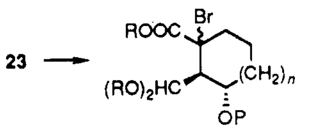

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(5)

in cases of the silyl ethers to provide approximately 1:1 diastereomeric mixtures of the corresponding bromo acetal esters **24** in high yields (Table II). The stereochemical outcome of the newly created sp^3 chiral center in the acetals **24** is inconsequential since the chirality at the carbon will be eventually eliminated in our projected synthesis. However, in the absence of nucleophilic solvents, the anthracycline precursors **33** and **35**, regardless of protection of the tertiary hydroxyl group, gave γ-lactone **36** (Table II, entries 7 and 8).

With enantiomerically pure acetal ester **34** and lactone **36** now secured by 1,2-functionalization of α,β-epoxy ketones through double dithiane addition and simple oxidative hydrolysis, efforts are being made to convert them to a 1,4-dipole equivalent for the subsequent condensation with a juglone derivative.

Acknowledgment. Financial support from the Korea Science and Engineering Foundation and the Organic Chemistry Research Center are appreciated.

Supplementary Material Available: Experimental procedures and spectral data of products and NMR spectra of compounds **30** and **36** (22 pages). Ordering information is given on any current masthead page.

Selective Functionalization in the Bay Region of Polycyclic Aromatic Hydrocarbons via Dilithiation

Arthur J. Ashe, III,* Jeff W. Kampf, and Paresh M. Savla
Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

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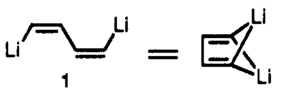
Summary: Sequential reaction of polycyclic aromatic hydrocarbons with butyllithium/TMEDA hexane and electrophiles allows preparation of derivatives functionalized in the bay region.

Several *cis,cis*-1,4-dilithiobutadiene derivatives **1** are known to adopt a symmetrical bridged structure **2** in the solid state.[1-3] Calculations indicate that structure **2** is highly stabilized in comparison to possible nonbridged geometries.[4-6] Schleyer and co-workers have demonstrated that this double lithium bridging can provide the thermochemical driving force for the otherwise surprising ortho-dilithiation of biphenyl (**3** → **4**) by *n*-BuLi in TMEDA/hexane.[7] A number of related lithium-directed metalations of aromatic compounds have been studied in detail.[8,9] We report here on the extension of this method to polycyclic aromatic hydrocarbons (PAH's). This procedure allows selective functionalization in the bay region of PAH's and can be used to prepare useful heterocycles efficiently.



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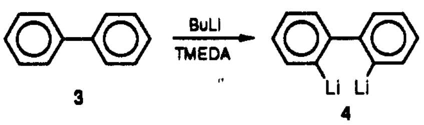

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Table I. **Relative Concentrations (%) of Deuterated PAH's after Sequential Reaction with BuLi/TMEDA and D_2O**

compound	d_0[a]	d_1[a]	d_2[a]	d_3[a]	d_4[a]	portion of d in Bay Region[b,c]
triphenylene (5)	2.5	12.3	60.6	23.9	0.7	85
phenanthrene (10)	0.9	12.8	64.4	19.0	2.9	41
chrysene (11)	0.9	10.7	69.5	18.3	0.6	62

[a] Determined by analysis of the appropriate EI mass spectral *m/e* values. Corrections were made for M − 1, M − 2 values, assuming random loss of *d*. See: Westmore, J. B.; Reimer, M. L. J.; Charlton, J. *Spectrosc: Int. J.* 1982, *1*, 86. [b] Determined from integration of appropriate signals in the ^{2}H NMR spectra. [c] The bay positions are defined as C_1,C_{12} of **5** and C_4,C_5 of **10** and **11**.

Thus, the reaction of triphenylene **5** with 5 equiv of *n*-butyllithium in TMEDA/hexane at 60 °C for 3 h gave a red solution of lithio derivatives. Quenching with D_2O afforded 95% of triphenylene which is predominantly d_2 although significant quantities of d_1 and d_3 were also present (see Table I). ^{2}H NMR spectroscopy indicates that 85% of the D is in the α-position.[10] Quenching the lithiation mixture with SCl_2 gives the known triphenyleno[4,5-*bcd*]thiophene **8**.[11] Purification[12] through oxidation with H_2O_2/HOAc to the unisolated sulfone, and column chromatographic separation from nonpolar impurities followed by reduction with $LiAlH_4$/THF allowed isolation of **8** in 53% yield. These data establish that 1,12-dilithiotriphenylene **6** is the major lithiated species.

Quenching **6** with I_2 afforded 30% of 1,12-diiodotriphenylene **9** as pale yellow crystals, mp 238–40 °C. The mass spectrum and the symmetrical ^{1}H NMR spectrum indicated structure **9**.[13] Since molecular mechanics calculations (SYBYL MAXIMIN2)[14] suggest that the aromatic rings of **9** should show gross distortions from pla-

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[1] Schubert, U.; Neugebauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1982**, 1184.

[2] An X-ray structure of the tetraphenyl derivative of **1** shows this bridged structure: Schleyer, P. v. R., private communication.

[3] Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

[4] Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 7928.

[5] Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355; **1984**, *56*, 151.

[6] Also see: Streitwieser, A., Jr.; Swanson, J. T. *J. Am. Chem. Soc.* **1983**, *105*, 2502. Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353.

[7] Neugebauer, W.; Kos, A. J.; Schleyer, P. v. R. *J. Organomet. Chem.* **1982**, *228*, 107.

[8] Neugebauer, W.; Clark, T.; Schleyer, P. v. R. *Chem. Ber.* **1983**, *116*, 3283. Bauer, W.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 970.

[9] Bauer, W.; Feigel, M.; Müller, G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 6033.

[10] The α-positions of triphenylene are known to be more acidic: Streitwieser, A., Jr.; Ziegler, G. R.; Mowery, P. C.; Lewis, A.; Lawler, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 1357.

[11] Klemm, L. H.; Lawrence, R. F. *J. Heterocycl. Chem.* **1979**, *16*, 599.

[12] Willey, C.; Iwao, M.; Castle, R. N.; Lee, M. L. *Anal. Chem.* **1981**, *53*, 400.

[13] **9**: MS *m/e* 456 (M^+ for $C_{18}H_{10}I_2$); H NMR ($CDCl_3$) 7.28 (t, J = 7.7 Hz, 2 H), 7.60 (sym. m, 2 H), 8.01 (d, J = 7.5 Hz, 2 H), 8.40 (sym. m, 2 H), 8.43 (d, J = 7.8 Hz, 2 H).

[14] SYBYL version 5.3, Triplos Assoc., St. Louis, MO.

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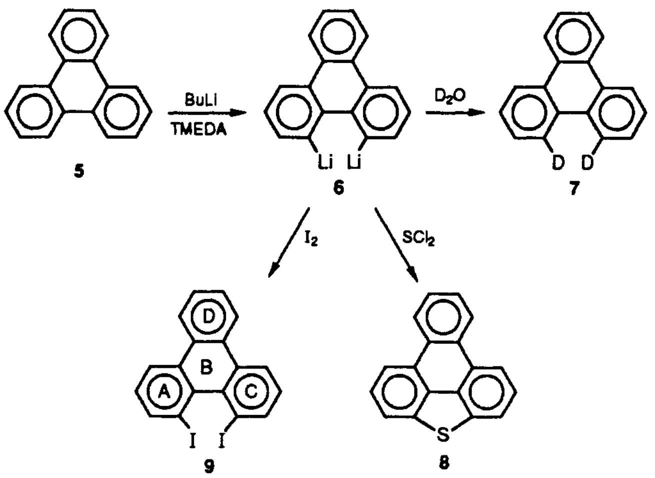
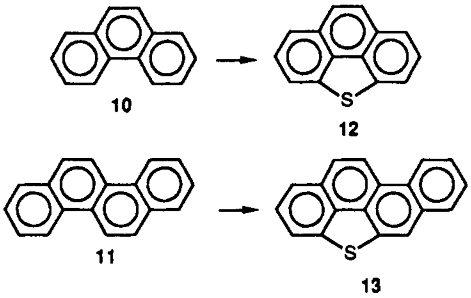


narity due to the crowding of the iodine atoms, we have obtained a crystal structure.[15] The molecular structure is illustrated in Figure 1. The nonbonded approach of the I atoms (3.683 (4) Å) is well below the van der Waals separation of 3.96 Å,[16] which might be consistent with an attractive non-bonded interaction.[17] The juxtaposition of the I atoms splays the A and C rings of **9** so that the average plane of ring A makes a dihedral angle of 33.5 (6)° with the corresponding plane of ring C. The distortion from planarity is seen most clearly by noting the torsional angles along the bonds connecting the two iodines: $\angle \mathrm{I1C1C18C17} = 23.5\ (7)^\circ$, $\angle \mathrm{C1C18C17C16} = 37\ (1)^\circ$ and $\angle \mathrm{C18C17C16I2} = 24\ (1)^\circ$. The distortion of **9** relative to **5** is similar to those shown by the better studied 4,5-disubstituted phenanthrenes.[18]



Similar dilithiations have been carried out with the bay region PAH's phenanthrene **10**[19] and chrysene **11**. In both cases, quenching with D_2O afforded as the major product the dideuterated hydrocarbon with predominant deuteration in the bay region. However, the selectivity of the dilithiations declines in the order **5** > **11** > **10**. Phenanthrene is least selective since approximately 40% of the deuterium was at the peri positions (C_1, C_9).

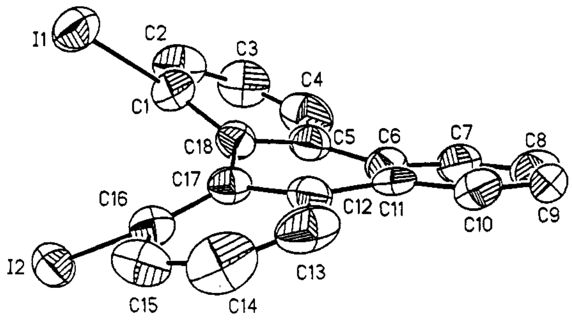


Figure 1. An ORTEP drawing of the molecular structure of 1,12-diiodotriphenylene, **9**.

Part of this lower selectivity is statistical since the portion of bay region hydrogen declines from 50% for **5** to 33% for **11** and 20% for **10**. However, it is also likely that the hydrogens of PAH's which are adjacent to fused rings are the most acidic.[10,20] Substantial primary lithiation at the peri positions of **10** and **11** is likely, while subsequent dilithiation might be directed to adjacent peri positions, in the manner which has been elegantly demonstrated for 1-lithionaphthalene.[8]

Quenching dilithio deviates of **10** and **11** with SCl_2 afforded 25% and 45% of the corresponding fused thiophenes **12**[21] and **13**,[22] respectively. These compounds have been identified in coal tars[23] and have been previously prepared by less efficient syntheses.[21,22] Chryseno[4,5-*bcd*]thiophene, **13**, is a suspected environmental mutagen,[24,25] although biological testing has been limited due to lack of adequate quantities.[26]

We intend to explore further the dilithiation of PAH's since it appears to be an excellent method for preparing interesting torsionally distorted aromatics and bay region functionalized PAH which may be useful in studies of carcinogenesis.

Acknowledgment. Supported in part by a grant from the University of Michigan Cancer Center's Institutional Grant from the American Cancer Society and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Crystallographic and SYBYL MAXIMIN2 data for **9** (19 pages). Ordering information is given on any current masthead page. Tables of observed and calculated structural factors are available from A.J.A. on request.

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(15) Pale yellow crystals of **9** were obtained from recrystallization from CCl_4: triclinic, $P\bar{1}$ space group, $Z = 4$ (2 independent molecules per assymetric unit), $a = 11.018\ (2)$ Å, $b = 11.411\ (5)$ Å, $c = 14.083\ (6)$ Å, $\alpha = 102.44\ (4)^\circ$, $\beta = 110.03\ (3)^\circ$, and $\gamma = 107.50\ (3)^\circ$. Refinement converged with $R = 0.0545$ and $R_w = 0.0744$.

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(18) Cosmo, R.; Hambley, T. W.; Sternhell, S. *J. Org. Chem.* **1987**, *52*, 3119.

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(25) Grünbauer, H. J. M.; Wegener, J. W. M. *Tox. Environ. Chem.* **1983**, *6*, 225.

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