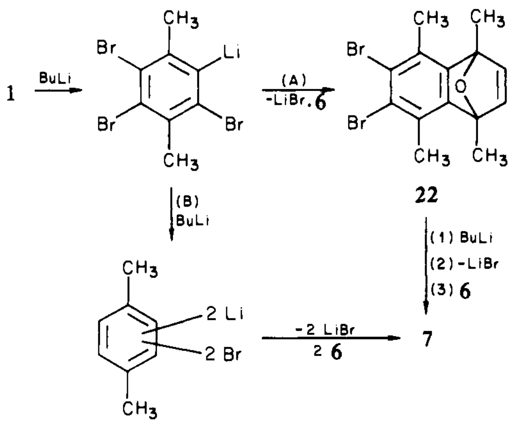
Scheme I



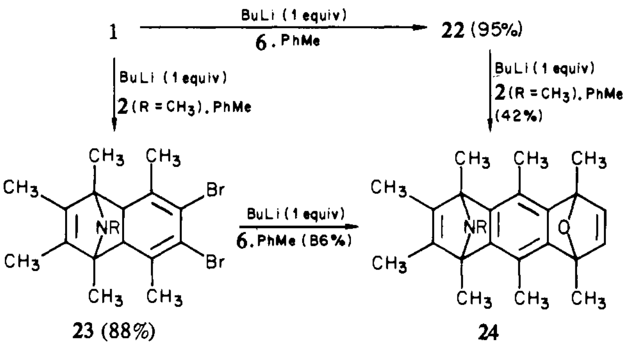
dropwise over about 2 h. The mixture is allowed to warm slowly to room temperature (several hours) and quenched with methanol. Workup usually involves extraction of the adduct into methylene chloride and purification by chromatography and/or recrystallization. In general, the yields are good; minor products include butylated or reduced arenes.[5]

We performed several experiments designed to determine whether the tetrabromoarenes are mono- or bismetalated (i.e., path A or B, Scheme I). The bisadduct **7** (entry 4, Table I) obtained from **1**, **6**, and 2 equiv of butyllithium was a mixture of anti and syn isomers, ratio 57:43.[6] When the monoadduct **22**, synthesized independently,[7] was treated with **6** and butyllithium, a quantitative yield of **7** with the same anti/syn ratio was obtained, consistent with path A. However, when a mixture of **1** and **6** in ether was treated with only *1* equiv of butyllithium, the product was still the bisadduct **7** (and recovered **1**); none of the monoadduct **22** could be isolated or detected in the crude product mixture. This result was consistent with path B or also with path A provided **22** is metalated faster than **1**. A mixture of **1**-d_6[9] and **22** (5 mmol each) was treated with excess **6** and 10 mmol of butyllithium (ether, −78 °C) to decide between these alternatives. Although the major product was again with the bisadduct, some monoadduct **22** was recovered (16%). It contained about 30–40% **22**-d_6.[10] This result proved that the annelation, in this example, is stepwise (path A).

We suspected that the greater solubility of the monoadducts (such as **22**) compared with their symmetric precursors (such as **1**) was the main reason why they could not be isolated when only 1 equiv of butyllithium was used. Being more soluble, they reacted preferentially with the butyllithium. We therefore sought a better solvent for the tetrabromoarenes, and found that with toluene and 1 equiv of butyllithium the monoadducts could be prepared, often in good yield (Scheme II),[11] thus adding versatility to the method in that the two new fused rings need not be identical.

The pyrrole- and furan-derived bisadducts (Table I) could be aromatized in various ways. For example, decamethylanthracene was obtained (72%) from **3** (R = NMe_2) and *m*-chloroperbenzoic acid (CH_3CN, 2 h, reflux).[12] When either **17** (entry 9) or **21** (entry 11) was heated at about 185 °C for 30 min, the nitrogen bridges were eliminated quantitatively[13] to give the corresponding anthracene[14] and tetracene,[15] respectively. Removal of the oxygen bridges from **7** (entry 4) gave the corresponding hexamethylanthracene.[16]

Scheme II



We envision bisaryne equivalents as versatile synthetic intermediates, though subject at present to the limitation that the substituents must be compatible with butyllithium.[17] But in view of the many alternate ways of generating benzynes,[18] it may be possible to overcome this limitation. Other uses for bisaryne equivalents can be anticipated through cycloadditions with 1,3-dipoles and (2 + 2) cycloadditions.[18] We are actively pursuing these possibilities.

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE 77-05956) and the National Institutes of Health (Grant GM 15977) for financial support of this research.

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[5] All new products described in the table and schemes were identified by their various spectra (particularly ^1H and ^{13}C NMR, which were especially diagnostic due to the high degree of symmetry) and in many cases by further chemical conversions. Details will appear in a full account.

[6] The major isomer had ^1H NMR singlets ($CDCl_3$) at δ 1.93 (12 H), 2.28 (6 H), and 6.78 (4 H) whereas those of the minor isomer were at δ 1.95, 2.34, and 6.75. The area ratios were measured at 180 MHz. We do not yet know which isomer is which, but crystals of the predominant isomer are being subjected to X-ray structure determination.

[7] 3,6-Dimethyl-4,5-dibromobenzediazonium carboxylate hydrochloride[8] and 2,5-dimethylfuran in 1,2-dichloroethane containing propylene oxide gave, on 3 h reflux, a 71% yield of **22**: mp 146–147 °C; ^1H NMR singlets ($CDCl_3$) at δ 1.42 (6 H), 2.48 (6 H), and 6.77 (2 H).

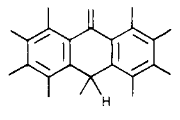
[8] Hart, H.; Ruge, B. *Tetrahedron Lett.* **1977**, 3143.

[9] Synthesized by brominating *p*-xylene-d_{10}; we are indebted to Dr. E. K. Fields, Amoco Chemical Co., for supplying us with the deuterated starting material.

[10] Determined by integrating the peaks at δ 1.42 and 2.48: see footnote 7.

[11] The ratio of the two isomers of **24** depended on the precursor, being 62:38 from **22** and 71:29 from **23** (determined by NMR integration).

[12] This represents a very substantial improvement over the previous method.[8] In addition, 12% of iv is also formed.



iv

[13] For similar reactions, see: Schultz, A. G.; Shen, M. *Tetrahedron Lett.* **1979**, 2969.

[14] For 9,10-dimethoxy-1,2,3,4,5,6,7,8-octamethylanthracene: mp 118–120 °C, ^1H NMR ($CDCl_3$) δ 2.38 (12 H, s), 2.76 (12 H, s), 3.33 (6 H, s).

[15] Overall yield 62% from **20**, up from the 8% previously reported by Sy, A.; Hart, H. *J. Org. Chem.* **1979**, *44*, 7.

[16] For 1,4,5,8,9,10-hexamethylanthracene: mp 196–198 °C; ^1H NMR (CCl_4) δ 2.70 (12 H, s), 2.83 (6 H, s), 6.87 (4 H, s).

[17] For some examples, see footnote 3 in Beak, P.; Brown, R. A. *J. Org. Chem.* **1979**, *44*, 4463.

[18] Hoffman, R. W. "Dehydrobenzene and Cycloalkynes", Academic Press: New York, 1967.

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Thiapen Chemistry: Synthesis of Higher Homologues of Tetrathiafulvalene

Sir:

Considerable interest has been shown in the chemistry of tetrathiafulvalenes (TTF) since some of these π-donors react with

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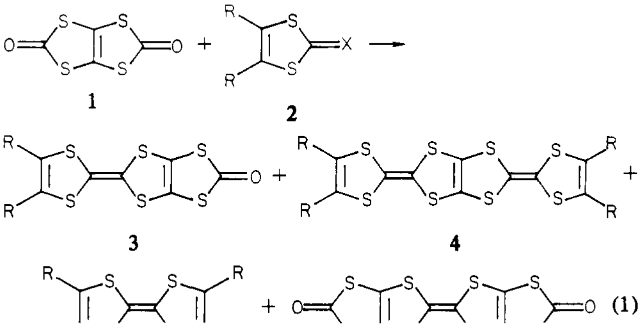
Table I. Experimental Data for 3, 4, 7, 9, and 11

compd	mp, °C	color (solvent)[a]	spectra[b]
3, R = CN	196 dec	magenta (CH_3CN)	(IR) 2210, 2205 (CN), 1675 (C=O)
3, R = CF_3	146-147	yellow (hexane)	(IR) 1680, 1665 (C=O), 1610, 1280, 1155 (CF_3); (^{19}F NMR) 49.6
4, R = CN	290 dec	black ($CHCl_3$ continuous extraction)	(IR) 2210 (CN)
4, R = CF_3	233-235	orange (benzene)	(IR) 1600, 1260, 1140 (CF_3)
7	252 dec	red (chlorobenzene)	(IR) 1605, 1270, 1165 (CF_3)
9, R = CO_2CH_3	204 dec	olive (nitrobenzene)	(IR) 1740, 1720, 1710 (ester), 1680 (C=O); (^1H NMR) 3.76, 3.80
11, R = CO_2CH_3	88-90	maroon (hexane)	(IR) 1725, 1710 (ester); (^1H NMR) 2.32, 3.72

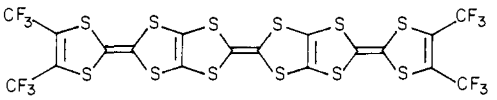
[a] Recrystallization solvent. [b] IR: KBr, cm^{-1}. ^{19}F NMR: $CHCl_3$, ppm relative to CCl_3F. ^1H NMR: ppm relative to Me_4Si.

acceptors to form the most conducting organic solids presently known.[1] The recent synthesis of 1,3,5,7-tetrathiapentalene-2,6-dione[2,3] (**1**, thiapendione) provided the possibility of elaborating a wide variety of novel TTF derivatives through cross-coupling reactions[4] with 1,3-dithioles (**2**) (eq 1).



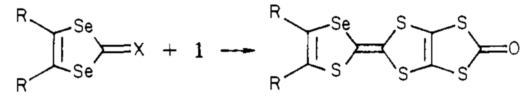
The cross-coupling reaction depends on the nature of the R and X substituents in dithiole **2**. Mono and bis capping of dithiapen to give products **3** and **4**, respectively, occurs when R = CO_2CH_3 or CF_3 and X = S and when R = CN and X = O. No cross-coupling was observed for R = alkyl and/or X = Se. In a typical reaction, a 2–4 mol excess of dithiole derivative to thiapendione was refluxed with excess trimethyl phosphite in dry benzene under N_2 for several hours. The products (**3**–**6**) were isolated by chromatography and by their solubility differences. Identification of the products was based on their spectral properties, mass spectral data (except for **4**) and elemental analysis. Table I summarizes some of this data.[5]

Selective high-yield preparations of either **3** or **4** could be achieved by modifying the cross-coupling reaction conditions. At 60 °C in neat triethyl phosphite,[6] thiapendione (**1**) does not undergo self-coupling to dithiapendione (**6**) whereas dithioles **2** readily self-couple to their respective TTF derivatives **5**. Because of solubility differences, addition of dithiole to a 60 °C solution of thiapendione in triethyl phosphite selectively precipitates in good yield (50–75%, based on thiapen) only monocapped product **3**, when R = CO_2CH_3, and only biscapped product **4**, when R = CF_3 or CN. In refluxing triethyl phosphite, monocapped product **3** (R = CF_3) self-couples to provide, in about 10% yield, the first example of a trisfused TTF derivative, bis(dithiolyidene)dithiapen (**7**).

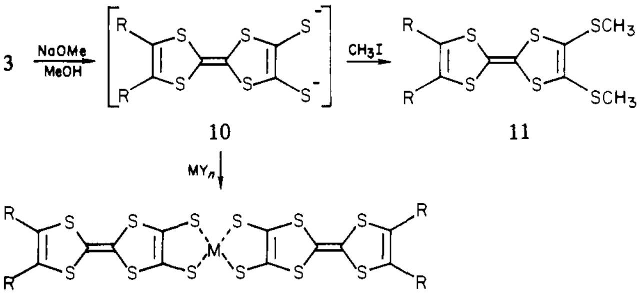


7

Extension of the cross-coupling reaction to 1,3-diselenoles (**8**, R = CO_2CH_3) failed when X = Se and led to a rearranged monocapped product **9** when X = S. As noted earlier[7] in the self-coupling of diselenole thiones, an interchange of a ring selenium with the carbonyl sulfur occurs to give a monocapped product (**9**) containing only one selenium.



Monocapped products can be converted in strong base (e.g., NaOMe) to the corresponding TTF dithiolate intermediates (**10**) which can then be treated with methyl iodide to provide unsymmetrically substituted TTF derivatives (**11**, R = CO_2CH_3). Alternately, treatment of **10** with transition-metal salts yielded a wide variety of novel metal dithiolene derivatives (**12**) which incorporate TTF as conjugated ligands.[8]



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[1] For reviews, see: (a) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, 7, 232 (1974); (b) A. N. Bloch, D. O. Cowan, and T. O. Poehler in "Energy and Charge Transfer in Organic Semiconductors", K. Masuda and M. Silver, Eds., Plenum Press, New York, 1974; (c) A. J. Heeger and A. F. Garito in "Low Dimensional Cooperative Phenomena", H. J. Keller, Ed., Plenum Press, New York and London, 1975; (d) E. M. Engler, *CHEMTECH*, **6**, 274 (1976); (e) M. Narita and C. U. Pittman, Jr., *Synthesis*, 489 (1976).

[2] R. R. Schumaker and E. M. Engler, *J. Am. Chem. Soc.*, **99**, 5521 (1977).

[3] For an alternate synthesis of the thiapen ring system, see: W. P. Krug, A. N. Bloch, and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 180 (1979).

[4] E. M. Engler, V. V. Patel, and R. R. Schumaker, *J. Chem. Soc., Chem. Commun.*. 516 (1979).

[5] For data on 3 and 4, R = CO_2CH_3, see ref 4.

[6] H. K. Spencer, M. V. Lakshmikanthan, M. P. Cava, and A. F. Garito, *J. Chem. Soc., Chem. Commun.*, 867 (1975).

[7] E. M. Engler, V. V. Patel, and R. R. Schumaker, *J. Chem. Soc., Chem. Commun.*, 835 (1977).

[8] For experimental details, see: N. Martinez Rivera, E. M. Engler, and R. R. Schumaker, *J. Chem. Soc., Chem. Commun.*, 184 (1979).

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Chemistry of Exciplexes. 10. Role of Excimers in Photocycloadditions of Arenes to 1,3-Dienes

Sir:

Photoexcited anthracenes and their catacondensed homologues form excimers,[1] and many are known to form exciplexes with