successively with ice water, sodium acetate, sodium bisulfite, sodium bicarbonate solutions and finally with ice-water. The chloroform solution was dried and concentrated under reduced pressure. The sirup crystallized from ether solution; yield 3.96 g., m.p. 95°, $[\alpha]^{25}\text{D}$ +199° ($CHCl_3$, *c* 6).

Anal. Calcd. for $C_{11}H_{15}O_{10}N$: C, 41.13; H, 4.70; N, 4.36. Found: C, 40.90; H, 4.66; N, 4.20.

Reduction of 2,3,4-Tri-*O*-acetyl-β-L-arabinopyranosyl Nitrate.—2,3,4-Tri-*O*-acetyl-β-L-arabinopyranosyl nitrate (10 g.) was treated with sodium borohydride in the same manner as 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl nitrate. The sirup (3.42 g.) was chromatographed as described previously. Zone I, located 105–130 mm. from the top of the column, was eluted with acetone, evaporated to a sirup and crystallized from a cold ether–petroleum ether solution; yield 0.09 g. No further work was done on this material.

Zone II, located 20–60 mm. from the top, was eluted with acetone, evaporated to a sirup and crystallized from a cold ether–petroleum ether solution; yield 0.83 g. After recrystallization, the melting point was 50–52° and $[\alpha]^{25}\text{D}$ +73.6° ($CHCl_3$, *c* 1.7). The melting point of 1,5 anhydro-2,3,4-tri-*O*-acetyl-D-arabinitol is 58°. Its rotation is −74.2° ($CHCl_3$).[23]

In another experiment, 6.36 g. of sirup, obtained from 10 g. of the nitrate, was chromatographed as described previously. Zone I, located 100–200 mm. from the top, yielded 0.5 g. of crystals from ether–petroleum ether solution. Zone II, located 45–100 mm. from the top, yielded 0.5 g. of crystals from ether–petroleum ether solution.

The crystals were combined and rechromatographed, as described previously. Zone I, located 80–100 mm. from the top, yielded 0.8 g. of crystals, m.p. 49–52° after several recrystallizations from ether–petroleum ether (b.p. 30–60°). Zone II, located 30–75 mm. from the top, yielded 0.20 g. of crystals from ether–petroleum ether solution. Its melting point was 74–75°, unchanged on admixture with a known sample of penta-*O*-acetyl-L-arabinitol.

The substance (0.4 g.) melting at 50–52° was deacetylated in the usual manner. The sirup was crystallized from an ethanol–ethyl acetate solution; yield 0.1 g., m.p. 95–96°, $[\alpha]^{25}\text{D}$ +101° (H_2O, *c* 1.8). The accepted values for 1,5-anhydro-D-arabinitol are m.p. 96–97°, $[\alpha]^{25}\text{D}$ −98.6° (H_2O).[23]

Attempted Reduction of Methyl 2,3,4-Tri-*O*-acetyl-α-D-glucopyranoside 6-Nitrate.—An amount of 5 g. of methyl-2,3,4-tri-*O*-acetyl-α-D-glucopyranoside 6-nitrate,[24] 25 ml. of *p*-dioxane, 25 ml. of water and 2 g. of sodium borohydride were combined and stirred at ice-water temperature for 8 hours and at room temperature overnight. Then the mixture was filtered, neutralized with glacial acetic acid and concentrated to dryness under reduced pressure. The residue was acetylated with 30 ml. of pyridine and 20 ml. of acetic anhydride. After 18 hours, the mixture was poured into ice-water. Crystals appeared which were filtered and recrystallized from ethanol; yield 4.51 g., m.p. 112°, unchanged on admixture with the starting material.

Preparation of 1,6-Di-*O*-benzoyl-D-mannitol 2,3,4,5-Tetranitrate.—1,6-Di-*O*-benzoyl-D-mannitol 2,3,4,5-tetranitrate was prepared by adding a cold solution of nitrating mixture consisting of 10 ml. of 99.6% nitric acid in 20 ml. of acetic anhydride[15] to 5 g. of 1,6-di-*O*-benzoyl-D-mannitol[25] dissolved in 10 ml. of chloroform and kept at ice-water temperature. After 10 minutes, the solution was poured into ice-water. Crystals which appeared were filtered and recrystallized from hot ethanol; yield, 2.3 g., m.p. 157°, $[\alpha]^{25}\text{D}$ +29.7° ($CHCl_3$, *c* 0.5).

Anal. Calcd. for $C_{20}H_{18}O_{16}N_4$: C, 42.12; H, 3.21; N, 9.82. Found: C, 42.36; H, 3.21; N, 9.62.

When the compound was reduced catalytically with hydrogen in the presence of palladium-on-charcoal[8] it yielded 1,6-di-*O*-benzoyl-D-mannitol.

Attempted Reduction of 1,6-Di-*O*-benzoyl-D-mannitol 2,3,4,5-Tetranitrate with Sodium Borohydride.—An amount of 5 g. of 1,6-di-*O*-benzoyl-D-mannitol 2,3,4,5-tetranitrate, 45 ml. of *p*-dioxane, 25 ml. of water and 2 g. of sodium borohydride were combined and stirred at ice-water temperature. After 6 hours, the mixture was filtered, neutralized with glacial acetic acid and refiltered. The filtrate was concentrated to dryness under reduced pressure below 40°. The residue was filtered with the aid of water and the residue was crystallized from hot ethanol; yield 3.61 g. (crude, after recrystallization the yield was 2.0 g.), m.p. 157° unchanged on admixture with the starting material.

Acknowledgment.—We wish to thank Dr. N. K. Richtmyer for the sample of polygalitol and Mrs. P. P. Wheeler for the elementary analyses.

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(23) H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **69**, 1672 (1947).

(24) E. K. Gladding and C. B. Purves, *ibid.*, **66**, 153 (1944).

(25) P. Brigl and H. Grüner, *Ber.*, **65**, 641 (1932).

INDIAN HEAD, MD.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Nitrocoumarans

BY CHARLES D. HURD AND ROSTYSLAW DOWBENKO[1]

RECEIVED APRIL 7, 1958

A number of alkyl substituted coumarans have been nitrated to give dinitrocoumarans. A phenyl substituted coumaran yielded a trinitro compound. Degradation of the nitration product of 2-methylcoumaran afforded evidence that the nitro groups were in the 5,7-positions.

In connection with other work[2] done in these laboratories a need arose for crystalline, easily accessible derivatives of alkyl and aryl substituted coumarans (2,3-dihydrobenzofurans) suitable for their characterization. Nitro derivatives seemed appropriate for this purpose. Curiously enough the literature has very little to say about nitration of coumarans or rules of orientation in this reaction.

Nitrocoumarans as a class of compound are virtually unknown. The only examples of nitration of coumarans are those reported by Arnold and McCool[3] and by Chatelus.[4] Arnold and McCool nitrated 5-acetamido-2-methylcoumaran expecting to obtain 5-acetamido-2-methyl-6-nitrocoumaran, but they obtained the 4-nitro derivative instead; on nitration of coumaran itself Chatelus obtained a dinitrocoumaran. The same author also nitrated chroman to obtain a dinitrochroman. He considered 6,8-dinitrochroman and 5,7-dinitrochroman as possible structures and preferred the former because of analogy to the nitration of tetralin. Assignment of structure to the nitration product of coumaran as 5,7-dinitrocoumaran then was made

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(1) Weyerhaeuser Timber Foundation Fellow, 1955–1957.

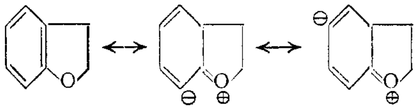
(2) To be published.

(3) R. T. Arnold and J. C. McCool, THIS JOURNAL, **64**, 1315 (1942).

(4) G. Chatelus, *Ann. chim.*, **4**, 505 (1949).

on the basis of similarity of coumaran to chroman. No real evidence was given supporting the assigned structure, however.

Two other arguments support the assignment of 5,7-orientation for the dinitrocoumaran. One is the fact that the resonance hybrid of coumaran shows a high electron density at positions 5 and 7.



The other is an observation of Marschalk[5] that coumaran is acylated at position 5. In the present work a detailed investigation of nitration of coumarans was carried out, with emphasis on the proof of structure.

Nitration of five coumarans that were substituted in the heterocyclic ring by a cold mixture of nitric and sulfuric acids resulted in formation of yellow to orange solid derivatives and pointed to the generality of the reaction. The compounds were highly crystalline and could be purified easily. Analysis showed them to be dinitro compounds, except for the 3-phenylcoumaran derivative which was a trinitro compound (*cf.* Table I). The infrared spectra lacked hydroxyl absorption, indicating that the dihydrofuran ring was intact and that the compounds were therefore dinitrocoumarans, the latter result being somewhat surprising in view of the relatively mild condition of nitration.

TABLE I

NITRO DERIVATIVES OF COUMARANS

Substd. coumaran	Product[a] Crude yield, g.	M.p., °C.	Formula	Analyses[e] Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
2-Methyl	2.0	96–97.5	$C_9H_8N_2O_5$	48.22	48.40	3.60	3.66	12.50	13.11
2,2-Dimethyl	1.9	149–150	$C_{10}H_{10}N_2O_5$	50.42	49.82	4.23	4.09	11.76	12.28
2,3-Dimethyl	0.3[b]	115–115.5	$C_{10}H_{10}N_2O_5$	50.42	50.24	4.23	4.25	11.76	12.84
2,2,3-Trimethyl	0.4[c]	96–97	$C_{11}H_{12}N_2O_5$	52.38	52.30	4.80	4.79	11.11	11.54
3-Phenyl	1.2[d]	194	$C_{14}H_9N_3O_7$	50.76	51.05	2.74	2.67	12.69	12.93

[a] From 1.5-g. samples. [b] The compound precipitated as an oil which crystallized on cooling to −30°. [c] Crude nitration product was an oil which was extracted with hot ethanol and the extract cooled to give a solid. [d] One-gram sample of the coumaran was nitrated at 15–20° for 10 min., since under the conditions of nitration of other coumarans oils were obtained; the compound was recrystallized from ethanol containing a small amount of acetone. [e] Analyses were performed by Miss Hilda Beck.

The determination of structure was limited at the outset to the derivative of the simplest representative, namely, 2-methylcoumaran, and was at first sought through its rational synthesis from compounds of known structure. The simplest route to 5,7-dinitro-2-methylcoumaran appeared to be through nitration of 2-allylphenol and ring closure of the resulting 2-allyl-4,6-dinitrophenol, the assumption being made that 2-allylphenol would nitrate in the required positions. Direct nitration of 2-allylphenol was unsuccessful. Carrying out the nitration in a mixture of concentrated nitric and sulfuric acids or of nitric and acetic acids under a variety of conditions led to intractable tars from which no definite compounds could be isolated. Similarly, the procedure of Baroni and Kleinau,[6] in which a substituted phenol is nitrated by a mixture of nitric acid and chloroform, led to equally unsatisfactory results.

The synthesis was therefore abandoned and the proof of structure was approached by degradation of the dinitro-2-methylcoumaran. This was accomplished by dehydrogenation of the compound and oxidation of the resulting dinitrobenzofuran to the known dinitrosalicylic acid. Dehydrogenation of dinitro-2-methylcoumaran was effected by use of N-bromosuccinimide. Dehydrobromination of the resulting bromo compound was accomplished by refluxing it with dimethylaniline.

Although the simple coumarans substituted only in the dihydrofuran ring react readily with N-bromosuccinimide to give satisfactory yields of bromocoumarans or of their dehydrobromination products,[7] it was found that dinitro-2-methylcoumaran reacted very sluggishly with this reagent. While the use of benzoyl peroxide as catalyst in carbon tetrachloride solution yielded a product of inferior quality, its use in acetone solution led to complete consumption of N-bromosuccinimide without reacting on the compound. Instead there was formed a strongly lachrymatory oil, probably bromoacetone. This result is in agreement with an example of sluggish bromination of *p*-nitrotoluene reported by Buu-Hoi.[8] Apparently the nitro groups in the ring deactivate the benzylic position toward reaction with N-bromosuccinimide. Satisfactory reaction conditions were found in the use of refluxing benzene as a solvent and by employing longer reaction times. The isolation of the resulting bromo compound was not attempted because of signs of dehydrobromination at the end of the reaction. Refluxing the bromination product with a solution of dimethylaniline in benzene gave a slightly yellowish crystalline compound, apparently the 5,7-dinitro-2-methylbenzofuran of Hale,[9] who condensed acetonylacetone with nitromalonic aldehyde, cyclized the resulting product, and nitrated the methylnitrobenzofuran.

Oxidation of benzofurans with potassium permanganate or with chromic acid was first reported by Stoermer and Richter[10] who demonstrated either non-reaction or complete destruction of the

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(5) C. Marschalk, *Ber.*, **43**, 1695 (1910); *cf.* also S. Kostanecki, V. Lampe and C. Marschalk, *ibid.*, **40**, 3665 (1907).

(6) E. Baroni and W. Kleinau, *Monatsh.*, **68**, 251 (1936).

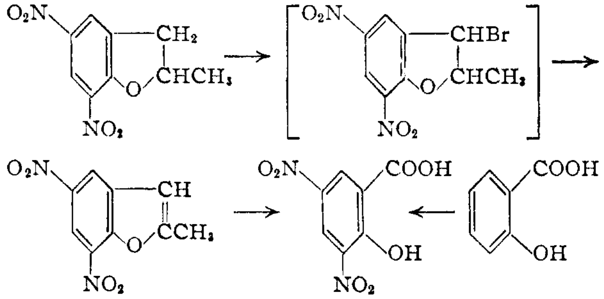
(7) Unpublished results; for use of N-bromosuccinimide in bromination of substituted coumarans *cf.* also T. A. Geissman, T. G. Halsall and E. Hinreiner, THIS JOURNAL, **72**, 4326 (1950), and M. F. Grundon and N. J. McCorkindale, *J. Chem. Soc.*, 2177 (1957).

(8) Ng. Ph. Buu-Hoi, *Ann.*, **556**, 1 (1944).

(9) W. J. Hale, *Ber.*, **45**, 1596 (1912).

(10) R. Stoermer and O. Richter, *ibid.*, **30**, 2094 (1897).

benzofuran molecule. On the other hand, Wacek and Zeisler[11] have shown that oxidation of benzofurans with chromic acid in acetic acid caused scission at positions 2,3. In our hands this reagent was less useful. In contrast, potassium permanganate in acetone in the presence of a small amount of water gave with dinitro-2-methylcoumaran an acidic compound as a sole product. This was indistinguishable from authentic 3,5-dinitro-2-hydroxybenzoic acid,[12] prepared by nitration of salicylic acid, in color, melting point and mixed melting point, ferric chloride test and infrared spectra. That the hydroxy acid itself was obtained instead of the acetoxy acid is not surprising in view of the alkalinity of the reaction medium.



From the fact that the dinitro-2-methylbenzofuran yields 3,5-dinitro-2-hydroxybenzoic acid on oxidation it must be concluded that the structure of the nitration product of 2-methylcoumaran is that of 5,7-dinitro-2-methylcoumaran. By analogy, therefore, the nitro groups in other dinitrocoumarans are attached to carbon atoms 5 and 7 in the coumaran ring. For 3-phenylcoumaran it is evident that the third nitro group is in the benzene ring and it is assumed that the structure of the nitration product is 5,7-dinitro-3-(*p*-nitrophenyl)-coumaran. In 3-phenylcoumaran the steric effect in the *o*-position of the 3-phenyl group would be of the same magnitude as, if not greater than, that in isopropylbenzene in whose nitration the ratio of *o*- to *p*-isomer is 14:86.[13] Therefore it is reasonable that the nitration in 3-phenylcoumaran would occur predominantly in the *p*-position of the 3-phenyl group.

Experimental[14]

The starting materials were prepared by methods described in the literature. 2-Methylcoumaran, b.p. 90° at 22 mm., n^{25}D 1.5274, was obtained by cyclization of 2-allylphenol.[15] 2,2-Dimethylcoumaran was prepared in a 68% yield from 2-methallylphenol[16] by an adaptation of method of ref. 15, b.p. 80.5° at 13.5 mm., n^{25}D 1.5190.

Dimer of 2-Methallylphenol; a Cryptophenol.—A by-product was separated in low yield in the last preparation. It was obtained by adding benzene–hexane to the residue after distillation of the 2,2-dimethylcoumaran, and it separated as a white powder; yield, about 10 g. from an original 140 g. of 2-methallylphenol. It melted at 137–138°, showed a band at 3.02 μ in the infrared, was insoluble in dilute sodium hydroxide although it was weakly acidic to a Davidson indicator[17] and showed a positive indophenol test[18]; ultraviolet spectrum (in methanol) (assuming mol. wt. of 292): shoulder at 295 mμ (ε 2820), λ_{max} 285 mμ (ϵ_{max} 5200), shoulder at 280 mμ (ε 5050), λ_{max} 237 mμ (ϵ_{max} 9500). The compound is probably a cryptophenol composed from two molecules of 2-methallylphenol such as 2-[2,2-dimethyl-3-(2-methyl-2-coumaranyl)]-propylphenol.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.81; H, 8.03.

1-Naphthylcarbamate of the cryptophenol had a m.p. of 114–115° (from hexane).

Anal. Calcd. for $C_{31}H_{31}NO_3$: C, 79.96; H, 6.71; N, 3.01. Found: C, 80.00; H, 6.54; N, 3.50.

2,3-Dimethylcoumaran, b.p. 76.5–78° at 6 mm., n^{25}D 1.5205, was prepared by a method of Claisen and Tietze.[19] 2,2,3-Trimethylcoumaran, b.p. 82–84° at 6.5 mm., was prepared by the method of Lauer and Moe.[20] For the preparation of 3-phenylcoumaran two methods were used. In one of these 2-chloro-3-phenylbenzofuran was reduced with sodium and ethanol[21] while in the other it was prepared from *o*-(1-phenyl-2-hydroxyethyl)-phenol by the method of Guss.[22] Both samples had b.p. 159–160° at 10 mm., m.p. 35–36°.

General Procedure of Nitration of Coumarans.—To a cooled (5°) mixture of 10 ml. each of concentrated nitric and sulfuric acids there was added dropwise 1.5 g. of the coumaran with cooling and stirring of the mixture. The resulting dark-cooled mixture was allowed to stand for 5 min. at 5° with occasional stirring and then it was poured onto 100 g. of ice. When the crude reaction product was a solid it was filtered off, washed well with cold water and recrystallized from ethanol. If it was an oil the supernatant aqueous layer was decanted and the oil purified by a method summarized in Table I.

Reaction of 5,7-Dinitro-2-methylcoumaran with N-Bromosuccinimide: 5,7-Dinitro-2-methylbenzofuran.—A mixture of 4.4 g. (0.020 mole) of 5,7-dinitro-2-methylcoumaran, 3.6 g. (0.020 mole) of N-bromosuccinimide, 0.05 g. of benzoyl peroxide and 200 ml. of benzene was refluxed for 26 hr., whereupon the solution gave only a faint test for free N-bromosuccinimide. The solution was cooled and poured into water (evolution of hydrogen bromide). The benzene layer was separated, washed well with water, dried and evaporated to a volume of 150 ml. It was then treated with 60 ml. of dimethylaniline and the resulting solution was refluxed for 18 hr. The reaction mixture was then cooled, washed with dilute solution of hydrochloric acid, sodium bicarbonate, and the benzene layer was dried. Evaporation of the benzene solution gave 3.9 g. of a tan solid. Chromatography on alumina and recrystallization from an acetone–methanol mixture gave 2.0 g. (50% of the theory) of light tan needles melting at 158–161°. Several recrystallizations from the same solvent gave the analytical sample as pale-yellow, small needles melting at 163–164° and having no halogen by the Beilstein test. The reported[9] m.p. of 5,7-dinitro-2-methylbenzofuran is 165°.

Anal. Calcd. for $C_9H_6N_2O_5$: C, 48.66; H, 2.72; N, 12.61. Found: C, 48.04; H, 3.08; N, 13.01.

Oxidation of 5,7-Dinitro-2-methylbenzofuran.—To a solution of 0.5 g. of 5,7-dinitro-2-methylbenzofuran in 100 ml. of acetone and 2 ml. of water there was added with mechanical stirring 1.4 g. of potassium permanganate in small portions. An additional 0.5 g. was added after 12 hr. After 2 days of stirring at room temperature the mixture was filtered. The filtrate was evaporated. The solid (MnO_2) was washed with sodium bicarbonate solution which was acidified, extracted with a mixture of ethyl acetate and ether and the resulting extract was evaporated. This residue was combined with that obtained from evaporation of the acetone solution. Several recrystallizations from a mixture of benzene and hexane containing a small amount of acetone gave 0.15 g. of yellowish needles melting at 173–

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(11) A. Wacek and F. Zeisler, *Monatsh.*, **83**, 5 (1952).

(12) R. Meldola, H. S. Foster and R. Brightman, *J. Chem. Soc.*, **111**, 533 (1917).

(13) G. Vavon and A. Collier, *Bull. soc. chim.*, [4] **41**, 357 (1927).

(14) The melting points are uncorrected.

(15) J. Entel, C. H. Ruof and H. C. Howard, THIS JOURNAL, **73**, 2365 (1951).

(16) O. Schales, *Ber.*, **70**, 116 (1937).

(17) D. Davidson, *J. Chem. Education*, **19**, 221 (1942).

(18) F. Feigl, "Spot Tests in Organic Analysis," Elsevier Publishing Co., Houston, Texas, 1956, p. 182.

(19) L. Claisen and E. Tietze, *Ber.*, **59**, 2351 (1926).

(20) W. M. Lauer and O. Moe, THIS JOURNAL, **65**, 291 (1943).

(21) R. Stoermer, *Ber.*, **36**, 3979 (1903).

(22) C. O. Guss, THIS JOURNAL, **73**, 608 (1951).

174° and giving a brown-red color with ferric chloride. The melting point of this compound was not depressed by admixture of authentic 3,5-dinitro-2-hydroxybenzoic acid.[12] The infrared spectra of the two compounds were indistinguishable.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY]

Synthesis of Hydrochrysenes. I. 1-Methoxy-10-keto-3,4,5,6,7,8,10,11,12,12a-decahydrochrysene from 1,7-Dimethoxynaphthalene

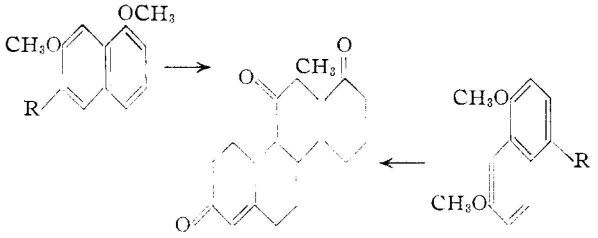
BY RODERICK A. BARNES AND WALTER M. BUSH[1]

RECEIVED APRIL 3, 1958

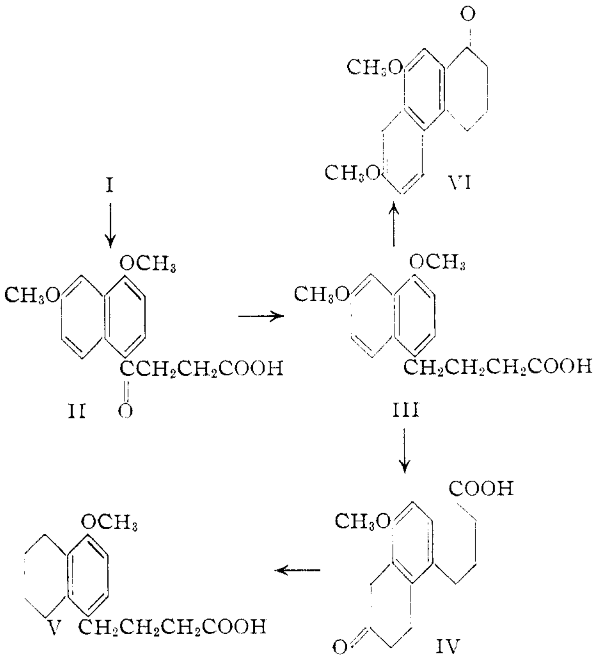
One of two possible synthetic routes from 1,7-dimethoxynaphthalene (I) toward 19-norsteroids with an oxygen function at position 11 has been investigated. The Friedel–Crafts reaction with succinic anhydride was observed to take place at the 4-position of I; further transformations of this reaction product led ultimately to 1-methoxy-10-keto-3,4,5,6,7,8,10,11,12,12a-decahydrochrysene.

Various modifications of a normal steroid structure such as addition of a 9-halogen atom or a 1,2-double bond and expansion of the D ring, have produced substances with enhanced biological activity. However, the structural modification in which the angular methyl group at position 19 is lacking cannot be accomplished in any simple way starting from the corresponding natural steroid. The reduction of estrone and related substances with an aromatic A ring, and subsequent transformations of the reduced product has been the most useful procedure for the preparation of 19-norsteroids.[2,3]

The experiments reported here were carried out to explore a possible synthetic route to the 19-norsteroids having an oxygen function at position 11. 1,7-Dimethoxynaphthalene (I) was chosen as the starting material, because, depending on the position which an entering substituent R might take, compound I could provide either rings C and D or B and C with the desired oxygen function properly located for either synthetic path.



The first substitution attempted with I was the Friedel–Crafts reaction with succinic anhydride. It seemed most likely that the bulky entering group, the succinic anhydride–aluminum chloride complex solvated with nitrobenzene, would react largely at the 4-position. The reaction product II was in fact mainly a single isomer and the small amount of acidic by-product was removed readily by recrystallization of II as the methyl ester. The reduction of the keto group of II by the Wolff–Kishner method produced considerable amounts of tarry products and a maximum of 25% of III; however, catalytic hydrogenation and hydrogenolysis using palladium-on-charcoal was nearly quantitative.



From III the ultimate synthetic goal could be achieved either by cyclization to VI or reduction to IV. Attempts to reduce III with sodium and alcohol failed, perhaps because of insolubility of the sodium salt. Reduction with lithium in liquid ammonia produced only 10% of IV. Although this route did not appear promising for the synthesis, the small amount of IV obtained provided a structure proof for II; Wolff–Kishner reduction of IV yielded acid V which was identical with a sample prepared by the method of Bachmann and Ness.[4] An attempt to prove the structure of II directly by oxidation was unsuccessful; the crystalline methyl ester of 4-methoxy-1,3,5-benzenetricarboxylic acid could not be isolated when the crude acidic oxidation product was treated with diazomethane.

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(1) Abstracted from a portion of the thesis presented by W. M. Bush to the Graduate Faculty for the Ph. D. degree, May, 1955.

(2) A. J. Birch, *J. Chem. Soc.*, 367 (1950); B. J. Magerlein and J. A. Hogg, THIS JOURNAL, **79**, 1508 (1957); F. B. Colton, L. N. Nysted, B. Riegel and A. L. Raymond, *ibid.*, **79**, 1123 (1957); A. Bowers, H. J. Ringold and R. I. Dorfman, *ibid.*, **79**, 4556 (1957).

(3) For an approach to the synthesis of 19-norsteroids from a derivative of strophanthidin see G. W. Barber and M. Ehrenstein, *J. Org. Chem.*, **19**, 365 (1954).

(4) W. Bachmann and A. B. Ness, THIS JOURNAL, **64**, 536 (1942).