[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Inter- and Intramolecular Acylations with Hydrogen Fluoride

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In a preliminary report by Calcott, Tinker and Weinmayr[2] it was stated that liquid anhydrous hydrogen fluoride can be used both in place of sulfuric acid and in cases where this reagent is ineffective to promote various peri condensations of aromatic compounds with acrolein. Since we recently worked on the preparation of perinaphthenone[3] by the sulfuric acid procedure,[4] the statement that hydrogen fluoride can be employed to effect the condensation of β-naphthol with acrolein led us to experiment with the reagent. Although our preliminary trials with this condensation were not promising, we soon became interested in exploring other possible synthetic uses of the reagent and found that liquid hydrogen fluoride can be used with distinct success for the cyclization of many acids to ketones of the α-hydrindone, α-tetralone, and anthrone types.

For a proper evaluation of the new method it seems desirable to call attention to certain limitations in the methods of cyclization already available. One of the most generally useful procedures consists in treating the acid in benzene, nitrobenzene, or chlorobenzene with phosphorus pentachloride, followed by aluminum chloride[5]; the use of thionyl chloride in the first step is perhaps less advantageous, for it may be necessary to conduct the reaction in ether with pyridine as a catalyst,[6] to remove the thionyl chloride very completely prior to the cyclization,[6a,7] and to avoid undesirable side reactions.[8] With a sufficiently reactive aromatic nucleus aluminum chloride can be replaced by the less destructive stannic chloride,[6b,d] and F. C. Novello in this Laboratory has recently found that in the preparation of 4′-keto-1,2,3,4-tetrahydro-3,4-benzpyrene the phosphorus pentachloride procedure[9] can be combined advantageously with treatment with stannic chloride[6b,7] (90–95% yield). The acid chloride method, while very generally serviceable, has failed in some instances, for example with γ-(4-methoxy-3-diphenyl)-butyric acid,[10] and in other cases has the disadvantage of giving rise to tars or to products of dehydrogenation. This is perhaps an even more serious objection to the method of cyclization by heating the free acid with stannic chloride at 120°[11] or with zinc chloride at 180°.[11a,12] Cyclization by heating the acid with these active condensing agents, or, in certain instances, by heating the pre-formed acid chloride alone,[13] is often destructive of the material and the yields are seldom high. A dehydrogenating action of the reagent was observed by Cook and Hewett[14] in the cyclization of α-naphthylpropionic acid with stannic chloride, or by treatment of the acid chloride with aluminum chloride.

The direct dehydration of γ-arylbutyric acids has been accomplished in some instances with phosphorus pentoxide in organic solvents such as benzene, or toluene,[15] or in sirupy phosphoric acid,[16] but the generality of the procedures has hardly been demonstrated. The method of ring closure with 85–95% sulfuric acid[17] is quite convenient, gives clean products, and in some cases the yields are good. Frequently, however, much material is lost by sulfonation. In the preparation of α-tetralone, for example, the yield as reported by various investigators[14,17b,18] is only 27-50% using sulfuric acid, as compared to 91%

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

(2) Calcott, Tinker and Weinmayr, THIS JOURNAL, **61**, 949 (1939).

(3) Our suggested nomenclature[4] for compounds of this series was unfortunately misquoted by Klyne and R. Robinson, *J. Chem. Soc.*, 1991 (1938).

(4) Fieser and Hershberg, THIS JOURNAL, **60**, 1658 (1938).

(5) An early instance of the use of this procedure is reported by v. Braun, Blessing and Cahn, *Ber.*, **57**, 908 (1924). Recent examples: Adelson and Bogert, THIS JOURNAL, **59**, 399 (1937); Burger and Mosettig, *ibid.*, **59**, 1302 (1937); Bachmann, *J. Org. Chem.*, **3**, 434 (1938); Fieser and Johnson, THIS JOURNAL, **61**, 168 (1939).

(6) (a) Fieser and Peters, *ibid.*, **54**, 4373 (1932); (b) Fieser and Fieser, *ibid.*, **57**, 782 (1935); (c) Carré, *Compt. rend.*, **199**, 1422 (1934); (d) Bachmann, Ref. 5.

(7) Fieser, Hershberg, Long and Newman, THIS JOURNAL, **59**, 475 (1937).

(8) Fieser and Desreux, *ibid.*, **60**, 2253 (1938).

(9) Vollmann, Becker, Corell and Streeck, *Ann.*, **531**, 1 (1937).

(10) Fieser and Bradsher, THIS JOURNAL, **58**, 1738 (1936).

(11) (a) Cook and Hewett, *J. Chem. Soc.*, 398 (1933); (b) Hoch, *Compt. rend.*, **205**, 65 (1937).

(12) Cook, *J. Chem. Soc.*, 1087 (1930).

(13) Schroeter, *Ber.*, **57**, 2003, 2025 (1924); Schroeter, Müller and Huang, *ibid.*, **62**, 645 (1929).

(14) Cook and Hewett, *J. Chem. Soc.*, 365 (1934).

(15) Examples: Haberland and co-workers, *Ber.*, **71**, 470, 2619 (1938); Wahl, *Compt. rend.*, **206**, 683 (1938); Weizmann, E. Bergmann and Kleinert, THIS JOURNAL, **60**, 1331 (1938).

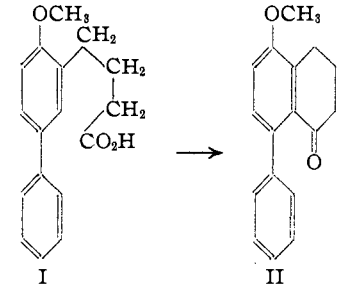
(16) Koebner and R. Robinson, *J. Chem. Soc.*, 1994 (1938).

(17) (a) W. v. Miller and Rohde, *Ber.*, **23**, 1887 (1890); (b) Krollpfeiffer and Shäfer, *ibid.*, **56**, 624 (1923); (c) Haworth, *J. Chem. Soc.*, 1125 (1932).

(18) Horne and Shriner, THIS JOURNAL, **55**, 4652 (1933).

by intramolecular Friedel and Crafts reaction.[19] As applied to the preparation of an anthrone or 1,2-benzanthrone, the method is often unsatisfactory both because of the sulfonating action of the reagent and because difficultly removed traces of this active acid promote decomposition and changes in the sensitive keto–enol system. This deleterious catalytic action is not overcome when sulfonation is inhibited by diluting the sulfuric acid with acetic acid or sirupy phosphoric acid.[20] A much superior method, particularly for the preparation of 1,2-benzanthracene derivatives, consists in catalytic cyclization in the presence of acetic anhydride and results in the formation of the anthranyl acetate. As catalyst Scholl and Meyer[21] used small amounts of hydrochloric or hydriodic acid, while the present authors[20,22] employed zinc chloride.[23,24] The only shortcoming of this scheme is that in case the anthrone is desired for synthetic operations its isolation from the anthranyl acetate by hydrolysis and isomerization is not easy and sometimes cannot be accomplished.[25] Catalytic cyclization with zinc chloride in acetic acid-anhydride has been applied successfully to some acids of the type $Ar(CH_2)_n$-COOH, giving ketones,[20,22] but some of the acids tried have been recovered unchanged. An as yet isolated instance of the cyclization of a γ-arylbutyric acid with hydriodic acid has been reported recently by R. Robinson and Walker.[26]

Bearing in mind this background of experiences with other reagents, we undertook to test the applicability of the method of cyclization with hydrogen fluoride in a few representative cases. The reactions were conducted simply by treating the organic acid in a platinum flask with about 10–30 parts of commercial anhydrous liquid hydrogen fluoride run from a cooled tank through a copper tube. The acids dissolved easily and stirring was not required. After standing at room temperature for a few hours or overnight, any hydrogen fluoride still present usually was largely removed by evaporation on the steam-bath. Soda was then added and the product collected or extracted and purified. Treated in this way γ-phenylbutyric acid gave pure α-tetralone in 92% yield and hydrocinnamic acid was converted into α-hydrindone in 73% yield. These results contrast with the poor yields of α-tetralone obtained in various laboratories by the sulfuric acid method, as noted above, and with the observation of v. Miller and Rohde[17a] that hydrocinnamic acid yields no α-hydrindone when treated with this reagent. With γ-(3-acenaphthyl)-butyric acid, cyclization with hydrogen fluoride gave pure ketotetrahydroacephenanthrene in 88% yield, a result comparable with that obtained by the action of aluminum chloride on the pure acid chloride[6a] (87%), and somewhat better than by catalytic cyclization with zinc chloride[22] (78%). γ-(4-Methoxy-3-diphenyl)-butyric acid (I) provided an interesting test case,



I II

for attempts to close the ring with sulfuric acid of various concentrations or through the acid chloride have been entirely unsuccessful.[6] With hydrogen fluoride the ketone II was obtained without difficulty.

Similar cyclizations with hydrogen fluoride have been carried out with distinct success by other workers in this Laboratory in the course of various investigations in progress. The results will be described later, but some idea of the generality of the method can be given by stating that excellent yields of ketones have been obtained from the following acids: γ-(9,10-dihydro-2-phenanthryl)-butyric acid, γ-(2-phenanthryl)-butyric acid, and γ-(9,10-dihydro-2-phenanthryl)valeric acid (W. S. Johnson); γ-(9-phenan-

(19) Martin and Fieser, *Org. Syntheses*, **15**, 77 (1935).

(20) Fieser and Hershberg, THIS JOURNAL, **59**, 1028 (1937).

(21) Scholl and Meyer, *Ber.*, **65**, 1398 (1932); Scholl, v. Hornuff and Meyer, *ibid.*, **69**, 707, 712 (1936); Scholl and Meyer, *ibid.*, **71**, 1482 (1938).

(22) Fieser and Hershberg, THIS JOURNAL, **60**, 1893 (1938).

(23) Scholl and Meyer (1938) suggest that this reagent suffers acetolysis with liberation of hydrogen chloride and that our method therefore may be a modification of theirs. Although adequate data are not yet available for comparison, we have made one experiment which provides some indication that zinc chloride probably is the active catalyst. γ-(3-Acenaphthyl)-butyric acid, which can be cyclized smoothly by our procedure,[22] was recovered unchanged on application of the method of Scholl and Meyer using hydrogen chloride as catalyst.

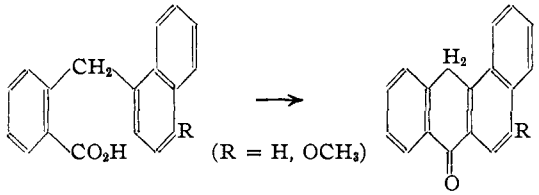
(24) A somewhat similar acetylative cyclization was accomplished with acetic anhydride-sulfuric acid by Beschke, *Ann.*, **384**, 143 (1911), in his synthesis of 6,12-diacetoxychrysene. An acetoxydihydrochrysene was similarly obtained by Newman, THIS JOURNAL, **60**, 2947 (1938), by cyclization of an unsaturated acid by the zinc chloride procedure.[20]

(25) Fieser and Seligman, *ibid.*, **60**, 170 (1938).

(26) R. Robinson and Walker, *J. Chem. Soc.*, 183 (1938).

thryl)-butyric acid (Dr. L. M. Joshel); γ-(3-pyrenyl)-butyric acid (F. C. Novello); β-(1-naphthyl)-propionic acid (M. D. Gates, Jr.). With acids having a saturated side chain, such as the γ-arylbutyric acids and β-arylpropionic acids, no instances of failure have as yet been encountered. A typical β-aroylpropionic acid was recovered unchanged. This was anticipated, since such acids are resistant to the ordinary methods of cyclization; the conversion of γ-(3-acenaphthoyl)-propionic acid into *peri*-succinoylacenaphthene[27] with molten sodium–aluminum chloride is probably the only example on record of such a reaction. On the other hand, it was somewhat surprising to find that *o*-benzoylbenzoic acid is completely unaltered by hydrogen fluoride. One ring closure of another type was investigated briefly by Dr. Joshel. 1-(β-1′-Naphthylethyl)-cyclohexanol underwent cyclodehydration under the influence of hydrogen fluoride and the product gave chrysene (in poor yield) on dehydrogenation with selenium (compare Cook and Hewett[14]).

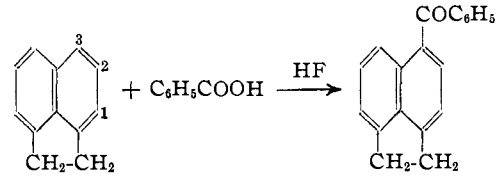
We were particularly interested in the possibility of preparing anthrones of use as intermediates in the synthesis of carcinogenic hydrocarbons. It was found that anthrone itself can be prepared in 82% yield by the action of liquid hydrogen fluoride on *o*-benzylbenzoic acid, but of course this parent substance is readily available by other methods. Of real importance is the observation that 2-(α-naphthylmethyl)-benzoic acid (III, R = H) can be converted by this method



III IV

into pure 1,2-benz-10-anthrone in 68–75% yield. Previous investigations have shown that cyclization of this acid with zinc chloride[12] or sulfuric acid[20] gives very crude products which cannot be purified, and the only previous route to the pure anthrone was by the laborious and somewhat wasteful process of cleaving the pure anthranyl acetate with a Grignard reagent and partially isomerizing the liberated anthranol.[20] By the present method the keto form is produced directly in such a condition that it can be purified with ease. Aside from the absence of a substitution akin to a sulfonation, hydrogen fluoride does not seem to have a destructive action on this sensitive type of product. Very good results were obtained also in the preparation of 3-methoxy-1,2-benz-10-anthrone[20] (IV, R = OCH_3), there being no attack on the methoxyl group. With this improvement in the preparation of the anthrones, the interesting carcinogens obtainable from them by the Grignard reaction are rendered very readily available.[27a] It now seems worth while to reinvestigate the possibility of synthesizing 9-alkyl-1,2-benzanthracenes by the same method.[25]

The success attained in effecting intramolecular acylations with the use of hydrogen fluoride suggested the possibility of condensing aromatic hydrocarbons with free carboxylic acids under the influence of this reagent. The choice of acenaphthene for first trial proved to be a fortunate one, for among the hydrocarbons thus far investigated this is one of the few which enter into reaction, at least at room temperature. From a mixture of acenaphthene and acetic acid, treated with a large volume of hydrogen fluoride and allowed to stand for about three days with occasional stirring until the hydrocarbon had dissolved, there was obtained in 94% yield a mixture of acetoacenaphthenes (see below). Benzoic acid, in an experiment continued for only two and one-half hours, gave nearly pure 3-benzoylacenaphthene in 62% yield, and less than 10% of unchanged acid was recovered. In a parallel experiment with benzoyl chloride conducted under the same



conditions the yield of distilled ketone was 87% and no acid was recovered. This condensation with an acid chloride, which proceeds in much the fashion of the Friedel and Crafts ketone synthesis and with the same orientation to the 3-position,[28] is similar to the alkylations of aromatic hydrocarbons with alkyl halides in the presence of hy-

(27) Fieser and Peters, THIS JOURNAL, **54**, 4347 (1932).

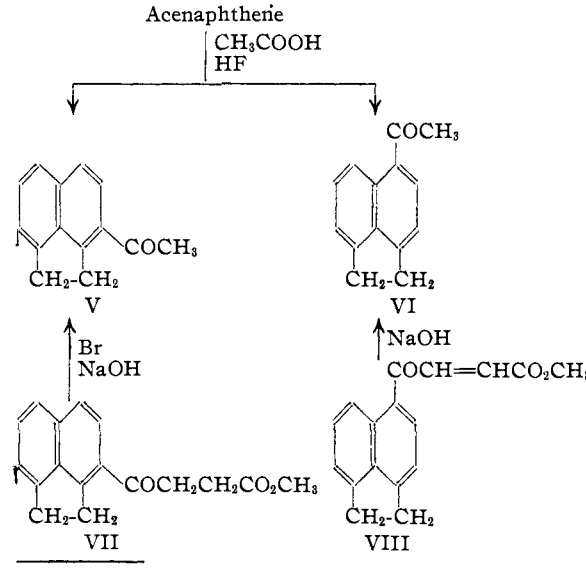
(27a) E. Bergmann and T. Berlin's recent statement that we[20] "found appreciable difficulty in introducing methyl radicals via their magnesium derivates into various anthrones" (in contrast to results with phenyl lithium) is misleading. With the anthrone available in the pure keto-form no difficulty is encountered in the actual condensation with alkylmagnesium halides.

(28) Graebe and Haas, *Ann.*, **327**, 91 (1903).

drogen fluoride described by Simons and Archer[29] in the course of their investigations of the use of this substance as a condensing agent. In the acylations conducted with a free carboxylic acid it is possible that this first undergoes dehydration and that the anhydride is the active acylating agent, but from present indications there seems to be but little advantage in the use of an acid chloride or anhydride rather than an acid. From succinic anhydride and acenaphthene we obtained by the hydrogen fluoride method a mixture consisting largely of β-(3-acenaphthoyl)-propionic acid with a smaller amount of the 1-isomer, the proportion being about the same as obtained with the use of aluminum chloride as the condensing agent.[27]

Acenaphthene also reacts with crotonic acid in the presence of hydrogen fluoride, but before commenting on certain interesting features of this reaction and of the acetylation it will be well to record the negative experiments with other hydrocarbons. Following the above procedure (excess hydrogen fluoride, room temperature), no reaction was noted between phthalic anhydride and benzene (two hours) or between benzoic acid and benzene (fourteen hours). The condensation of benzoic acid with hydroquinone yielded hydroquinone monobenzoate, which is an indication that hydrogen fluoride, at least at a low temperature, does not promote the Fries rearrangement of an acyl group into a benzenoid nucleus. Naphthalene, under the usual conditions, failed to condense with succinic anhydride or crotonic acid (up to twenty hours). Benzene and naphthalene are of course less reactive than acenaphthene, but it was surprising to obtain negative results with certain of the higher hydrocarbons, particularly in view of the successful cyclizations involving substitution even into a benzenoid nucleus. Phenanthrene was recovered unchanged after treatment with the reagent in nitrobenzene solution or on adding β-chloropropionyl chloride to a suspension of the hydrocarbon in hydrogen fluoride, although the addition caused it to dissolve (Mary Fieser). Solution of the hydrocarbon without any noticeable reaction was also observed on attempted condensation with acetyl chloride (W. S. Johnson). Negative results were also obtained with 9,10-dihydrophenanthrene and acetyl chloride (W. S. Johnson), anthracene and chloroacetyl chloride (H. M. Irwin), and with 1,2-benzanthracene and oxalic acid (E. B. H.) Further experiments of course will be required to define the limits of the reaction even under the set of conditions employed and it remains to be seen if condensation can be caused to occur by raising the temperature, using solvents, or employing added catalysts. The present results, however, do indicate that acenaphthene occupies a rather unique position among the hydrocarbons mentioned.[29a] We have noted further that acenaphthene in the presence of liquid hydrogen fluoride seems to react with acrylic acid, maleic anhydride, malonic acid, and formic acid, but the conditions appeared too drastic in these cases and in the preliminary tests no pure products were isolated.

As was noted above, the orientation in both the benzoylation and succinoylation of acenaphthene is exactly the same in the condensations with hydrogen fluoride as in the Friedel and Crafts reaction, the 3-isomer being the sole product in the former case and the predominant isomer in the latter. This parallelism does not hold for the acetylation. The distilled product from the hydrogen fluoride reaction when crystallized from alcohol or ether–ligroin yielded in the less soluble fraction an easily isolated and purified ketone melting at 105°, and this proved to be the hitherto unknown 1-acetoacenaphthene (V). In contrast



(29) Simons, Archer, *et al.*, THIS JOURNAL, **60**, 986, 2952, 2953, 2955, 2956 (1938).

(29a) Since this paper was written hydrindene and perinaphthane have been found to condense smoothly with benzoyl chloride and with acetic acid under the influence of hydrogen fluoride and the acylation of less reactive hydrocarbons has been accomplished at higher temperatures.

to the results of all previous acylations of the hydrocarbon, the yield of the 1-isomer amounted to no less than 25% of the theoretical. From the mother liquors a considerable quantity of the 3-isomer (VI) was isolated in the form of an orange picrate. The identity of the two ketones was established by reference to the known products of the succinoylation of the hydrocarbon.[27] Methyl β-(3-acenaphthoyl)-propionate was previously[27] converted by bromination and elimination of hydrogen bromide into methyl β-(3-acenaphthoyl)-acrylate (VIII). It has now been found that this unsaturated keto ester is cleaved smoothly by alcoholic alkali to 3-acetoacenaphthene (VI), paralleling the behavior of β-benzoylacrylic acid.[30] The substance can be obtained in an equally pure condition by the action of alcoholic alkali on crude methyl β-bromo-β-(3-acenaphthoyl)-propionate. The ketone, which was further characterized by conversion to the known 3-acenaphthoic acid and iodoform, proved to be identical with the more soluble isomer obtained in the acetylation with hydrogen fluoride. A ketone identical with the less soluble isomer (V) was similarly obtained by the alkaline cleavage of the crude bromination product from methyl β-(1-acenaphthoyl)-propionate[27] (VII).

By the Friedel and Crafts reaction of acenaphthene and acetyl chloride in carbon bisulfide solution, Graebe and Haas[28] obtained a substance melting at 75° which they regarded as pure 3-acetoacenaphthene, and the same melting point has been observed by other workers.[31] Our ketone, prepared either by the degradation of an acid of established purity and structure or from the purified picrate obtained from the acetylation mixture, exists in two interconvertible polymorphic forms melting at 57 and 70°. Since the Friedel and Crafts reaction product has not previously been purified by the apparently efficacious method of conversion to the picrate, we investigated this point and found that the product of reaction in nitrobenzene solution yields a large amount of an orange picrate identical with that of our sample of 3-acetoacenaphthene; from the mother liquor there was isolated a very small amount of 1-acetoacenaphthene. It is therefore probable that the substance obtained by previous workers and purified merely by distillation and crystallization consisted largely of 3-acetoacenaphthene, but was contaminated with a small amount of the less soluble 1-isomer.

Heretofore the best route to 1-substituted acenaphthene derivatives has been by the nitration of the hydrocarbon in a large volume of acetic anhydride according to Morgan and Harrison,[32] but the process is tedious and the yield low, the crude 1-nitro compound obtained in 22% yield requiring extensive purification. The Sandmeyer reactions of the 1-amine proceed either rather poorly (halides[32,33]) or to a negligible extent (cyanide, observation of present authors), and the reactions of the Grignard and lithium derivatives are far from smooth.[33,34] The discovery of a very simple and rapid method of preparing the pure 1-aceto compound in 25% yield is therefore of considerable practical importance. The ketone has been converted smoothly into the new 1-acenaphthoic acid, and other derivatives are under investigation, particularly those affording new routes to the synthesis of cholanthrenes and other hydrocarbons of interest as possible carcinogens.

By the condensation of acenaphthene with crotonic acid in the presence of hydrogen fluoride we obtained in 62% yield (pure) a nicely crystalline ketone (m. p. 167°) having the composition of a crotonylacenaphthene but giving no tests for unsaturation. This suggested the presence of a new ring, and the observation that the low-melting hydrocarbon obtained on Clemmensen reduction gave no crystalline product on dehydrogenation with selenium or palladium charcoal provided some indication, but clearly no proof, that this is either a five-membered or peri ring. On oxidation with dichromate the ketone was converted into an acetonaphthalene tricarboxylic acid, and this on hypohalite oxidation gave a naphthalene tetracarboxylic acid. The latter acid readily formed a dianhydride but proved to be quite different from the known naphthalene-1,4,5,8-tetracarboxylic acid, an observation which eliminates the possibility of a peri condensation. The new ring therefore must have been closed across either the 1,2- or 2,3-position. The acetyl group of the initial oxidation product must have arisen from the fragment —$CH(CH_3)$—, the carbon atom joined to the nucleus being that in the β-position of the crotonyl group. In order to locate this fragment further the aceto com-

(30) H. v. Pechmann, *Ber.*, **15**, 885 (1882); Bougault, *Ann. chim.*, [8] **15**, 502 (1902).

(31) Dziewoński and Reiss, *Bull. intern. acad. polon. sci.*, **A**, 62 (1930).

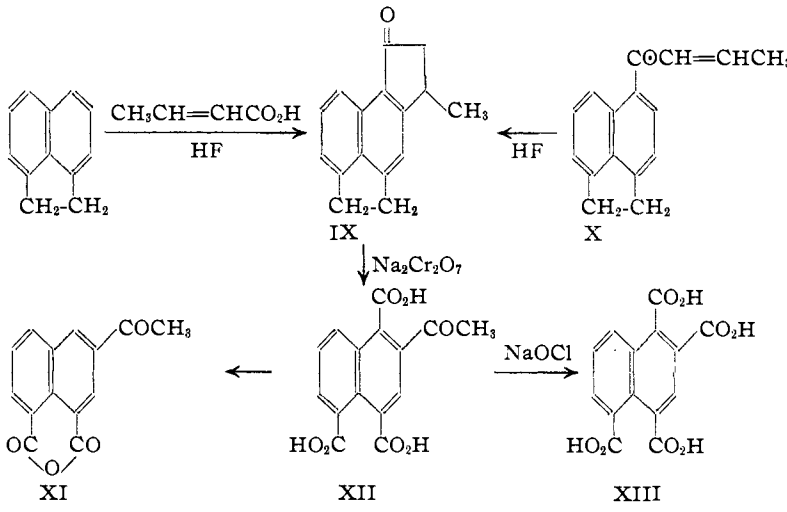
(32) Morgan and Harrison, *J. Soc. Chem. Ind.*, **49**, 413T (1930).

(33) Fieser and Hershberg, THIS JOURNAL, **57**, 1681 (1935).

(34) Cook, Haslewood and Robinson, *J. Chem. Soc.*, 667 (1935).

pound was partially decarboxylated; the product proved to be the anhydride of an acetonaphthalene dicarboxylic acid different from the known 4-aceto-1,8-naphthalic anhydride,[35] which rules out a possible addition of acenaphthene at the 3-position to the unsaturated acid, with subsequent intramolecular acylation. There remained the possibility of a similar ring formation at positions 2 and 3, or initial acylation in either the 1- or 3-position followed by intramolecular addition to the double bond of the side chain.

Since the second mode of reaction seemed the more likely, acenaphthene was converted by the Friedel and Crafts reaction into a crotonyl derivative and the presence of the substituent at the 3-position was established by permanganate



oxidation to the anhydride of naphthalene-1,4,5-tricarboxylic acid. It was then found that 3-crotonylacenaphthene (X) can be cyclized with hydrogen fluoride and yields a product identical with the ketone in question. The substance therefore is 1′-methyl-3′-keto-2,3-cyclopentenoacenaphthene, IX, and the structures of the various degradation products are as shown in the chart.

It thus appears that the initial reaction with crotonic acid consists in an acylation at the 3-position and that the orientation is the same as with benzoic acid rather than acetic acid. It is hard to say whether the unsaturated character of the two similarly acting acids is significant or merely coincidental, but it is at least interesting that succinic anhydride behaves to some extent like acetic acid in giving an appreciable amount of 1-substitution. That hydrogen fluoride effects the cyclization of the 3-crotonyl derivative (X) is not surprising, but the direction of the ring closure would hardly have been anticipated. From the ready formation of 3,4-dinitroacenaphthene[32] and the peri cyclization of β-(3-acenaphthoyl)-propionic acid,[27] it would seem that the more normal direction of ring closure would be to the peri position. Mayer and Müller[36] formulated as 1,2-cyclopentenonaphthalene derivatives various ketones obtained by crotonylation and subsequent ring closure with aluminum chloride or sulfuric acid, but the structures were not established; no cyclization product was obtained from acenaphthene. The ready conversion of the hydrocarbon into a ketone on reaction with crotonic acid and hydrogen fluoride suggests other applications, although the negative results recorded above indicate that the reaction may be specific to a restricted type of structure. Even where the initial substitution fails, however, the reagent may have some value for the cyclization of unsaturated ketones obtained by other methods, although the observation that methyl β-(3-acenaphthoyl)-propionate (VIII) was recovered unchanged in a trial experiment may indicate that there are limitations in this step as well.

Experimental Part[37]

The following experiments were conducted in an open platinum container without provision for reflux. Commercial anhydrous hydrogen fluoride obtained from Kinetic Chemicals, Inc., was used without purification and stored in a cold room at 5°. The vessel containing the acid to be cyclized was tared on a rough balance in the hood and charged with the required weight of reagent run from the inverted tank through a copper tube, using goggles and rubber gloves. If the material did not dissolve at once or after occasional stirring with a metal spatula a mechanical metal stirrer could be inserted. If much reagent still remained after allowing ample time for reaction, the excess usually was evaporated by gentle heating over a steam-bath. The solution also can be poured into water containing a little ice and the product quickly extracted with ether or collected by suction filtration, although in

(35) Dziewoński and Piasecki, *Bull. intern. acad. polon. sci.*, **A**, 287 (1932).

(36) Mayer and Müller, *Ber.*, **60**, 2278 (1927).

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

general it seemed best to remove or neutralize the reagent before making a transfer to glass.

α-Tetralone.—γ-Phenylbutyric acid (5 g.) dissolved in hydrogen fluoride (100 g.) to give a light yellow solution which had become orange-brown after standing for sixteen hours at room temperature. The excess reagent was evaporated and the residue was taken up in ether and poured into a separatory funnel containing dilute alkali. Distillation of the neutral fraction gave 4.1 g. (92%) of α-tetralone, b. p. 121–123° at 8 mm.

α-Hydrindone.—Treated as above for twenty-six hours, 5 g. of hydrocinnamic acid gave 3.2 g. (73%) of the ketone, b. p. 118–119° at 10 mm.

1-Keto-1,2,3,4-tetrahydro-8,9-acephenanthrene.—A solution (deep reddish-brown) of 7 g. of γ-(3-acenaphthyl)-butyric acid in 200 g. of hydrogen fluoride was allowed to stand for three and one-half hours and poured onto ice. The precipitated solid was collected quickly, washed well, and crystallized from dilute acetic acid, giving 5.7 g. (88%) of the ketone in the form of long flat needles, m. p. 143–145°.

5-Methoxy-8-phenyltetralone-1 (II) was obtained from 1 g. of γ-(4-methoxy-3-diphenyl)-butyric acid (I) and 30 g. of hydrogen fluoride. After five hours the red-orange solution was evaporated and the residue treated with ether and sodium carbonate solution. Two crystallizations of the neutral product from ether–ligroin gave 0.15 g. of colorless leaflets, m. p. 120–120.5°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.94; H, 6.39. Found: C, 80.80; H, 6.51.

1,2-Benz-10-anthrone.—2-(α-Naphthylmethyl)-benzoic acid (5 g.) was dissolved in hydrogen fluoride (50 g.) and after ten minutes the solution was poured onto ice. The moist solid was dissolved in 400 cc. of acetone, and after clarification with Norite the solution was concentrated to about 200 cc. and cooled slowly to −10°. This gave 3.5 g. (75%) of pale yellow needles of the anthrone, m. p. 181–182°. In another experiment with 13.5 g. of the acid (one hour) the yield was 68%.

Since **10-methyl-1,2-benzanthracene** heretofore has not been prepared in quantity from the pure anthrone, the following experiment may be recorded. A suspension of 10 g. of 1,2-benz-10-anthrone in 75 cc. of benzene was added to a stirred solution of Grignard reagent from 3 g. of magnesium and excess methyl chloride. After refluxing overnight and distilling the hydrolyzed product there was obtained 9.3 g. of yellow solid, b. p. 230–240° at 1 mm. When a benzene solution of this material was passed through a tower of activated alumina there was a significant yellow zone which appeared to consist of 1,2-benz-10-anthranol, probably arising from the isomerizing action of the Grignard reagent. The filtrate was concentrated and diluted with ligroin, giving 5.3 g. of very pure hydrocarbon in the form of long needles, m. p. 140–141°, and a smaller crop (0.3 g.), m. p. 138–140°, was obtained from the mother liquor; yield 56%. The main product was more nearly colorless than any of the samples previously prepared in this Laboratory[20,38] and is distinctly less colored than any of the homologs described[20] except the *n*-propyl compound. The latter is completely devoid of color; the present sample of the methyl compound is very nearly so, but by careful observation of the material in bulk one can discern a faint yellowish tinge in the channels of the crystalline mass.

Anthrone, prepared as above and crystallized from benzene–ligroin, was obtained as pale greenish-yellow prisms, m. p. 154–156°; yield 82%.

3-Methoxy-1,2-benz-10-anthrone.—The material from 2.2 g. of 2-(4′-methoxy-1′-naphthylmethyl)-benzoic acid and 50 g. of hydrogen fluoride was dissolved while moist in 200 cc. of acetone, the solution was concentrated to about 50 cc. and diluted with a little water. This gave 1.2 g. (58%) of the anthrone in the form of pale yellow needles, m. p. 176–177°.

3-Benzoylacenaphthene.—The orange-red solution resulting from 3 g. of powdered acenaphthene, 2.4 g. of benzoic acid, and 40 g. of hydrogen fluoride was poured onto ice after two and one-half hours and the product taken up in ether. Extraction with soda gave 0.2 g. of benzoic acid and the neutral fraction yielded 2.9 g. (62%) of solid distillate, m. p. 88–93°. Crystallized from benzene, the ketone melted at 98.5–99.5° (compare 101°).[28]

In another experiment 2.7 g. of benzoyl chloride was added to a suspension of 3 g. of acenaphthene in 100 g. of hydrogen fluoride and after two and one-half hours the product was worked up as before, giving 4.4 g. (87%) of distillate. The crystallized material (3.5 g., 70%) melted at 98–99°.

Acenaphthene and Succinic Anhydride.—A mixture of 3 g. of the hydrocarbon, 1.95 g. of the anhydride, and 100 g. of reagent was evaporated after fifteen hours, giving 2.4 g. (49%) of crude solid, m. p. 193–197°. Separation through the sodium salt[27] gave 2 g. of γ-(3-acenaphthoyl)-propionic acid, m. p. 202–205°, while the 1-isomer was recovered from the mother liquor material by conversion to the methyl ester (0.15 g.), m. p. 122–124°.

Hydroquinone monobenzoate was obtained as a product of the reaction of hydroquinone (5.5 g.) with benzoic acid (6.1 g.) in hydrogen fluoride (100 g.), continued for twenty hours. After evaporation, the portion not extracted by bicarbonate was crystallized from hot water, giving 1 g. (9%) of the monobenzoate, m. p. 165–166°.

1-Acetoacenaphthene (V).—A mixture of 15.4 g. of powdered acenaphthene and 6 g. of acetic acid in 300 g. of hydrogen fluoride was allowed to stand for sixty hours, with occasional stirring at the start. The deep green solution was evaporated and the residue washed in ether with sodium carbonate solution and distilled. There was obtained 18.4 g. (94%) of oil, b. p. 154–155° at 1 mm., which solidified in the receiver. After two crystallizations from methanol (50 cc.) and one from ether–ligroin, the top fraction melted at 102–104°; yield, 4.9 g. (25%). Crystallized to constant melting point from ether–ligroin, 1-acetoacenaphthene formed thick prisms, m. p. 104.7–105.2°.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.73; H, 6.17. Found: C, 85.78; H, 6.40.

On the addition of picric acid to the alcoholic mother liquor there was obtained 3.8 g. of the orange picrate (m. p. 94–96°) of 3-acetoacenaphthene, identified by comparison with the sample described below. A small amount of a yellow picrate was also encountered; a further study of this substance, and of other derivatives and proper-

(38) Fieser and Newman, THIS JOURNAL, **58**, 2376 (1936).

ties of the two ketones, has been undertaken by Dr. J. Cason and will be reported later.

1-Acenaphthoic Acid.—Iodine–potassium iodide solution was added to a solution of 1 g. of the above ketone in 50 cc. of dioxane at room temperature. There was an immediate discharge of color, and after an excess of reagent had been added the solution was warmed to 60°, diluted, filtered from precipitated iodoform, and acidified. The crude acid (0.7 g.) was crystallized twice from acetic acid and once from toluene to give small colorless prisms, m. p. 256–257°.

Anal. Calcd. for $C_{13}H_{10}O_2$: C, 78.76; H, 5.09. Found: C, 78.51; H, 5.14.

Preparation of the Acetonaphthalenes by Other Methods (L. F. F.) (a) 3-Acetoacenaphthene.—In the first experiments on the alkaline cleavage of methyl β-(3-acenaphthoyl)-acrylate[27] or methyl β-bromo-β-(3-acenaphthoyl)-propionate[27] only the low-melting form of 3-acetoacenaphthalene was encountered. Thus 0.5 g. of either the unsaturated ester or the bromo ester (powdered) was suspended in 5 cc. of alcohol and treated with 3 cc. of 25% sodium hydroxide solution and allowed to stand overnight, stirring occasionally at the start until the solid had dissolved. The weakly yellow solution on dilution with water gave an emulsion, and on cooling and scratching the oil solidified to a yellowish crystalline solid. This was dissolved in methanol and the solution was clarified with Norite, cooled, and diluted well with water; the resulting emulsion on standing slowly gave rise to glistening, colorless plates (0.17 g.). The samples from both sources melted at 57–58°. A sample for analysis was prepared from 5 g. of the bromo ester in the same way, extracted with ether and distilled, giving 1 g. of light yellow oil which soon solidified. This was crystallized from petroleum ether (very soluble, yellow product, m. p. 57–58°), twice from dilute methanol (colorless plates, m. p. 58.5–59°), and finally from petroleum ether, giving clusters of heavy prisms, m. p. 59–59.5°.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.73; H, 6.17. Found: C, 85.88; H, 6.35.

On a later (one week) occasion a sample was prepared by adding alkali to a suspension of the ester (1 g.) in boiling alcohol and, when the material had all dissolved, diluting the brown solution to a volume of about 75 cc. The oil slowly crystallized and when collected on the next day and washed well with water there was obtained 0.37 g. of colorless solid, m. p. 66–67°. Crystallized twice from dilute alcohol this formed thin plates resembling the earlier samples but melting at 69.5–70°. The above analytical sample was then reëxamined and found to melt sharply at 69.5–70° when heated slowly, but showing some prior softening when introduced above 60°. There was no depression, and both samples were then found to solidify very slowly and to then remelt at temperatures below 70°. After several repetitions, or after briefer heating at a higher temperature, solidification occurred very rapidly and the melting point became constant at 57–57.5°.

An **orange picrate of 3-acetoacenaphthene** was obtained from alcohol as a crust of orange prisms, m. p. 97.5–98° (constant).

Anal. Calcd. for $C_{14}H_{12}O \cdot C_6H_3O_7N_3$: N, 9.88. Found: N, 9.82.

The **trinitrobenzene derivative** crystallized from alcohol as clusters of rather stout yellow needles, m. p. 112–113°.

Anal. Calcd. for $C_{14}H_{12}O \cdot C_6H_3O_6N_3$: N, 10.26. Found: N, 10.40.

For further characterization the ketone was treated with hypoiodite in dioxane and gave iodoform (m. p. 121–122°) and **3-acenaphthoic acid,** m. p. 222–223°.

(b) 1-Acetoacenaphthene by Degradation.—Methyl β-(1-acenaphthoyl)-propionate was brominated as described for the isomer[27] and the bromo ester crystallized once from ligroin (yellowish prisms, m. p. 103°, dec.). Without further purification this crude bromo ester (2 g.) was stirred with alcohol and alkali as above until dissolved, and after several hours the solution was diluted. The product was sticky but gave good needles from dilute alcohol, m. p. 102.5–103.5° (0.22 g.). Recrystallized from methanol, this formed prisms, m. p. 103–104°, giving no depression with the sample obtained in the acetylation with hydrogen fluoride.

(c) Friedel and Crafts Reaction.—In an orienting experiment carried out chiefly to see if both ketones are produced in the reaction, 15.4 g. of acenaphthene in 90 cc. of nitrobenzene was iced and treated with 8 g. of acetyl chloride and 14 g. of aluminum chloride (two hours in the ice-bath and three hours at 25°). Since a considerable amount of a granular complex had separated this was collected on a sintered glass funnel and washed with benzene. The resulting clean orange powder when decomposed with dilute acid gave 7.4 g. of nearly colorless ketone, m. p. 61–65°. Treated with an equal weight of picric acid in alcohol this gave 9.9 g. of the orange picrate of 3-acetoacenaphthene, m. p. 94–95°. After three recrystallizations the sample melted at 97–97.5° and did not depress the above sample; the recovered ketone was crystallized repeatedly from dilute alcohol and from ether (clusters of plates) and melted constantly at 69.5–70° and, after several repetitions of the fusion, at 57–57.5°. On removing the picric acid from the material in the first alcoholic mother liquor and crystallizing the ketone mixture several times from alcohol there was obtained a small amount of 1-acetoacenaphthene in the form of colorless prisms, m. p. 103.5–104.5° (no depression with above sample). This ketone shows no change on repeated fusion and the melt solidifies at once.

The nitrobenzene filtrate from the reaction mixture was worked up as usual; the distilled product (6.9 g., m. p. 50–53°) gave 11.9 g. of crude orange picrate of the 3-aceto compound, and a small amount of the yellow picrate observed in the hydrogen fluoride reaction.

The experiment shows that the 3-isomer is the chief product but that a small amount of the 1-isomer is also formed. Since the 3-isomer is much the more soluble of the two, purification by crystallization[28,31] does not seem feasible; the separation of the aluminum halide complex, at least from nitrobenzene, is incomplete and seems to offer little advantage. The 3-isomer, however, can be isolated in a pure form through the picrate; indeed Graebe and Haas[28] obtained a picrate (m. p. 95°) of nearly the same properties as ours from a ketone preparation (m. p. 75°) which probably contained some of the higher melting isomer.

1′-Methyl-3′-keto-2,3-cyclopentenoacenaphthene (IX). (a) From Acenaphthene.—A mixture of 30.8 g. of powdered

acenaphthene and 17.2 g. of crotonic acid in 200 g. of hydrogen fluoride was allowed to stand at room temperature for twenty-four hours (occasional stirring at the start) and the deep reddish-brown solution was then evaporated to dryness. The residue was taken up in benzene, extracted with soda solution, and distilled, giving 37.1 g. of pale yellow liquid, b. p. 185–200° at 2 mm., which soon solidified. On crystallization from benzene–ligroin there was obtained 27.6 g. (62%) of colorless flat needles, m. p. 165–167° and on further purification from this solvent or methanol the substance melted constantly at 167–167.5°. The compound is unaffected by bromine in chloroform or permanganate in acetone.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.50; H, 6.35; mol. wt., 222. Found: C, 86.55; H, 6.59; mol. wt. (Rast), 227.

(b) **From 3-Crotonylacenaphthene.**—From 1 g. of the unsaturated ketone, after treatment with hydrogen fluoride for twenty-four hours, there was obtained by extraction of the residue and crystallization from methanol 0.5 g. of the ketone IX, m. p. 163–164°. The recrystallized product melted at 166.5–167° and gave no depression with the sample described in (a).

3-Crotonylacenaphthene was prepared from 15.4 g. of acenaphthene and 10.5 g. of crotonyl chloride in 200 cc. of carbon bisulfide, treated at 10–15° with 14 g. of aluminum chloride, added slowly. A dark brown complex separated after a short time, and this was collected, washed with carbon bisulfide, and decomposed with ice and acid. Extraction with ether and distillation gave 9.5 g. (43%) of oil, b. p. 188–190° at 2 mm., which slowly solidified. Crystallization from dilute methanol and then from methanol alone with good cooling afforded 5.2 g. (23%) of nearly colorless crystalline aggregates, m. p. 63–63.5°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.50; H, 6.35. Found: C, 86.34; H, 6.34.

To establish the structure, 0.5 g. of finely powdered ketone was shaken for fifteen hours with 2.5 g. of potassium permanganate in 100 cc. of water containing 0.5 cc. of 6 *N* sodium hydroxide. The solution was then filtered (colorless), made acid with sulfuric acid, and boiled. It soon became cloudy and the **anhydride of naphthalene-1,4,5-tricarboxylic acid** separated. This crystallized from acetic acid containing a few drops of acetic anhydride in the form of yellow leaflets, m. p. 274–275° (75 mg.), and it did not depress the m. p. of a known sample.[27]

1′-Methyl-2,3-cyclopentenoacenaphthene.—Reduction of the ketone IX (5 g.) with amalgamated zinc using water (10 cc.), concentrated hydrochloric acid (25 cc., with 35 cc. added later), toluene (15 cc.), and acetic acid (0.5 cc.) was conducted for twenty-four hours at the boiling point. The organic layer was separated and distilled, giving 4 g. (85%) of colorless oil, b. p. 143–148° at 1 mm., which solidified after standing overnight. It crystallized from dilute methanol as colorless cottony needles, m. p. 38–38.5°.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.51; H, 8.12.

The **trinitrobenzene derivative** formed slender, bright orange needles from alcohol, m. p. 113–114°.

Anal. Calcd. for $C_{16}H_{16}\cdot C_6H_3O_6N_3$: N, 9.98. Found: N, 10.21.

2-Acetonaphthalene-1,4,5-tricarboxylic Acid.—A solution of 5 g. of the ketone IX in 100 cc. of glacial acetic acid was treated with 40 g. of anhydrous sodium dichromate, added in portions with some cooling to keep the temperature below 100°. After the initial vigorous reaction had subsided the solution was refluxed for two and one-half hours and the viscous green solution was then diluted with 300–400 cc. of water and 100 cc. of concentrated hydrochloric acid, boiled for one hour, and allowed to stand at room temperature. The separation of the oxidation product was very slow, but after two days a quantity of the material had crystallized in the form of light yellow prisms; yield, 1.95 g. (29%). The sample melted when inserted into a bath at 160°, but when heated slowly it melted at 189–191°. As the substance could not be recrystallized very satisfactorily owing to the tendency to form the anhydride, the sample was analyzed as obtained.

Anal. Calcd. for $C_{15}H_{10}O_7$: C, 59.59; H, 3.33; neut. equivalent (tribasic), 101. Found: C, 59.11; H, 3.42; neut. equivalent, 103.

The **anhydride** was prepared by heating the acid at 200–220° for a few minutes and crystallizing the product from benzene. It formed small, pale yellow aggregates which became opaque on drying, m. p. 217–218°.

Anal. Calcd. for $C_{15}H_8O_6$: C, 63.39; H, 2.84. Found: C, 63.61; H, 3.07.

The **monomethyl ester anhydride** was obtained by allowing a suspension of the tribasic acid in an ethereal solution of diazomethane to stand at 0° for eight hours, the solid changing in appearance and forming a powder. After evaporating the ether the residue was crystallized from benzene, giving colorless needles, m. p. 261–262°.

Anal. Calcd. for $C_{16}H_{10}O_6$: C, 64.42; H, 3.39. Found: C, 64.12; H, 3.62.

3-Aceto-1,8-naphthalic Anhydride (XI).—A solution of 0.5 g. of the anhydride of 2-acetonaphthalene-1,4,5-tricarboxylic acid in 2 cc. of refluxing quinoline was treated with successive small portions of basic copper carbonate. Gas evolution was rapid at first but diminished considerably after ten minutes, and since the solution then began to darken the process was stopped. The quinoline was extracted with dilute acid from a black residue, and this was collected and crystallized from acetic acid, using a liberal quantity of Darco. Greenish-yellow prisms resulted, m. p. 215–217°, and further crystallization from benzene gave glistening yellow diamond-shaped prisms, m. p. 217.5–218.5°.

Anal. Calcd. for $C_{14}H_8O_4$: C, 70.00; H, 3.36. Found: C, 69.90; H, 3.53.

Naphthalene-1,2,4,5-tetracarboxylic Acid.—A solution of 0.8 g. of 2-acetonaphthalene-1,4,5-tricarboxylic acid in 50 cc. of water and 5 cc. of 6 *N* alkali was allowed to stand at room temperature for three hours with excess sodium hypochlorite solution. After short warming, the pale yellow solution was cooled, treated with bisulfite, and acidified. On standing overnight 0.65 g. of the tetrabasic acid separated in a good condition as a pale tan microcrystalline product. Titration with alkali gave the neutralization equivalent 74 (calcd. for a tetrabasic acid, 76), but the carbon value was about 1% too high, indicating the presence of some anhydride. The crude acid melts at

once when immersed in a bath at 250°, but melts at 262–262.5° when heated slowly.

The **dianhydride** was obtained as straw colored needles, m. p. 262.5–263°, by crystallization of the tetrabasic acid from glacial acetic acid containing a few drops of acetic anhydride.

Anal. Calcd. for $C_{14}H_4O_6$: C, 62.68; H, 1.50. Found: C, 62.52; H, 1.71.

A **dimethyl ester anhydride** was obtained on treating 0.2 g. of the tetrabasic acid with diazomethane in ether (six hours at 0° with occasional shaking). The residue left on evaporation when crystallized twice from benzene formed glistening colorless plates, m. p. 219.5–220.5°.

Anal. Calcd. for $C_{16}H_{10}O_7$: C, 61.16; H, 3.21. Found: C, 61.03; H, 3.40.

Summary

Liquid hydrogen fluoride is an excellent reagent for the cyclization of a number of γ-arylbutyric acids and β-arylpropionic acids. A particularly significant use of the reagent is in the preparation of 1,2-benz-10-anthrones by the cyclization of appropriate acids, for these important intermediates in the synthesis of carcinogenic hydrocarbons are thereby rendered readily available in the pure keto form.

Certain intermolecular hydrocarbon acylations with free acids, anhydrides, or acid chlorides also can be brought about under the influence of hydrogen fluoride at room temperature. The reaction is not general under these conditions for negative results have been obtained with several common hydrocarbons. Acenaphthene reacts readily, giving benzoyl, acetyl, and succinoyl derivatives in good yield. In most cases the orientation is the same as in the Friedel and Crafts reaction, but the condensation with acetic acid takes a different course. Due to this fortunate circumstance and to favorable solubility relationships, the hitherto unknown 1-acetoacenaphthene can be prepared easily in 25% yield.

Acenaphthene reacts smoothly with crotonic acid in the presence of hydrogen fluoride to give 1′-methyl-3′-keto-2,3-cyclopentenoacenaphthene.

CONVERSE MEMORIAL LABORATORY
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The Reduction of α-Diketones

BY R. B. THOMPSON

Since dimesityl diketone was first synthesized,[1] several papers have appeared showing that it fails to undergo many of the reactions typical of α-diketones. Thus Kohler and Baltzly[1] found that it forms a monoxime with difficulty, and does not undergo a benzilic acid rearrangement, give a quinoxaline derivative with *o*-phenylenediamine, react with Grignard reagents, or undergo reduction by hydrogen and platinum. Shortly afterward Fuson and Gray[2] prepared the diketone by a different method and confirmed its inertness toward the usual reagents.

A priori, there is no reason why reduction of dimesityl diketone should be difficult, since the hydrogen may add to the ends of the conjugated system. Numerous experiments have shown that the failure of mesityl compounds to participate in addition reactions is confined to those reactions in which the atoms attached to the ring are involved. Thus mesityl carboxylic acid is esterified with difficulty, but, in contrast, mesityl acetic acid reacts readily.[3] Even if reduction does not proceed through a 1,4-mechanism, 1,2-addition is entirely possible, since it has been shown that dimesityl ketone, in which hindrance to the carbonyl is at a maximum, is not especially difficult to reduce.[1]

$$(CH_3)_3C_6H_2COC_6H_2(CH_3)_3 \longrightarrow (CH_3)_3C_6H_2CH(OH)C_6H_2(CH_3)_3$$

Actually the reduction of dimesityl diketone proceeds readily in absolute methyl alcohol in the presence of platinum. The reaction stops when one mole of hydrogen has been absorbed, and the solution becomes colorless; in contact with air, however, it becomes yellow at once, and concentration of the solution gives the diketone in 95% yield.[4]

The only explanation for this anomaly is that the ene-diol II, in contrast with most compounds of its type, is unusually persistent.[5] The presence

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

(2) Fuson and Gray, *ibid.*, **56**, 739 (1934).

(3) Meyer, *Ber.*, **27**, 510 (1894); Meyer and Sudborough, *ibid.*, **27**, 1587 (1894).

(4) This experiment was completed in January, 1937, while the author was working under the direction of the late Professor E. P. Kohler.

(5) Fuson and Corse, THIS JOURNAL, **61**, 975 (1939).