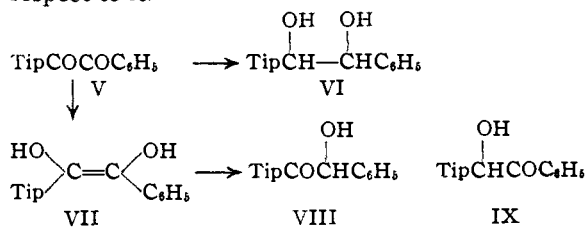
$$\text{CH}_3$$
$$\text{TipCOCH}_2\text{C}_6\text{H}_5 \qquad \overset{|}{\text{TipCOCHC}_6\text{H}_5}$$
$$\text{III} \qquad\qquad\qquad \text{IV}$$

group in the *beta* position (by analogy with enol II) likewise failed to stabilize the enol. α-Phenylethyl 2,4,6-triisopropylphenyl ketone (IV) could be enolized by the Grignard reagent but the enol could not be detected even in solution.

Finally, an enol was sought in which the *beta* carbon atom held a phenyl radical and a hydroxyl group. This would permit comparison with the stilbenediols illustrated by compound I. To this end phenyl 2,4,6-triisopropylphenyl diketone (V) was prepared and subjected to hydrogenation. Evidence of the existence of the enediol (VII) in solution was abundant but the compound could not be isolated. It ketonized readily to yield the benzoin (VIII). It is interesting that the benzoin is obtained also by hydrolysis of the diacetate of the enediol.

The structure of the benzoin was made certain by the fact that it gave nearly two moles of gas in the Grignard machine.[4] The isomeric benzoin would undergo extensive addition. The validity of this method of structure proof was established by a study of the mesityl analogs of these benzoins.[5]

The rearrangement of the enediol (VII) to 2,4,6-triisopropylbenzoin (VIII) rather than to its isomer (IX) constitutes proof that the stabilizing effect of the triisopropylphenyl radical is exerted to a greater degree on the hydroxyl group in the *beta* than on that in the *alpha* position with respect to it.

$$\overset{\text{OH}\quad\text{OH}}{\text{TipCOCOC}_6\text{H}_5 \longrightarrow \text{TipCH—CHC}_6\text{H}_5}$$
$$\downarrow \text{V} \qquad\qquad\qquad \text{VI}$$

$$\underset{\text{Tip}}{\overset{\text{HO}}{>}}\text{C}=\text{C}\underset{\text{C}_6\text{H}_5}{\overset{\text{OH}}{<}} \longrightarrow \overset{\text{OH}}{\text{TipCOCHC}_6\text{H}_5} \qquad \overset{\text{OH}}{\text{TipCHCOC}_6\text{H}_5}$$
$$\text{VII} \qquad\qquad \text{VIII} \qquad\qquad \text{IX}$$

(3) The 2,4,6-triisopropylphenyl radical is represented by Tip.
(4) Kohler and Richtmyer, THIS JOURNAL, **52**, 3736 (1930).
(5) Weinstock and Fuson, *ibid.*, **58**, 1986 (1936).

The structure of the benzil (V) follows from the fact that it was produced by the oxidation of benzyl 2,4,6-triisopropylphenyl ketone (III) with selenium dioxide. It was formed also by oxidation of the benzoin (VIII). Hydrogenation of the benzil under high pressure yielded not only the benzoin but the glycol (VI) as well. Attempts to dehydrate the latter failed to yield any pure products.

The instability of the enediol (VII) shows that in stilbenediols *both* aryl radicals must provide hindrance similar to that furnished by the mesityl radical. In other words, each of the carbon atoms of the enediol group, being *beta* to an enolic hydroxyl group, must hold a radical such as mesityl or triisopropylphenyl in addition to the hydroxyl group.

Experimental

Benzyl Triisopropylphenyl Ketone (III).—This ketone[3] was subjected to analysis in the Grignard machine.[4] It was found to yield nearly a mole of methane.

α-Phenylpropionic Acid.—This acid was made by oxidation of the corresponding aldehyde[6] with potassium permanganate. The aldehyde was prepared from acetophenone and ethyl chloroacetate by way of ethyl β-phenylglycidate.[7]

α-Phenylethyl 2,4,6-Triisopropylphenyl Ketone (IV).—Five grams of α-phenylpropionic acid was allowed to stand overnight with 16 g. of thionyl chloride. The mixture was then heated at 60° for two hours and distilled. The α-phenylpropionyl chloride boiled at 75–76° (3 mm.); n^{20}D 1.5232; yield 5 g.

A solution of the acid chloride (5 g.) in 8 cc. of 1,3,5-triisopropylbenzene was added dropwise, with stirring, to a mixture of 4.1 g. of anhydrous aluminum chloride, 6 cc. of the triisopropylbenzene and 10 cc. of carbon disulfide. During the addition the reaction flask was cooled in an ice-bath. After the addition was completed the mixture was stirred at room temperature for one and one-half hours then heated, with stirring, under reflux for thirty minutes. The mixture was decomposed in the usual way. Distillation of the product gave 6 cc. of triisopropylbenzene and an oil which, when allowed to stand in the icebox with a small amount of low-boiling petroleum ether, formed 6.5 g. of white needles. The ketone was purified by recrystallization from ethanol; m. p. 83–84° (cor.).

Anal.[8] Calcd. for $C_{24}H_{32}O$: C, 85.64; H, 9.61; mol. wt., 336. Found: C, 83.90, 86.23; H, 9.57, 9.65; mol. wt., 309.

The ketone was treated with sodium ethoxide for twenty-four hours at the reflux temperature, but no enol could be isolated. Attempts to make an acetate and a benzoate of the enol also failed. Analysis in the Grignard machine[4] showed the presence of one active hydrogen atom.

(6) Claisen and Feyerabend, *Ber.*, **38**, 704 (1905).
(7) Darzens, *Compt. rend.*, **139**, 1216 (1904).
(8) Microanalyses by Miss Margaret McCarthy and Miss Theta Spoor.

Phenyl Triisopropylphenyl Diketone (V).—A mixture of 60 g. of benzyl triisopropylphenyl ketone,[1] 30 g. of selenium dioxide, 500 cc. of dioxane and 5 cc. of water was heated under reflux for eight hours. The product crystallized from ethanol in bright yellow needles; m. p. 121.5–122.2° (cor.); yield 85%.

Anal. Calcd. for $C_{23}H_{28}O_2$: C, 82.07; H, 8.39. Found: C, 81.68, 81.83; H, 8.26, 8.54.

1-Phenyl-2-(2,4,6-triisopropylphenyl)-ethylene Glycol (VI).[9]—Twelve grams of the diketone (VI), hydrogenated in the presence of copper chromite at 175° and a pressure of 2000 lb., yielded 10 g. of crude glycol melting at 126–127.5°. It was purified by recrystallization from alcohol; m. p. 133.5–134° (cor.).

Anal. Calcd. for $C_{23}H_{32}O_2$: C, 81.18; H, 9.41. Found: C, 81.26; H, 9.23.

The diacetate was prepared by treating the glycol with acetic anhydride in pyridine. After recrystallization from alcohol it melted at 113–114° (cor.).

Anal. Calcd. for $C_{27}H_{36}O_4$: C, 76.38; H, 8.55. Found: C, 76.39; H, 8.49.

Dehydration of the Glycol (VI).—A solution of the glycol in a mixture of 9 cc. of concentrated hydrochloric acid and 40 cc. of glacial acetic acid was refluxed three hours. Decomposition of the mixture by addition of ice produced a brownish, semi-solid mass. The crude material melted at 90–98°. When the solid was sublimed *in vacuo* there was obtained a sticky, white substance which melted over the same range. It was very soluble in all usual solvents except water; mixed solvents containing water gave a non-crystalline material.

Hydrogenation of the Diketone (V).—Attempts to prepare an *enediol* (VII) from the diketone by hydrogenation were unavailing. That an enediol was formed was proved, however, by the fact that the solution of the hydrogenation product gave the indophenol test. This test showed that the enediol persisted in solution for several days. When the method of Thompson[10] was used in the reduction of the diketone a diacetate was produced. The reduction was carried out in acetic anhydride with a platinum catalyst, three drops of hydrochloric acid and 0.03 g. of fused zinc chloride. At the end of seven hours the mixture was poured into water. The diacetate was purified by crystallization from methanol; m. p. 161–161.5° (cor.).

Anal. Calcd. for $C_{27}H_{34}O_4$: C, 76.74; H, 8.11. Found: C, 76.96; H, 8.06.

The diacetate was also prepared by the method of Thiele.[11]

In an attempt to isolate the enediol the reduction was carried out in low-boiling petroleum ether. A white precipitate appeared in about fifteen minutes. When it was removed from the flask it turned yellow immediately, being converted to the benzil.

In another hydrogenation experiment in which ether was used as the solvent the reaction mixture was filtered and the solvent allowed to evaporate. The residue crystallized from ethanol in white needles which proved to be the benzoin (VIII); m. p. 117.5–118.5°.

(9) The high-pressure reduction was carried out by Mr. J. M. Stewart.

(10) Thompson, THIS JOURNAL, **61**, 1281 (1939).

(11) Thiele, *Ann.*, **306**, 142 (1899).

Anal. Calcd. for $C_{23}H_{30}O_2$: C, 81.66; H, 8.88. Found: C, 81.60; H, 9.03.

Analysis of the benzoin in the Grignard machine[4] showed that one mole of the benzoin produced 1.83 moles of methane and that 0.17 mole of the Grignard reagent had reacted additively.

The benzoin was also prepared by high-pressure hydrogenation of the benzil.[12] A copper chromite catalyst was used; the initial temperature was 150°, the pressure 1500–2000 lb. After thirty minutes the mixture was removed and filtered while hot. The benzoin was obtained by concentrating the filtrate; m. p. 115–116.5°.

The best method for making the benzoin was a modification of the procedure of Apitzasch.[13] A part of the benzil was dissolved in ethanol and a little zinc dust was added along with hydrochloric acid. The addition of zinc dust was continued until the solution became colorless. The mixture was heated to bring the solid into solution, then cooled. The product melted at 114–115.5°. A mixed melting point showed it to be identical with the other samples of the benzoin.

The benzoin was prepared in very pure form by the hydrolysis of the enediol diacetate. A solution of the diacetate in methanol, containing hydrochloric acid and water, was refluxed in an atmosphere of nitrogen until it became clear (about three hours). The benzoin (VIII) was collected on a filter; m. p. 116–118°.

The benzoin was oxidized to the benzil by several methods. Heating on a steam cone overnight with dilute sulfuric acid or water; heating for five hours with pyridine and copper sulfate; standing for five hours with a 10% solution of sodium hydroxide (alcohol–water mixture); and refluxing with acetic anhydride were attended by benzil formation.

The acetate of the benzoin was made by allowing it to stand overnight in a 40% solution of acetic anhydride in pyridine. The mixture was diluted and allowed to stand. The solid acetate crystallized from ethanol in white needles; m. p. 120–120.5°.

Anal. Calcd. for $C_{25}H_{32}O_3$: C, 78.95; H, 8.42. Found: C, 78.80; H, 8.77.

Acetylation of the benzoin was also accomplished by heating it with acetic anhydride for one hour in an atmosphere of nitrogen.

Summary

It has been established that the enol forms of benzyl 2,4,6-triisopropylphenyl ketone and α-phenylethyl 2,4,6-triisopropylphenyl ketone undergo ketonization immediately. The enediol obtained by catalytic hydrogenation of phenyl 2,4,6-triisopropylphenyl diketone can be detected in solution but rearranges rapidly to 2,4,6-triisopropylbenzoin.

It is concluded that the stability of an unchelated enol is due in greater degree to space exigency at the *beta* than at the *alpha* carbon atom.

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(12) This hydrogenation was carried out by Mr. J. C. Robinson, Jr.

(13) Apitzasch. *Ber.*, **40**, 1803 (1907).