Anal. Calcd. for $C_{31}H_{50}O_5$: C, 74.06; H, 10.02. Found: C, 74.03; H, 9.94.

(b) *From Cholestan-3α,5α-diol-6-one-5-acetate* (VIII). Cholestan-3α,5α-diol-6-one-5-acetate (50 mg.) was dissolved in 10 ml. of acetic anhydride and 3 ml. of pyridine and allowed to stand at room temperature for 18 hr. Water was then added, the suspension cooled, and the resulting solid was filtered, washed with water, air-dried, and recrystallized from ethanol-water, yielding 39 mg. (71.5%) of cholestan-3α,5α-diol-6-one-3,5-diacetate, m.p. 180–182°. Recrystallization from ethanol-water gave pure diacetate, m.p. 186–187°, mixed m.p. undepressed with that prepared in (a) above.

URBANA, ILL.

[CONTRIBUTION FROM THE SUMMIT RESEARCH LABORATORIES, CELANESE CORP. OF AMERICA]

Some 3,9-Dicarboxylic Acids of 2,4,8,10-Tetroxaspiro[5.5]undecane

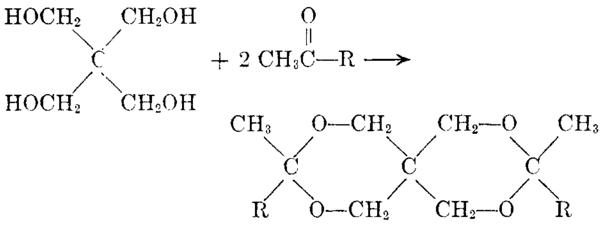
JOHN B. CLEMENTS AND LEONARD M. RICE[1]

Received July 1, 1959

A series of 3,9-disubstituted 2,4,8,10-tetroxaspiro[5.5]undecanes has been prepared by the condensation of pentaerythritol with aldehydes and acetals which contain other functions such as nitrile or ester groups. Hydrolysis of the derived nitriles and esters has led to a variety of 3,9-dicarboxylic acids. Attempts to prepare the desired acids by replacement of the halogens of 3,9-bis(halomethyl)-2,4,8,10-tetroxaspiro[5.5]undecane with appropriate nucleophiles were unsuccessful because of the extreme inertness of the halide. Finally, a very convenient method for removing dipentaerythritol from commercial pentaerythritol has been developed.

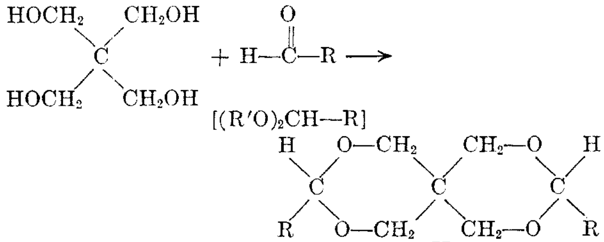
In connection with another project, it was necessary to prepare a series of 3,9-dibasic acids of 2,4,8,10-tetroxaspiro[5.5] undecane upon which we would like to report at this time. These spiro acids were prepared from pentaerythritol and a suitable aldehyde or its corresponding acetal.

Some 30 years ago, Boeseken and Felix[2] condensed pentaerythritol with various keto esters to obtain a series of diesters (I).


I

In all of these products, positions 3 and 9 were substituted with a methyl group in addition to the fatty acid ester residue, R.

For the purpose of our investigation we were interested in the spiro acids where the 3,9 positions were not substituted by alkyl and possessed only a carboxyl or carboxyalkyl group. We took advantage in our syntheses of the condensation of pentaerythritol with aldehydes or acetals as shown in the following figure:


II

R = Carboxyl or Carboxyalkyl

The preparation of the 3,9-disubstituted 2,4,8,10-tetroxaspiro[5.5]undecanes (II) was realized by condensing pentaerythritol with a variety of aldehydes and acetals which also had an ester or nitrile function in their molecule. Thus, pentaerythritol was condensed with methyl dimethoxyacetate, ethyl 2,2-diethoxypropionate, 1,1-diethoxy-3-cyanopropane, 1,1-dimethyl-3-cyanobutyraldehyde, and 1,1-diethyl-3-cyanobutyraldehyde to give the corresponding diester or dinitrile, all in good yields. Each diester or dinitrile was hydrolyzed to the corresponding diacid. The various diesters, dinitriles, and dicarboxylic acids are listed in Table I together with pertinent data.

The condensation of methyl dimethoxyacetate with pentaerythritol to give ester V and its hydrolysis to acid VI is worthy of special note. Even though the conditions for carrying out the condensation are rather drastic, *i.e.*, 3 hr. reflux with concentrated hydrochloric acid, the ester itself is somewhat water sensitive. Thus, the diester is hydrolyzed completely to the diacid by short reflux with water alone and this was the most convenient method of preparation of the diacid. Except for this water sensitivity, the ester is not otherwise labile and remains unchanged at ordinary room conditions using no special precautions.

In all of the other condensations a small amount of *p*-toluene sulfonic acid was used as a catalyst. For the condensation of the acetals with pentaerythritol the reactants were refluxed until homogeneous and for the aldehydes the reactions were performed in refluxing toluene using a Dean-Stark trap for removal of the water as it formed. Dinitriles XI and XIII were hydrolyzed with potassium hydrox-

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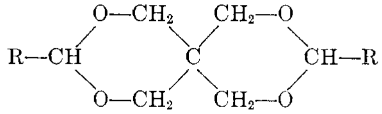
[1] Present address: Wyeth Laboratories, Radnor, Pa.

[2] J. Boeseken and B. B. C. Felix, *Ber.*, 61B, 787 and 1855 (1928).

TABLE I

3,9-DERIVATIVES OF 2,4,8,10-TETROXASPIRO[5.5]UNDECANE



				Analyses					
				Carbon		Hydrogen		Acid No.	
No.	R	Formula	M.P.	Calcd.	Found	Calcd.	Found	Calcd.	Found
V	—$COOCH_3$	$C_{11}H_{16}O_8$	135–136	47.82	47.4, 47.6	5.84	5.81, 5.96	138	138, 139[a]
VI	—COOH	$C_9H_{12}O_8$	234–234.5	43.55	43.4, 43.5	4.88	4.80, 4.81	124	124
VII	—$CH_2COOC_2H_5$[b]	$C_{15}H_{24}O_8$	81.5–82	54.21	54.3, 54.4	7.28	7.31, 7.40		
VIII	—CH_2COOH	$C_{11}H_{16}O_8$	220–221	47.82	47.9, 47.7	5.84	5.90, 6.04	138	138, 138
IX	—CH_2CH_2CN	$C_{13}H_{18}N_2O_4$	73–74	58.63	58.9, 58.8	6.81	6.90, 6.86	10.52	10.37, 10.44[c]
X	—CH_2CH_2COOH	$C_{13}H_{20}O_8$	207–208	51.31	51.6, 51.8	6.63	6.60, 6.77	152	151, 153
XI	—$C(CH_3)_2CH_2CH_2CN$	$C_{19}H_{30}N_2O_4$	103–104	65.11	65.3, 65.2	8.63	8.56, 8.56		
XII	—$C(CH_3)_2CH_2CH_2COOH$	$C_{19}H_{32}O_8$	257–258	58.74	58.5, 58.7	8.30	8.49, 8.45	194	195, 196
XIII	—$C(C_2H_5)_2CH_2CH_2CN$	$C_{23}H_{38}N_2O_4$	89.5–90.5	67.94	67.7, 67.8	9.42	9.52, 9.55		
XIV	—$C(C_2H_5)_2CH_2CH_2COOH$	$C_{23}H_{40}O_8$	164–165	62.14	61.6, 61.7	9.07	8.90, 9.03	222	222

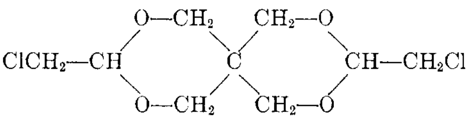
[a] Saponification No. [b] See Ref. 7. [c] Nitrogen analysis.

ide in 85% aqueous ethyl Cellosolve. All other esters and nitriles were hydrolyzed in aqueous base.

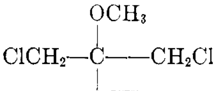
Attention is directed to the unexpected differences in physical properties between acids XII and XIV of Table I. The small structural difference at the carbon atom alpha to the spiran ring causes a great difference in melting point and in solubility characteristics. Replacement of the ethyls by methyls causes an increase of 93° in melting point and a large reduction in solubility in organic solvents. Acid XIV is easily soluble in many common solvents, recrystallizing very easily from methanol or ethanol, but acid XII dissolves only in the higher boiling solvents such as ethyl Cellosolve, ethylene glycol, and dimethyl formamide. Recrystallization from boiling dimethyl formamide was found to be the most suitable method for purification.

Early in this work attempts were made to utilize the readily available[3] 3,9-bis(chloromethyl)-2,4,8,-10-tetroxaspiro[5.5]undecane (III) in conventional reactions. If the halogen were replaceable by groups such as nitrile, a convenient path to the corresponding acid would be available. In spite of numerous attempts to replace the chlorine atom of this compound only limited success was achieved. Thus, cyanation with sodium cyanide and amination, both with ammonia and by the Gabriel method, resulted either in recovery of starting material or intractable products which could not be characterized. The only successful displacement reaction was the exchange iodination of the chloride using sodium iodide which required a rather high boiling solvent, ethyl Cellosolve, and extended reaction time. This diiodide was also very inert as shown by its failure to undergo cyanation.

An interesting analogy can be drawn between the halide unreactivity of III and IV, the dimethyl ketal of 1,3-dichloroacetone.



III



$ClCH_2—C(OCH_3)_2—CH_2Cl$

IV

In each case the halogen atom is located on a carbon alpha to a carbon atom carrying two alkoxy groups and peculiar unreactivity toward nucleophilic displacement has been found. Thus, chloride IV is unaffected by secondary amines under fairly drastic conditions, *i.e.*, at 100° under pressure. Also, sodium iodide fails to react with IV indicating it to be even less reactive toward displacement than either III or the corresponding iodide. At present no mechanism or explanation can be offered for these interesting observations.

Because it was thought contamination by dipentaerythritol, present to some extent in all commercially available pentaerythritol, might yield impure products in our syntheses, a very convenient procedure was developed for the preparation of monopentaerythritol free of dipentaerythritol. The procedure, an adaptation of the method of Simecek,[4] takes advantage of the facile condensation of commercial pentaerythritol with acetal for the preparation of pentaerythritol bisacetal. This bisacetal was carefully purified by vacuum distillation to give a product of sharp boiling point. The infrared spectrum of this material showed the absence of

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[3] V. G. Mkhitaryan, *J. Gen. Chem.* (*U.S.S.R.*), **9**, 1923 (1939); *Chem. Abstr.* **34**, 4381 (1940).

[4] J. Simecek, *Chem. Listy*, **47**, 1673 (1954); *Chem. Abstr.*, **49**, 856h (1955).

hydroxyl group indicating dipentaerythritol and dipentaerythritol condensation products to be absent. The bisacetal was hydrolyzed with dilute aqueous hydrochloric acid to give pure pentaerythritol. Subsequently in our work we found that both commercial pentaerythritol and the purified pentaerythritol gave identical results in our syntheses.

EXPERIMENTAL[5]

3,9-Dicarbomethoxy-2,4,8,10-tetroxaspiro[5.5]undecane. A mixture of 272 g. (2.0 mol.) of pentaerythritol, 590 g. (4.4 mol.) of methyl dimethoxyacetate and 500 ml. of concentrated hydrochloric acid was refluxed for 3 hr. The reaction mixture was transferred to a large evaporating dish and left overnight on a steam bath. On treating the resulting thick oil with 400 ml. of methanol a colorless semisolid cake was formed. Recrystallization of the entire cake from methanol resulted in 292 g. (52.8%) of colorless solid melting at 133.5–134.5°. The analytical sample was prepared by recrystallizing from methanol as long colorless needles.

The *diamide*, prepared by treatment of the diester with concentrated aqueous ammonium hydroxide, was recrystallized from water as colorless flakes. The melting point was above 300°.

Anal. Calcd. for $C_9H_{14}N_2O_6$: C, 43.87; H, 5.73; N, 11.38. Found: C, 44.0, 43.7; H, 6.01, 5.78; N, 11.25, 11.29.

The *bis-N-benzylamide*, prepared from benzylamine using NH_4Cl catalysis, yielded colorless flakes melting at 180–181°, after recrystallization from methanol.

Anal. Calcd. for $C_{23}H_{26}N_2O_6$: C, 64.75; H, 6.15; N, 6.57. Found: C, 64.6, 64.5; H, 6.18, 6.30; N, 6.49, 6.53.

The *dihydrazide* was prepared from the ester and hydrazine hydrate. It was recrystallized from aqueous methanol as colorless flakes melting at 208–210°.

Anal. Calcd. for $C_9H_{16}N_4O_6$: N, 20.29. Found: N, 20.10, 20.19.

3,9-Dicarboxy-2,4,8,10-tetroxaspiro[5.5]undecane. A solution of 55.3 g. (0.20 mol.) of 3,9-dicarbomethoxy-2,4,8,10-tetroxaspiro[5.5]undecane in 165 ml. of water was refluxed for 2 hr. and allowed to stand overnight. Upon cooling, 39.5 g. (79.5%) of colorless crystals, melting at 233.5–234.5° (gas evolution), precipitated. Two recrystallizations from water raised the melting point to 234–234.5° (gas evolution).

3,9-Biscarbethoxymethyl-2,4,8,10-tetroxaspiro[5.5]undecane. A mixture of 36.0 g. (0.19 mol.) of ethyl β,β-diethoxypropionate,[6] 11.9 g. (0.086 mol.) of pentaerythritol and 0.2 g. of *p*-toluenesulfonic acid monohydrate was refluxed for 8 hr. Upon cooling a pasty, colorless solid appeared which was recrystallized from ethanol to give 16.6 g. (58.3%) of colorless crystals melting at 79.5–81°. Another recrystallization from ethanol raised the melting point to 81.5–82°. Croxall, Van Hook, and Luckenbaugh[7] report a melting point of 79° for this ester.

3,9-Biscarboxymethyl-2,4,8,10-tetroxaspiro[5.5]undecane. A mixture of 9.56 g. (0.029 mol.) of 3,9-biscarbethoxymethyl-2,4,8,10-tetroxaspiro[5.5]undecane, 7 g. of potassium hydroxide and 50 ml. of water was refluxed for 3 hr. The yellow solution was charcoaled, cooled, and acidified with concentrated hydrochloric acid. A colorless solid, weighing 6.13 g. (77.0%) and melting at 220–221° (gas evolution), was collected. Recrystallization from water did not raise the melting point.

3,9-Bis(2-cyanoethyl)-2,4,8,10-tetroxaspiro[5.5]undecane. A mixture of 33.1 g. (0.243 mol.) of pentaerythritol, 84.0 g. (0.535 mol.) of 1,1-diethoxy-3-cyanopropane,[8] and 0.66 g. of *p*-toluenesulfonic acid monohydrate was refluxed for 4 hr., ethanol removed on a steam bath, and the resulting red oil crystallized by cooling in ice. The reaction product was recrystallized from ethanol to give 56.8 g. (88.0%) of nearly colorless crystals melting at 67–69.5°. Several recrystallizations from ethanol raised the melting point to 73–74°.

3,9-Bis(2-carboxyethyl)-2,4,8,10-tetroxaspiro[5.5]undecane. A mixture of 37.9 g. (0.142 mol.) of 3,9-bis(2-cyanoethyl)-2,4,8,10-tetroxaspiro[5.5]undecane, 31.8 g. of potassium hydroxide, and 225 ml. of water was refluxed overnight. The reaction product was charcoaled, cooled, brought to *p*H 7 with concentrated hydrochloric acid and allowed to stand at room temperature overnight. The cloudy solution was filtered using a diatomaceous earth filter aid and made strongly acid with concentrated hydrochloric acid. The precipitate, after filtering and drying, weighed 38.1 g. (88.2%) and melted at 208–211°. The analytical sample was prepared by recrystallizing from water as glistening needles melting at 207–208°.

The *dimethyl ester*, prepared by overnight reflux of the diacid with methanol and sulfuric acid, recrystallized from methanol as thick, colorless needles melting at 92–93°.

Anal. Calcd. for $C_{15}H_{24}O_8$: C, 54.21; H, 7.28. Found: C, 53.8, 53.8; H, 7.47, 7.42.

3,9-Bis(1,1-dimethyl-3-cyanopropyl)-2,4,8,10-tetroxaspiro[5.5]undecane. A mixture of 104 g. (0.765 mol.) of pentaerythritol, 206 g. (1.65 mol.) of 2,2-dimethyl-4-cyanobutyraldehyde,[9] 4.25 g. of *p*-toluenesulfonic acid monohydrate, and 750 ml. of toluene was refluxed overnight under a Dean-Stark trap. The theoretical amount of water separated. The reaction product was partially cooled, neutralized with sodium methoxide, and filtered using a diatomaceous earth filter aid. Removal of the solvent from the filtrate gave an oil which readily crystallized to a light yellow solid. Recrystallization of this material from methanol yielded 218.1 g. (83.2%) of nearly colorless crystals melting at 101.5–102.5°.

3,9-Bis(1,1-dimethyl-3-carboxypropyl)-2,4,8,10-tetroxaspiro[5.5]undecane. A mixture of 156.5 g. (0.45 mole) of 3,9-bis(1,1-dimethyl-3-cyanopropyl)-2,4,8,10-tetroxaspiro[5.5]-undecane, 165 g. of potassium hydroxide, 185 ml. of water, and 380 ml. of ethyl Cellosolve was refluxed overnight. The reaction mixture was diluted with about 1 l. of water and made acid with concentrated hydrochloric acid. The pasty precipitate, after partially drying by distillating with benzene, weighed 185.3 g. and melted at 251–255°. The product was very insoluble, failing to dissolve in the following solvents (cold or hot): methanol, ethanol, *n*-propyl alcohol, water ethyl acetate, acetonitrile, methylene chloride, chloroform, carbon tetrachloride, tetrahydrofuran, acetone, and nitromethane. It partially dissolved in hot dimethyl formamide, hot ethyl Cellosolve, and hot ethylene glycol. The analytical sample was prepared by leaching 30 g. of the crude product with boiling dimethyl formamide, filtering hot, and collecting 15.1 g. of brown precipitate melting at 257–258° (slight gas evolution). Two further recrystallizations from dimethyl formamide followed by a methanol wash did not raise the melting point and this material was directly analyzed.

The *dimethyl ester*, prepared by overnight reflux of the diacid with methanol and sulfuric acid, recrystallized from methanol as colorless flakes melting at 136–136.5°.

Anal. Calcd. for $C_{21}H_{36}O_8$: C, 60.55; H, 8.71. Found: C, 60.6, 60.5; H, 8.63, 8.78.

3,9-Bis(1,1-diethyl-3-cyanopropyl)-2,4,8,10-tetroxaspiro[5.5]undecane was prepared in a 96.2% yield from pentaerythritol and 2,2-diethyl-4-cyanobutyraldehyde[10] using a

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(5) All melting points are corrected.

(6) A. N. Nesmeyanov, R. Kh. Freedlina, and L. I. Zakharkin, *Doklady Akad. Nauk S.S.S.R.*, **97**, 91 (1954); *Chem. Abstr.*, **49**, 8793e (1955).

(7) W. J. Croxall, J. O. Van Hook, and R. Luckenbaugh, *J. Am. Chem. Soc.*, **71**, 2741 (1949) prepared this ester in an analogous manner using sodium bisulfate catalysis.

(8) R. H. F. Manske, *Can. J. Res.*, **5**, 529 (1931).

(9) We wish to thank Eastman Chemical Products, Kingsport, Tenn., for a generous sample of this aldehyde.

(10) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **66**, 56 (1944).

procedure similar to that for the preparation of 3,9-bis(1,1-dimethyl-3-cyanopropyl)-2,4,8,10-tetroxaspiro[5.5]undecane.

3,9-Bis(1,1-diethyl-3-carboxypropyl)-2,4,8,10-tetroxaspiro-[5.5]undecane was prepared in a 93.8% yield by basic hydrolysis of the dinitrile in aqueous Cellosolve. It recrystallized very easily from methanol.

3,9-Bis(iodomethyl)-2,4,8,10-tetroxaspiro[5.5]undecane. A mixture of 102.4 g. (0.40 mol.) of 3,9-bis(chloromethyl)-2,4,8,10-tetroxaspiro[5.5]undecane, 240 g. (1.60 mol.) of sodium iodide, and 1 l. of ethyl Cellosolve was refluxed for 24 hr. The reaction product, obtained by dilution with water, weighed 153.5 g. (87.5%) and melted at 144.5–145.5°. Recrystallization from ethanol gave colorless flakes melting at 146.5–147.5°.

Anal. Calcd. for $C_9H_{14}I_2O_4$: C, 24.55; H, 3.21. Found: C, 24.4, 24.6; H, 3.22, 3.29.

Attempts to cyanate the above diiodide with a three-fold excess of potassium cyanide in refluxing ethyl Cellosolve yielded only tars which could not be characterized. Use of cuprous cyanide in pyridine gave similar results.

Attempts to replace the chlorine of *3,9-bis(chloromethyl)-2,4,8,10-tetroxaspiro[5.5]undecane.* (a) *Amination.* Heating the dichloride with a saturated methanolic ammonia solution at 130° resulted in intractable tars which could not be characterized.

(b) *Cyanation.* Refluxing a solution of the dichloride with sodium cyanide and a small amount of sodium iodide in either ethanol or ethyl Cellosolve resulted in quantitative recovery of starting material.

(c) *Gabriel reaction.* Heating a mixture of the dichloride with potassium phthalimide in dimethyl formamide on a steam bath for 1 hr. resulted in recovery of the starting material. Refluxing for 20 hr. gave an oil which could not be characterized nor hydrolyzed to the amine.

Attempts to replace the chlorine of *1,3-dichloro-2,2-dimethoxypropane.* (a) *Reaction with secondary amines.* Heating a methanolic solution of the dichloride with excess dimethyl amine at 100° for 8 hr. resulted in the recovery of the starting material.

(b) *Iodination.* Attempts to replace the chlorine with iodine, using conditions similar to those used in preparing 3,9-bis(iodomethyl)-2,4,8,10-tetroxaspiro[5.5]undecane, resulted in the recovery of starting halide.

Monopentaerythritol. 3,9-Dimethyl-2,4,8,10-tetroxapiro-[5.5]undecane (pentaerythritol bisacetal) was prepared from commercial pentaerythritol and acetaldehyde diethyl acetal according to the method of Mkhitaryan.[3] Three careful vacuum fractional distillations gave a product boiling at 113.0–113.5°/18 mm. The over-all yield was 56%. No hydroxyl groups could be detected in the infrared spectrum. Steam distillation of a weakly acidic (HCl) aqueous solution of the bisacetal resulted in complete hydrolysis to pentaerythritol. The pentaerythritol was isolated by evaporation of the reaction mixture to incipient crystallization, cooling thoroughly, and filtering. One recrystallization from the minimum amount of water gave 69% of product melting at 263–265°. The literature has reported melting points from 260°[11] to 269°.[12] Others[4,13] have reported intermediate values.

SUMMIT, N. J.

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(11) W. Friedrich and W. Brun, *Ber.*, **63B**, 6281 (1930).

(12) G. Desseigne, *Mem. des Poudres*, **33**, 169 (1951); *Chem. Abstr.*, **48**, 1954i (1954).

(13) P. Ebert, *Ber.*, **64**, 114 (1931); B. W. Lew, M. L. Wolfrom, and R. M. Goepp, *J. Am. Chem. Soc.*, **86**, 1449 (1946).

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

Synthesis of 6-Fluoro-, 7-Fluoro-, and 6-Methoxy-10-methyl-1,2-benzanthracenes[1]

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Received July 2, 1959

The syntheses of 6-fluoro-, 7-fluoro-, and 6-methoxy-10-methyl-1,2-benzanthracenes are described. The ratio of isomeric keto acids formed from reactions of 1,2-naphthalic anhydride with *p*-fluorophenylmagnesium bromide and with fluorobenzene in the Friedel-Crafts condensation were determined and the results are compared with those obtained with 3-methyl- and 3-chlorophthalic anhydrides. On hydrolysis of methyl 1-*p*-fluorobenzoyl-2-naphthoate with aqueous methanolic potassium hydroxide, an unexpectedly high yield of 1-*p*-methoxybenzoyl-2-naphthoic acid was obtained.

In continuation of a previously described program of synthesis designed to provide all of the monofluoro-10-methyl-1,2-benzanthracenes[2] for studies on carcinogenicity, we have prepared 6-fluoro-10-methyl-1,2-benzanthracene (III) and 7-fluoro-10-methyl-1,2-benzanthracene (IV) by routes essentially the same as those used for the synthesis of the corresponding 6- and 7-chloro analog.[3,4]

The condensation of *p*-fluorophenylmagnesium bromide with 1,2-naphthalic anhydride yielded 1-*p*-fluorobenzoyl-2-naphthoic acid (I) and 2-*p*-fluorobenzoyl-1-naphthoic acid (II) in the approximate ratio of 1 to 2.6. The ratio of product II, resulting from reaction at the unhindered carbonyl group, to that of I, arising from reaction of the hindered carbonyl group is thus similar to that ratio obtained in the reactions of *p*-chlorophenylmagnesium bromide[3] and of *m*-chlorophenylmagnesium bromide[4] with 1,2-naphthalic anhydride, and of phenylmagnesium bromide with 3-methylphthalic anhydride.[5] It appears then that in the

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(1) This work was supported by a grant from the National Institutes of Health.

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

(3) M. S. Newman and M. Orchin, *J. Am. Chem. Soc.*, **61**, 244 (1939).

(4) M. S. Newman and M. Orchin, *J. Am. Chem. Soc.*, **60**, 586 (1938).

(5) M. S. Newman and C. D. McCleary, *J. Am. Chem. Soc.*, **63**, 1542 (1941).