extract was dried and concentrated to afford the diketone coronands **6**. Further purification was achieved by thick layer chromatography. Table III summarizes the physical and spectral data.

Complexation of 5 with Cobalt(II) Chloride. A solution of **5** (58.8 mg, 0.1 mmol) in $CHCl_3$ was added to a solution of $CoCl_2 \cdot 6H_2O$ (0.1 mmol) in MeOH (5 mL). After 4 h at reflux, the mixture was concentrated in vacuo to a volume of 5 mL, and the remaining solvent was allowed to evaporate slowly.

X-ray Experimental Methods. Intensity data for **5** and **9** were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Variable scan rates were employed in the ω–2θ scans in order to achieve approximately equal relative precision for all observable data. One quadrant of data was collected for the monoclinic crystal; one hemisphere for the triclinic crystal. Crystal data and angular limits for each compound are given in Table V. Data reduction included corrections for background, Lorentz, and polarization effects. Absorption corrections for the complex were based on ψ scans of reflections near χ = 90°. Equivalent data were averaged and reflections having $I > 3\sigma(I)$ were used in the refinements.

Structures were solved using MULTAN 78[24] and refined by full-matrix least squares based on F with weights $w = \sigma^{-2}(Fo)$. Non-hydrogen atoms were treated anisotropically; H atoms were located by difference maps and included as fixed contributions. Final R factors and residual electron densities are given in Table V.

Acknowledgment. We wish to thank the National Science Foundation, the National Institutes of Health, and LSU Center for Energy Studies for partial support of this work.

Supplementary Material Available: Coordinates for non-hydrogen atoms for **5** and **9**, bond distances and angles for **5** and **9**, coordinates for hydrogen atoms for **5** and **9**, anisotroic thermal parameters for **5** and **9**, and stereoscopic drawing of **5** (11 pages). Ordering information is given on any current masthead page.

(24) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M., "MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data"; Universities of York (England) and Louvain (Belgium), 1978.

[2 + 2] and [2 + 4] Cycloadditions of Difluoromethylenecyclopropanes

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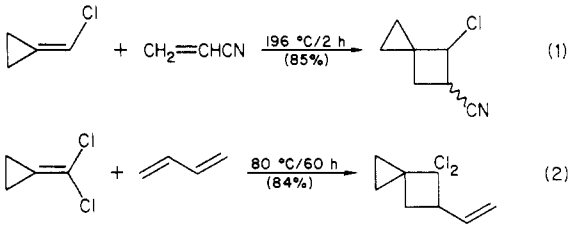
An improved synthesis of 2,2-difluoromethylenecyclopropane (**1**) is reported and its thermal cycloaddition reactions are compared with those of its isomer, (difluoromethylene)cyclopropane (**2**). 2,2-Difluoromethylenecyclopropane readily reacts with dienes in a [2 + 4] manner, whereas **2** predominantly undergoes [2 + 2] cycloadditions, including cyclodimerization. The factors that influence the reactivities of **1** and **2** are discussed.

Methylenecyclopropanes are relatively unreactive addends in cycloadditions. Some undergo thermal [2 + 2] dimerizations forming cyclobutanes,[2] as exemplified by methylenecyclopropane itself which will cyclodimerize in a head-to-head manner, but only to the extent of about 20% in 48 h at 245 °C.[2b] Certain radical-stabilizing substituents greatly enhance reactivity. (Dichloromethylene)cyclopropane, for instance, readily cyclodimerizes in high yield at 100 °C.[2d] The dimerizations, however, are quite sensitive to steric effects, inasmuch as that ethylidenecyclopropane,[3] isopropylidenecyclopropane,[2a] and 2,2-dimethylmethylenecyclopropane[2a] do not thermally cyclodimerize.

Methylenecyclopropanes also have been reported to undergo other [2 + 2] cycloadditions as shown in eq 1 and 2, although the examples are few.[2c,4]



(1)

(2)

The [2 + 2] cycloaddition reactions of methylenecyclopropanes are presumed to proceed via a two-step, biradical mechanism wherein the first step involves σ-bond formation to the highly strained sp^2-hybridized carbon of the methylenecyclopropane to give the most stable biradical intermediate, which determines the favored regiochemistry.[5] This mechanism is exemplified in eq 3 for the reaction of (dichloromethylene)cyclopropane with butadi-

(1) Contribution No. 3866.

(2) (a) Dolbier, W. R., Jr.; Lomas, D.; Garza, T.; Harmon, C.; Tarrant, P. *Tetrahedron* **1972**, *28*, 3185. (b) Binger, P. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 433. (c) Bottini, A. T.; Cabral, L. J. *Tetrahedron* **1978**, *34*, 3187. (d) Dolbier, W. R., Jr.; Lomas, D.; Tarrant, P. *J. Am. Chem. Soc.* **1968**, *90*, 3594. (e) Le Perchec, P.; Conia, J. M. *Tetrahedron Lett.* **1970**, 1587.

(3) Chesick, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 2720.

(4) Bartlett, P. D.; Wheland, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 2145.

(5) An exceptional case is the reported [2 + 2] cycloaddition of 4-phenyl-1,2,4-triazoline-3,5-dione to *trans*-2,3-dimethylmethylenecyclopropane[6a] for which a biradical mechanism is unlikely.[6b,c]

(6) (a) Pasto, D. J.; Chen, A. F. T. *Tetrahedron Lett.* **1972**, 2995. (b) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6385. (c) Cheng, C.-C.; Seymour, C. A.; Petti, M. A.; Greene, F. D.; Blount, J. F. *J. Org. Chem.* **1984**, *49*, 2910.

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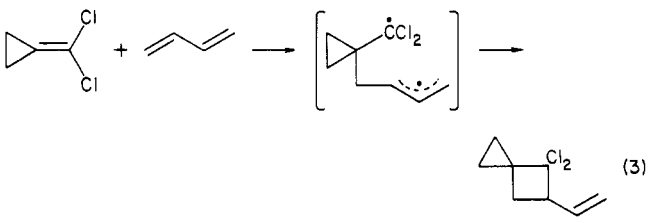
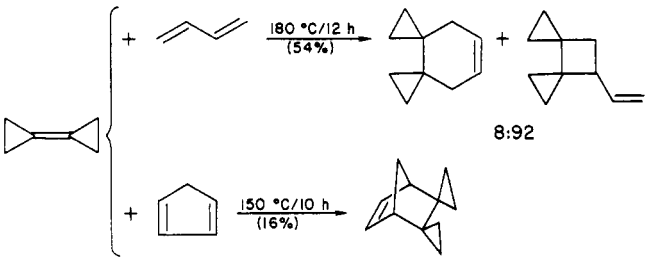
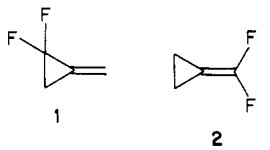


(3)

ene.[4] Not unexpectedly, methylenecyclopropanes also have been shown in isolated cases to participate in [2 + 4] cycloadditions.[7]



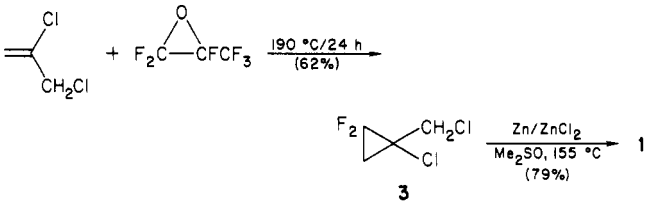
It is well-known that geminal fluorine substituents enhance the reactivity of olefins in biradical [2 + 2] cycloadditions.[8] It is now recognized that the major driving force for cycloaddition is the thermodynamic gain obtained from converting a vinyl CF_2 group to an alkyl CF_2 group.[9] Bartlett and Wheland[4] have emphasized the similarity between *gem*-difluoroalkenes and methylenecyclopropanes in thermal [2 + 2] cycloadditions and have argued that the double bonds in these olefins are similarly rehybridized and weakened relative to a normal alkene double bond. It therefore was somewhat surprising to find that perfluoromethylenecyclopropane,[10] which by analogy might be expected to behave like tetrafluoroethylene, does not undergo biradical [2 + 2] cycloadditions but is exceptionally reactive in [2 + 4] cycloadditions. It thus was of interest to investigate the cycloaddition reactions of the two partially fluorinated methylenecyclopropanes 1 and 2.[11] Whereas methylenecyclopropane 2 is predicted to be



especially reactive in [2 + 2] cycloadditions, much like tetrafluoroethylene, 1 should have no special [2 + 2] reactivity but should be a good dienophile, in part because of the electron-withdrawing inductive effect of the geminal allylic fluorines.

Results

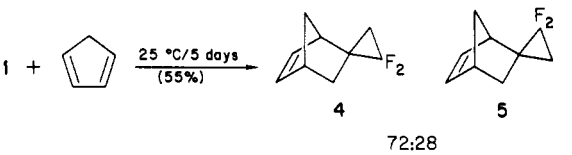
Synthesis of 2,2-Difluoromethylenecyclopropane (1) and (Difluoromethylene)cyclopropane (2). 2,2-Difluoromethylenecyclopropane was synthesized in two steps and 49% overall yield from 2,3-dichloropropene. Difluorocarbene, generated thermally from hexafluoropropylene oxide, was added to 2,3-dichloropropene to give 1-chloro-1-(chloromethyl)-2,2-difluorocyclopropane (3) in 62% yield. The dichloride was dehalogenated with Zn/$ZnCl_2$ in Me_2SO at 155 °C to give 1 in 79% yield. Interesting, no other dechlorination procedures proved effective.[12] This synthesis provides multigram quantities of 1 and is far superior to the method reported earlier,[11] which involved adding difluorocarbene to allene.



(Difluoromethylene)cyclopropane 2 was prepared by equilibrating 1 at 260–300 °C for about 30 min in a sealed tube. Under these conditions, 2 comprised about 70% of the mixture, and it was isolated by GLPC. Exact thermodynamic and kinetic parameters for this thermal equilibration have been reported.[11] Both 1 and 2 were fully characterized by their ^1H, ^{19}F, and ^{13}C NMR spectra.

Cycloadditions of 2,2-Difluoromethylenecyclopropane (1). 2,2-Difluoromethylenecyclopropane was found to be a quite reactive dienophile in Diels–Alder cycloadditions but was reluctant to undergo [2 + 2] cycloadditions.

With cyclopentadiene, 1 formed two isomeric [2 + 4] adducts in a total yield of 55% after 5 days at 25 °C. The identities of products 4 and 5 were established by ^1H, ^{19}F, and ^{13}C NMR, IR, and mass spectral data.



Proton NMR spectra, specifically the chemical shifts of the cyclopropane ring protons and the exo and endo protons at C_6, proved particularly useful in assigning the structures 4 and 5. For 4, the exo and endo protons were bunched together at about δ 1.64, whereas they appeared at δ 2.1 (d of d) and δ 1.2 (m) for 5. On the basis of predictions derived from spectra of exo and endo isomers of model compounds, 5-methylnorbornene[14] and 5-(trifluoromethyl)norbornene,[15] the structure assigned to 5 is more consistent with the observed separation of the exo and endo protons. Also consistent with the structural assignments of 4 and 5 are the chemical shifts of their respective cyclopropyl protons (δ 1.3 and 1.0). The methyl proton resonances in exo- and endo-5-methylnorbornene (δ 1.03 and 0.78, respecitvely) exhibit a similar difference in chemical shifts.[14]

In a similar reaction, 1 cycloadded to furan, albeit at higher temperature and in lower yield. The structures of 6 and 7 were assigned in a manner similar to and consistent with those of 4 and 5. Diphenylisobenzofuran (8) reacted

(7) Kaufman, D.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 159.
(8) (a) Roberts, J. D.; Sharts, C. M. *Org. React. (N. Y.)* **1962**, *12*, 1. (b) Sharkey, W. H. *Fluorine Chem. Rev.* **1968** *2*, 1. (c) Bartlett, P. D. *Q. Rev.* **1970**, *24*, 473.
(9) Dolbier, W. R., Jr.; Medinger, K. S. *Tetrahedron* **1982**, *38*, 2415.
(10) (a) Smart, B. E. *J. Am. Chem. Soc.* **1974**, *96*, 927. (b) Smart, B. E. *J. Am. Chem. Soc.* **1974**, *96*, 929.
(11) Dolbier, W. R., Jr.; Fielder, T. H., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 5577.
(12) 1-Chloro-1-(chloromethyl)-2,2-difluorocyclopropane (3) was inert to "activated"[13] Zn/$ZnCl_2$ in refluxing DMF, dioxane, diglyme, or acetic anhydride and to Mg/I_2 in refluxing THF. When 3 was heated to 160 °C in sulfolane, a rearrangement produce (1,3-dichloro-1,1-difluorobut-3-ene) was isolated in 26% yield. In the successful dechlorination with Me_2SO solvent, variable amounts of $(CH_3)_2S$ also were generated, depending upon the temperature. At 150–155 °C, more than an equivalent of $(CH_3)_2S$ per equivalent of 3 was generated. (Zn/$ZnCl_2$ and Me_2SO alone at 150–155 °C generated little $(CH_3)_2S$).
(13) Shriner, R. L.; Neumann, F. W. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 73.
(14) Moen, R. V.; Makowski, H. S. *Anal. Chem.* **1971**, *43*, 1629.
(15) Gaede, B.; Balthazor, T. M. *J. Org. Chem.* **1983**, *48*, 276.

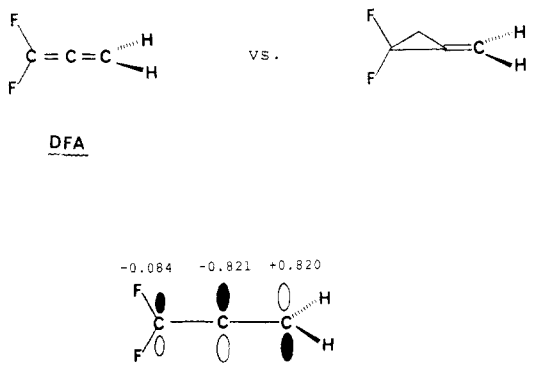
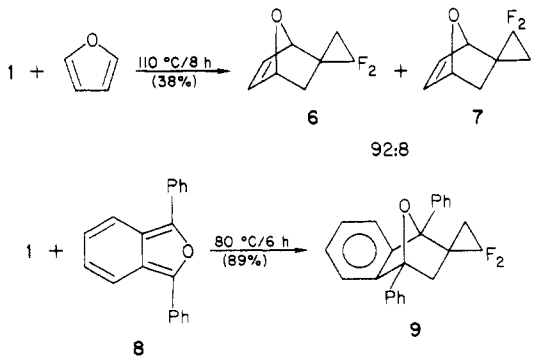
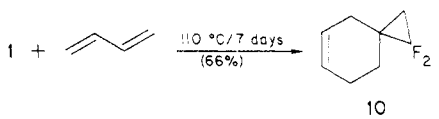


Figure 1. Extended Hückel AO coefficients for the difluoroallene (DFA) LUMO.

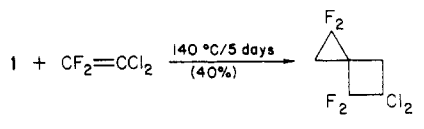
with 1 to give only one [2 + 4] adduct in 89% yield. Its NMR spectrum was consistent with the "endo" isomer **9**.



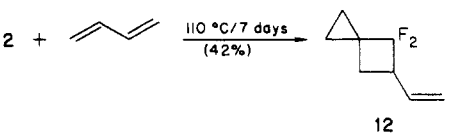
Butadiene was significantly less reactive than the cyclic dienes, and its reaction with **1** required 7 days at 110 °C to produce the single product **10** in 66% yield.



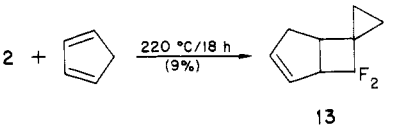
In the above reactions of **1** where there was potential competition between [2 + 2] and [2 + 4] processes, *only* [2 + 4] cycloadditions were observed. Only with one of the more reactive [2 + 2] addends, 1,1-dichloro-2,2-difluoroethylene, was **1** induced to undergo a [2 + 2] reaction. This reaction proceeded regiospecifically in low yield and the dimer of 1,1-dichloro-2,2-difluoroethylene was competitively formed under the reaction conditions.



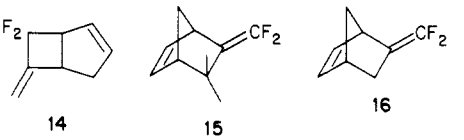
Cycloadditions of (Difluoromethylene)cyclopropane (2). In contrast to **1**, its isomer **2** preferentially underwent [2 + 2] cycloadditions with dienes. (Difluoromethylene)cyclopropane reacted with butadiene under the same conditions as did **1**, but **2** gave regiospecifically a single [2 + 2] adduct, **12**, in 42% yield.



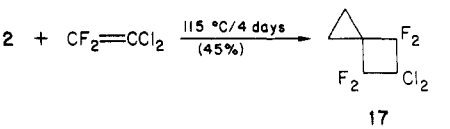
With cyclopentadiene, **2** reacted slowly at 220 °C to give in 9% yield a single cycloadduct, which proved to be the [2 + 2] adduct **13**.



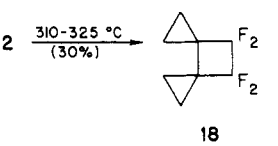
The structure of **13** could be differentiated from that of the alternative [2 + 4] adduct by comparing its ^{1}H, ^{19}F, and ^{13}C NMR spectra were those of model compounds. The spectra assigned to **13** were consistent with those of related compounds **12** and **14** but were inconsistent with those of the bicyclo[2.2.1]heptenes **15** and **16**. Most notably, the bicyclo[2.2.1]hept-2-ene systems exhibit an apparent single vinyl proton resonance, whereas the bicyclo[3.2.0]hept-2-ene systems show two distinct vinyl proton resonances.



(Difluoromethylene)cyclopropane proved to be considerably more reactive than **1** with 1,1-dichloro-2,2-difluoroethylene. It formed a single [2 + 2] adduct, **17**, in 45% yield after 4 days at 115 °C. It also was found that



2 cyclodimerized in 30% yield after 3.5 h at 310–325 °C to give the head-to-head dimer 7,7,8,8-tetrafluorodispiro[2.0.2.2]octane (**18**). Although **1** comprises about 30% of



the equilibrium mixture of **1** and **2** under these conditions, neither a cyclodimer of **1** nor a [2 + 2] cycloadduct between **1** and **2** was detected. No appreciable dimer **18** was formed at temperatures below 300 °C.

Discussion

2,2-Difluoromethylenecyclopropane (**1**) is a moderately reactive dienophile in Diels–Alder reactions. This is consistent with expectations for a normal concerted mechanism in that the two allylic fluorine substituents should activate the double bond by lowering the energy of its LUMO. A similar effect is observed for 3,3,3-trifluoropropene, which is somewhat less reactive than **1** but is a much more reactive dienophile than ethylene or propylene.[15,16] The inductive effect in **1** may be more pronounced because of its relatively short C_1–C_2 bond. More important, the methylenecyclopropane double bond should be activated toward cycloaddition because of the release of approximately 13 kcal/mol of strain[17] upon σ-bond formation at C_1. The combined inductive and strain effects makes **1** a much better dienophile than simple alkenes.

It is interesting that the adduct with the CF_2 group endo is preferred over that with CF_2 exo in the reaction of **1** with cyclopentadiene, furan, or **8**. This finding may relate to the reported regiospecific [2 + 4] and 1,3-dipolar cycloadditions to the nonfluorinated π-bond in 1,1-difluoro-

(16) McBee, E. T.; Hsu, C. G.; Pierce, O. R.; Roberts, C. W. *J. Am. Chem. Soc.* **1955**, *77*, 915.
(17) Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395.

allene (DFA).[18] The importance of C–F σ-bond interaction on the shape of the LUMO in DFA (Figure 1) was supported by extended Hückel[18a] and ab initio[18c] MO calculations. Since **1** is structurally somewhat analogous to DFA, there indeed may be a similar contribution of the C–F σ-bonds to the LUMO of **1**, which would give rise to the endo preference observed for the CF_2 group. A 4:1 preference for the endo over the exo [2 + 4] cycloadduct from 3,3,3-trifluoropropene and cyclopentadiene also has been reported[15] and may similarly reflect the importance of secondary C–F orbital interactions.

In contrast, (difluoromethylene)cyclopropane underwent [2 + 2] rather than [2 + 4] cycloadditions. This is consistent with the general observation that fluorinated ethylenes are very poor dienophiles[19] but are reactive [2 + 2] addends.[8] Indeed, the behavior of **2** parallels that of tetrafluoroethylene (TFE) in accord with the hypothesis of Bartlett and Wheland.[4] Like TFE, **2** cyclodimerizes, smoothly [2 + 2] cycloadds to 1,1-dichloro-2,2-difluoroethylene, and reacts with butadiene to give only a single, [2 + 2] cycloadduct. Although quantitative comparisons cannot be made, qualitatively **2** is somewhat less reactive than TFE in [2 + 2] cycloadditions. For instance, TFE rapidly dimerizes at 200 °C[20]—**2** requires over 300 °C; TFE cycloadds to butadiene in 90% yield after 8 h at 125 °C[21]—**2** cycloadds but in only 42% yield after 7 days at 110 °C; TFE cycloadds to 1,1-dichloro-2,2-difluoroethylene in 50% yields after 20 h at 200 °C[22]—**2** cycloadds in 40% yield after 5 days at 140 °C.

The behavior of **1** and **2** compared with that of perfluoromethylenecyclopropane[10] indicates that the reactivity of the latter is dominated by its four allylic fluorines, which so enhance [2 + 4] reactivity that its geminal vinyl fluorines have little effect. The failure of both **1** and perfluoromethylenecyclopropane to cyclodimerize further suggests that the ring fluorine substituents impart a rate-retarding steric effect on biradical [2 + 2] reactivity.[10b]

In conclusion, methylenecyclopropanes undergo thermal [2 + 2] cycloadditions mainly because of their highly strained double bonds. This reactivity can be markedly enhanced by sterically modest, radical-stabilizing substituents such as Cl on the vinyl carbon, but *any* geminal substituents on the ring carbons markedly decrease biradical [2 + 2] reactivity. Fluorine substituents on the vinyl carbon modestly increase [2 + 2] reactivity, but direct relative rate comparisons with methylenecyclopropane itself were not made. Methylenecyclopropanes are to a lesser extent reactive in Diels–Alder additions. Allylic fluorine substituents as in **1** or perfluoromethylenecyclopropane dramatically increase this reactivity, whereas vinyl fluorine substituents as in **2** do not. With the absence of similar studies on Diels–Alder reactions of methylenecyclopropane itself, however, the actual kinetic effect of the fluorines in **2** on [2 + 4] reactivity cannot be ascertained.

Experimental Section

Infrared spectra were determined either as films between KBr plates or in solution with matched liquid cells (0.1 mm). NMR chemical Shifts for ^1H spectra are reported in parts per million downfield from internal Me_4Si in $CDCl_3$ solution. Chemical shifts for ^{19}F spectra are reported in parts per million upfield from internal $CFCl_3$ in $CDCl_3$ solution. Chemical shifts for ^{13}C spectra are reported in parts per million downfield from internal Me_4Si in $CDCl_3$ solution. Reported exact masses are an average of at least five scans.

1-(Chloromethyl)-1-chloro-2,2-difluorocyclopropane (3). A 500-mL stainless steel rocker bomb was charged with 35.0 g (0.272 mol) of 2,3-dichloropropene and 60.0 g (0.362 mol) of hexafluoropropylene oxide and heated at 189 °C for 24 h. After cooling and venting, the bomb was opened and washed with 62 mL of CH_2Cl_2. The resulting solution was washed with water and then a saturated NaCl solution and dried over $MgSO_4$. The CH_2Cl_2 was removed on a rotary evaporator, and the residual liquid was fractionated to afford 31.2 g (62%) of **3**: bp 62–64 °C (100 mm); ^1H NMR δ 1.83–1.92 (m, 2 H), 3.85 (br d, 2 H); ^{19}F NMR ϕ 133.1 and 138.0 (AB with further splitting, J_{FF} = 156.8 Hz); ^{13}C NMR δ 110.8 (t, J_{CF} = 293.6 Hz, CF_2), 46.8 (t, J_{CF} = 6.1 Hz, CH_2Cl), 45.7 (t, J_{CF} = 11.6 Hz, C_1), 26.0 (t, J_{CF} = 10.4 Hz, CH_2); IR (film) 3097, 3012, 2964, 1457, 1449, 1367, 1283, 1250, 1212, 1176, 1057, 1032, 1000 (s), 987 (s), 895 cm^{-1}. Anal. Calcd for $C_4H_4Cl_2F_2$: C, 29.84; H, 2.51; F, 23.60. Found: C, 30.05; H, 2.61; F, 23.95.

2,2-Difluoromethylenecyclopropane (1) and 1,3-Dichloro-1,1-difluorobut-3-ene. All glassware was oven-dried beforehand. A three-necked, 500-mL, round-bottomed flask was equipped with a magnetic stirrer bar, a pressure equalizing addition funnel, and a vertical water condenser that was attached to a bubbler containing a saturated aqueous solution of mercuric acetate, which in turn was attached to two traps at −78 °C. The flask was charged with Zn dust (34.0 g, 520 mmol), anhydrous $ZnCl_2$ (7.0 g, 51.3 mmol), and dry Me_2SO (100 mL). 1-(Chloromethyl)-1-chloro-2,2-difluorocyclopropane (**3**) (16.0 g, 100 mmol) was added dropwise over 30 min to this mixture, which was stirred as rapidly as possible while the pot temperature was maintained at 155 °C. The reaction mixture was kept at 155 °C for 3 h, after which time the additional funnel was replaced with a N_2 gas inlet. The system was then maintained under a slow flow of N_2 for an additional 2 h. The flow of N_2 through the system should be adjusted so that the dimethyl sulfide which is produced during the reaction is efficiently trapped by the mercuric acetate solution. The 7.09 g (79%) of liquid that collected in the first −78 °C trap was ca. 98% pure **1** by GLPC (15 ft × $^1/_4$ in 20% SE-30 column, 60 °C): bp 23–24 °C; ^1H NMR δ 1.92–1.98 (m, 2 H), 5.65–5.68 (m, 1 H), 5.97–6.00 (m, 1 H); ^{19}F NMR ϕ 132.2 (m, 2 F); ^{13}C NMR δ 127.9 (t, $^2J_{CF}$ = 7.9 Hz, C_1), 111.4 (s, $=CH_2$), 106.3 (t, J_{CF} = 288.1 Hz, CF_2), 18.6 (t, J_{CF} = 12.8 Hz, CH_2); IR (gas) 3080 (w), 2963, 1775, 1457, 1448, 1440, 1288 (s), 1215 (s), 1090, 1021, 795, 714 (s) cm^{-1}; mass spectrum, m/z (relative intensity) 91 (M^+ + 1, 1.5) 90 (M^+, 34), 64 (100), 51 (25), 46 (7), 45 (8), 39 (53), 38 (10).

If the above experimental procedure was followed using dry sulfolane in place of Me_2SO, then 1,3-dichloro-1,1-difluorobut-3-ene was produced in 26% yield: ^1H NMR δ 3.32 (t, with further splitting, J_{HF} = 12.1 Hz, 2 H), 5.46 (br s, 1 H), 5.55 (br s, 1 H); ^{19}F NMR ϕ 51.5 (t, J_{HF} = 12.1 Hz); ^{13}C NMR δ 131.5 (s, C_3), 127.1 (t, J_{CF} = 293.8 Hz, CF_2Cl), 119.8 (s, $=CH_2$), 50.5 (t, J_{CF} = 26.2 Hz, CH_2); IR (gas) 2964, 1640, 1426, 1363, 1259, 1207, 1180, 1160, 1101 (s), 1019 (s), 988, 894, 794, 714 cm^{-1}; mass spectrum, m/z (relative intensity) 165 (0.2), 164 (5.0), 163 (1.3), 162 (32.3), 161 (2.3), 160 (M^+, 50) 127 (34), 125 (94), 111 (29), 89 (100), 85 (22), 75 (25), 61 (26), 39 (72).

(Difluoromethylene)cyclopropane (2). A thick-walled glass tube charged with 2,2-difluoromethylenecyclopropane (**1**) (1.03 g, 11.44 mmol) was sealed under vacuum and heated at 260 °C for 40 min. The tube was then cooled to liquid N_2 temperature, opened, and rapidly connected to a vacuum system. The products (0.95 g, 92%) were transferred to a cold finger and then separated by GLPC (15 ft × $^1/_4$ in. 20% SE-30 column, 25 °C) to give **1** (0.28 g) and (difluoromethylene)cyclopropane (**2**) (0.66 g): ^1H NMR δ 1.36 (t, J_{HF} = 4.2 Hz, 4 H); ^{19}F NMR ϕ 88.4 (quintet, J_{HF} = 4.2 Hz, 2 F); ^{13}C NMR δ 150.4 (t, J_{CF} = 275.3 Hz, $=CF_2$), 67.8 (t, J_{CF} = 37.8 Hz, C_1), 3.1 (s, CH_2); IR (gas) 2962, 1860 (s), 1257 (s), 1238, 1090, 1015 (s), 793 (s), 714 (s) cm^{-1}; mass spectrum, m/z (relative intensity) 91 (M^+ + 1, 3.0), 90 (M^+, 66) 89 (11), 75 (12), 64 (100),

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51 (24), 40 (22), 39 (58), 38 (15).

***endo*- and *exo*-1′,1′-Difluorospiro[bicyclo[2.2.1]hept-2-ene-5,2′-cyclopropane] (4 and 5).** Into an evacuated glass tube cooled in liquid N_2 was condensed 0.141 g (2.14 mmol) of cyclopentadiene along the 0.096 g (1.07 mmol) of **1**. The tube was sealed under vacuum and allowed to warm to room temperature. After 5 days at room temperature, the tube was placed in a dry ice bath, opened, and quickly stoppered with a septum. The reaction mixture was separated by GLPC on a $^1/_4$ in. × 15 ft 20% TCP column. The slower eluting product, 0.066 g (39.5%), was collected and identified as **4**: ^{1}H NMR δ 1.29 (m, 2 H), 1.55 (m, 2 H), 1.67 (m, 2 H), 2.5 (br s, 1 H), 3.02 (br s, 1 H), 6.18 (m, 2 H); ^{19}F NMR ϕ 134.25 and 136.13 (AB with further splitting, J_{FF} = 158.6 Hz); ^{13}C NMR ϕ 136.9 (s, C_2), 134.6 (s, C_3), 115.8 (t, J_{CF} = 287.8 Hz, C_9) 49.3 (s, C_7), 48.1 (s, C_4), 42.2 (s, C_1), 34.5 (s, C_5), 34.0 (t, $^2J_{CF}$ = 9.1 Hz, C_6), 20.6 (t, $^2J_{CF}$ = 10.2 Hz, C_8); IR (neat) 1470, 1150, 1005, 890, 700 cm^{-1}; mass spectrum gave M$^+$ = 156.0738 ± 0.0008 (5.6 ppm), calcd for $C_9H_{10}F_2$ 156.0750 dev 0.0012 (7.9 ppm).

The minor component, 0.026 g (15.6%), also was collected and identified as **5**: ^{1}H NMR δ 1.02 (m, 2 H), 1.19 (m, 1 H), 1.45–1.6 (m, 2 H), 2.08 (br d, 1 H), 2.6 (br s, 1 H), 3.0 (br s, 1 H), 6.15 (d of d, 1 H), 6.32 (d of d, 1 H); ^{19}F NMR ϕ 132.9 and 138.8 (AB with further splitting, J_{FF} = 150.7 Hz); ^{13}C NMR δ 136.9 (s, C_2), 134.6 (s, C_3), 115.8 (t, J_{CF} = 287.8 Hz, C_9), 49.3 (s, C_7), 48.1 (s, C_4), 42.7 (s, C_1), 34.5 (s, C_5), 34.0 (t, $^2J_{CF}$ = 9.1 Hz, C_6), 18.6 (t, $^2J_{CF}$ = 10.3 Hz, C_8); IR(neat) 1470, 1150, 1005, 890, 700 cm^{-1}; mass spectrum gave M$^+$ = 156.0745 ± 0.0018 (12 ppm), calcd for $C_9H_{10}F_2$ 156.0750 dev 0.0005 (3.3 ppm).

***endo*- and *exo*-1′,1′-Difluoro-7-oxaspiro[bicyclo[2.2.1]-hept-2-ene-5,2′-cyclopropane] (6 and 7).** The same procedure described above was used to react 0.392 g (5.76 mmol) of furan and 0.130 g (1.44 mmol) of **1** for 4 h at 140 °C. The products were separated on a $^1/_4$ in. × 20 ft 20% TCP column. Thus, 0.079 g (35%) of the earlier eluting fraction was collected and identified as **6**: ^{1}H NMR δ 1.42 (br q, 1 H), 1.63 (m, 1 H), 1.68 (br d, 1 H), 2.0 (m, 1 H), 4.53 (br s, 1 H), 5.17 (br d, 1 H), 6.48 (m, 2 H); ^{19}F NMR ϕ 134.3 and 136.2 (AB with further splitting, J_{FF} = 160.7 Hz); ^{13}C NMR δ 136.3 (s, C_2), 134.3 (s, C_3), 113 (t, t J_{CF} = 280.2 Hz, C_8), 82.2 (s, C_4), 79.8 (s, C_1), 33.7 (t, $^2J_{CF}$ = 9.8 Hz, C_6), 33.3 (s, C_5) 20.1 (t, $^2J_{CF}$ = 10.2 Hz, C_7); C_7); IR (neat) 885, 910, 1110, 1120, 1380 cm^{-1}; mass spectrum gave M$^+$ = 158.0465 ± 0.0026 (17 ppm), calcd for $C_8H_8F_2O$ 158.0465 dev 0.00001 (0.02 ppm).

A later fraction, 0.007 g (3%), also was collected and identified as **7**: ^{1}H NMR δ 1.12–1.34 (m, 3 H), 2.29 (d of d, 1 H), 4.70 (br s, 1 H), 5.13 (d, 1 H), 6.45 (d of d, 1 H), 6.56 (d of d, 1 H); ^{19}F NMR ϕ 134.5 and 138.6 (AB with further splitting, J_{FF} = 155.1 Hz); ^{13}C NMR δ 139.2 (s, C_2), 135.4 (s, C_3), 113.5 (t, J_{CF} = 287.1 Hz, C_8), 80.8 (s, C_4), 80.2 (s, C_1), 34.4 (t, $^2J_{CF}$ = 10.1 Hz, C_6), 34.2 (s, C_5), 17.5 (t, $^2J_{CF}$ = 10.3 Hz, C_7); IR (neat) 660, 890, 910, 1090, 1210, 1370 cm^{-1}; mass spectrum gave M$^+$ = 158.0470 ± 0.0002 (16.6 ppm), calcd for $C_8H_8F_2O$ 158.0465 dev 0.0005 (3.7 ppm).

***endo*-1,4-Epoxy-1′,1′-difluoro-1,2,3,4-tetrahydro-1,4-diphenylspiro[naphthalene-2,2′-cyclopropane] (9).** A sealed tube containing a mixture of 0.300 g (1.11 mmol) of diphenylisobenzofuran, 0.281 g (3.12 mmol) of **1**, and 4.3 mL of $CHCl_3$ was heated for 6 h at 80 °C. The volatiles were removed under vacuum, and the residual solid was purified by column chromatography to give 0.357 g (89%) of **9**: ^{1}H NMR δ 1.28 (m, 2 H) 2.65 (m, 2 H), 8.0–9.0 (m, 14 H); ^{19}F NMR ϕ 127.6 and 139.5 (AB with further splitting, J_{FF} = 163.6 Hz); ^{13}C NMR δ 128.5–127.1 (Ar), 123.3 (t, J_{CF} = 291.5 Hz, C_7), 119.4 (s, C_2), 119.3 (s, C_3), 88.9 (s, C_1), 87.6 (s, C_4), 42.3 (s, C_5), 41.3 (t, $^2J_{CF}$ = 11.1 Hz, C_6), 18.5 (t, $^2J_{CF}$ = 10.0 Hz, C_8); IR ($CDCl_3$) 3070, 3040, 2965, 1610, 1461, 1450, 1371, 1314, 1270, 1165, 1117, 1095, 983, 699 cm^{-1}; mass spectrum gave M$^+$ = 360.1230 ± 0.0025 (7 ppm), calcd for $C_{24}H_{18}F_2O$: 360.1232 dev 0.0002 (0.1 ppm).

1,1-Difluorospiro[2.5]oct-5-ene (10). A mixture of 0.10 g (1.86 mmol) of butadiene and 0.084 g (0.93 mmol) of **1** was heated for 7 days in a sealed tube at 110 °C. The product mixture was chromatographed on a $^1/_4$ in. × 20 ft 15% DNP column to give 0.0884 g (63%) of **10**: ^{1}H NMR δ 1.04 (complex d, 2 H), 1.75 (d of d, 2 H), 2.13 (m, 4 H), 5.75 (complex d, 2 H); ^{19}F NMR ϕ 139.5 and 142.5 (AB with further splitting, J_{FF} = 163.2 Hz); IR (neat), 1475, 1200, 1010, 960, 900, 700, 650 cm^{-1}; mass spectrum gave M$^+$ = 144.0756 ± 0.0021 (15 ppm), calcd for $C_8H_{10}F_2$ 144.0750 dev 0.0006 (4.4 ppm).

5,5-Dichloro-1,1,4,4-tetrafluorospiro[2.3]hexane (11). A sealed tube containing 0.103 g (1.14 mmol) of **1** and 0.30 g (2.28 mmol) of 1,1-dichloro-2,2-difluoroethylene was heated for 5 days at 140 °C. The reaction mixture was separated on a $^1/_4$ in. × 10 ft 20% SE-30 column to give 0.093 g (40%) of the [2 + 2] adduct **11**: ^{1}H NMR δ 1.62 (m, 1 H), 2.02 (septet, 1 H), 2.68 (septet, 1 H), 3.2 (m, 1 H); ^{19}F NMR ϕ 100.1 and 101.8 (AB with further splitting, cyclobutyl fluorines, J_{FF} = 180.1 Hz), 130.5 and 139.9 (AB with further splitting, cyclopropyl fluorines, J_{FF} = 163.9 Hz); ^{13}C NMR δ 115.3 (dd, $^1J_{CF}$ = 297.3, 287.5 Hz, C_4), 110.2 (t, $^1J_{CF}$ = 289.9 Hz, C_1), 86.5 (t, $^2J_{CF}$ = 28.1 Hz, C_5), 37.1 (t, $^2J_{CF}$ = 24.3 Hz, C_2), 35.4 (m, C_3), 20.7 (t, $^3J_{CF}$ = 10.3 Hz, C_6); IR (neat) 1485, 1395, 1300, 1250, 1220, 1000, 980, 910, 900, 825 cm^{-1}; mass spectrum gave M$^+$ − 20 = 201.9580 ± 0.0032 (16 ppm), calcd for $C_6H_3F_3Cl_2$ 201.9600 dev 0.0016 (8.2 ppm).

4,4-Difluoro-5-vinylspiro[2.3]hexane (12). A sealed tube containing 0.104 g (1.15 mmol) of **2** and 0.11 g (2.12 mmol) of butadiene was heated at 110 °C for 7 days. The reaction mixture was separated on a $^1/_4$ in. × 20 ft 20% TCP column to give 0.069 g (41.6%) of **12**: ^{1}H NMR δ 0.7 (br s, 2 H), 1.0 (d of d, 2 H), 2.1 (complex d, 2 H), 3.5 (m, 1 H), 5.2 (m, 2 H), 6.0 (m, 1 H); ^{19}F NMR ϕ 94.1 and 110.7 (AB with further splitting, J_{FF} = 189.7 Hz); ^{13}C NMR ϕ 133.0 (s, C_2), 124.2 (t, J_{CF} = 279.1 Hz, C_4), 117.0 (s, C_1), 48.7 (t, $^2J_{CF}$ = 22.6 Hz, C_3), 28.3 (s, C_6),27.1 (t, $^2J_{CF}$ = 7.1 Hz, C_5), 9.5 (s, C_7), 8.5 (s, C_8); IR (neat) 660, 705, 910, 970, 1000, 1200, 1475 cm^{-1}; mass spectrum gave M$^+$ = 144.069 ± 0.0012 (8.3 ppm), calcd for $C_8H_{10}F_2$ 144.070 dev 0.0007 (0.5 ppm).

2,2-Difluorospiro[bicyclo[3.2.0]hept-4-ene-1,1′-cyclopropane] (13). To a 150-mL thick-walled glass tube containing cyclopentadiene dimer (3.00 g, 22.7 mmol) was condensed 0.43 g (4.77 mmol) of **2**. The tube was chilled, sealed under vacuum, and heated at 220 °C for 18 h. On cooling to room temperature, the contents of the tube partially solidified. The tube was chilled and opened, and the product was transferred to a cold finger under vacuum to give 1.53 g (45%) of colorless liquid. A white polymeric solid residue (1.57 g, 46%) remained in the tube. The volatile liquid was analyzed by GLPC (8 ft × $^1/_4$ in. 20% SE-30 column, 150 °C) and was found to comprise starting materials and several other components. Preparative scale GLPC afforded three fluorine-containing products. Two were identified as [2 + 4] adducts of cyclopentadiene and **1** (**4** and **5**). The other isolated fluorine-containing adduct, 66 mg (9% yield based on recovered **2**), was identified as **13**: ^{1}H NMR δ 0.40–0.49 (m, 1 H), 0.55–0.64 (m, 1 H), 0.72–0.79 (m, 1 H), 0.98–1.04 (m, 1 H) (four cyclopropyl protons), 1.85 and 2.13 (AB with further splitting, J_{HH} = 8.9 Hz, 2 H), 2.19 (br s, 1 H), 6.16 (m, 1 H), 6.53 (m, 1 H); ^{19}F NMR ϕ 98.0 and 106.8 (AB with further splitting, J_{FF} = 212 Hz); ^{13}C δ 140.8 (d, J = 2.6 Hz, C_5), 131.8 (dd, J = 5.8, 18 Hz, C_4), 130.8 (t, J_{CF} = 254.5 Hz, C_2), 51.1 (dd, J = 25.2, 22.6 Hz, C_6), 49.0 (dd, J = 3.3, 1.7 Hz, C_7), 47.9 (dd, J = 2.8, 1.0 Hz, C_6), 31.9 (t, J_{CF} = 23.7 Hz, $C_{1,1'}$), 8.7 (d, J = 9.6 Hz, C_2, or $C_{3'}$), 7.4 (dd, J = 6.6, 1.9 Hz, C_3 or $C_{2'}$); mass spectrum, m/z (relative intensity) 157 (M$^+$ + 1, 1.36), 156 (M$^+$, 14), 141 (10), 127 (15), 92 (19), 91 (26), 66 (100), 51 (10), 39 (15); mass spectrum gave M$^+$ = 156.0727 ± 0.0013 (8.8 ppm), calcd for $C_9H_{10}F_2$ 156.0750 dev 0.0022 (14.5 ppm).

5,5-Dichloro-4,4,6,6-tetrafluorospiro[2.3]hexane (17). A mixture of 0.103 g (1.14 mmol) of **2** and 0.300 g (2.28 mmol) of 1,1-dichloro-2,2-difluoroethylene in a sealed tube was heated for 4 days at 115 °C. The reaction mixture was separated on a $^1/_4$ in. × 20 ft TCP column to give 0.115 g (44.9%) of **17**: ^{1}H NMR δ 1.2 (s, 4 H); ^{19}F NMR ϕ 107.1 (s); IR ($CDCl_3$) 1380, 1310, 1190, 900, 730, 650 cm^{-1}; mass spectrum gave M$^+$ = 221.8961 ± 0.0041 (18.5 ppm), calcd $C_6H_4F_4Cl_2$ 221.9026 dev 0.0064 (2.4 ppm).

7,7,8,8-Tetrafluorodispiro[2.0.2.2]octane (18). 2,2-Difluoromethylenecyclopropane (**1**) (2.30 g, 25.6 mmol) was sealed under vacuum in a thick-walled 165-mL glass tube. The tube was heated at 312 °C for 3.5 h, then cooled to liquid N_2 temperature, and opened, and the contents (1.75 g, 76%) were transferred to a cold finger under vacuum. A quantity of polymeric material remained in the tube. The material that collected on the cold finger was thawed and trap-to-trap distilled to yield 0.38 g of ca. a 70/30 mixture of **2** and **1** by ^{19}F NMR and a white solid residue. The solid was sublimed under reduced pressure to give 0.68 g (30%) of the white crystalline head-to-head cyclodimer **18**: mp 64–65 °C; ^{1}H NMR δ 0.51–0.58 (m, 2 H), 1.06–1.10 (m, 2 H); ^{19}F NMR ϕ 119.4 (br t, J_{HF} = 2.8 Hz); ^{13}C NMR δ 120.4 (tt, J_{CF} =

289.3, 26.7 Hz, CF_2), 29.4 (m, $C_{3,4}$), 7.0 (s, $C_{1,2,5,6}$): IR (CCl_4) 3088 (w), 3012, 1401, 1342, 1331, 1256, 1168, 1138 (3), 1112, 1053 (s), 1016, 974 cm^{-1}; mass spectrum, m/z (relative intensity) 160 ($M^+ - 20$, 7.0), 145 (100), 127 (33), 116 (31), 115 (70), 111 (50), 109 (77), 101 (60), 90 (58), 77 (63), 75 (42), 64 (43), 51 (59) and 39 (80).

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Registry No. **1**, 67884-63-3; **2**, 67884-64-4; **3**, 100207-83-8; **4**, 100207-84-9; **5**, 100296-07-9; **6**, 100207-85-0; **7**, 100296-08-0; **8**, 5471-63-6; **9**, 100207-86-1; **10**, 100207-87-2; **11**, 100207-88-3; **12**, 100207-89-4; **13**, 100207-90-7; **17**, 100207-92-9; **18**, 100207-93-0; $H_2C{=}C(Cl)CH_2Cl$, 428-59-1; $H_2C{=}CHCH{=}CH_2$, 106-99-0; $F_2C{=}CCl_2$, 79-35-6; $ClCF_2CH_2C(Cl){=}CH_2$, 100207-91-8; hexafluoropropylene oxide, 428-59-1; cyclopentadiene, 542-92-7; furan, 110-00-9; cyclopentadiene dimer, 7313-32-8.

Synthesis of 1,5-Diamino-1,5-dihydrobenzo[1,2-*d*:4,5-*d*']bistriazole (DABT) and Its Use as a 1,4-Benzadiyne Equivalent[1]

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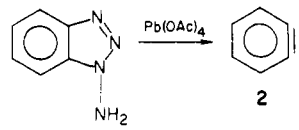
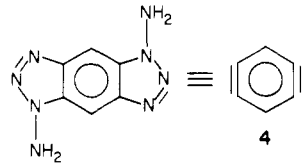
Amination of 1,5-dihydrobenzo[1,2-*d*:4,5-*d*']bistriazole (**9**) gives the 1,5- and 1,7-diamino derivatives **3** and **10**, both useful as 1,4-benzadiyne equivalents, as well as the 1,6 isomer **11** and the recyclable monoamino derivatives **12** and **13**. Sixteen examples of the synthetic utility of DABT (**3**) with lead tetraacetate in bisannulations are described (Table I). The aryne-trapping dienes include ester, halogen, and carbonyl functionality; often the reactions are quite regio- and stereoselective as a consequence of the stepwise nature of the annulations.

Oxidation of 1-aminobenzotriazole (**1**) with lead tetraacetate has long been known as a useful way of generating benzyne (**2**) under mild conditions.[2,3] We will describe



1 2

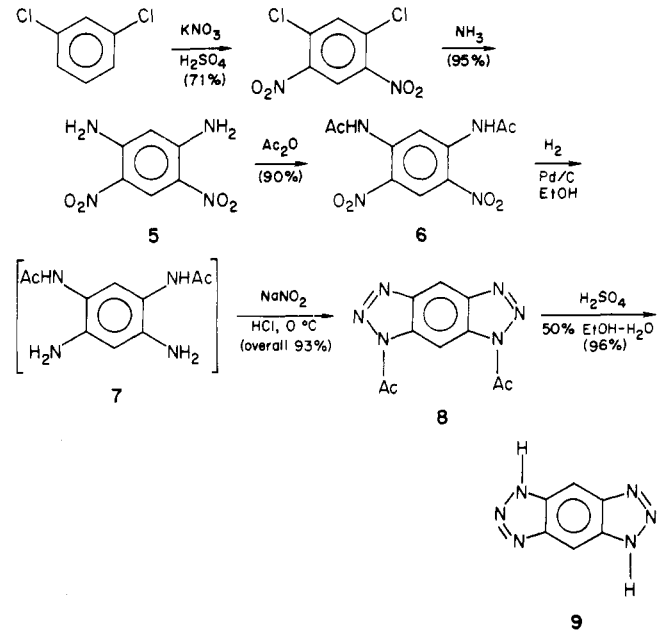
here the synthesis of **3** (1,5-diamino-1,5-dihydrobenzo-[1,2-*d*:4,5-*d*']bistriazole for which we use the acronym DABT) and its use via similar oxidations as the synthetic equivalent of 1,4-benzadiyne (**4**).



3 4

We have recently described the use of 1,2,4,5-tetrabromobenzene and analogous polyhaloarenes as synthetic equivalents of **4** as a consequence of metal–halogen exchange with butyllithium and subsequent aryne formation by lithium bromide elimination.[4,5] One limitation of this method when applied to biscycloadditions is that the diene cannot contain functionality that will react with butyllithium and, hence, prevent aryne formation. In practice, this means that the diene usually cannot contain certain carbonyl functions, halogens, and so on. It was thought that **3** would be useful as a benzadiyne equivalent in these instances and this notion has turned out to be correct.

Scheme I



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(1) For a preliminary account, see: Hart, H.; Ok, D. *Tetrahedron Lett.* **1984**, *25*, 2073.

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(5) Other di-aryne equivalents which have seen limited use include (a) 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), (b) treatment of bis(*o*-bromotosylates) with strong base (LeHoullier, C. S.; Gribble, G. W. *J. Org. Chem.* **1983**, *48*, 1682), and (c) thermal cycloadditions to bis(1,4-epoxyarenes) (Hart, H.; Raju, N.; Meador, M. A.; Ward, D. L. *J. Org. Chem.* **1983**, *48*, 4357).

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