hydrogenation to Δ^{22}-stigmasten-3-one and Δ^{22}-coprostigmasten-3-one, as well as other products. Reduction of the former ketone gave Δ^{22}-stigmasten-3β-ol (5,6-dihydrostigmasterol), and of the latter, Δ^{22}-coprostigmasten-3α-ol.

The changes in molecular rotation associated with the hydrogenation of the steroidal side chain 22(23)-ethylenic linkage have been discussed.

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

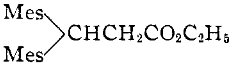
Conjugate Addition of Mesitylmagnesium Bromide to Ethyl 2,4,6-Trimethylcinnamate and to Mesitalacetomesitylene

BY REYNOLD C. FUSON AND HAROLD L. JACKSON[1]

A mesityl radical in the *beta* position in an α,β-unsaturated carbonyl compound is known not to block the entry of hydrocarbon radicals into that position in reactions with Grignard reagents.[2] In particular it has been shown that the mesityl radical likewise can enter the *beta* position in such molecules.[3]

The present work was designed to determine whether mesitylmagnesium bromide would attack a *beta* carbon atom already holding a mesityl group in carbonyl compounds in which the carbonyl group is not blocked by hindering radicals, *i. e.*, is free to react in the normal manner. When ethyl 2,4,6-trimethylcinnamate (I) was treated with an excess of the Grignard reagent, ethyl β,β-dimesitylpropionate (II) was formed. Although the experiment was run on a small scale, it was possible to isolate the product in 47% yield. No other organic product could be detected.

$\text{MesCH=CHCO}_2\text{C}_2\text{H}_5$
I

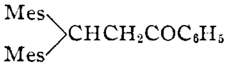


$\begin{matrix}\text{Mes}\\ \text{Mes}\end{matrix}\!\!>\!\text{CHCH}_2\text{CO}_2\text{C}_2\text{H}_5$
II

The structure of the dimesityl ester was established by hydrolysis; the β,β-dimesitylpropionic acid which formed was found to be identical with an authentic sample.[4]

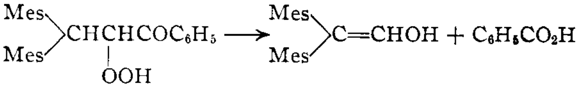
Mesitalacetophenone (III) reacted with mesitylmagnesium bromide to give an 84% yield of the conjugate addition product, β,β-dimesitylpropiophenone (IV).

$\text{MesCH=CHCOC}_6\text{H}_5$
III

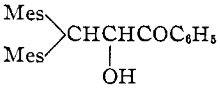


$\begin{matrix}\text{Mes}\\ \text{Mes}\end{matrix}\!\!>\!\text{CHCH}_2\text{COC}_6\text{H}_5$
IV

The structure of the new ketone was confirmed by the preparation of the oxime and reduction to the carbinol. By treatment of the solution of the enol with oxygen, it was possible also to prepare the hydroperoxide (V), which when heated above its melting point decomposed to dimesitylvinyl alcohol (VI) and benzoic acid.



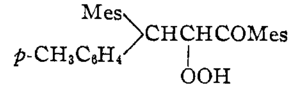
$\begin{matrix}\text{Mes}\\ \text{Mes}\end{matrix}\!\!>\!\text{CH}\underset{\text{OOH}}{\underset{|}{\text{C}}}\text{HCOC}_6\text{H}_5 \longrightarrow \begin{matrix}\text{Mes}\\ \text{Mes}\end{matrix}\!\!>\!\text{C=CHOH} + \text{C}_6\text{H}_5\text{CO}_2\text{H}$
V VI



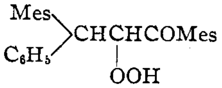
$\begin{matrix}\text{Mes}\\ \text{Mes}\end{matrix}\!\!>\!\text{CH}\underset{\text{OH}}{\underset{|}{\text{C}}}\text{HCOC}_6\text{H}_5$
VII

Reduction of the hydroperoxide with either a mixture of potassium iodide and acetic acid or hydrogen over a platinum catalyst gave a product which melted at 137.0–139.5° and had the composition indicated by formula VII.

The formation of the hydroperoxide was surprising since no hindering radical is attached to the carbonyl carbon and since hydrogen, rather than a hydrocarbon residue, is attached to the *alpha* carbon atom.



$\begin{matrix}\text{Mes}\\ p\text{-CH}_3\text{C}_6\text{H}_4\end{matrix}\!\!>\!\text{CH}\underset{\text{OOH}}{\underset{|}{\text{C}}}\text{HCOMes}$
VIII



$\begin{matrix}\text{Mes}\\ \text{C}_6\text{H}_5\end{matrix}\!\!>\!\text{CH}\underset{\text{OOH}}{\underset{|}{\text{C}}}\text{HCOMes}$
IX

The infrared absorption spectrum[5] of the hydroperoxide (V) shows a strong band at 1678 cm.$^{-1}$. Compounds VIII and IX[6] had absorption bands at 1685 and 1680 cm.$^{-1}$, respectively. Infrared absorption in this region is indicative of the presence of the singly conjugated carbonyl group. These results are in agreement with the recent findings of Rigaudy.[7] Because ultraviolet absorption spectra showed the presence of a carbonyl group, this author assigned the hydroperoxide structure rather than the cyclic peroxide structure suggested by Kohler[8] for such stable peroxides.

Experimental[9]

Ethyl β,β-Dimesitylpropionate (II).—A well-stirred, cold solution of mesitylmagnesium bromide, prepared from 32 g. of bromomesitylene, 3.9 g. of magnesium and 50 ml.

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[1] Socony-Vacuum Oil Company Fellow 1948–1949. Present address: E. I. du Pont de Nemours and Company, Wilmington, Delaware.

[2] Kohler and Blanchard, THIS JOURNAL, **57**, 367 (1935).

[3] Fuson and Meek, *J. Org. Chem.*, **10**, 551 (1945).

[4] Fuson and Jackson, THIS JOURNAL, **72**, 351 (1950).

[5] The infrared absorption spectra were determined and interpreted by Miss Elizabeth M. Peterson.

[6] Fuson and Tan, THIS JOURNAL, **70**, 602 (1948).

[7] Rigaudy, *Compt. rend.*, **226**, 1993 (1948).

[8] Kohler, *Am. Chem. J.*, **36**, 185 (1906).

[9] The microanalyses were performed by Miss Emily Davis and Miss Rachel Kopel.

of dry ether, was treated with 7.0 g. of ethyl 2,4,6-trimethylcinnamate[10] dissolved in 35 ml. of dry benzene and 35 ml. of dry ether. After the mixture was heated under reflux for one and one-half hours, it was decomposed with a saturated solution of ammonium chloride. Subsequently to the steam-distillation of the organic layer, the gummy residue was distilled to give ethyl β,β-dimesitylpropionate, b. p. 184–189° (2.3 mm.). Treatment of the product with Darco and crystallization from dilute methanol gave white crystals which melted at 78.5–80.0°; yield 47%.

Anal. Calcd. for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found C, 81.71; H, 8.78.

Hydrolysis of this ester produced an acid which melted at 167.0–168.5° and did not depress the melting point of β,β-dimesitylpropionic acid.

Mesitalacetophenone.—To a solution of 10.5 g. of sodium hydroxide in 250 ml. of ethanol was added 30 g. of freshly distilled acetophenone followed by 37.0 g. of freshly distilled mesitaldehyde, the mixture being cooled 0° before the addition of the aldehyde. The reaction mixture was stirred continuously during these operations. At the end of three hours it had become a light yellow slurry. After an additional fifteen hours, during which the temperature was held at 15–20°, stirring was discontinued and the mixture allowed to stand overnight in the icebox. The mesitalacetophenone was recrystallized from ethanol; m. p. 97.5–98.5°; yield 55.6 g. (87%). This compound was made first by Kohler and Blanchard[2] by condensing mesitaldehyde with acetophenone but the procedure was not described. These authors reported that the compound melted at 96°.

β,β-Dimesitylpropiophenone.—To a Grignard reagent, prepared from 60 g. of bromomesitylene, 7.3 g. of magnesium and 200 ml. of dry ether, was added 55.6 g. of mesitalacetophenone dissolved in a mixture of 100 ml. of dry benzene and 100 ml. of dry ether. When the addition was completed, the mixture was stirred and heated under reflux for two hours. After the mixture was hydrolyzed by a saturated solution of ammonium chloride, the organic layer was distilled with steam and the resulting yellow residue was crystallized from ethanol to give 46.7 g. (84%) of white crystals melting at 142–144°. Two additional crystallizations of the ketone from methanol raised the melting point to 145.5–146.0°.

Anal. Calcd. for $C_{27}H_{30}O$: C, 87.52; H, 8.16. Found: C, 87.71; H, 8.21.

When β,β-dimesitylpropiophenone was treated with hydroxylamine hydrochloride in pyridine, it formed a white *oxime* which crystallized from methanol; m. p. 174–176°.

Anal. Calcd. for $C_{27}H_{31}NO$: C, 84.11; H, 8.11; N, 3.63. Found: C, 84.16; H, 8.35; N, 3.88.

3,3-Dimesityl-1-phenyl-1-propanol.—This compound was prepared by treating a solution of β,β-dimesitylpropiophenone in methylcyclohexane with hydrogen under 100 atmospheres of pressure in the presence of copper chromium oxide catalyst at a temperature of 150°. After the catalyst was removed by filtration, the solvent was distilled under reduced pressure. The colorless residue was crystallized from dilute methanol and then from nitromethane; m. p. 134.5–135.0°.

Anal. Calcd. for $C_{27}H_{32}O$: C, 87.05; H, 8.66. Found: C, 86.86; H, 8.79.

The reduction of β,β-dimesitylpropiophenone with sodium and 1-butanol was also a good method for the preparation of this carbinol.

Treatment of β,β-Dimesitylpropiophenone Enol with Oxygen.—A solution of 13.0 g. of mesitalacetophenone in a mixture of 50 ml. of ether and 50 ml. of benzene was added to a solution of mesitylmagnesium bromide, prepared from 24.0 g. of bromomesitylene, 2.9 g. of magnesium and 150 ml. of absolute ether. The mixture was heated under reflux for one hour and then poured into an ice-hydrochloric acid mixture. After the layers had been separated, the aqueous portion was extracted with cold, low-boiling petroleum ether. The organic layer was united with the petroleum ether extracts, washed with cold water and placed in a large graduated cylinder supported in an ice-bath. Oxygen was bubbled through the solution for eight hours and the solvents were removed under a jet of air. The residue was washed with three portions of low-boiling petroleum ether. The 15 g. of white solid obtained by this method was recrystallized from petroleum ether; m. p. 140–141° (dec.).

Anal. Calcd. for $C_{27}H_{30}O_3$; C, 80.56; H, 7.51. Found: C, 80.38; H, 7.70.

A sample of this product underwent only slight decomposition when allowed to stand in a stoppered bottle for forty-five days. When it was heated gently, it melted and then decomposed suddenly yielding a puff of acrid fumes and a light brown oil. Dimesitylvinyl alcohol and benzoic acid were isolated from the oil.

A mixture of 4.0 g. of the hydroperoxide, 7.5 g. of powdered potassium iodide and 45 ml. of glacial acetic acid was shaken for six hours at room temperature. The color of iodine appeared immediately. When the mixture was poured into 200 ml. of water containing 6 g. of sodium bisulfite, a white solid separated. Recrystallization of this product from ethanol gave white crystals melting at 187.0–139.5°; yield 2.3 g.

The same product was obtained by shaking a solution of the hydroperoxide in ethanol with platinum catalyst in an atmosphere of hydrogen for six hours.

Anal. Calcd. for $C_{27}H_{30}O_2$: C, 83.90; H, 7.82. Found: C, 84.14; H, 8.04.

The composition of this compound corresponds to that of the expected α-hydroxy ketone (VII); however, attempts to cleave it with periodic acid or lead tetraacetate were fruitless.

Summary

The presence of a mesityl radical in the *beta* position of an α,β-unsaturated ester or unhindered ketone does not prevent conjugate addition of mesitylmagnesium bromide. Ethyl 2,4,6-trimethylcinnamate and mesitalacetophenone have been found to react with the mesityl Grignard reagent to yield, respectively, ethyl β,β-dimesitylpropionate and β,β-dimesitylpropiophenone.

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(10) Prepared according to the procedure of Bock, Lock and Schmidt, *Monatsh.*, **64**, 399 (1934).