Quantitative Determination.—Fully methylated corn fiber gum, 100 mg., was heated at 100° in a sealed tube with 5 ml. of 5% hydrogen chloride in methanol for 12 hr. The solution was neutralized, filtered and the solvent removed to produce a brown sirup. This sirup was heated at 100° for 8 hr. in a sealed tube with 5 ml. of 0.5 *N* hydrochloric acid solution. The solution was neutralized with silver carbonate, filtered and the excess silver ions precipitated with hydrogen sulfide. The solution was concentrated to a sirup and chromatographed. Papers were developed with solvent A and the methylated sugars eluted with methanol. Quantities of the methylated sugars were determined by the alkaline hypoiodite method.[15] Amounts of each methylated sugar found in the hydrolyzate are given in Table I.

Acknowledgments.—The authors wish to thank K. W. Kirby who determined the uronic acid content of the polysaccharide and G. E. Lauterbach who made an electrophoretic pattern of the hemicellulose.

[15] S. K. Chanda, E. L. Hirst, J. K. N. Jones and E. G. V. Percival, *J. Chem. Soc.*, 1289 (1950).

LAFAYETTE, INDIANA

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

Fluoranthene Derivatives. III. 2-Nitrofluoranthene and 2-Aminofluoranthene[1]

BY MILTON C. KLOETZEL, WILLIAM KING AND JOHN H. MENKES

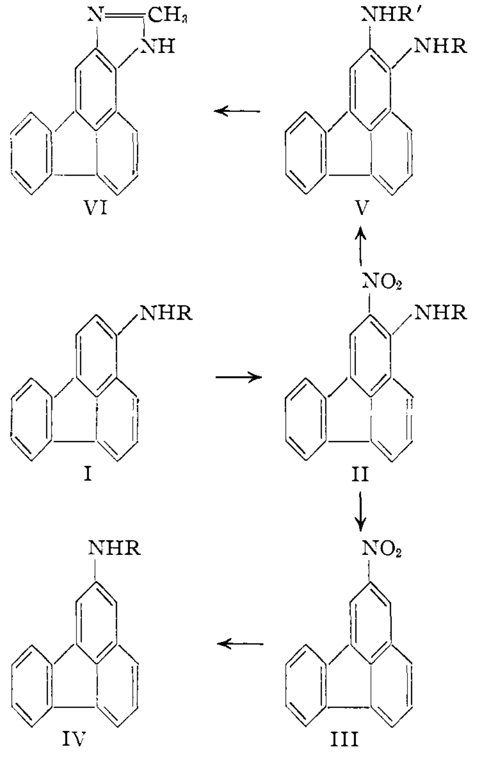
RECEIVED SEPTEMBER 23, 1955

3-Acetylaminofluoranthene has been shown to undergo nitration in the 2-position. Several new 2,3-disubstituted fluoranthene derivatives have been prepared. 2-Nitrofluoranthene, 2-aminofluoranthene and several derivatives of each have been synthesized and their structures ascertained.

Since the elucidation of the structure of fluoranthene[2] numerous reports have described the preparation of 3- and 8-fluoranthyl derivatives by direct substitution of the hydrocarbon and derivatives with substituents in other positions by methods of nuclear synthesis.[3] Only two compounds have been reported, however, in which fluoranthene carries a single substituent in the 2-position. 2-Methylfluoranthene was prepared through nuclear synthesis[4] and an impure sample of 2-fluoranthenecarboxylic acid was described by Campbell and Wang.[5]

2-Nitrofluoranthene (III) has now been prepared in 39% over-all yield from commercially-available fluoranthene through a sequence involving initial nitration in the 3-position and reduction of the nitro group to the amino group. The directive influence of the latter was subsequently employed to promote nitration in the 2-position (compound II, R = $COCH_3$) and the amino group was finally eliminated by reduction of the corresponding diazonium salt. Catalytic reduction of 2-nitrofluoranthene yielded 2-aminofluoranthene (IV, R = H).

Nitration of fluoranthene was accomplished in a manner similar to that described by Garascia, Fries and Ching.[6] In addition to 3-nitrofluoranthene, we were able to isolate a small quantity of the 8-isomer from the reaction mixture. von Braun and Manz[7] indirectly demonstrated the formation of a little 8-nitrofluoranthene during nitration of fluoranthene but the compound has not been isolated heretofore. The identity of 8-nitrofluoranthene was confirmed by its conversion to the known 8-aminofluoranthene[7] and 8-acetylaminofluoranthene.[7-9]



3-Aminofluoranthene (I, R = H) formed solid salts in 96–98% yields when ether solutions of the amine were treated with hydrogen chloride, hydrogen bromide, 57% hydriodic acid or concentrated sulfuric acid. Reaction with ethyl chloroformate produced the urethan (I, R = $COOC_2H_5$). Cold acetic anhydride converted the amine to the amide (I, R = $COCH_3$) while hot acetic anhydride in the

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[1] Partially abstracted from the M.S. thesis of John H. Menkes. The numbering system for fluoranthene herein employed is that adopted by *Chemical Abstracts*.

[2] J. von Braun and E. Anton, *Ber.*, **62**, 145 (1929).

[3] S. H. Tucker and M. Whalley, *Chem. Revs.*, **50**, 483 (1952).

[4] S. H. Tucker, *J. Chem. Soc.*, 803 (1952).

[5] N. Campbell and H. Wang, *ibid.*, 1513 (1949).

[6] R. J. Garascia, E. F. Fries and C. Ching, *J. Org. Chem.*, **17**, 226 (1952).

[7] J. von Braun and G. Manz, *Ann.*, **496**, 170 (1932).

[8] Ng. Ph. Buu-Hoi and P. Cagniant, *Rec. trav. chim.*, **62**, 719 (1943).

[9] N. Campbell, W. K. Leadill and J. F. K. Wilshire, *J. Chem. Soc.*, 1404 (1951).

presence of sulfuric acid readily yielded the diacetylamine.

3-Acetylaminofluoranthene (I, R = $COCH_3$) was nitrated in excellent yield at room temperature, or more rapidly at 75°, to give 3-acetylamino-2-nitrofluoranthene (II, R = $COCH_3$). This substance was reduced catalytically to 3-acetylamino-2-aminofluoranthene (V, R = $COCH_3$, R′ = H), which formed an imidazole VI upon being heated with hydrochloric acid. The structures ascribed to II and V clearly are in accord with this behavior.

Alkaline or acidic hydrolysis of 3-acetylamino-2-nitrofluoranthene (II, R = $COCH_3$) readily provided 3-amino-2-nitrofluoranthene (II, R = H). Oxidation of this nitro amine to 1-fluorenonecarboxylic acid[10] confirmed the fact that nitration had occurred in the ring bearing the amino group.

When the diazonium salt of 3-amino-2-nitrofluoranthene was reduced with hypophosphorous acid,[11] 2-nitrofluoranthene (III) was produced in excellent yield. In the manner characteristic of other nitrofluoranthenes[6,12,13] the unsubstituted ring of the naphthalenic nucleus in 2-nitrofluoranthene was cleaved upon oxidation to produce 3-nitro-1-fluorenonecarboxylic acid, which subsequently was decarboxylated to give the previously described[14] 3-nitrofluorenone. Consequently the position of the nitro group in 2-nitrofluoranthene is established.

Relatively little is known regarding the orientation of disubstituted fluoranthene derivatives. Holbro and Tagmann[15] and Campbell and his associates[9,13,16–18] in a series of illuminating papers, have discerned two types of orientation. (1) A *meta*-directing substituent in the 3-position of fluoranthene causes a second substituent to enter position 9. (2) An *ortho-para*-directing substituent in the 3-position of fluoranthene causes introduction of a second substituent in the 8-position. The nitration of 3-acetylaminofluoranthene in the 2-position appears to be the first reported instance of still a third type of orientation in the fluoranthene nucleus, in which a substituent (the acetylamino group) so intensely activates the ring to which it is attached that the second substituent enters the same ring. This result is not unexpected. However, it indicates that the orientation rule of Campbell and Keir[13] is oversimplified to the extent that the rule does not take into account the effects of intensely activating substituents.

Experimental[19]

Nitration of Fluoranthene.—Concentrated nitric acid (150 ml. in 150 ml. of acetic acid) was added dropwise over a period of 1.5 hours to a mechanically-stirred suspension of fluoranthene (306 g.) in glacial acetic acid (1900 ml.) heated to 65°. Heat was liberated and the temperature of the reaction mixture was maintained at 69–70° by means of external cooling. Stirring at 70° was continued for 1.5 hours after addition of nitric acid and the solution was then filtered at 65° from 199 g. (56% yield) of **3-nitrofluoranthene** which had separated as a yellow-orange precipitate.

After cooling to 40°, the filtrate was again filtered from a small quantity of dark solid and was then allowed to stand at room temperature. The yellow precipitate (57 g.) which separated yielded, after a number of crystallizations from nitroethane, **8-nitrofluoranthene**, which separated from nitroethane in yellow needles, m.p. 158–160° (and depressed the m.p. of 3-nitrofluoranthene approximately 30°).

Anal. Calcd. for $C_{16}H_9NO_2$: N, 5.66. Found: N, 5.53.

A mixture of 469 mg. of 8-nitrofluoranthene, 85 ml. of absolute ethanol and 50 mg. of platinum oxide absorbed 95% of the calculated volume of hydrogen at approximately atmospheric pressure within 20 minutes. The product was precipitated with water and crystallized from a mixture of benzene and petroleum ether to yield 399 mg. (97%) of **8-aminofluoranthene**, m.p. 167–169°. von Braun and Manz[7] reported a m.p. of 168–170°.

8-Acetylaminofluoranthene precipitated when a mixture of the amine (1.0 g.), acetic anhydride (5 ml.) and sulfuric acid (1 drop) was heated to 60° for 1 minute and then poured into water. Crystallization from diluted ethanol yielded 670 mg. (56%) of yellow leaflets. Melting points of 190–191°, 190°, and 199–201° have been reported for this compound.[7–9] We were unable to obtain a m.p. higher than 192.5–193° even after chromatographic purification.

Hydrogenation of 3-nitrofluoranthene (21 g.) suspended in absolute ethanol (150 ml.) was accomplished within 40 minutes at a pressure of 3 atmospheres over platinum oxide (500 mg.); yield 16 g. (87%) of 3-aminofluoranthene, isolated as described for the 8-isomer. Recrystallization from a mixture of benzene and petroleum ether gave a sample melting at 115–116°. von Braun and Manz,[20] who prepared this amine by reduction of the nitro compound with stannous chloride and hydrochloric acid, reported a m.p. of 111–112°. Campbell, Leadill and Wilshire[9] prepared the amine by hydrolysis of its acetyl derivative, which was obtained from the reaction of 3-acetylfluoranthene with sodium azide and trichloroacetic acid, and reported it to melt at 113–115°.

Salts of 3-aminofluoranthene were precipitated in 96–97% yields when dry hydrogen chloride or hydrogen bromide was passed into a solution of the amine in anhydrous ether and were analytically pure after trituration with anhydrous ether. The m.p. (285–287°) of the **hydrochloride** was raised 1 degree when the salt was dissolved in absolute ethanol and reprecipitated with dry ether. Melting points of 285° and 285–288° were reported previously.[9,20]

The **hydrobromide** melted at 308–310° dec.

Anal. Calcd. for $C_{16}H_{12}BrN$: C, 64.44; H, 4.05; N, 4.70. Found: C, 64.50; H, 4.09; N, 4.94.

The **hydriodide** separated as a gray precipitate when 57% hydriodic acid was added to a solution of the amine in dry ether until fluorescence disappeared. After trituration with dry ether the salt melted at 315–317° dec.; yield 97%.

Anal. Calcd. for $C_{16}H_{12}IN$: C, 55.67; H, 3.50; N, 4.06. Found: C, 55.70; H, 3.70; N, 4.32.

The **sulfate** separated in 98% yield when a solution of concentrated sulfuric acid (0.5 ml.) in dry ether (1 ml.) was added to a solution of the amine (1.25 g.) in dry ether (100 ml.); m.p. 344–345° dec.

Anal. Calcd. for $C_{16}H_{13}NO_4S$: C, 60.93; H, 4.15; N, 4.44. Found: C, 61.09; H, 4.39; N, 4.42.

Ethyl N-3-fluoranthylcarbamate (I, R = $COOC_2H_5$) separated from a solution of 3-aminofluoranthene (1.0 g.), ethyl chloroformate (1 ml.) and pyridine (1 ml.) in benzene (50 ml.) which was boiled for 0.5 minute and then allowed to stand at room temperature. Recrystallization from benzene and then from absolute ethanol yielded 0.9 g. (68%) of colorless urethan, m.p. 168–169°.

Anal. Calcd. for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 79.40; H, 5.57; N, 4.60.

3-Acetylaminofluoranthene (I, R = $COCH_3$) was produced in quantitative yield when the amine in benzene solu-

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(10) Compare L. F. Fieser and A. M. Seligman, This Journal, **57**, 2174 (1935).

(11) N. Kornblum, *Organic Reactions*, **2**, 262 (1944).

(12) N. Campbell and J. F. K. Wilshire, *J. Chem. Soc.*, 867 (1954).

(13) N. Campbell and N. H. Keir, *ibid.*, 1233 (1955).

(14) F. E. Bardout, *C. A.*, **26**, 1275 (1932). See also F. E. Bardout, *ibid.*, **29**, 5437 (1935).

(15) T. Holbro and E. Tagmann, *Helv. Chim. Acta*, **33**, 2178 (1950).

(16) N. Campbell, W. W. Easton and J. L. Rayment, *Nature*, **165**, 76 (1950).

(17) N. Campbell, W. W. Easton, J. L. Rayment and J. F. K. Wilshire, *J. Chem. Soc.*, 2784 (1950).

(18) N. Campbell, W. H. Stafford and J. F. K. Wilshire, *ibid.*, 1137 (1951).

(19) Microanalyses are by Mr. W. J. Schenck. Melting points are uncorrected.

(20) J. von Braun and G. Manz, *Ann.*, **488**, 111 (1931).

tion was treated with acetic anhydride at room temperature; m.p. 242–245°. The m.p. previously reported[9] was 244–245°.

3-Diacetylaminofluoranthene was formed when a mixture of the 3-amine or the 3-acetylamine (2.0 g.), acetic anhydride (75 ml.) and concentrated sulfuric acid (4 drops) was boiled for 2 minutes and poured into water. Recrystallization from absolute ethanol yielded 1.6 g. (69%) of colorless needles, m.p. 168–169°.

Anal. Calcd. for $C_{20}H_{15}NO_2$: C, 79.71; H, 5.02; N, 4.65. Found: C, 79.65; H, 5.24; N, 4.61.

3-Acetylaminofluoranthene, m.p. 240–241°, separated when a mixture of 200 mg. of the 3-diacetylaminofluoranthene, 10 ml. of absolute ethanol and 5 ml. of 20% aqueous sodium hydroxide was heated to reflux for 1 hour and then cooled.

3-Acetylamino-2-nitrofluoranthene (II, R = $COCH_3$).—3-Acetylaminofluoranthene (2 g.) was dissolved in glacial acetic acid (100 ml.) by warming and to the solution which had then been cooled to room temperature was added a solution of concentrated nitric acid (0.84 ml.) in acetic acid (10 ml.). After standing at room temperature for 12 hours the mixture was diluted with water (300 ml.) to complete precipitation of the product; yield 2.20 g. (94%), m.p. 279–280°. Pure nitro amide separated from acetic acid in yellow needles, m.p. 282–283°.

Anal. Calcd. for $C_{18}H_{12}N_2O_3$: C, 71.04; H, 3.97; N, 9.20. Found: C, 71.42; H, 4.22; N, 9.29.

A similar nitration effected in 30 minutes at 75° gave an 88% yield, m.p. 280–281°.

When treated with acetic anhydride and sulfuric acid as described for 3-acetylaminofluoranthene, 3-acetylamino-2-nitrofluoranthene gave an 83% yield of **3-diacetylamino-2-nitrofluoranthene**, which separated from absolute ethanol in yellow needles, m.p. 164–165°.

Anal. Calcd. for $C_{20}H_{14}N_2O_4$: C, 69.36; H, 4.07; N, 8.09. Found: C, 69.46; H, 4.22; N, 8.29.

Hydrolysis of 3-acetylamino-2-nitrofluoranthene was accomplished in 91–94% yield either by heating to reflux for 15 minutes a mixture of the amide (25.1 g.), ethylene glycol (250 ml.), potassium hydroxide (8.5 g.) and water (35 ml.) and then diluting with water (850 ml.), or by heating to reflux for 5 hours a mixture of amide (15 g.), 95% ethanol (1200 ml.) and concentrated hydrochloric acid (1200 ml.) and then neutralizing with 10% sodium hydroxide solution. The precipitated **3-amino-2-nitrofluoranthene** (II, R = H) melted at 235–236° after recrystallization from chlorobenzene in orange microcrystals.

Anal. Calcd. for $C_{16}H_{10}N_2O_2$: C, 73.27; H, 3.84; N, 10.68. Found: C, 73.58; H, 3.99; N, 10.39.

Oxidation of 1.0 g. of 3-amino-2-nitrofluoranthene with chromic anhydride, essentially by the method described for fluoranthene,[10] yielded 490 mg. of 1-fluorenonecarboxylic acid which did not depress the m.p. of an authentic sample.

Hydrogenation of 3-acetylamino-2-nitrofluoranthene (8.3 g.), suspended in absolute ethanol (200 ml.), at 3 atmospheres pressure in the presence of platinum oxide (100 mg.) was complete within 46 hours. The suspended product was brought into solution by the addition of more ethanol (200 ml.) and heating. Evaporation of the filtered solution and dilution with water yielded 7.3 g. (98%) of yellow **3-acetylamino-2-aminofluoranthene** (V, R = $COCH_3$, R′ = H), m.p. 198–200°. Recrystallization from pyridine or xylene raised the m.p. to 201–203°.

Anal. Calcd. for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 79.15; H, 5.33; N, 10.14.

2,3-Bisacetylaminofluoranthene (V, R = R′ = $COCH_3$), m.p. 268–269° after crystallization from glacial acetic acid.

Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.85. Found: C, 76.00; H, 5.26; N, 8.64.

2-Methylfluorantho[b,d]imidazole (VI).—To a hot solution of 3-acetylamino-2-aminofluoranthene (1.2 g.) in acetic acid (50 ml.) was added concentrated hydrochloric acid (5 ml.) and the mixture was heated to reflux for 1 hour. Filtration of the cooled mixture yielded a solid salt which decomposed above 350° and was shown to contain ionic chlorine. The imidazole, liberated by means of sodium carbonate from a hot aqueous solution of the salt, separated from ethanol in solvated form; yield 600 mg., m.p. 178–180° with gas evolution, resolidification, and finally melting at 267–268°. An analytical sample was heated to 210° and then dried *in vacuo* at 140°.

Anal. Calcd. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72; N, 10.93. Found: C, 84.21; H, 4.98; N, 11.06.

An acetyl derivative of the imidazole was obtained in 90% yield when an acetic anhydride solution of the imidazole was boiled for 3 minutes and then diluted with water. Recrystallization from absolute ethanol gave yellow needles, m.p. 168–170°.

Anal. Calcd. for $C_{20}H_{14}N_2O$: C, 80.51; H, 4.73; N, 9.39. Found: C, 80.79; H, 4.90; N, 9.63.

2-Nitrofluoranthene (III).—Powdered 3-amino-2-nitrofluoranthene (11.5 g.) was added slowly with stirring to a solution of sodium nitrite (4 g.) in concentrated sulfuric acid (140 ml.) and water (10 ml.) at −5°. After standing at −5° for 30 minutes the resulting solution was diluted with precooled 50% hypophosphorous acid (300 ml.) at such a rate (3 hours) that the temperature of the reaction mixture at no time exceeded 5°. After standing for 4 days at 3° the mixture was diluted with 3 volumes of water to precipitate 10 g. (92%) of product, m.p. 145–148°. Recrystallization from glacial acetic acid yielded flat yellow needles, m.p. 153–153.5°.

Anal. Calcd. for $C_{16}H_9NO_2$: C, 77.72; H, 3.67; N, 5.66. Found: C, 78.02; H, 3.94; N, 5.65.

Oxidation of 2-nitrofluoranthene (1.2 g.) was accomplished by heating to reflux for 3 hours with sodium dichromate (8 g.) and acetic acid (40 ml.). After dilution with 6 *N* sulfuric acid (300 ml.) the mixture was extracted with benzene, then with ether, and the combined organic extracts shaken with aqueous sodium carbonate. Acidification of the carbonate solution precipitated 250 mg. of yellow **3-nitro-1-fluorenonecarboxylic acid**, m.p. 200–205°; after crystallization from a mixture of xylene and petroleum ether, m.p. 204–205°

Anal. Calcd. for $C_{14}H_7NO_5$: N, 5.20. Found: N, 5.06.

Vigorous evolution of carbon dioxide occurred when a mixture of 3-nitro-1-fluorenonecarboxylic acid (850 mg.), quinoline (5 ml.) and copper–bronze (200 mg.) was gradually heated at 170–220° over a period of 45 minutes. The filtered solution was extracted with 18% hydrochloric acid to leave a solid residue of crude **3-nitrofluorenone**. Five crystallizations from ethanol finally yielded 50 mg. of the pure nitro ketone,[21] m.p. 229–230°.

Rapid separation of red crystals occurred when phenylhydrazine (10 drops) was added to a boiling solution of 3-nitrofluorenone (80 mg.) in acetic acid (10 ml.) which had been diluted with water to the point of incipient cloudiness; m.p. 228–233° dec. Recrystallization from ethanol or benzene yielded **3-nitrofluorenone phenylhydrazone**, m.p. 231–233° dec.

Anal. Calcd. for $C_{19}H_{13}N_3O_2$: N, 13.33. Found: N, 13.55.

Authentic 3-Nitrofluorenone.—To a mixture of 2-amino-3-nitrofluorenone (2 g.), prepared by the method of Eckert and Langecker,[22] concentrated sulfuric acid (20 ml.) and water (2 ml.), cooled to 0°, was added sodium nitrite (0.62 g.) with stirring. After 20 minutes an additional quantity (2 g.) of powdered 2-amino-3-nitrofluorenone was added with stirring over a period of 20 minutes. After standing at 0° for 30 minutes the resulting solution was diluted by dropwise addition of 50% hypophosphorous acid (30 ml.) with mechanical stirring. During the addition considerable gas evolution occurred and the temperature was maintained at 0–6°. After standing for 3 days at 3° the mixture was diluted with 200 ml. of water and the precipitated nitro ketone (1.70 g.) was purified as described for that obtained by decarboxylation of 3-nitro-1-fluorenonecarboxylic acid; m.p. 230–231° alone and 229–230° when mixed with 3-nitrofluorenone from the decarboxylation reaction.

3-Nitrofluorenone prepared from 2-amino-3-nitrofluorenone also formed the phenylhydrazone, m.p. 231–233° dec.

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(21) A much better yield (400 mg.) of material melting in the vicinity of 210°, the m.p. reported for this nitro ketone by Eckert and Langecker[22] and also by Schmidt and Söll,[23] was obtained readily after only two crystallizations. However, repeated crystallization raised the m.p. to that described by Bardout.[14]

(22) A. Eckert and E. Langecker, *J. prakt. Chem.*, [2] **118**, 263 (1928).

(23) J. Schmidt and J. Söll, *Ber.*, **41**, 3679 (1908).

2-Aminofluoranthene (IV, R = H) was best obtained by rapid hydrogenation of 2-nitrofluoranthene (2 g.) in absolute ethanol (75 ml.), in the presence of decolorizing charcoal (1 g.) and platinum oxide (350 mg.), at a pressure of 45 lb./sq. in. Precipitation with water yielded 1.45 g. (82%) of amine, which separated from a mixture of benzene and petroleum ether in yellow needles, m.p. 128–129°. Solutions of the amine are sensitive to light and darken rapidly upon standing.

Anal. Calcd. for $C_{16}H_{11}N$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.18; H, 5.16; N, 6.64.

2-Acetylaminofluoranthene (IV, R = $COCH_3$) was obtained when 2-nitrofluoranthene (1 g.) suspended in 50 ml. of benzene was hydrogenated as before and the resulting solution was filtered directly into a solution of acetic anhydride (10 ml.) in benzene (50 ml.). When the solution was boiled for several minutes and then cooled, 400 mg. (38%) of the amide separated in orange–yellow microcrystals; m.p. 225–226° after recrystallization from glacial acetic acid.

Anal. Calcd. for $C_{18}H_{13}NO$: N, 5.40. Found: N, 5.65.

Ethyl N-2-fluoranthylcarbamate (IV, R = $COOC_2H_5$) was formed when a mixture of 2-aminofluoranthene (600 mg.), ethyl chloroformate (0.6 ml.), pyridine (0.6 ml.), benzene (30 ml.) and decolorizing charcoal (1 g.) was heated for 10 minutes at 50° and then allowed to stand in the dark for 12 hours. The precipitated urethan was separated from charcoal by solution in warm benzene from which it separated in yellow plates, m.p. 135–136°; yield 500 mg. (63%).

Anal. Calcd. for $C_{19}H_{15}NO_2$: N, 4.84. Found: N, 5.12.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NORTHWESTERN UNIVERSITY]

The Stereochemistry of the Ketonization Reaction of Enols.[1] II[2]

BY HOWARD E. ZIMMERMAN

RECEIVED SEPTEMBER 15, 1955

The study of the stereochemistry of ketonization has been extended to include the 2-methyl-3-phenylindanone system. The enol of 2-methyl-3-phenylindanone was found to lead preferentially to the less stable stereoisomeric product, *cis*-2-methyl-3-phenylindanone (IIa). Furthermore, enolization of IIa proved to be more facile than that of the *trans*-isomer IIb. These results are discussed in light of our previous findings which led to the conclusion that ketonization proceeds by protopic attack on the less hindered side of the enolic double bond.

Previously we have discussed[2] the kinetically controlled ketonization reaction of enols, which very frequently leads to the formation of the thermodynamically less stable of two possible stereoisomers. It was proposed that the reaction geometry results from a preferential attack of the proton donor on the less hindered side of the enolic double bond. This hypothesis was supported by experimental evidence in the 1-phenyl-2-benzoylcyclohexane series and also by six examples cited from the literature. It was therefore of interest to devise further tests of this hypothesis not only to strengthen its validity but also to further define the limits of its generality. The present study was concerned with the enol (I) of 2-methyl-3-phenylindanone (II).

2-Methyl-3-phenylindanone has been described in the literature by several researchers. Bergmann reported[3] the reduction of 2-methyl-3-phenylindone (III) with phosphorus and hydriodic acid to yield 2-methyl-3-phenylindanone (II), m.p. 64–65°. Somewhat later Ingold by catalytic hydrogenation of III obtained an oil which was considered[4] to be II. Finally, Shoppee[5] reported the formation of 2-methyl-3-phenylindanone (II) by reaction of 2-methyl-3-phenylind-2-en-1-yl acetate with aqueous base; again II was obtained as an oil. Both this oil and that of Ingold yielded 2,4-dinitrophenylhydrazones, m.p. 179° and 176–177°, respectively, the latter in unstated yield.

For the present study it was necessary first to prepare *cis*- and *trans*-2-methyl-3-phenylindanone (IIa and IIb) in reasonable quantities and to establish their configurations before proceeding with a consideration of the ketonization of I to yield these products. It was found that catalytic hydrogenation of 2-methyl-3-phenylindone (III) with PtO_2 in either benzene or ethyl acetate yielded *cis*-2-methyl-3-phenylindanone (IIa), m.p. 60.0–60.5°, while hydrogenation with the same catalyst in an ethanol–ethyl acetate mixture containing sodium hydroxide led to *trans*-2-methyl-3-phenylindanone, m.p. 61.0–62.0°. These stereoisomers exhibited a large mixed melting point depression and possessed similar solution infrared spectra which however differed markedly at several wave lengths in the 8–15 μ region. Both isomers yielded the same 2,4-dinitrophenylhydrazone, isomerization having occurred under the strongly acidic reaction conditions. Also, the same products of *alpha* bromination were obtained from IIa and IIb. The assignment of the *cis*-configuration to the isomer obtained by hydrogenation under non-alkaline conditions[6] was supported by equilibration experiments. Treatment of *cis*-2-methyl-3-phenylindanone (IIa) with 0.8 *N* methanolic sodium methoxide at room temperature for 2.5 hours yielded a mixture of IIa and IIb shown by infrared analysis[8] to consist

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[1] Presented at the Organic Division, Minneapolis A.C.S. Meeting, Sept., 1955.

[2] Paper I of this series: *J. Org. Chem.*, **20**, 549 (1955). Literature examples of this phenomenon are cited in this paper.

[3] E. Bergmann and H. Taubadel, *Ber.*, **65**, 467 (1932).

[4] C. Ingold and C. Wilson, *J. Chem. Soc.*, 1498 (1933).

[5] H. Burton and C. Shoppee, *ibid.*, 1156 (1935).

[6] Hydrogenation under neutral or acidic conditions generally proceeds by *cis*-addition to the olefinic double bond. Note ref. 7 for a discussion of the effect of basicity on the hydrogenation of α,β-unsaturated ketones. Alkaline conditions allow epimerization at the α-carbon atom; and regardless of mechanism the more stable isomer (IIb) should result.

[7] H. Weidlich and M. Meyer-Delius, *Ber.*, **74**, 1195 (1941).

[8] The method of quantitative estimation of relative amounts of IIa and IIb in various mixtures is described in the experimental section.