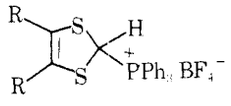
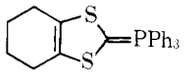
5, 6, or 7, with the formation of an intermediate of the type 8; addition of triethylamine brought about the elimination of triphenylphosphine and the formation of the monobenzotetrathiofulvalenes **9**, **10**, and **11**, respectively. Symmetrical TTFs corresponding to the individual 1,3-dithiole units were not detected, and the products were readily purified.

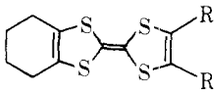
The new procedure is not limited to the synthesis of monobenzotetrathiafulvalene derivatives. Thus, the tetramethylene-1,3-dithiolium fluorophosphate (**7**) added triphenylphosphine to give the corresponding phosphonium salt **12a**; reaction of the latter with *n*-butyllithium at −78 °C and reaction of the intermediate phosphorane **13** with 1,3-di-



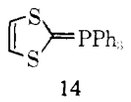
12a, R = $-(CH_2)_4-$
b, R = H



13



15, R = H
16, R = Me



14

thiolium fluoborate (**5**) or 4,5-dimethyl-1,3-dithiolium fluoborate (**6**)[4b] gave, after triethylamine treatment, the mixed TTF derivatives **15** and **16**, respectively. Finally, the same derivative **15** was prepared in the reverse manner from 4,5-tetramethylene-1,3-dithiolium ion (**7**) and the phosphorane **14** derived from the unsubstituted 1,3-dithiolium phosphonium salt **12b**.

In a typical procedure, phosphonium salt **2** (360 mg, 0.72 mmol) was suspended in dry THF (25 mL) at −78 °C, and a solution of *n*-butyllithium (0.72 mmol) in hexane was added, After 2 h at −78 °C, fluoborate **5** (137 mg, 0.72 mmol) was added. After the red solution lightened to yellow, excess triethylamine was introduced and the mixture was stirred for 3 h at −78 °C, and then allowed to come to room temperature. Removal of solvent, followed by silica chromatography (hexane eluant), afforded **9** in 40% yield.

The extension of this method to the synthesis of unsymmetrical selenathiafulvalenes is under investigation in our laboratory.

The physical measurements and preparation of organic conductors based on these donors will be reported separately.

Acknowledgment. This work was supported by the National Science Foundation MRL program under Grant No. DMR 76-00678.

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Received September 27, 1977

A New 7,12-Dimethylbenz[*a*]anthracene Synthesis: 9-Methoxy- and 10-Methoxy-7,12-dimethylbenz[*a*]anthracene

Summary: Hydrolysis of the reaction product of 2-(2-lithio-4-methoxyphenyl)-4,4-dimethyl-2-oxazoline with methyl 2-naphthyl ketone affords 5-methoxy-3-methyl-3-(2-naphthyl)phthalide which is converted by three known steps to 9-methoxy-7,12-dimethylbenz[*a*]anthracene. Similarly, methyl 1-naphthyl ketone affords 10-methoxy-7,12-dimethylbenz[*a*]anthracene.

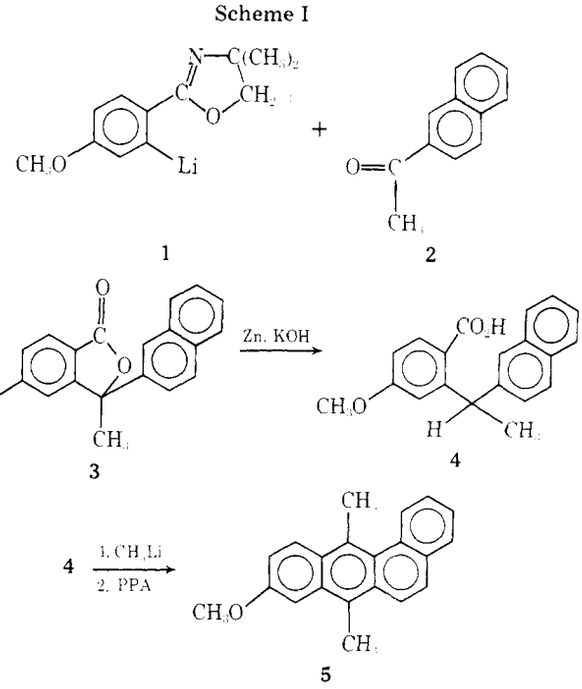
Substituted 7,12-dimethylbenz[*a*]anthracenes are of importance in studies on carcinogenesis. Present synthetic routes involve fundamentally the following condensation reactions: a substituted phenyl organometallic reagent with 1,2-naphthalic anhydride; a phenyl organometallic reagent with a substituted 1,2-naphthalic anhydride; a substituted naphthyl organometallic reagent with phthalic anhydride; or a naphthyl organometallic reagent with a substituted phthalic anhydride. Friedel–Crafts condensations of analogous appropriate compounds have also been used. In three of the above cases difficultly separable mixtures of keto acids of the *o*-benzoylbenzoic acid type are obtained. The two carbons in the anhydride function become the meso carbons in the anthracene moiety of the final compound.

We describe herein a new synthesis in which the two carbons which become the meso carbons are initially present in different reactants. The advantages of the new route are the following: no difficultly separable mixtures of isomeric compounds are formed; fewer steps are required to reach the final benz[*a*]anthracenes; and the reaction components are easier to obtain than the unsymmetrical anhydrides.

The new synthesis is outlined in Scheme I.

The key reagent is 2-(2-lithio-4-methoxyphenyl)-4,4-dimethyl-2-oxazoline (**1**) prepared by lithiation[3] of 2-(4-methoxyphenyl)-4,4-dimethyl-2-oxazoline.[4] In a typical reaction a solution of 0.1 mol of **1**, prepared as described,[3] in 300 mL of dry ether was added dropwise during 5 min to a solution of 0.1 mol of **2** in 100 mL of ether at 0 °C. After 18 h at room temperature and 1 h at reflux, the products of the reaction, isolated in a conventional way, were heated at reflux for 18 h with 8% aqueous ethanolic sulfuric acid[4] to yield 62% of 5-

Scheme I



methoxy-3-methyl-3-(2-naphthyl)phthalide (**3**) as a colorless oil, IR absorption at 5.7 μm (five-membered lactone carbonyl). Zinc dust in alkali reduction[5] of **3** readily afforded 4-methoxy-2-(α-2-naphthylethyl)benzoic acid* (**4**), mp 176.5–177.5 °C, which by reaction[5] with CH_3Li was converted into the corresponding methyl ketone, in turn cyclized to 9-methoxy-7,12-dimethylbenz[*a*]anthracene* (**5**) mp 204.5–205.5 °C (33% overall yield from **1**), by treating with polyphosphoric acid at room temperature for 3 h.

In a similar sequence starting with 1 and methyl 1-naphthyl ketone there was obtained 10-methoxy-7,12-dimethylbenz-[*a*]anthracene,[6] mp 135.0–136.0 °C, in 27% overall yield from **1**. In this case, the PPA cyclization required 40 min at 95 °C.

The application of this new synthesis to the synthesis of other methoxy- and fluoro-substituted benz[*a*]anthracenes is under study.

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(7) All new compounds marked with an asterisk gave satisfactory elemental analyses and NMR spectra.

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N-Bromosuccinimide Oxidation of Silyl Ethers[1]

Summary: *N*-Bromosuccinimide converts the trimethylsilyl (Me_3Si) ethers of primary alcohols into esters and the Me_3Si ethers of secondary alcohols into ketones. An aldehyde and a Me_3Si ether give a "mixed" ester in the presence of NBS.

Sir: Oxidation of alcohols is a fundamental transformation of organic chemistry which is attracting much current interest.[2] Since the hydrogens on a carbon atom attached to oxygen are labile in the free radical sense,[3] we reasoned that conversion of an alcohol into an unsymmetrical ether and treatment with *N*-bromosuccinimide (NBS) would effect the desired oxidation (eq 1).[4] In order to have the proper regiochemistry,

$$RR'CHOH \rightarrow RR'CHOR'' \xrightarrow{NBS} [RR'CBrOR''] \rightarrow RCOR' \quad (1)$$

R″ cannot possess α hydrogens and thus might be *tert*-butyl;[5] however, treating the *tert*-butyl ether of 1-hexanol with NBS under a variety of conditions gives only traces of hexanal and *N*-chlorosuccinimide fails to react at all. In addition, neither bromine nor sulfuryl chloride causes oxidation of *tert*-butyl 1-hexyl ether.

We decided to examine the analogous trimethylsilyl (Me_3Si) ethers[6] readily available in high yield from alcohols by treatment with chlorotrimethylsilane and pyridine or triethylamine.[7a] When a Me_3Si ether is dissolved in CCl_4 and stirred with NBS under the irradiation of an ordinary sun lamp, a reaction occurs. The results with a variety of systems are summarized in Table I. Thus, the trimethylsilyl ether of 1-

Table I. Oxidation of Silyl Ethers

Reactant	Conditions	Product	Yield, g (%)[a]
$CH_3(CH_2)_5OSiMe_3$	$h\nu$, 0 °C, 5 h	$CH_3(CH_2)_4CO_2(CH_2)_5CH_3$	1.90 (80)
$C_6H_5CH_2OSiMe_3$	$h\nu$, −20 °C, 2.5 h	C_6H_5CHO	1.06 (48)
$C_6H_5CH(OSiMe_3)CH_3$	$h\nu$, Pyr, rt, 3.5 h	$C_6H_5COCH_3$	1.37 (76)
$CH_3(CH_2)_5CH(OSiMe_3)CH_3$	$h\nu$, Pyr, rt, 3.5 h	$CH_3(CH_2)_5COCH_3$	1.05 (55[b])

[a] Refers to pure, isolated products. Yields not optimized. [b] Based on 36% recovery of starting material.

Table II. Oxidation of Silyl Ethers in the Presence of Aldehydes

Aldehyde	Silyl ether (equiv)	Conditions	Product	Yield, g (%)
$CH_3(CH_2)_8CHO$	$CH_3CH_2OSiMe_3$ (2.0)	$h\nu$, 0 °C, 2.5 h	$CH_3(CH_2)_8CO_2CH_2CH_3$	0.96 (83)
$CH_3(CH_2)_4CHO$	$CH_3CH_2OSiMe_3$ (1.3)	$h\nu$, 0 °C, 3.5 h	$CH_3(CH_2)_4CO_2CH_2CH_3$	0.81 (58)
C_6H_5CHO	$CH_3CH_2OSiMe_3$ (1.0)	$h\nu$, 0 °C, 2.5 h	$C_6H_5CO_2CH_2CH_3$	0.90 (45)
C_6H_5CHO	$CH_3CH_2OSiMe_3$ (2.5)	$h\nu$, 0 °C, 2.5 h	$C_6H_5CO_2CH_2CH_3$	1.78 (89)
CH_3CH_2CHO	c-$C_6H_{11}OSiMe_3$ (1.0)	$h\nu$, 0 °C, 2.5 h	c-$C_6H_{11}O_2CCH_2CH_3$	2.72 (68)
$CH_3(CH_2)_8CHO$	$(CH_3)_3COSiMe_3$ (2.0)	$h\nu$, 0 °C, 2.5 h	$CH_3(CH_2)_8CO_2C(CH_3)_3$	1.28 (44)
$CH_3(CH_2)_4CHO$	$(CH_3)_3COSiMe_3$ (3.0)	$h\nu$, 0 °C, 2.5 h	$CH_3(CH_2)_4CO_2C(CH_3)_3$	0.97 (42)

[a] Refers to pure, isolated products. Yields not optimized.

0022-3263/78/1943-0371$01.00/0