Bismabenzene. The Reaction of Group V Heteroaromatic Compounds with Hexafluorobutyne

Sir:

Our interest in the problem of incorporating heavier atoms in aromatic rings has led us to try to obtain the group V heteroaromatic compounds **1a**–**1e**. These compounds should provide a graded series in which carbon is multiply bonded to an entire column of elements. A comparative study of their spectra and chemistry should provide detailed information about bonding in heterocyclic aromatic systems as a function of increasing atomic number of the heteroatom. The first four members of this series, pyridine **1a**, phosphabenzene[1] **1b**, arsabenzene[1] **1c**, and stibabenzene[2] **1d**, are now available. We now wish to report on our attempts to prepared bismabenzene (bismin) **1e**.

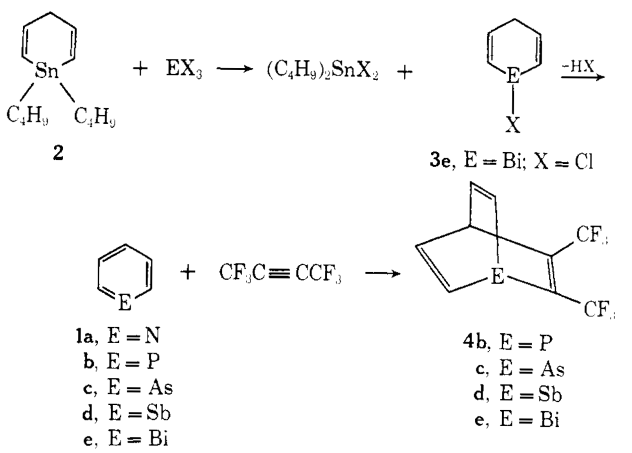
The exothermic reaction of 1,4-dihydro-1,1-dibutylstannabenzene (**2**)[3] and bismuth trichloride gave a precipitate of 1,4-dihydro-1-chlorobismabenzene (**3e**). Recrystallization from THF afforded a 75% yield of yellow crystals: mp 144–145° dec; nmr (THF-d_8) τ 5.5 (m, 2 H), 3.3 (d of t, J = 12, 4 Hz, 2 H), 2.5 (d of t, J = 12, 2 Hz, 2 H). *Anal.* Calcd for C_5H_6BiCl: C, 19.34; H, 1.95. Found: C, 19.36; H, 2.05.

Treating a THF solution of **3e** with 1,5-diazabicyclo-[4.3.0]non-5-ene caused an exothermic loss of HCl with the production of polymeric material. While it is tempting to suppose that bismabenzene has transient existence in this system, our attempts at isolation have failed.

On the other hand, addition of hexafluorobutyne after precipitation of the hydrochloride of the base gave an adduct which could be isolated by glpc. This 1:1 adduct was assigned structure **4e** on the basis of its spectra.[4] *Anal.* Calcd for $C_9H_5BiF_6$: C, 24.79; H, 1.15. Found: C, 24.81; H, 1.25.

The proton nmr spectrum (CCl_4) shows a one-proton triplet at τ 4.05 (J = 8 Hz) due to the bridgehead proton and a two-proton triplet at τ 2.24 (J = 8 Hz) assigned to the protons at C_5 and C_8, while the doublet at τ 1.55 (J = 8 Hz) is due to the protons adjacent to the metal atom.[5] Formation of adduct **4e** is consistent with the intermediacy of bismabenzene.

For comparison we have examined the reaction of the other group V heteroaromatics with hexafluorobutyne. Pyridine does not show Diels–Alder reactions but instead gives nucleophilic addition to dienophiles.[6] In contrast 2,4,6-trisubstituted phosphabenzenes are reported to form the corresponding 1-phosphabarrelene adducts when treated with hexafluorobutyne at 100° for 2 days.[7] The parent phosphabenzene reacts under the same conditions to give a 1:1 adduct. *Anal.* Calcd for $C_9H_5PF_6$: C, 41.86; H, 1.95. Found: C, 41.63; H, 2.02.



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3e, E = Bi; X = Cl

1a, E = N
b, E = P
c, E = As
d, E = Sb
e, E = Bi

4b, E = P
c, E = As
d, E = Sb
e, E = Bi

The ^1H nmr spectrum (CCl_4) allows structural assignment as the symmetrical adduct **4b**. The bridgehead proton occurs as a triplet at τ 4.57 (J = 7 Hz), while the two-proton quartet at τ 2.41 (J = 7 Hz) is assigned to the protons at C_5 and C_8. The protons at C_6 and C_7 are a doublet of doublets centered at τ 3.05 ($J_{^1H-^{31}P}$ = 56 Hz, $J_{^1H-^1H}$ = 7 Hz).[5] Irradiation at the ^{31}P frequency removes the phosphorus coupling, collapsing the signal at τ 3.05 to a doublet and that at τ 2.41 to a triplet.

Arsabenzene gave a similar adduct at room temperature.[8] *Anal.* Calcd for $C_9H_5AsF_6$: C, 35.76; H, 1.65. Found: C, 35.75; H, 1.74.

Again the ^1H nmr spectrum allowed structural assignment as the 1,4-adduct **4c**. The vinyl protons are a complex multiplet centered at τ 2.71, while the bridgehead proton occurs as a triplet at τ 4.44 (J = 6 Hz).[5] Stilbabenzene reacts rapidly with hexafluorobutyne at 0° to give **4d**: ^1H nmr (CCl_4) τ 4.34 (t of t, J = 7, 2 Hz, 1 H), 2.80 (d of d, J = 8.5, 7 Hz, 2 H), 2.58 (d of d, J = 8.5, 2 Hz, 2 H).[5] *Anal.* Calcd for $C_9H_5SbF_6$: C, 30.98; H, 1.44. Found: C, 31.00; H, 1.70.

Qualitatively the heavier heterocycles react more rapidly with hexafluorobutyne. Relative reactivity of benzocyclic aromatic compounds in the Diels–Alder reaction has been correlated with the loss of resonance energy from isolating the 1 and 4 positions from the ring.[9] Even assuming the same mechanism, one cannot expect to find so simple a correlation for compounds **1b**, **1c**, **1d**, and **1e** since the products each contain different C–E bonds. Thus, it should be expected that reactivity will be proportional to the difference between the loss of resonance energy of **1** and the gain of bond strength of the formed C–E single bond in **4**. At least for the trimethyl derivatives of the group V elements, C–E single bond strength decreases as atomic number increases.[10] Since reactivity of compounds **1** increases with atomic number, the resonance energy must decrease.

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[1] A. J. Ashe, III, *J. Amer. Chem. Soc.*, **93**, 3293 (1971).

[2] A. J. Ashe, III, *ibid.*, **93**, 6690 (1971).

[3] A. J. Ashe, III, and P. Shu, *ibid.*, **93**, 1804 (1971).

[4] The pmr spectra were taken using TMS as an internal standard. The spectrum of **3e** was recorded using a Varian T-60 instrument while all other spectra were from a Varian HR-100 and were calibrated by the side-band technique. Microanalyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

[5] The chemical-shift values of the protons α to the heteroatom of **4** are shifted to progressively lower field for the heavier metal atoms. This shift is similar to that already noted for compounds **1a**, **1b**, **1c**, and **1d**. See ref 1 and 2.

[6] See R. Huisgen, *Top. Heterocycl. Chem.*, 223 (1969).

[7] G. Märkl and F. Leib, *Angew. Chem., Int. Ed. Engl.*, 7, 733 (1968).

[8] 9-Arsaanthracene gives a similar adduct with maleic anhydride: P. Jutzi and K. Deuchert, *Angew. Chem., Int. Ed. Engl.*, **8**, 991 (1969).

[9] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 432–438.

[10] G. O. Doak and L. D. Freedman, "Organometallic Compounds of Arsenic, Antimony and Bismuth," Wiley, New York, N. Y., 1970, p 8.

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Incremental Substituent Effects Leading to Steric Blockade of the Boat-Like Six-Center Cope Rearrangement of *cis*-1,2-Dialkenylcyclobutanes[1]

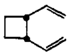
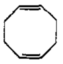
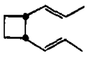
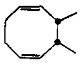
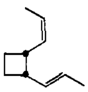
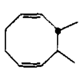
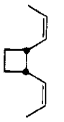
Sir:

Although the rate of the chair-like, four-center Cope rearrangement of acyclic biallyls is faster than that of the boat-like, six-center one by a factor greater than exp((6000 cal/mol)/RT),[2] there are several cases in the literature in which the order of preference is qualitatively reversed. Among the earliest examples so interpreted are the thermal transformations of *cis*-1,2-dialkenylcyclobutanes to *cis,cis*-cycloocta-1,5-dienes.[3,4] The normal preference for the chair-like pathway in these systems should be diminished because of the high strain energy[5] of the product, a *cis,trans*-cycloocta-1,5-diene. Although the transient intermediacy of that substance cannot be excluded on purely energetic grounds,[6] the present results strongly support the formulation[3,4,8] of the rearrangement of *cis*-1,2-divinylcyclobutane to *cis,cis*-cycloocta-1,5-diene as a direct process *via* a boat-like transition state. Moreover, they show how *cis*-1,2-dialkenylcyclobutanes, already deprived of the normal chair-like pathway by product strain, can be subjected to incremental steric effects that gradually deny access even to the "second-best" boat-like reaction.

Successive treatments of dimethyl *cis*-1,2-cyclobutanedicarboxylate with $NaAlH_2(OCH_2CH_2OCH_3)_2$ and $CH_3CH{=}PPh_3$, followed by gas chromatographic (gc) separation on a $AgNO_3$–Carbowax 200 column, give *cis*-1,2-*trans,trans*-, *cis*-1,2-*cis,trans*-, and *cis*-1,2-*cis,cis*-dipropenylcyclobutanes (cTT, cCT, and cCC).[7] These substances are identified by nuclear magnetic resonance (nmr) and especially by infrared (ir) spectroscopy ($\lambda\lambda_{max}$ cTT, 965 cm^{-1}; cCC, 740 and 695 cm^{-1}; cCT, 965 and 715 cm^{-1}).

Table I records the rates and products observed on pyrolysis of these three reactants and of *cis*-1,2-divinylcyclobutane[3] (cDV) at 146.5° in the liquid phase.

Table I. Rates and Products of Pyrolyses of *cis*-1,2-Dialkenylcyclobutanes

	Boat		Crossover	
Reactant	Product	k_b, rel	Product	k_c, rel
 cDV	 1	181,000[a]		
 cTT	 2	41,800[b]	3	
 cCT	 3	435[c]	2	24[c]
 cCC	2	1[c,d]	3	200[c]

[a] Calculated from published activation parameters.[3] [b] Measured directly. [c] Calculated as the product of the observed overall first-order rate constant for disappearance of cCT (or cCC) and the fraction of the indicated 3,4-dimethylcycloocta-1,5-diene in the product mixture, which also contains *trans*-1,2-*cis,trans*- (respectively, *cis,-cis*)-dipropenylcyclobutanes from cCT and cCC, as well as piperylene and 3-methyl 4-propenylcyclohexenes. [d] k_b(abs) = 1.3 × 10^{-7} sec^{-1}.

The data show that methyl substitution at the terminal carbons of the vinyl groups of cDV produces a regular decline in the rate of the boat-like rearrangement. In the transition state of cTT → **2**, the major steric difference as compared to the case of cDV → **1** is the methyl–methyl interaction, MM. The same conformation in the case of cCT → **3** replaces this with two methyl–hydrogen interactions, MH, but also introduces a methyl–ring interaction, MR. Finally, the reaction cCC → **2** has one MM and two MR interactions. On the assumption that the interaction free energies remain constant in the series, the relative rate data of Table I for the boat-like reactions can be expressed in the form of the following parameters (in kcal/mol): $\Delta\Delta F_{MH}{}^{\ddagger} = 0.29$; $\Delta\Delta F_{MM}{}^{\ddagger} = 1.22$; $\Delta\Delta F_{MR}{}^{\ddagger} = 4.43$. These steric effects, when combined with the observed stereochemistry of the products (both double bonds cis, methyl configurations cis from cTT and cCC, trans from cCT), strongly suggest boat-like transition states for the Cope rearrangements of cDV, cTT, and the major portion of cCT.

By far the largest steric effect is the methyl–ring interaction,[8] which comes into play in the boat-like transition states from the reactants having cis propenyl groups (cCT and cCC). Not only does this depress strongly the rate of the unperturbed boat-like reaction of cDV, but by doing so, it permits the observation of a much slower "crossover" process which gives a different product. The crossover and boat-like reactions are distinguished by the configuration of the methyl groups in the product 3,4-dimethylcycloocta-1,5-diene.[9] Undetectable in the Cope rearrangement of cTT, crossover begins to emerge in the cCT case (95% boat-like, 5% crossover) and becomes dominant in cCC (0.5% boat-like, 99.5% crossover).

Two mechanisms for the crossover reaction are presently under consideration. The first is a direct

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[1] We thank the National Science Foundation (Grant No. GP11017X) and the Hoffmann-La Roche Foundation for partial support of this work.

[2] W. von E. Doering and W. Roth, *Tetrahedron*, **18**, 67 (1962).

[3] G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, **86**, 899 (1964).

[4] D. J. Trecker and J. P. Henry, *ibid.*, **86**, 902 (1964).

[5] A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *ibid.*, **89**, 4024 (1967).

[6] For a discussion, see W. von E. Doering, M. Franck-Neumann, D. Hasselmann, and R. L. Kaye, *ibid.*, **94**, 3833 (1972), ref 45.

[7] Elemental analysis confirms the composition.

[8] Qualitative evidence for a large retarding effect of this type has been provided recently by W. Grimme, *J. Amer. Chem. Soc.*, **94**, 2525 (1972).

[9] Ozonolyses of **2** and **3** give succinic acid and (respectively) *meso*- and *rac*-2,3-dimethylsuccinic acids.