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

CONJUGATE ADDITION REACTIONS OF 5-MESITOYLACENAPHTHYLENE

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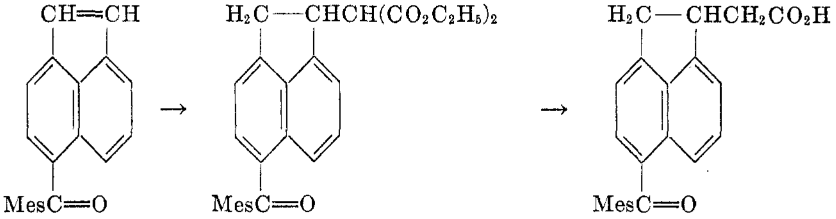
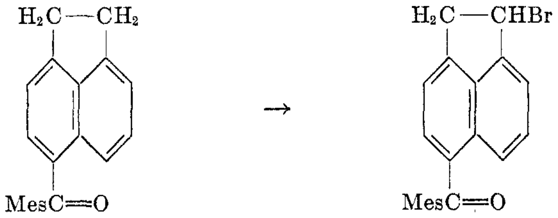
Alkylation of duryl phenyl ketone (1) and similar compounds at the *para* position, which corresponds to 1,6 addition of the Grignard reagent, suggests that it might be possible to achieve conjugate addition involving the 8 position of a ketone of this type which holds an ethylenic group in the *para* position. To test this idea we have prepared 5-mesitoylacenaphthylene (I) and subjected it to the action of various reagents known to enter into reactions of the conjugate type.



I II III

Perhaps the most interesting reaction observed with 5-mesitoylacenaphthylene (I) is the Michael condensation with ethyl malonate to produce a keto ester (II). When degraded in the conventional manner, the ester gave the corresponding keto acid (III). A similar transformation was realized with ethyl cyanoacetate, the end product being the same keto acid (III).

5-Mesitoylacenaphthene was made by treating acenaphthene with mesitoyl chloride in the presence of aluminum chloride. Bromination of the saturated ketone (IV), carried out with N-bromosuccinimide, yielded 1-bromo-5-mesitoylacenaphthene (V), which gave the unsaturated ketone (I) when dehydrobrominated. The bromide was regenerated by treating the unsaturated compound with hydrogen bromide. Piperidine was found to combine in a similar way with



IV V

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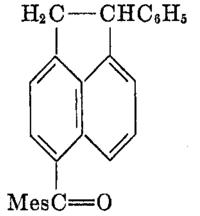
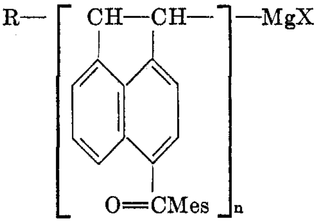
[1] Henry Strong Fellow, 1949-1950.

the olefinic compound. Benzene reacts with either the bromide or the olefin to give 1-phenyl-5-mesitoylacenaphthene (VI).

Grignard reagents attack 5-mesitoylacenaphthylene, but the products are complex. It is believed that they are polymers, perhaps of the type represented by formula VII.



VI



VII

The assumption that, in all the reactions mentioned which involve the *peri* bridge the 1 position is attacked, has been proved to be correct in the case of the Michael adducts by an independent synthesis of the final product, 5-mesitoyl-1-acenaphtheneacetic acid (III). This synthesis is described in the following paper (2).

EXPERIMENTAL[2]

5-Mesitoylacenaphthene.[3] A solution of 91.2 g. of acenaphthene and 109.5 g. of mesitoyl chloride in 450 ml. of carbon disulfide was added, over a period of 5 hours, with stirring, to a suspension of 100 g. of aluminum chloride in 300 ml. of carbon disulfide. During the addition the reaction vessel was cooled by an ice-bath. The mixture was stirred at room temperature for 9 hours, at the end of which time the evolution of hydrogen chloride had ceased. The 5-mesitoylacenaphthene, isolated by conventional procedures, crystallized from benzene in almost colorless plates; m.p. 177–179°; yield 70%.

Anal. Calc'd for $C_{22}H_{20}O$: C, 87.96; H, 6.71.

Found: C, 87.82; H, 6.74.

When heated with palladium on charcoal at 300° the ketone was unchanged. Treatment at higher temperatures or with sulfur produced only tarry materials.

1-Bromo-5-mesitoylacenaphthene.[3] A solution of 72 g. of 5-mesitoylacenaphthene, 43.2 g. of N-bromosuccinimide, 0.5 g. of benzoyl peroxide, and 1200 ml. of carbon tetrachloride was heated under reflux for 20 minutes. When the mixture was cooled to room temperature, succinimide separated in nearly quantitative yield. Removal of solvent by distillation left the bromo ketone as a yellow gum, which was crystallized from high-boiling petroleum ether after treatment with Darco. By repeated recrystallization from this solvent the product was obtained in nearly colorless needles; m.p. 151–165° (decomp.).

Anal. Calc'd for $C_{22}H_{10}BrO$: C, 69.66; H, 5.05.

Found: C, 69.36; H, 5.26.

This compound was also produced by adding hydrogen bromide to 5-mesitoylacenaphthylene. A mixture of 15 ml. of 48% hydrobromic acid and 6.7 ml. of acetic anhydride was added slowly, with cooling, to 1.5 g. of the acenaphthylene. The red solution was allowed to stand for 4 hours and was poured into 500 ml. of water. The yellow precipitate was washed with water, dried, and recrystallized first from methyl ethyl ketone then from high-boiling

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

[3] This preparation was carried out by Dr. Russell Gaertner.

petroleum ether; m.p. 158.5–160° (decomp.); yield 80%. Practically the same results were obtained when the addition was carried out in the presence of a small amount of benzoyl peroxide. The infrared spectrum[4] of this compound was identical with that of the product obtained by bromination with N-bromosuccinimide.

5-Mesitoylacenaphthylene. A mixture of 37.9 g. of 1-bromo-5-mesitoylacenaphthene and 75 ml. of dry pyridine was slowly heated to boiling. When the temperature reached about 50° the solid dissolved and as the temperature rose a solid mass of quaternary ammonium salt precipitated from solution. The mixture was heated under reflux for 12 hours, cooled, and combined with 75 ml. of chloroform. The solution was washed three times with 200-ml. portions of 2 *N* hydrochloric acid and once with a saturated solution of sodium chloride. The chloroform was distilled and the residue was extracted five times with 100-ml. portions of high-boiling petroleum ether. The solid left by evaporation of the petroleum ether, after repeated recrystallization from isopropyl alcohol, formed yellow plates; m.p. 130–131°.

Anal. Calc'd for $C_{22}H_{18}O$: C, 88.55; H, 6.08.
Found: C, 88.36; H, 6.23.

Hydrogenation of 5-mesitoylacenaphthylene at room temperature with the Adams catalyst reconverted it to 5-mesitoylacenaphthene (m.p. 176–178°). A mixture melting point with an authentic specimen showed no depression.

5-Mesitoylacenaphthylene reacted with the benzyl, *sec*-butyl, phenyl, mesityl, and *p*-chlorobenzyl Grignard reagents to give products which appeared to be polymeric.

The unsaturated ketone combined with piperidine to give an amine, which was isolated as the hydrochloride. A solution of 0.30 g. of 5-mesitoylacenaphthylene in 6 ml. of piperidine was allowed to stand at room temperature for 2 days. When shaken with a mixture of 20 ml. of benzene and 35 ml. of 6 *N* hydrochloric acid the hydrochloride of the tertiary amine was precipitated; yield 0.27 g. It crystallized from absolute ethanol in needles, which melted with decomposition in the range 260–275°. Analysis showed that it contained a molecule of ethanol. The presence of a hydroxyl group was indicated by a band at 3315 cm.$^{-1}$ in the infrared spectrum.

Anal. Calc'd for $C_{27}H_{30}ClNO$: C, 74.73; H, 7.79; N, 3.01.
Found: C, 74.68; H, 7.80; N, 3.14.

1-Phenyl-5-mesitoylacenaphthene. 5-Mesitoylacenaphthylene (1.5 g.) and aluminum chloride (1.0 g.) were added to 50 ml. of anhydrous benzene previously saturated with dry hydrogen chloride. The mixture, which assumed a dark red color, was shaken for 4 hours at room temperature in a stoppered container and was poured into a mixture of ice and hydrochloric acid. The 1-phenyl-5-mesitoylacenaphthene, isolated by conventional procedures, was recrystallized repeatedly from methyl ethyl ketone. It formed pale yellow needles; m.p. 184–185.5°.

Anal. Calc'd for $C_{28}H_{24}O$: C, 89.32; H, 6.43.
Found: C, 89.37; H, 6.25.

The same compound was obtained by treating 1-bromo-5-mesitoylacenaphthene (1.8 g.) with benzene (50 ml.) in the presence of aluminum chloride (1.0 g.) by a procedure very similar to that described for the olefinic compound. In either case the yield was about 80%. The two products were shown to be identical by a mixture melting point determination.

5-Mesitoyl-1-acenaphtheneacetic acid. To a solution of 0.46 g. of sodium in 10 ml. of absolute ethanol was added a solution of 4 g. of ethyl malonate and 5 ml. of absolute ethanol followed by a solution of 1.5 g. of 5-mesitoylacenaphthylene in 5 ml. of dry benzene. The resulting dark green solution was boiled gently under reflux for 90 minutes; 15 ml. of 2 *N* hydrochloric acid was added and the organic layer was removed, washed repeatedly with water, and dried over magnesium sulfate.

To the mixture of ethyl malonate and the adduct, left when the solvent was evaporated, was added a solution 5 g. of potassium hydroxide in 6 ml. of water and the mixture was

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[4] The infrared absorption spectra were recorded and interpreted by Miss Elizabeth Petersen.

heated on a steam-bath (at 90–95°) for 45 minutes. The dibasic acid was precipitated by slow addition of 7.0 ml. of concentrated hydrochloric acid, collected on a filter, and air dried; yield 1.7 g. A gas was evolved when the crude dibasic acid was heated.

A solution of the dibasic acid (1.7 g.), 4.5 ml. of concentrated hydrochloric acid, and 30 ml. of glacial acetic acid was heated under reflux for 4 hours. The monobasic acid, precipitated by addition of water, crystallized from nitromethane in almost colorless needles; m.p. 201–205°; yield 50% (based on the 5-mesitoylacenaphthylene). An analytical sample was obtained by recrystallization of the compound twice from nitromethane and then three times from ethyl acetate; m.p. 205–206.5°.

Anal. Calc'd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19.
Found: C, 80.21; H, 6.02.

The infrared spectrum has bands at 1710 cm.$^{-1}$ and 1657 cm.$^{-1}$ assignable, respectively, to a carboxyl group and a hindered carbonyl group.

This acid was obtained also when ethyl cyanoacetate was employed instead of ethyl malonate, the procedure being essentially the same as that just described. A mixture of the two samples showed no melting point lowering.

SUMMARY

5-Mesitoylacenaphthylene reacts with ethyl malonate and ethyl cyanoacetate in the conjugate manner corresponding to 1,8 addition.

URBANA, ILLINOIS

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(2) FUSON AND FREY, *J. Org. Chem.*, **19**, following paper (1954).