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A Comparison of Certain Dimesitylmethyl Derivatives with the Corresponding Triarylmethyl Compounds

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The dimesitylmethyl radical has been found to exhibit a behavior which is reminiscent of that of the triarylmethyls. For example, when a benzene solution of dimesitylchloromethane is shaken with molecular silver in an inert atmosphere, there is produced a highly colored solution with the halochromic characteristics of a benzene solution of a hexaarylethane.[2] We have found that the unusual behavior of certain dimesitylmethyl derivatives may be accounted for by assuming the ready formation of the dimesitylmethyl carbonium ion. Evidence for the existence of this ion is the deep violet-red color, which is exhibited by dimesitylcarbinol in the presence of salts or electrophilic reagents such as aluminum chloride, calcium chloride and sulfuric acid. Further evidence was obtained by pouring a solution of dimesitylcarbinol in 100% sulfuric acid into cold methanol; a quantitative yield of dimesitylmethyl methyl ether was obtained. The methyl ether of triphenylcarbinol is formed by the same procedure[3] although it was found that benzohydrol gave none of the methyl ether when treated in the same manner. The mechanism of the formation of the ether is presumably as follows

$$\mathrm{Mes_2CHOH + 2H_2SO_4 \longrightarrow Mes_2CH^+ + H_3O^+ + 2HSO_4^-}$$

$$\mathrm{Mes_2CH^+ + CH_3OH \longrightarrow Mes_2CHOCH_3 + H^+}$$

Like triphenylchloromethane,[4] dimesitylchloromethane may be used as an alkylating agent. The magnesiumethoxy derivative of ethyl malonate reacted with dimesitylchloromethane to give an 84% yield of ethyl dimesitylmethylmalonate (I). Attempts to introduce a second alkyl group with either dimesitylchloromethane or benzyl chloride proved unavailing. The corresponding benzohydryl derivative, ethyl benzohydrylmalonate, gave ethyl dibenzohydrylmalonate when treated with benzohydryl bromide.[5]

The structure of the new malonic ester (I) was established by hydrolysis and decarboxylation. The resulting β,β-dimesitylpropionic acid (II), a new compound, was converted to methyl β,β-dimesitylpropionate by way of the crystalline acid chloride.

$\mathrm{Mes_2CHCH(CO_2C_2H_5)_2}$ I

$\mathrm{Mes_2CHCH_2COOH}$ II

Because the dimesitylmethyl group is known to exhibit the characteristics of a free radical,[2,6] it seemed likely that it could enter into coupling reactions with less hindered radicals in the presence of a metal. All attempts, however, to bring about a reaction of triphenylchloromethane or benzohydryl bromide with dimesitylchloromethane in the presence of mercury were fruitless, although it is known that under the same conditions benzohydryl bromide does react with triphenylmethyl chloride to give a high yield of pentaphenylethane.[7] Triphenylmethylsodium and dimesitylchloromethane gave a mixture from which no pure products could be isolated. Efforts to prepare a Grignard reagent from dimesitylchloromethane were ineffective also.

The dimesitylcarbinol which was used in this work was prepared by two new methods. The condensation of mesitaldehyde with mesitylmagnesium bromide is a satisfactory procedure. Still better results were obtained, however, by allowing the mesityl Grignard reagent to react with ethyl formate. This latter result is in contrast to that of Lapkin who reported the product to be a mixture of dimesitylmethane and dimesityl ketone, no carbinol being formed.[8]

Dimesitylchloromethane was formed from dimesitylcarbinol by treating a benzene solution of the carbinol with dry hydrogen chloride or by allowing a benzene solution of the carbinol to stand for several days in contact with a 37% aqueous solution of hydrochloric acid. The method used for the preparation of triarylmethyl halides from an acetyl halide failed to yield the corresponding dimesitylmethyl derivative.

The chloride could be hydrolyzed by heating for a short time with dilute sodium hydroxide or with water containing Dreft. Ethers of dimesitylcarbinol were formed easily from dimesitylchloromethane and a warm alkaline solution of the appropriate alcohol.

Two other hindered carbinols, didurylcarbinol and di-(4-methoxy-2,6-xylyl)-carbinol, were also prepared from the corresponding Grignard reagents and ethyl formate.

In one experiment dimesitylcarbinol was heated with aniline hydrochloride in acetic acid. The product was a hydrocarbon (m. p. 238–239°) having the composition of tetramesitylethylene (A). This compound, however, showed none of the typical reactions of an ethylene, resisted ozonization and could not be hydrogenated.

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(2) Coops, Nauta, Ernsting and Faber, *Rec. trav. chim.*, **59**, 1109 (1940).

(3) Smith and Smith, THIS JOURNAL, **70**, 2400 (1948).

(4) Coles, *ibid.*, **59**, 2468 (1937).

(5) Cope, *ibid.*, **56**, 721 (1934).

(6) Nauta and Wuis, *Rec. trav. chim.*, **56**, 535 (1937); **57**, 41 (1938).

(7) Bachmann and Wiselogle, *J. Org. Chem.*, **1**, 376 (1936).

(8) Lapkin, *J. Gen. Chem.* (*U. S. S. R.*), **16**, 729 (1946).

When it was oxidized with sodium dichromate in concentrated sulfuric acid, acetic acid was the only product identified. The same hydrocarbon was obtained when dimesitylchloromethane was used in the reaction mixture in place of the carbinol. A compound, which had the composition of tetradurylethylene, was obtained when didurylcarbinol was heated with aniline hydrochloride and acetic acid. Similar treatment of mesitylphenylcarbinol, mesityl-2,4-xylylcarbinol or di-(4-methoxy-2,6-xylyl)-carbinol with acetic acid and aniline hydrochloride yielded only intractable oils. When triphenylcarbinol is treated in the same manner, *p*-aminotetraphenylmethane is produced.[9]

A similar experiment with dimesitylchloromethane in which phenol replaced the mixture of aniline hydrochloride and acetic acid yielded another hydrocarbon (B) (m. p. 204–206°; mixture m. p. with A, 190–200°) which had the same composition as A. When a mixture of phenol and dimesitylcarbinol was heated under reflux, the higher melting product (A) was isolated. The mesityl group was the only significant structural unit indicated by either the infrared or the ultraviolet spectra of A and B. The infrared spectra of A and B were very similar. The structures of A and B are, therefore, in doubt.

Experimental[10]

Dimesitylcarbinol. (A) From Mesitylmagnesium Bromide and Mesitaldehyde.—To an ice-cold solution of mesitylmagnesium bromide, prepared from 100 g. of bromomesitylene, 12 g. of magnesium and 500 ml. of dry ether, was added with stirring 52 g. of freshly distilled mesitaldehyde. An ether-insoluble complex formed. After the mixture had been stirred for four hours, it was poured into a mixture of ice and acetic acid. The ether layer was filtered to remove the suspended carbinol. Recrystallization of the crude, gray carbinol from ethanol yielded 70 g. (75%) of white crystals, m. p. 146–147°. One additional recrystallization of the carbinol from ethanol raised the melting point to 149.5–150.0°. Kohler and Baltzly,[11] who prepared dimesitylcarbinol by the reduction of dimesityl ketone, reported a melting point of 150°.

(B) From Mesitylmagnesium Bromide and Ethyl Formate.—To a Grignard reagent, prepared from 300 g. of bromomesitylene, 36 g. of magnesium and 1500 ml. of dry ether and cooled to 0°, was added 28 g. of ethyl formate in 100 ml. of dry ether. During the thirty minutes required for the addition of the ester, the reaction mixture was stirred vigorously and maintained at 0–5°. It was then allowed to attain room temperature and the stirring was continued for one hour. Hydrolysis was effected by pouring the reaction mixture into ice and hydrochloric acid; the carbinol, which separated from the ether layer as a white solid, was isolated by filtration, yield 74.5 g. When the ether filtrate was allowed to stand overnight, an additional 13.0 g. of the carbinol precipitated; the over-all yield was 86%. After four recrystallizations from ethanol, the compound melted at 149.0–149.5°.

Didurylcarbinol.—The synthesis of didurylcarbinol was effected by the treatment of ethyl formate with an excess of durylmagnesium bromide according to procedure B above. It crystallized from ethanol in white prisms; m. p. 163–165° (reported[3] 162°), yield, 44%.

Di-(4-methoxy-2,6-xylyl)-carbinol.—This compound was synthesized from ethyl formate and the Grignard reagent prepared from 4-bromo-3,5-dimethylanisole. Recrystallization from methanol gave 54% of the theoretical amount of the carbinol, m. p. 93.5–94.0°.

Anal. Calcd. for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05. Found: C, 76.04; H, 8.29.

Dimesitylchloromethane.—(A) Dimesitylcarbinol was converted to the chloride by the procedure of Nauta and Wuis.[6] The dimesitylchloromethane was recrystallized from high-boiling petroleum ether; m. p. 103–105°, yield, 86%.

(B) **Dimesitylchloromethane** was prepared also by allowing a benzene solution of dimesitylcarbinol to stand in contact with concentrated hydrochloric acid for two days, the mixture being shaken frequently. Removal of the solvent from the benzene layer gave an almost quantitative yield of the chloride. The procedure was adapted from that described by Reid[12] for the preparation of di-(*o*-tolyl)-methyl chloride. The product obtained by this method was not as pure as that obtained by method A.

Dimesitylchloromethane was hydrolyzed in nearly quantitative yields to dimesitylcarbinol by heating under reflux for thirty minutes with either a 2% sodium hydroxide solution or with water containing a trace of Dreft to act as an emulsifying agent.

Dimesitylmethyl Methyl Ether.—The procedure was similar to that described by Smith and Smith[3] for the preparation of the methyl ether of triphenylcarbinol. To 12 g. of 100% sulfuric acid was added 2 g. of dimesitylcarbinol. The deep red solution which formed was added dropwise to 30 ml. of methanol maintained at −10° in an ice–salt-bath. After the resulting solution was poured into a mixture of ice and water, the white solid which separated was crystallized from methanol to give colorless prisms; m. p. 57–59°, yield 2.1 g. (98%). Two recrystallizations of the ether from methanol raised the melting point to 60.0–60.5°. A mixture melting point with a known sample of dimesitylmethyl methyl ether showed no depression.

Anal. Calcd. for $C_{20}H_{26}O$: C, 85.06; H, 9.28. Found: C, 85.08; H, 9.38.

This ether was prepared also by warming dimesitylchloromethane with a methanolic solution of sodium methoxide.

Dimesitylmethyl Ethyl Ether.—One gram of dimesitylchloromethane was heated for three hours in a refluxing solution of 0.5 g. of potassium hydroxide, 20 ml. of ethanol and 10 ml. of dry benzene. The cooled mixture was poured into water and the organic solvent removed under a stream of air. Crystallization of the resulting oil from ethanol gave 0.5 g. of the ether; m. p. 63–64°.

Anal. Calcd. for $C_{21}H_{28}O$: C, 85.10; H, 9.54. Found: C, 85.36; H, 9.24.

Ethyl Dimesitylmethylmalonate.—Eleven grams of dimesitylchloromethane, dissolved in the minimum amount of warm benzene, was added slowly to a solution of magnesiomalonic ester prepared from 7.0 g. of ethyl malonate, 5 ml. of dry ether, 5 ml. of absolute ethanol, 1.07 g. of magnesium and 0.1 ml. of carbon tetrachloride. After the reaction mixture was heated under reflux for three hours, it was cooled to room temperature and shaken with cold, dilute sulfuric acid. The organic layer was washed with water and dried. The solvent was removed under water-pump pressure, and the residue was dissolved in 30 ml. of methanol. When this solution was cooled, 12.5 g. of white crystals separated, m. p. 94–95°. Concentration of the mother liquor yielded an additional 1.5 g. of the ester. The over-all yield was 84%. The analytical sample melted at 97–98°.

Anal. Calcd. for $C_{26}H_{34}O_4$: C, 76.06; H, 8.33. Found: C, 76.18; H, 8.05.

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(9) Ullmann and Munzhuber, *Ber.*, **36**, 404 (1903).

(10) The microanalyses were carried out by Miss Emily Davis and Miss Jane Wood.

(11) Kohler and Baltzly, THIS JOURNAL, **54**, 4015 (1932).

(12) Reid, *ibid.*, **61**, 3238 (1939).

Attempts to alkylate ethyl dimesitylmethylmalonate with either dimesitylchloromethane or benzyl chloride were unsuccessful.

Dimesitylmethylmalonic Acid.—A mixture of 4.0 g. of ethyl dimesitylmethylmalonate, 20 ml. of water, 40 ml. of ethanol and 5.0 g. of sodium hydroxide was heated under reflux for eight hours. The cooled solution was poured into 500 ml. of cold water; a small white suspension formed and was removed by filtration. Acidification of the clear filtrate gave 3.0 g. of white crystals which melted with decomposition at 173.5–174.0°.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.35; H, 7.56.

β,β-Dimesitylpropionic Acid.—Dimesitylmethylmalonic acid was heated in an oil-bath at a temperature of 180–190° until the evolution of gas was completed. The light brown melt, when it was allowed to cool, formed a glass which was crystallized from benzene. Treatment of the crystalline product with Darco and four crystallizations from benzene gave white crystals which melted at 166.5–167.0°.

Anal. Calcd. for $C_{21}H_{26}O_2$: C, 81.69; H, 8.46. Found: C, 81.83; H, 8.46.

Methyl β,β-Dimesitylpropionate.—Fifteen grams of β,β-dimesitylpropionic acid was heated under reflux with 15.0 ml. of purified thionyl chloride for two hours. The excess thionyl chloride was removed under water-pump pressure, and the colorless residue was crystallized from high-boiling petroleum ether. The yield of colorless crystals was 14.0 g. (88%); m. p. 116.5–118.0°. A mixture of 8.0 g. of β,β-dimesitylpropionyl chloride and 200 ml. of dry methanol was heated under reflux for two hours. The volume of the resulting solution was reduced to 75 ml. under a take-off condenser, and the solution was allowed to cool. The white crystals which separated melted at 164–165°; yield 6.7 g. (87%).

Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.28; H, 8.72.

This compound was prepared also by esterification of β,β-dimesitylpropionic acid with methanol in the presence of sulfuric acid.

Reaction of Dimesitylcarbinol in the Presence of Acetic Acid and Aniline Hydrochloride.—A mixture of 10.8 g. of dimesitylcarbinol, 4.3 g. of dry aniline hydrochloride and 35 ml. of glacial acetic acid was heated under reflux for four hours. The solid which formed was collected on a filter, washed with water and ethanol, dissolved in high-boiling petroleum ether and treated with Darco. The decolorized solution was boiled under a take-off condenser in order to remove excess solvent. When this solution was cooled, 3.1 g. of a white solid precipitated. The melting point of this product was 237.5–238.5°. Four recrystallizations of the hydrocarbon from high-boiling petroleum ether raised the melting point to 238–239°.

Anal. Calcd. for $C_{38}H_{44}$: C, 91.14; H, 8.86; mol. wt., 500.7. Found: C, 90.84; H, 9.05; mol. wt., 505, 533.

Dimesitylchloromethane was substituted for dimesitylcarbinol in the preparation with no decrease in yield of the hydrocarbon.

Only unchanged hydrocarbon was isolated when the product was treated with hydrogen at 155° for two hours under a pressure of 2300 lb. per sq. in. over a Raney nickel catalyst. The hydrocarbon was not altered by treatment with a stream of oxygen-containing ozone. Oxidation of the hydrocarbon with a mixture of sodium dichromate and concentrated sulfuric acid gave acetic acid.

Reaction of Didurylcarbinol in the Presence of Acetic and Aniline Hydrochloride.—Didurylcarbinol was treated with acetic acid and aniline hydrochloride in the manner described above. After the reaction mixture was cooled, the crystals which separated were recrystallized from ethanol, m. p. 132.0–133.0°. This compound has the composition of tetradurylethylene.

Anal. Calcd. for $C_{42}H_{52}$: C, 90.59; H, 9.41. Found: C, 90.90; H, 9.58.

Reaction of Dimesitylchloromethane in the Presence of Phenol.—Three grams of dimesitylchloromethane and 4.7 g. of phenol were heated under reflux for three hours. The mixing of the reactants was accompanied by the formation of a dark red solution and the evolution of hydrogen chloride. A gum formed when the reaction mixture was poured slowly into 250 ml. of cold water. The white solid, which separated when the gum was boiled with ethanol, was recrystallized from high-boiling petroleum ether; yield 1.2 g. of white crystals, m. p. 204–206°.

Anal. Calcd. for $C_{38}H_{44}$: C, 91.14; H, 8.86. Found: C, 90.86; H, 8.95.

Treatment of Methanol with a Solution of Benzohydrol in 100% Sulfuric Acid.—To 150 ml. of methanol maintained at −10° was added with stirring an orange solution of 10 g. of benzohydrol in 75 g. of 100% sulfuric acid. After the resulting solution was poured into a mixture of ice and water, the cloudy mixture was extracted with four 50-ml. portions of ether. The combined ether extracts were washed with sodium carbonate solution and dried over Drierite. Distillation of the liquid residue, which remained after removal of the ether, gave 1.3 g. of a colorless liquid; b. p. 178–182° (16 mm.).

Anal. Found: C, 86.16, 86.25; H, 6.10, 5.79.

This compound was not the methyl ether of benzohydrol, which boils at 147–148° (17 mm.),[13] and has the following composition: C, 84.8; H, 7.12.

There remained in the reaction vessel 3.4 g. of a dark brown liquid residue which solidified to a hard resin when it was allowed to cool to room temperature. All attempts to crystallize or identify this solid were unavailing.

Summary

The behavior of dimesitylcarbinol in the presence of electrophilic reagents, such as sulfuric acid, has been interpreted by assuming the formation of the dimesitylmethyl carbonium ion. The carbinol is quantitatively converted to the methyl ether when its solution in 100% sulfuric acid is treated with methanol.

Ethyl malonate was monoalkylated with dimesitylchloromethane to give ethyl dimesitylmethylmalonate, which in turn was converted to the free malonic acid, β,β-dimesitylpropionic acid and methyl β,β-dimesitylpropionate.

Two new syntheses of dimesitylcarbinol from mesitylmagnesium bromide are described.

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[13] Bergmann and Hervey, *Ber.*, **62B**, 893 (1929).