Anal. Calcd. for $C_{12}H_{27}Sb$: Sb, 41.6. Found: Sb, 41.4.

Attempted preparation of the distibine using di-*n*-butylantimonylithium also resulted in 22% tri-*n*-butylstibine. In both reactions an antimony mirror was noted in the distilling flask. The distillation residue was a black solid which contained butyl groups (infrared) and which also gave a qualitative test for antimony. Upon standing in the air, this black solid turned white. The similarities in physical properties between polymeric methylstibine (see ref. 4, p. 5) and this material strongly suggest that it is polymeric *n*-butylstibine.

An Abnormal Fluorination with Sulfur Tetrafluoride

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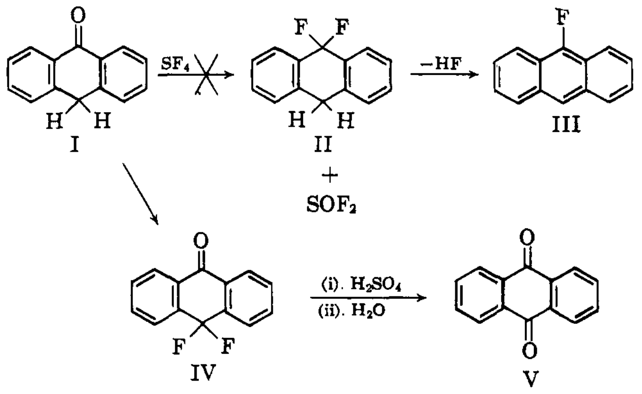
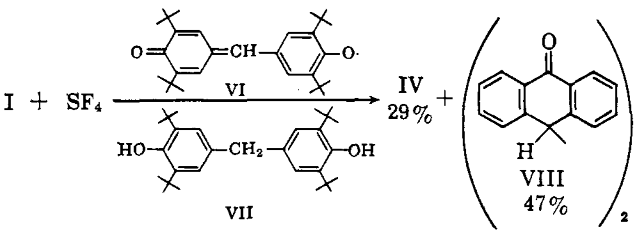
The recent discovery and exploitation of the general reaction of sulfur tetrafluoride with the carbonyl function to produce *gem*-difluorides[1] suggested a feasible synthesis of 9-fluoroanthracene, which was required for another investigation. Sulfur tetrafluoride would be expected to convert anthrone (I) to 9,9-difluoro-9,10-dihydroanthracene (II), which should easily lose the elements of hydrofluoric acid under conditions of either acid or base catalysis to give 9-fluoroanthracene (III). The product of the reaction was, however, neither II nor III, but 10,10-difluoroanthrone (IV). Compound IV was identified by its carbon–hydrogen analysis, by the presence in the infrared spectrum of an absorption at 1677 cm.$^{-1}$ characteristic of aromatic ketones,[2] and by the absence of n.m.r. signals characteristic of diarylmethylene protons.[3] The position of the fluorine substituents was confirmed by the hydrolysis of IV to anthraquinone (V) under acid conditions, a reaction typical of *gem*-difluorides which can form conjugated ketones by hydrolysis.[4] The best yield (85%) of IV was obtained when methylene chloride was employed as a solvent. In the absence of solvent, the yield of IV was 48%.



Although sulfur tetrafluoride is an oxidizing agent under some circumstances,[5] it has not been observed before to attack the carbon–hydrogen bond under mild conditions. Such attack suggests a free-radical chain mechanism analogous to halogenations by molecular chlorine and bromine. To test this hypothesis, the fluorination was run in the presence of small amounts of the radical scavenger, 2,6-di-*t*-butyl-α-(3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy radical (VI)[6] and the antioxidant, 4,4′-dihydroxy-3,5,3′,5′-tetra-*t*-butyldiphenylmethane (VII). It was expected that methylenic fluorination would be inhibited and recovery of starting material would be possible. If this had been the case, the reaction with sulfur tetrafluoride would have been repeated in the presence of VI and VII at increased temperatures in the hope that the normal carbonyl fluorination would occur. The result, however, of the addition of VI and VII to the reaction mixture was to cause the formation of 10,10′-bianthrone (VIII) in 47% yield. The yield of IV was reduced to 29%. Compound I was recovered quantitatively from a control experiment in which an ethylene chloride solution of I, containing small amounts of VI and VII, was heated at the temperatures used in the inhibited fluorination of I.



The fact that VI and VII inhibit to some extent the formation of IV supports the proposed radical chain mechanism. To account for the formation of VIII, an ionic Friedel–Crafts reaction of fluoroanthrone with the phenolic tautomer of anthrone may be suggested, but the matter has been investigated no further in this work.

Experimental[7]

10,10-Difluoroanthrone (IV).—Anthrone, 19.4 g. (0.100 mole), was purged with nitrogen under vacuum in a 183-ml. stainless steel reaction bomb, 24.5 g. (0.226 mole) of sulfur tetrafluoride (E. I. du Pont de Nemours and Co., Organic Chemicals Dept., technical) and 5.5 g. (0.28 mole) of anhydrous hydrofluoric acid were distilled into the bomb, and 75 ml. of cold methylene chloride was injected through the bomb port with a hypodermic syringe. After 16.3 hr. at 69°, 34.2 g. of dark solid was washed out of the bomb with water. Sublimation at 80° and 0.2 mm. pressure of 10.0 g. of the dark solid gave 5.72 g. (85% yield) of 10,10-difluoroanthrone (IV), m.p. 130–149° dec., identified by comparison of its infrared spectrum with that of an analytical sample. An analytical sample, m.p. 141–142°, was prepared by several recrystallizations from cyclohexane followed by sublimation.

Anal. Calcd. for $C_{14}H_8F_2O$: C, 73.04; H, 3.50. Found: C, 72.97; H, 3.57.

The carbonyl absorption of IV occurred at 1677 cm.$^{-1}$ in the infrared (KBr disk). The n.m.r. spectrum had a multiplet cen-

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[2] L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 137.

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[6] (a) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962); (b) M. S Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

[7] Melting points are uncorrected. We thank P. McMahon, D. Johnson, and associates for the infrared spectra; O. Norton, D. Johnson, and associates for the n.m.r. spectra; and J. Nemeth and associates for the microanalyses. Details may be found in the Ph.D. thesis of R. Searle, University of Illinois, 1963.

tered at τ 1.7 (area 1) and another multiplet centered at τ 2.2 (area 3.2). A small amount of IV was dissolved in concentrated sulfuric acid. Water was added and the resulting precipitate was identified as anthraquinone by comparison of its infrared spectrum with that of an authentic sample.

In another experiment, 19.4 g. (0.100 mole) of anthrone, 39.6 g. (0.366 mole) of sulfur tetrafluoride, and a small amount of anhydrous hydrofluoric acid were heated together in a 185-ml. stainless steel bomb at 75° for 11 hr. and at 98° for 50 min. The crude product was extracted with hexane to give 14.6 g. of dark solid. Sublimation of 3.00 g. of the solid with 76% recovery gave a 48% yield of 10,10-difluoroanthrone, m.p. 100–143°, identified by comparison of its infrared spectrum with that of an analytical sample.

2,6-Di-*t*-butyl-α-(3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy radical (VI) was prepared by the method of Kharasch,[6b] oxidation of 4,4′-dihydroxy-3,5,3′,5′-tetra-*t*-butyldiphenylmethane (VII, Ethyl Corporation, antioxidant 702) with potassium ferricyanide, and was used without purification.

Reaction of Anthrone with Sulfur Tetrafluoride in the Presence of Radical Scavengers.—To 9.00 g. (0.0464 mole) of anthrone, purged with nitrogen in a 183-ml. stainless steel reaction bomb, was added 25.2 g. (0.234 mole) of sulfur tetrafluoride, 0.42 g. (0.0010 mole) of VI, 0.31 g. (0.00073 mole) of VII, 70 ml. of methylene chloride, and 0.5 ml. (0.03 mole) of water. The bomb was heated at 70° for 40 min., allowed to remain at room temperature for 23 hr., and then heated at 70° for 19 hr. The bomb contents were extracted with methylene chloride, and the extract was washed with sodium carbonate solution and water, dried, and evaporated to leave 10.3 g. of brown solid. 10,10-Difluoroanthrone (IV), identified by comparison of its infrared spectrum with that of an authentic sample, was obtained with 25% recovery (29% yield) from 1.10 g. of the crude product by sublimation. Of the crude product, 2.00 g. was washed with 3:1 benzene–hexane to leave 0.825 g. of 10,10′-bianthrone (VIII, 47% recovery, 47% yield), identified by comparison of its infrared spectrum with that of an authentic sample. Recrystallization of 0.749 g. of crude VIII from benzene without change in infrared spectrum gave 0.459 g. (29% yield) of a sample, m.p. 263–271° dec., lit.[8] m.p. *ca.* 270–275° dec.

Control for the Reaction of Anthrone with Sulfur Tetrafluoride in the Presence of Radical Scavengers.—A solution of 1.00 g. (0.00515 mole) of anthrone, 0.050 g. (0.00012 mole) of VI, and 0.040 g. (0.000094 mole) of VII in 9 ml. of ethylene chloride was heated at 70–75° for 17.2 hr. The solvent was evaporated to leave 0.934 g. (93%) of anthrone, identified by comparison of its infrared spectrum with that of an authentic sample. Recrystallization from benzene–hexane produced a sample, 0.569 g. (57%), with m.p. 151–167° (no blackening up to 300°), whose infrared spectrum was unchanged.

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund. We are also indebted to the National Science Foundation for partial support.

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d-Betuligenol from *Rhododendron maximum* L.

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d-Betuligenol is *d*-4-(*p*-hydroxyphenyl)-2-butanol.[1] The levoratatory enantiomorph, *l*-betuligenol, was first isolated from the bark of the white birch (*Betula alba*) as the β-*d*-glucopyranoside called *betuloside*.[2] Rhododendrin, a glycoside from *Rhododendron fauriae* leaves,[3] and its aglycone, rhododendrol, were subsequently shown to be identical with betuloside and *l*-betuligenol, respectively.[4] It has been unequivocally established that the carbohydrate moiety is attached *via* the aliphatic hydroxyl group.[5] Sosa[1] apparently assumed that the betuligenol he found co-occurring with the glucoside in *Betula alba* was the *l*-form since he reported no specific rotation for it. The isolation of *d*-betuligenol from *R. maximum* in this laboratory was incidental to another investigation, but its occurrence in a species so closely related to one from which the levorotatory isomer had been previously isolated as the glucoside is considered of sufficient interest to warrant this report. The identity of the *d*-betuligenol is established by the data in Table I. Its isolation did not involve conditions which would have hydrolyzed a glucoside.

TABLE I

PHYSICAL PROPERTIES OF BETULIGENOLS

	From betuloside[a]	From *R. maximum*
M.p., °C.	81.5	81–83
[α]D in ethanol	−18.5° (*c* 3.88)	+17.1° (*c* 2.0)
M.p. of monobenzoate, °C.	68–69	65–66
[α]D of monobenzoate in ethanol	−12.8° (*c* 1.69)	+14.0° (*c* 1.0)

[a] By either acidic or enzymatic hydrolysis. The data are from ref. 1.

Experimental[6]

Isolation of *d*-Betuligenol.—Fresh *Rhododendron maximum* leaves and twigs (730 lb.) collected in North Carolina in February were ground and extracted by the procedure of Wood, *et al.*[7]

The final chloroform extract was concentrated to a viscous dark green syrup. This was dissolved in 2 l. of methanol–water (9:1) and washed with 2 l. of *n*-hexane. Addition of 4 l. of chloroform to the aqueous methanol layer caused separation of a small aqueous layer, which was discarded. After the solvent was stripped from the methanol–chloroform solution, the 180 g. of dark sirupy residue was dissolved in 500 ml. of ethyl acetate and chromatographed on a column made from 1 kg. of Davison No. 950 silica gel (60–200 mesh) and eluted with ethyl acetate. The first 2.5 l. of eluate collected was concentrated to give 19.1 g. of residue, which was rechromatographed on a similar column of 400 g. of the adsorbent. The first 800 ml. of ethyl acetate eluate gave 12.44 g. of oily crystalline residue. Recrystallization of this from chloroform gave 8.74 g. of *d*-betuligenol having the properties given in Table I.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.07; H, 8.36.

The infrared spectrum (chloroform, Beckman IR 4) contained a sharp hydroxyl band at 2.75 and a broader one near 3.00 μ. An aromatic doublet appeared at 6.20 and 6.25, and a sharp intense band was present at 6.58 μ. The ultraviolet spectrum (ethanol) contained peaks at 224 mμ (ϵ 7960) and 279 (1910) as well as a shoulder near 284. The compound gave a positive iodoform test.

***d*-Betuligenol Benzoate.**—*d*-Betuligenol (500 mg.) was dissolved in 10 ml. of 10% sodium hydroxide and 1 ml. of benzoyl chloride was added. The reaction mixture was shaken vigorously for 10 min. The white solid which precipitated was removed by filtration, washed thoroughly with water, dried, and recrystallized from cyclohexane. The yield of monobenzoate with the properties recorded in Table I was 410 mg.

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