

styrene bromohydrin by acetylation and dehydrohalogenation.

5. Attempts to polymerize a variety of α -

and β -substituted styrenes have been unsuccessful.

URBANA, ILLINOIS

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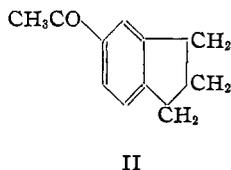
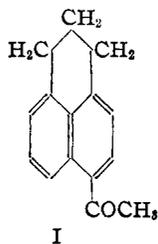
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Further Observations on the Use of Hydrogen Fluoride in Acylations and Cyclizations

BY LOUIS F. FIESER AND E. B. HERSHBERG¹

In a first paper² on this subject it was reported that acenaphthene can be acylated smoothly by reaction with various free acids, acid anhydrides and acid chlorides in the presence of liquid anhydrous hydrogen fluoride at room temperature. Under the same conditions, entirely negative results were obtained with benzene, naphthalene, phenanthrene, anthracene and 1,2-benzanthracene. These observations have now been extended, partly in the hope of casting further light on the remarkable specificity of acenaphthene in the reaction, and partly to see if any additional examples could be found of unusual orientations of practical synthetic value, as encountered in the acetylation of the above hydrocarbon by the hydrogen fluoride method.² We may state at the outset that no such applications have been discovered and that the theoretical interpretation still seems obscure.

Two other aromatic hydrocarbons which, like acenaphthene, contain an alicyclic side ring, have been found amenable to acylation under the above conditions. Perinaphthane reacted fairly readily with either acetic acid or acetic anhydride to give as the chief product a substance identified as the 4-aceto derivative I by oxidative degradation.



The orientation is thus the same as in the benzoylation of the hydrocarbon by the Friedel and Crafts (Perrier) method.³ Satisfactory condensation also occurred in the presence of hydrogen

fluoride between hydrindene and either acetic acid or benzoyl chloride, and again substitution took the normal course and gave the 5-derivatives, such as II. The direct substitution of an α -naphthoyl group in the 4-position of hydrindene would give a known ketone⁴ which is easily convertible into cholanthrene, but the total ketonic reaction product obtained with α -naphthoic acid and hydrogen fluoride yielded no hydrocarbon on pyrolysis and afforded on purification a crystalline substance which evidently is the 5-derivative.

It was next found that certain of the hydrocarbons which do not react at room temperature and atmospheric pressure can be acylated by conducting the condensation in an iron pressure vessel under reflux at temperatures up to that of the steam-bath. The acetylation of acenaphthene under these conditions was investigated for comparison and because of the usefulness in syntheses of the 1-aceto compound made available by this reaction. The condensation proceeded smoothly and 1-acetoacenaphthene was obtained in even better yield (37%) than at room temperature. The ketone was converted through the acid to the new 1-acenaphthaldehyde by the Rosenmund reaction. Using the pressure apparatus naphthalene and acetic anhydride gave a mixture of the α - and β -aceto compounds somewhat richer in the β -isomer than that obtained by the Friedel and Crafts method in carbon bisulfide solution⁵; the hydrocarbon did not react with succinic anhydride at moderate temperatures and tar formation occurred on attempting to push the reaction. At 50–55° phenanthrene and acetic anhydride gave a mixture from which the 2- and 3-acetyl compounds were isolated, as with aluminum chloride.⁶ A condensation of the hydrocarbon with crotonic acid was also effected giving an oil which appears to be a mixture of isomeric methylketo-

(1) Research Fellow on funds from the National Cancer Institute and the Eli Lilly Company.

(2) Fieser and Hershberg, *THIS JOURNAL*, **61**, 1272 (1939).

(3) Fieser and Hershberg, *ibid.*, **60**, 1658 (1938).

(4) Fieser and Seligman, *ibid.*, **57**, 2174 (1935).

(5) Fieser, Holmes and Newman, *ibid.*, **58**, 1055 (1936).

(6) Mosettig and van de Kamp, *ibid.*, **52**, 3704 (1930).

cyclopentenophenanthrenes. The special susceptibility shown by acenaphthene, perinaphthene and hydrindene in the acylation reaction, while still appearing rather remarkable, is thus seen to be a matter of degree rather than of kind.

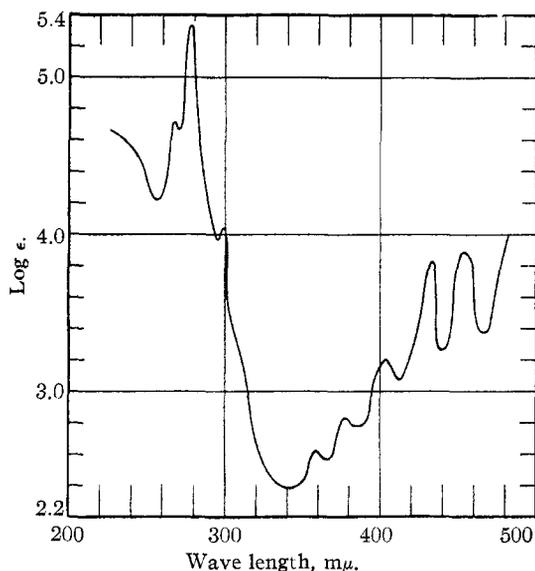
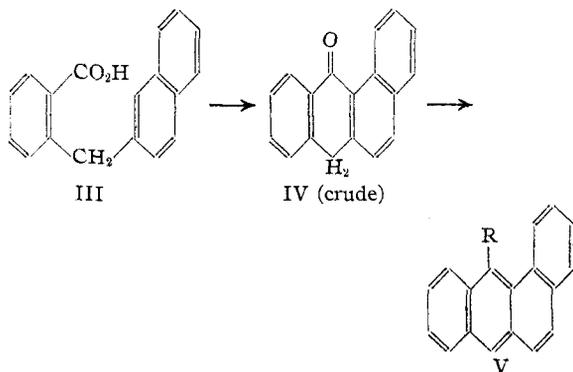


Fig. 1.—1',10-Dimethyl-2,3-benzanthracene in absolute alcohol. Principal maxima in $m\mu$ ($\log \epsilon$ values in parentheses): 278 (5.33), 299 (4.03), 359 (2.61), 378 (2.82), 403 (3.20), 433 (3.82), 454 (3.90).

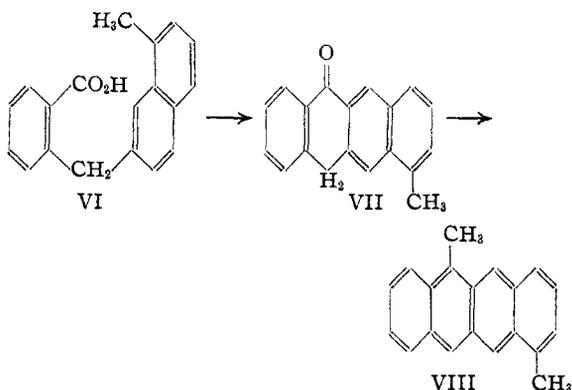
The hydrogen fluoride method² of cyclizing aromatic compounds with acidic side chains has found many useful applications.⁷ In view of the success in the preparation of 1,2-benzanthrones by this method in a condition suitable for the introduction of 10-alkyl substituents by the Grignard reaction,² we have investigated this possible route to 9-alkyl-1,2-benzanthracenes, with particular reference to the unknown 1',9-dimethyl



(7) For additional examples, see (a) Fieser and Johnson, *THIS JOURNAL*, **61**, 1647 (1939); (b) Fieser and Cason, *ibid.*, **61**, 1740 (1939); (c) Fieser, Joshel and Seligman, *ibid.*, **61**, 2134 (1939); (d) Fieser and Joshel, *ibid.*, **61**, 2959 (1939); (e) Calcott, Tinker and Linch, U. S. Patent 2,174,118 (1939).

compound. *o*-(β -Naphthylmethyl)-benzoic acid (III) was found to undergo rapid cyclization in hydrogen fluoride at room temperature, but the anthrone IV proved to be a very sensitive substance and was not isolated as such. By pumping the mixture to dryness decomposition and isomerization attendant upon the manipulation of the material was minimized, and on treating the crude residue with Grignard reagent it was possible to obtain substituted hydrocarbons in significant if low yields. The known 9-methyl-1,2-benzanthracene⁸ was isolated in 14% yield, and the 9-allyl compound was obtained in 35% yield.

These results seemed sufficiently promising to warrant a further attempt to synthesize 1',9-dimethyl-1,2-benzanthracene from the previously described intermediate VI.⁹ It had been estab-



lished that on cyclization with zinc chloride and acetic anhydride this acid gives a 1,2-benzanthranlyl-10-acetate, but this could not be converted satisfactorily into the corresponding anthrone. On using hydrogen fluoride in the hope of obtaining the anthrone directly we were surprised to find that ring closure largely takes the alternate course and gives chiefly the naphthacene derivative VII and only a very small amount of the angular isomer (characterized as the quinone). The anthrone VII, like the parent substance,¹⁰ is stable in the ketonic form and easily purified, and on reaction with methylmagnesium chloride it gave a hydrocarbon which crystallized either in bronze plates or in the form of fiery red needles of striking beauty.

That the substance has the linear rather than the angular structure was at once apparent from the ultraviolet absorption spectrum, kindly de-

(8) Newman, *THIS JOURNAL*, **59**, 1003 (1937); Cook, Robinson and Goulden, *J. Chem. Soc.*, 393 (1937).

(9) Fieser and Seligman, *THIS JOURNAL*, **60**, 170 (1938).

(10) Fieser, *ibid.*, **63**, 2329 (1931).

terminated by Mr. D. M. Bowen. The curve (Fig. 1) bears no resemblance to that of 1,2-benzanthracene but corresponds well in form with the absorption curve of naphthacene as reported by Radulescu and co-workers¹¹ and by Clar.¹² Compared with the parent hydrocarbon, the maxima for the dimethyl compound VIII are shifted about 7–8 $m\mu$ (av.) in the direction of longer wave lengths. The extinction coefficients found for VIII correspond with the values for naphthacene given by Clar rather than the distinctly lower values reported by Radulescu. Chemical evidence for the linear structure was also obtained, for the anthrone VII gave on oxidation a quinone isomeric with the known 1'-methyl-1,2-benzanthraquinone⁹ and exhibiting the resistance to alkaline hydrosulfite characteristic of naphthacene-quinone.¹⁰

Experimental Part¹³

3-Acetoperinaphthane (I).—A mixture of 10 g. of perinaphthane³ in 5 cc. of dry ether, 6.1 g. of acetic anhydride, and 200 g. of hydrogen fluoride was stirred mechanically for sixty hours at room temperature, fresh hydrogen fluoride being added to replace that lost by evaporation. The solution was then evaporated on the steam-bath and the product taken up in benzene, washed with dilute alkali, and distilled. A fore-run of 1.3 g. (perinaphthane) was collected up to 160° (2 mm.) and the ketone fraction boiled at 170–175°; yield 9.1 g. (71%).

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.69; H, 6.72. Found: C, 85.28; H, 6.66.

Acetic acid gave similar results. Trial runs with no solvent to serve as a diluent were less satisfactory.

The ketone forms an easily dissociated picrate in ether-ligroin and no complex was obtained in methanol.

The **trinitrobenzene derivative** separated from methanol in yellow needles of m. p. 114–114.5°.

Anal. Calcd. for $C_{15}H_{14}O \cdot C_6H_3O_6N_3$: N, 10.22. Found: N, 9.82.

Oxidation to **4-aceto-1,8-naphthalic anhydride** was accomplished by warming a solution of 1.0 g. of the ketone and 7.5 g. of anhydrous sodium dichromate in 25 cc. of acetic acid to 75–90° until the first vigorous reaction was over and then refluxing for two hours. The anhydride slowly separated after cooling and three crystallizations from benzene-ligroin gave yellow micro-needles, m. p. 193–195°. The substance has been reported as melting at 189°¹⁴ or 191–192°¹⁵; the 2-aceto isomer^{7b} melts considerably higher.

3-Perinaphthoic acid was obtained by shaking the ketone with potassium hypochlorite solution until dissolved.

(11) Radulescu, Ostrogovich and Barbulescu, *Ber.*, **64**, 2240 (1931).

(12) Clar, *ibid.*, **65**, 503 (1932).

(13) All melting points are corrected. Microanalyses by Lyon Southworth and Herbert S. Wight.

(14) Graebe and Haas, *Ann.*, **327**, 94 (1903).

(15) Dziewonski and Piasecki, *Bull. intern. acad. polon. sci. classe sci. math. nat.*, **A**, 287 (1932).

The acid after four crystallizations from benzene-ligroin formed pale yellow needles, m. p. 188.4–189°.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.25; H, 5.70. Found: C, 78.89; H, 5.83.

Acylation of Hydrindene. (a) **5-Aceto Compound.**—From 46.4 g. of hydrindene, 27 g. of acetic acid, and 600 g. of hydrogen fluoride there was obtained after a reaction time of sixty-four hours at room temperature 46.2 g. (73%) of 5-acetohydrindene, b. p. 134–137° (8 mm.). A 2-g. portion of the material, oxidized with hot hypochlorite solution, gave 1.3 g. of hydrindene-5-carboxylic acid, m. p. 172–178°; recrystallized from dilute alcohol, m. p. 179.5–181.5° (compare 178–179°¹⁶; the 4-isomer melts at 152.5–153.5°).¹⁷

(b) **Benzoylation.**—Treated with one equivalent of benzoyl chloride and excess hydrogen fluoride at room temperature for thirty-six hours, 11.6 g. of hydrindene gave 16.5 g. (75%) of a colorless ketone, b. p. 203–204° (8 mm.) and 1.75 g. of benzoic acid was recovered from the alkaline extract. The material seems to consist very largely of 5-benzoylhydrindene, for 1.0 g. of the ketone treated with hydroxylamine in pyridine-alcohol gave 1.1 g. of once crystallized oxime which, after a second crystallization from benzene-ligroin, melted at 149–152° (compare 153–154°).¹⁸

(c) **5-(α -Naphthoyl)-hydrindene** was prepared as above from the hydrocarbon (7 g.) and α -naphthoic acid (9.8 g.). After seventy-two hours at room temperature, 2.1 g. of α -naphthoic acid was recovered and the ketone, b. p. 255–265° (8 mm.), obtained as a pale yellow oil amounted to 11.0 g. (90%, allowing for the recovered acid). The oil crystallized after standing for several weeks and on recrystallization from ether-petroleum ether it formed rosetts of colorless needles, m. p. 71–72°.

Anal. Calcd. for $C_{20}H_{18}O$: C, 88.21; H, 5.92. Found: C, 88.23; H, 6.14.

Pyrolysis of the total distilled ketone under conditions suited for the Elbs reaction gave only tars and no cholanthrene could be detected.

Acetylation of Acenaphthene under Pressure.—The reaction vessel used was a welded steel cylinder with $\frac{1}{8}$ in. (3-mm.) walls. This was connected to a stainless steel condenser tube carrying a glass water jacket by means of a wrought steel union with a brass seat (large stainless steel unions could not be as easily disconnected after exposure to hydrogen fluoride). A tee connection at the top of the condenser tube carried a 200-lb. (13 atm.) pressure gage, but this did not withstand corrosion very well and was used only in pilot runs and then disconnected and a plug substituted. To the horizontal opening of the tee connection there was fitted a stainless steel needle valve leading, through a second wrought steel union, to a steel receiver which could be closed by a separate brass needle valve. A mixture of 61.6 g. of acenaphthene, 22 cc. of acetic anhydride, and 120 g. of hydrogen fluoride was heated in this pressure vessel under reflux on the steam-bath for one and one-half hours at a gage pressure of 60 lb. (4 atm.). The hydrogen fluoride was then allowed to distill into the receiver and the residue was taken up in

(16) Von Braun, Kirschbaum and Schuhmann, *Ber.*, **53**, 1155 (1920).

(17) Fieser and Seligman, *This Journal*, **59**, 394 (1937).

(18) Borsche and Pommer, *Ber.*, **54**, 102 (1921).

benzene, washed thoroughly but rapidly with water in a glass separatory funnel and distilled. The total ketone fraction, b. p. 190–200° at 6 mm., weighed 54.7 g. (78%) and on two crystallizations from methanol afforded 23.6 g. of 1-acetoacenaphthene, m. p. 103–104.5°, and 2.3 g., m. p. 101.5–104.5° (yield, 37%). A fore-run of 6.7 g. consisted largely of acenaphthene.

1-Acenaphthaldehyde.—A solution of 7.5 g. of 1-acenaphthoyl chloride in 75 cc. of xylene, to which was added 0.35 g. of 2% palladium catalyst on barium sulfate and 0.075 cc. of the quinoline-sulfur reagent,¹⁹ was stirred mechanically at 150–160° while passing in hydrogen. The evolution of hydrogen chloride continued for five and one-half hours, when 88% of the theoretical amount had been produced. After filtration and removal of the solvent at reduced pressure the product was distilled and the crude aldehyde (5 g., b. p. 150–165° at 2 mm.) dissolved in ether-benzene and stirred overnight with 75 cc. of saturated sodium bisulfite solution. The solid addition product was collected by centrifugation and decomposed with sodium carbonate solution, giving 4.5 g. (72%) of aldehyde, m. p. 93–99°. After five crystallizations from ether-oleum ether, the substance formed faintly yellowish dles, m. p. 99.5–100.5°.

Anal. Calcd. for $C_{13}H_{10}O$: C, 85.72; H, 5.54. Found: C, 85.29; H, 5.56.

β -Naphthaldehyde was obtained by the same procedure in 84% yield.

Naphthalene and Acetic Anhydride.—The hydrocarbon (12.8 g.) and anhydride (10.2 g.) were heated with hydrogen fluoride (100 g.) in the pressure bomb at 50–60° for sixty-eight hours. Distillation of the recovered and washed product gave a small fore-run of naphthalene and 4.9 g. of acetonaphthalene mixture, b. p. 155–165° (9 mm.). Oxidation with hypochlorite afforded 4.7 g. of naphthoic acid mixture, m. p. 145–168°, and on two crystallizations from dilute alcohol 2.9 g. of β -naphthoic acid, m. p. 182–184°, was obtained.

Phenanthrene and Acetic Anhydride.—From 35.6 g. of phenanthrene, 11 cc. of the anhydride, and 150 g. of hydrogen fluoride heated one hundred hours at 50–55° there was obtained 25.8 g. of recovered hydrocarbon and 9.3 g. (77% based on material consumed) of ketone, b. p. 180–210° (3 mm.). Crystallization from ether and from benzene-ligroin afforded 1.2 g. of 2-acetophenanthrene, m. p. 144–145°; the mother material when purified from methanol gave 3.6 g. of the 3-isomer, m. p. 70.5–71.5°. The latter substance gave a large depression when mixed with 9-acetophenanthrene (m. p. 74°).

Phenanthrene (17.8 g.) and crotonic acid in equivalent amounts were heated with hydrogen fluoride (100 g.) for forty-three hours at 40–50 lb. (3 atm.) pressure. The reagent was evaporated, the product taken up in benzene, and the blue organic layer washed with alkali and distilled, giving 8.4 g. of phenanthrene, b. p. 140–200° (2 mm.), and 6.4 g. of ketone, b. p. 210–240°. The redistilled material was an orange oil, b. p. 215–225° (2 mm.).

Anal. Calcd. for $C_{13}H_{14}O$: C, 87.78; H, 5.73. Found: C, 87.42; H, 5.88.

(19) Rosenmund and Zetzsche, *Ber.*, **54**, 425 (1921).

***o*-(β -Naphthoyl)-benzoic acid** was prepared from 29 g. of β -bromonaphthalene and 23 g. of phthalic anhydride by the Grignard procedure²⁰ in 37% yield. It crystallized from benzene in small needles containing combined solvent; this complex melted at 129–131° with loss of benzene, resolidified and melted at 166–167° (compare 168°).²⁰

Anal. Calcd. for $C_{13}H_{12}O_3 \cdot \frac{1}{2}C_6H_6$: C, 80.00; H, 4.79. Found: C, 80.14; H, 5.01.

***o*-(β -Naphthylmethyl)-benzoic Acid (III).**—The keto acid (9 g.) was refluxed for sixteen hours with 200 cc. of water containing 20 g. of sodium hydroxide, 12 g. of zinc dust and a trace of copper sulfate. Capryl alcohol (2–3 cc.) was helpful in preventing foaming and was distilled off prior to filtration and acidification. The product was taken up in ether-benzene and the solution extracted with soda; precipitation gave 7.3 g. (97%) of good acid, m. p. 134–138°. After two crystallizations from dilute acetic acid the substance formed glistening white leaflets melting at 134–136°, and remelting after solidification at 139.5–140°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 82.42; H, 5.34. Found: C, 82.59; H, 5.47.

The acid was previously prepared in poor yield by another method by King²¹ (m. p. 136–137°).

9-Methyl-1,2-benzanthracene.—The best procedure found consisted in dissolving 2.5 g. of the acid III in 18 g. of hydrogen fluoride in a platinum cylinder, allowing the solution to stand at room temperature for one hour, and removing the reagent by placing the cylinder in a large glass test-tube and evaporating at the water pump. An ethereal solution of methylmagnesium chloride from 2.5 g. of metal was then added to the residue in the platinum container and after suitable time for reaction the mixture was worked up in the usual manner²² and the hydrocarbon obtained as bright yellow prisms, m. p. 136–137.5°; yield 0.32 g. (14%). This did not depress the melting point of Newman's material.⁸

9-Allyl-1,2-benzanthracene was prepared from 3.8 g. of III as above but allowing only twenty minutes for cyclization before evaporating the hydrogen fluoride and adding the Grignard reagent (16 g. allyl bromide). The yield of hydrocarbon, m. p. 111–115°, was 1.4 g. (35%). The purified substance separated from ligroin in pale yellow aggregates, m. p. 115–116°.

Anal. Calcd. for $C_{21}H_{18}$: C, 94.00; H, 6.01. Found: C, 94.26; H, 6.23.

***o*-(8-Methyl-2-naphthylmethyl)-benzoic Acid (VI).**⁹—In repeating the previous synthesis 1-methyl-7-bromonaphthalene was prepared from 100 g. of the dihydride according to Fieser and Seligman,⁹ and after fractionation the naphthalene derivative was isolated from the mixture as the trinitrobenzene derivative. The complex forms yellow blades from methanol, m. p. 92.5–93°.

Anal. Calcd. for $C_{11}H_9Br \cdot C_6H_5O_2N_3$: N, 9.70. Found: N, 9.35.

This was cleaved by reduction with stannous chloride in hydrochloric acid, giving 10.9 g. of pure 1-methyl-7-

(20) Weizmann, Bergmann and Bergmann, *J. Chem. Soc.*, 1367 (1935).

(21) King, *This Journal*, **49**, 562 (1927).

(22) Fieser and Hershberg, *ibid.*, **59**, 1028 (1937).

bromonaphthalene (liquid). On reaction with magnesium and then phthalic anhydride, this afforded 11.4 g. of hydrated keto acid, m. p. 110–120° (76%, assuming the substance to be a monohydrate). Reduction as above gave the acid VI, m. p. 142–143.5°, in 60% yield.

1'-Methyl-2,3-benz-10-anthrone (VII).—One gram of the methyl-naphthylmethylbenzoic acid VII was treated with hydrogen fluoride at room temperature and after seven minutes was poured onto ice and the light yellow solid was quickly collected and washed. A portion was crystallized from acetone and obtained in two polymorphic forms of the same m. p. 174–176°. Prisms separated when a saturated solution was cooled rapidly in the ice box, while slow crystallization at room temperature gave rise to needles. Recrystallized slowly, the anthrone formed pale yellow needles, melting at 175–176° when heated slowly but liquefying when immersed in a bath at 171°.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.35; H, 5.46. Found: C, 88.80; H, 5.63.

With alcoholic alkali the anthrone gives a characteristic¹⁰ purplish color which fades on shaking with air.

1'-Methyl-2,3-benzanthraquinone was obtained by oxidation of 100 mg. of the anthrone with 55 mg. of chromic anhydride in acetic acid. The substance crystallized from this solvent in orange-yellow needles, m. p. 227–229°. It gave no red color with aqueous hydrosulfite-alkali.

Anal. Calcd. for $C_{19}H_{12}O_2$: C, 83.80; H, 4.45. Found: C, 83.68; H, 4.66.

1',10-Dimethyl-2,3-benzanthracene (VIII).—After treatment of the crude anthrone VII with excess methylmagnesium chloride the collected product was passed in benzene solution through a tower charged with alumina mixed with Super-cel. On slow crystallization from absolute alcohol the hydrocarbon then formed brilliant, fiery red needles, m. p. 138–139°. When the alcoholic solution is cooled rapidly by cooling in ice the hydrocarbon separates in another modification which forms small, bronze-colored plates. This form melts when inserted in a

bath at 133° and then solidifies and remelts at the higher temperature. The solution in concentrated sulfuric acid is olive-green.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.82; H, 6.35.

The picrate forms purplish-black needles from absolute alcohol, m. p. 164–165°.

Anal. Calcd. for $C_{20}H_{16} \cdot C_6H_3O_7N_3$: N, 8.66. Found: N, 8.59.

The trinitrobenzene derivative resembles the picrate in appearance, m. p. 166.5–167.5° (absolute alcohol).

Anal. Calcd. for $C_{20}H_{16} \cdot C_6H_2O_6N_3$: N, 8.94. Found: N, 9.04.

When the total crude product of cyclization was treated with Grignard reagent there was obtained in addition to the hydrocarbon a small amount of 1'-methyl-1,2-benzanthraquinone.⁹

Summary

Perinaphthane and hydrindene can be acetylated in the presence of hydrogen fluoride at room temperature, and the acylation of naphthalene and phenanthrene can be accomplished in a pressure bomb at somewhat higher temperatures.

9-Methyl- and 9-allyl-1,2-benzanthracene were synthesized successfully by cyclizing *o*-(β -naphthylmethyl)-benzoic acid with hydrogen fluoride and treating the crude anthrone with Grignard reagent, but when this process was applied to *o*-(8-methyl-2-naphthylmethyl)-benzoic acid ring closure occurred chiefly in the alternate direction, giving rise to the linear isomer. 1',10-Dimethyl-2,3-benzanthracene exists in two modifications, one of which has a striking red color.

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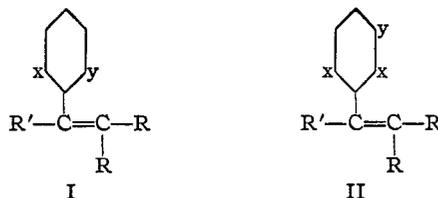
Restricted Rotation in Aryl Olefins. I. Preparation and Resolution of β -Chloro- β -(2,4,6-trimethyl-3-bromophenyl)- α -methylacrylic Acid

BY ROGER ADAMS AND M. W. MILLER¹

Molecular dissymmetry due to restricted rotation between the ring and the olefinic carbon in appropriately substituted aryl olefins of types I and II was postulated in a previous communication.² Synthetic difficulties in preparing such compounds proved to be great and no procedure was found which gave successful results. The

(1) Portion of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in chemistry; Eastman Kodak Fellow, 1939–1940.

(2) Maxwell and Adams, *THIS JOURNAL*, **52**, 2960 (1930).



introduction of an atom or group other than hydrogen for the R' was complicated when R, x and y represented substituents other than hydrogen.