to yield a white solid (1.0 g.), m.p. 156–159° (from benzene-ethanol). This material had an infrared spectrum identical with that of authentic 1,2-benzanthracene (lit.,[23] m.p. 155–157°). The melting points of the derived 2,4,7-trinitrofluorenone complex (221–223°) and the picrate (136–138°) were not depressed on admixture with those prepared from pure 1,2-benzanthracene.

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[23] W. E. Bachmann, *J. Org. Chem.*, **1**, 347 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

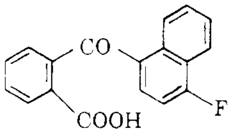
An Unusual Halogen Exchange Reaction

E. D. BERGMANN, J. BLUM, AND S. BUTANARO

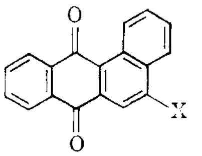
Received January 6, 1961

The cyclization of *o*-(4-fluoro-1-naphthoyl)benzoic acid (I) with benzoyl chloride yields 3-chloro-1,2-benzanthraquinone, while benzoyl *fluoride* gives the expected 3-fluoro analog. This type of reaction appears to be specific for *o*-benzoylbenzoic acids carrying a fluorine atom in *para* to the carbonyl group. The mechanism of the reaction is discussed.

In an attempt to cyclize *o*-(4-fluoro-1-naphthoyl)benzoic acid (I) to the corresponding 1,2-benzanthraquinone derivative (II, X = F) by means of benzoyl chloride,[1] a 50% yield of 3-chloro-1,2-benzanthraquinone (II. X = Cl) was obtained.



I

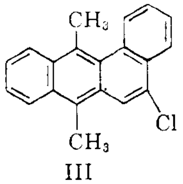


II

The structure of the product was established by analysis, the infrared spectrum (C = O frequency at 1680 cm.$^{-1}$) and its conversion into 9,10-dimethyl-3-chloro-1,2-benzanthracene (III) by the usual[2] method: treatment of the Grignard adduct with methylmagnesium iodide with hydriodic acid and reductive deiodination of the 3-chloro-10-iodomethyl-9-methyl-1,2-benzanthracene so formed. The melting point of II(X = Cl) (184°) was in agreement with that reported by Heller (180–181.5°),[3] but not that given by Waldmann (207.5°)[4] for the same compound. Therefore, the quinone (II. X = Cl) was synthesized by condensing 4-chloro-1-naphthylmagnesium bromide with phthalic anhydride and cyclization of the keto acid (I, Cl instead of F) with benzoyl chloride.[5] The melting point of the product so obtained was 184°.

The desired product (II, X = F) could be obtained easily when instead of benzoyl chloride, benzoyl fluoride[6,7] was used as cyclizing agent. This is, in our knowledge, the first time that this compound has been employed as a cyclizing agent.

In order to show whether the observed exchange reaction is general, analogs of (I) were studied: *o*-(3-fluoro-1-naphthoyl)benzoic acid (IV), *o*-(4-fluorobenzoyl)benzoic acid (VI), and *o*-(3-fluorobenzoyl)benzoic acid (VIII). The first was prepared in analogy to Newman and Galt[8] from phthalic anhydride and 3-fluoro-1-naphthylmag-



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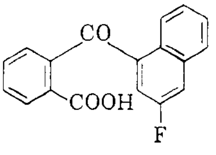
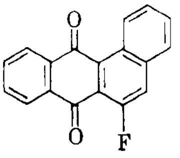
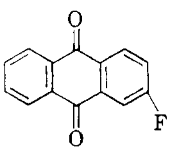


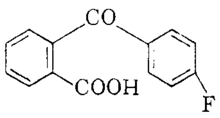
IV



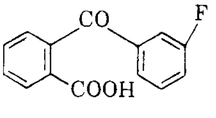
V



VII



VI



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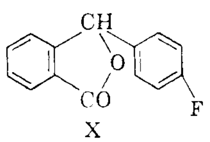
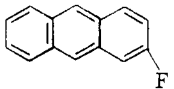
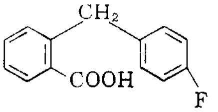


X



IX



XI

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(1) G. M. Badger and J. W. Cook, *J. Chem. Soc.*, 802 (1939), J. L. Wood and L. F. Fieser, *J. Am. Chem. Soc.*, **73**, 4494 (1951).

(2) R. B. Sandin and L. F. Fieser, *J. Am. Chem. Soc.*, **62**, 3098 (1940).

(3) G. Heller, *Ber.*, **45**, 665 (1912).

(4) H. Waldmann, *J. prakt. Chem.* [2], **127**, 201 (1930), quoted by Elsevier, Encyclopedia of Organic Chemistry, **14**, 338 (1940).

(5) The same acid has been obtained by Heller (ref. 3) by Friedel-Crafts reaction between phthalic anhydride and 1-chloronaphthalene.

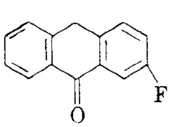
(6) A. Borodine, *Ann.*, **126**, 58 (1863).

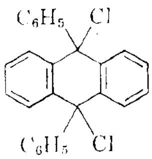
(7) Ch.-L. Tseng and Sh.-W. Mai, *Chem. Abstr.*, **30**, 2943 (1936).

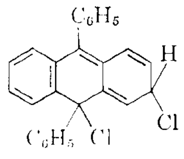
(8) M. S. Newman and R. H. B. Galt, *J. Org. Chem.*, **25**, 214 (1960).

nesium bromide and gave with benzoyl chloride exclusively (96%) 4-fluoro-1,2-benzanthraquinone (V)—without any halogen exchange. Also VIII, prepared from phthalic anhydride and *m*-fluorophenylmagnesium bromide gave only (97%) 2-fluoroanthraquinone (VII). From VI,[9] however, a beautifully crystallized molecular compound (1:1) of 2-fluoro- and 2-chloroanthraquinone was obtained. This same compound was also obtained when the two quinones were recrystallized together from ethyl acetate and did not dissociate when sublimed *in vacuo.*

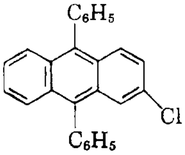
The cyclization of VIII can theoretically lead to both 1- and 2-fluoroanthraquinone. The product is, however, different from 1-fluoroanthraquinone, for which Hahn and Reid[9] give m.p. 128–129°, and Bergmann and Berkovic[10] 223–224°, but identical with 2-fluoroanthraquinone.[9,10] Furthermore, the product of the cyclization of VIII was reduced to 2-fluoroanthracene (IX) which was prepared by the following unambiguous route: VI was reduced *via* the lactone (X) to *o*-(4-fluorobenzyl)benzoic acid (XI); cyclization gave 2-fluoro-9-anthrone (XII) and subsequent reduction IX. The ultraviolet spectrum of IX shows a slight bathochromic shift (383 mμ) as compared with the spectrum of anthracene (375 mμ).[11]

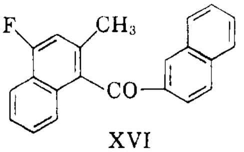

XII

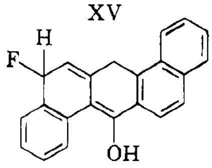

XIII

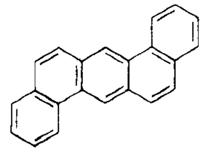

XIV

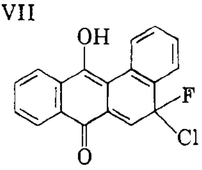
Regarding the mechanism of this unexpected halogen-exchange reaction, two prior observations appear to bear on this problem: the rearrangement occurring in heating 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene (XIII) to 2-chloro-9,10-diphenylanthracene (XV), assumed to proceed *via* XIV[12,13] and the dehalogenations occurring in the Elbs reaction of certain halogenated polycyclic ketones, *e.g.*, the formation of 1,2,5,6-dibenzanthracene (XVIII) from 4-fluoro-2-methyl-1-(β-naphthoyl)naphthalene (XVI) assumed to proceed *via* XVII.[14,15]


XV


XVI


XVII


XVIII


XIX

In analogy, one might assume that the hydrogen chloride liberated in the cyclization of I with benzoyl chloride would add to I or another precursor of the quinone system to give XIX which loses hydrogen fluoride in preference to hydrogen chloride. Obviously, such a reaction is only possible, if the fluorine atom is located in the *para-* position to the carbonyl group.

EXPERIMENTAL

3-Chloro-1,2-benzanthraquinone (II, X = Cl). A mixture of 5 g. of I[16,17] was heated with 5 ml. of benzoyl chloride at 140° and after addition of 3 drops of concd. sulfuric acid at 175° for 3 hr. The resulting product was cooled to 100° and poured into 100 ml. of $5N$ sodium hydroxide solution, filtered, heated with 10% sodium carbonate solution and water, filtered again, and dried. Recrystallization of the crude product (2.3 g.; 50%) from nitromethane or ethyl acetate and subsequent sublimation (170°, 2 mm.) gave long, yellow needles of m.p. 184°.

Anal. Calcd. for $C_{18}H_9ClO_2$: C, 73.8; H, 3.1; Cl, 12.0. Found: C, 73.4; H, 3.2; Cl, 11.9.

The alkaline washings gave, upon acidification with hydrochloric acid, 1.6 g. (37%) of unchanged I.

o-(4-Chloro-1-naphthoyl)benzoic acid (I, Cl instead of F). A Grignard solution, prepared from 18 g. of 1-bromo-4-chloronaphthalene[18] and 2.4 g. of magnesium in 100 ml. of ether, was added with vigorous agitation to a suspension of 12 g. of phthalic anhydride in 80 ml. of benzene and the mixture refluxed for 3 hr. and decomposed with 10% hydrochloric acid. The organic solvents were removed by steam distillation, and the residue was extracted with 10% sodium carbonate solution. Acidification of the filtered extract and recrystallization from toluene gave 15.5 g. (65%) of the desired keto acid, m.p. 174° (lit.[3]: 172–174°).

Cyclization with concentrated sulfuric acid at 165° or benzoyl chloride at 190° gave a quinone which after sublimation at 170° and 3 mm., melted at 184°. This melting point was not depressed by admixture of the product described above.

3-Fluoro-1,2-benzanthraquinone (II, X = F). A mixture of 6 g. of I and 6 g. of benzoyl fluoride (b.p. 145°)[6,7] was heated at 150°; a few drops of concentrated sulfuric acid

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(9) F. C. Hahn and E. E. Reid, *J. Am. Chem. Soc.*, **46**, 1645 (1920).

(10) E. D. Bergmann and S. Berkovic, *J. Org. Chem.*, **26**, 919 (1961).

(11) P. K. Seshan, *Proc. Indian Acad. Sci.*, **3A**, 148 (1936).

(12) E. Bergmann and O. Blum-Bergmann, *J. Am. Chem. Soc.*, **59**, 1439 (1937).

(13) Ch. Dufraisse, A. Etienne, and J. Salmon, *Bull. Soc. Chim. Belges*, **62**, 21 (1953).

(14) E. D. Bergmann and J. Blum, *J. Org. Chem.*, **25**, 474 (1960).

(15) E. D. Bergmann and J. Blum, *J. Org. Chem.*, **26**, 3214 (1961).

(16) M. S. Newman, D. Mac Dowell, and S. Swaminathan, *J. Org. Chem.*, **24**, 509 (1959).

(17) E. D. Bergmann and J. Blum, *J. Org. Chem.*, **26**, 3214 (1961).

(18) L. F. Fieser and V. Desreux, *J. Am. Chem. Soc.*, **60**, 2255 (1938).

were added and the heating was continued for 90 min. Work-up as in the preceding experiment and recrystallization from ethanol gave yellow needles of m.p. 138° in a yield of 20%.

Anal. Calcd. for $C_{18}H_9FO_2$: C, 78.3; H, 3.3; F, 6.9. Found: C, 78.7; H, 3.6; F, 6.5.

o-(3-Fluoro-1-naphthoyl)benzoic acid (IV) has been prepared by Newman and Galt[8] from phthalic anhydride and 3-fluoro-1-naphthylmagnesium bromide in tetrahydrofuran. Using ether-benzene as solvent, as above, from 2.3 g. of 1-bromo-3-fluoronaphthalene[8,15] and 1.5 g. of phthalic anhydride, 2.1 g. (72%) of IV was obtained after two recrystallizations from toluene; m.p. 187° (lit.[8] m.p. 187–189°).

4-Fluoro-1,2-benzanthraquinone (V). A mixture of 2 g. of IV and 2 ml. of benzoyl chloride was heated, until a clear solution had formed, and after addition of 3 drops of concd. sulfuric acid kept at 190° for 10 hr. The mixture was poured, while still warm, into 100 ml. of 5*N* sodium hydroxide solution and the solid product filtered and recrystallized from ethyl acetate. The compound (1.8 g.; 90%) so obtained was sublimed *in vacuo* and formed orange-yellow needles of m.p. 199–200°.

Anal. Calcd. for $C_{18}H_9FO_2$: C, 78.2; H, 3.3; F, 6.9. Found: C, 78.0; H, 3.5; F, 6.9.

Reaction of VI *with benzoyl chloride.* o-(4-Fluorobenzoyl)-benzoic acid (VI) was prepared according to Hahn and Reid.[9] A mixture of 3 g. of VI and 3 ml. of benzoyl chloride was heated to dissolution and after addition of 3 drops of concd. sulfuric acid kept at 180° for 6 hr. Work-up as in the foregoing experiment, recrystallization from ethyl acetate and sublimation at 160° (2 mm.) afforded 1.2 g. (40%) of light-yellow needles of m.p. 210°, which according to the analysis were a molecular compound (1:1) of 2-fluoroanthraquinone (VII) and 2-chloroanthraquinone.

Anal. Calcd. for $C_{14}H_7FO_2 + C_{14}H_7ClO_2$: C, 71.7; H, 3.0; F, 4.1. Found: C, 72.0; H, 3.3; F, 4.3.

The same product (no depression in melting point) was obtained when 0.5 g. of 2-chloroanthraquinone[19] (m.p. 210°; lit. m.p. 204°[19]; 208–209°[20]; 211°[21]) and 0.5 g. of 2-fluoroanthraquinone (see below) were recrystallized together from boiling ethyl acetate. Sublimation of the molecular compound at 160° (3 mm.) did not change the melting point or the composition of the crystals.

o-(3-Fluorobenzoyl)benzoic acid (VIII). A Grignard solution prepared from 1.2 g. of magnesium and 8 g. of *m*-bromofluorobenzene in 80 ml. of ether, was added to a well agitated suspension of 7.5 g. of phthalic anhydride in 80 ml. of benzene. The mixture was refluxed for 2 hr. and worked up as described in the prepartion of (I, Cl instead of F). Recrystallization from toluene or benzene-cyclohexane gave 8.5 g. (76%) of VIII, which formed colorless, glistening needles of m.p. 148.5°.

Anal. Calcd. for $C_{14}H_9FO_3$: C, 68.9; H, 3.7; F, 7.8. Found: C, 69.1; H, 4.0; F, 7.8.

2-Fluoroanthraquinone (VII). As in previous examples, 4.5 g. of the acid (VIII), 4.5 ml. of benzoyl chloride, and 3 drops of concd. sulfuric acid were heated at 195° for 10 hr. The product was recrystallized from ethyl acetate; 3.5 g. (80%) of yellowish needles were obtained which melted at 204° after an additional sublimation. The melting point was not depressed by admixture of an authentic specimen.[10]

Anal. Calcd. for $C_{14}H_7FO_2$: C, 74.3; H, 3.1; F, 8.4. Found: C, 74.0; H, 3.3; F, 8.3. From the alkaline washing, 0.6 g. (14%) of VIII was recovered.

Lactone X *of o-(α-hydroxy-4-fluorobenzyl)benzoic acid.* Under the conditions specified by Hahn and Reid[9] VI could not be reduced to XI directly; nor is the melting point given for XI by these authors (148–149°) correct for either XI or the lactone (X) which is actually formed.

(a) A mixture of 12.2 g. of VI,[9] 150 ml. of 25% ammonia solution and 10 g. of zinc dust, activated with 0.1 g. of cupric sulfate and 2 g. of sodium hydroxide, was heated for 4 hr. at 70° and the solution filtered and acidified with 10% hydrochloric acid. The precipitate was recrystallized from aqueous ethanol or cyclohexane and formed colorless cubic crystals of m.p. 105°; yield, 11 g. (96%). Already the fact that the product was insoluble in 10% sodium carbonate solution, but dissolved slowly upon heating with 30% sodium hydroxide solution, indicated that the lactone (X) had formed. This was supported by the analysis and the infrared spectrum (λ_{max}^{KBr} 1750; 1765 cm.$^{-1}$).

Anal. Calcd. for $C_{14}H_9FO_2$: C, 73.7; H, 3.9; F, 8.3. Found: C, 73.9; H, 4.1; F, 8.2.

(b) When instead of the ammonia solution 10% sodium hydroxide solution was used, a yield of 9.5 g. (83%) of X, m.p. 105°, was obtained.

(c) From 12.7 g. of VI, 10 g. of 40% sodium amalgam and 200 ml. of water (70°; 10 hr.), 9 g. (79%) of X was obtained.

(d) Clemmensen reduction: A mixture of 12.2 g. of VI, 20 g. of amalgamated mossy zinc, 50 ml. of concd. hydrochloric acid, 20 ml. of toluene, and 8 ml. of glacial acetic acid was refluxed for 24 hr.; every 6 hr., 10 ml. of concd. hydrochloric acid was added. After addition of 50 ml. of benzene, the layers were separated, and the solid product as well as the aqueous layer was extracted three times with 50 ml. of benzene. The residue from the combined organic solutions was fractionally recrystallized from a mixture of benzene and cyclohexane. Thus, 5.9 g. (52%) of X, m.p. 105°, and 4 g. of a high-melting (m.p. (277–279°) product were obtained, the structure of which has not been elucidated.

o-(4-Fluorobenzyl)benzoic acid (XI). A mixture of 5 g. of the lactone (X), 4 g. of red phosphorus, 3 ml. of concd. hydriodic acid, 100 ml. of glacial acetic acid, and 2 ml. of water was refluxed for 6 hr. and the solution filtered and poured into 500 ml. of water, containing 1 g. of sodium hydrogen sulfite. Recrystallization from methanol, ethanol, or cyclohexane gave 4.8 g. (93%) of XI, colorless platelets of m.p. 127°.

Anal. Calcd. for $C_{14}H_{11}FO_2$: C, 73.0; H, 4.8; F, 8.3. Found: C, 73.1; H, 5.0; F, 8.6.

2-Fluoro-9-anthrone (XII). When 5 g. of the foregoing acid (XI) was kept at room temperature with 15 ml. of concd. sulfuric acid, a green solution resulted, which was poured after 3 hr. into 200 ml. of ice-cold water. The precipitate was washed with warm 10% sodium carbonate solution and recrystallized from ethanol or benzene. Thus, 3.2 g. (70%) of XII, m.p. 147–148° was obtained. In potassium bromide, the compound shows both the carbonyl absorption (1675 cm.$^{-1}$.) and that of the enol form (3500 cm.$^{-1}$). $\lambda_{max}^{CHCl_3}$ 243 (4.44); 258 (inflection; 4.54); 268 (4.68); 276 (4.72); 287 (4.97); 297 (5.00); 347 (3.86); 365 (3.98); 380 mμ (3.85). The spectrum resembles closely that of anthrone.[22]

Anal. Calcd. for $C_{14}H_9FO$: C, 79.3; H, 4.2; F, 9.0. Found: C, 79.7; H, 4.4; F, 8.5.

2-Fluoroanthracene (IX). (a) A mixture of 1 g. of XII, 1 g. of zinc dust, activated by cupric sulfate, 30 ml. of 15% sodium hydroxide solution, and 10 ml. of toluene was refluxed for 18 hr. (until the red color of the hydroquinone ion had disappeared). The layers were separated and both the solid and the aqueous layer extracted with 20 ml. of toluene. Concentration of the combined toluene solutions and chromatography of the residue from benzene on activated alumina gave 0.9 g. (97%) of the intensely fluorescent, colorless platelets of 2-fluoroanthracene, m.p. 212°. The product sublimes before the m.p. $\lambda_{max}^{CHCl_3}$ 253 (5.10); 283 (inflection; 3.04); 287 (inflection; 2.88); 298 (2.75); 303 (2.81); 316 (3.18); 330 (3.48); 345 (3.65); 364 (3.71); 383 mμ (3.72).

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(19) A. Rée, *Ann.*, **233**, 216 (1886).

(20) F. Kaufler, *Ber.*, **37**, 63 (1904).

(21) P. H. Groggins, *Ind. Eng. Chem.*, **22**, 626 (1930).

(22) E. Martin, *Ann. combustibles liquides*, **12**, 97 (1937); quoted by Elsevier, Encyclopedia of Organic Chemistry, Vol. 13, p. 327 (1946).

Anal. Calcd. for $C_{14}H_9F$: C, 85.7; H, 4.6; F, 9.7. Found: C, 85.7; H, 4.9; F, 9.9.

(b) A mixture of 0.2 g. of the cyclization product of (VIII), believed to be VII, 1 g. of tin, 15 ml. of concd. hydrochloric acid, and 5 ml. of toluene was refluxed for 3 hr. and the solution filtered and poured into water. The precipitate was refluxed for 24 hr. with 30 ml. of 10% sodium hydroxide solution, 1 g. of zinc dust, activated with cupric sulfate, and 10 ml. of toluene. The toluene layer was concentrated and the residue sublimed at 170° (30 mm.). The product melted at 212° and was identical with the one obtained by method (a).

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[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

Further Observations on the Elbs Reaction

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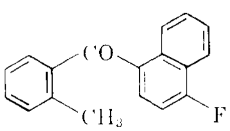
Received December 27, 1960

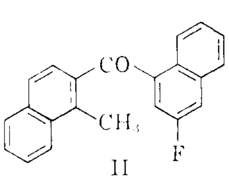
Elbs reactions of diaryl ketones containing a fluorine atom *para* to the carbonyl group (such as I) are accompanied by elimination of the halogen atom. If the fluorine atom is situated *meta* to the carbonyl group, the products of the Elbs reaction sometimes retain the halogen atom, sometimes lose it.

In a previous publication,[1] attention was drawn to the fact that the Elbs reaction of diaryl ketones, which contained a fluorine atom in the *para*-position to the carbonyl group, was accompanied by the elimination of fluorine; similar observations have been recorded before (see ref. 1) regarding such substituents as chlorine or methoxyl groups. The mechanism suggested then would imply that fluorine in other positions than *para*, relative to the carbonyl group, would not be eliminated in the course of the pyrolysis. It has now been shown that there are cases in which, under these conditions, fluorocompounds are obtained in the Elbs reaction; however, this is not always the case, and additional dehalogenation mechanisms must be operative.

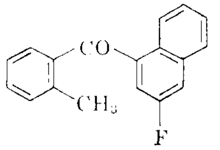
The previous experiments on compounds containing fluorine *para* to the carbonyl have been supplemented by the pyrolysis of 1-fluoro-4-(*o*-toluoyl)naphthalene (I), prepared from 4-fluoro-1-naphthylmagnesium bromide and *o*-tolunitrile; this pyrolysis gave a 32% yield of 1,2-benzanthracene. The following four additional cases have been investigated: 3-fluoro-1′-methyl-1,2′-dinaphthyl ketone (II), 3-fluoro-1-(*o*-toluoyl)naphthalene (III), 1-(*m*-fluorobenzoyl)-2-methylnaphthalene (IV), and 4-(3-fluoro-1-naphthoyl)-7-methylindane (V). Only from II, the expected 4-fluoro-1,2,5,6-dibenzanthracene (VI) was obtained. The aromatic products from III and V were 1,2-benzanthracene and methylcholanthrene, respectively; no fluorine derivatives of these systems could be detected. IV did not undergo the Elbs reaction. However, from III and II, two interesting by-products were obtained which are likely to shed some light on the mechanism of the Elbs reaction. From III, a fluorine-containing oily substance was isolated which gave the analysis and showed the absorption spectrum of 4-fluoro-5,5a,6,7,8,8a,9,10-octahydro-1,2-benzanthracene (VII)—its formation indicates that hydrogen transfer and, therefore, hydrogenation is plausible during an Elbs reaction—and from II 4-fluoro-1,2,5,6-dibenzanthr-9-one (VIII) was isolated. Its structure was demonstrated by reduction to VI. The formation of such ketones has been observed before.[2-4]



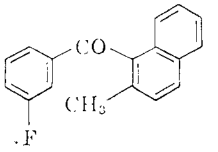
I



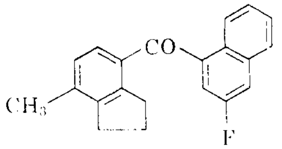
II



III



IV



V

For the synthesis of II, 1-methyl-2-naphthoic acid[5] was converted *via* the amide into the nitrile (IX) and the latter treated with the magnesium derivative of 3-fluoro-1-bromonaphthalene which we have prepared approximately by the same method as Newman and Galt.[6] The same magnesium organic

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