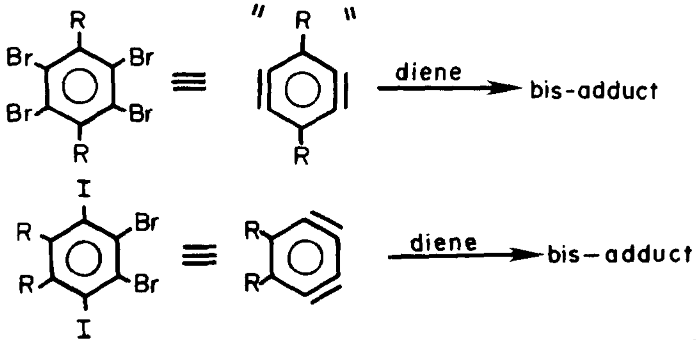
Tetrahedron Letters,Vol.24,No.51,pp 5721-5724,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

THE DILITHIATION MECHANISM IN THE REACTIONS OF POLYHALOARENES AS DI-ARYNE EQUIVALENTS

Harold Hart* and Godson C. Nwokogu
Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA

Abstract: The preparation of certain 1,4-dilithio-tetrahaloarenes is described; they react with electrophiles at low temperatures or form arynes at higher temperatures.

1,2,4,5- and 1,2,3,4-Tetrahalobenzenes are synthetically useful di-aryne equivalents.[1] For example, when treated with two equivalents of an organolithium reagent in the presence of a receptor diene they form bis-adducts.

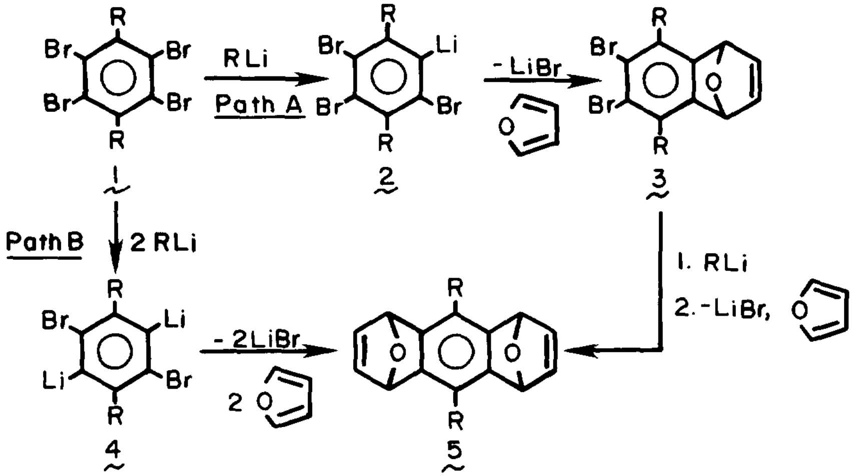


These reactions have been used to synthesize anthracenes[1,2] and higher acenes,[1,3] phenanthrenes[4] and iptycenes[5,6] from readily available precursors in two or three steps.

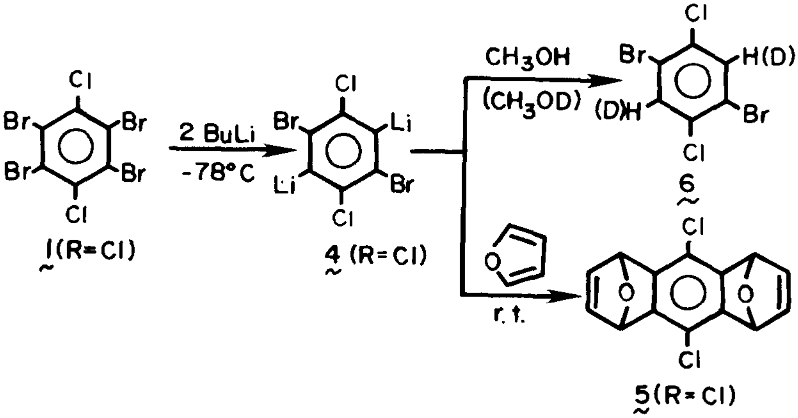
In principle at least two mechanisms are possible for these reactions, illustrated in Scheme I for the reaction of 1,2,4,5-tetrabromobenzenes, furan, and organolithium. Treatment of 1 with two equivalents of organolithium reagent can give either a monolithio derivative 2 (Path A) or a dilithio derivative 4 (or its 1,3-isomer; Path B). These paths are readily distinguishable experimentally because in Path A the monoadduct 3 is a discreet, isolable or detectable intermediate, whereas Path B leads directly to the bis-adduct 5.[7]

In our first publication on this subject we showed that when R=CH_3 Path A is followed.[1] We now report that when R is an electron-withdrawing substituent such as Cl, reaction proceeds via Path B with 4 (R=Cl) as a stable, detectable and synthetically useful dilithio intermediate.

Scheme I



Addition of 2.2 equivalents of *n*-BuLi (0.4 M in hexane) to a mixture of 1 (R=Cl; 5 mmol),[8] ether (100 mL) and furan (5g) at -78°C over 1.5 h, followed by quenching with methanol gave only 1,4-dibromo-2,5-dichlorobenzene 6, mp 147-149°C.[9] With CH_3OD, the corresponding dideuteroarene was obtained. But if the reaction mixture was warmed to room temperature (6h) before quenching with methanol, the product was the bis-adduct 5 (R=Cl), mp 227-231°C.[10]

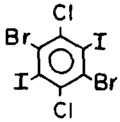
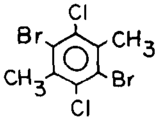
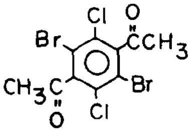
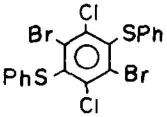
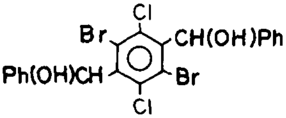
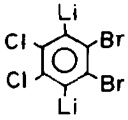
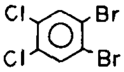
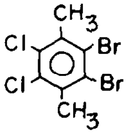
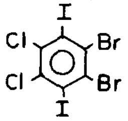


These results show that metallation of 1 (R=Cl) gives the dilithio compound 4 (R=Cl). The bromines are replaced in preference to chlorines, the lithiums are exclusively *para*, the dilithioarene is stable at -78°C but when warmed eliminates lithium bromide (not chloride) to give arynes. To illustrate the low temperature stability of 4 (R=Cl) we have trapped it with various electrophiles (Table I).

Tetrabromo-*o*-dichlorobenzene also gave a dilithio derivative 7 with butyllithium; again, only the 1,4-isomer was observed. Its reactions with certain electrophiles are shown in Table I. Tetrabromo-difluorobenzenes gave similar results. Hexabromobenzene and excess *n*-BuLi (4 eq.) gave, after a low temperature methanol quench, only 1,2,4,5-tetrabromobenzene (71%) showing again that the lithiums are *para*.

We attribute the *para* orientation in all of these dilithiobenzenes to minimization of

Table I. Reaction of Dilithiobenzenes with Various Electrophiles.

Dilithioarene	Electrophile	Product	Yield(%)[a]	mp,°C (ref)
4 (R=Cl)	$CH_3OH(D)$	**6**	61-64	147-149 (9)
	I_2		72	265-267 (10)
	$(CH_3)_2SO_4$		97	229-231 (11)
	$(CH_3CO)_2O$ or CH_3COCl		30	241-243 (10)
	PhS-SPh		39	209-212 (10)
	PhCH=O		33	242-246 (10)
	$BrCH_2CO_2Et$	**1** (R=Cl)	64	280-281 (8)[12]
 **7**	CH_3OH		55	150-152 (10)
	$(CH_3)_2SO_4$		93	236-238 (10)
	I_2		48	268-270 (10)

---

[a] Of pure crystalline product, not optimized.

repulsion between the two negative (or partial negative) charges. Di- and polylithioarenes have been reported before,[13] including examples with lithiums 1,3- or even 1,2-, but these species usually contain 3 or 4 stabilizing Cl or F substituents.

We conclude that di-aryne equivalents of the tetrabromoarene type[1] may react via either mono- or dilithio intermediates, depending on the nature of the remaining substituents. Extensions of these studies are in progress.

Acknowledgement. We are indebted to the National Institutes of Health (GM 15997) and the National Science Foundation (CHE 80-17746) for financial support.

References and Notes

1. Hart, H.; Lai, C-Y.; Nwokogu, G.; Shamouilian, S.; Teuerstein, A.; Zlotogorski, C. J. Am. Chem. Soc. **1980**, 102, 6649.
2. Hart, H.; Nwokogu, G. J. Org. Chem. **1981**, 46, 1251.
3. Sy, A.; Hart, H. J. Org. Chem. **1979**, 44, 7.
4. Hart, H.; Shamouilian, S. J. Org. Chem. **1981**, 46, 4874.
5. Hart, H.; Shamouilian, S.; Takehira, Y. J. Org. Chem. **1981**, 46, 4427.
6. Hart, H.; Raju, N.; Meador, M. A.; Ward, D. L. J. Org. Chem. **1983**, in press.
7. Path B does not necessarily imply a di-aryne intermediate, since loss of the two equivalents of lithium bromide and reaction with the diene can still occur in a stepwise manner.
8. Hugel, G.; Lerer, M.; Fabre, C. Bull. Soc. Chim. France, **1954**, 836.
9. Varma, P. S.; Shankarnarayanan, J. Ind. Chem. Soc. **1936**, 13, 31.
10. All new compounds gave correct elemental analyses and spectra consistent with the assigned structures.
11. Beacall, T. Trans. Faraday Soc. **1945**, 41, 472.
12. Reaction occurs with displacement at bromine, not at carbon, to give the starting tetrabromo-p-dichlorobenzene.
13. For examples, see Haiduc, I.; Gilman, H. Rev. Roum. Chim. **1971**, 16, 907; Dua, S. S.; Gilman, H. J. Organomet. Chem. **1974**, 64, Cl; Tamborski, C.; Soloski, E. J. J. Organomet. Chem. **1969**, 20, 245.

(Received in USA 1 September 1983)