Methylation of Disaccharides.—The disaccharide octaacetate was converted to the α-glycosyl chloride with titanium tetrachloride.[7] By treatment with silver carbonate and methanol the glycosyl chloride was converted to the methyl heptaacetyl-β-glycoside. The heptaacetyl compound was methylated in acetone solution with dimethyl sulfate and 50% sodium hydroxide solution using a relatively large excess of these reagents. The methylation was completed by two treatments with sodium and methyl iodide according to the procedure of Pacsu and Trister.[8] By this method, methyl heptamethyl-β-lactoside, m. p. 84.5–85.2°, methyl heptamethyl-β-cellobioside, m. p. 86–87.5°, methyl heptamethyl-β-melibioside, m. p. 105–106°, methyl heptamethyl-β-gentiobioside, m. p. 105–106° and methyl heptamethylmaltoside, b. p. 143° (0.05 mm.), $n^{25}D$ 1.4620, were prepared. The final yields based on disaccharide octaacetate were in all cases 40–60% of the theoretical.

Acknowledgment.—The authors wish to express their appreciation to the Corn Products Refining Company for financial assitance, to G. E. Hilbert of the U. S. Northern Regional Research Laboratory for a generous sample of levoglucosan, and to B. Clifford Hendricks of the University of Nebraska for seed crystals of tetramethylgalactose.

Summary

1. A new method for the separation of the hydrolysis products of completely methylated disaccharides has been developed. This involves the introduction of azoyl (p-phenylazobenzoyl) groups into the positions opened by hydrolysis.

2. A similar method has been developed based on methyl alcoholysis of methylated disaccharides followed by azoylation of one of the products.

3. Both methods have been applied to five completely methylated disaccharides.

4. Crystalline azoyl derivatives of the eight methyl trimethyl-D-glucopyranosides have been obtained by chromatographic separation of the α and β mixtures.

Iowa City, Iowa Received November 17, 1944

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[7] Pacsu, *Ber.*, **61**, 1508 (1928).

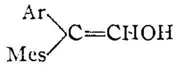
[8] Pacsu and Trister, This Journal, **61**, 2442 (1939).

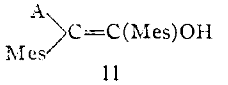
[Contribution from the Noyes Chemical Laboratory, University of Illinois]

Vinyl Alcohols. XV.[1] Trisubstituted Vinyl Alcohols

By Reynold C. Fuson, L. J. Armstrong, David H. Chadwick, J. Wayne Kneisley,[2] Stanley P. Rowland,[3] W. J. Shenk, Jr., and Quentin F. Soper

The vinyl alcohols dealt with in this series of papers, unique in that they contain only hydrocarbon substituents,[4] fall into two separate categories which may be designated as aldehyde enols and ketone enols. The stable aldehyde enols which have been made so far are 2,2-diarylvinyl alcohols in which one or both of the radicals is mesityl or isoduryl. They may be represented by formula I.


I

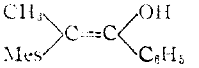

II

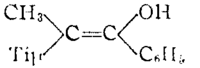
The ketone enols differ widely in the tendency to ketonize,[5] their stability depending on the nature of the three substituents. Those which are stable have a mesityl or a similar radical[6] in the *beta* as well as the *alpha* position and may be represented by formula II. Moreover, from a consideration of known examples, it appears that A may be any hydrocarbon residue but not hydrogen.[7]

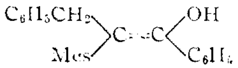
The purpose of the present work was to discover the structural elements which are necessary and sufficient to stabilize this type of enol. Eight new trisubstituted vinyl alcohols have been examined in which the structure has been varied systematically. They fall into two classes which may be designated as disubstituted acetophenones and disubstituted acetones.

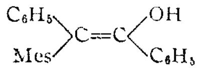
Enols of Disubstituted Acetophenones

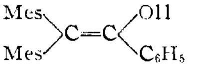
The acetophenone enols are represented by formulas III to VII.

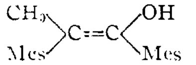

III


IV


V


VI


VII


VIII

The first of these, 2-mesityl-1-phenyl-1-propen-1-ol (III), differs structurally from the known

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[1] For the preceding communication in this series see Fuson, Byers, Rowland, Southwick and Sperati, This Journal, **66**, 1873 (1944).

[2] Present address: Hercules Powder Company, Wilmington, Delaware.

[3] du Pont Fellow in Chemistry, 1942–1943.

[4] The enol form of 9-formylfluorene is stable [Wislicenus and Waldmüller, *Ber.*, **42**, 785 (1909), Wislicenus and Russ, *ibid.*, **43**, 2719 (1910)] and, if the aldehyde is classed as a diarylacetaldehyde would constitute an exception to this statement.

[5] Up to this time the relative tendencies of vinyl alcohols to ketonize have not been measured accurately. Enols which can be isolated and characterized are said to be "stable."

[6] Other radicals which have been found to resemble mesityl in their stabilizing influence are duryl, isoduryl and 3-bromomesityl.

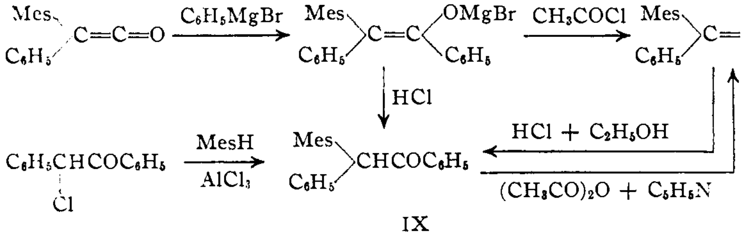
[7] Enols are known in which A is methyl or phenyl. It is interesting to note that when A is hydroxyl the vinyl alcohol is a stable enediol. Although not a hydrocarbon residue, the radical MesCOCH$_2$— in the stable enol, 1,2,4-trimesityl-1-buten-4-on-1-ol, of Lutz and Kibler (This Journal, **62**, 365 (1940)) should be mentioned in this connection.

stable enol, 1,2-dimesityl-1-propen-1-ol (VIII),[8] by having a phenyl rather than a mesityl group on the *alpha* carbon atom. The replacement of the mesityl radical by a phenyl group was attended by marked diminution in the stability of the vinyl alcohol. Enol III did exist in solution, however, and yielded a peroxide.

The second enol, 1-phenyl-2-tipyl-1-propen-1-ol (IV), differed from the first (III) by having increased crowding at the *beta* position, *i. e.*, a tipyl[9] group was introduced in place of the mesityl radical in that position. This enol was similar to III; it was not isolated from solution but did yield a peroxide.

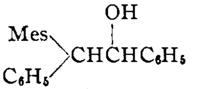
In view of an earlier observation that a benzyl group was more effective than a methyl group in the *beta* position[1] an attempt was made to prepare the benzyl analog of enol III. The Grignard method[1] was used. Condensation of phenylmagnesium bromide with α-mesitylvinyl phenyl ketone did not yield the expected enol, 2-mesityl-1,3-diphenyl-1-propen-1-ol (V). However, benzoic acid was formed in the mixture after exposure to air, indicating that the enol had undergone oxidative cleavage.

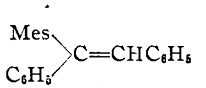
Most surprising was the discovery that 2-mesityl-1,2-diphenyl-vinyl alcohol (VI) was unstable. Its synthesis was attempted by the condensation of phenylmagnesium bromide with mesitylphenylketene. The results are shown by the following outline.



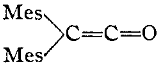
The ketone, α-mesityldesoxybenzoin (IX), appeared to undergo enolization readily but no stable enol form was found. It was isolated only in the form of the peroxide. The structure of the ketone was confirmed by an independent synthesis, which involved condensation of desyl chloride with mesitylene. Moreover, the infrared absorption spectrum[10] showed a maximum at 5.90 μ, demonstrating the presence of a carbonyl group.

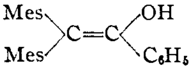
In one attempt to prepare the enol form of α-mesityldesoxybenzoin, isopropylmagnesium bromide was used as the enolizing agent. The reaction was, however, one of reduction rather than enolization. The reduction product, 2-mesityl-1,2-diphenylethanol (X), was isolated as the acetate. Treatment with ethanolic hydrochloric acid caused hydrolysis of the acetate and dehydration of the resulting carbinol, presumably to 1-mesityl-1,2-diphenylethylene (XI).

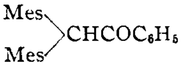

X


XI

In the search for a stable ketone enol without a hindering radical in the *alpha* position there remained the possibility of increasing still further the hindrance at the *beta* position. To test this idea we condensed dimesitylketene (XII) with phenylmagnesium bromide and with lithium phenyl. The resulting enol, 1-phenyl-2,2-dimesitylvinyl alcohol (XIII), was stable. It could be ketonized, however, by treatment with methanolic hydrogen chloride. The ketone, α,α-dimesitylacetophenone (XIV), which was formed also by the condensation of dimesitylacetyl chloride with phenylmagnesium bromide, underwent enolization when heated in the presence of sodium ethoxide. The stability of this vinyl alcohol shows that excessive hindrance at the *beta* position can stabilize a ketone enol which has no hindering radical in the *alpha* position.


XII

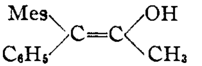

XIII

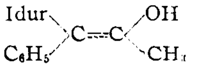

XIV

This enol is the first to be made which cannot exist in *cis* and *trans* forms. Consequently, the isolation of the corresponding ketone (XIV) proves the structure of the enol by the principle of exclusion.

Enols of Disubstituted Acetones

It was of especial interest to determine the effect of an alkyl group in the *alpha* position. To this end we have carried out experiments designed to produce the enolic forms of certain disubstituted acetones. The first to be studied were 1-mesityl-1-phenyl-1-propen-2-ol (XV) and its isoduryl analog (XVI). The only products which could be isolated, however, were ketones rather than enols. Thus when methylmagnesium iodide was added to mesitylphenylketene, the product was 1-mesityl-1-phenyl propanone (XVII). Addition of acetyl chloride to the reaction mixture produced an acetate, indicating that the reaction proceeded by addition of the reagent to


XV


XVI

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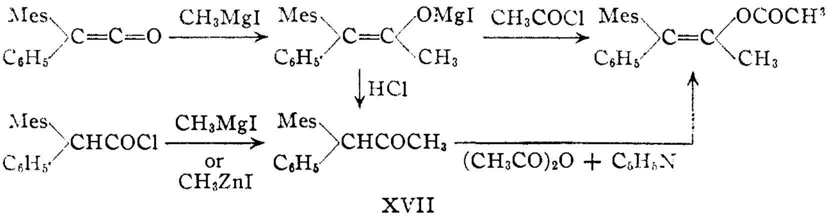
[8] Fuson, Byers and Rabjohn, THIS JOURNAL, **63**, 2639 (1941). Samples of this vinyl alcohol and of 1-duryl-2-mesityl-1-propen-1-ol, kept under nitrogen in sealed tubes, were found to be unchanged after two and one-half years.

[9] For convenience in presentation the 2,4,6-triisopropylphenyl radical is designated as *tipyl* and represented by *Tip*.

[10] The authors are indebted to Professor W. H. Rodebush, Dr. M. M. Sparks and Dr. R. M. Whitney for the measurement and interpretation of the infrared spectra mentioned in this paper.

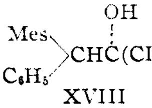
the carbonyl group. However, the enol was not stable and rearranged at once to the ketone. The acetate could be formed also by heating the ketone with acetic anhydride in pyridine. This is evidence of the ready interconvertibility of the ketone and the unstable enol.



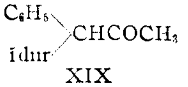
XVII

When mesitylphenylacetyl chloride was condensed with methylmagnesium or methylzinc iodide the product was a mixture of 1-mesityl-1-phenylpropanone (XVII) and a hydrocarbon corresponding to the dehydration product of the carbinol (XVIII) that would be formed by the action of excess reagent on the methyl ketone. The methyl ketone formed a 2,4-dinitrophenylhydrazone. Also, its infrared absorption spectrum[10] indicated the presence of a carbonyl group. In the Grignard machine[11] it gave approximately one-half mole of methane, indicating that addition was accompanied by enolization. This is especially interesting in view of the observation that the isomeric ketone, α-mesitylpropiophenone (corresponding to enol III), reacted with the Grignard reagent entirely by addition.

The condensation of methylzinc iodide with isodurylphenylacetyl chloride followed the course outlined for mesitylphenylacetyl chloride. The product was 1-isoduryl-1-phenylpropanone (XIX).



XVIII

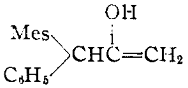


XIX

It was planned to prepare the methyl ketones from the corresponding benzohydrols through the Grignard reagents and acetyl chloride. The work was, however, not carried beyond the first step. Reduction of benzoylisodurene yielded isodurylphenylcarbinol but the chief products from benzoylmesitylene were two solids believed to be the meso and racemic forms of mesitylphenylmethyl ether.

On the basis of the evidence at hand it appears probable that methyl groups in the *alpha* position do not stabilize these vinyl alcohols. In particular, the enol form of the methyl ketone (XVII) appears to be unstable. This applies especially to the enol formed by way of the ketene, which would be expected to have the structure represented by XV. Since the acetate prepared from the corresponding enolate and that made by treating the ketone (XVII) with acetic anhydride and pyridine were identical, it appears that the enol formed by enolization of the ketone also has the structure XV.

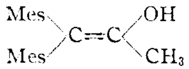
There is evidence that the isomeric enol (XX) may be formed also by enolization of the ketone. In one experiment in which the ketone was subjected to prolonged heating with sodium methoxide in the presence of air it was converted partially to mesitylphenylacetic acid. Although the mechanism of this change is obscure, it presumably involves the intermediate formation of the peroxide of enol XX. Enolization of a similar type was encountered by Whitmore and Lester[12] in a study of the steric effect of the dineopentylcarbinyl group. They found that in compounds of type XXI enolization by the Grignard reagent occurred only if R contained a hydrogen atom in the *alpha* position. It is clear that in the ketones which they examined enolization involved a hydrogen atom from R rather than that in the dineopentylcarbinyl radical.



XX

$[(CH_3)_3CCH_2]_2CHCOR$

XXI



XXII

Finally, the enol form of 1,1-dimesitylacetone (XXII) was prepared by the condensation of methylmagnesium iodide with dimesitylketene. As with the phenyl analog (XIII) the two mesityl radicals served to render the enol stable. This remarkable enol could be ketonized by treatment with methanolic hydrogen chloride. Thus, it seems certain that a 2,2-dimesitylvinyl alcohol of this type will be stable regardless of the nature of the third hydrocarbon radical.

The dimesitylketene employed in the preparation of the vinyl alcohol was made from dimesitylacetic acid, the acid chloride being an intermediate. The procedure was similar to that given for mesitylphenylketene.[13] An attempt to make dimesitylketene by the method of Smith and Hoehn[14] yielded dimesitylacetic acid.

Generalization

The information now available with reference to trisubstituted vinyl alcohols makes it possible to state in general terms the necessary and sufficient conditions for their stability. These are the presence of two radicals of the mesityl type. The position of these two and the size of the third radical are immaterial.

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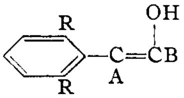
(11) Kohler and Richtmyer, This Journal, **52**, 3736 (1930).

(12) Whitmore and Lester, *ibid.*, **64**, 1247 (1942).

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

(14) "Organic Syntheses," **20**, 47 (1940).

It is possible also to set down a generalization concerning all types of vinyl alcohols, including enediols. Those which are stable have the following type of structure in which A or B is an aryl group. If A is a radical of the mesityl type



B may be any hydrocarbon radical or a hydrogen atom. If B is a radical of the mesityl type, A may be hydroxyl or any hydrocarbon radical, but not hydrogen.

Experimental

Phenyl 2,4,6-Trimethylbenzyl Ketone.—This compound was prepared by heating mesityl phenyl diketone with zinc dust in glacial acetic acid by the method of Weinstock and Fuson.[15] In one experiment the chief product was a high-melting solid, which crystallized from chloroform in glistening white needles; m. p. 249–250°.

Anal.[16] Calcd. for $C_{34}H_{38}O_2$: C, 85.31; H, 8.00; Found: C, 85.47; H, 8.21.

This compound was probably the bimolecular reduction product, **1,4-dimesityl-2,3-diphenylbutan-2,3-diol.** In keeping with its formulation as a glycol was the observation that reduction with hydriodic acid converted it to a derivative corresponding to the expected olefin, **1,4-dimesityl-2,3-diphenyl-2-butene.** One gram of the glycol was heated under reflux with 10 ml. of hydriodic acid (sp. gr. 1.50) and 50 ml. of glacial acetic acid. When the yellow crystals, which separated when the mixture was cooled, were collected on a filter it was noticed that they liberated iodine and gradually became colorless. The butene crystallized from methanol in hard plates; m. p. 180–181°; yield 0.6 g.

Anal. Calcd. for $C_{34}H_{36}$: C, 91.84; H, 8.16. Found: C, 91.94; H, 7.85.

α-Mesitylvinyl Phenyl Ketone.—A mixture of 16 g. of phenyl 2,4,6-trimethylbenzyl ketone, 6 g. of paraformaldehyde, 2.5 g. of anhydrous potassium carbonate and 150 ml. of ethanol was heated, with stirring, at 65° for five hours. At the end of this time 4 g. of paraformaldehyde and 2 g. of potassium carbonate were added. Twelve hours later one-half these quantities was added. The heating and stirring were continued for an additional twenty-four hours and the mixture was poured into water. The mixture was acidified and filtered. The α-mesitylvinyl phenyl ketone was recrystallized from methanol; m. p. 84–85°; yield, 13.5 g.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.50; ,H, 7.38.

Oxido α-Mesitylvinyl Phenyl Ketone.—To a solution of 1 g. of the unsaturated ketone in 25 ml. of methanol were added 1.5 ml. of 2 N sodium hydroxide solution and 2 ml. of 30% hydrogen peroxide. After twelve hours the oxido compound was collected and recrystallized from methanol; m. p. 71.5–72.5°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.28; H, 6.73.

2-Mesityl-1-phenyl-1-propen-1-ol (II).—A mixture of 0.5 g. of α-mesitylvinyl phenyl ketone, 40 ml. of ethanol and 0.015 g. of platinum oxide catalyst absorbed the theoretical amount of hydrogen in twenty minutes. Filtration of the mixture and evaporation of the solvent left the vinyl alcohol as an oil which did not crystallize. Attempts to prepare a benzoate by treating the vinyl alcohol with benzoyl chloride in the presence of pyridine were unsuccessful.

The crude vinyl alcohol was dissolved in an ether–petroleum ether mixture and a stream of oxygen was bubbled through the solution for twenty-four hours. The solvents were removed and the peroxide was recrystallized from high-boiling petroleum ether; m. p. 122–123°; yield, 1.3 g.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.20; H, 7.28.

At the end of several months the peroxide was found to have undergone extensive decomposition.

α-Mesitylpropiophenone.—A sample of crude 2-mesityl-1-phenyl-1-propen-1-ol was distilled under nitrogen at 174–175° (4–5 mm.). The distillate was the keto isomer, α-mesitylpropiophenone. After recrystallization from petroleum ether the ketone melted at 79.5–80°.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.51; H, 7.61.

A sample of the vinyl alcohol, sealed under nitrogen and kept at room temperature, changed to the keto form in the course of a week; m. p. 74–76°.

In one experiment 4 g. of α-mesitylvinyl phenyl ketone in 90 ml. of absolute ethanol was reduced in the presence of a platinum oxide catalyst. The mixture was filtered, and a stream of dry hydrogen chloride was passed for one hour into the filtrate at 0°. After the resulting solution had been heated under reflux for eight hours it was poured into water. There was obtained 3.5 g. of α-mesitylpropiophenone.

The **phenylhydrazone** was formed by heating a mixture of 2 g. of α-mesitylpropiophenone, 1 ml. of phenylhydrazine and 75 ml. of ethanol under reflux for twelve hours. It was purified by recrystallization from 90% ethanol; m. p. 79.5–80°.

Anal. Calcd. for $C_{24}H_{26}N_2$: C, 86.16; H, 8.11. Found: C, 86.10; H, 8.21.

The **2,4-dinitrophenylhydrazone** was prepared in a similar manner. It was recrystallized from ethyl acetate; m. p. 224–225°.

Anal. Calcd. for $C_{24}H_{24}N_{24}O_4$: C, 66.79; H, 5.37. Found: C, 66.91; H, 5.43.

The **oxime**, prepared in the usual manner, was recrystallized from 80% methanol; m. p. 154.5–155.5°.

Anal. Calcd. for $C_{18}H_{21}NO$: N, 5.24. Found: N, 5.10.

In the Grignard machine α-mesitylpropiophenone gave no gas and used one mole of the reagent.

Phenyl 2,4,6-Triisopropylbenzyl Ketone.—A mixture of 1 g. of phenyl tipyl diketone,[17] 25 ml. of hydriodic acid (sp. gr. 1.50) and 75 ml. of glacial acetic acid was heated under reflux for one hour and poured into water. The yield of the desoxybenzoin, m. p. 108–110°, was nearly quantitative. The compound crystallized from aqueous methanol in white prisms; m. p. 113.5–114.5° (cor.).

Anal. Calcd. for $C_{23}H_{30}O$: C, 85.66; H, 9.38. Found: C, 85.60; H, 9.46.

Phenyl 2,4,6-triisopropylbenzyl ketone was made in nearly quantitative yield from 2,4,6-triisopropylbenzoin.[17] A mixture of 2.5 g. of the benzoin, 150 ml. of glacial acetic acid, 50 ml. of hydriodic acid (sp. gr. 1.50) and a little red phosphorus was heated under reflux for eight hours. The desoxybenzoin made in this way was shown by the method of mixed melting points to be the same as that prepared from the diketone.

This ketone was also made, although in low yield, by the condensation of 2,4,6-triisopropylphenylacetyl chloride with diphenylcadmium.

An attempt to obtain phenyl 2,4,6-triisopropylbenzyl ketone by reducing phenyl 2,4,6-triisopropylphenyl diketone with zinc and acetic acid yielded a mixture. The only product which was isolated in pure form melted at 121–122° (cor.), and proved to be the acetyl derivative of 2,4,6-triisopropylbenzoin.[17]

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(15) Weinstock and Fuson, THIS JOURNAL, **58**, 1233 (1936).

(16) The microanalyses reported in this paper were carried out by Miss Margaret McCarthy, Miss Theta Spoor and Miss Dorothy Schneider.

(17) Fuson and Soper, THIS JOURNAL, **65**, 915 (1943).

An attempt was made to prepare the desoxybenzoin by condensing phenacyl chloride with triisopropylbenzene in the presence of aluminum chloride. The reaction product was a tar from which a little phenyl 2,4,6-triisopropylphenyl diketone was eventually isolated. It would appear that the desired desoxybenzoin had been formed and subsequently oxidized.

Phenyl 2,4,6-Triisopropylphenyl Diketone Hydrazone.—A mixture of 5.2 g. of hydrazine sulfate, 11 g. of sodium acetate and 25 ml. of water was boiled for five minutes and filtered. The filtrate was heated to 60° and added to a hot solution of 8 g. of the diketone in 75 ml. of ethanol. The mixture was heated under reflux for thirty minutes. The crude hydrazone weighed 8 g. and melted at 193–197°, with decomposition. It was recrystallized from methanol. The melting point, determined in a sealed tube, was 207.5–208.5° (cor.), with decomposition.

Anal. Calcd. for $C_{23}H_{30}N_2O$: C, 78.81; H, 8.63; mol. wt., 340. Found: C, 78.79; H, 8.83; mol. wt. (ebullioscopic in chloroform), 328.

Phenyl α-(Triisopropylphenyl)-vinyl Ketone.—A mixture of 1 g. of phenyl 2,4,6-triisopropylbenzyl ketone, 1.5 g. of paraformaldehyde, 0.5 g. of anhydrous potassium carbonate and 70 ml. of ethanol was stirred and heated (65°) for twenty-three hours. An additional 1 g. of paraformaldehyde and 0.5 g. of potassium carbonate were added, and the heating and stirring continued for thirty hours longer. By pouring the mixture into 100 ml. of water containing 5 ml. of concentrated hydrochloric acid there was obtained a 96% yield of the vinyl ketone. It crystallized from methanol in white needles; m. p. 139–139.5° (cor.). Dilute acetic acid and ethanol could be used as recrystallization solvents.

Anal. Calcd. for $C_{24}H_{30}O$: C, 86.17; H, 9.04. Found: C, 86.45; H, 9.29.

A solution of 0.5 g. of the vinyl ketone in 30 ml. of ethyl acetate was subjected for three and one-half hours to hydrogen at atmospheric pressure in the presence of a platinum oxide catalyst. One mole of hydrogen was absorbed. After the mixture had been filtered the solvent was removed in a stream of air. The peroxide of the enol, 1-phenyl-2-tipyl-1-propen-1-ol (IV), left as a residue was recrystallized from high-boiling petroleum ether. It formed transparent prisms which melted at 127–128° (cor.), with decomposition.

Anal. Calcd. for $C_{24}H_{32}O_3$: C, 78.22; H, 8.75. Found: C, 77.75; H, 8.97.

The peroxide decomposed in the course of several months.

α-(2,4,6-Triisopropylphenyl)-propiophenone.—In a subsequent experiment 5 g. of phenyl α-(2,4,6-triisopropylphenyl)-vinyl ketone was subjected to hydrogenation as before. The solvent was removed by an air blast and the product allowed to stand. In addition to a small amount of solid, presumably the peroxide, there was a large amount of oil. It was separated into two fractions by distillation. The first of these fractions appeared to be the enol; on continued exposure to air it changed to the enol peroxide.

The second fraction consisted of the keto form, α-(2,4,6-triisopropylphenyl)-propiophenone. It boiled at 173–174° (2 mm.) and melted at 117–118°. It separated from methanol in large, transparent plates.

Anal. Calcd. for $C_{24}H_{32}O$: C, 85.66; H, 9.59. Found: C, 85.80; H, 9.89.

The **2,4-dinitrophenylhydrazone** was purified by one recrystallization from a mixture of chloroform and ethyl acetate followed by several recrystallizations from acetic acid. It formed yellow needles melting at 238–240°.

Anal. Calcd. for $C_{30}H_{36}N_4O_4$: C, 69.74; H, 7.03. Found: C, 67.82; H, 6.92.

Attempts to Prepare 2-Mesityl-1,3-diphenyl-1-propen-1-ol.—To a cold solution of Grignard reagent prepared from 1.6 g. of magnesium, 10 g. of bromobenzene and 50 ml. of dry ether was added a solution of 5 g. of α-mesitylvinyl phenyl ketone in 90 ml. of dry benzene. The mixture was heated overnight and decomposed with a solution of ammonium chloride. The viscous yellow oil which was isolated failed to crystallize. Crystals of benzoic acid were obtained from it by sublimation; it appeared that the enol had been cleaved in the usual way by atmospheric oxidation.

α-Mesityldesoxybenzoin.—Mesitylphenylketene (9.5 g.) was added dropwise, with stirring, to a solution of phenylmagnesium bromide made from 1.52 g. of magnesium, 9.7 g. of bromobenzene and 40 ml. of dry ether. The addition was complete in twenty minutes, and the mixture was then heated for two hours under reflux. One-half of the enolate solution was then treated according to the procedure used in making 1,2-dimesityl-2-phenylvinyl alcohol.[18] The product was freed from biphenyl by steam distillation and recrystallized from aqueous ethanol; m. p. 113–114° (cor.).

Anal. Calcd. for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found: C, 87.58; H, 7.09.

This same compound was produced by the condensation of desyl chloride with mesitylene by a slight modification of the directions of Maxwell and Adams.[19] A solution of 17 g. of the chloride in 45 ml. of mesitylene was added, dropwise and with stirring, to a mixture of 15 g. of anhydrous aluminum chloride and 15 ml. of mesitylene. The mixture was heated at 45–60° during the hour required to complete the addition and for four hours afterward, then poured into an ice–hydrochloric acid mixture. The aqueous layer was washed with a mixture of benzene and ether, the solution thus obtained being combined with the organic layer. The resulting solution was washed with water, 5% sodium carbonate solution and again with water. After removal of the solvents and unchanged mesitylene by steam distillation, the α-mesityldesoxybenzoin was crystallized from ethanol; it melted at 109–112° and weighed 21 g. (90%). It was purified by recrystallization from 125 ml. of ethanol. It formed colorless cubes; m. p. 113–114° (cor.); yield 18 g.

Treatment of α-mesityldesoxybenzoin with phenylmagnesium bromide converted it to an oil that could not be induced to crystallize. A similar observation was recorded by Maxwell and Adams.[19]

The Acetate of 2-Mesityl-1,2-diphenylvinyl Alcohol.—To the remaining half of the enolate solution prepared from mesitylphenylketene and phenylmagnesium bromide was added, dropwise, a solution of 4 ml. of acetyl chloride in 10 ml. of dry ether. After the resulting mixture had been heated for ten minutes under reflux, it was decomposed in the usual way. The acetate, after recrystallization from ethanol, melted at 134.5–135° and weighed 4 g.

Anal. Calcd. for $C_{25}H_{24}O_2$: C, 84.22; H, 6.79. Found: C, 84.52; H, 6.91.

The acetate was prepared from α-mesityldesoxybenzoin in two different ways.

(A) A solution of 0.35 g. of the ketone, 4.5 ml. of dry pyridine and 1.7 ml. of acetic anhydride was heated under reflux for forty minutes.

(B) A solution of 4.7 g. of the ketone, 8.5 g. of freshly fused potassium acetate and 90 ml. of acetic anhydride was heated under reflux for three hours.

The acetate obtained by either of these two procedures crystallized from ethanol in square prisms; m. p. 134–135°. It did not depress the melting point of a sample of the acetate made from the ketene.

Heating with ethanolic hydrochloric acid for three hours reconverted the acetate to α-mesityldesoxybenzoin; m. p. 113–114°.

2-Mesityl-1,2-diphenylvinyl Alcohol Peroxide.—Four and one-half grams of mesitylphenylketene was added to a solution of phenylmagnesium bromide containing about double the amount of reagent required to produce the enolate. The mixture was heated under reflux for one hour and poured into ice and hydrochloric acid. The layers were separated and the water layer was extracted

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(18) Fuson, Armstrong, Kneisley and Shenk, THIS JOURNAL, **66**, 1464 (1944).

(19) Maxwell and Adams, *ibid.*, **52**, 2959 (1930).

with 150 ml. of cold low-boiling petroleum ether. The combined organic portions were then washed three times with ice water, and a rapid stream of oxygen was passed through the solution for twenty hours. The peroxide, in the form of a light yellow oil, remained after the solvent had been removed by a slow stream of air. It could not be induced to crystallize.

When 1 g. of the peroxide was heated it decomposed in the manner characteristic of peroxides. The oil resulting from the decomposition was dissolved in 50 ml. of ether and the solution extracted with 10% sodium carbonate solution. Acidification of the carbonate solution precipitated a small amount of solid which, after recrystallization from 60% ethanol, melted at 169–171° and did not depress the melting point of mesitylphenylacetic acid.

The ethereal solution was shaken with 6% potassium hydroxide solution and the extract acidified. Phenol was produced. It was identified by conversion to tribromophenol.

The neutral portion of the product could not be induced to crystallize.

Reduction of α-Mesityldesoxybenzoin with Isopropylmagnesium Bromide.—A solution of 3 g. of the ketone in 10 ml. of dry ether and 15 ml. of dry benzene was added dropwise over a 30-minute period to a solution of Grignard reagent prepared from 0.72 g. of magnesium, 4.2 g. of isopropyl bromide and 30 ml. of absolute ether. The reaction mixture was heated under reflux for two hours, and a solution of 4 ml. of acetyl chloride in 10 ml. of dry ether was added slowly. The acetate crystallized from low-boiling petroleum ether in colorless plates. The **2-mesityl-1,2-diphenylethyl acetate** was purified by recrystallization from 80% ethanol; m. p. 126–127°. A mixture with 2-mesityl-1,2-diphenylvinyl acetate melted at 100–105°.

Anal. Calcd. for $C_{25}H_{26}O_2$: C, 83.76; H, 7.31. Found: C, 83.87; H, 7.84.

When a mixture of 0.35 g. of the acetate (m. p. 123–125°), 7.5 ml. of ethanol and 1.5 ml. of concentrated hydrochloric acid was heated under reflux for three and one-half hours, the carbinol, 2-mesityl-1,2-diphenylethanol, was liberated and dehydrated. The product, 1-mesityl-1,2-diphenylethylene, separated from ethanol in white crystals; m. p. 141–142°.

Anal. Calcd. for $C_{23}H_{22}$: C, 92.57; H, 7.43. Found: C, 92.26; H, 7.49.

Mesitil Monohydrazone.—Two grams of 85% hydrazine hydrate solution was dropped into a hot solution of 6 g. of mesitil in 100 ml. of methanol. After being heated for twelve hours under reflux the solution was cooled to 0°. The hydrazone separated in white needles (4 g.) which were purified by recrystallization from alcohol; m. p. 208–209°.

Anal. Calcd. for $C_{20}H_{24}N_2O$: C, 77.87; H, 7.83. Found: C, 78.08; H, 7.92.

When treated with acetic anhydride the hydrazone formed an **acetyl derivative.** It crystallized from methanol in pale yellow plates; m. p. 161.5–162.5°.

Anal. Calcd. for $C_{22}H_{26}N_2O_2$: C, 75.38; H, 7.48. Found: C, 75.43; H, 7.29.

Dimesitylacetic Acid

(a) **From Mesitil Monohydrazone.**—A finely ground mixture of 2.5 g. of mesityl monohydrazone, 2 g. of yellow mercuric oxide and 1 g. of anhydrous calcium sulfate was stirred for twenty-four hours in 100 ml. of dry benzene. The resulting cherry-red mixture was filtered in such a way that the filtrate dropped into a 15-ml. modified Claisen distilling flask kept in a metal bath at 110°. After the benzene was distilled the flask was cooled rapidly, and 2 ml. of water and 15 ml. of ether were added to the residue. After the mixture had stood for an hour it was extracted three times with ether. The ether solution was extracted twice with potassium carbonate solution. Acidification of the latter with dilute hydrochloric acid yielded 0.1 g. of dimesitylacetic acid. It crystallized from dilute methanol in fine needles; m. p. 197–198°.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.17; neut. equiv., 296. Found: C, 81.09; H, 8.02; neut. equiv., 297.

(b) **From Mesitylglycolic Acid.**—This procedure is a modification of that of Gyr.[20] One hundred four grams of stannic chloride was added slowly to a warm (60–70°) solution of 40 g. of mesitylglycolic acid in 200 ml. of mesitylene. The resulting solution was maintained for four hours at 60–70° and decomposed with water. The dimesitylacetic acid, isolated by usual procedures, was crystallized once from methanol; m. p. 193–194°; yield 86%. The pure acid did not depress the melting point of the sample from the ketene.

Dimesitylketene.—One gram of pyridine was added to a cool solution of 18 g. of dimesitylacetic acid, 7.3 g. of thionyl chloride and 100 ml. of dry benzene. The solution was heated under reflux for eight hours and decanted from the precipitated pyridine hydrochloride. Removal of the solvent on the water pump left 16.5 g. of the crude product. After several recrystallizations from high-boiling petroleum ether and treatment with Norite, the yellow, crystalline solid melted at 126–127°.

Anal. Calcd. for $C_{40}H_{44}O_2$: C, 86.28; H, 7.97. Found: C, 86.70; H, 7.25.

Ethyl Dimesitylacetate.—This ester was prepared in high yield by heating dimesitylacetyl chloride or dimesitylketene with absolute ethanol for seven or eight hours. It was recrystallized from ethanol; m. p. 113–114°.

Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.63; H, 8.74.

Methyl Dimesitylacetate.—A solution of 11 g. of dimesitylketene in 50 ml. of methanol was heated under reflux for one-half hour; and the ester, which crystallized when the mixture was cooled, was recrystallized from methanol; m. p. 130.5–131.5°.

Anal. Calcd. for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.46; H, 8.93.

It is interesting from the standpoint of hindrance that an attempt to esterify dimesitylacetic acid directly by use of methanolic hydrogen chloride was unsuccessful.

2,2-Dimesityl-1-phenylvinyl Alcohol.—A solution of 5.6 g. of dimesitylketene in 100 ml. of absolute ether was added over a period of forty-five minutes to a Grignard reagent prepared from 4.8 g. of bromobenzene, 0.74 g. of magnesium and 75 ml. of dry ethyl ether. After the reaction had been heated under reflux for ten hours the ethyl ether was replaced by n-butyl ether and the heating under reflux continued for two hours. The vinyl alcohol, isolated in the usual way, was treated with Norite and recrystallized from ethanol; m. p. 155–156°; yield 3 g.

Anal. Calcd. for $C_{26}H_{28}O$: C, 87.60; H, 7.92. Found: C, 87.58; H, 8.17.

The **acetate** of this vinyl alcohol, prepared by the use of acetic anhydride and pyridine, melted at 191–192° after recrystallization from n-butyl ether.

Anal. Calcd. for $C_{28}H_{30}O_2$: C, 84.38; H, 7.59. Found: C, 84.00; H, 7.57.

The **benzoate**, made by treatment of the vinyl alcohol with benzoyl chloride, was also recrystallized from n-butyl ether; m. p. 179.5–180°.

Anal. Calcd. for $C_{33}H_{32}O_2$: C, 86.05; H, 7.00. Found: C, 86.11; H, 7.09.

α,α-Dimesitylacetophenone (A) from 2,2-Dimesityl-1-phenylvinyl Alcohol.—Dry hydrogen chloride was bubbled for thirty hours through a solution of 3 g. of the vinyl alcohol in 100 ml. of absolute methanol. The product, α,α-dimesitylacetophenone, was recrystallized from ethanol; m. p. 160.5–161.5°; yield 2.8 g. A mixture of the ketone and the parent enol melted at 132–142°.

(B) **From Dimesitylacetyl Chloride.**—A solution of 22.7 g. of dimesitylacetyl chloride in 75 ml. of dry ethyl ether was added over a period of four hours to a Grignard reagent prepared from 7.85 g. of bromobenzene, 1.22 g. of magnesium and 75 ml. of dry ethyl ether. The reaction

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[20] Gyr, *Ber.*, **41**, 4321 (1908).

mixture was heated under reflux during the time of addition and then overnight. The ether was replaced by benzene and the heating under reflux continued for two hours. By suitable manipulation of the tarry products small amounts of two crystalline products were isolated. One of them was shown by the method of mixed melting points to be **ethyl dimesitylacetate**. The other was **α,α-dimesitylacetophenone**. It was recrystallized from ethanol; m. p. 160.5–161.5°. A mixed melting point determination showed it to be the same as the ketone prepared by ketonization of the vinyl alcohol.

Anal. Calcd. for $C_{26}H_{28}O$: C, 87.60; H, 7.92. Found: C, 87.74; H, 8.02.

An attempt was made to prepare α,α-dimesitylacetophenone by the condensation of lithium phenyl with dimesitylacetyl chloride. The product, obtained in small amount, melted at 150–153° and appeared to be impure 2,2-dimesityl-1-phenylvinyl alcohol. Its identity was confirmed by conversion to the benzoate, which melted at 179–180° and did not depress the melting point of an authentic sample.

Enolization of α,α-dimesitylacetophenone was effected by the use of sodium ethoxide. A solution of 1.5 g. of the ketone in 40 ml. of 10% sodium ethoxide solution was heated overnight under reflux. The product was recrystallized from ethanol; m. p. 154–155.5°; yield 1.1 g. A mixed melting point determination showed it to be 2,2-dimesityl-1-phenylvinyl alcohol.

1-Mesityl-1-phenylpropanone (from **Mesitylphenylketene**).—A solution of 1 g. of the ketene in 30 ml. of dry ether was added rapidly to a solution of methylmagnesium iodide, prepared from 3.5 g. of methyl iodide and 0.6 g. of magnesium. Immediate reaction occurred and the solution developed a brown color. Stirring was continued for two hours during which time nitrogen was passed over the reaction mixture. It was poured into a mixture of 300 g. of ice and 10 ml. of acetic acid. The ether solution was washed successively with water, dilute potassium carbonate solution and water and dried over calcium chloride. The residue from evaporation of the ether was dissolved in low-boiling petroleum ether. The solution was treated with Norite, filtered and allowed to stand. The 1-mesityl-1-phenylpropanone separated in white needles; m. p. 82–83°.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.70; H, 7.71.

Acetyl Derivative of 1-Mesityl-1-phenyl-1-propen-2-ol.—When the iodomagnesium enolate, prepared from 4 g. of mesitylphenylketene and an excess of methylmagnesium iodide, was treated with acetyl chloride an acetate was obtained.

The same acetate formed when 1-mesityl-1-phenylpropanone was treated with acetic anhydride and pyridine as described for the preparation of 2-mesityl-1,2-diphenylvinyl acetate. It was recrystallized from aqueous ethanol; m. p. 69–69.5°.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.58; H, 7.54. Found: C, 81.68; H, 7.50.

1-Mesityl-1-phenylpropanone (from **Mesitylphenylacetyl Chloride**).—A mixture of 10 g. of the acid chloride, 25 ml. of dry benzene and 10 ml. of anhydrous ether was added, with stirring and at 0°, to a solution of methyl Grignard reagent made from 1.25 g. of magnesium, 7.25 g. of methyl iodide and 30 ml. of anhydrous ether. The addition was completed in thirty minutes, and the solution was stirred overnight at 20° and for an additional hour at 50°. The mixture was decomposed and the benzene–ether solution was extracted with aqueous alkali to remove the mesitylphenylacetic acid (1.1 g.). Distillation of the neutral products yielded a light brown oil; b. p. 158–160° (5 mm.). It crystallized from high-boiling petroleum ether (m. p. 79.5–80°) and proved to be identical with the 1-mesityl-1-phenylpropanone prepared from mesitylphenyl ketene.

From the mother liquors was isolated a second product. It crystallized from 90% ethanol in white plates; m. p. 65.5°.

Anal. Calcd. for $C_{19}H_{22}$: C, 91.14; H, 8.86. Found: C, 91.23; H, 9.07.

The composition of this hydrocarbon is that of 1-mesityl-2-methyl-1-phenylpropene, a dehydration product of the 1-mesityl-2-methyl-1-phenyl-2-propanol which might have been expected.

The yield of 1-mesityl-1-phenylpropanone was higher (50 to 65%) when the acid chloride was condensed with methylzinc iodide by the Blaise method.[21]

The **2,4-dinitrophenylhydrazone** of 1-mesityl-1-phenylpropanone formed when the ketone (1 g.) was heated for nine hours with 2,4-dinitrophenylhydrazine (1.2 g.) in 75 ml. of ethanol. The product was repeatedly dissolved in 95% ethanol and precipitated by the addition of water. It formed an orange powder which sintered at 174° and melted at 184–186°.

Anal. Calcd. for $C_{24}H_{24}N_4O_4$: C, 66.64; H, 5.60. Found: C, 67.33; H, 5.40.

In the Grignard machine[11] the ketone gave 0.54 mole of gas and consumed an additional 0.62 mole of reagent.

In one experiment it was possible to obtain a benzoyl derivative from the 1-mesityl-1-phenylpropanone. A mixture of 1 g. of the ketone, 2 ml. of benzoyl chloride, 6 ml. of dry pyridine and 3 ml. of chloroform was warmed on a steam-bath for a few minutes and allowed to stand at room temperature for twenty-four hours. Ether was added and the mixture was stirred with water. The ether solution was dried over calcium chloride and the solvent evaporated. The benzoate was recrystallized from methanol; 115–116°.

Anal. Calcd. for $C_{25}H_{24}O_2$: C, 84.23; H, 6.79. Found: C, 84.01; H, 6.97.

Isodurylphenylacetyl Chloride.—A mixture of 9 g. of isodurylphenylacetic acid and 25 ml. of thionyl chloride was allowed to stand at room temperature for eighteen hours. Purification in the conventional manner gave a 65% yield of the acid chloride, melting at 108.5–109°. The crystals were purified by recrystallization from high-boiling petroleum ether and decolorized by the use of Norite. The compound formed small, white plates.

Anal. Calcd. for $C_{18}H_{19}OCl$: C, 75.37; H, 7.68. Found: C, 75.57; H, 7.69.

Treatment with ethanol converted the acid chloride to ethyl isodurylphenylacetate.[22] Hydrolysis of the ester regenerated the acid, m. p. 196–198°.

1-Isoduryl-1-phenylpropanone.—The condensation of isodurylphenylacetyl chloride with methylzinc iodide, carried out by the Blaise procedure, afforded a 65% yield of 1-isoduryl-1-phenylpropanone. The ketone boiled at 182–184° (5 mm.) and melted at 74–75°. It crystallized from aqueous methanol in transparent, colorless plates.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.75; H, 8.27.

Isodurylphenylcarbinol.—This alcohol was prepared in 70% yield by the method of Wiselogle and Sonneborn for benzohydrol.[23] The procedure was modified as follows. The gummy solid, which separated when the reaction mixture was poured into ice-hydrochloric acid, was separated mechanically, and the aqueous solution was extracted with three 100-ml. portions of benzene. The solid was added to the benzene solution and purified in the usual way. The carbinol could be distilled at 180–185° (4 mm.). It crystallized from high-boiling petroleum ether in white cubes; m. p. 78–78.5°.

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 85.11; H, 8.52.

Benzylisodurene.—Isodurylphenylmethyl chloride was made by shaking the carbinol for two days with concentrated hydrochloric acid. A 67% yield was obtained of chloride boiling at 174–177° (5 mm.). The redistilled ma-

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(21) Blaise, *Bull. soc. chim.*, [4] **9**, 1 (1911).

(22) Fuson, Armstrong, Wallace and Kneisley, THIS JOURNAL, **66**, 1274 (1944).

(23) Wiselogle and Sonneborn, "Organic Syntheses," Coll. Vol. I, ed. 2, 1941, p. 90.

terial boiled at 165–166° (4 mm.); $n^{20}D$ 1.5899. Analysis showed it to be impure. In an effort to convert it to the nitrile the procedure of Newman[24] for 1-naphthonitrile was applied. Among the products was a solid which had the composition of benzylisodurene. It distilled at 154–160° (5 mm.) and crystallized from ethanol from which it separated in glistening white plates; m. p. 57.5–58.5°.

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 91.08; H, 9.14.

Mesitylphenylmethyl Ether.—Reduction of 129 g. of benzoylmesitylene according to the procedure of Wiselogle and Sonneborn[23] for benzohydrol gave 80 g. of a liquid which set to a glassy solid in the receiver. By means of fractional crystallization of this material from acetone two compounds were obtained. They are thought to be the meso and racemic modifications of mesitylphenylmethyl ether. The less soluble isomer formed prisms melting at 168.5–169°.

Anal. Calcd. for $C_{32}H_{34}O$: C, 88.43; H, 7.89. Found: C, 88.59; H, 7.83.

The more soluble isomer was recrystallized repeatedly from methanol; m. p. 135–136.5° (cor.). It formed fine, white needles.

Anal. Calcd. for $C_{32}H_{34}O$; C, 88.43; H, 7.89. Found: C, 88.59; H, 7.69.

This substance appears to be the same as that reported by Louise,[25] as melting at 137°.

1,1-Dimesityl-1-propen-2-ol.—A solution of 8.4 g. of dimesitylketene in 75 ml. of dry benzene was added over a period of one hour to a Grignard reagent prepared from 3.0 ml. of methyl idodide, 1.2 g. of magnesium and 75 ml. of dry ethyl ether. The mixture was stirred under reflux during the addition and at 50° for thirty hours thereafter. The crude enol, isolated in the usual way, melted at 94–97° and weighed 7 g. It was recrystallized from ethanol; m. p. 97–98°.

Anal. Calcd. for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 86.16; H, 9.20.

The infrared absorption spectrum showed the presence of a hydroxyl group.

The **acetate**, prepared by the use of acetic anhydride and pyridine, was recrystallized from ethanol; m. p. 114–115°.

Anal. Calcd. for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 82.31; H, 8.61.

Dry hydrogen chloride was passed for thirty hours through a solution of 5 g. of 1,1-dimesityl-1-propen-2-ol in 75 ml. of dry methanol. The product, **α,α-dimesitylacetone**, was recrystallized from ethanol; m. p. 145.5–146.5°; yield 2.4 g.

Anal. Calcd. for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 85.68; H, 9.23.

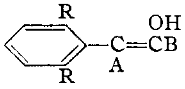
Efforts to prepare this ketone by treating dimesitylacetyl chloride with methylmagnesium iodide or lithium methyl were unsuccessful.

Summary

Eight new vinyl alcohols have been studied, two of which proved to be stable. From a consideration of the behavior of these and other enols examined previously the following generalization emerges.

The necessary and sufficient condition for stability in a trisubstituted vinyl alcohol is the presence of two radicals of the mesityl type. The position of these two and the size of the third radical are immaterial.

Stable vinyl alcohols of all types and the related enediols have the following structure in which A or B is an aryl radical.



URBANA, ILLINOIS RECEIVED NOVEMBER 9, 1944

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[24] Newman, "Organic Syntheses," **21**, 84 (1941).

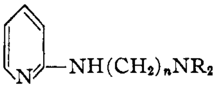
[25] Louise, *Ann. chim. phys.*, [6] **6**, 213 (1885).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Heterocyclic Basic Compounds. I. 2-Aminoalkylamino-pyridines[1]

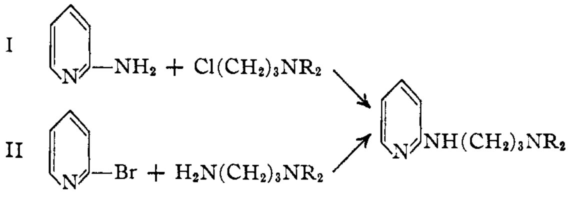
BY FRANK C. WHITMORE, HARRY S. MOSHER,[2,3] DALE P. J. GOLDSMITH,[2,3,4] AND ANTON W. RYTINA

In this paper compounds of the following general type are reported



in which the side chain is varied to include radicals of aminoalkylamines, dialkylaminoalkylamines, heterocyclic aminoalkylamines, and side chains which are interrupted with nitrogen and oxygen.

Two methods were available for the preparation of these compounds, either the action of an amino-alkyl halide on 2-aminopyridine as in I, below, or the action of an aminoalkylamine on a halopyridine as in II.



It is a well established fact that sodamide should be used in the first type reaction if substitution on the ring nitrogen via the imino form of α-amino-pyridine is to be prevented.[5] The synthesis of 2-(γ-morpholinopropylamino)-pyridine by both methods has been accomplished and the structure of this product is thus proved. The

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[1] Presented before the Organic Division of The American Chemical Society at Detroit, April 12, 1943.

[2] The material herein presented is taken in part from theses presented by Dale P. J. Goldsmith and Harry S. Mosher to The Pennsylvania State College in partial fulfillment of the requirements for the Ph.D. degree.

[3] Parke, Davis and Company Research Fellow, 1942.

[4] Present Address: Research and Development Department, Merck and Company, Rahway, New Jersey.

[5] Tschitschibabin, Konovalova and Konovalova, *Ber.*, **54**, 814 (1921).