isomer not implied). The concept of stabilization of a cyclobutadiene system through complex formation is not new,[12] although significant stabilization in such a loosely bound state as that in a charge-transfer or π-complex would be a novel and intriguing circumstance. The inordinate stabilities of the biphenylene complexes and, more pertinently, the requirement of a geometry somewhat different from that of the substituted benzene complexes as imposed by the different isokinetic relationship, are easily reconciled to the new geometry. We do not advocate this dibenzocyclobutadiene-tetracyanoethylene π-complex more vigorously because a clear physical interpretation and a definition of the limits of applicability of the enthalpy-entropy correlation have not yet been described.

We hope that work in progress will establish the geometry of other more firmly associated complexes of the biphenylenes.

CAMBRIDGE 40, MASS.

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(12) R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959).

[CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

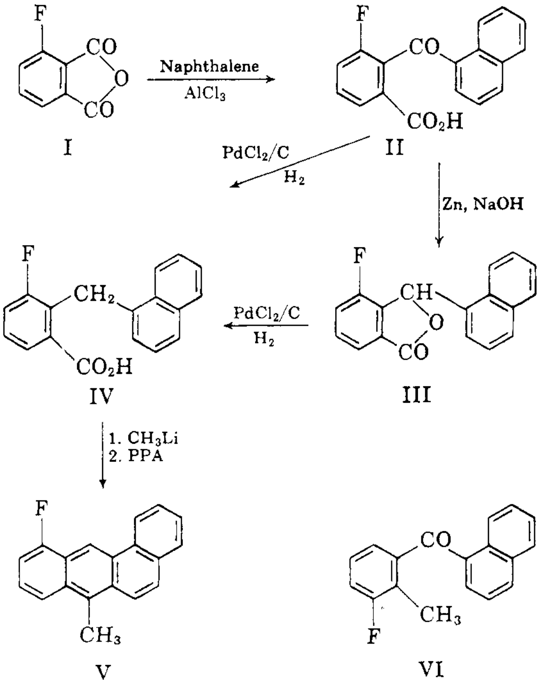
Synthesis of 8-Fluoro-10-methyl-1,2-benzanthracene[1]

MELVIN S. NEWMAN AND EDWARD H. WISEMAN[2]

Received January 5, 1961

The synthesis of 8-fluoro-10-methyl-1,2-benzanthracene is described. The elimination of a fluorine atom during the Elbs pyrolysis of 1-(3-fluoro-2-methylbenzoyl)naphthalene (VI) is noted.

In this paper we report the synthesis of 8-fluoro-10-methyl-1,2-benzanthracene (V), in continuation of a previously described program[3] to provide all of the monofluoro-10-methyl-1,2-benzanthracenes for carcinogenic studies.



The 3-fluorophthalic anhydride needed for the synthesis was prepared by oxidation of 2,3-dimethylfluorobenzene, obtained by decomposition of 2,3-dimethylbenzenediazonium hexafluorophosphate.[4] As a byproduct in this reaction, 2,2'-3,3'-tetramethylbiphenyl was isolated, the identity of which was established by synthesis from the known[5] 2,3-dimethyliodobenzene.

2,3-Dimethylfluorobenzene was oxidized to 3-fluorophthalic acid in high yield by potassium permanganate in aqueous pyridine solution. Distillation of the acid gave the required 3-fluorophthalic anhydride (I). The anhydride (I) was also prepared by heating 3-chlorophthalic anhydride with potassium fluoride, a method described[6] while our work was in progress. In our hands,[7] however, the yields obtained with small quantities could not be reproduced on a larger scale.

Attempts to oxidize 2,3-dimethylfluorobenzene with nitric acid led to the formation of 2-methyl-3-fluorobenzoic acid, the structure of which was established by decarboxylation to *o*-fluorotoluene and by conversion to 3-fluoro-2-methylaniline[8] by the Schmidt Reaction.[9]

Condensation of the anhydride (I) with naphthalene under Friedel-Crafts conditions gave 2-(1-naphthoyl)-3-fluorobenzoic acid (II) exclusively. This parallels the reaction[10] of 3-chlorophthalic anhydride, in that condensation occurs at the

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[1] This work was supported by Grant C-4395 from the National Institutes of Health.

[2] One of us (E.H.W.) gratefully acknowledges the receipt of a Travel Grant from the Wellcome Trust, London W. 1, England.

[3] M. S. Newman, D. MacDowell, and S. Swaminathan, *J. Org. Chem.*, **24**, 509 (1959).

[4] K. Rutherford, paper to be published in *Canadian Journal of Research.*

[5] A. Klages and C. Liecke, *J. prakt. Chem.*, (2) **61**, 323 (1900).

[6] A. Heller, *J. Org. Chem.*, **25**, 834 (1960).

[7] This work was carried out by Mr. V. DeVries.

[8] G. Lock, *Ber.*, **69**, 2253 (1936).

[9] K. F. Schmidt, *Z. angew. Chem.*, **36**, 511 (1923).

hindered carbonyl group.[11] The structure of the keto acid II was established by decarboxylation to a ketone which was shown to be 1-(*o*-fluorobenzoyl)naphthalene.

The keto acid, II, was smoothly reduced to 2-(1-naphthylmethyl)-3-fluorobenzoic acid (IV) by hydrogen in the presence of palladium chloride on charcoal,[12] in ethanol solution. Clemmensen reduction of the keto acid II under conditions described[13] for analogous compounds, gave only the lactone of 2-(α-hydroxynaphthylmethyl)-3-fluorobenzoic acid (III) even under prolonged reaction conditions. Lactone III was also smoothly reduced catalytically to IV over the above palladium catalyst. To our knowledge, these are the first examples of low pressure catalytic hydrogenation of these types of compounds to acids of the *o*-benzylbenzoic acid type.

With excess methyllithium, acid IV yielded the corresponding methyl ketone, which was immediately cyclodehydrated[3] with polyphosphoric acid to give 8-fluoro-10-methyl-1,2-benzanthracene (V).

In connection with this program,[3] an entry into the 5-fluoro-1,2-benzanthracene series was envisaged by the Elbs Reaction on 1-(2-methyl-3-fluorobenzoyl)naphthalene (VI). This ketone VI was prepared by condensing the Grignard reagent of 2-chloro-6-fluorotoluene with 1-naphthonitrile. 2-Chloro-6-fluorotoluene was obtained from 3-chloro-2-methylaniline *via* the diazonium hexafluorophosphate,[4] the overall yield being slightly better than that obtained[14] from the corresponding diazonium fluoborate.

On heating the ketone VI at 400° for several hours, a small yield of 1,2-benzanthracene was obtained, the fluorine atom having been eliminated. The elimination of a methyl group at the 5-position in the Elbs reaction has been reported,[15] and also that of a fluorine atom in an attempted[16] synthesis of a fluorinated 1,2,5,6-dibenzanthracene. However, since in our compound the fluoro-substituent is carried in the *meta*-position with regard to the carbonyl group, the explanation of the loss of fluorine advanced[16] cannot apply in this case.

EXPERIMENTAL[17]

2,3-Dimethylfluorobenzene. 2,3-Dimethylaniline hydrochloride[18] (78.8 g.) dissolved in water (1000 ml.) containing concentrated hydrochloric acid (42 ml.) was diazotized below 5° with sodium nitrite (34.8 g.) in water (50 ml.). Addition of hexafluorophosphoric acid[19] (80.4 g.; *ca.* 65% solution) gave a heavy yellow precipitate. This was washed with water, methanol, and ether successively, the dry salt (98.1 g.) melting with decomposition at 105–110°. Decomposition as described,[20] followed by fractional distillation gave 2,3-dimethylfluorobenzene, (26.4 g.; 43%), b.p. 146–148°.

Anal. Calcd. for C_8H_9F: C, 77.4; H, 7.3. Found: C, 77.4; H, 7.3.

Further distillation gave *2,2',3,3'-tetramethylbiphenyl* (4.5 g. see below), b.p. 132–134° at 2 mm. Recrystallization from ethanol gave white needles, m.p. 115–117°.

2,2',3,3'-Tetramethylbiphenyl. 2,3-Dimethyliodobenzene[5] (21.0 g.) and copper powder (20.0 g. Venus-copper bronze) were heated at 150° for 40 hr. The organic phase was separated and distilled to give starting material (7.2 g.), b.p. 80–82° at 2 mm., and 2,2',3,3'-tetramethylbiphenyl (4.3 g.), b.p. 130–133° at 2 mm. Recrystallization of the latter from ethanol afforded white crystals, m.p. 115–117°, alone and when mixed with the product above.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.4; H, 8.6. Found: C, 91.5; H, 8.7 (for decarboxylation product); C, 91.2; H, 8.7 (for synthesized product).

2-Methyl-3-fluorobenzoic acid. 2,3-Dimethylfluorobenzene (68.0 g.), nitric acid (140 ml., s.g. 1.42) and water (280 ml.) were stirred at reflux for 66 hr. The mixture on cooling yielded unchanged starting material (10.8 g.) and 2-methyl-3-fluorobenzoic acid (49.7 g., 59%), m.p. 156–157° (from water containing a trace of ethanol).

Anal. Calcd. for $C_8H_7FO_2$: C, 62.3; H, 4.6. Found: C, 62.7; H. 4.8.

p-Nitrobenzyl ester of above acid, m.p. 126–126.5° from ethanol.

Anal. Calcd. for $C_{15}H_{12}FNO_4$: C, 62.3; H, 4.2. Found: C, 62.6; H, 4.2.

The Schmidt reaction[9] on the above acid (5.1 g.) gave 3-fluoro-2-methylaniline (3.2 g.), b.p. 50–53° at 2 mm. (lit.[8] b.p. 89.5–90.5° at 15 mm.), characterized as the hydrochloride, m.p. 237–238° (from 50% hydrochloric acid), (*Anal.* Calcd. for C_7H_9ClFN: C, 52.1; H, 5.6. Found: C, 52.4; H, 5.6) and as the acetyl derivative, m.p. 130–131° (from) benzenecyclohexane) (lit. m.p. 132°).

Anal. Calcd. for $C_9H_{10}FNO$: C, 64.7; H, 6.0. Found: C, 64.4; H, 6.1.

The acid above (3.0 g.) was decarboxylated by heating with copper powder (1.5 g.; Venus-copper bronze) and quinoline (25 ml.). The product (1.1 g.) b.p. 114–116°, had an infrared spectrum identical with that of an authentic sample of *o*-fluorotoluene.

3-Fluorophthalic acid. A solution of 2,3-dimethylfluorobenzene (30.0 g.) in pyridine (350 ml.) and water (250 ml.) was heated just to reflux. With no external heating, potassium permanganate (175 g.) was added, portionwise, over a period of 1 hr., so that gentle reflux was maintained. The mixture was refluxed for a further 30 min., excess permanganate destroyed with sodium bisulphite, and the warm solution filtered. The filtrate was acidified and continuously extracted with ether for 16 hr. Evaporation and recrystalliza-

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(10) M. S. Newman and P. G. Scheurer, *J. Am. Chem. Soc.*, **78**, 5004 (1955).

(11) For discussion see footnotes 4–7, ref. 10.

(12) R. Mozingo, *Org. Syntheses*, **Coll. Vol. III**, p. 688, Note 13.

(13) M. S. Newman, S. Swaminathan, and R. Chatterji, *J. Org. Chem.*, **24**, 1961 (1959).

(14) H. Willstaedt, *Ber.*, **64**, 2688 (1931).

(15) L. F. Fieser and J. Cason, *J. Am. Chem. Soc.*, **61**, 1740 (1939).

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

(17) All melting points are uncorrected. Analyses are by the Schwarzkopf Laboratories. The term "worked up in the usual way" means that an ether-benzene extract of the organic products was washed with acid and/or alkali as required, saturated sodium chloride solution, dried with magnesium sulfate, and filtered; the solvents were removed and the residue treated as described.

(18) Eastman Kodak Co., Practical Grade, used without further purification.

(19) Obtained from the Ozark Mahoning Company, Tulsa, Okla.

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

tion from aqueous ethanol gave 3-fluorophthalic acid (36.1 g.; 81%), m.p. 167–168°.

Anal. Calcd. for $C_8H_5FO_4$: C, 52.2; H, 2.7. Found: C, 52.3; H, 3.0.

3-Fluorophthalic anhydride (I). 3-Fluorophthalic acid (34.0 g.) was distilled at 210–215° to give I (30.2 g., 98%), m.p. 157–158°.[6] Recrystallization could be effected from either acetic anhydride or toluene.

2-(1-Naphthoyl)-3-fluorobenzoic acid (II). To a solution of 3-fluorophthalic anhydride (8.3 g.) and naphthalene (7.7 g.) in *o*-dichlorobenzene (100 ml.), anhydrous aluminum chloride (14.7 g.) was added portionwise during 30 min., and the dark-red solution was held at 85–90° for 2 hr. The mixture was poured onto ice and hydrochloric acid, and solvent and excess naphthalene removed by steam distillation. The product, worked up in the usual manner, gave crude acid (13.1 g. 93%), m.p. 176–178°. Recrystallization gave pure II, m.p. 198–199.5°, with little loss, from ethanol.

Anal. Calcd. for $C_{18}H_{11}FO_3$: C, 73.4; H, 3.7. Found: C, 73.5; H, 3.9.

This reaction also proceeded in tetrachloroethane. Yields however were lower (*ca.* 60%) and the product proved difficult to isolate in a pure state.

Methyl 2-(1-naphthoyl)-3-fluorobenzoate was prepared by refluxing the above acid with methanol saturated with hydrogen chloride. Recrystallization from petroleum ether (b.p. 60–70°) gave colorless needles, m.p. 95–96°.

Anal. Calcd. for $C_{19}H_{13}FO_3$: C, 74.0; H, 4.3. Found: C, 74.0; H, 4.6.

Decarboxylation of II. A mixture of II (4.0 g.), copper powder (1.0 g.; Venus-copper bronze), and quinoline (25 ml.) were refluxed for 1.5 hr. The organic phase, in ether, was worked up in the usual way, the neutral fraction yielding 1-(*o-fluorobenzoyl*)*naphthalene* (2.3 g.), b.p. 195–197° at 4 mm. The *2,4-dinitrophenylhydrazone* (from glacial acetic acid) had m.p. 281–282°, alone and in admixture with the authentic sample prepared below.

Preparation of ketones. Condensation of naphthalene with *o*- and *m*-fluorobenzoyl chloride respectively under Friedel-Crafts conditions gave 1-(*o-fluorobenzoyl*)- and 1-(*m-fluorobenzoyl*)*naphthalene* in over 80% yields. The *o*-isomer was also prepared from *o*-fluorobenzonitrile and 1-bromonaphthalene under Grignard conditions in 55% yield. The *ortho*-isomer was a colorless viscous oil, b.p. 212–213° at 6 mm. The *meta*-isomer crystallized as fine white needles from alcohol, m.p. 122–123°.

Anal. Calcd. for $C_{17}H_{11}FO$: C, 81.6; H, 4.4. Found: *o*-isomer, C, 81.7; H, 4.5; *m*-isomer, C, 81.7; H, 4.7.

The *2,4-dinitrophenylhydrazones* of the above ketones were prepared in alcohol solution, and recrystallized from glacial acetic acid. The orange *ortho*-isomer melted at 282–283°, and the orange-red *meta*-isomer at m.p. 262–264°.

Anal. Calcd. for $C_{23}H_{15}FN_4O_4$: C, 64.2; H, 3.5. Found: *ortho*-isomer, C, 64.3; H, 3.8; *meta*-isomer, C, 64.4; H, 3.8.

The specimens of ketone prepared by decarboxylation of 2-(1-naphthoyl)-3-fluorobenzoic acid, II, and from *o*-fluorobenzoyl chloride and from *o*-fluorobenzonitrile were shown to be identical both by comparison of infrared spectra and by mixed melting point determinations on the derived 2,4-dinitrophenylhydrazones.

Lactone of 2-(α-hydroxy-1-naphthylmethyl)-3-fluorobenzoic acid (III). A mixture of II (6.5 g.), water (100 ml.), potassium hydroxide (18.5 g.), and zinc dust (20.0 g.), activated with a few drops of cuprammonium sulphate solution, were stirred together under reflux for 18 hr. Isolation in the usual manner gave III (5.1 g. 83%), m.p. 172–173.5° (from methanol).

Anal. Calcd. for $C_{18}H_{11}FO_2$: C, 77.7; H, 4.0; F, 6.8. Found: C, 77.7; H, 3.9; F, 6.8.

2-(1-Naphthylmethyl)-3-fluorobenzoic acid (IV). (a) *From* III. The lactone III (5.0 g.) in ethanol (250 ml.) was hydrogenated[12] (initial pressure 34 p.s.i.) in the presence of palladium chloride (1.0 g.) adsorbed on charcoal (Darco G-60; 5.0 g.) for 7 hr. The mixture was filtered, and the ethanol removed under reduced pressure. After the usual workup, the acid fraction, recrystallized from benzene–petroleum ether (b.p. 90–100°) gave pure IV (4.8 g., 95%), m.p. 144.5–145.5°.

Anal. Calcd. for $C_{18}H_{13}FO_2$: C, 77.1; H, 4.6; F, 6.8. Found: C, 77.2; H, 4.6; F, 6.8.

(b) *From* II. The acid II (9.0 g.) in ethanol (250 ml.) was reduced as in (a) with hydrogen in the presence of palladium chloride (1.9 g.) on charcoal (10 g.) over a period of 13 hr. Isolation as before gave pure IV (7.0 g. 82%), m.p. 144.5–145.5°, identical with the above product.

8-Fluoro-10-methyl-1,2-benzanthracene (V). To the methyllithium solution prepared from lithium (1.8 g.) and methyl iodide (12.0 g.) in ether was added, at 0°, a solution of IV (3.5 g.) in ether (150 ml.). The deep purple reaction mixture was stirred at room temperature for 30 min., and then decomposed with ice-water. The ether layer was removed, and the aqueous layer extracted once with ether-benzene. The extracts were combined and evaporated to yield an almost colorless oil, which was stirred into polyphosphoric acid[21] (35 g.). The mixture was heated at 100° for 1 hr., and stood overnight at room temperature. Water was added, and the mixture extracted with benzene. The benzene extracts were concentrated, passed once through a short alumina column, and the product recrystallized from ethanol-benzene to give V (0.9 g.; 31%), m.p. 130.5–131.0°.

Anal. Calcd. for $C_{19}H_{13}F$: C, 87.7; H, 5.0; F, 7.3. Found: C, 87.8; H, 5.0; F, 7.5.

The *2,4,7-trinitrofluorenone complex*, m.p. 212–213.5°, dec., was obtained in, and recrystallized from, benzene.

Anal. Calcd. for $C_{32}H_{18}FN_3O_7$: C, 66.8; H, 3.1. Found: C, 66.8; H, 3.3.

2-Chloro-6-fluorotoluene. 3-Chloro-2-methylaniline (220.0 g.) in water (3500 ml.) containing concentrated hydrochloric acid (300 ml.) was diazotized below 5° with sodium nitrite (130 g.) in water (400 ml.). Addition of hexafluorophosphoric acid[19] (430 g.; *ca.* 65% solution) gave a copious precipitate, dec. point 130–132°. Decomposition as before,[20] followed by fractional distillation gave 2-chloro-6-fluorotoluene (103.4 g.; 47%), b.p. 152–153° (lit.[14] 153–154°). Further distillation gave 2-hydroxy-6-chlorotoluene (65.3 g. 29%), b.p. 212–215°. Recrystallization from petroleum ether (b.p. 60–70°) gave white needles, m.p. 86–87° (lit.,[22] m.p. 86°).

Anal. Calcd. for C_7H_7ClO: C, 58.9; H, 4.9. Found: C, 58.9; H, 5.1.

1-(2-Methyl-3-fluorobenzoyl)naphthalene (VI). The Grignard Reagent from 2-chloro-6-fluorotoluene (83.4 g.) and magnesium (17.2 g.) was prepared in dry tetrahydrofuran (400 ml.). The solution was forced by dry nitrogen into a solution of 1-naphthonitrile (88.0 g.) in dry tetrahydrofuran (100 ml.). After 1 hr. at reflux, the tetrahydrofuran was replaced by benzene, and refluxing continued for 16 hr. The reaction mixture was decomposed with ice and saturated ammonium chloride solution, and the organic phase extracted with sulfuric acid (4*N*, 4 × 150 ml.). Evaporation of the extracted organic layer gave unchanged 1-naphthonitrile (28.2 g.). The combined acid extracts were refluxed for 3 hr. and extracted with ether, subsequent distillation giving VI (84.6 g.; 43.1%), b.p. 181–184° at 4 mm.

Anal. Calcd. for $C_{18}H_{13}FO$: C, 81.8; H, 4.9. Found: C, 81.8; H, 4.8.

Elbs reaction on VI. The ketone VI (2.0 g.) was heated at 400–410° for 2 hr. The solid product (1.2 g.) was distilled from the reaction mixture, and converted with 2,4,7-trinitrofluorenone to the red complex (2.4 g.), m.p. 220–224° (ethanol). A solution of this complex in benzene was passed through a short alumina column, and the eluant evaporated

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(21) Obtained from the Victor Chemical Co., to whom we are indebted for a generous gift.

(22) E. Noelting, *Ber.*, **37**, 1015 (1904).

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.

Columbus 10, Ohio

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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

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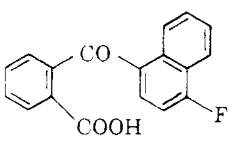
The cyclization of *o*-(4-fluoro-1-naphthoyl)benzoic acid (I) with benzoyl chloride yields 3-chloro-1,2-benzanthraquinone, while benzoyl *fluoride* gives the expected 3-fluoro analog. This type of reaction appears to be specific for *o*-benzoylbenzoic acids carrying a fluorine atom in *para* to the carbonyl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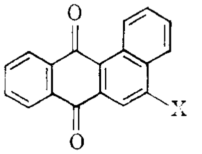
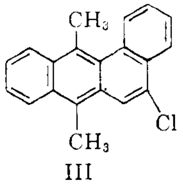

II

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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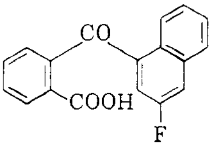
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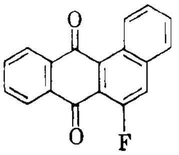
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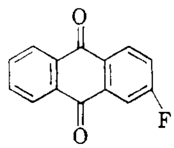
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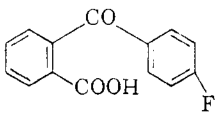
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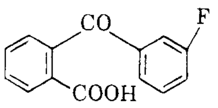
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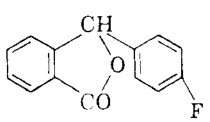
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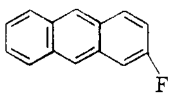
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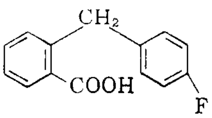
XI

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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.

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