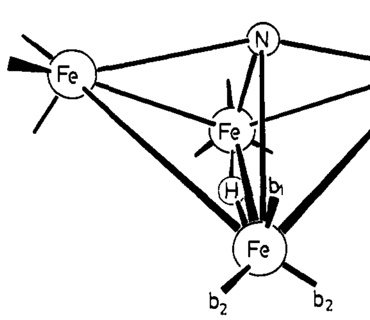

(A)

and 2.54 (2) Å (basal–basal), and the average iron–nitrogen distances were 1.77 (1) (apical iron) and 1.92 (2) Å (basal iron). The dihedral angle between the two Fe(apical)-2Fe(basal) planes was 101°, and the Fe(apical)–N–Fe(apical) angle was 178.4 (6)°. The basicity of the nitrogen atom in **2** was not high.[12b] However, this complex did dissolve in pure CF_3SO_3H, indicating protonation of the cluster, but the site of protonation could not be established by NMR because of fast intermolecular proton exchange.

All three Fe_5N clusters, **3–5**, appeared to have square-pyramidal geometry. An X-ray crystallographic analysis[13] of $HFe_5N(CO)_{14}$ (**5**) established a square-pyramidal arrangement of iron atoms, Fe–Fe = 2.58 (2) Å average, with the nitride nitrogen atom located near the basal plane (Figure 1). Actually, the nitrogen atom was precisely 0.093 (2) Å below the basal plane away from the apical iron atom, a slightly greater extension than for the carbide carbon atom in the isoelectronic carbide analogue, $Fe_5C(CO)_{15}$.[9] With respect to the disposition of peripheral ligands in **5**, the apical iron atom had three terminal carbonyls, the basal iron atoms each had two terminal carbonyls, three of the basal edges were unsymmetrically bridged by one carbonyl, and the remaining edge was bridged by a hydride ligand. By taking into account the smaller nitrogen atom radius, there was a close parallel in the iron–nitrogen distances of this nitride cluster to the iron–carbon distances in the $Fe_5C(CO)_{15}$[9] analogue: apical Fe–N = 1.913 (2) Å, Fe–C = 1.96 (3) Å and basal Fe–N = 1.836 (3) Å, Fe–C = 1.88 (1) Å. In the only other first row cluster nitride,[2] $[Co_6N(CO)_{15}^-]$, the average Co–N distance was 1.938 Å.

The anionic nitride, $[Fe_5N(CO)_{14}^-]$ (**3**), is isoelectronic with $[Fe_5C(CO)_{14}^{2-}]$, and the dynamic ^{13}C NMR spectra of these two species were analogous; both showed two ^{13}C resonances of relative intensities 3:11 of which the more intense resonance broadened at low temperatures. These patterns of ^{13}C CO resonances can be rationalized in terms of an intermediate exchange system in which CO exchange between basal and apical iron atom sites is slow on the NMR time scale while interiron CO exchange is fast among the basal set of iron atoms. A precise structural model for **3** is $[RhFe_4C(CO)_{14}^-]$, whose tetraethylammonium salt was crystallographically defined earlier.[15] The metal atom framework was square pyramidal with a CO bridging a basal edge and two terminal CO ligands at these two basal metal atom sites and with three terminal CO ligands at the remaining metal atom sites. Presumably, the $[HFe_5N(CO)_{13}^{2-}]$ cluster ion (**5**) has a structure similar to that established for $HFe_5N(CO)_{14}$ (**4**), where the bridging carbonyl opposite the bridging hydride in **4** is absent.

Acknowledgment. The work at Argonne National Laboratory was sponsored by the Office of Basic Energy Sciences of the U.S. Department of Energy. This collaborative research was also funded in part by the National Science Foundation Grant CHE-78-20698 to J.M.W. and E.L.M. and Grant CHE-79-03933 to E.L.M.

Supplementary Material Available: A listing of positional and thermal parameters derived from full-matrix least-squares refinements, structure factor tables, and relevant bond angles and lengths (31 pages). Ordering information is given on any current masthead page.

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[12] (a) X-ray analysis for $HFe_4N(CO)_{12}$: mol wt 574.5 amu; triclinic space group $P\bar{1}$, $Z = 2$, $a = 7.491$ (2), $b = 9.214$ (3), $c = 13.974$ (6) Å, $\alpha = 88.09$ (3), $\beta = 86.98$ (3), $\gamma = 73.76$ (3)°, and $V_{calcd} = 924.5$ (6) Å^3 at 298 K. Unit-cell parameters were determined from 17 reflections. With a Syntex $P2_1$ automated diffractometer, 2169 independent reflections were collected (4.0° $\leq 2\theta \leq$ 40.0°). A total of 1415 unique reflections had $F_o^2 \geq \sigma F_o^2$. Absorption corrections were made ($\mu_c = 31.38$ cm^{-1}), and transmission factors ranged from 0.80 to 0.83. The structure was solved with MULTAN and Patterson functions. The structure of $HFe_4N(CO)_{12}$ was disordered with disordered molecules related by a near twofold rotation inversion axis which resulted in a superposition of the molecules. The iron cluster core was resolved by using least-squares refinements in which the iron–iron superposition gave a site separation of ~0.50 Å. The difference maps contained iron ellipsoids which also indicated disorder. Final refinement led to $R(F_o) = 0.071$, $R_w(F_o^2) = 0.078$, and GOF = 1.40. The successful least-squares refinement yielded a structural model with chemically reasonable distances and angles (a full discussion of Fe_4X butterfly structures will be published by us). (b) This is expected because in the analogous and neutral complex $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ the C–H hydrogen atom is removed as a proton by methanol (M. Tachikawa, unpublished data).

[13] X-ray analysis for $HFe_5N(CO)_{14}$: mol wt 686.4 amu; monoclinic, space group $P2_1/n$, $Z = 4$, $a = 8.473$ (2), $b = 15.056$ (3), $c = 16.048$ (3) Å, $\beta = 95.42$ (2)°, μ(Mo Kα) = 36.38 cm^{-1}. One quadrant, 4945 reflections, of data was collected on a Syntex $P2_1$ automated diffractometer at 173 K. Solution of the structure was accomplished by using MULTAN,[14] and the hydrogen atom was located in a difference Fourier synthesis. All atomic positional and thermal parameters refined successfully (anisotropic temperature factors except for hydrogen atoms) and convergence were realized at an agreement factor of $R_w(F_o) = 0.031$ for 3967 reflections where $F_o^2 > \sigma F_o^2$.

[14] A. Germain, P. Main, and M. M. Wolfson, *Acta Crystallogr.*, **19**, 1014 (1954).

[15] M. Tachikawa, A. C. Sievert, E. L. Muetterties, M. R. Thompson, C. S. Day, and V. W. Day, *J. Am. Chem. Soc.*, **102**, 1725 (1980).

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Received June 27, 1980

Bisannelation of Arenes with Bisaryne Equivalents

Sir:

We have found that tetrabromo derivatives[1] of 1,4-disubstituted benzenes function as bisaryne equivalents,[2,3] allowing one to readily convert benzenes to anthracenes in two steps. The method is broad in scope and is generally useful for synthesizing polynuclear aromatic compounds and for other novel structures. Table I gives illustrative examples.

In a typical procedure, 10 mmol of the bisaryne equivalent and 20 mmol (or excess) of the diene in 100 mL of carefully dried solvent are cooled to −78 °C[4] and stirred (argon atmosphere) as *n*-butyllithium (30 mL in hexane, approximately 0.8 M) is added

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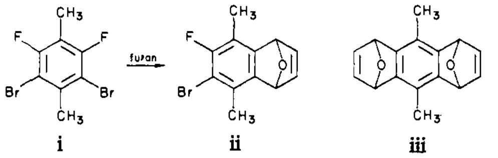
[1] Other halo drivatives, such as dibromo–diiodo or tetraiodo, also work, and other possibilities are being explored. The tetrabromo derivatives, however, are usually the most easily accessible.

[2] The only previous similar reaction of which we are aware is the conversion of i to iii: Wittig, G.; Hārle, H. *Justus Liebigs Ann. Chem.* **1959**, *623*, 17. With magnesium in THF, i gave mainly the monoadduct ii (34%) and only 5% of the bisadduct iii. With butyllithium, the yield of iii increased to 15%, but no ii was isolated.



i ii iii

[3] Bisarynes have been postulated as intermediates in certain mass spectral fragmentations and to rationalize products from the copyrolysis of benzene with pyromellitic or mellophanic dianhydrides (Fields, E. K.; Meyerson, S. *Adv. Phys. Org. Chem.* **1968**, *6*, 18–21), but alternate explanations are possible.

[4] Often some of the bisaryne equivalent crystallizes out during this cooling, but dissolves as the butyllithium is added.

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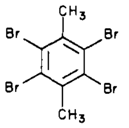
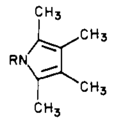
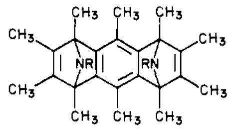
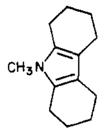
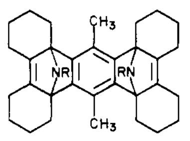
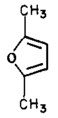
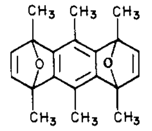
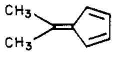
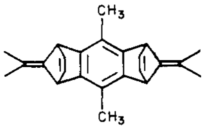
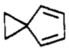
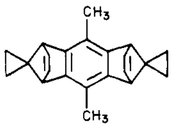
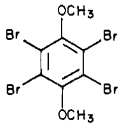
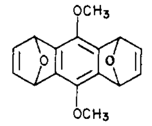
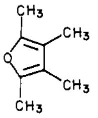
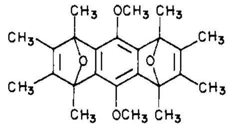
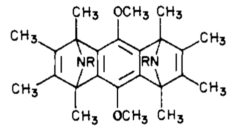
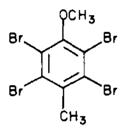
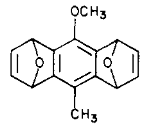
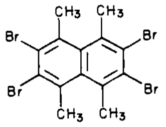
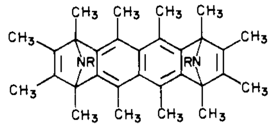
Table I. Bisadducts of Bisaryne Equivalents

entry	bisaryne equiv	diene	solvent[a]	bisadduct (yield, %)
1	 1	 2, R = CH_3	E	 3, R = CH_3 (78)[b]
2	1	2, R = NMe_2	T	3, R = NMe_2 (76)
3	1	 4	THF	 5, R = CH_3 (76)[b]
4	1	 6	E, T	 7, (78, 93)[c]
5	1	 8	THF	 9 (70)[b]
6	1	 10	T	 11 (68)[b]
7	 12	 13	E	 14 (72)[b]
8	12	 15	THF	 16 (59)[b]
9	12	2, R = NMe_2	THF	 17 (71)[b]
10	 18	13	E	 19 (62)[b]
11	 20	2, R = NMe_2	THF	 21 (62)[b]

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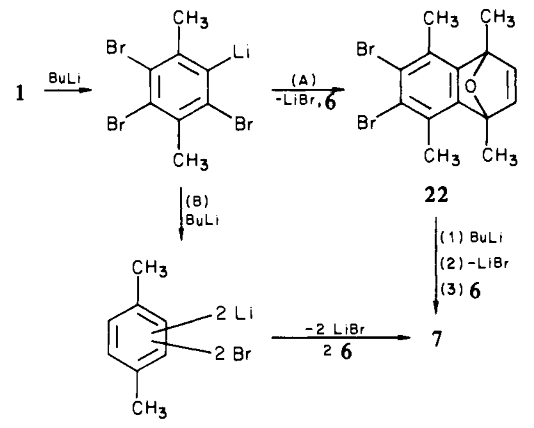
[a] E = ether, T = toluene, THF = tetrahydrofuran. [b] A mixture of two stereoisomers. [c] 57:43 mixture of stereoisomers.

Scheme I



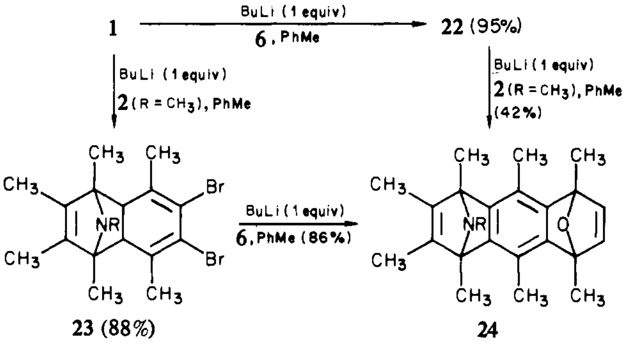
dropwise over about 2 h. The mixture is allowed to warm slowly to room temperature (several hours) and quenched with methanol. Workup usually involves extraction of the adduct into methylene chloride and purification by chromatography and/or recrystallization. In general, the yields are good; minor products 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 ^{1}H 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 ^{1}H 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; ^{1}H NMR singlets ($CDCl_3$) at δ 1.42 (6 H), 2.48 (6 H), and 6.77 (2 H).

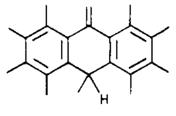
(8) Hart, H.; Ruge, B. *Tetrahedron Lett.* **1977**, 3143.

(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, ^{1}H 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; ^{1}H 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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Received June 2, 1980

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

0002-7863/80/1502-6651$01.00/0