except that a sharper peak and a suggestion of a fine structure is shown (see Fig. 2). This material does not yield vitamin A or anhydro vitamin A on pyrolysis.



Fig. 2.—Absorption spectrum of material recovered from antimony trichloride reaction product of kitol, about 0.0027% in ethanol.

We have found small amounts of kitol in shark liver oil (commercial product) and in the oil extracted from the liver of a lamb. The liver oil from a northern pike, containing vitamin A_2 , was treated by the above-mentioned procedure for concentrating kitol and showed the presence of a substance which had an absorption band at 310 $m\mu$ and whose antimony trichloride color showed an absorption band at 510 $m\mu$. This substance on heating gave rise to a material whose antimony trichloride reaction product had an absorption band at 690 $m\mu$. In our opinion, the 690 chromogen is vitamin A₂ and its progenitor should be called kitol₂.

Kitol is a provitamin A in the strict sense of the word in that kitol itself has no biological activity but when subjected to a simple physical process is transformed into vitamin A. Due to the fact that vitamin A itself is very unstable to heat, it is likely that this process, if carried out on a large scale, should be performed in a molecular still so that the vitamin A as it is formed can be removed immediately.

Summary

Kitol, a dihydric alcohol with the approximate formula $C_{40}H_{60}O_2$, has been found in considerable quantities in whale liver oil. This substance has little or no biological activity, but is transformed into vitamin A upon heating to temperatures above 200°.

Rochester, N. Y.

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

Vinyl Alcohols. VI.¹ 1,4-Dehydrogenation

BY REYNOLD C. FUSON AND ROBERT E. FOSTER

A remarkable property of vinyl alcohols is the ability to undergo 1,4-dehydrogenation. Thus certain oxidizing agents convert 1,2-dimesityl-1-propen-1-ol (I) to mesityl α -mesitylvinyl ketone (II).² In this reaction the vinyl alcohols may be



likened to enediols, which show a pronounced tendency to give up hydrogen and revert to the corresponding benzils. The oxidation of 1,2-dimesitylacetylene glycol (III) to mesitil (IV)³ is an example.

(2) Fuson, Byers and Rabjohn, *ibid.*, **63**, 2639 (1941).

(3) Fuson and Corse, ibid., 61, 975 (1939).

$$\begin{array}{cccc} OH & OH & O & O \\ & & & & \\ MesC & & \hline \\ III & & IV \end{array} \xrightarrow{} MesC & CMes \end{array}$$

It seemed probable that the ease of 1,4-dehydrogenation of a propenol such as I would prove to depend chiefly on the firmness of attachment of the hydrogen atoms of the methyl group. To test this suggestion it was planned to replace one of these hydrogen atoms by a phenyl group. The resulting vinyl alcohol would possess a benzyl radical in place of the methyl group. The benzyl radical would, of course, lose a hydrogen atom more readily than the methyl group and hence enhance the ease of 1,4-dehydrogenation.

An enol of the type in question was sought in the following way. Benzyl duryl ketone (V) was condensed with benzaldehyde, and the resulting

⁽¹⁾ For the preceding communication in this series see Fuson, Lindsey and Welldon, THIS JOURNAL, **54**, 2888 (1942).

unsaturated ketone (VI) was subjected to catalytic hydrogenation. The ketone was found to take up one mole of hydrogen but no enol (VII) could be isolated. In fact, the starting material was always recovered unchanged.

 $C_{6}H_{5}CH O$ $C_{6}H_{5}CH_{2}CODur \longrightarrow C_{6}H_{5}C CDur \longrightarrow VI$ $C_{6}H_{5}CH_{2}OH \qquad C_{6}H_{5}CH_{2}OH$ $C_{6}H_{5}CH_{2}OH \qquad C_{6}H_{5}CH_{2}O$ $C_{6}H_{5}C CDur \longrightarrow C_{6}H_{5}CH_{2}OUr$ $VII \qquad VIII$

The simplest way to explain this result was to assume that the enol, although formed in the expected manner, was dehydrogenated immediately when exposed to the air. In support of this hypothesis, it was found that if the hydrogenation mixture was allowed to stand for forty-eight hours, the product was the saturated ketone (VIII). Evidently the enol had ketonized.

Although the existence of the enol in solution was thus clearly demonstrated, all attempts to isolate it were unsuccessful. The freshly prepared solutions obtained by hydrogenation of the unsaturated ketone failed also to yield derivatives of the alcohol. Treatment with acetic anhydride and pyridine, for example, did not produce an acetate. This was true even when the whole operation was conducted in the absence of oxygen. Even hydrogenation of the vinyl ketone in acetic anhydride failed to yield an acetate.

It was found that enolization of the saturated ketone (VIII) could be effected by use of the Grignard reagent. The saturated ketone gave a mole of gas in the Grignard machine.⁴ Addition of water to the resulting solution of the enolate, however, failed to produce a stable enol.

Three similar vinyl ketones— α,β -diphenylvinyl 2,4,6-triisopropylphenyl ketone, duryl α -phenyl- β -(p-chlorophenyl)-vinyl ketone and mesityl α -phenyl- β -(p-chlorophenyl)-vinyl ketone—were found to undergo hydrogenation in the same manner. Each absorbed a mole of hydrogen and yielded the corresponding saturated ketone only if the solution was allowed to stand for two days. Immediate exposure to the air always caused the hydrogenation product to revert to the parent vinyl ketone.

It must be concluded that these enols ketonize readily and, like the acetylene glycols, undergo 1,4-dehydrogenation in contact with oxygen. Experimental

Benzyl Duryl Ketone.—This ketone was prepared by the Friedel-Crafts method. From 277 g. of phenylacetyl chloride and 241 g. of durene was obtained 332 g. of benzyl duryl ketone. It was purified by recrystallization from ethanol; m. p. 110-111° (cor.).

Anal.⁵ Caled. for $C_{18}H_{20}O$: C, 85.71; H, 7.94. Found: C, 85.59; H, 7.79.

 α,β -Diphenylvinyl Duryl Ketone.—A mixture of 10 g. of benzyl duryl ketone, 10 g. of freshly distilled benzaldehyde, 30 cc. of 10% aqueous sodium hydroxide and 250 cc. of ethanol was stirred for four hours at room temperature. The mixture was cooled to 0° and the α,β -diphenylvinyl duryl ketone which separated was removed by filtration and crystallized from ethanol; m. p. 150–151° (cor.); yield 70%.

Anal. Calcd. for $C_{25}H_{24}O$: C, 88.23; H, 7.06. Found: C, 88.06; H, 7.06.

 α,β -Diphenylvinyl 2,4,6-Triisopropylphenyl Ketone.— Benzyl 2,4,6-triisopropylphenyl ketone was made from phenylacetyl chloride and triisopropylbenzene by the Friedel-Crafts method.⁶ The product was an oil which solidified when allowed to stand with a small amount of ethanol; m. p. 60.5-61° (cor.).

Anal. Calcd. for C23H30O: C, 85.71; H, 9.32. Found: C, 85.75; H, 9.48.

Benzyl 2,4,6-triisopropylphenyl ketone was condensed with benzaldehyde by the procedure just described for the duryl ketone except that the time of reaction was eight hours instead of four. The α,β -diphenylvinyl 2,4,6-triisopropylphenyl ketone crystallized from an ethanol-water mixture in pale yellow needles; m. p. 117-119° (cor.); yield 70%.

Anal. Calcd. for C₃₀H₃₄O: C, 87.81; H, 8.29. Found C, 87.73; H, 8.31.

Duryl α -Phenyl- β -(p-chlorophenyl)-vinyl Ketone.—The condensation of benzyl duryl ketone with p-chlorobenzaldehyde, according to the foregoing procedure, was complete in two and one-half hours. The duryl α -phenyl- β -(p-chlorophenyl)-vinyl ketone crystallized from ethanol in pale yellow needles; m. p. 138–140° (cor.); yield 81%.

Anal. Caled. for $C_{25}H_{25}OC1$: C, 80.11; H, 6.14 Found: C, 80.27; H, 5.99.

Mesityl α -Phenyl- β -(p-chlorophenyl)-vinyl Ketone. By use of the above procedure benzyl mesityl ketone was converted to the p-chlorobenzal derivative in a yield of 83%. The mesityl α -phenyl- β -(p-chlorophenyl)-vinyl ketone crystallized from ethanol in pale yellow needles; m. p. 138-140° (cor.).⁷

Anal. Caled. for $C_{24}H_{21}OC1$: C, 79.89; H, 5.83. Found: C, 79.89; H, 5.73.

Hydrogenation of α,β -Diphenylvinyl Duryl Ketone.— The hydrogenation was carried out with the Adams and Voorhees⁸ apparatus. A mixture of 0.3 g. of the un-

(4) Kohler and Richtmyer, THIS JOURNAL, 52, 3736 (1930).

⁽⁵⁾ Microanalyses by Miss Margaret McCarthy and Miss Theta Spoor.

⁽⁶⁾ This synthesis was carried out by Mr. R. S. Voris.

Weinstock and Fuson, THIS JOURNAL, 58, 1233 (1936).
(8) Adams and Voorhees, "Org. Syntheses," Coll. Vol. I, second

⁽⁸⁾ Adams and Voornees, "Org. Syntheses," Coll. Vol. 1, second edition, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 61.

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 C₂₅H₂₆O: 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 C₈₀H₃₆O: 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 C₂₅H₂₀OC1: 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 $C_{24}H_{23}OC1$: 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.

$$\begin{array}{ccc} \text{ArCH} & \text{O} & \text{ArCH}_2 \text{ OH} & \text{ArCH}_2 \\ \text{ArC} & & \text{CAr'} & \longrightarrow & \text{ArCHCOAr'} \\ \text{ArC} & & \text{B} & \text{C} \end{array}$$

If the solution of the enol is allowed to stand the corresponding ketone (C) is formed.

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[CONTRIBUTION FROM THE NOVES 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.



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.

⁽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).