TABLE II

UNSATURATED AND SATURATED ACIDS IN EXTRACTED "MOLINILLO" SEED OIL

Acids	In unsatd. acids, %	In satd. acids, %	In original oil, %	Glycerides in oil, %
Linoleic	15.56		11.91	12.39
Oleic	84.44		64.64	67.55
Myristic		8.90	1.29	1.36
Palmitic		82.75	11.98	12.57
Stearic		8.35	1.21	1.26

Palmitic Acid (m. p. 62°).—From fractions 1, 2, 3, 4, 5 an acid melting between 56 and 62° was obtained. Anilide derivatives prepared from these acids had a m. p. 88.5°. Palmitic acid anilide melts at 89.5°.

Stearic Acid (m. p. 69.2°).—No pure stearic acid could be isolated from fractions 3, 4 and 5. After several recrystallizations these fractions yielded products melting at 64, 65 and 67°, respectively, which were mixtures of stearic and palmitic acids. The residue, however, yielded pure stearic acid m. p. 69.2°. An anilide prepared from this acid melted at 93°. Stearic acid anilide melts at 93°.

Summary

The characteristics and composition of "molinillo" (*Leonotis nepetaefolia* L.) seed oil have been determined.

SAN JUAN, PUERTO RICO RECEIVED JUNE 29, 1945

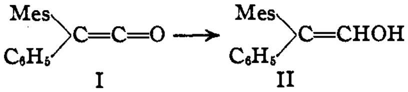
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Vinyl Alcohols. XVI. Reduction of Hindered Diaryl Ketenes by the Grignard Reagent

BY REYNOLD C. FUSON, ROBERT E. FOSTER, W. J. SHENK, JR., AND E. W. MAYNERT

It has been found that excellent yields of 2,2-diarylvinyl alcohols can be obtained by reduction of the corresponding diaryl ketenes with the Grignard reagent. The reaction was discovered in connection with the preparation of various trisubstituted vinyl alcohols by condensation of ketenes with Grignard reagents.[1,2] The methyl, phenyl and mesityl reagents were observed to react normally and to afford satisfactory yields of the expected trisubstituted vinyl alcohols.

When mesitylphenylketene (I) was treated with cyclohexylmagnesium chloride, however, the reaction took a different course. The ketene was reduced to 2-mesityl-2-phenylvinyl alcohol (II) in a yield of 80% of the theoretical. The reaction seems to be general.



$$\text{Mes}(C_6H_5)C{=}C{=}O \longrightarrow \text{Mes}(C_6H_5)C{=}CHOH$$

I II

t-Butylmagnesium chloride also afforded excellent yields of the vinyl alcohols. For example, this reagent reduced dimesitylketene to 2,2-dimesitylvinyl alcohol; the yield was 86%. In addition, two new ketenes were reduced to the corresponding vinyl alcohols: durylphenyl- and 3-bromomesitylphenylketene yielded, respectively, 2-duryl-2-phenylvinyl alcohol and 2-(3-bromomesityl)-2-phenylvinyl alcohol. The 2-(3-bromomesityl)-2-phenylvinyl alcohol, although not obtained in pure form, yielded an acetate which gave a satisfactory analysis.

Before the reduction method was discovered an attempt had been made to prepare 2-duryl-2-phenylvinyl alcohol by the glycol method. 1-Duryl-2-phenylethylene glycol was made by hydrogenation of duryl phenyl diketone and subjected to the usual treatment with a mixture of glacial acetic acid and concentrated hydrochloric acid. In the single experiment which was carried out, no vinyl alcohol could be isolated from the resulting mixture.

The procedure used to make the alcohol, starting with acetodurene, is described in the experimental part and will serve to illustrate the relative ease with which such compounds can be produced. In particular, the procedure described for the reduction of durylphenylketene is illustrative of the method now being reported.

In view of the improved methods which have been developed for the production of hindered ketoketenes[2] the reduction method is by far the most direct procedure for the synthesis of 2,2-diarylvinyl alcohols. It not only gives high yields but produces the vinyl alcohols under conditions most favorable for their isolation.

The reduction of ketenes by Grignard reagents has not been reported previously. In fact, there seems to be no record of the reduction of a ketene by any method. From the results presently reported it is not clear what if any relationship exists between the reduction and the steric hindrance provided by the mesityl, 3-bromomesityl or duryl radical.

Experimental

Durylglycolic Acid.—Acetodurene was prepared in 88% yield by the method of Smith and Guss[3] and oxidized with selenium dioxide in dioxane. The solvent was removed by distillation *in vacuo*. The crude durylglyoxal obtained from 78 g. of acetodurene was added to 500 ml. of 10% potassium hydroxide solution and the mixture was heated on a steam-bath for ten hours. It was cooled and filtered to remove a dark brown, gummy solid (6 g.), and the filtrate was extracted with ether and then treated with Norite. The durylglycolic acid was precipitated from the solution by the addition of dilute hydrochloric acid and

---

[1] Fuson, Byers, Rowland, Southwick and Sperati, THIS JOURNAL, **66**, 1873 (1944).

[2] Fuson, Armstrong, Chadwick, Kneisley, Rowland, Shenk and Soper, *ibid.*, **67**, 386 (1945).

[3] Smith and Guss, *ibid.*, **59**, 804 (1937).

recrystallized from water; m. p. 162.5–163°. This constant is in agreement with that given by Riebsomer.[4]

Durylphenylacetic Acid. A. From Durylglycolic Acid.—The procedure was a modification of that of Gyr[5] similar to that described for the preparation of dimesitylacetic acid.[2] To a boiling solution of 22.5 g. of durylglycolic acid in 200 ml. of benzene was added dropwise 65 g. of fuming stannic chloride. The mixture was heated for twelve hours and poured into 200 ml. of water. Two hundred milliliters of ether was added and the durylphenylacetic acid (4.3 g.) which precipitated was removed by filtration; m. p. 223.5–227°. The non-aqueous layer was extracted with 5% potassium hydroxide solution. Acidification of the alkaline extract yielded 21.5 g. of product. The two batches of crystals were combined and recrystallized three times from acetic acid. The durylphenylacetic acid formed fine needles melting at 231–233° (aluminum block); yield 21.5 g. (74%).

B. From Duryl Phenyl Diketone.—A mixture of 18 g. of hydrazine sulfate, 36 g. of hydrated sodium acetate and 90 ml. of water was boiled for about ten minutes and cooled to about 60°. Ninety milliliters of ethanol was added and the mixture filtered to remove the precipitate. The filtrate was mixed with a solution of 21.2 g. of duryl phenyl diketone[6] in 100 ml. of warm ethanol. The mixture was made homogeneous by the addition of more alcohol, heated under reflux for forty-five hours and cooled in a refrigerator. The **monohydrazone** was recrystallized from ethanol. It melted with decomposition at 184–187°; yield, 10 g. The decomposition point *in vacuo* of the analytical sample was 203–204°.

Anal. Calcd. for $C_{18}H_{20}N_2O$: C, 77.11; H, 7.19; N, 9.99. Found: C, 77.32; H, 7.19; N, 10.63.

An alcohol-insoluble by-product, after recrystallization from pyridine, decomposed *in vacuo* at 303–305° (uncor.). It weighed 3 g. and had the composition of the **dihydrazone.**

Anal. Calcd. for $C_{18}H_{22}N_4$: C, 83.43; H, 7.53; N, 19.03. Found: C, 83.60; H, 7.92; N, 19.35.

The monohydrazone of duryl phenyl diketone was converted to durylphenylacetic acid by oxidation with mercuric oxide by a procedure similar to that used to convert mesitil monohydrazone to dimesitylacetic acid.[2] A mixture of 2.8 g. of the hydrazone, 3.2 g. of mercuric oxide and 1.4 g. of calcium sulfate in benzene was stirred for five days, a few drops of potassium ethoxide being added every second day. After filtration, the benzene solution was introduced dropwise into a Claisen flask maintained at 115° by an oil-bath. When all the solvent had been removed in this manner, the dark brown, viscous residue was heated at 125° under an atmosphere of nitrogen for two hours. Yellow crystals, presumably the ketene, collected in the cool neck of the flask. The flask was cooled, wet ether was poured on the residue and the mixture was extracted with 10% sodium hydroxide solution. The basic solution was acidified and the solid acid reprecipitated from potassium carbonate solution. It separated from dilute acetic acid; in white crystals; m. p. 231–233° (aluminum block) yield 2%. A mixture with the sample of **durylphenyl aceticacid** prepared from the glycolic acid showed no lowering of the melting point.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51; neut. equiv., 268. Found: C, 80.43; H, 7.75; neut. equiv., 265.

Durylphenylketene.—A mixture of 15 g. of durylphenylacetic acid, 7.4 g. of thionyl chloride, 1 ml. of pyridine and 200 ml. of benzene was heated under reflux for twelve hours. The pyridine hydrochloride was removed by filtration and the solvent was evaporated *in vacuo*. The ketene was a yellow oil boiling at 134–137° (1 mm.) which solidified slowly. A redistilled sample was analyzed.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 85.62; H, 7.29.

The melting point of the analytical sample was not sharp. After being recrystallized several times from dry high-boiling petroleum ether, the ketene melted at 83–84°. However, after an additional recrystallization it was found to contain durylphenylacetic acid.

2-Duryl-2-phenylvinyl Alcohol.—A Grignard reagent, prepared from 9.3 g. of *t*-butyl chloride, 2.4 g. of magnesium and 200 ml. of dry ether, was heated to boiling and to it was added a solution of 8 g. of the ketene in 50 ml. of dry ether. The mixture was maintained under reflux during the addition and for ninety minutes afterward and then poured into a mixture of ice and hydrochloric acid. The ether layer was removed and the aqueous layer extracted with ether. The solvent was evaporated in a stream of air, and the 2-duryl-2-phenylvinyl alcohol was recrystallized from a mixture of high- and low-boiling petroleum ether; m. p. 86–87°; yield 6.5 g. (80%).

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.86; H, 8.10.

The acetate, prepared by the reaction of acetic anhydride with the alcohol, crystallized from ethanol in needles melting at 130–130.5°.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.54. Found: C, 81.67; H, 7.82.

1-Duryl-2-phenylethylene Glycol.—An ethanol solution of 10 g. of duryl phenyl diketone[5] was subjected for eight hours at 150° to a hydrogen pressure of 1850 lb. in the presence of a copper chromite catalyst.[7] Two moles of hydrogen was absorbed for each mole of diketone used. The solution was treated with Norite and filtered. When the solvent was evaporated and the residual, viscous liquid was cooled, white crystals were formed. Exposure to air, however, caused the crystals to become gummy and later very hard. When water was added to the mother liquor more crystals were precipitated, which exhibited the same remarkable behavior. This may possibly be due to loss of alcohol of crystallization. Recrystallization of the glycol from high-boiling petroleum ether yielded fine white needles melting at 98–99°. The yield was 70% of the theoretical.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.97; H, 8.20. Found: C, 80.07; H, 8.27.

The **diacetate** was prepared by allowing a mixture of 1 g. of the glycol, 15 ml. of pyridine and 3 ml. of acetic anhydride to stand overnight in a closed flask. The diacetate was recrystallized from ethanol; m. p. 114–115°. The yield was nearly quantitative.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.66; H, 7.36.

Dehydration of the glycol was attempted by heating a mixture of 5 ml. of glacial acetic acid, 1 ml. of concentrated hydrochloric acid and 0.25 g. of 2-duryl-1-phenylethane-1,2-diol. The heating was continued for two and one-half hours under reflux and the mixture poured into water. The solid which formed was dissolved in benzene, and the solution washed with dilute potassium carbonate solution and with water. Removal of the solvent with an air blast left a gummy residue which crystallized from dilute ethanol in long white needles melting at 108–110°. This compound was shown by the method of mixed melting points to be different from the glycol. It gave no coloration with ferric chloride. The compound was not investigated further.

3-Bromomesitylphenylacetic Acid.—From 179 g. of bromomesitylene and 50 g. of mandelic acid was obtained 63 g. (57%) of 3-bromomesitylphenylacetic acid melting at 193–194°. It separated from ethanol in white, granular crystals; m. p. 194–195° (aluminum block).

Anal. Calcd. for $C_{17}H_{17}BrO_2$: C, 61.27; H, 5.14; Br, 23.98; neut. equiv., 333. Found: C, 61.28; H, 5.30; Br, 24.23; neut. equiv., 330.

This acid was made also by direct bromination in carbon tetrachloride. From 15 g. of mesitylphenylacetic acid was obtained 16 g. of the bromo acid. It was purified by recrystallization from nitromethane.

---

(4) Riebsomer, THIS JOURNAL, **60**, 2974 (1938).

(5) Gyr, *Ber.*, **41**, 4321 (1908).

(6) Fuson, Byers, Sperati, Foster and Warfield, *J. Org. Chem.*, **10**, 69 (1945).

(7) The reduction was carried out by Dr. J. C. Robinson.

3-Bromomesitylphenylketene.—Thirty grams of 3-bromomesitylphenylacetic acid was covered with 50 ml. of thionyl chloride and the mixture allowed to stand two days. The yield of acid chloride was 27 g. (85.5% of the theory); m. p. 84–87°. The chloride was recrystallized repeatedly from a mixture of low- and high-boiling petroleum ether. It formed light orange crystals; m. p. 85.5–87°.

Anal. Calcd. for $C_{17}H_{16}BrClO$: C, 58.06; H, 4.58. Found: C, 58.42; H, 4.67.

When the acid chloride was heated with a little pyridine, the ketene was obtained as a golden yellow oil boiling at 155–157° (1 mm.).

A more convenient method for preparing the ketene was to treat 3-bromomesitylphenylacetic acid with thionyl chloride and pyridine as illustrated in the synthesis of durylphenylketene. From 31.9 g. of the acid was obtained 12.7 g. of the twice-distilled ketene; b. p. 163° (2 mm.).

Anal. Calcd. for $C_{17}H_{15}BrO$: C, 64.77; H, 4.80. Found: C, 64.65; H, 4.92.

The ketene gave a grayish-black precipitate of silver when treated with silver nitrate.

2-(3-Bromomesityl)-2-phenylvinyl Alcohol.—When 2.8 g. of the ketene was treated with an excess of *t*-butylmagnesium chloride, 2.3 g. of 2-(3-mesityl)-2-phenylvinyl alcohol was obtained. Repeated recrystallization failed to yield a product with a satisfactory melting point; the values varied from 94° to 108° and the range was always wide.

Anal. Calcd. for $C_{17}H_{17}BrO$: C, 64.36; H, 5.40. Found: C, 64.34; H, 6.09.

The acetate, prepared by treating the alcohol with acetic anhydride and pyridine, was recrystallized from ethanol; m. p. 100.5–101.5°.

Anal. Calcd. for $C_{19}H_{19}BrO_2$: C, 63.51; H, 5.33. Found: C, 63.38; H, 5.30.

Summary

Mesitylphenyl-, dimesityl-, durylphenyl- and 3-bromomesitylphenylketene have been reduced by the action of cyclohexyl- or *t*-butylmagnesium chloride to the corresponding 2,2-diarylvinyl alcohols.

The preparation of 2-duryl-2-phenylvinyl alcohol has been described to illustrate the method.

URBANA, ILLINOIS RECEIVED AUGUST 23, 1945

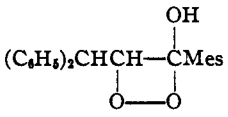
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

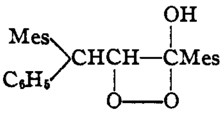
Vinyl Alcohols. XVII.[1] Cleavage of Enol Peroxides

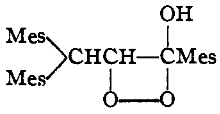
BY REYNOLD C. FUSON, E. W. MAYNERT AND W. J. SHENK, JR.

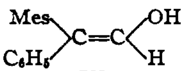
One of the most important questions to be answered in connection with the chemistry of 2,2-diarylvinyl alcohols concerns the possibility of the existence of the corresponding aldehydes. As yet they have not been obtained either by isomerization of the vinyl alcohols or by methods designed to produce them directly.

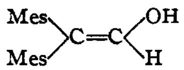
A particularly interesting aldehyde synthesis was discovered by Kohler and Thompson[2] who found that thermal decomposition of the peroxide of the enol form of benzohydrylacetomesitylene (I) yielded diphenylacetaldehyde.


I


II


III

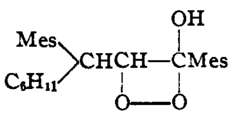

IV


V

If this method could be applied to peroxides such as II or III, the products might be expected to be aldehydes of the desired type. The discovery that phenyl- and mesitylmagnesium bromide condense in the 1,4-manner with mesitalacetomesitylene[3] opened a way to the synthesis of peroxides II and III, for example, and made it possible to test the usefulness of these peroxides for the synthesis of aldehydes. The results are of special interest due to the fact that the products *were not the expected aldehydes but the corresponding vinyl alcohols.*

By the condensation of benzalacetomesitylene and mesitalacetomesitylene with mesitylmagnesium bromide and subsequent treatment of the enol solutions with oxygen, peroxides II and III, respectively, were obtained. Decomposition of the first (II) yielded 2-mesityl-2-phenylvinyl alcohol (IV) and mesitoic acid. The second (III) gave 2,2-dimesitylvinyl alcohol (V) and mesitoic acid. It is difficult to see how the vinyl alcohols could be produced directly from the peroxides. It seems probable that the aldehydes are formed initially and that they enolize spontaneously.

2-*p*-Chlorophenyl-2-mesitylvinyl alcohol, a new compound, was also made by the peroxide method. In an effort to replace the phenyl group by the cyclohexyl group 1,3-dimesityl-3-cyclohexyl-1-propen-1-ol peroxide (VI) was prepared and de-


VI

---

[1] For the preceding communication in this series see Fuson, Kneisley, Rowland, Shenk and Soper, THIS JOURNAL, **67**, 1937 (1945).

[2] Kohler and Thompson, *ibid.*, **59**, 887 (1937).

[3] Fuson and Meek, *J. Org. Chem.*, in press.