

cyclohexen-1-one has been synthesized through cyclization of the Michael addition product of anisalacetone and ethyl acetoacetate. ANN ARBOR, MICHIGAN RECEIVED NOVEMBER 17, 1945

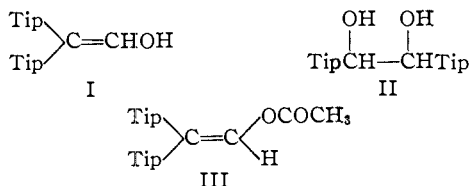
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Vinyl Alcohols. XVIII.¹ Increased Hindrance

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The study of the influence of structure on the stability of trisubstituted vinyl alcohols, summarized in an earlier paper of this series,³ consisted chiefly in a search for the minimum hindrance which would render a vinyl alcohol stable. In the present work an effort was made to bring the amount of hindrance to a maximum. As a result it has been possible to prepare an aldehyde enol with two 2,4,6-triisopropylphenyl⁴ radicals and a ketone enol with three mesityl radicals.

Ditipylvinyl Alcohols.—2,2-Ditipylvinyl alcohol (I) was made by dehydration of 1,2-ditipylethylene glycol (II). Experiment showed that either the hydrobenzoin (II) or the isohydrobenzoin could be dehydrated successfully in a manner similar to that used with the mesityl and isoduryl analogs.⁵ The rearrangement product formed an acetate (III), from which it could



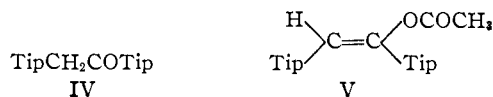
be regenerated by hydrolysis. By analogy with enols obtained in a similar manner, the compound was identified as 2,2-ditipylvinyl alcohol (I).

The study of the oxidation and reduction of 2,2-ditipylvinyl alcohol, though contributing little to the problem of structure determination, gave very interesting results. Thus, hydrogen peroxide, chromic anhydride and ozone converted the alcohol to ditipyl ketone, ditipyl diketone and the corresponding benzoin, respectively. Reduction with hydrogen iodide converted the vinyl alcohol to 1,2-ditipylethylene.

In unsuccessful efforts to prepare a ditipylvinyl chloride the 2,2-ditipylvinyl alcohol was treated with thionyl chloride and with phosphorus pentachloride. Another experiment which might have been expected to yield a ditipylvinyl chloride was the dehydrochlorination of 1,2-ditipyl-1,2-dichlo-

roethane. The elimination of hydrogen chloride took place with unexpected ease. Simple heating converted the compound to a hydrocarbon which had approximately the composition of ditipylacetylene.

It appears probable that with very bulky substituents such as the tipyl radical 1,2-disubstituted vinyl alcohols might prove to be stable. An attempt was made to isolate an enol form of the hexaisopropyl desoxybenzoin (IV). The enol acetate (V) was made by treatment of the desoxy derivative with methylmagnesium iodide and then with acetyl chloride. Hydrolysis of the new acetate converted it to the original desoxy compound, showing that the corresponding enol was unstable.



In an attempted hydrogenation, 2,2-ditipylvinyl alcohol (I) was subjected to high pressure in the presence of hydrogen and Raney nickel; the result was not hydrogenation but merely isomerization. From the reaction mixture was isolated a new ditipylvinyl alcohol. It formed an acetate from which it could be regenerated by hydrolysis, and, in general, behaved like the original 2,2-ditipylvinyl alcohol. By the principle of exclusion it would be the missing stereoisomer of the unstable enol form of the desoxy compound—presumably the *trans* form (VI). It would follow



that in the *trans* configuration the two triisopropylphenyl groups afford enough hindrance to stabilize the enol whereas in the *cis* arrangement (VII) the crowding is less favorable to the existence of an enol.

Because of the great importance of this point, much effort has been expended in an attempt to confirm the structures assigned to the two stable ditipylvinyl alcohols. Degradation methods were found to be of little value. Reagents which attack the central ethylenic linkage often produce migration of a tipyl radical. Thus each of the isomers gave rise to both 1,2 and 2,2 derivatives. For example, reduction with hydrogen iodide converted both vinyl alcohols to 1,2-ditipylethylene.

(1) For the preceding communication in this series see Fuson, Maynert and Shenk, *THIS JOURNAL*, **67**, 1939 (1945).

(2) Abbott Fellow, 1941-1942.

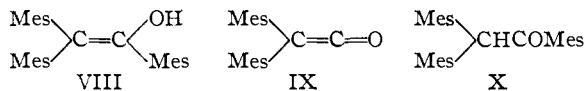
(3) Fuson, Armstrong, Chadwick, Kneisley, Rowland, Shenk and Soper, *THIS JOURNAL*, **67**, 386 (1945).

(4) For convenience in presentation the 2,4,6-triisopropylphenyl radical will be called *tipyl* and will be represented by *Tip*.

(5) Fuson and Southwick and Rowland, *THIS JOURNAL*, **66**, 1109 (1944).

This result does show, of course, that the tipyl radicals themselves have not isomerized.

Trimesitylvinyl Alcohol.—The synthesis of trimesitylvinyl alcohol (VIII) was accomplished by condensing mesitylmagnesium bromide with dimesitylketene (IX). This vinyl alcohol is remarkable in a number of ways. It cannot be ketonized and is insensitive to heat and oxygen. It was found to be unchanged after two and one-half years during which time it had been allowed to stand in contact with the air. Even acetylation requires prolonged treatment.



The preparation of trimesitylethanone (X) was of particular interest since space exigency in the molecule would be extreme. Perhaps because of this property, efforts to make the ketone were fruitless. Treatment of dimesitylacetyl chloride with mesitylmagnesium bromide and with mesitylene in the presence of aluminum chloride failed to yield the ketone.

In an attempt to effect condensation between α -chloromesitylacetyl chloride and mesitylene by the Friedel-Crafts method, it was noticed that deep-seated change occurred, but the ketone could not be isolated. Similarly, an attempted condensation of α -bromodesoxymesityoin gave a complex mixture from which the trimesityl ketone could not be isolated. The pure products which were isolated in these experiments bore no apparent relation to the parent materials or to the expected product. These anomalous results are reminiscent of the discovery that phenyl-*p*-tolylacetyl chloride and benzene yielded diphenylmethane.⁶ Triphenylcarbinol and triphenylmethane were also reported as products of this reaction.⁷

In work done in this Laboratory it was noted that mesitylacetyl chloride and mesitylphenylacetyl chloride, when treated with benzene in the presence of aluminum chloride, yielded diphenylmethane. Isodurylphenylacetyl chloride appeared to behave in a similar manner. Finally, tipylacetyl chloride with benzene yielded a wholly anomalous product along with the expected phenyl 2,4,6-triisopropylbenzyl ketone.

Enol Forms of Desoxybenzoins.—The isolation of a ditipylvinyl alcohol corresponding to the enol form of hexatriisopropyldeoxybenzoin led to attempts to obtain stable enol forms of other desoxybenzoins. It had been shown earlier that both the *cis* and *trans* forms of desoxymesityoin were unstable.⁸ Another possible method of making enols of this type is by the action of Grignard reagents⁹ or of magnesium

halides¹⁰ on the corresponding desyl bromides. The bromides of mesityl 2,4,6-triethylbenzyl ketone and duryl 2,4,6-trimethylbenzyl ketone were made and treated with sodium ethoxide; no stable enols could be isolated. Treatment of the duryl compound with ethylmagnesium bromide yielded duryl 2,4,6-trimethylbenzyl ketone.

Infrared Absorption Spectra

Infrared absorption data are now available for additional compounds which have been described in this series of papers. The spectrum of 2-mesityl-2-phenylvinyl alcohol¹¹ exhibits absorption peaks at 2.76 and 2.84 μ ; that of trimesitylvinyl alcohol at 2.78 and 2.86 μ . These values are very nearly the same as those observed earlier for 2,2-dimesitylvinyl alcohol,¹² 1,2-dimesityl-2-phenylvinyl alcohol¹³ and 1,1-dimesityl-1-propen-2-ol.³ It is interesting that the values for 2,2-dimesitylethanol⁵—2.76 and 2.85 μ —do not differ appreciably from those of the vinyl alcohols. However, concentration studies with this alcohol indicated intermolecular hydrogen bonding.

Absorption in the region 2.84–2.86 μ is characteristic of the bonded hydroxyl group. Association of the vinyl alcohols through intermolecular hydrogen bonding seems to be excluded, however, since concentration studies showed no relative changes in the intensities of the two peaks.

The following compounds have been found not to absorb light in this region of the spectrum: ethyl isodurylphenylacetate,¹⁴ 1-mesityl-1-phenylpropanone³ and 2-mesityl-2-phenylvinyl methyl ether.¹¹ These data, which exclude the possibility of the presence of hydroxyl groups, are consistent with the structures assigned.

The authors are indebted to Professor W. H. Rodebush, Dr. M. M. Sparks and Dr. R. M. Whitney for the measurement and interpretation of these absorption spectra.

Experimental

2,2-Ditipylvinyl Alcohol. (I).—This compound was made by the dehydration of the 1,2-ditipylethylene glycols (II),¹⁵ various procedures being employed.

(a) **Sulfuric Acid.**—Either the high- or the low-melting glycol, when heated with sulfuric acid, yielded the vinyl alcohol. Two grams of the high-melting glycol, for example, was heated on a steam-bath for thirty-six hours with 24 ml. of concentrated sulfuric acid and 18 ml. of water. The needle-like crystals of the glycol appeared to become wet by the solution and to react; the vinyl alcohol crystallized in hard white cubes. It was recrystallized from glacial acetic acid; m. p. 114–115°.

Anal. Calcd. for C₂₂H₄₈O: C, 85.65; H, 10.78. Found: C, 85.79; H, 10.70.

(b) **Phosphorus Pentoxide.**—An alternative method involved the use of phosphorus pentoxide. Two grams

(10) Schönberg and Moubasher, *J. Chem. Soc.*, 462 (1944).

(11) Fuson, Rabjohn and Byers, *THIS JOURNAL*, **66**, 1272 (1944).

(12) Fuson and Rowland, *ibid.*, **65**, 992 (1943).

(13) Fuson, Armstrong, Kneisley and Shenk, *ibid.*, **66**, 1464 (1944).

(14) Fuson, Armstrong, Wallace and Kneisley, *ibid.*, **66**, 1274 (1944).

(15) Fuson, Horning, Ward, Rowland and Marsh, *ibid.*, **64**, 30 (1942).

(6) Koelsch, *THIS JOURNAL*, **54**, 2049 (1932).

(7) McKenzie and Widdows, *J. Chem. Soc.*, **107**, 702 (1915); McKenzie, Roger and McKay, *ibid.*, 2597 (1932).

(8) Fuson, Armstrong and Shenk, *THIS JOURNAL*, **66**, 964 (1944).

(9) Kohler and Johnston, *Am. Chem. J.*, **33**, 35 (1905).

of the high-melting glycol was dissolved in 50 ml. of dry benzene and 5 g. of phosphorus pentoxide was added. After the mixture had been allowed to stand for twelve hours at room temperature, it was poured into water. The product was identical with the vinyl alcohol made by the use of sulfuric acid.

The low-melting glycol, when subjected to this treatment, also yielded the vinyl alcohol.

(c) **Acetic Acid-Hydrochloric Acid.**—A mixture of 1 g. of the high-melting glycol, 20 ml. of glacial acetic acid and 6 ml. of concentrated hydrochloric acid was heated under reflux for three hours. The vinyl alcohol was deposited in white cubes when the solution was allowed to cool. The result was the same when the low-melting glycol was used.

(d) **Heat.**—When 10 g. of the low-melting glycol was distilled *in vacuo*, the vinyl alcohol came over in high yield, at 175–176° (6 mm.). The compound was purified by recrystallization from glacial acetic acid; m. p. 114–115°.

Reduction.—Reduction of 2,2-ditipylvinyl alcohol with hydrogen iodide yielded 1,2-ditipylethylene. A mixture of 1 g. of the alcohol, 30 ml. of glacial acetic acid and 10 ml. of hydriodic acid (sp. gr. 1.50) was heated on the steam-bath for twenty-four hours. The ethylene was removed by filtration and recrystallized from methanol. It formed long colorless needles, melting at 146–147°, which did not depress the melting point of an authentic specimen of 1,2-ditipylethylene.¹¹ Treatment of the vinyl alcohol with phosphorus and iodine likewise produced the ethylene. It is interesting that 1,2-ditipylethylene was obtained also by the reduction of the isomeric 1,2-ditipylethylene glycols with hydrogen iodide or with phosphorus and iodine. Even hydrobromic acid alone effected the same transformation. The structure of the ethylene was proved by ozonization; 2,4,6-triisopropylbenzoic acid was isolated.

Oxidation. (a) **Chromic Anhydride.**—One gram of 2,2-ditipylvinyl alcohol was allowed to stand at room temperature for twenty-four hours with chromic anhydride (2.5 g.) in glacial acetic acid (80 ml.). A small amount of yellow crystals was isolated; when recrystallized from methanol, this compound melted at 152–154°. A mixed melting point test identified this product as 1,2-ditipyl diketone.¹⁶

(b) **Hydrogen Peroxide.**—Five grams of 2,2-ditipylvinyl alcohol was dissolved in 300 ml. of ethanol, and a mixture of 25 ml. of 30% hydrogen peroxide and 10 ml. of 20% sodium hydroxide solution was added. The mixture was allowed to stand for forty-eight hours at room temperature. The solid product, when recrystallized from ethanol, formed colorless crystals melting at 140–141°. This substance was shown by the mixed melting point method to be ditipyl ketone.

(c) **Potassium Permanganate.**—To a solution of 1 g. of 2,2-ditipylvinyl alcohol in 250 ml. of dioxane was added gradually over a period of thirty minutes a solution of 4 g. of potassium permanganate in 80 ml. of water. Stirring was employed during the mixing and for two hours longer. The product melted at 140–141° and proved to be ditipyl ketone.

(d) **Ozone.**—A stream of oxygen containing 4% ozone was passed for two hours at room temperature through a solution of 3 g. of 2,2-ditipylvinyl alcohol in 40 ml. of chloroform. The deep red color produced at the beginning changed to orange at the end of the reaction period. The chloroform solution was poured into 200 ml. of 1% sodium hydroxide solution and the mixture heated under reflux for three hours. From the chloroform layer was isolated a yellow compound, melting at 152–154°. A mixed melting point test showed it to be ditipyl diketone.

When the chloroform solution from the ozonization was poured into water, instead of sodium hydroxide solution, and heated for two hours under reflux, the product (m. p. 125–126°) was the benzoin¹⁶ corresponding to ditipyl diketone.

When the benzoin was heated with alcoholic potassium hydroxide, it was converted to the diketone. The ozoni-

zation product was evidently the benzoin, which was changed to the benzil when the alkali treatment was used.

(e) **Selenium Dioxide.**—Treatment of 2,2-ditipylvinyl alcohol with selenium dioxide in dioxane gave a very small amount of ditipyl diketone; m. p. 152–154°.

Bromination.—A mixture of 3 g. of 2,2-ditipylvinyl alcohol, 50 ml. of chloroform and 1 g. of bromine was stirred at room temperature for eight hours. Copious quantities of hydrogen bromide were evolved. The reaction mixture was poured into water and the bromination product isolated by the usual procedure. It was recrystallized from an ethanol-benzene mixture; m. p. 187–188°.

Anal. Calcd. for C₃₂H₄₆OBr₃: C, 56.07; H, 6.62. Found: C, 56.12; H, 6.10.

Attempts to acetylate the bromine derivative were unsuccessful.

The Acetate of 2,2-Ditipylvinyl Alcohol (III).—This compound was prepared by the use of acetic anhydride and pyridine. It was crystallized from ethanol; m. p. 115–116°.

Anal. Calcd. for C₃₃H₅₀O₂: C, 83.21; H, 10.27. Found: C, 83.40; H, 10.25.

The vinyl alcohol (m. p. 114–115°) was regenerated by hydrolysis of the acetate. The acetate was unaffected by treatment with an acetone solution of potassium permanganate but yielded ditipyl ketone when treated with alkaline hydrogen peroxide.

Ditipyl Ketone.—A solution of 26.6 g. of 2,4,6-triisopropyl benzoyl chloride in 75 ml. of dry ether was added slowly to a Grignard reagent prepared from 2.6 g. of magnesium, 75 ml. of dry ether and 30 g. of tipyl bromide. After being heated under reflux for eight hours, the reaction mixture was worked up in the usual manner. The ditipyl ketone was purified by recrystallization from ethanol; m. p. 140–141°.

Anal. Calcd. for C₃₁H₄₆O: C, 85.65; H, 10.67. Found: C, 85.80; H, 10.58.

Isomerization by Treatment with Ethanolic or Methanolic Hydrogen Chloride.—Two grams of 2,2-ditipylvinyl alcohol was added to 80 ml. of absolute ethanol which had been saturated with hydrogen chloride at room temperature. After the mixture had been heated for eight hours under reflux it was allowed to cool. The product, after recrystallization from methanol, melted at 171–172°.

Anal. Calcd. for C₃₂H₄₈O: C, 85.65; H, 10.78. Found: C, 85.67; H, 10.93.

The same product was obtained when methanolic hydrogen chloride was used. The compound failed to yield an acetate, could not be hydrolyzed and failed to give gas in the Kohler-Richtmyer apparatus.¹⁷ It did not undergo catalytic reduction. Reduction with hydriodic acid in glacial acetic acid, however, converted it to 1,2-ditipylethylene, m. p. 146–147°. From its behavior it was thought that the compound might be 1,2-ditipylethylene oxide.

Attempts to Make a Ditipylvinyl Chloride. (a) **From 2,2-Ditipylvinyl Alcohol.**—By the action of thionyl chloride or phosphorus pentachloride the vinyl alcohol was converted to tarry materials from which no pure compound could be isolated.

(b) **From 1,2-Ditipylethylene Glycol.**—One gram of the glycol (m. p. 285–286°) was heated on a steam cone for thirty minutes with 30 ml. of phosphorus oxychloride and 1 g. of phosphorus pentachloride. The mixture was allowed to cool and was poured into water. The product appeared to be a mixture presumably of the stereoisomeric 1,2-ditipyl-1,2-dichloroethanes. By repeated recrystallization of the product from absolute ethanol, one of these was obtained in pure form; m. p. 213–215°, with dec.

Anal. Calcd. for C₃₂H₄₈Cl₂: C, 76.29; H, 9.61. Found: C, 76.00; H, 9.72.

The same dichloro compound was obtained when the low-melting glycol (m. p. 186–187°) was used.

It was prepared also by the action of methylmagnesium

(16) Fuson and Horning, *THIS JOURNAL*, **62**, 2962 (1940).

(17) Kohler and Richtmyer, *ibid.*, **52**, 3736 (1930).

iodide on 2,4,6-triisopropylbenzal chloride according to the method used with mesital chloride.¹⁸ 2,4,6-Triisopropylbenzal chloride was prepared in 76% yield by the action of phosphorus pentachloride (42 g.) on the corresponding aldehyde (46 g.); b. p. 169–170° (21 mm.). Treatment with methylmagnesium iodide in the usual way¹⁹ converted it to a mixture of dichlorides one of which melted at 213–215° and proved to be identical with that from the glycol. The two dichlorides were separated and purified by repeated recrystallizations from absolute ethanol.

The other dichloride, presumably a stereoisomer of the first, melted at 175–176°.

Anal. Calcd. for C₃₂H₄₈Cl₂: C, 76.29; H, 9.61. Found: C, 76.58; H, 9.27.

One gram of 1,2-ditriptyl-1,2-dichloroethane (m. p. 213–215°) was heated at 215–230° for one hour. Hydrogen chloride was evolved. The product, after recrystallization from methanol, melted at 180–182°. It was halogen-free and had approximately the composition of di-(2,4,6-triisopropylphenyl)-acetylene.

Anal. Calcd. for C₃₂H₄₆: C, 89.24; H, 10.76. Found: C, 88.41; H, 11.17.

Trimesitylvinyl Alcohol. (VIII).—This compound was made by the addition of mesitylmagnesium bromide to dimesitylketene.³ A solution of 12 g. of dimesitylketene in 150 ml. of dry ether was added to a Grignard solution prepared from 18 g. of bromomesitylene, 2.2 g. of magnesium and 200 ml. of dry ether. After the mixture had been heated under reflux for two and one-half hours the ether was distilled and replaced by benzene. Heating under reflux was continued for an additional two hours. The trimesitylvinyl alcohol, isolated by conventional procedures, was recrystallized from ethanol; m. p. 155–157°; yield 10 g. Further purification was effected by recrystallization from low-boiling petroleum ether; m. p. 157–158°.

Anal. Calcd. for C₂₉H₃₄O: C, 87.39; H, 8.60. Found: C, 87.84; H, 8.69.

The acetate of trimesitylvinyl alcohol was made by heating a mixture of 15 g. of the vinyl alcohol, 5 ml. of acetic anhydride and 15 ml. of pyridine for five hours under reflux. It was recrystallized from ethanol; m. p. 181.5–182.5°.

Anal. Calcd. for C₃₁H₃₆O₂: C, 84.50; H, 8.24. Found: C, 84.66; H, 8.41.

When the acetate was heated under reflux for five hours with methanolic potassium hydroxide, the vinyl alcohol was regenerated in high yield.

α-Bromodesoxybenzoin.—A solution of 21 g. of desoxybenzoin in 125 ml. of dry ether was added slowly to a Grignard reagent prepared from 2.4 g. of magnesium, 12 g. of ethyl bromide and 60 ml. of dry ether. After the mixture had been heated under reflux, with stirring, for three hours, it was cooled by an ice-bath and a solution of 17.6 g. of bromine in 100 ml. of ether added gradually. The mixture was stirred for one hour after the addition was complete, the temperature being allowed to rise to that of the room. Finally, the mixture was heated under reflux for an additional hour. The bromodesoxybenzoin, isolated by conventional procedures, was recrystallized from ethanol; m. p. 105–106°; yield 14 g.

Anal. Calcd. for C₂₀H₃₀OBr: C, 66.85; H, 6.45. Found: C, 67.21; H, 6.68.

Dimesitylacetyl Chloride.—A mixture of 20 g. of dimesitylacetic acid, 50 ml. of thionyl chloride and 10 ml. of chloroform was heated to initiate reaction and allowed to stand for one day at room temperature. The temperature was then brought to 40° and held there while the excess thionyl chloride was removed at the pump a few milliliters of chloroform was added to the residue and removed at the pump to sweep out any remaining traces of thionyl chloride. The acid chloride was washed re-

peatedly with cold, low-boiling petroleum ether and dried in a vacuum desiccator; m. p. 91–94°; yield 14.5 g. Repeated recrystallization of the compound from petroleum ether brought the melting point to 93–94°.

Anal. Calcd. for C₂₀H₂₂OCl: C, 76.29; H, 7.36. Found: C, 76.44; H, 7.62.

Attempts to Prepare Trimesitylethanone (X). α-Chloromesitylacetyl Chloride.—A mixture of 19.4 g. of mesitylglycolic acid and 100 ml. of thionyl chloride was allowed to stand overnight, then was heated under reflux for three hours. The α-chloromesitylacetyl chloride boiled at 103–108° (2–3 mm.); n_D²⁰ 1.5487; yield 85% of the theoretical. Analysis showed the compound to be slightly impure.

Anal. Calcd. for C₁₁H₁₂OCl₂: C, 57.16; H, 5.24. Found: C, 57.79; H, 5.56.

Condensation of α-Chloromesitylacetyl Chloride with Mesitylene.—The condensation was carried out in the presence of anhydrous aluminum chloride and without solvent. The semi-solid product was dark green in color and exceedingly difficult to purify. Repeated recrystallization of this material from an ethanol-butyl ether solvent yielded a small amount of yellow needles melting at 164–166°. Analysis showed the compound to be a hydrocarbon; it was not investigated further.

Anal. Calcd. for C₁₇H₁₈: C, 91.84; H, 8.16. Found: C, 91.87; H, 8.07.

Condensation of Dimesitylacetyl Chloride with Mesitylene.—A procedure similar to that employed with α-chloromesitylacetyl chloride yielded a complex mixture from which a small amount of crystalline material was isolated. It was purified by recrystallization from benzene; m. p. 265–270° (copper block). The product proved to be a hydrocarbon but was not further studied.

Anal. Calcd. for C₁₇H₁₈: C, 91.84; H, 8.16. Found: C, 91.91; H, 8.51.

An attempt to carry out the condensation in carbon disulfide as a solvent also led to a complex product. By suitable manipulation of this mixture two pure compounds were isolated. One was recrystallized from ethanol; m. p. 148.5–149.5°. Its structure was not determined.

Anal. Calcd. for C₂₀H₂₆O: C, 85.05; H, 9.28. Found: C, 85.01; H, 9.16.

The second product, after recrystallization from ethanol, melted at 60.5–62°. It was not identified.

Anal. Calcd. for C₂₀H₂₆O: C, 85.05; H, 9.28. Found: C, 85.20; H, 9.33.

Condensation of Mesitylacetyl Chloride with Benzene.—To a mixture of 70 g. of anhydrous aluminum chloride and 350 ml. of dry benzene at room temperature was added slowly, with stirring, a solution of 80 g. of mesitylacetyl chloride in 350 ml. of dry benzene. The mixture was warmed for three hours, allowed to stand overnight and decomposed with iced hydrochloric acid. The product, after being recrystallized three times from methanol, melted at 161–162°; yield 7 g. A mixed melting point showed it to be phenyl 2,4,6-trimethylbenzyl ketone.²⁰

By evaporation of the initial methanol filtrate and distillation of the oily residue there was isolated 15 g. of a liquid boiling at 135–140° (23 mm.); n_D¹⁶ 1.571. This substance was identified as diphenylmethane by oxidation with chromic anhydride in glacial acetic acid. The resulting benzophenone was identified by reference to the semicarbazone. The yield of diphenylmethane, collected over the 5° range, was 22% of theoretical.

Condensation of Isodurylphenylacetyl Chloride with Benzene.²¹—A mixture of 11 g. of isodurylphenylacetyl chloride, 30 ml. of thionyl chloride and 20 ml. of dry chloroform was heated gently to effect solution and allowed to stand overnight at room temperature. The solvent was removed by distillation under diminished pressure. Dry benzene was added and distillation resumed. The crude

(18) Asinger and Lock, *Monatsh.*, **62**, 323 (1933).

(19) Fuson and Ross, *THIS JOURNAL*, **55**, 720 (1933).

(20) Weinstock and Fuson, *ibid.*, **55**, 1233 (1936).

(21) This experiment was carried out by Dr. W. J. Shenk, Jr.

acid chloride, remaining after all the benzene had been distilled, was dissolved in 20 ml. of dry benzene and the resulting solution was added dropwise, with stirring, to a mixture of 10 g. of anhydrous aluminum chloride and 15 ml. of benzene. The addition was carried out at room temperature and required twenty-five minutes. Stirring was continued for five and one-half hours, and the reaction mixture was decomposed in the usual way. From the red organic layer, which had a peculiar, fruity odor, was obtained 5 g. of an oil which boiled at 103–104° (3 mm.). It had the odor characteristic of diphenylmethane.

Condensation of 2,4,6-Triisopropylphenylacetyl Chloride with Benzene.²²—A solution of 10 g. of the acid chloride in 50 ml. of dry benzene was added, dropwise and with stirring, to a mixture of 10 g. of anhydrous aluminum chloride and 50 ml. of dry benzene. The mixture was stirred for five hours after the addition was completed. The product was an oil boiling at 176–178° (3 mm.).

Anal. Calcd. for $C_{23}H_{30}O$: C, 85.66; H, 9.38. Found: C, 86.17; H, 7.83.

The compound did not react with hydroxylamine.

Enol Benzoate of Duryl 2,4,6-Trimethylbenzyl Ketone.²³—The bromomagnesium enolate from 3 g. of the ketone and an excess of ethylmagnesium bromide was treated with 1.8 g. of benzoyl chloride. The benzoate, isolated in the usual way did not give a color with ferric chloride or cupric acetate and was not hydrolyzed by cold, dilute alcoholic potassium hydroxide solution. It was purified by recrystallization from ethanol; m. p. 148.5–149° (cor.).

Anal. Calcd. for $C_{28}H_{30}O_2$: C, 84.38; H, 7.59. Found: C, 84.16; H, 7.75.

α -Bromo-2,4,6-trimethylbenzyl Duryl Ketone.²³ (a) From the Desoxybenzoin.—The bromomagnesium enolate of duryl 2,4,6-trimethylbenzyl ketone was prepared by adding 10 g. of the ketone in 75 ml. of dry ether to a solution of ethylmagnesium bromide and 30 ml. of dry ether. After the mixture had been heated, under reflux and with stirring, for one hour a solution of 1.9 ml. of dry bromine in 10 ml. of dry ether was added. Decomposition of the mixture in the usual way yielded 6.1 g. of the crude bromo ketone. It was recrystallized from ethanol; m. p. 130.5–131.5°.

Anal. Calcd. for $C_{21}H_{22}OBr$: C, 67.54; H, 6.75. Found: C, 67.42; H, 6.92.

(b) From α -Bromomesitylacetyl Bromide.—The acid bromide, made by treating mesitylglycolic acid with phosphorus tribromide,⁸ boiled at 130–133° (5 mm.) and melted at 58–60°. Condensation of the bromide with durene by the Friedel-Crafts method gave an 11% yield of the bromo ketone. A mixed melting point determination showed this sample to be identical with that made by bromination of the ketone.

Treatment of the bromo ketone with ethylmagnesium bromide yielded the halogen-free desoxybenzoin. Sodium ethoxide converted the bromo compound to an intractable tar.

α -Bromo-2,4,6-triethylbenzyl Mesityl Ketone.²³—This compound was prepared from the desoxybenzoin and from α -bromo-2,4,6-triethylphenylacetyl bromide (b. p. 168–171° (6–8 mm.); n_D^{20} 1.5713) by procedures similar to those indicated for the preparation of α -bromo-2,4,6-trimethylbenzyl duryl ketone. The ketone was recrystallized from ethanol; m. p. 134.5–135.5° (cor.).

Anal. Calcd. for $C_{23}H_{26}OBr$: C, 68.81; H, 7.29. Found: C, 69.00; H, 7.31.

Treatment of the bromo desoxybenzoin with sodium ethoxide produced tars.

2,2',4,4',6,6'-Hexaisopropylidenebenzoin (IV).—This ketone was made by condensation of tipylacetyl chloride with triisopropylbenzene by the Friedel-Crafts method. The product was crystallized from methanol; m. p. 131–132°.

(22) This experiment was carried out by Dr. Quentin F. Soper.

(23) This compound was made by Dr. Carleton A. Sperati.

Anal. Calcd. for $C_{32}H_{48}O$: C, 85.65; H, 10.78. Found: C, 85.91; H, 10.88.

The desoxybenzoin was made also by condensing tipylmagnesium bromide with tipylacetyl chloride.

A third method involved high-pressure hydrogenation of the corresponding diketone. One gram of the ditipyl diketone¹⁶ in 20 ml. of absolute ethanol was heated for twelve hours at 250° and 6000 lb. of hydrogen pressure in the presence of a copper chromite catalyst.

A Zerewitinoff determination showed the desoxybenzoin to possess one active hydrogen. Long treatment with acetic anhydride and pyridine failed to produce an acetate. An acetate was prepared, however, by the following procedure. A sample of the desoxybenzoin was heated at 90–95° for four hours in a butyl ether solution containing approximately a ten-fold excess of methylmagnesium iodide. An excess of acetyl chloride was added and the mixture heated for twelve hours at 90–95°. The acetate crystallized from methanol; m. p. 168–169°.

Anal. Calcd. for $C_{34}H_{50}O_2$: C, 83.21; H, 10.27. Found: C, 83.21; H, 10.13.

The acetate was shown by a Zerewitinoff determination to have no active hydrogen, and copper acetate in ether failed to yield a copper derivative. Hydrolysis of the acetate with potassium hydroxide regenerated the hexaisopropylidenebenzoin.

1,2-Ditipylvinyl Alcohol (VI).—Two grams of the 2,2-ditipylvinyl alcohol was dissolved in 20 ml. of absolute ethanol and the solution placed with 1 g. of Raney nickel catalyst in a small hydrogenation bomb. The mixture was heated at 175° for twelve hours under a pressure of 4500 pounds of hydrogen. The catalyst was removed by filtration and the ethanol solution concentrated to a small volume. The new vinyl alcohol was crystallized from ethanol; m. p. 129–130°.

Anal. Calcd. for $C_{32}H_{48}O$: C, 85.65; H, 10.78. Found: C, 85.95; H, 10.96.

Reduction with hydriodic acid was carried out as indicated for the 2,2-isomer except that heating was continued only six hours. The product was 1,2-ditipylethylene, melting at 146–147°.

1,2-Ditipylvinyl Acetate.—The acetate was formed when the alcohol was heated with acetic anhydride and pyridine. After several recrystallizations from methanol it was obtained in colorless needles; m. p. 103–104°.

Anal. Calcd. for $C_{34}H_{50}O_2$: C, 83.21; H, 10.27. Found: C, 83.40; H, 10.25.

Hydrolysis of the acetate with potassium hydroxide in aqueous ethanol regenerated the parent vinyl alcohol; m. p. 129–130°.

Catalytic hydrogenation of the acetate produced 2,2-ditipylvinyl alcohol. A mixture of 0.5 g. of the acetate, 15 ml. of absolute ethanol and 0.25 g. of Raney nickel catalyst was heated in a bomb for ten hours at 200° under a pressure of 4800 pounds of hydrogen. After recrystallization from glacial acetic acid, the product melted at 114–115°. It did not depress the melting point of an authentic sample of 2,2-ditipylvinyl alcohol.

Summary

2,2-Ditipylvinyl alcohol has been synthesized by dehydration of 1,2-ditipylethylene glycol. An isomeric compound, believed to be 1,2-ditipylvinyl alcohol, has been prepared from the 2,2-isomer by rearrangement. The behavior of this isomer suggests that the high degree of crowding provided by the tipyl groups makes up for the absence of the third substituent radical, previously thought to be necessary in a stable ketone enol.

Trimesitylvinyl alcohol has been synthesized; it could not be ketonized.