trimethylbenzaldehyde is replaced by a larger group or atom. This aldehyde, and others containing two ortho methyl groups, gives typical aldehyde reactions albeit at reduced rates,[17] whereas the corresponding ketones and acid derivatives are characteristically unreactive. Thus the aldehyde group must be just on the border line between groups capable of free rotation and those not. However, as soon as a larger group, such as methyl or chlorine, is substituted for the aldehydic hydrogen, the steric hindrance to free rotation is greatly increased so that a coplanar orientation, favorable for a perpendicular approach, is no longer possible under moderate reaction conditions. In this connection it is interesting to note that mesitoyl chloride, although extremely reactive to alcoholysis,[18] does not react with diazomethane.[19] The explanation is that the former reaction undoubtedly involves ionization to yield an oxocarbonium ion,[20] $(CH_3)_3C_6H_2C^+{=}O$ which would not be sterically hindered according to the above arguments, whereas the latter reaction involves addition to the carbonyl group.

The author has applied the rule of six as above outlined and modified to a number of experimental observations in the literature and found that many seemingly anomalous facts are readily explained thereby. The utility of this rule seems to be undeniable but it is beyond the scope of this article to point out further examples or to go into further detail at present.[21]

Finally, it should be pointed out that the application of the rule of six and of the concept of the perpendicular approach is not necessarily limited to carbonyl-containing functions but may be applied to all doubly-bonded functions. For example, the resistance of *asym*-dineopentylethylene (six-number 18) to oxidation[22] is undoubtedly due to steric hindrance. In the steroid field, the lesser reactivity of the double bond in between carbons 22 and 23 of stigmasterol as compared to the double bond between carbons 5 and 6 may be explained by the widely differing six-numbers.[23]

Summary

An empirical rule for the estimation of steric hindrance to addition reactions at a doubly-bonded aliphatic function is enunciated. If one numbers the atoms in branched compounds starting with the atom of the doubly-bonded function most distant from the chain then *the greater the number of atoms in the six position the greater the steric hindrance to addition.* Applications of this rule to many experimental facts are reviewed. Refinements of the rule are discussed.

COLUMBUS 10, OHIO RECEIVED APRIL 7, 1950

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(17) L. I. Smith and J. Nichols, *J. Org. Chem.*, **6**, 489 (1941); Gattermann, *Ann.*, **347**, 374 (1906); however see G. Lock and E. Bayer, *Ber.*, **72**, 1064 (1939).

(18) J. F. Norris and H. H. Young, Jr., THIS JOURNAL, **57**, 1420 (1935).

(19) W. E. Bachmann and W. S. Struve in "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1942, Vol. I, ref. 18, p. 43.

(20) M. S. Newman and H. Gildenhorn, THIS JOURNAL, **70**, 317 (1948).

(21) It has been tacitly assumed, but not specifically stated, that all of the counted atoms involved in a chain are carbon or hydrogen. However, many other possibilities exist. In considering other atoms polar effects may overshadow steric effects.

(22) P. D. Bartlett, G. L. Fraser and R. B. Woodward, *ibid.*, **63**, 495 (1941).

(23) E. Fernholz, *Ann.*, **507**, 128 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Fluoranthene Derivatives. II. The Reaction of Acenaphthylene with Butadiene Derivatives[1]

BY MILTON C. KLOETZEL AND HOLLY E. MERTEL

Substitution reactions of fluoranthene (VI) result in formation of mixtures of 3- and 8-fluoranthyl derivatives, from which it is usually difficult to isolate either isomer in good yield.[2,3,4] In order to circumvent this difficulty, or to obtain fluoranthene derivatives containing substituents in positions other than 3 and 8, several methods have been developed for the synthesis of the fluoranthene nucleus with a group attached in the desired position.[5-11] For example, two highly-arylated fluoranthene derivatives were reported[11] from the reaction of acenaphthylene with complex cyclopentadienones at 250–300°.

We have now found that acenaphthylene reacts with simple butadiene derivatives, at 145–175°, to yield tetrahydrofluoranthenes (I–V) which can be dehydrogenated readily to the corresponding aromatic fluoranthene derivatives (VI–X).

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[1] Abstracted from the dissertation submitted by Holly E. Mertel to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the degree of Doctor of Philosophy. For the previous paper in this series, see Kloetzel and Chubb, THIS JOURNAL, **72**, 150 (1950).

(2) von Braun and Manz, *Ann.*, **488**, 111 (1931).

(3) von Braun, Manz and Kratz, *ibid.*, **496**, 170 (1932).

(4) Campbell and Easton, *J. Chem. Soc.*, 340 (1949).

(5) Dilthey and Henkels, *J. prakt. Chem.*, **149**, 85 (1937).

(6) France, Tucker and Forrest, *J. Chem. Soc.*, 7 (1945).

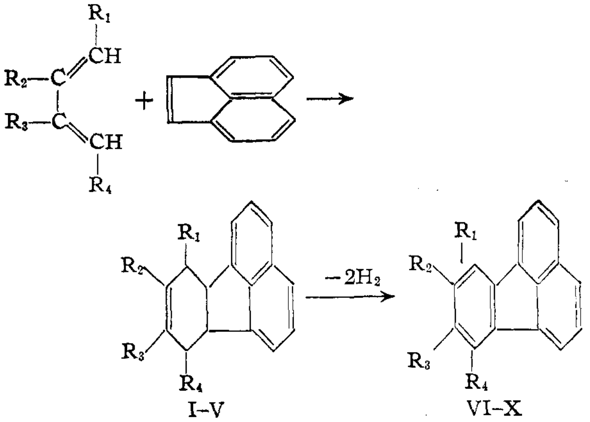
(7) Forrest and Tucker, *ibid.*, 1137 (1948).

(8) Bergmann and Orchin, THIS JOURNAL, **71**, 1917 (1949).

(9) Campbell and Wang, *J. Chem. Soc.*, 1513 (1949).

(10) Campbell and Gow, *ibid.*, 1555 (1949).

(11) Dilthey, Henkels and Schaefer, *Ber.*, **71**, 974 (1938).



I and VI, $R_1 = R_2 = R_3 = R_4 = H$
II and VII, $R_1 = CH_3$; $R_2 = R_3 = R_4 = H$
III and VIII, $R_2 = CH_3$; $R_1 = R_3 = R_4 = H$
IV and IX, $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$
V and X, $R_1 = CH_3$; $R_4 = COOC_2H_5$; $R_2 = R_3 = H$

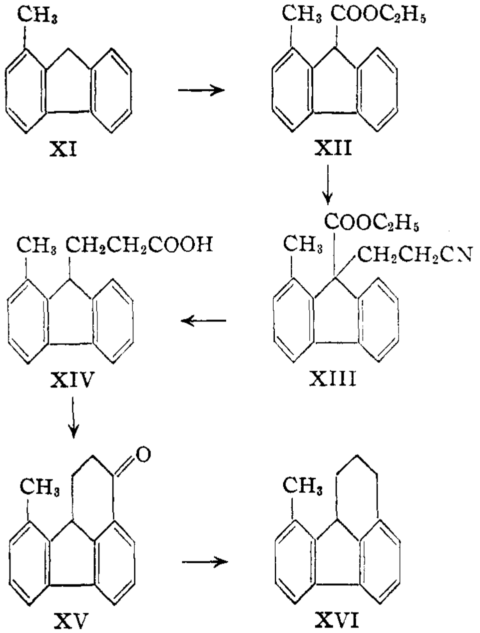
In most instances the adduct (I–V) from the Diels–Alder reaction was separated from accompanying polymeric material by selective solution in methanol and subsequent sublimation or distillation in vacuum. With the exception of the liquid product from acenaphthylene and isoprene, the adducts were colorless solids which showed no visible fluorescence when viewed in ultraviolet light. All hydrocarbon adducts yielded colored molecular addition products with picric acid, 1,3,5-trinitrobenzene or 2,4,7-trinitrofluorenone.

The position of the ethylenic linkage with respect to the carboethoxyl group in adduct V was not ascertained. It has been reported that in certain Diels–Alder reactions, the double bond may migrate in order to produce a conjugated system in the adduct.[12]

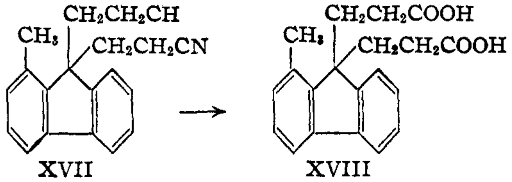
Dehydrogenation of the adducts was effected in good yield with palladium-on-barium sulfate catalyst.[13] In this manner there was obtained fluoranthene (VI), 7-methylfluoranthene (VII), 8-methylfluoranthene (VIII), 8,9-dimethylfluoranthene (IX) and ethyl 10-methyl-7-fluoranthenecarboxylate (X). Dehydrogenation of ester V was also accomplished by refluxing the adduct with chloranil in xylene, but the yield of X in this instance was only 21%.

The 7-methylfluoranthene obtained *via* the Diels–Alder reaction was shown to be identical with that obtained by an alternate sequence, starting from 1-methylfluorene (transformations XI to XVI).

1-Methylfluorenone[14] was reduced to 1-methylfluorene (XI) in 80% yield, following the general Huang-Minlon modification of the Wolff–Kishner method.[15] Reduction of 1-methylfluorenone with red phosphorus and hydriodic acid was found by Lothrop and Goodwin[14] to yield only 22% of hydrocarbon XI. Conversion of XI to 1-methyl-9-fluorenecarboxylic acid was accomplished in 88% yield by metalation with potassium amide, in a mixture of liquid ammonia and ether, and subsequent carbonation with Dry Ice, following essentially the procedure described by Yost and Hauser[16] for the preparation of diphenylacetic acid.



Ethyl 1-methyl-9-fluorenecarboxylate (XII), obtained by esterification of the aforementioned acid with ethanol and sulfuric acid, condensed readily with acrylonitrile, in the presence of sodium hydroxide and pyridine, to give ethyl 9-(2-cyanoethyl)-1-methyl-9-fluorenecarboxylate (XIII). For our purpose, the direct condensation of acrylonitrile with 1-methylfluorene could not be employed, for this reaction, catalyzed by benzyltrimethylammonium hydroxide, produced a 70% yield of 9,9-bis-(2-cyanoethyl)-1-methylfluorene (XVII).[17] Hydrolysis of dinitrile XVII with 20% potassium hydroxide produced the corresponding dibasic acid (XVIII) in 97% yield.



Hydrolysis of cyano ester XIII and partial decarboxylation of the resulting dibasic acid afforded 3-(1-methyl-9-fluoryl)-propionic acid (XIV), the acid chloride of which yielded 3-keto-10-methyl-1,2,3,10b-tetrahydrofluoranthene (XV)

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(12) Kloetzel, *Organic Reactions*, **4**, 16 (1948).

(13) Schmidt, *Ber.*, **52**, 409 (1919); Houben, "Die Methoden der organischen Chemie," 3rd Ed., Vol. II, Verlag Georg Thieme, Leipzig, 1930, p. 500.

(14) Lothrop and Goodwin, THIS JOURNAL, **65**, 363 (1943).

(15) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

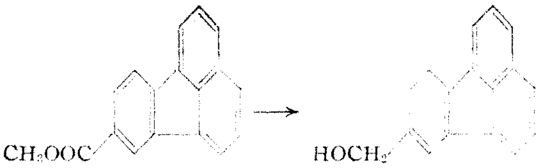
(16) Yost and Hauser, *ibid.*, **69**, 2325 (1947).

(17) Compare Bruson, *ibid.*, **64**, 2457 (1942).

upon intramolecular acylation with aluminum chloride in nitrobenzene. Clemmensen reduction of the cyclic ketone then produced 10-methyl-1,2,3,10b-tetrahydrofluoranthene (XVI) which was catalytically dehydrogenated to form 7-methylfluoranthene (VII).

7-Methylfluoranthene was also the product when 10-methyl-7-fluoranthenecarboxylic acid, obtained by hydrolysis of the corresponding ester X, was decarboxylated by heating with quinoline and copper powder. Since X was obtained by dehydrogenation of adduct V, this result provided evidence that the Diels–Alder condensation of acenaphthylene with ethyl sorbate proceeded in the normal fashion.

The identity of 8-methylfluoranthene (VIII) was established by its independent synthesis from methyl 8-fluoranthenecarboxylate (XIX). Treatment of fluoranthene with oxalyl chloride and aluminum chloride in carbon disulfide, nitroethane, or, best, nitrobenzene, yielded a mixture of carboxylic acids. This mixture was esterified and from the resulting mixture of methyl esters there was finally isolated, by selective adsorption on a column of alumina,[4] a sample of methyl 8-fluoranthenecarboxylate. Reduction of this ester (XIX) with lithium aluminum hydride[18] afforded 8-fluoranthylcarbinol (XX) in 84% yield. Hydrogenolysis of the carbinol was accomplished by heating with palladium-on-barium sulfate catalyst and 9,10-dihydroanthracene (as a source of hydrogen). 8-Methylfluoranthene prepared in this way was found to be identical with that obtained from dehydrogenation of adduct III.



XIX XX

Under no conditions were we able to obtain more than a 45% yield of acenaphthylene from the reaction of 1-acenaphthenol with thionyl chloride and pyridine.[19] However, when 1-acetoxyacenaphthene was treated under carefully controlled conditions with warm 48% hydrobromic acid containing pyridine hydrobromide, consistent 55–60% yields of acenaphthylene were obtained.

Experimental[20]

Acenaphthylene. (a) **From 1-Acetoxyacenaphthene.**—To a solution of 10 g. of 1-acetoxyacenaphthene[21] in 100 cc. of benzene, heated to boiling, was added a hot (80°) mixture of 100 cc. of 48% hydrobromic acid and 10 cc. of pyridine. Ten grams of potassium bromide was then added and the mixture was shaken for one hour (the temperature was allowed to drop spontaneously to 30° during the period of shaking). After addition of 100 cc. of water, the layers were separated and the aqueous layer was extracted with 30 cc. of benzene. The combined benzene solution was washed with 5% hydrochloric acid, then with dilute ammonium chloride solution and was finally dried over sodium sulfate. To the hot solution, which had been decolorized with charcoal, was added a hot solution of 8 g. of anhydrous picric acid in 100 cc. of benzene. Separation of acenaphthylene picrate began immediately, and continued while the solution cooled. This picrate, combined with several additional crops obtained by concentrating the mother liquor, was recrystallized from dry benzene; yield 11.5 g. of golden yellow needles, m. p. 200–202°. Cleavage of the picrate, in benzene solution, was effected with alumina, and yielded 4.3 g. (60%) of yellow acenaphthylene, m. p. 91–92°. Behr and van Dorp[22] reported a m. p. of 92–93° for acenaphthylene.

It was found necessary to adhere strictly to the afore-described procedure in order to obtain yields of 55–60% consistently. The addition of potassium bromide increased the average yield about 5%.

(b) **From 1-Acenaphthenol.**—To a solution of 25 g. of 1-acenaphthenol[21] in 200 cc. of dry benzene was added 6 cc. of dry pyridine. The solution was heated to boiling and 17.5 g. of thionyl chloride was added dropwise with stirring. After washing the reaction mixture with 5% sodium bicarbonate and drying over calcium chloride, the solvent was removed under reduced pressure and the residue distilled at 0.5 mm. until hydrogen chloride began to be evolved. From the distillate was isolated 10.1 g. (45%) of pure acenaphthylene.

Fluoranthene (VI).—A mixture of 5 g. of acenaphthylene, 30 g. of butadiene and 0.5 g. of hydroquinone was heated in a sealed tube at 170–175° for thirty-six hours. The reaction mixture, diluted with benzene, was extracted with dilute sodium hydroxide to remove hydroquinone, and solvents were then removed under reduced pressure. By treatment with hot methanol, there was extracted from the residue 3.5 g. of yellow oily material which was then evaporatively distilled at 0.1 mm. The first fraction (yellow oil) was discarded and the second fraction (2.1 g. of yellow solid, m. p. 65–67°) was crystallized from 95% ethanol. **6b,7,10,10a-Tetrahydrofluoranthene** (I) separated in colorless blades, m. p. 68–68.5°; yield 1.9 g. (28%, based upon acenaphthylene).

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.32; H, 6.71.

The 1,3,5-trinitrobenzene derivative of 6b,7,10,10a-tetrahydrofluoranthene separated from absolute ethanol in yellow needles, m. p. 126.5–127.5°.

Anal. Calcd. for $C_{22}H_{17}O_6N_3$: C, 63.00; H, 4.08. Found: C, 63.21; H, 4.23.

The picrate separated from absolute ethanol in orange needles, m. p. 109–110°.

Anal. Calcd. for $C_{22}H_{17}O_7N_3$: C, 60.68; H, 3.93. Found: C, 60.35; H, 4.31.

The 2,4,7-trinitrofluorenone complex[23] separated from acetic acid in crimson blades, m. p. 142–143°.

Anal. Calcd. for $C_{29}H_{19}O_7N_3$: C, 66.79; H, 3.67. Found: C, 67.10; H, 3.77.

When 0.79 g. of 6b,7,10,10a-tetrahydrofluoranthene (I) was heated with 0.71 g. of palladium-on-barium sulfate catalyst[18] hydrogen evolution began at 190° and ceased after thirty minutes at 270–290°. Fluoranthene (0.70 g., 91% yield) separated from ethanol in colorless plates, m. p. 109.5–110.5° alone and also when mixed with purified fluoranthene from coal tar.[24] The picrate of the synthetic fluoranthene melted at 185–186° (von Braun

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[18] Nystrom and Brown, THIS JOURNAL, **69**, 1197 (1947).

[19] Marquis, *Compt. rend.*, **182**, 1227 (1926).

[20] All m. p.'s are uncorrected. Analyses are by Dr. Adalbert Elek, Elek Micro Analytical Laboratories, Los Angeles, California, and by the Microchemical Laboratory, California Institute of Technology, Pasadena, California.

[21] Cason, *Org. Syntheses*, **21**, 1 (1941).

[22] Behr and van Dorp, *Ber.*, **6**, 753 (1873).

[23] Orchin and Woolfolk, THIS JOURNAL, **68**, 1727 (1946); Orchin, Reggel and Woolfolk, *ibid.*, **69**, 1225 (1947).

[24] Reilly Tar and Chemical Corporation, Indianapolis, Ind.

and Anton[25] reported 184–185°) and the 1,3,5-trinitrobenzene addition product melted at 205–206° alone and also when mixed with the derivative of authentic fluoranthene (Sinomiya[26] reported a m. p. of 205° for this derivative).

7-Methylfluoranthene (VII). (a) From 1-Methylfluorene.—1-Methylfluorenone[14] was reduced to 1-methylfluorene (XI) in 80% yield, following the general Huang-Minlon modification of the Wolff-Kishner method.[15] 1-Methylfluorene separated from dilute ethanol in colorless plates, m. p. 86–87°. Lothrop and Goodwin,[14] who prepared this hydrocarbon by another method, reported a m. p. of 87°.

Conversion of 1-methylfluorene to 1-methyl-9-fluorenecarboxylic acid was accomplished in 88% yield by metalation with potassium amide, and subsequent carbonation, following essentially the procedure described by Yost and Hauser[16] for the preparation of diphenylacetic acid. **1-Methyl-9-fluorenecarboxylic acid** separated from benzene–petroleum ether in colorless needles, m. p. 223–224°.

A solution of 20 g. of the aforedescribed acid in 200 cc. of absolute ethanol and 200 cc. of benzene, containing 10 cc. of concentrated sulfuric acid, was refluxed for thirty-four hours. During the reflux period, portions of solvent were allowed to distil until a total of 250 cc. of distillate had been collected. The reaction mixture was then diluted with 300 cc. of benzene and extracted with 10% aqueous sodium carbonate to recover 8.4 g. of unchanged carboxylic acid. **Ethyl 1-methyl-9-fluorenecarboxylate** (XII) distilled at 150–156° at 0.5 mm. and then separated from ethanol in colorless prisms, m. p. 67–68°; yield 84% based upon carboxylic acid consumed.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.90; H, 6.25.

A mixture of 7.9 g. of the aforedescribed ester, 2.5 g. of acrylonitrile, 20 cc. of pyridine and 4 cc. of 50% sodium hydroxide solution was shaken, with cooling, and finally allowed to stand at room temperature for thirty minutes. The reaction mixture was diluted with 240 cc. of water, acidified, and extracted with benzene. After being washed with dilute hydrochloric acid and with water, the benzene extract was distilled to yield 7.4 g. (78%) of **ethyl 9-(2-cyanoethyl)-1-methyl-9-fluorenecarboxylate (XIII)**, b. p. 190–196° at 1 mm., which crystallized from ethanol in colorless prisms, m. p. 92–93°.

Anal. Calcd. for $C_{20}H_{19}O_2N$: C, 78.66; H, 6.27. Found: C, 78.67; H, 6.21.

When a 7.0-g. sample of the cyano ester (XIII) was refluxed for ten hours with 100 cc. of 20% aqueous potassium hydroxide and the resulting solution was acidified, there was precipitated 6.6 g. of crude **9-(2-cyanoethyl)-1-methyl-9-fluorenecarboxylic acid.** Decarboxylation was effected by heating this acid to 200° and finally to 260° for ten minutes. **3-(1-Methyl-9-fluoryl)-propionic acid (XIV)** crystallized from benzene–heptane in colorless needles, m. p. 136–136.5°; yield 3.4 g. (59%, from XIII).

Preparation and cyclization of 3-(1-methyl-9-fluoryl)-propionyl chloride by methods analogous to those previously described[27] for phenanthrylpropionyl chlorides afforded a 54% yield of **3-keto-10-methyl-1,2,3,10b-tetrahydrofluoranthene** (XV). The ketone separated from ethanol in colorless prisms, m. p. 182–183.5°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.14; H, 6.02. Found: C, 86.66; H, 6.14.

The cyclic ketone (XV) yielded an **oxime** which separated from dilute ethanol in colorless prisms, m. p. 222–224° with decomposition.

Anal. Calcd. for $C_{17}H_{15}ON$: C, 81.90; H, 6.06. Found: C, 82.23; H, 6.09.

The aforedescribed ketone was reduced by the Clemmensen method, as described by Bachmann and Edgerton[28] for reduction of 1-keto-4-methyl-1,2,3,4-tetrahydrophenanthrene. There was obtained an 89% yield of **10-methyl-1,2,3,10b-tetrahydrofluoranthene (XVI)** which separated from ethanol in colorless needles, m. p. 148–149°.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.79; H, 7.22.

Dehydrogenation of hydrocarbon XVI (0.2 g.) by heating to 200–290° with palladium-on-barium sulfate catalyst (0.05 g.) gave **7-methylfluoranthene (VII)**, which separated from absolute ethanol in faintly-yellow plates, m. p. 136–137°; yield 0.16 g. (81%). The hydrocarbon shows a strong blue fluorescence in ultraviolet light.

Anal. Calcd. for $C_{17}H_{12}$: C, 94.40; H, 5.59. Found: C, 94.38; H, 5.55.

7-Methylfluoranthene picrate separated from absolute ethanol in yellow needles, m. p. 201–202°.

Anal. Calcd. for $C_{23}H_{15}O_7N_3$: C, 62.02; H, 3.39. Found: C, 61.78; H, 3.44.

(b) 7-Methylfluoranthene from Acenaphthylene and 1,3-Pentadiene.—Acenaphthylene (5 g.) was heated for twenty hours at 170–175° with 1,3-pentadiene (60 cc.) and the reaction mixture was treated as previously described for the reaction with butadiene. **7-Methyl-6b,7,10,10a-tetrahydrofluoranthene (II)** separated from 95% ethanol in colorless blades, m. p. 94–95°; yield 4 g. (55%).

Anal. Calcd. for $C_{17}H_{16}$: C, 92.67; H, 7.32. Found: C, 92.49; H, 7.46.

The 1,3,5-trinitrobenzene derivative crystallized from absolute ethanol in orange-yellow needles, m. p. 97–98.5°.

Anal. Calcd. for $C_{23}H_{19}O_6N_3$: C, 63.73; H, 4.42. Found: C, 63.83; H, 4.70.

The 2,4,7-trinitrofluorenone derivative separated from acetic acid in vermilion needles, m. p. 136.5–137°.

Anal. Calcd. for $C_{30}H_{21}O_7N_3$: C, 67.28; H, 3.95. Found: C, 67.54; H, 4.09.

Dehydrogenation of II, as described for I, yielded 80% of **7-methylfluoranthene** which showed no depression of m. p. when mixed with 7-methylfluoranthene prepared from 1-methylfluorene.

8-Methylfluoranthene (VIII). (a) From Fluoranthene.—A solution of 24.5 g. of oxalyl chloride in 100 cc. of nitrobenzene was added to a solution of 20.2 g. of fluoranthene and 33 g. of anhydrous aluminum chloride in 200 cc. of nitrobenzene at 0°. The reaction temperature was allowed to rise spontaneously to 25° during a period of twelve hours and 6.7 g. (27%) of mixed fluoranthenecarboxylic acids, m. p. 256–278°, was isolated in the customary manner. In nitroethane as solvent, the yield of mixed acids was 7%, and in carbon disulfide,[3] only 2%.

Esterification of the crude acids (10 g.) was accomplished by first refluxing for ten hours with methanol (200 cc.) and benzene (100 cc.) and then slowly distilling off solvents over a period of twenty hours, adding fresh methanol as necessary to retain approximately constant volume. The solution was finally concentrated to 75 cc., diluted with 175 cc. of benzene and extracted with dilute sodium carbonate to remove any unchanged acid. Distillation in vacuum yielded a crude ester from which, by selective adsorption on alumina[4] and crystallization from methanol, there was finally obtained 1.1 g. of pure methyl 8-fluoranthenecarboxylate (XIX), m. p. 99–100°. Campbell and Easton[4] reported a m. p. of 93–95°.

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.29; H, 4.67.

Reduction of methyl 8-fluoranthenecarboxylate (0.8 g.) was effected with lithium aluminum hydride (1 g.) following the generalized conditions described by Nystrom and Brown[18] for reduction of ether-soluble compounds. **8-Fluoranthylcarbinol (XX)** separated from ethanol in faintly-green needles, m. p. 140–141°, showing a blue fluorescence in ultraviolet light; yield 0.6 g. (84%).

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(25) von Braun and Anton, *Ber.*, **62**, 145 (1929).

(26) Sinomiya, *Bull. Chem. Soc. Japan*, **15**, 259 (1940) [*C. A.*, **34**, 7900 (1940)].

(27) Bachmann and Kloetzel, THIS JOURNAL, **59**, 2207 (1937).

(28) Bachmann and Edgerton, *ibid.*, **62**, 2219 (1940).

Anal. Calcd. for $C_{17}H_{12}O$: C, 87.90; H, 5.20. Found: C, 88.51; H, 5.23.

Hydrogenolysis of 0.2 g. of 8-fluoranthylcarbinol was accomplished by heating with 2.5 g. of 9,10-dihydroanthracene and 0.2 g. of palladium-on-barium sulfate catalyst to 290–300° for thirty minutes.

To the decolorized benzene solution of reaction products was added 5 g. of maleic anhydride and the solution was refluxed for twenty hours. The bulk of the anthracene adduct separated upon cooling and the remainder was removed by extracting the benzene solution with dilute sodium hydroxide. When the residual crude hydrocarbon was again heated briefly with palladium-on-barium sulfate catalyst, a small additional quantity of hydrogen was evolved. Treatment of the resulting product as before, with 1.5 g. of maleic anhydride, followed by passage of the benzene solution of hydrocarbon through an alumina column finally yielded *8-methylfluoranthene* (0.06 g.), which crystallized from ethanol in nearly colorless needles, m. p. 93–94°, showing a blue fluorescence in ultraviolet light.

Anal. Calcd. for $C_{17}H_{12}$: C, 94.40; H, 5.59. Found: C, 94.30; H, 5.65.

8-Methylfluoranthene picrate separated from absolute ethanol in orange-yellow needles, m. p. 156–157°.

Anal. Calcd. for $C_{23}H_{15}O_7N_3$: C, 62.02; H, 3.39. Found: C, 62.19; H, 3.39.

The 1,3,5-trinitrobenzene addition product crystallized from absolute ethanol in yellow needles, m. p. 171–173.5°.

Anal. Calcd. for $C_{23}H_{15}O_6N_3$: C, 64.33; H, 3.52. Found: C, 64.21; H, 3.57.

(b) **8-Methylfluoranthrene from Acenaphthylene and Isoprene.**—The reaction of acenaphthylene with isoprene, effected as in the case of butadiene, yielded after fifteen hours 43% of a yellow, oily adduct which could not be induced to crystallize. **The 1,3,5-trinitrobenzene addition compound of 8-methyl-6b,7,10,10a-tetrahydrofluoranthrene**, prepared in the customary manner from the oily adduct, crystallized from absolute ethanol in yellow prisms, m. p. 108–110°.

Anal. Calcd. for $C_{23}H_{19}O_6N_3$: C, 63.73; H, 4.42. Found: C, 64.38; H, 4.57.

The 2,4,7-trinitrofluorenone derivative of 8-methyl-6b,7,10,10a-tetrahydrofluoranthene separated from acetic acid in vermilion prisms, m. p. 112–114°.

Anal. Calcd. for $C_{30}H_{21}O_7N_3$: C, 67.28; H, 3.95. Found: C, 67.50; H, 4.10.

Dehydrogenation of the yellow liquid 8-methyl-6b,7,-10,10a-tetrahydrofluoranthene (III), as described for I, produced a quantitative yield of **8-methylfluoranthene** (VIII), m. p. 93–94°. The m. p.'s of this material and its 1,3,5-trinitrobenzene derivative were not depressed upon admixture with 8-methylfluoranthene prepared from fluoranthene, and its 1,3,5-trinitrobenzene derivative, respectively.

8,9-Dimethylfluoranthene (IX).—The reaction of acenaphthylene with 2,3-dimethyl-1,3-butadiene was carried out as described for butadiene, except that the mixture was heated for thirty-six hours at 150–155°. **8,9-Dimethyl - 6b,7,10,10a - tetrahydrofluoranthene** (IV, 60% yield) crystallized from absolute ethanol in colorless blades, m. p. 69–70°.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.10; H, 7.92.

The 2,4,7-trinitrofluorenone derivative separated from acetic acid in vermilion needles, m. p. 137–138°.

Anal. Calcd. for $C_{31}H_{23}O_7N_3$: C, 67.75; H, 4.21. Found: C, 68.26; H, 4.05.

8,9-Dimethylfluoranthene (IX) was produced in 78% yield by dehydrogenation of the aforedescribed adduct in the usual manner, and separated from 95% ethanol in yellow prisms, m. p. 144–145°.

Anal. Calcd. for $C_{18}H_{14}$: C, 93.87; H, 6.12. Found: C, 94.05; H, 6.00.

The 1,3,5-trinitrobenzene derivative separated from absolute ethanol in yellow needles, m. p. 208–209°.

Anal. Calcd. for $C_{24}H_{17}O_6N_3$: C, 65.00; H, 3.86. Found: C, 64.62; H, 3.89.

Ethyl 10-Methyl-7-fluoranthenecarboxylate (X).—A mixture of 5 g. of acenaphthylene, 30 g. of ethyl sorbate[29] and 0.5 g. of hydroquinone was heated in a nitrogen atmosphere at 145–150° for twenty-four hours. Hydroquinone was removed by alkaline extraction as before and solvents were removed by reduced pressure distillation (finally by heating to 100° at 0.5 mm. pressure). Approximately 3 g. of **ethyl 10-methyl-6b,7,10,10a-tetrahydro-7-fluoranthenecarboxylate** (V) then sublimed when the residue was heated at 0.1 mm. pressure, and separated from ethanol in colorless plates, m. p. 105–106°; yield 2.4 g. (25%).

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.52; H, 6.95.

Catalytic dehydrogenation of the aforedescribed adduct yielded 56% of **ethyl 10-methyl-7-fluoranthenecarboxylate** (X), which crystallized from ethanol in pale yellow needles, m. p. 83–84°. The aromatic ester was obtained in only 21% yield when dehydrogenation was effected by refluxing for twenty-four hours a solution of 2.4 g. of adduct V and 4.2 g. of chloranil in 50 cc. of xylene.

Anal. Calcd. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.44; H, 5.60.

10-Methyl-7-fluoranthenecarboxylic acid was precipitated when 0.5 g. of the ethyl ester (X) was refluxed with 20% aqueous potassium hydroxide for eight hours and the resulting solution was acidified with dilute sulfuric acid. Crystallization of the crude acid from 70% aqueous acetic acid and then from benzene yielded 0.3 g. (67%) of colorless prisms, m. p. 249–250°.

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.52; H, 4.72.

Decarboxylation of the aforedescribed acid was accomplished by refluxing 0.2 g. of the acid, 0.05 g. of copper powder and 30 cc. of quinoline for fifteen minutes. The cooled solution was diluted with 50 cc. of ether, filtered, and repeatedly extracted with 20% sulfuric acid. Evaporation of the washed ether solution yielded a residue which was recrystallized from ethanol; yield 0.02 g. (12%) of 7-methylfluoranthene (VII), m. p. 136–137° alone and also when mixed with 7-methylfluoranthene prepared as previously described.

9,9-Bis(2-cyanoethyl)-1-methylfluorene (XVII).—Acrylonitrile was allowed to react with 1-methylfluorene as described by Bruson[17] for the reaction with fluorene. 9,9 - Bis - (2 - cyanoethyl) - 1 - methylfluorene (70% yield) crystallized from dilute ethanol in colorless needles, m. p. 105–106°.

Anal. Calcd. for $C_{20}H_{18}N_2$: C, 83.88; H, 6.33. Found: C, 83.57; H, 6.32.

Hydrolysis of 1 g. of dinitrile XVII, by refluxing for three hours with 20% potassium hydroxide solution, yielded 1.1 g. (97%) of the corresponding dibasic acid (XVIII), which separated from acetone–water in colorless needles, m. p. 248–248.5°; neut. equiv. calcd., 162.2; found, 160.7.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.05; H, 6.21. Found: C, 73.88; H, 6.19.

Summary

Acenaphthylene is obtained in 55–60% yield from the reaction of 1-acetoxyacenaphthene with warm 48% hydrobromic acid containing pyridine hydrobromide.

Acenaphthylene reacts with simple butadiene derivatives at 145–175° to yield tetrahydrofluoranthenes which can be dehydrogenated to the

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[29] Rigg and Rosenthal, THIS JOURNAL, 71, 2865 (1949).

corresponding fully aromatic fluoranthene derivatives. In this manner were prepared fluoranthene, 7-methylfluoranthene, 8-methylfluoranthene, 8,9-dimethylfluoranthene and ethyl 10-methyl-7-fluoranthenecarboxylate.

Los Angeles, Calif. Received April 3, 1950

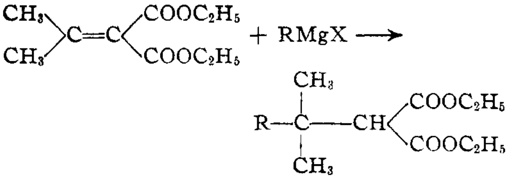
[Contribution from the Noyes Chemical Laboratory, University of Illinois]

A Synthesis of Ethyl *t*-Alkylcyanoacetates

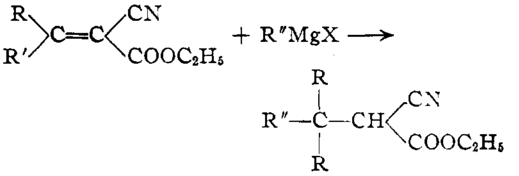
By Elliot R. Alexander, John D. McCollum and Donald E. Paul

In general, the preparation of substituted acetoacetic, malonic, or cyanoacetic esters by an alkylation procedure is suitable only for the introduction of primary or secondary alkyl groups. Under the alkaline conditions employed, *t*-alkyl halides readily dehydrohalogenate to form alkenes. Ethyl *t*-butylcyanoacetate, for example, appears to be unknown.

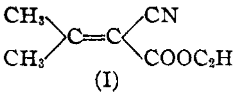
Recently, however, the synthesis of ethyl *t*-alkylmalonates has been reported[1] by the conjugate addition of Grignard reagents to ethyl isopropylidenemalonate (equation 1). It was the object of this work to explore the scope and limitations of this reaction in the synthesis of ethyl *t*-alkylcyanoacetates (equation 2).

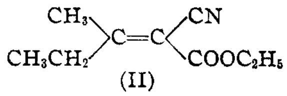

(1)

(R = methyl and butyl)

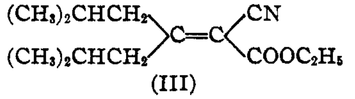

(2)

In Table I are summarized the ethyl *t*-alkylcyanoacetates which were prepared by the conjugate addition of Grignard reagents to ethyl 1-methylethylidenecyanoacetate (I) and ethyl 1-methylpropylidenecyanoacetate (II). With ethyl 1-methylethylidenecyanoacetate the method appears to be quite general for *n*-alkyl or phenyl groups and the yields of pure *t*-alkylcyanoacetates range from 42–75%. Experiments were also carried out with isopropylmagnesium bromide and *t*-butylmagnesium chloride, but in each case the reaction led to a mixture of products which could not be separated by distillation through an eight-inch electrically heated column packed with glass helices. It is interesting that in the one case that was studied, namely, the addition of methylmagnesium iodide to ethyl 1-methylethylidenecyanoacetate, there appeared to be no tendency for a second molecule of Grignard reagent to add either to the nitrile group or to the carbethoxyl group. Thus, when a 10 molar excess of methylmagnesium iodide was employed and the reaction mixture was allowed to stir overnight, the yield of ethyl *t*-butylcyanoacetate was the same (57%) as that obtained by using a 1.2 molar excess of methylmagnesium iodide. With the isopropyl or *t*-butyl Grignard reagents, however, (where the reaction failed) infrared analysis showed the presence of hydroxyl groups in the mixture of products which was obtained.


(I)


(II)

Just as the reaction fails with the secondary or tertiary Grignard reagents which were employed, there is a limiting unsaturated ester for the synthesis. The reaction between ethyl 1-methylpropylidene cyanoacetate and methylmagnesium iodide proceeded normally (Table I) and again treatment with isopropylmagnesium bromide led to inseparable mixtures. With ethyl 1-isobutyl-3-methylbutylidenecyanoacetate (III), however, mixtures were obtained even from methylmagnesium iodide and benzylmagnesium chloride.


(III)

Acknowledgment.—We are indebted to Miss Theta Spoor, Miss Rachel Kopel and Miss Emily Davis for the microanalyses which are reported in this paper.

Experimental[2]

Ethyl Alkylidenecyanoacetates.—The unsaturated esters which are mentioned in this paper were prepared by the method of Cope and Hofmann[3] which is based upon a Knoevenagel condensation of ethyl cyanoacetate with the appropriate ketone. Before use, all of the esters were distilled to constant refractive index through an eight-inch electrically heated column packed with glass helices.

Ethyl *t*-Butylcyanoacetate.—The experiments summarized in Table I were carried out according to the following procedure. It is illustrated here with the preparation of ethyl *t*-butylcyanoacetate.

In a dry 500-ml. three-necked flask fitted with a stirrer, an addition funnel, and a condenser protected from the

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[1] Wideqvist, *Arkiv. Kemi, Mineral. Geol.*, **22B**, No. 4 (1946); *C. A.* **41**, 1615 (1947).

[2] All melting points and boiling points are uncorrected.

[3] Cope and Hofmann, This Journal, **63**, 3457 (1941).