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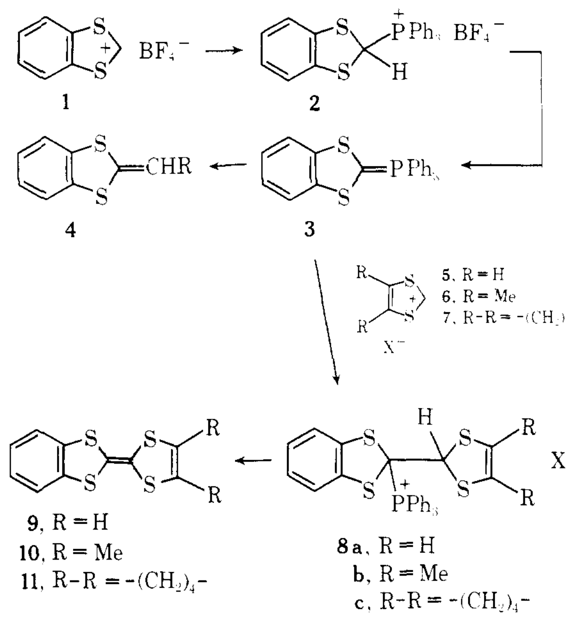
Communications

Organic Metals: a General Synthesis of Unsymmetrical Tetrathiafulvalenes

Summary: A number of unsymmetrical tetrathiafulvalenes have been prepared by the use of a new and general synthesis. This synthesis, which involves a phosphorane intermediate, allows the overall specific coupling of two different 1,3-dithiolium salts.

Sir: Tetrathiafulvalene (TTF) and its derivatives are heterocycles of great current interest in view of their ability to act as π donors in the preparation of organic charge-transfer salts having metallic properties.[1] Almost all known TTF derivatives are symmetrical about the central double bond, due to the fact that general methods for their synthesis have involved the coupling or condensation of two identical S_2 containing moieties, usually a 1,3-dithiol-2-thione (or selone) or a 1,3-dithiolium ion.[2] With the exception of monoethyl- and monocarboxytetrathiofulvalene (prepared from lithiated TTF),[3] the few known unsymmetrical TTF derivatives have been prepared by random coupling or condensation; their separation from symmetrical co-products was the result of fortuitous crystallization properties in two cases,[4] and sufficient polarity differences to allow chromatographic separation[5] in a third case. We now report the discovery of a fundamentally new TTF synthesis which allows the preparation of a wide range of unsymmetrical TTF derivatives from two different 1,3-dithiolium cations without the concomitant formation of symmetrical byproducts.

Scheme I



A recent report has described the reaction of 1,3-benzodithiolium fluoborate (1) with triphenylphosphine to give the phosphonium salt 2 (Scheme I); deprotonation of the latter with *n*-butyllithium at −78 °C and reaction of the resulting unstable phosphorane 3 with various aldehydes afforded 1,4-benzodithiafulvalenes (4) in good yield.[6,7] Our attempts to couple phosphorane 3 with various 1,3-dithiol-2-thiones (or selones) were unsuccessful. However, the red color of 3 was discharged at −78 °C upon addition of the 1,3-dithiolium salts

Table I

TTF derivative	Mp, °C (uncorr)	Yield,[a] %	NMR[e] ($CDCl_3$), δ	UV-visible, nm (log ϵ)
9	135–136 (lit.[5] 138.5–140)	40	*d*	
10	190–191	30	1.9 (s, 6 H) 7.1–7.2 (m, 4 H)	247 (3.84), 253 (3.94), 259.5 (4.00), 292 (4.15), 319 (4.11), 454 (2.5)
11	207–208	31	1.7–2.4 (m, 8 H) 7.1–7.3 (m, 4 H)	258 (3.83), 265 (3.89), 271 (3.91), 281 (3.98), 293 (4.04), 307 (4.00), 319 (3.99), 456 (2.28)
14	105–106	18[b] 41[c]	1.6–2.5 (m, 8 H) 6.25 (s, 2 H)	274 (3.84), 299 (4.02), 310 (3.99), 322 (3.98), 364 (3.18), 460 (2.41)
15	174–175	43	1.5–2.4 (m, 8 H) 1.9 (s, 6 H)	286 (4.01), 298 (4.05), 314 (4.02), 323 (3.98), 478 (2.33)

[a] Isolated, crystallized yield, based on phosphonium salt. [b] Based on 13. [c] Based on 12. [d] In accord with ref 5. [e] In units downfield from Me_4Si.

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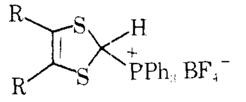
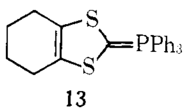
5, **6**, or **7**, with the formation of an intermediate of the type **8**; addition of triethylamine brought about the elimination of triphenylphosphine and the formation of the monobenzotetrathiofulvalenes **9**, **10**, and **11**, respectively. Symmetrical TTFs *corresponding to the individual* 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-dithiolium 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**.



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



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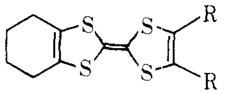
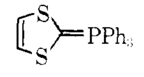


15, R = H
16, R = Me



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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.

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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.

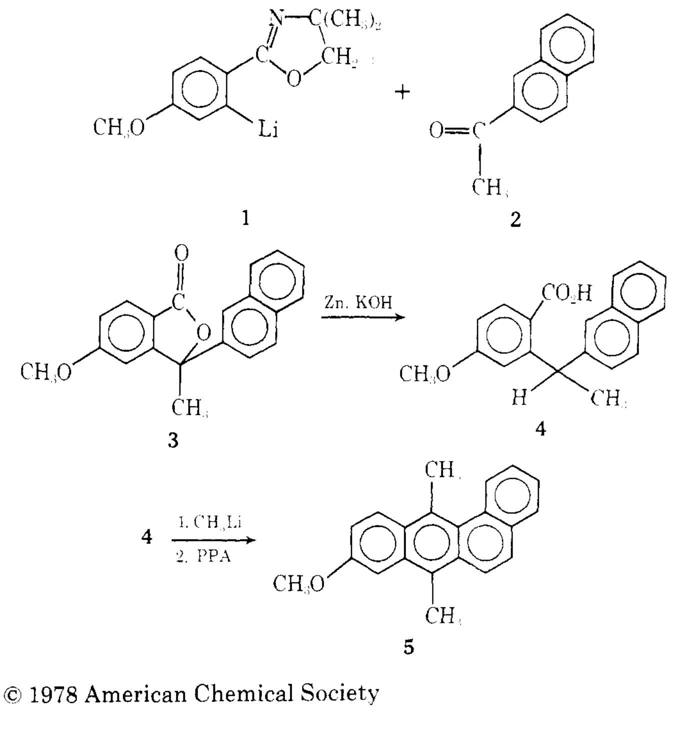
Substituted 7,12-dimethylbenz[*a*]anthracenes are of importance in studies on carcinogenesis. Present synthetic routes involve fundamentally the following condensation reactions: a substituted phenyl organometallic reagent with 1,2-naphthalic anhydride; a phenyl organometallic reagent with a substituted 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



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