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

1,5-DISUBSTITUTED ACENAPHTHENES. 5-MESITOYL-1-ACENAPHTHENEACETIC ACID

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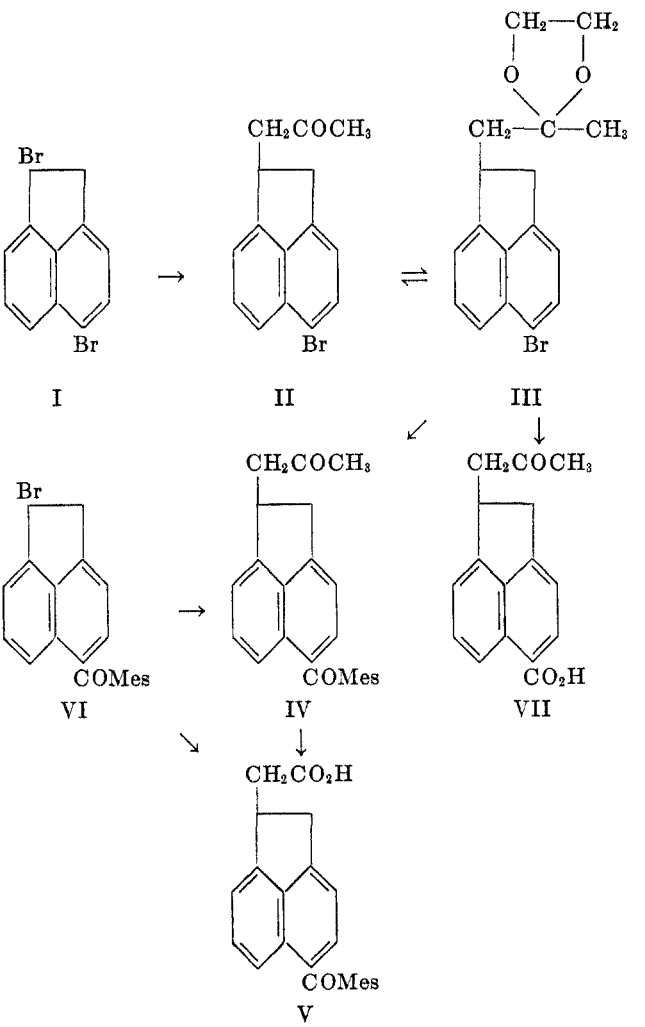
Received October 16, 1953

The study of conjugate addition reactions of 5-mesitoylacenaphthylene reported in the preceding communication (1) was greatly impeded by the lack of reference compounds especially in the 1,5 series. The present paper reports experiments designed to fill this gap and, in particular, to provide an unequivocal synthesis of 5-mesitoyl-1-acenaphtheneacetic acid (V), the key compound in the study of the Michael reaction (1).

The synthesis of this acid has been carried out by the following reaction sequence, no step of which seems to be open to question:



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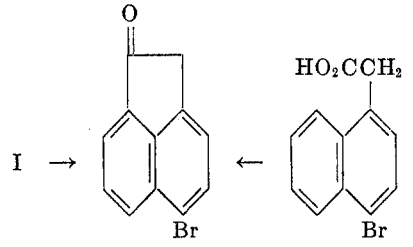
The structure of the dibromide (I) is established by replacement of the 1-bromine atom by the acetoxy group, hydrolysis to the alcohol, and oxidation to 5-bromoacenaphthenone (VIII) (2) which corresponds to the product obtained when 4-bromo-1-naphthaleneacetic acid (IX) is cyclized (3).

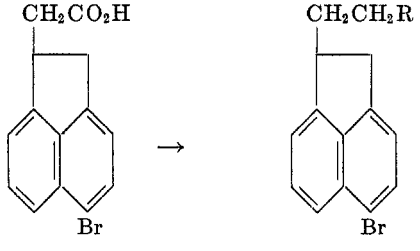


VIII IX

The conversion of the dibromide to the bromoketone (II) was achieved by the use of ethyl acetoacetate, ketonic cleavage of the keto ester being effected by treatment with potassium hydroxide. The cyclic ketal (III) was prepared by azeotropic distillation, toluene being used as solvent and *p*-toluenesulfonic acid monohydrate as the catalyst. Replacement of the bromine atom of the ketal by a mesitoyl group was accomplished by exchanging the bromine for lithium with *n*-butyllithium and allowing the lithium compound to react with mesitoyl chloride. Acid hydrolysis served to produce the diketone (IV). The final step consisted in oxidative degradation of the diketone (IV) to the acetic acid (V) by the action of hypoiodite.

The acetic acid was made also from 5-mesitoylacenaphthene by the malonic ester method, the 1-bromo ketone (VI) being an intermediate. The bromo ketone (VI) was converted to the diketone (IV) by the acetoacetic ester method. The acid (VII) was prepared from the cyclic ketal by carbonation of the intermediate formed by the exchange of the bromine atom for lithium with *n*-butyllithium.

Degradation of the acetic acid (V) by cleavage with orthophosphoric acid was abandoned when work with model compounds, 5-mesitoylacenaphthene and 1-mesitoylnaphthalene, showed that the mesitoyl group was removed instead of the mesityl radical.



X

XI (R = OH)
XII (R = Br)
XIII (R = C_2H_5O)
XIV (R = $(C_6H_5)_3CO$)
XV (R = *p*-$ClC_6H_4CH_2O$)

Condensation of the 1,5-dibromo derivative (I) with ethyl malonate provided a route to the bromo acid (X), which was reduced to the corresponding alcohol (XI). The bromide (XII) was prepared as well as three ethers (XIII, XIV, and XV). Unsuccessful attempts were made to replace the bromine atom by the mesitoyl group in the triphenylmethyl ether (XIV).

5-Bromoacenaphthene, serving as a model compound, was converted to the mesitoyl derivative by bromine replacement.

5-Nitroacenaphthene was converted to the corresponding acenaphthylene. The latter, however, failed to react additively with hydrogen bromide or with ethyl malonate.

Apparently the conditions employed for the hypohalite oxidation of the bromo ketone (II) to the acid (X) were too vigorous, since 4-bromophthalic anhydride was produced.

EXPERIMENTAL[2]

1,5-Dibromoacenaphthene (I). This compound was made by treating 35 g. of 1-acetoxyacenaphthene (4) with 26.4 g. of bromine in glacial acetic acid. The dibromide crystallized from petroleum ether (b.p. 65–110°) in nearly colorless needles; m.p. 117.5–120.5°. The melting point given by Gault and Kalopissus, who developed the method (5), is 116–117°.

Anal.[3] Calc'd for $C_{12}H_8Br_2$: C, 46.19; H, 2.58.

Found: C, 46.02; H, 2.65.

1-Acetonyl-5-bromoacenaphthene (II). The procedure was patterned after that of Campbell, Corrigan, and Campbell (6) for 1-acetonylacenaphthene. To a solution of sodium ethoxide, prepared by dissolving 3.96 g. of sodium in 100 ml. of ethanol, was added 22.4 g. of ethyl acetoacetate. The solution was heated under reflux for 15 minutes and cooled in an ice-bath. A cold solution of 26.88 g. of 1,5-dibromoacenaphthene in a mixture of 115 ml. of anhydrous ether and 140 ml. of dry benzene was added and the resulting mixture was allowed to stand, with occasional shaking, for 40 hours in the refrigerator. It was then heated 4 hours under reflux; the solvents were distilled; and the residue was treated with 300 ml. of 1.2 *N* hydrochloric acid and extracted with three 75-ml. portions of ether. The ether solution was washed with 75 ml. of water, dried over sodium sulfate, concentrated to about 33 ml., and added, with stirring, over a period of 45 minutes to a boiling solution of 70 g. of potassium hydroxide in 370 ml. of water. The mixture was maintained at 95–105° for 5 hours, cooled, and extracted with three 150-ml. portions of ether. The ether solution was washed with 150 ml. of water and dried over magnesium sulfate. Removal of the solvent left a solid residue which crystallized from petroleum ether (b.p. 40–60°) in colorless needles; m.p. 61–62.5°; yield 75%.

Anal. Calc'd for $C_{15}H_{13}BrO$: C, 62.30; H, 4.53.

Found: C, 62.35; H, 4.63.

Oxidation of 1.0 g. of the methyl ketone (II) with potassium hypochlorite, prepared from 15 g. of calcium hypochlorite, was conducted by heating the mixture at 60–90° for 1 hour. The product was recrystallized from dilute acetic acid; m.p. 221.5–223°. The melting point of 4-bromonaphthalic anhydride was reported as 218–219° (7).

Anal. Calc'd for $C_{12}H_5BrO_3$: C, 52.01; H, 1.82.

Found: C, 52.24; H, 1.84.

The *dioxolane* (III) was prepared by the procedure of Stork and Conroy (8). A mixture of 6.31 g. of the bromo ketone (II), 20 ml. of ethylene glycol, 100 ml. of toluene, and 0.60 g.

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[2] All melting points are corrected.

[3] Microanalyses by Miss Emily Davis, Mrs. Jean Fortney, Mrs. K. Pih, Mrs. Esther Fett, Mrs. Lucy Chang, and Mr. Joseph Nemeth.

of *p*-toluenesulfonic acid monohydrate was heated under reflux for 17 hours under conditions permitting gradual distillation of water and of ethylene glycol. The toluene solution was treated with 4 g. of potassium carbonate and 50 ml. of water and the toluene layer was freed of solvents by evaporation. The dioxolane was a light yellow oil; b.p. 190–193° (0.6–0.7 mm.); n_D^{23} 1.6122; yield 86%.

Anal. Calc'd for $C_{17}H_{17}BrO_2$: C, 61.27; H, 5.14.
Found: C, 61.29; H, 5.29.

The 1-acetonyl-5-bromoacenaphthene was regenerated by heating a solution of the dioxolane in 50% ethanol with a little hydrochloric acid.

1-Acetonyl-5-mesitoylacenaphthene (IV) *A. From the dioxolane.* An ether solution of 0.042 mole of *n*-butyllithium (9) was added over a period of 10 minutes to a solution of 6.70 g. of the bromodioxolane (III) in 150 ml. of anhydrous ether. The mixture, which as the addition progressed changed from yellow to red then to brown, was stirred for 20 minutes, heated under reflux for 20 minutes, and cooled to below −50° with a mixture of acetone and solid carbon dioxide. The cooling and subsequent operations were conducted in an atmosphere of dry nitrogen. To the cold solution was added over a 5-minute period a solution of 17 g. of mesitoyl chloride in 30 ml. of anhydrous ether. The refrigeration was discontinued after 90 minutes and the dark brown mixture was stirred at room temperature for an additional 5 hours, cooled, and treated with a mixture of 30 g. of crushed ice and 30 ml. of concentrated hydrochloric acid. The ether layer was washed with 5% sodium bicarbonate solution to remove mesitoic acid, then washed with water, and dried over sodium sulfate. Removal of solvent left the diketone (IV) as a crystalline solid which, after repeated recrystallization from 95% ethanol, formed nearly colorless crystals; m.p. 145–149°.

B. From 1-bromo-5-mesitoylacenaphthene (VI). The procedure was very similar to that employed with the dibromide (I). From 16.95 of the bromoketone (VI), prepared by the method of Fuson and Mange (1), was obtained 9.80 g., or 57% of the diketone; m.p. 128–148°. Repeated recrystallization of this product from 95% ethanol raised the melting point to 146–150°.

Anal. Calc'd for $C_{25}H_{24}O_2$: C, 84.23; H, 6.79.
Found: C, 84.48; H, 6.76.

A mixture melting point determination with a sample of the diketone made from the dioxolane (III) showed no depression. The two samples have identical infrared spectra, with absorption bands at 1723 cm.$^{-1}$ and at 1651 cm.$^{-1}$ attributable to an ordinary ketone group and a hindered ketone group, respectively.[4]

5-Mesitoyl-1-acenaphtheneacetic acid (V) *A. From the diketone* (IV). From a haloform reaction on 2.14 g. of the diketone (VI) was obtained 0.05 g. of product; m.p. 191–199°. This material separated from ethyl acetate as yellow crystals; m.p. 205–208°. A mixture melting point with the compound obtained from 5-mesitoylacenaphthylene and ethyl malonate (1) showed no depression. The two samples have identical infrared spectra with absorption bands attributable to the acid group (1706 cm.$^{-1}$) and a hindered carbonyl group (1655 cm.$^{-1}$).

B. From the bromo ketone (VI). The procedure was very similar to that employed with ethyl acetoacetate. The crude ester formed from 9.6 g. of ethyl malonate and 11.37 g. of the bromo ketone (VI) was hydrolyzed with aqueous potassium hydroxide and the resulting acid was decarboxylated by heating with concentrated hydrochloric acid in glacial acetic acid. Dilution of the mixture with water precipitated the keto acid as a yellow powder; m.p. 196–202°; yield 74%. Several recrystallizations from ethyl acetate, treatment with decolorizing charcoal, and further recrystallization from nitromethane gave yellow crystals melting at 202–206°. A mixture melting point with the compound obtained from 5-mesitoylacenaphthylene and ethyl malonate (1) showed no depression. The infrared spectra of the two samples were identical, with absorption bands at 1706 cm.$^{-1}$ and at 1655 cm.$^{-1}$ attributable to the carboxyl group and a hindered carbonyl group, respectively.

[4] The infrared absorption spectra were determined and interpreted by Miss Helen P. Miklas.

1-Acetonyl-5-acenaphthenecarboxylic acid (VII). The lithium derivative of the dioxolane, prepared as in the synthesis of the diketone (IV), was poured on crushed solid carbon dioxide. The crude acid, isolated in 63% yield by usual procedures, separated from 95% ethanol as colorless crystals; m.p. 193.5–196°.

Anal. Calc'd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55.

Found: C, 75.52; H, 5.68.

Cleavage of 1-mesitoylnaphthalene. A mixture of 1.0 g. of the ketone and 40 ml. of 85% phosphoric acid was heated under reflux for 36 hours and then made slightly basic by addition of 20% sodium hydroxide solution. When subjected to steam-distillation the alkaline mixture yielded 0.35 g. (75%) of naphthalene. No acidic product was found.

Cleavage of 5-mesitoylacenaphthene. When 1.0 g. of this ketone was subjected to the cleavage procedure, acenaphthene was formed; m.p. 87–90°; yield 81%. A second cleavage product was not isolated.

4-Bromo-1-naphthaleneacetic acid (IX). The procedure given by Ogata, Okano, and Kitamura (10) was employed in this preparation. The bromination of 100 g. of 1-naphthaleneacetic acid in glacial acetic acid gave 37 g., or 26% of the bromo acid; m.p. 173–177°.

The *amide* separated from 95% ethanol as fine white needles; m.p. 196.5–198.5°. The melting point reported by Mayer and Sieglitz is 182° (3).

Anal. Calc'd for $C_{12}H_{10}BrNO$: C, 54.57; H, 3.82; N, 5.30.

Found: C, 54.56; H, 3.98; N, 5.22.

The bromo acid (IX) was obtained from the amide by hydrolysis with aqueous sodium hydroxide at reflux temperature.

5-Bromoacenaphthenone (VIII). A mixture of 8.30 g. of 4-bromo-1-naphthaleneacetic acid and 6.50 g. of phosphorus pentachloride gave, after removal of the phosphorus oxychloride, 9.6 g. of acid chloride. The crude acid chloride was dissolved in 20 ml. of carbon disulfide and added with stirring over a period of 10 minutes to a mixture of 6 g. of anhydrous aluminum chloride in 20 ml. of carbon disulfide. The mixture was stirred under reflux for 90 minutes and cooled. The complex was collected and decomposed with dilute hydrochloric acid. The bromo ketone, crystallized from benzene, amounted to 4.25 g., or 55% m.p. 173–177°. The melting point is given (3) as 174–175°.

5-Bromo-1-acenaphtheneacetic acid (X). The procedure given by Bachmann and Sheehan (11) for 1-acenaphtheneacetic acid was followed in this preparation. From 26.84 g. of the dibromide (I) was obtained 15.58 g., or 62% of the bromoacid (XI); m.p. 150.5–152°. Kalopissus and Gault, who described this compound, reported (2) a melting point of 158–159°.

Anal. Calc'd for $C_{14}H_{11}BrO_2$: C, 57.75; H, 3.81.

Found: C, 57.97; H, 3.83.

The *amide* separated from 50% ethanol as colorless crystals; m.p. 163.5–165.5°. The melting point given by Kalopissus and Gault (2) is 160°.

The bromo acid was regenerated from the amide by hydrolysis under reflux with aqueous sodium hydroxide.

1-(2-Hydroxyethyl)-5-bromoacenaphthene (XI). The procedure of Nystrom and Brown (12) was employed for the reduction of the bromoacid (XI) with lithium aluminum hydride. From 2.91 g. of the bromo acid there was obtained 2.25 g. (81%) of the alcohol; m.p. 86.5–89.5° after recrystallization of the crude product from a mixture of one part benzene and two parts petroleum ether (b.p. 65–110°).

Anal. Calc'd for $C_{14}H_{13}BrO$: C, 60.67; H, 4.73.

Found: C, 60.97; H, 4.68.

1-(2-Bromoethyl)-5-bromoacenaphthene (XII). A mixture of 4.15 g. of the alcohol (XI), 5 ml. of 48% hydrobromic acid, and 6 drops of concentrated sulfuric acid was heated under reflux for 1 hour. The mixture was extracted with ether, freed of acid, and dried. The bromide distilled as a yellow oil (b.p. 173–194° [0.35–0.40 mm.]) and solidified when allowed to stand. It was recrystallized from 95% ethanol; yield 57%; m.p. 51–59°. Further recrystallization of this material from 95% ethanol gave white needles; m.p. 65–67°.

Anal. Calc'd for $C_{14}H_{12}Br_2$: C, 49.44; H, 3.56.

Found: C, 49.63; H, 3.81.

1-(2-Ethoxyethyl)-5-bromoacenaphthene (XIII). A solution of 15.03 g. of the bromide (XII) in 400 ml. of absolute ethanol was added to a solution of sodium ethoxide prepared by adding 8.0 g. of sodium to 300 ml. of absolute ethanol and the resulting mixture was heated under reflux for 4 hours. Distillation of the solvent gave an ether-soluble residue which was washed and dried. The product was obtained in 88.5% yield as a yellow oil; b.p. 146–156° (0.25 mm.); n_D^{20} 1.6140.

Anal. Calc'd for $C_{16}H_{17}BrO$: C, 62.96; H, 5.62.

Found: C, 63.29; H, 5.52.

1-(2-Triphenylmethoxyethyl)-5-bromoacenaphthene (XIV). This ether was prepared from the alcohol (XI) by the method of Green and Green (13). A mixture of 8.31 g. of the alcohol, 8.37 g. of triphenylchloromethane, and 75 ml. of pyridine was heated under reflux for 1 hour. The product, precipitated by the addition of water, crystallized from acetone as tiny white needles; m.p. 144.5–146.5°; yield 51%.

Anal. Calc'd for $C_{33}H_{27}BrO$: C, 76.30; H, 5.24.

Found: C, 76.08; H, 5.39.

1-[2-(p-Chlorobenzyloxy)-ethyl]-5-bromoacenaphthene (XV). A mixture of 5.26 g. of the alcohol (XI), 0.43 g. of sodium, and 30 ml. of dry toluene was heated under reflux for 20 minutes and a solution of 3.85 g. of p-chlorobenzyl bromide in 20 ml. of toluene was added over ten minutes. The mixture was heated under reflux for 2 hours, extracted with ether, washed, and dried. The crude ether was distilled; b.p. 207–246° (0.25–0.3 mm.); m.p. 60–70°; yield 23.8%. The product separated from petroleum ether (b.p. 40–60°) as fine light yellow needles; m.p. 74–76°.

Anal. Calc'd for $C_{21}H_{18}BrClO$: C, 62.78; H, 4.52.

Found: C, 62.74; H, 4.62.

Replacement of the bromine atom in the triphenylmethyl ether (XIV) with the mesitoyl group was attempted in a manner very similar to the preparation of the diketone (IV) from the dioxolane. From 5.19 g. of the ether in a reaction performed at room temperature a crude product was obtained which was distilled. From the residue after distillation was was obtained 1.27 g. (52%) of triphenylmethane; m.p. 76–94°. The product separated from 95% ethanol as colorless crystals; m.p. 91–94°. None of the desired compound was isolated.

5-Mesitoylacenaphthene A. Grignard reaction. Acylation of the Grignard reagent from 2.33 g. of 5-bromoacenaphthene with 3.46 g. of mesitoyl chloride gave a few crystals of 5-mesitoylacenaphthene; m.p. 169.5–179°. The reported melting point (1) is 177–179°.

B. With n-butyllithium. According to the procedure used for the preparation of the diketone (IV) from the dioxolane, 6.23 g. of 5-bromoacenaphthene gave 0.88 g. (10.9%) of the ketone; m.p. 168.5–179°. Crystallization from methyl ethyl ketone gave white crystals; m.p. 175–179°.

1-Bromo-5-nitroacenaphthene. Nitration of 30.2 g. of acenaphthene according to the method of Morgan and Stanley (14) gave 24.4 g., or 61% of the product; m.p. 103–104.5°. Treatment of 6.0 g. of 5-nitroacenaphthene with N-bromosuccinimide according to a procedure given earlier (1) gave 2.4 g. (28.8%) of a yellow solid; m.p. 134–139°. The bromide separated from petroleum ether (b.p. 65–110°) in yellow crystals; m.p. 137–140°.

Anal. Calc'd for $C_{12}H_8BrNO_2$: C, 51.82; H, 2.90; N, 5.04.

Found: C, 51.99; H, 3.19; N, 5.18.

5-Nitroacenaphthylene. A mixture of 2.8 g. of the bromonitro compound and 15 ml. of pyridine was heated for 5 hours on a steam-cone and then heated under reflux for 2 hours. The isolation of the product was achieved by the procedure used for 5-mesitoylacenaphthylene (1). The product separated from 95% ethanol as red needles; m.p. 113–114.5°; yield 60%.

Anal. Calc'd for $C_{12}H_7NO_2$: C, 73.09; H, 3.58; N, 7.10.

Found: C, 73.03; H, 3.82; N, 7.12.

Neither hydrogen bromide nor ethyl malonate could be condensed with the acenaphthylene as in the case of the 5-mesitoylacenaphthylene (1).

SUMMARY

5-Mesitoyl-1-acenaphtheneacetic acid has been synthesized by two independent methods. The preparation of 5-nitroacenaphthylene and of several 1,5-disubstituted acenaphthenes has been described.

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