[JOINT CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT BRANCH, OFFICE OF SYNTHETIC LIQUID FUELS, U. S. BUREAU OF MINES, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

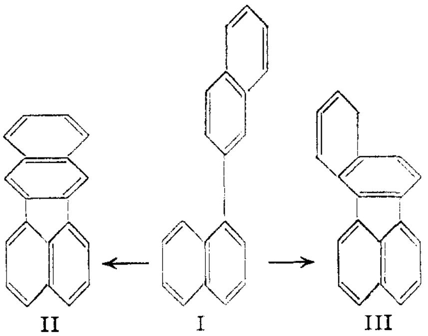
Synthesis of Benz[j]fluoranthene and Benz[k]fluoranthene[1]

BY MILTON ORCHIN[2] AND LESLIE REGGEL[2]

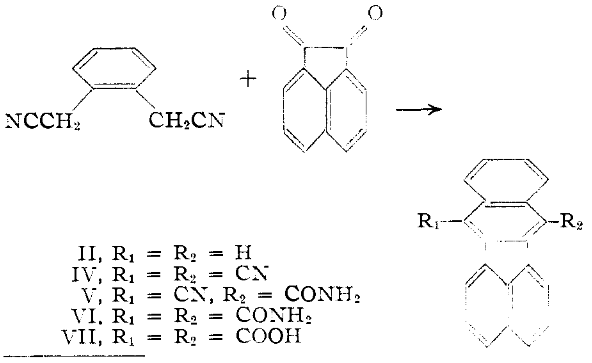
The two benzfluoranthenes secured by the cyclodehydrogenation of 1,2′-dinaphthyl have been synthesized. Condensation of acenaphthenequinone with *o*-phenylenediacetonitrile gave 7,12-dicyanobenz[k]fluoranthene, which was saponified to benz[k]fluoranthene-7,12-dicarboxamide. Treatment of benz[k]fluoranthene-7,12-dicarboxamide with phosphoric acid at 200° gave benz[k]fluoranthene.

A new method for the production of 1,2-benzfluorenone from 2-naphthylamine has been developed. The Reformatsky reaction on the benzfluorenone gave 1,2-benzfluorenyl-9-acetic acid, which was converted to β-(1,2-benzfluorenyl-9)-propionic acid by the Arndt–Eistert reaction. Cyclization of β-(1,2-benzfluorenyl-9)-propionic acid gave 3-keto-12c,1,2,3-tetrahydrobenz[j]fluoranthene which was reduced and then dehydrogenated to benz[j]fluoranthene.

It has previously been shown[3] that cyclodehydrogenation of 1,2′-dinaphthyl (I) leads to two isomeric hydrocarbons, of melting point 166° and 217°, to which the structures of benz[k]fluoranthene (II) and benz[j]fluoranthene (III), respectively, were tentatively assigned.[4] We now wish to report the synthesis of the two isomers. Comparison of the synthetic samples with those secured by cyclodehydrogenation has shown that our previous assignment of structures should be reversed.


II I III

The method of synthesis of II was essentially that of Moureu, Chovin and Rivoal.[5] These authors reported the synthesis of 7-cyanobenz[k]fluoranthene-12-carboxamide (V) by the condensation of *o*-phenylenediacetonitrile and acenaphthenequinone. Their assignment of the structure V to the product was based on the nitrogen content; however, the dicyano compound IV, the cyanoamide V, and the diamide VI all have approximately the same nitrogen content. Our investigation showed the condensation product to be contaminated by a small amount of an oxygen-containing material (possibly unconverted acenaphthenequinone); careful purification resulted in an oxygen-free material whose composition was consistent with its formulation as 7,12-dicyanobenz[k]fluoranthene (IV). The dicyano compound, IV, was inert to acid hydrolysis but was converted to benz[k]fluoranthene-7,12-dicarboxamide (VI) by alkaline saponification. All attempts to convert the diamide, VI, to the diacid, VII, were unsuccessful; VI was recovered unchanged after treatment with acids or alkali and was converted by nitrous-sulfuric acids into a compound which was apparently a mononitrosobenz[k]fluoranthenedicarboxylic acid. However, treatment of VI with phosphoric acid at 200° led to hydrolysis and decarboxylation, giving benz[k]fluoranthene, (II), in high yield. The product, melting point 217.0–217.3°, was identical with one of the benzfluoranthenes obtained by cyclodehydrogenation of 1,2′-dinaphthyl.[3] The properties of our hydrocarbon were also identical with those reported[6] by Moureu, Chovin and Rivoal, who published the conversion of V (or IV?) to II at about the time our experiments were completed.



II, $R_1 = R_2 = H$
IV, $R_1 = R_2 = CN$
V, $R_1 = CN$, $R_2 = CONH_2$
VI, $R_1 = R_2 = CONH_2$
VII, $R_1 = R_2 = COOH$

The starting material for the synthesis of benz[j]fluoranthene (III), was 1,2-benzfluorenone (XI). It appeared that the simplest preparation of XI would be the degradation of chrysene; but since the latter was unavailable at the time this work was begun, and since none of the other available methods[7,8] for the preparation of XI seemed promising for large-scale work, a new synthesis of XI was developed. Treatment of 2-benzoylaminonaphthalene (VIII) with benzoyl chloride and stannic chloride at 100° gave 1-benzoyl-2-benzoylaminonaphthalene (IX) which was saponified to 1-benzoyl-2-naphthylamine (X). Diazotization of X, followed by treatment with copper, gave XI. The over-all yield of XI from 2-naphthylamine was

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[1] Not subject to copyright. The material reported here is part of a thesis submitted to the University of Pittsburgh by L. R. in partial fulfillment of the requirements for the Doctor of Philosophy degree. We wish to thank Prof. Klaus Hofmann for his kind interest and coöperation during the course of this investigation.

[2] U. S. Bureau of Mines, Bruceton, Pa.

[3] Orchin and Reggel, THIS JOURNAL, **69**, 505 (1947).

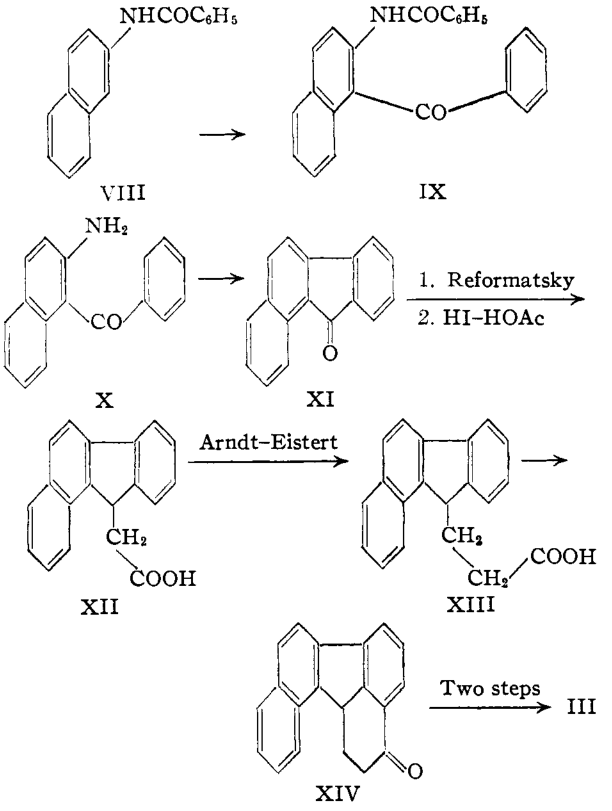
[4] II and III were previously called 8,9-benzfluoranthene and 7,8-benzfluoranthene. We now feel that the systematic Ring Index nomenclature is preferable.

[5] Moureu, Chovin and Rivoal, *Bull. soc. chim. France*, 106 (1946).

[6] Moureu, Chovin and Rivoal, *Compt. rend.*, **223**, 951 (1946); *ibid.*, **225**, 501 (1947); *Bull. soc. chim. France*, 99 (1948).

[7] Graebe, *Ber.*, **29**, 826 (1896); Cook and Hewett, *J. Chem. Soc.*, 365 (1934); Cook, Hewett, Mayneord and Roe, *ibid.*, 1727 (1934), Lothrop and Goodwin, THIS JOURNAL, **65**, 363 (1943).

[8] Cook and Preston, *J. Chem. Soc.*, 553 (1944).



20%.[9] The position of the benzoyl group in X has been previously proven[10] by conversion to the known 1-benzoyl-2-naphthol. Our conversion of X to the known 1,2-benzfluorenone (XI) substantiates the assigned structure. It is of interest to note that treatment of 2-naphthylamine or 2-acetylaminonaphthalene with acetic anhydride and aluminum chloride in carbon disulfide results in acylation in the 6- and 8-positions.[11]

The Reformatsky reaction on 1,2-benzfluorenone (XI), followed by reductive hydrolysis[8] of the crude hydroxy-ester, gave 1,2-benzfluorenyl-9-acetic acid (XII) in high yield. The structure of XII was confirmed by decarboxylation to the known, strongly estrogenic,[12] 9-methyl-1,2-benzfluorene.

Conversion of XII to the corresponding propionic acid, XIII, by the Arndt–Eistert method proved both difficult and erratic; the acid chloride of XII was easily converted to an oily diazoketone, but the rearrangement to give β-(1,2-benzfluorenyl-9)-propionic acid (XIII) (or its ester), proceeded in poor yield and with irreproducible results (see Experimental).

Ring closure of XIII by the inverse Friedel–Crafts method[13] in either benzene or carbon disulfide as solvent gave an almost quantitative yield of neutral material, from which the ketone XIV could be isolated in fair yield by chromatography or *via* the semicarbazone; the nature of the by-products was not investigated. Clemmensen–Martin reduction of XIV gave a non-crystalline tetrahydrobenz[j]fluoranthene, which was dehydoogenated with palladium-on-charcoal to give a very small yield of benz[j]fluoranthene (III), isolated as the *s*-trinitrobenzene complex, brown needles, m. p. 213.0–216.5°. The *s*-trinitrobenzene complex of benz[j]fluoranthene isolated from the cyclodehydrogenation experiments[3] was orange-yellow, but of the same melting point; a mixed melting point of the two samples gave no depression. The identity of the two *s*-trinitrobenzene complexes was confirmed by comparison of the ultraviolet absorption spectra (Fig. 1). Apparently the brown complex contains a very small amount of a dark impurity which affects neither the melting point nor the ultraviolet absorption spectrum. Insufficient material prevented further characterization or purification.

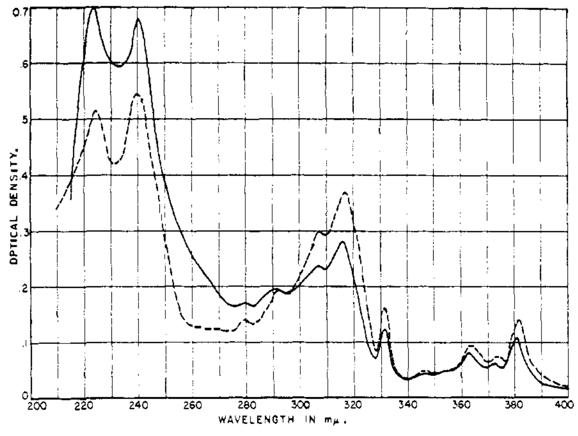


Fig. 1.—Ultraviolet absorption spectra; ---- benz[j]fluoranthene from 1,2′-dinaphthyl[3]; —— *s*-trinitrobenzene complex of benz[j]fluoranthene, this investigation; both spectra in 95% ethanol as solvent.

In another attempt to convert the ketone XIV to III, the ketone was reduced (both catalytically and with lithium aluminum hydride) and then dehydrogenated; small amounts of unidentified products were obtained. The problem was not investigated further, and III was never obtained as the hydrocarbon in the present investigation. We believe, however, that the structure of benz[j]fluoranthene for the hydrocarbon of melting point 166° obtained from 1,2′-dinaphthyl is quite certain.

After the experimental work described here had been completed, a paper by Zinke and Pack[14] appeared in which the action of aluminum chloride on dinaphtho[2,1,1′,2′]furan was reinvestigated. It was shown that zinc-dust distillation of the compound formerly regarded as 1-hydroxyperylene did not give perylene but, instead, an isomeric yellow hydrocarbon, m. p. 165–167°, to which the structure of benz[j]fluoranthene (III) was assigned. These properties agree with those of our hydrocarbon. No ultraviolet absorption data were given.

In another experiment designed as an alternate route to the benz[j]fluoranthene nucleus, the modi-

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(9) Drs. Clair J. Collins and A. Russell Jones, who were supplied with the details of this experimental procedure, have informed us that the yield of XI can be somewhat improved by omitting purification of the intermediates.

(10) Dziewoński, Kwieciński and Sternbach, *Bull. intern. acad. polonaise, Classe sci. math. nat.*, *A*, 329 (1934); *C. A.*, **29**, 1084^5 (1935).

(11) Leonard and Hyson, *J. Org. Chem.*, **13**, 164 (1948); THIS JOURNAL, **71**, 1392 (1949).

(12) Badger, *J. Chem. Soc.*, 535 (1941); Haddow and Kon, *Brit. Med. Bull.*, **4**, 314 (1947).

(13) Johnson and Glenn, THIS JOURNAL, **71**, 1092 (1949).

(14) Zinke and Pack, *Monatsh.*, **80**, 213 (1949).

fied Stobbe reaction[15] with 1,2-benzfluorenone was found to give 1,2-benzfluorenylidene-9-succinic acid as the only identifiable product. In view of the superior results of the Reformatsky reaction, this approach was not investigated further.

The air oxidation of an alkaline solution of fluorene-9-carboxylic acid has been shown[16] to give fluorene and fluorenone. We have found that both fluorenyl-9-acetic acid and 1,2-benzfluorenyl-9-acetic acid, under the same conditions, give a mixture of the corresponding fluorene and fluorenone. We plan to investigate further this elimination of the side chain from 9-substituted fluorenes.

Experimental[17]

7,12-Dicyanobenz[k]fluoranthene (IV).—To a solution of 5.00 g. of acenaphthenequinone[18] in 25 ml. of piperidine, there was added rapidly with stirring a solution of 4.60 g. of *o*-phenylenediacetonitrile[19] in 25 ml. of piperidine. Another 25 ml. of piperidine was used to rinse the funnel. After a few minutes the solution became cloudy and evolved heat. The flask was placed in an ice-bath and stirred for 1 hour; then the ice-bath was removed, and stirring was continued for 4 hours at room temperature. The mixture was allowed to stand for 63 hours, then poured into 400 ml. of water and acidified with 70 ml. of concentrated hydrochloric acid. The yellow-green solid was filtered and washed with water, placed in a 1-liter flask with 110 g. of sodium metabisulfite, 190 ml. of water, and a few ml. of alcohol, and the mixture refluxed two hours (considerable foaming). The solid was filtered, the treatment with sodium metabisulfite was repeated, and the yellow solid was filtered and washed with water and alcohol. There was obtained 6.03 g. of IV, m.p. 358–362°. Two recrystallizations from about 200 ml. of *s*-tetrachloroethane gave 5.43 g. (65%) of small, yellow crystals, m.p. 356–360°. The crystals of IV shrink markedly from about 320° to 350°, but the actual melting point is fairly sharp and reproducible. For analysis, a sample was recrystallized again from tetrachloroethane; it melted at 357–359°. *Anal.* Calcd. for $C_{22}H_{10}N_2$: C, 87.4; H, 3.3; N, 9.3. Found: C, 87.2; H, 3.5; N, 9.5.

If the treatment with sodium bisulfite was omitted, the melting point of the product was not changed, but the material contained about 1.5% oxygen; the impurity may be acenaphthenequinone. IV did not form a complex with 2,4,7-trinitrofluorenone.[20]

Benz[k]fluoranthene-7,12-dicarboxamide (VI).—A mixture of 2.24 g. of IV, 45 g. of potassium hydroxide, 225 ml. of ethylene glycol monoethyl ether (distilled from sodium) and 18 ml. of water was refluxed for 48 hours in a copper flask. The clear orange solution was poured onto ice, allowed to stand two hours, filtered, and washed with water. The resulting material (2.36 g., m.p. 318–323° (gas)) was dissolved in 400 ml. of acetic acid, and the solution was concentrated to 110 ml. There was obtained 1.70 g. of pale-yellow plates, m.p. 399–401° (dec.); the melting point depended somewhat upon the rate of heating. The mother liquor gave an additional 0.37 g., m.p. 391–396° (dec.); total yield 2.07 g., 83%. A sample recrystallized for analysis and then sublimed at 325–335° (1 mm.) had m.p. 395.5–397° (dec.). *Anal.* Calcd. for $C_{22}H_{14}O_2N_2$: C, 78.1; H, 4.2; N, 8.3. Found: C, 78.5; H, 4.0; N, 8.1.

When the dicyano compound, IV, was refluxed with acetic–sulfuric acids, acetic–hydrochloric acids, ethanol saturated with hydrogen chloride, or ethylene glycol saturated with hydrogen chloride, it was recovered unchanged (melting point and mixed melting point).

Attempted Conversion of Benz[k]fluoranthene-7,12-dicarboxamide (VI) to Benz[k]fluoranthene-7,12-dicarboxylic Acid (VII). (a) **Acid Hydrolysis.**—A solution of 470 mg. of VI in 50 ml. of acetic acid and 5 ml. of 65% sulfuric acid (by weight) was refluxed for 48 hours and then poured onto ice. The precipitate was digested, cooled, filtered, and washed with water; 0.43 g., m.p. 352–355° (dec.). The acetic acid filtrate was analyzed for nitrogen by the Kjeldahl method and found to contain less than 1 mg. of ammonia; hydrolysis of the diamide to the diacid would have produced 47 mg. of ammonia. The precipitate was recrystallized three times from acetic acid, yielding 225 mg., m.p. 361.5–368° (dec.). Since the melting point had not reached a constant value, the material was not analyzed; however, the Kjeldahl determination indicates that hydrolysis of the amide linkages did not take place.

(b) **Treatment with Nitrous Acid.**—To a solution of 541 mg. of VI in 70 ml. of acetic acid, there was added 2.0 ml. sulfuric acid followed by a solution of 1.40 g. sodium nitrite in 10 ml. water. After 50 minutes at room temperature, the solution was heated on the steam-bath for 30 minutes and then allowed to cool; a copious precipitate of small yellow needles formed. Another portion of 1.40 g. of sodium nitrite in 10 ml. of water was added, the mixture allowed to stand 30 minutes at room temperature, heated 30 minutes on the steam-bath, and left overnight in the refrigerator. The yellow precipitate was filtered to give 411 mg. of material which decomposed slowly on heating but did not melt. A sample dissolved in ethylene glycol monoethyl ether and titrated with sodium hydroxide gave a neutral equivalent of about 193; the solution was very dark and the end-point of the titration difficult to determine. The material was very insoluble in acetic acid; recrystallization from ethylene glycol monoethyl ether gave a small amount of material which decomposed slowly (300–400°) without melting. The analysis is suggestive of an impure mononitrosobenzfluoranthenedicarboxylic acid. *Anal.* Calcd. for $C_{22}H_{11}O_5N$: C, 71.6; H, 3.0; N, 3.8. Found: C, 69.0, 69.2; H, 3.5, 3.8; N, 3.8, 3.6; ash, 0.7, 0.6.

When fluorenone-1-carboxamide was treated with nitrous acid in the same manner, there was obtained a 97% yield of fluorenone-1-carboxylic acid.

Benz[k]fluoranthene (II).—A mixture of 2.296 g. of VI and 85 ml. of 100% phosphoric acid[21] was heated at 190–210° for eight hours with frequent swirling. The mixture was poured into water and extracted with benzene. The benzene solution was washed with water, sodium bicarbonate solution, water, and saturated sodium chloride and dried over calcium chloride. (In a previous experiment, extraction with Claisen alkali showed the absence of acidic products.) The benzene solution was taken to dryness, giving 1.749 g. of a brownish crystalline material. This was dissolved in benzene, chromatographed on alumina–supercel (1:1), developed with benzene, and the column extruded. The blue-fluorescent, less strongly adsorbed band gave 1.633 g. (95%) of benz[k]fluoranthene (II) m.p. 215.5–217.6°. Recrystallization from benzene gave 1.25 g. of small, pale-yellow needles, m.p. 217.0–217.3°, and a second crop, 0.18 g., m.p. 216.8–217.3°. The mixed melting point with the benzfluoranthene of melting point 217.0–217.4° obtained from cyclodehydrogenation of 1,2′-dinaphthyl[3] was 217.1–217.6°. The ultraviolet absorption spectra of the two samples were identical.

The complex with 2,4,7-trinitrofluorenone formed small orange-red needles, m.p. 251.5–253.5° (from benzene); reported[3] m.p. 252.0–253.0. Attempts to prepare the picrate and s-trinitrobenzene complex[3] of II in benzene, ethanol, or benzene–ethanol gave only mixtures.

2-Benzoylaminonaphthalene, VIII.—The reaction of benzoyl chloride with 2-naphthylamine in pyridine gave VIII in 89% yield. A sample recrystallized from acetic acid and then twice from absolute ethanol formed snow-white needles, m.p. 160.8–162.2° (reported[22] m.p. 162–163°). The 2,4,7-trinitrofluorenone[20] complex of VIII formed elongated orange prisms (from benzene–alcohol) m.p. 137.0–138.4°

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[15] Johnson and co-workers, THIS JOURNAL, **67**, 1357, 1360, 1366 (1945), and subsequent papers.

[16] Wislicenus and Ruthig, *Ber.*, **46**, 2770 (1913); Jeanes and Adams, THIS JOURNAL, **59**, 2620 (1937).

[17] Microanalyses were performed by G. L. Stragand, University of Pittsburgh. Kjeldahl macroanalysis was done by R. Raymond, Bureau of Mines. The authors are indebted to R. A. Friedel, Lois Pierce, Lois Harnack and Marion Springer for the ultraviolet absorption spectra. All melting points are corrected.

[18] Maxwell and Allen, *Org. Syntheses*, **24**, 1 (1944).

[19] Fieser and Pechet, THIS JOURNAL, **68**, 2577 (1946); Moore and Thorpe, *J. Chem. Soc.*, **93**, 165 (1908).

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

[21] Berger and Olivier, *Rec. trav. chim.*, **46**, 600 (1927).

[22] Heilbron, "Dictionary of Organic Compounds," Vol. 3, Oxford University Press, New York, 1943, p. 33.

TABLE I

UNSUCCESSFUL ATTEMPTS TO PREPARE 1-BENZOYL-2-BENZOYLAMINONAPHTHALENE BY THE FRIEDEL–CRAFTS REACTION USING BENZOYL CHLORIDE WITH 2-NAPHTHYLAMINE OR AN ACYLATED 2-NAPHTHYLAMINE

Starting material	Catalyst	Solvent	Temp., °C.	Time, hr.	Products isolated
2-Acetylaminonaphthalene	$AlCl_3$	CS_2	0	23	2-Acetylaminonaphthalene, benzoic acid
2-Acetylaminonaphthalene	$AlCl_3$	CS_2	20	3.5	2-Acetylaminonaphthalene, benzoic acid, other non-ketonic product (not investigated)
			Reflux	3	
2-Naphthylamine	$ZnCl_2$	CS_2	20	48	2-Naphthylamine 2-Benzoylaminonaphthalene
2-Naphthylamine	$ZnCl_2$	None	180	5 min.	2-Benzoylaminonaphthalene
2-Benzoylaminonaphthalene	$AlCl_3$	$CHCl_2CHCl_2$	95	5	Tar, benzoic acid
			20	15	
2-Benzoylaminonaphthalene	$SnCl_4$	$CHCl_2CHCl_2$	20	140	2-Benzoylaminonaphthalene

with sintering from 128°. *Anal.* Calcd. for $C_{30}H_{18}O_8N_4$: N, 10.0. Found: N, 10.5.

1-Benzoyl-2-benzoylaminonaphthalene (IX).—In a one-liter three-necked flask fitted with mercury-sealed stirrer, reflux condenser, and dropping funnel, there was placed 98.8 g. of 2-benzoylaminonaphthalene, VIII, and 160 ml. of distilled benzoyl chloride. The mixture was stirred and held at 100–110° (oil-bath temperature), while 234 ml. of distilled stannic chloride was added during 30 minutes. Hydrogen chloride was evolved, and the mixture became black. After addition of the stannic chloride was complete, the mixture was stirred and heated at 100–110° for 12 minutes and then poured into 3 liters of water (violent reaction). The material clinging to the reaction flask was dissolved in hot acetone and the acetone solution added to the main mixture. The brown granular solid was filtered, dissolved in about 1 liter of benzene, the benzene solution washed twice with 500-ml. portions of 10% hydrochloric acid, water, 10% sodium hydroxide and water, and then filtered through paper (gravity). The solution was concentrated to remove most of the water, treated with charcoal, the benzene replaced with ethanol, and the product allowed to crystallize from 500 ml. of ethanol. There was obtained 96.4 g. of IX as a tan solid, m.p. 155.0–156.8°, which was pure enough for use in the next step. The ethanol mother liquor was distilled *in vacuo* to give 14.4 of a red gum, boiling point about 270–300° at 1–3 mm. The distillate was recrystallized from ethanol, giving 7.6 g. of material, m.p. 153.4–155.2°. The total yield was 104.0 g. (74%).

For analysis, a sample was recrystallized from ethanol, giving very pale tan needles, m.p. 155.5–157.2°. *Anal.* Calcd. for $C_{24}H_{17}O_2N$: C, 82.0; H, 4.9; N, 4.0. Found: C, 82.2; H, 4.8; N, 4.3.

When the reaction was carried out at 140–160°, the yield dropped to 65%. The use of temperatures lower than 100° was not tried, but, since the reaction fails at room temperature (Table I) some intermediate optimum temperature may exist. The action of a smaller amount of stannic chloride was not investigated.

For preparing large quantities of IX, the reaction was carried out using one and one-half the quantities given above, but this was found to be rather inconvenient. It was preferable to do several experiments in the manner described, crystallize the first crop of material from each, and then combine and distil the mother liquors.

An attempt to prepare the 2,4,7-trinitrofluorenone[20] complex of IX in benzene–ethanol or in acetic acid gave only mixtures.

1-Benzoyl-2-naphthylamine (X).—To a refluxing solution of 96.4 g. of IX in 750 ml. of ethanol, there was added slowly a solution of 100 g. of potassium hydroxide in 150 ml. of water and 200 ml. of ethanol.[9] The solution was refluxed 12 to 16 hours; during this time, a yellow solid precipitated. After cooling to room temperature, the crystals were filtered, washed with water until neutral, and then washed by decantation with 100 ml. of absolute ethanol, giving 58.9 g. of X, m.p. 168.2–170.0°. The ethanol washing and the original alkaline ethanol filtrate were combined, concentrated, and diluted with hot water. After standing overnight, the precipitate was filtered, washed with water, and recrystallized twice from ethanol (charcoal) giving 3.45 g. of X, m.p. 167.5–169.5°. The total yield was 62.35 g. (92%). A sample for analysis was recrystallized from ethanol, giving bright-yellow needles, m.p. 168.8–169.8°. *Anal.* Calcd. for $C_{17}H_{13}ON$: C, 82.6; H, 5.3; N, 5.7. Found: C, 82.5; H, 5.1; N, 5.7.

On a larger scale it was found convenient to saponify 200 g. of IX, filter off the first crop of crystals, and precipitate the second crop as done previously. The second crops from two 200-g. runs were then combined and distilled (b.p. 200–240° at 1 mm.) and the distillate was recrystallized once from ethanol. The yield was about the same (93%).

An attempt to prepare the 2,4,7-trinitrofluorenone complex[20] of X in benzene or benzene–ethanol gave only mixtures. Use of acetic acid as solvent gave dark-purple needles, m.p. 220–232° (not analyzed).

1,2-Benzfluorenone (XI).—In a three-liter, three-necked flask fitted with a dropping funnel, mercury-sealed stirrer, and reflux condenser, were placed 49.4 g. of X, 1500 ml. of acetic acid, and 21 ml. of sulfuric acid. To the stirred mixture there was added during two minutes a solution of 53.0 ml. of isoamyl nitrite in 250 ml. of acetic acid. During the addition the yellow solid dissolved, giving a clear red solution. After stirring for 30 minutes, the flask was cooled in an ice-bath, and 25.5 g. of copper powder was added; some gas was evolved. The mixture was stirred 30 minutes, the ice-bath removed, and stirring continued for 2.5 hours at room temperature and then for 3.0 hours on the steam-bath. The mixture was then allowed to stand overnight. About 1200 ml. of acetic acid was distilled off and the residue filtered (gravity) into about 1 liter of water; a black, tarry material precipitated. The copper was extracted three times with 100-ml. portions of hot benzene. The water was decanted from the tar, and the aqueous phase was extracted with the benzene washings of the copper. The tar was then extracted with three 175-ml. portions of hot benzene–ether (1:1) (not all of the tar dissolved). The organic extracts were combined and washed with 250-ml. portions of 10% hydrochloric acid (twice), water, 10% sodium hydroxide containing a little ammonium hydroxide (twice), water, and saturated sodium chloride and dried over calcium chloride. (Usually it was necessary to filter the organic layer with suction once or twice during the washings because of the formation of emulsions and the precipitation of tar.) The solvents were removed and the residue was distilled. After a small forerun there was obtained 21.24 g. of orange material, b.p. 210–235° at 2–4 mm. (bath 270–300°) which solidified immediately. This was recrystallized from 400 ml. of 95% ethanol, giving 12.27 g. of XI, m.p. 133.2–134.8°. The second crop (3.17 g., m.p. 130.0–132.0°) was recrystallized to give 2.67 g. of good material. The total yield was 14.94 g. (33%). A sample recrystallized again from ethanol formed thin orange needles, m.p. 134.5–135.0° (literature, 130°,[23a] 132.5°,[23b] 131–132°,[23c] 133°[23d]).

The above reaction was run several times. Fractional crystallization of the mother liquor gave no pure compound. Neither the hydrochloric acid washings nor the sodium hydroxide washings contained an appreciable amount of material. A Claisen alkali extract of the crude XI did not remove any acidic material. The procedure gave consistent yields of 33% as described or when twice the above quantities were

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(23) (a) Bamberger and Kranzfeld, *Ber.*, **18**, 1931 (1885); Graebe. *ibid.*, **27**, 952 (1894); Graebe, *ibid.*, **29**, 826 (1896); (b) Bamberger and Burgdorf, *ibid.*, **23**, 2433 (1890); Graebe, *Ann.*, **335**, 122 (1904); (c) Cook and Hewett, *J. Chem. Soc.*, 365 (1934); (d) Kruber, *Ber.*, **70B**, 1556 (1937).

used. A 5.00-g. run gave a yield of 44%; this was never duplicated on a larger scale. In one run the copper was added to the diazonium solution at room temperature; the mixture became hot, and the yield was decreased to 11%. Use of ethanol as solvent gave a very low yield; addition of sodium hypophosphite[24] in either ethanol or acetic acid as solvent gave very low yields. Use of less acetic acid (20.0 g. of X in a total of 300 ml. of acetic acid) lowered the yield of XI to 26%; the influence of more acetic acid was not tried. The use of dioxane as solvent[25] was not investigated.

The complex of XI with 2,4,7-trinitrofluorenone[20] formed yellow-orange needles, m.p. 218.0–220.0°, after recrystallization from acetic acid. *Anal.* Calcd. for $C_{30}H_{15}O_8N_3$: N, 7.7. Found: N, 7.7.

The oxime of XI was prepared in pyridine–ethanol and recrystallized from benzene; it formed bright-yellow prisms, m.p. 193.2–194.0° (dec.) (reported, 190°,[23a] 202°.[23b]

The 2,4-dinitrophenylhydrazone of XI formed red needles (from pyridine), m.p. 325.0–326.0° (dec.) with previous darkening. It was extremely insoluble in isopropyl alcohol or in acetic acid. *Anal.* Calcd. for $C_{23}H_{14}O_4N_4$: N, 13.7. Found: N, 12.8.

The semicarbazone of XI was prepared in pyridine–ethanol and recrystallized from pyridine, forming bright-yellow crystals, m.p. 263.5–266.5° (dec.) with previous darkening. It was extremely insoluble in benzene and in isopropyl alcohol. *Anal.* Calcd. for $C_{18}H_{13}ON_3$: N, 14.6. Found: N, 14.3.

1,2-Benzfluorenylidene-9-succinic Acid.—To a solution of 1.02 g. of potassium in 20 ml. of *t*-butyl alcohol (nitrogen atmosphere) there was added a mixture of 4.60 g. of XI and 6.97 g. of diethyl succinate; an additional 5-ml. portion of *t*-butyl alcohol was used to rinse the mixture into the reaction flask. The resulting deep-red solution was refluxed 1.5 hours and then decomposed by the addition of a mixture of 5 ml. of hydrochloric acid and 25 ml. of water. The *t*-butyl alcohol was then removed by distillation at the water-pump. The red, oily residue was taken up in ether and extracted with 10% sodium bicarbonate. The bicarbonate extracts were acidified and the red oil taken up in ether, washed well with water and saturated sodium chloride solution, and dried over calcium sulfate. After removal of the solvent, the residue was distilled at 1 mm. (bath temperature 290°). There was obtained 5.12 g. (72%) of a black viscous gum, presumed to be β-carboethoxy-β-(1,2-benzfluorenylidene-9)-propionic acid, which could not be crystallized. It was dissolved in a mixture of 30 ml. of acetic acid, 20 ml. of 48% hydrobromic acid, and 10 ml. of water, and refluxed for six hours. The solution was extracted with benzene–ether and the organic layer washed with water and then separated into neutral and acidic fractions by extraction with 5% sodium bicarbonate. The neutral portion was dried with sodium sulfate and the solvents removed, leaving 1.25 g. of oil which was not further investigated. The bicarbonate extracts were acidified and the precipitate filtered and dried, giving 3.90 g. of a tan solid, m.p. 158–200°. This material was insoluble in benzene but very soluble in ethanol. Recrystallization from benzene–ethanol gave 1.20 g. of 1,2-benzfluorenylidene-9-succinic acid, m.p. 233–237° (dec.). For analysis, the material was recrystallized again from benzene–ethanol, giving 0.66 g. of tan crystals, m.p. 237.5–239.5° (dec.). *Anal.* Calcd. for $C_{21}H_{14}O_4$: C, 76.4; H, 4.3; neut. equiv., 165. Found: C, 76.3; H, 4.4; neut. equiv. (L.R.), 167.

The solvents were removed from the mother liquor of the 1.20 g. (above) and the residue recrystallized from aqueous acetic acid, giving 1.26 g. of brown crystals, m.p. 154.0–157.5° (dec.) (sintering from 150°). Two recrystallizations from aqueous acetic acid gave material of melting point 169.5–175.0° (not constant). This material was not further investigated; it may be an impure stereoisomer of β-(1,2-benzfluorenylidene-9)-propionic acid or it may be a stereoisomer of the succinic acid; both of these compounds could exist in *cis* and *trans* forms.

1,2-Benzfluorenyl-9-acetic Acid (XII).—To 11.76 g. of granulated zinc and a crystal of iodine there was added about 20 ml. of a solution of 27.60 g. of 1,2-benzfluorenone, XI, and 32.76 g. of ethyl bromoacetate in 540 ml. of dry, thiophene-free benzene (nitrogen atmosphere). The mixture was stirred and refluxed while the remainder of the solution of XI and bromoester was added during 1.25 hours; the mixture was then stirred and refluxed for 24 hours. The solution was poured onto a mixture of ice and 45 ml. of concentrated sulfuric acid; ether was added and the organic layer washed three times with 200-ml. portions of 5% sulfuric acid and then with water, sodium bicarbonate solution, and saturated sodium chloride solution. The solvents were carefully distilled and the residual crude hydroxy-ester was then refluxed for 24 hours with 150 ml. of 55% hydriodic acid and 600 ml. of acetic acid.[8] About 400 ml. of acetic acid was then distilled off and the residue poured into iced sodium metabisulfite. The pale-yellow precipitate was filtered, air-dried, and dissolved in a mixture of 225 ml. of Claisen alkali and 675 ml. of water. (Use of undiluted Claisen alkali led to the formation of solid matter, probably the potassium salt of the acid.) The alkaline solution was extracted with 300 ml. of benzene and then poured onto 300 ml. of iced hydrochloric acid. The precipitate was filtered, air-dried, placed in a Soxhlet thimble, and extracted for 5 hours with 650 ml. of toluene. On cooling, the toluene extract gave 25.90 g. of XII, m.p. 191.5–192.5° (softening at 190°). The mother liquor was used to re-extract the material remaining in the thimble and then concentrated to give 3.90 g. of XII, m.p. 189.8–191.6° (softening at 189°). The total yield was 29.80 g. (91%). (This method of crystallization was found to be more convenient than simply dissolving the crude product in toluene, as the acid dissolved rather slowly.) A sample recrystallized from toluene formed clusters of white needles, m.p. 191.0–193.5° (sintering at 190°). *Anal.* Calcd. for $C_{19}H_{14}O_2$: C, 83.2; H, 5.1. Found: C, 83.3; H, 5.1.

A mixture of 1,2-benzfluorenyl-9-acetic acid and 1,2-benzfluorene had a melting point of 160–170° (cloudy until about 190°).

The 2,4,7-trinitrofluorenone[20] complex of XII formed small orange-yellow crystals (from acetic acid), m.p. 169.0–170.0° (sintering from 168.5°). *Anal.* Calcd. for $C_{32}H_{19}O_9N_3$: N, 7.1. Found: N, 7.1.

Ethyl 1,2-benzfluorenyl-9-acetate formed almost colorless plates, m.p. 69.4–70.6° (from ethanol). *Anal.* Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.6; H, 6.0.

1,2-Benzfluorenyl-9-acetamide formed pink crystals, m.p. 235.0–237.0° (from acetic acid). *Anal.* Calcd. for $C_{19}H_{15}ON$: N, 5.1. Found: N, 5.6.

9-Methyl-1,2-benzfluorene.—A mixture of 1.0 g. of 1,2-benzfluorenyl-9-acetic acid, XII, 10 ml. of quinoline and 0.5 g. of copper powder was refluxed 1.25 hours. The product was taken up in benzene, filtered, washed with hydrochloric acid, water, and sodium chloride, dried, and concentrated to small volume. There was obtained 0.27 g. of starting material, m.p. 191.0–192.4°, mixed melting point 191.5–192.6°. This was combined with its mother liquor and the benzene removed. An additional 0.10 g. of 1,2-benzfluorenyl-9-acetic acid was dissolved in a few ml. of alcohol and treated with a solution of 0.5 g. copper sulfate in a few ml. of water. The green precipitate of the copper salt was filtered and dried in a vacuum desiccator. The recovered XII, the copper salt, 0.5 g. of copper, and 15 ml. of 2,7-dimethylquinoline were refluxed 4.5 hours. The product was taken up in benzene, washed with hydrochloric acid, water, sodium hydroxide, water, and sodium chloride, dried, and chromatographed on alumina. The column was eluted with benzene–petroleum ether (1:1). The first fraction of the percolate was taken to dryness and the residual solid recrystallized from ethanol, giving 0.15 g. (18%) of 9-methyl-1,2-benzfluorene, m.p. 111.5–121.0°. Recrystallization from ethanol gave very pale yellow plates, m.p. 124.0–124.9° (literature,[12] 120.5–122.5°).

β-(1,2-Benzfluorenyl-9)-propionic Acid (XIII).—To a cold solution of diazomethane (prepared from 76 g. of N-nitroso-N-methylurea; titration showed about 6.83 g. of diazomethane) in 600 ml. of benzene–ether (1:1) there was added dropwise with stirring a solution of crude, solid 1,2-benzfluorenyl-9-acetyl chloride (prepared from 10.74 g. of acid using phosphorus pentachloride) in 100 ml. of benzene. After stirring for 2 hours, the solution was allowed to stand in the ice-bath for 17 hours. The solvents were then distilled off at the water-pump (dry nitrogen atmosphere), the flask being kept in a bath maintained at 50–55°. There was obtained a dark-brown oil, insoluble in petroleum ether, very soluble in benzene, which could not be crystallized. A

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(24) Ruggli and Staub, *Helv. Chim. Acta*, **20**, 37 (1937).

(25) Cassaday and Bogert, THIS JOURNAL, **61**, 2461, 3055, 3058 (1939).

small portion of the oil was dissolved in a few drops of acetic acid, and a drop of hydrochloric acid was added; gas was evolved vigorously, indicating the presence of the diazoketone. The oily diazoketone was dissolved in 300 ml. of absolute ethanol and the solution heated in a water-bath at 55–60° and stirred vigorously while an ethanol slurry of silver oxide (prepared from 60 ml. of 10% silver nitrate solution) was added in small portions during 35 minutes. After stirring for an additional 25 minutes, the mixture was refluxed with stirring for 1 hour. The mixture was filtered, the ethanol removed at the water pump (nitrogen atmosphere), and the residue distilled at 1–2 mm. (bath temperature 290°). There was obtained 9.29 g. of a brown oil, presumably ethyl β-(1,2-benzfluorenyl-9)-propionate, which could not be crystallized. The ester was hydrolyzed by refluxing for 24 hours with 100 ml. of acetic acid and 50 ml. of hydrochloric acid. The dark crystals which formed on cooling were recrystallized from benzene–acetic acid, giving 5.04 g. of XIII, m.p. 192.5–195.0° (sintering at 183°). The mother liquors were combined and concentrated, and the resulting very dark crystalline material was recrystallized from benzene–acetic acid to give an additional 1.23 g. of XIII, m.p. 191.5–195.5°. The total yield was 6.27 g. (56%). A sample recrystallized from benzene formed brown plates, m.p. 192.0–195.5° (sintering at 190.5°). *Anal.* Calcd. for $C_{20}H_{16}O_2$: C, 83.3; H, 5.6. Found: C, 83.3; H, 5.2.

A mixture of β-(1,2-benzfluorenyl-9)-propionic acid and 1,2-benzfluorenyl-9-acetic acid melted at 165–185°.

The experiment described above was the best of nine attempts to convert XII to XIII. In one experiment a very small quantity of the diazoketone was dissolved in dioxane and added to a mixture of silver oxide, sodium thiosulfate, and water at 65°; there was obtained a small amount of the propionic acid, XIII. Two attempts to repeat this preparation on a large scale (5 g. of XII) failed to give any XIII; the products were mainly neutral materials which did not evolve gas when treated with acid and hence were not unchanged diazoketone. An attempt to convert XII to XIII by the benzyl alcohol–isoquinoline method of Wilds and Meader[26] also failed to give any acidic material; this experiment was done on a small scale and could not be repeated because of lack of a sufficient supply of XII.

Action of Alkali on 1,2-Benzfluorenyl-9-acetic Acid (XII).—A solution of 0.50 g. of XII in 100 ml. of 5% aqueous sodium hydroxide was refluxed for 2.5 hours. A small amount of white solid formed in the solution, and a small amount of orange solid distilled into the condenser. The mixture was extracted with benzene and then with benzene–ether (1:1). Acidification of the alkaline solution gave 0.46 g. of starting acid (92%). The organic extracts were washed with hydrochloric acid, water, and sodium chloride and evaporated to dryness. There was obtained 0.036 g. of an orange oil. Analysis by means of the ultraviolet absorption spectrum showed that this material consisted of 11% 1,2-benzfluorene and 13% 1,2-benzfluorenone; the balance was unidentifiable.

3-Keto-12c,1,2,3-tetrahydrobenz[j]fluoranthene (XIV).—A solution of the oily acid chloride prepared (phosphorus pentachloride) from 2.50 g. of XIII was dissolved in 20 ml. of benzene and added dropwise with stirring during 15 minutes to a mixture of 1.62 g. of aluminum chloride and 40 ml. of benzene maintained at 5–8°. The first drop produced an immediate orange color. The mixture was stirred for 2.25 hours at 5°, and then for one hour at 10°. It was then cooled to about 3–5°, 50 ml. of ether was added, and then 100 ml. of cold 1:1 hydrochloric acid was added dropwise; the orange color disappeared. The organic layer was washed with water, sodium bicarbonate solution, and saturated sodium chloride, and dried over sodium sulfate. The bicarbonate extract gave only a trace of material on acidification. The neutral portion was insoluble in petroleum ether and could not be induced to crystallize from methanol–benzene. It was dissolved in 50 ml. absolute ethanol, 4.85 g. of semicarbazide hydrochloride and 5 ml. of dry pyridine were added, the solution was refluxed 2.5 hours, concentrated to about 25 ml., and cooled. The tan crystals were filtered and boiled with water for a few minutes to remove any biurea present, filtered, and then hydrolyzed by refluxing for 30 minutes with 25 ml. of water and 50 ml. of hydrochloric acid. The resulting oil was taken up in benzene, washed with water and sodium chloride, dried over sodium sulfate, and the material crystallized from benzene–methanol, giving 0.46 g. of the ketone XIV, m.p. 96.4–98.0°. A sample recrystallized from methanol formed pink plates, m.p. 97.0–98.2°. *Anal.* Calcd. for $C_{20}H_{14}O$: C, 88.9; H, 5.2. Found: C, 88.7; H, 5.3.

The mother liquor of the semicarbazone deposited more material on standing; this was hydrolyzed as before, giving 0.87 g. of XIV as a dark oil which was used for the Clemmensen reduction.

In another experiment, the acid chloride prepared from 4.03 g. of XIII was dissolved in 33 ml. of carbon disulfide and added dropwise with stirring during 45 minutes to a mixture of 2.65 g. of aluminum chloride and 65 ml. of carbon disulfide maintained at 2–5°. After stirring 2.5 hours at 2–5° the reaction mixture was decomposed as before. The neutral fraction was distilled at 1–3 mm. (bath temperature 300–330°) to give 2.47 g. of a dark gum. This was chromatographed on alumina and the column eluted first with benzene–petroleum ether mixtures and then with benzene. There was obtained a blue-fluorescent band which gave 0.15 g. of a yellow solid, m.p. 88–130°, not further investigated; a more strongly adsorbed, dark, non-fluorescent band, which gave 0.03 g. of purple solid, not further investigated; and, as the most strongly adsorbed fraction, a green-fluorescent band which gave 1.34 g. of a red oil. Crystallization from methanol–benzene gave 0.73 g. of XIV, m.p. 95.6–98.0°, and a second crop, 0.23 g., m.p. 92.0–97.0°. The total yield was 0.96 g. (25%).

Benz[j]fluoranthene (III).—(a) To a solution of 0.87 g. of impure XIV (see above) in 5 ml. of acetic acid and 10 ml. of toluene there was added 10 g. of amalgamated zinc, 7.5 ml. of water and 10 ml. of hydrochloric acid. The mixture was refluxed 3 hours; 5 ml. of hydrochloric acid was added and refluxing continued for another 16 hours. The product was taken up in benzene, washed with water, sodium bicarbonate solution, and sodium chloride, and dried by concentration to small volume. The solution was then chromatographed on alumina. The less strongly adsorbed, blue-fluorescent band gave 0.11 g. of a yellow oil, presumably 12c,1,2,3-tetrahydrobenz[j]fluoranthene, which did not form a picrate. Twenty mg. of a 30% palladium-on-charcoal catalyst[27] was added to the oil. The mixture was heated for 45 minutes at 300–320°, and the temperature then raised to 350° during 20 minutes. The product was dissolved in benzene, filtered, and chromatographed on alumina. The less strongly adsorbed, blue-fluorescent band gave 0.007 g. of material, not further investigated. The more strongly adsorbed, yellow-fluorescent band gave 0.027 g. of solid, which was treated with 0.027 g. of *s*-trinitrobenzene in methanol–ethanol solution. There was obtained 0.028 g. of brown needles (*s*-trinitrobenzene complex of III), m.p. 213.0–216.5° after sintering at 194°. A mixture with the orange-yellow *s*-trinitrobenzene complex (m.p. 219.8–220.5°) of the lower-melting benzfluoranthene (m.p. 166.0–166.4°) obtained from 1,2′-dinaphthyl[3] melted at 215.5–219.0°. Comparison of the ultraviolet absorption spectra of the brown complex of III and of the benzfluoranthene from 1,2′-dinaphthyl confirmed the identity of the two hydrocarbons. The reason for the striking color difference is not known; it may be due to a small amount of a very dark impurity in the synthetic sample of III.

The more strongly adsorbed, blue-fluorescent band obtained from the chromatogram of the Clemmensen reduction product gave 0.34 g. of a brownish oil, which crystallized when refluxed with methanol. The yellowish solid obtained began to sinter at 198° and melted at about 206–214°. Recrystallization from benzene–ethanol gave a first crop of material m.p. 260–270° (indefinite) and a second crop m.p. 216–226° (indefinite). The analysis is consistent with that of a polymer of dihydrobenz[j]fluoranthene. *Anal.* Calcd. for $(C_{20}H_{14})_n$: C, 94.5; H, 5.6. Found: C, 94.3; H, 5.7. This material was not further investigated; the impure ketone used may have contained polymeric material resulting from aldol condensations, or polymerization may have taken place during the Clemmensen reduction.

(b) A mixture of 1.1 g. of powdered lithium aluminum hydride and 75 ml. of dry ether was refluxed with stirring for 1.0 hour; then a slurry of 0.54 g. of XIV in 100 ml. of dry ether was added and refluxing and stirring continued for

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[26] Wilds and Meader, *J. Org. Chem.*, **13**, 763 (1948).

[27] Linstead and Thomas, *J. Chem. Soc.*, 1127 (1940); catalyst-d.

another 3.5 hours. Thirty ml. of dilute (1:5) acetic acid was added, followed by 5 ml. of 10% hydrochloric acid. The organic layer was washed with water and sodium chloride, dried over sodium sulfate, and evaporated to dryness. The white solid was extracted with several portions of warm benzene, the benzene evaporated, the product dehydrogenated by treatment with 0.50 g. of palladium-on-charcoal catalyst[27] at 300–350° for 30 minutes, and then chromatographed on alumina. The least strongly adsorbed blue-fluorescent band gave 0.11 g. of tan solid which was sublimed at 180° (1 mm.) and then treated with 0.08 g. *s*-trinitrobenzene in benzene–ethanol. There was obtained 15 mg. of orange-brown plates, m.p. 158–179°. The more strongly adsorbed, purple-fluorescent band of the chromatogram gave 0.07 g. dark solid which was sublimed at 180° (1 mm.) and then treated with 0.08 g. of *s*-trinitrobenzene in benzene–alcohol. There was obtained 67 mg. of black needles, m.p. 233.0–235.0°. The ultraviolet absorption spectra showed that neither of the two products was benz[j]-fluoranthene; they were not further investigated.

(c) A solution of 0.41 g. of XIV in 15 ml. of absolute ethanol was hydrogenated in the presence of 50 mg. of Adams catalyst. During 3.5 hours, 35.9 ml. (S.T.P.) of hydrogen was absorbed (105% of theoretical for the conversion of XIV to the carbinol). The product was heated with 0.30 g. of palladium-on-charcoal catalyst[27] at 300–310° for 50 minutes; a small amount of tarry material which sublimed during this period was discarded. The product was then sublimed at 300° (2–3 mm.) and the dark-purple plates dissolved in benzene–ethanol and treated with 0.10 g. of 2,4,7-trinitrofluorenone.[30] The black crystals obtained had m.p. 250.5–255.5° (reported[3] for the orange-red 2,4,7-trinitrofluorenone complex of III, m.p. 255–256°; no material was available for a mixed melting point). The complex was chromatographed on alumina and eluted with benzene, and the deep red eluate shaken with 25 ml. of concentrated sulfuric acid for about 5 minutes. The resulting colorless solution was washed with water, 10% sodium bicarbonate solution, and saturated sodium chloride, dried over calcium chloride, and evaporated to dryness. There was obtained 0.0060 g. of a pale violet oil. The ultraviolet absorption spectrum showed that the product was not III; it was not further investigated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Demonstration of Exchange and Friedel–Crafts Reactions of Gaseous Organic Chlorides on Solid Aluminum Chloride

BY MONTE BLAU AND JOHN E. WILLARD

Recent work in our laboratory[1] has shown that rapid exchange of chlorine occurs between solid aluminum chloride and liquid carbon tetrachloride. The observed characteristics of the reaction have suggested strongly that it, and possibly also certain related Friedel–Crafts type reactions, must occur on the solid surface rather than through the medium of dissolved aluminum chloride molecules or CCl_3^+ and $AlCl_4^-$ ions in solution. The purpose of the present communication is to report: (1) experiments on the exchange of chlorine between six different gaseous organic halides and solid aluminum chloride which demonstrate with certainty that this type of reaction can occur on an aluminum chloride surface without the necessity for a solvent; (2) an experiment which shows that a Friedel–Crafts reaction between carbon tetrachloride and benzene can take place between gaseous reactants in contact with solid aluminum chloride.

Experimental

All of the experiments reported here were carried out on a vacuum line using techniques similar to the most rigorous described in the previous work.[1] In each test a sample of the vapor of the organic halide to be tested was admitted from a reservoir of the carefully degassed liquid through a phosphorus pentoxide drying train to a 500-ml. flask coated on the inside with ten to twenty mg. of radioactive aluminum chloride. The pressure of the vapor used was in each case below its vapor pressure at the reaction temperature. Pressures were measured with a closed-end mercury manometer. The aluminum chloride was prepared *in situ* by heating aluminum with silver chloride containing radiochlorine (Cl^{36}) and subliming the product into the flask where it was condensed on the walls with the aid of liquid air.

When the organic vapor had stood in contact with the aluminum chloride for the desired length of time it was frozen out in a side tube and sealed off. The tube so removed was opened, and while the contents were still frozen a mixture of water and carbon tetrachloride was added to dissolve both inorganic and organic products. The radioactivity in the aqueous and in the organic fraction was then determined with a solution counter, the count in the organic fraction being corrected for the lower counting efficiency due to the higher density of the solution.

After the desired number of runs had been made with a given preparation of aluminum chloride, the flask was opened and the residual activity was determined by dissolving and counting the aluminum chloride. In those cases where a non-volatile organic product was left with the aluminum chloride, qualitative tests were made of its solubility in different solvents.

Blank determinations showed that no detectable amount of aluminum chloride was sublimed from the reaction flask to the side tubes when they were cooled with liquid air for the purpose of condensing and sealing off the reaction products. Check determinations also showed that hydrolysis during the washing procedure could not have contributed significantly to the amount of inorganic chloride found.

Except for *n*-propyl and *n*-amyl chlorides the organic chlorides were used as they came from the manufacturers' bottles, without further purification other than vacuum distillation through phosphorus pentoxide. The types used were: Mallinckrodt "Low Sulfur" carbon tetrachloride; Baker "Analyzed" chloroform; Eastman ethyl chloride, and benzyl chloride. The amyl and propyl chlorides were purified by washing with concentrated sulfuric acid, sodium carbonate solution, and water, followed by drying over calcium chloride and distillation from phosphorus pentoxide through a Vigreux column. The second 5 ml. of distillate from 15 ml. of compound was used in the experiments. In the case of the amyl chloride the refractive index was checked and found to be 1.4119^{20}_{D}, in agreement with literature values. Runs with unpurified material gave essentially the same results as those with purified reagents.

Results

Exchange Reactions and Hydrogen Chloride Formation.—The data of Table I show that under the conditions of these experiments exchange of chlorine occurred readily between solid aluminum chloride and gaseous carbon tetrachloride, chloroform, ethyl chloride, *n*-propyl chloride, *n*-amyl chloride and benzyl chloride with a contact time of a few minutes at room temperature. Exchange was observed at −10° in run 5 with carbon

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[1] Wallace and Willard, THIS JOURNAL, 72, 5275 (1950).