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DIAMINO-BENZO[1,2-d:4,5-d']BISTRIAZOLE (DABT), A NEW USEFUL 1,4-DIBENZYNE EQUIVALENT

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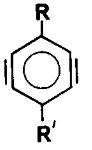
Abstract: *The title compound, when treated with two equivalents of lead tetraacetate, is the synthetic equivalent of 1,4-dibenzyne; bis-cycloadducts are formed with dienes and 1,3-dipoles.*

1,2,4,5- and 1,2,3,4-Tetrahaloarenes are useful synthetic equivalents of 1,4- and 1,3-diarynes (**1** and **2**, respectively).[1] When treated with two equivalents of an organolithium reagent in the presence of certain dienes, they readily form products which correspond formally to bis-cycloadducts of **1** and **2**. The reaction is particularly useful for simultaneously fusing two new rings to an arene.



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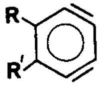
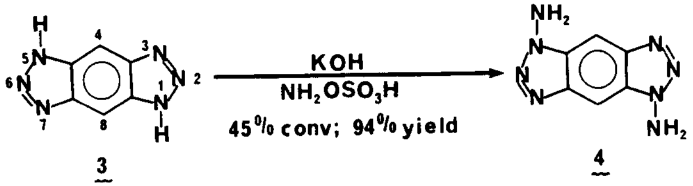


2

One synthetic limitation of this method, however, is that the receptor diene may not contain functionality which will compete with the tetrahaloarene for the organolithium reagent.[2,3] In practice this means that the diene usually must not contain carbonyl, halogen or similar groups.

It has long been known that 1-aminobenzotriazole, when treated with lead tetraacetate (LTA), is a moderately effective benzyne precursor.[4,5] We synthesized the analogous 1,5-diamino-benzo[1,2-d:4,5-d']bis-triazole (DABT) **4** from the known precursor **3**,[6-8] and found that with two equivalents of LTA it is an excellent 1,4-dibenzyne



equivalent. DABT is formulated here as the 1,5-isomer (the aromatic protons appear as a sharp singlet at δ 8.24 in DMSO-d_6). However, whether the structure is 1,5- or 1,7- or a mixture,[9] does not affect the utility as a dibenzyne equivalent.

Table I shows examples of the use of 4 as a 1,4-dibenzyne equivalent. The diene precursors in entries 1-4 contain carbonyl functions which presumably would be incompatible with the butyllithium used to generate arynes from tetrahaloarenes. But with DABT-LTA they give bis-adducts in good yield. The bromofuran (entry 5), which would also have problems with previous methods, works well with DABT-LTA.

Although regio isomers are possible for entries 2-6 the 'trans' arrangement of like substituents seems preferred (the aromatic proton signals in the central ring in each product appear as singlets). Although the product melting points are fairly sharp, occasional, minor extraneous peaks in the ^{13}C NMR spectra for adducts in entries 2, 4 and 5 indicate that both syn and anti bridges may be present, but with one isomer predominant. Entry 6 presents the first example of 1,3-dipolar addition to a diaryne equivalent; although four regio and stereoisomers are possible, the product appears to be a single substance (the oxygens are 1,4; the phenyl substituents are probably trans).

The remarkable degree of regio and stereospecificity in these cycloadditions strongly suggests that they occur stepwise. We are continuing to explore the reasons for these specificities, as well as further synthetic applications of DABT and related dibenzyne equivalents.

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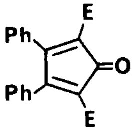
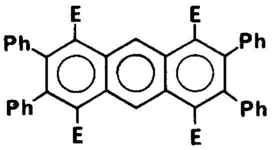
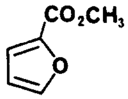
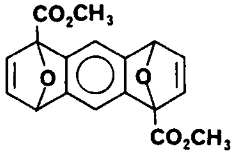
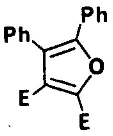
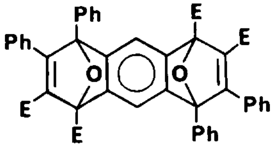
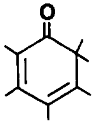
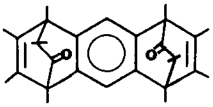
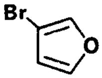
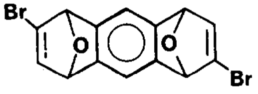
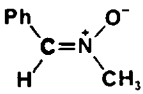
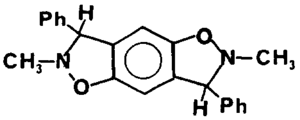
References and Notes

1. Sy, A,; Hart, H. J. Org. Chem. **1979**, 44, 7; Hart, H.; Lai, C-Y.; Nwokogu, G.; Shamouilian S.; Teuerstein, A.; Zlotogorski, C. J. Am. Chem. Soc. **1980**, 102, 6649; Hart, H.; Nwokogu, G. J. Org. Chem. **1981**, 46, 1251; Hart, H.; Shamouilian, S.; Takehira, Y. J. Org. Chem. **1981**, 46, 4427; Hart, H.; Shamouilian, S. J. Org. Chem. **1981**, 46, 4874; Hart, H.; Nwokogu, G. Tetrahedron Lett. **1983**, 24, 5721.

Table I. Examples of DABT bis-Cycloadditions[10]

Entry	Diene	Adduct[11]	mp, °C	Yield (%)
1.	 $(E = CO_2CH_3)$		375-376	93
2.			236-242	47
3.	 $(E = CO_2CH_3)$		283-287	78
4.			338 (dec.)	79
5.			115 (dec.)	69
6.			142-143	91

2. Other di-aryne equivalents which have been used in very limited circumstances include the treatment of 1,4-dibromoarenes with strong base (Cadogan, J. I. G.; Harger, M. J. P.; Sharp, J. T. *J. Chem. Soc. B* **1971**, 602; Stringer, M. B.; Wege, D. *Tetrahedron Lett.* **1980**, *21*, 3831), the treatment of bis-*o*-bromotosylates with strong base (LeHoullier, C. S.; Gribble, G. W. *J. Org. Chem.* **1983**, *48*, 1682) and thermal cycloadditions of bis-1,4-diepoxyarenes (Hart, H.; Raju, N.; Meador, M. A.; Ward, D. L. *J. Org. Chem.* **1983**, *48*, 4357).
3. Obvious di-aryne precursors would be the bis-diazonium carboxylates derived from appropriate diamino tere- or isophthalic acids. So far, attempts to tetrazotize these bis-anthranilic acids have failed (Hart, H.; Ok, D., unpublished results), but the attractiveness of these di-aryne equivalents warrants further study.
4. Campbell, C. D.; Rees, C. W. *J. Chem. Soc. C* **1969**, 742, 748, 752; Houghton, P. G.; Rees, C. W. *J. Chem. Res.* **1980**, (S) 303, (M) 3888.
5. Hoffmann, R. W. "Dehydrobenzene and Cycloalkynes", Academic Press, New York, 1967, p. 81.
6. (a) Muzik, F.; Allan, Z. J. *Coll. Czech. Chem. Comm.* **1959**, *24*, 474; (b) Coburn, M. D.; Berlin, J. K. *Synthesis* **1974**, 869.
7. Improvements in the literature[6b] synthesis of **3** will be described in detail in a full account. The most important of these involves the conversion of 1,5-bis[acetylamino]-2,4-dinitrobenzene to 1,7-diacetylbenzo[1,2-d:4,5-d']bistriazole, where the yield has been improved from 60 to 97%; the key difference from the literature procedure is to carry out the catalytic hydrogenation in ethanol containing concentrated hydrochloric acid (instead of in acetic acid).
8. The procedure for **4**: Bistriazole **3** (6.0 g, 0.0375 mol) was dissolved in a solution of KOH (0.3 mol) in water (200 mL) at 60°C. Hydroxylamine-O-sulfonic acid (16.95 g, 0.15 mol) was added in portions (1 h) with the temperature maintained at 66-68°C. The mixture was stirred (1 h, 60°C), cooled and filtered. The alkaline solution was continuously extracted with ether for 48 h. Evaporation of the ether and recrystallization from ethanol gave 3.21 g of **4**, mp 292°C (dec). After extraction, the alkaline solution was acidified with 10% hydrochloric acid to precipitate 3.13 g of **3** which can be recycled.
9. Treatment of **3** with 2,4,6-trinitrofluorobenzene, for example, gives both the 1,5- (56%) and 1,7- (44%) bistrinitrophenyl derivatives (Berlin, J. K.; Coburn, M. D. *J. Heterocycl. Chem.* **1975**, *12*, 235).
10. A sample procedure for entry 2 follows: To a mixture of DABT (1 g, 5.26 mmol) in 100 mL THF under Ar was added 1.46 g (11.57 mmol) of methyl 2-furoate, and the mixture was stirred 30 min. LTA (5.13 g, 11.57 mmol) suspended in 60 mL THF was added at room temperature in portions over 30 min. After 10 min additional stirring, the lead diacetate was filtered, the filtrate was diluted with water (800 mL) and extracted with chloroform (3 X 100 mL). Following washes with $NaHCO_3$, NaCl and drying ($MgSO_4$), the solvent was removed and the residue purified by chromatography on silica gel (75% hexane: 25% ethyl acetate) to give the bis adduct (entry 2), which was recrystallized from ether.
11. All adducts gave satisfactory elemental analyses and spectra consistent with the illustrated structures.

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