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).

JERUSALEM, ISRAEL

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

Further Observations on the Elbs Reaction

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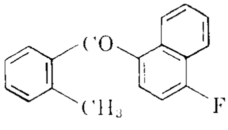
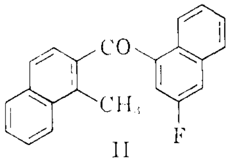
Elbs reactions of diaryl ketones containing a fluorine atom *para* to the carbonyl group (such as I) are accompanied by elimination of the halogen atom. If the fluorine atom is situated *meta* to the carbonyl group, the products of the Elbs reaction sometimes retain the halogen atom, sometimes lose it.

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.

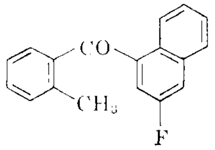
The previous experiments on compounds containing fluorine *para* to the carbonyl have been supplemented by the pyrolysis of 1-fluoro-4-(*o*-toluoyl)naphthalene (I), prepared from 4-fluoro-1-naphthylmagnesium bromide and *o*-tolunitrile; this pyrolysis gave a 32% yield of 1,2-benzanthracene. The following 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



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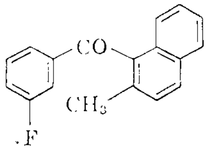

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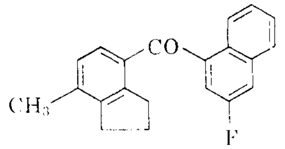

V

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

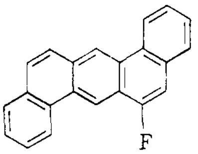
[2] G. T. Morgan and E. A. Coulson, *J. Chem. Soc.*, 2551 (1929).

[3] L. F. Fieser and M. A. Peters, *J. Am. Chem. Soc.*, **54**, 3742 (1932).

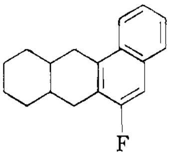
[4] L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **62**, 1640 (1940).

[5] H. Gilman and J. E. Kirby, *J. Am. Chem. Soc.*, **51**, 3475 (1929).

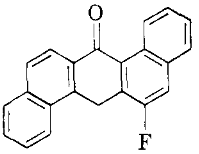
[6] M. S. Newman and R. H. B. Galt, *J. Org. Chem.*, **25**, 214 (1960).



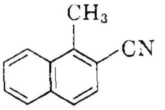
VI



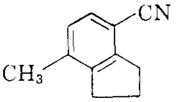
VII



VIII



IX



X

compound gave III with *o*-tolunitrile and V with 4-cyano-7-methylindane (X). From *m*-fluorophenylmagnesium bromide and 2-methyl-1-naphthonitrile the ketone IV was obtained.

EXPERIMENTAL

1-Fluoro-4-(o-toluoyl)naphthalene (I). A solution of 6 g. of *o*-tolunitrile in 50 ml. of benzene was added, with vigorous agitation, to a Grignard solution prepared from 1.2 g. of magnesium and 11.2 g. of 1-bromo-4-fluoronaphthalene in a mixture of 40 ml. of ether and 10 ml. of benzene. The mixture was refluxed for 24 hr., decomposed with 100 g. of ice and 30 ml. of concd. hydrochloric acid, and treated with steam. The remaining dark oil was separated mechanically and refluxed for 3 hr. with 50 ml. of acetic acid, 60 ml. of toluene, 50 ml. of concentrated hydrochloric acid and 100 ml. of water. After addition of 100 ml. of water, the toluene layer was separated and the aqueous phase extracted with benzene. The solvent was removed from the combined organic solutions with steam and the resulting oil distilled. The fraction boiling at 180–195° (0.5 mm.) crystallized and was recrystallized first from ethanol-benzene (10:1), then from pure ethanol. M.p. 88–88.5°; yield, 5.4 g. (20%).

Anal. Calcd. for $C_{18}H_{13}FO$: C, 81.8; H, 4.9; F, 7.2. Found: C, 81.5; H, 5.1; F, 7.2.

Pyrolysis of I. A mixture of 4 g. of I and 2 g. of zinc dust was heated at 400–405° for 2 hr. and flash-distilled under 1 mm. pressure. The distillate was brought to crystallization by treatment with a mixture of ethanol and benzene, and the product chromatographed on alumina (solvent: benzene; eluent: benzene–petroleum ether (b.p. 60–80°) 3:1)). The colorless plates so obtained (1.1 g.; 32%), m.p. 160°, had analytical values of 1,2-benzanthracene.

Anal. Calcd. for $C_{18}H_{12}$: C, 94.7; H, 5.3. Found: C, 94.6; H, 5.4.

1-Methyl-2-naphthamide. A mixture of 10 g. of 1-methyl-2-naphthoic acid[5] (m.p. 178°) and 40 ml. of thionyl chloride was refluxed for 3 hr., and the excess of thionyl chloride distilled. The residue was dissolved in 100 ml. of ether and treated with ammonia gas for 30 min. The amide crystallized and was filtered, washed with water and recrystallized from a mixture of benzene and ethanol. Colorless needles of m.p. 204°; yield, 8 g. (80%).

Anal. Calcd. for $C_{12}H_{11}NO$: C, 77.8; H, 5.9; N, 7.6. Found: C, 77.8; H, 6.2; N, 7.4.

1-Methyl-2-naphthonitrile (IX). When a mixture of 7 g. of the foregoing compound and 20 ml. of thionyl chloride was refluxed for 2 hr. and poured onto 100 g. of ice, a product was obtained which was filtered, washed with cold water, dried, and recrystallized from petroleum ether. The nitrile (5.3 g.; 84%) formed colorless needles of m.p. 64–64.5°.

Anal. Calcd. for $C_{12}H_9N$: C, 86.2; H, 5.4; N, 8.4. Found: C, 86.2; H, 5.7; N, 8.1.

1-Bromo-3-fluoronaphthalene.[6] To a solution of 100 g. of 4-bromo-1-acetnaphthalide[7] in 800 ml. of glacial acetic acid, there was added at 45° and with vigorous stirring, 28 g. of fuming nitric acid in two portions. The mixture, from which *4-bromo-2-nitro-1-acetnaphthalide* began to separate immediately, was kept for 5 min. at 65–70°, cooled and filtered. The precipitate was washed with 100 ml. of cold alcohol and then 200 ml. of petroleum ether. The nitro compound (82 g.; 70%) melted at 242° (lit.[8,9] m.p. 232°); it formed yellowish crystals, the melting point of which was not changed by recrystallization from glacial acetic acid.

Hydrolysis of 80 g. of the product with a boiling mixture of 400 ml. of ethanol and 400 ml. of 50% sulfuric acid for 6 hr. afforded 63.5 g. (92%) of *4-bromo-2-nitro-1-naphthylamine,* orange-colored plates of m.p. 199° (lit.[10,11] m.p. 197°). Deamination of the amine was carried out both by the method of Hodgson and Elliott[10] and Cava and Stucker.[11] The *1-bromo-3-nitronaphthalene* obtained (70–75% yield) was suitable, without further purification, for the reduction step if in the deamination no hypophosphoric acid was used (ref. 10); if this acid were used (ref. 11), the product had to be distilled *in vacuo;* b.p. 180–181° (4 mm.); m.p. 133°. In this latter case recrystallization from ethyl acetate and formic acid did not suffice to remove the inhibitor of catalytic reduction. Reduction was effected in absolute ethanol as solvent and with either platinum oxide or palladium on charcoal (10%) as catalyst. The solution obtained was filtered and poured into 18% hydrochloric acid. On cooling, *1-bromo-3-naphthylamine hydrochloride* precipitated; it was purified by precipitation of its aqueous solution with concentrated hydrochloric acid and formed colorless platelets of m.p. 214°. The yield from the *distilled* nitro compound was quantitative, otherwise it varied between 60 and 75%.

Anal. Calcd. for $C_{10}H_9BrClN$: C, 46.4; H, 3.5; N, 5.4. Found: C, 46.3; H, 3.1; N, 5.2.

For the preparation of *1-bromo-3-fluoronaphthalene,* 50 g. of 1-bromo-3-naphthylamine hydrochloride was diazotized with 14 g. of sodium nitrite and 50 ml. of 50% fluoroboric acid added to the resulting solution. The fluoroborate (59 g.; 95%) was filtered and dried (dec. pt. 151°), and decomposed in the usual manner. The product was dissolved in benzene, washed with 10% sodium hydroxide solution and water, and isolated by distillation; b.p. 96° (1.5 mm.). The distillate solidified slowly upon standing; the product (27 g.; 62%, calculated on the hydrochloride) could be recrystallized at low temperature from a little petroleum ether and formed large colorless plates of m.p. 31.5°.

Anal. Calcd. for $C_{10}H_6BrF$: C, 53.3; H, 2.7; F, 8.5. Found: C, 53.6; H, 3.0; F, 8.7.

3-Fluoro-1'-methyl-1,2'-dinaphthyl ketone (II). A solution of 17 g. of (IX) in 100 ml. of benzene was added to the Grignard reagent prepared from 22.5 g. of 1-bromo-3-fluoronaphthalene and 2.4 g. of magnesium in a mixture of 150 ml. of ether and 30 ml. of benzene. The ether was removed from the mixture, 100 ml. of benzene added and the mass refluxed for 12 hr. with efficient agitation. When the decomposition was carried out as described for the preparation of I, the ketimine hydrochloride corresponding to II remained as a solid; it was hydrolyzed by heating it for 3 hr. with a mixture of 50 ml. of concd. hydrochloric acid, 50 ml. of glacial acetic acid, 50 ml. of toluene and 100 ml. of water. The ketone boiled at 225–235° (2mm.) (23 g.; 73%) and was recrystallized from a mixture of ethanol and benzene. M.p. of the slightly yellowish crystals 104°.

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(7) R. Meldola, *Ber.*, **11**, 1904 (1878).

(8) C. Liebermann, *Ann.*, **183**, 225 (1876).

(9) H. H. Hodgson and S. Birtwell, *J. Chem. Soc.*, 321 (1943).

(10) H. H. Hodgson and R. L. Elliott, *J. Chem. Soc.*, 1850 (1935).

(11) M. P. Cava and J. F. Stucker, *J. Am. Chem. Soc.*, **79**, 1706 (1957).

Anal. Calcd. for $C_{22}H_{15}FO$: C, 84.1; H, 4.8; F, 6.7. Found: C, 84.3; H, 4.9; F, 6.1.

Pyrolysis of II. (a) The dark product obtained from 1.5 g. of II by heating at 390–400° for 30 min. was extracted with benzene and the solution chromatographed twice on alumina; as eluent benzene was used first, then its 1:1 mixture with cyclohexane. The first fractions crystallized upon trituration with benzene-methanol (1:20); thus, 80 mg. (5%) of *4-fluoro-1,2,5,6-dibenzanthracene* (VI) was obtained in yellowish needles (m.p. 226–229°). It was purified by conversion into its *picrate* (in benzene), orange needles from benzene, m.p. 178°, and decomposition of the latter with dilute aqueous ammonia solution. Recrystallization of the product from a mixture of benzene and methanol (3:1) gave crystals of m.p. 240.5°. The ultraviolet spectrum (in chloroform) showed the following maxima: 280 (4.70); 290 (5.02); 299 (5.16); 324 (4.32); 337 (4.23); 353 (4.10); 375 (3.08); 385 (2.75); 395 mμ (2.73) and was thus practically identical with the spectrum of 1,2,5,6-dibenzanthracene.[12]

Anal. Calcd. for $C_{22}H_{13}F$: C, 89.2; H, 4.4; F, 6.4. Found: C, 89.1; H, 4.4; F, 6.7.

(b) When 15 g. of II was heated at 380–385° for 15 min., the same work-up as above afforded 580 mg. (4%) of *4-fluoro-1,2,5,6-dibenzanthr-9-one* (VIII) as a yellowish solid, which melted at 246° after chromatography from benzene solution and recrystallization from the same solvent. The carbonyl absorption was observed at 1660 cm.$^{-1}$

Anal. Calcd. for $C_{22}H_{13}FO$: C, 84.6; H, 4.2; F, 6.1. Found: C, 84.7; H, 4.2; F, 5.8. No other defined compound could be isolated from the pyrolysis product.

Reduction of VIII *to* VI. A mixture of 450 mg. of VIII, 1 g. of zinc dust (activated by a drop of cupric sulfate solution), 1 ml. of toluene, and 100 ml. of 10% sodium hydroxide solution was refluxed and stirred for 8 hr. The organic material was extracted into boiling benzene and the solution washed with 10% hydrochloric acid and concentrated sodium chloride solution, and concentrated. The product was purified as above *via* the picrate and recrystallized from a mixture of benzene and methanol. Thus, 0.32 g. (75%) of VI, m.p. and mixed m.p. 240.5°, was obtained.

3-Fluoro-1-(o-toluoyl)naphthalene (III). To the Grignard solution, prepared from 20 g. of 1-bromo-3-fluoronaphthalene, 11 g. of *o*-tolunitrile was added; the ether was distilled (by heating the mass to 70°) and replaced by benzene, and the mixture refluxed for 12 hr. and worked up as indicated for the preparation of I. The ketone (III) formed a yellowish oil of b.p. 192° (2 mm.); yield, 4.3 g. (19%). The distillation residue was a dark resin.

Anal. Calcd. for $C_{18}H_{13}FO$: C, 81.8; H, 4.9; F, 7.2. Found: C, 81.7; H, 5.1; F, 7.2.

Pyrolysis of III. A mixture of 3.5 g. of III and 1 g. of zinc-dust was gradually heated to a bath temperature of 395–405°, maintained at this temperature for 2 hr. and flash-distilled in a vacuum of 2 mm. The product was extracted with benzene, the benzene evaporated and the residue, dissolved in petroleum ether, chromatographed on alumina. The first fraction (0.38 g., 11%) was a colorless, viscous oil which showed a violet-blue fluorescence and could not be induced to crystallize. Its analysis and the ultraviolet spectrum—corresponding to a naphthalene derivative—[248 (3.86); 313 (infl.; 2.93); 320 mμ (3.04)] indicated that the compound was *4-fluoro-5,5a,6,7,8,8a,9,10-octahydro-1,2-benzanthracene* (VII).

Anal. Calcd. for $C_{18}H_{19}F$: C, 85.0; H, 7.5; F, 7.5. Found: C, 84.6; H, 7.4; F, 7.2.

A second fraction of the chromatographed material (60 mg., 2%) crystallized in large, colorless platelets; after recrystallization from benzene-methanol, they melted at 160° and were identified by mixed melting point, analysis and the typical violet fluorescence as 1,2-benzanthracene.

Anal. Calcd. for $C_{18}H_{12}$: C, 94.7; H, 5.3. Found: C, 94.4; H, 5.6.

The balance of the material subjected to pyrolysis was ill-defined and could not be characterized.

1-(m-Fluorobenzoyl)-2-methylnaphthalene (IV). In the manner described, the condensation of 17 g. of 2-methyl-1-naphthonitrile[13] and the magnesium derivative of 17 g. of *m*-bromofluorobenzene was carried out in benzene; the mixture was refluxed for 20 hr. and the hydrolyzed product fractionated: 11.5 g. of 2-methyl-1-naphthonitrile was recovered and 3.5 g. (13%) of (IV) obtained, which boiled at 170–190° (0.5 mm) and crystallized from ethanol in colorless cubes of m.p. 82.5–83.5°.

Anal. Calcd. for $C_{18}H_{13}FO$: C, 81.8; H, 4.9; F, 7.2. Found: C, 81.5; H, 4.9; F, 7.5. When this ketone was refluxed at 350° bath temperature for 6 hr. with or without zinc dust, no pyrolysis took place, and the starting material was recovered unchanged.

4-(3-Fluoro-1-naphthoyl)-7-methylindane (V). To the Grignard reagent, prepared from 90 g. of 1-bromo-3-fluoronaphthalene and 2 g. of magnesium in 50 ml. of ether and 50 ml. of benzene, 4-cyano-7-methylindane[14] was added and the mixture refluxed for 14 hr. with vigorous agitation. The product was then decomposed by means of 10 g. of ice and 50 ml. of concd. hydrochloric acid and the ketimine hydrochloride of V isolated by steam distillation of the organic solvents. It formed a brownish-yellow solid and was hydrolyzed by refluxing it for 2 hr. with a mixture of 100 ml. of glacial acetic acid, 100 ml. of concd. hydrochloric acid, 100 ml. of toluene, and 200 ml. of water. The toluene layer was separated and the aqueous phase extracted with 50 ml. of toluene. To the combined solutions some aqueous alkali was added and the toluene removed by steam distillation. The remaining oil was extracted with ether and distilled *in vacuo*. The product (b.p. 205–215° (0.5 mm.)) was dissolved in a mixture of 20 ml. of benzene and 20 ml. of ethanol and the yellowish solid obtained on cooling, recrystallized from ethanol. Thus 9.5 g. (71%) of colorless crystals (m.p. 95°) was obtained.

Anal. Calcd. for $C_{21}H_{17}FO$: C, 82.9; H, 5.6; F, 6.2. Found: C, 82.6; H, 5.6; F, 6.3.

Pyrolysis of V. A quantity of 6.5 g. of the ketone (V) was heated for 40 min. at 405–415° and the product flash-distilled in a vacuum of 0.5 mm. The solid distillate in 50 ml. or benzene was chromatographed on alumina, benzene–petroleum ether (3:1) serving as eluent. The yellowish product so obtained melted after repeated recrystallization from benzene-ethanol at 180° and was identified as 20-methylcholanthrene by analysis and mixed melting point. Yield, 2.1 g. (37%).

Anal. Calcd. for $C_{21}H_{16}$: C, 94.0; H, 6.0. Found: C, 93.7; H, 6.1.

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(13) R. C. Fuson, C. H. McKeever and L. C. Behr, *J. Am. Chem. Soc.*, **63**, 2648 (1941).

(14) L. F. Fieser and A. M. Seligman, *J. Am. Chem. Soc.*, **58**, 2482 (1936).