7   8

Energetic considerations favor the triplet recombination mechanism as well. Two sets of circumstances have to be distinguished: In the first case, the triplet energies of the sensitizers lie below the ion-pair energies but above the triplet level of **3**. In the second case, for which pyrene and anthracene serve as examples, the sensitizer triplets are well below that of **3**. These two types of sensitizer families can conveniently be identified from either CIDNP studies or quantum efficiency studies of isomerization: for the second family (namely pyrene and anthracene), with $E_T(\text{sensitizer}) < E_T(3)$, the CIDNP effects are rather weak, and in parallel, the quantum efficiency for isomerization (**3** → **4**) is at least tenfold smaller than for sensitization with donors of the first family (i.e., phenanthrene or triphenylene).[6] This sensitivity of either CIDNP or quantum efficiency to relative positions of triplet energies is not expected for a reaction mechanism involving rearranging radical anions of **3**. Instead, these results support the triplet recombination mechanism, as did earlier flash photolysis experiments,[6] which revealed that upon quenching of pyrene fluorescence with **3**, pyrene radical cations as well as pyrene triplets are generated.

The remaining uncertainty deals with the selection between two lower-lying triplet states, which in principle are both accessible following the decay of the ion pairs. The energy gap law[18] would predict population of the triplet lying closest to the energy of the ion pair.[19] Unfortunately, the present results do not allow an unambiguous test of the energy gap law because of the following uncertainties: If the triplet of the sensitizer with $E_T(S) > E_T(3)$ is generated on recombination, subsequent triplet energy transfer from ^3S to ^{33} would populate the triplet state of **3** in competition with direct population of ^{33} from the ion pair. Therefore, isomerization of ^{33} could occur in any event.

The system stilbene/fumaronitrile provides another example in which ion-pair formation/triplet recombination results in favored isomerization and stronger CIDNP of the component with the lower triplet energy (stilbene).[7,21] It should be noted, however, that the dynamics of electron transfer (backtransfer) may involve changes in geometry for these systems, so that arguments based upon energetics alone are likely to be incomplete. A settlement of this point has to await studies of systems that do not involve geometrical changes.

Experimental Section

Electron-donor sensitizers were commercially available and were recrystallized before use. Phenanthrene was further purified by repeated recrystallization from toluene and methanol and finally zone refining. The norbornadiene derivative **3** was prepared and converted to the valence isomer by direct irradiation as previously reported.[22]

CIDNP experiments were carried out by using solutions with 1×10^{-4} M sensitizer and 0.02–0.10 M of **3** and commercial acetonitrile-d_3 as solvent. Concentrations of **3** were chosen such that >50% of the sensitizer fluorescence was quenched (as deduced from Stern–Volmer plots[6]). The NMR spectra were recorded in a slightly modified Varian HA 100 spectrometer (operating at 60 MHz) in an all-quartz probe during UV irradiation with the $NiSO_4$-filtered light (290–360 nm)[23] from a high-pressure mercury–xenon lamp (1000W, Hanovia Model 977 B-1). The modification of the probe allowed irradiation through the paddle holes via a light guide.

# Dianions of 2-Methyl-1,5-hexadiene: Evidence against Y Aromaticity

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Abstract: The dimetalation of 2-methyl-1,5-hexadiene results in the formation of two linearly conjugated hexatriene dianion derivatives (**5/6**), a cross-conjugated dianion with extended conjugation (**10**), and a dianion best characterized as containing two isolated allylic monoanions (**9**). With two different metalating systems (*n*-butyllithium/tetramethylethylenediamine and *n*-butyllithium/potassium *tert*-butoxide) the species formed initially in largest concentration was **9**. Dianion **10** was the thermodynamic product, formed at the expense of **9** and **5/6**. At no time was the 6π Y-aromatic dianion **4** detected. The stability of **10** is best explained by a consideration of REPA's (resonance energy per atom).

Neutral linearly conjugated systems are generally recognized to possess greater stabilization than the isomeric cross-conjugated systems.[1] Frequently, though, with polyanionic systems, this tendency is reversed.[2] For example, we found that when 2-methyl-2-butene was treated with 2 equiv of *n*-butyllithium/tetramethylethylenediamine (TMEDA), the thermodynamic product was the cross-conjugated anion **2**.[3] By the use of ^{1}H NMR spectroscopy and periodic quenches with methyl iodide,

it was possible to observe the initial formation of linearly conjugated anion **1** with subsequent and complete isomerization of it to the anion **2**.

1   2
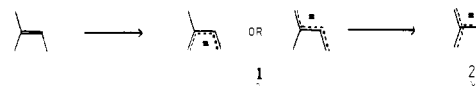
These results are explained by the theory of Y aromaticity,[4,5] which states that certain polyanions tend to adopt a closed-shell, Y-delocalized 6π-electron configuration. We decided to probe further this tendency by dimetalating an alkadiene that could form

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Table I. Metalation of 2-Methyl-1,5-hexadiene

metalating system[a] (mol)[b]	duration of metalation, h	products[c] (%)[d]
n-BuLi (2); TMEDA (2)	1	11 (3); 12 (4); 13 (37); 14/15 (16); 16 (38)
n-BuLi (2); TMEDA (2)	7	11 (5); 12 (11); 13 (32); 14/15 (17); 16 (32)
n-BuLi (2); TMEDA (2)	24	11 (3); 12 (9); 13 (31); 14/15 (21); 16 (31)
n-BuLi (2); TMEDA (2)	132	11 (1); 12 (6); 13 (14); 14/15 (16); 16 (47); 17 (7); 18 (8)
n-BuLi (2); TMEDA (2)	192	11 (3); 12 (3); 13 (19); 14/15 (8); 16 (56); 17 (10); 18 (5)
n-BuLi (2); TMEDA (2)	434	11 (1); 12 (5); 13 (0); 14/15 (8); 16 (68); 17 (15); 18 (3)
n-BuLi (2); *t*-OBuK (2)	1	11 (44); 12 (6); 13 (28); 14/15 (10); 16 (7); 18 (5)
n-BuLi (2); *t*-OBuK (2)	18	11 (42); 12 (6); 13 (27); 14/15 (8); 16 (14); 18 (3)
n-BuLi (2); *t*-OBuK (2)	96	11 (31); 12 (8); 13 (20); 14/15 (12); 16 (19); 18 (8)

[a] The reaction was performed in hexane at 0 °C. [b] Moles relative to the substrate. [c] After treatment with *n*-butyl bromide. [c] After treatment with *n*-butyl bromide. [d] % of dialkylated product.

Table II. Dianion Formation during Metalation

metalating system (mol)	duration of metalation, h	dianion (%)
n-BuLi (2); TMEDA (2)	1	9 (40); 5/6 (20); 10 (38)
n-BuLi (2); TMEDA (2)	7	9 (37); 5/6 (28); 10 (32)
n-BuLi (2); TMEDA (2)	24	9 (34); 5/6 (30); 10 (31)
n-BuLi (2); TMEDA (2)	132	9 (15); 5/6 (22); 10 (62)
n-BuLi (2); TMEDA (2)	192	9 (18); 5/6 (11); 10 (71)
n-BuLi (2); TMEDA (2)	434	9 (1); 5/6 (13); 10 (86)
n-BuLi (2); *t*-OBuK (2)	1	9 (72); 5/6 (16); 10 (12)
n-BuLi (2); *t*-OBuK (2)	18	9 (69); 5/6 (14); 10 (17)
n-BuLi (2); *t*-OBuK (2)	96	9 (51); 5/6 (20); 10 (27)

dianion (REPA = 0.028β). There is, however, another dianion possible by isomerization of dianions 4–8, the cross-conjugated dianion 10. The REPA for this species (0.065β)[8] suggests that

it rather than the Y-aromatic dianion **4** should be the most thermodynamically stable species from the parent alkene. Our investigation therefore evaluated the relative stabilities of dianions **4, 5–8, 9,** and **10** in order to evaluate the importance of Y aromaticity.

Metalation of 2-methyl-1,5-hexadiene (**3**) for less than a day with 2 equiv of *n*-butyllithium in the presence of an equimolar amount of TMEDA followed by alkylation with *n*-butyl bromide gave (Table I) a 1:3 mixture of mono- and dialkylated products. The dialkylated product mixture consisted of the following dienes: **11,** (*Z*)-2-pentyl-1,4-decadiene; **12,** (*Z*)-3-butyl-5-methyl-1,4-decadiene; **13,** 4-butyl-2-pentyl-1,5-hexadiene; **14,** (*Z,Z*)-6-methyl-6,8-tetradecadiene; **15,** (*E,Z*)-6-methyl-6,8-tetradecadiene; and **16,** (*Z*)-3-butyl-2-pentyl-1,4-hexadiene.

either a cross-conjugated 6π dianion or a linearly conjugated 8π hexatriene dianion. Deprotonation of the parent hexadiene to give the hexatriene dianion is kinetically more favorable than the analogous formation of the isobutylene dianion, since the hexatriene dianion forms 3–7 times faster than the isobutylene dianion.[6] In a system incorporating both hexatriene and isobutylene dianionic systems, formation of hexatriene dianion would be the kinetic process, while formation of the isobutylene dianion would be expected to be the thermodynamic process. Observation of the progress of the reaction would allow us to ascertain the relative thermodynamic stability of the cross-conjugated 6π dianion and its Y aromaticity insofar as relative thermodynamic stability is a criterion of aromaticity.[7]

The system chosen for examination was 2-methyl-1,5-hexadiene (**3**) which would yield upon direct dimetalation six possible dianionic species: **4,** the 6π cross-conjugated dianion, four linearly conjugated dianions, **5–8,** and a dianion, **9,** which is in reality two isolated monoanions.
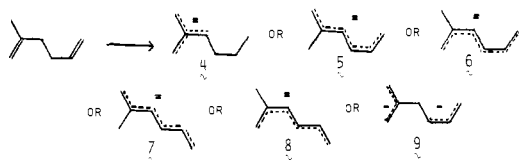
An alternative method for the evaluation of the stability of polyanions involves a consideration of the resonance energy per atom (REPA).[8] The relationship between thermodynamic stability and a larger REPA for polyanions has already been demonstrated for the isomeric C$_4$ dianions:[3] the isobutylene dianion (REPA = 0.034β) and the butadiene dianion (REPA = –0.040β). By this criterion, the cross-conjugated 6π dianion (REPA = 0.046β)[9] would be expected to be more stable than the hexatriene

When the reaction mixture was quenched after 24–434 h, two new products were formed: **17,** 5-pentyl-2,4-decadiene, and **18,** (*E*)-5-methyl-2-pentyl-1,3-nonadiene. The dienes can be grouped into three categories, each of which reflects the dianion from which each dialkylated product was formed. Dienes **11** and **13** were formed by alkylation of dianion **9, 12–14** by alkylation of **5** or **6,** and **16–18** by alkylation of dianion **10.**
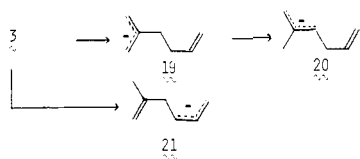
An examination of the amount of each dianion formed with time (Table II) shows that the amount of dianion **10** in the reaction mixture increases from approximately 35% at short time periods to 86% after 434 h, and this increase is at the expense of **5/6** and dianion **9.** The presence of dianion **9,** which is in reality two isolated allylic monoanions, suggests that the initial metalation occurs with the most acidic hydrogen to give monoanion **19.** This monoanion is next in a large fraction of the cases metalated a second time to give dianion **9.** The formation of 3-butyl-2-methyl-1,5-hexadiene as 24% of the reaction mixture after 1 h

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(9) We agree with a referee that the appropriate method for calculating the REPA for **4** would be to include all six atoms of the π system of **4,** giving $^2/_3$ × REPA (isobutylene dianion). The REPA of the isobutylene dianion is in error in ref 8 (personal communication from L. Schaad) and should be +0.069β rather than +0.034β. The REPA value of **4** should be 0.046β.

Evidence against Y Aromaticity

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Scheme I

suggests that transmetalation of **19** to give monoanion **20** also occurs early in the reaction. Monoanion **21** is formed more slowly from **3**, giving **9** and **5/6** after a second metalation. Dianion **20** also appears to be rapidly dimetalated to give linearly conjugated dianions (20% of the reaction mixture after an hour). Dianion **10** then is formed by transmetalation of **5/6** or **9**.

The sequence can be substantiated by an examination of ^{1}H NMR spectra of the metalation mixture after varying periods of time. Although analysis of the spectrum was complicated by overlap of anion peaks with solvent and TMEDA, it was possible to verify the presence after 10 min of monoanions **19** and **21** and dianion **9** by observation of their chemical shifts and coupling constants and by evaluation of the change in the spectrum of the starting alkene.
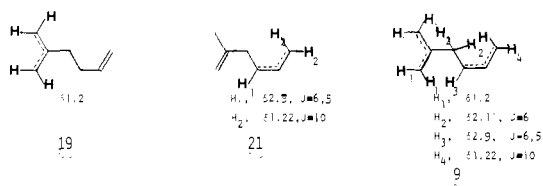
Initial formation of **19** was apparent from the changes in the vinyl region of the spectrum of the starting alkene, changes specifically in the positions of the protons of the geminally disubstituted double bond, and from the appearance of a singlet at δ 1.2, corresponding well with the chemical shift for the analogous protons in the crotyl anion.[10] Anion **21** formed at a slower rate than **19** but was verified by the doublet for the methylene group of the allylic anion at δ 1.22, $J = 10$ Hz, and, more importantly, by the doublet of triplets for the methinyl proton at the other end of the allylic system at δ 2.9, $J = 6$(d), 5(t) Hz. The formation of anion **20** could not be verified or refuted because its NMR spectrum is similar to that of **19** and because of solvent overlap in crucial areas of the spectrum. Within 10 min after addition of alkene to the metalating system, dianion **9** was visible in the NMR spectrum. That **9** was indeed being formed and that the spectrum was not simply overlapping spectra of **19** and **21** were apparent from the diminished size of the methyl group at δ 1.71 of the unmetalated hexadiene and the altered vinyl pattern of starting material. Dianions **5/6** were visible after 21 min, characterized primarily by their similarity to the hexatriene dianion.[6]
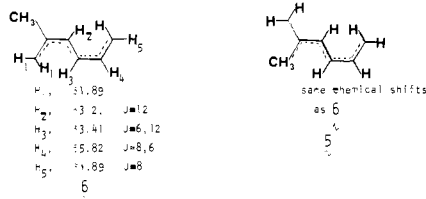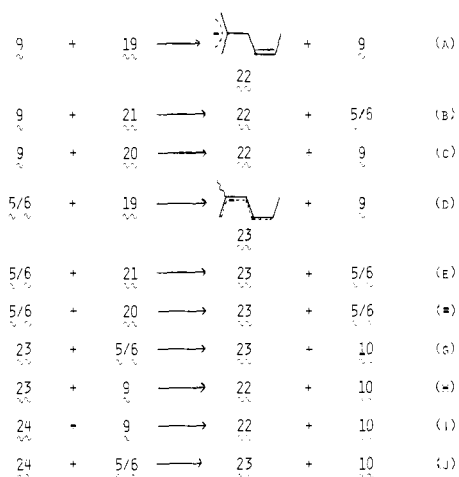
Peaks for dianion **9** appear to diminish with the growth of **5/6**, as evidenced primarily by the diminished peak at δ 2.11. Dianion **10** was the major dianionic species after 48 h and was charac-
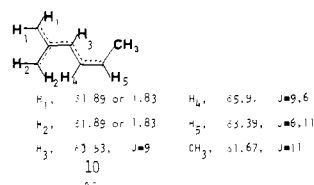
(10) Bates, R. B.; Beavers, W. A. *J. Am. Chem. Soc.* **1974**, *96*, 5001.

terized by chemical shifts/coupling constants and by the similarity of its spectrum to that of the dianion from 2-methyl-1,4-pentadiene.[6]

Metalation of 2-methyl-1,5-hexadiene by butylpotassium takes a slightly different course. Treatment of the starting alkene with 2 equiv of *n*-butyllithium and an equimolar amount of potassium *tert*-butoxide[11] followed by alkylation with *n*-butyl bromide gives a 1:4 mixture of mono- and dialkylated alkenes. The diadducts were found to be the same as in the metalation with *n*-butyllithium/TMEDA with one exception, the absence of **16**. The change in the percentage composition of dialkylated products with time is given in Table I. Again, it is possible to group those products into three categories on the basis of the dianions from which they were formed. Products from dianion **10** formed only a small portion of the reaction mixture, 12% of the dialkylated products after 1 h, with an increase to 27% after 96 h. The relative concentration of dianions **5/6** after 1 h was also low (16%), and the increase in relative concentration with time (20% after 96 h) was much less than for dianion **10**. Interestingly, products from alkylation of dianion **9** comprised a very significant portion of the reaction mixture, 72% after 1 h dropping to 51% after 96 h. Our explanation for this phenomenon is based on the ionic character of the potassium–carbon bond and the corresponding lack of solubility of dipotassioalkenes in the pentane/metalating solvent system. Dianion **9** must be formed initially, probably via monoanion **19**, and the transmetalation required to give **5/6** and **10** would be expected to be slow in the heterogeneous reaction mixture. The reluctance of dipotassioalkenes to undergo transmetalation under these conditions is also reflected in the relatively invariant ratios of dipotassioalkadienes from 2,5-dimethyl-2,4-hexadiene with time.[12]

In an attempt to discover the major species through which transmetalation occurs, we removed the supernatant from the reaction mixture and quenched it with *n*-butyl bromide. The only dialkylated products were **14** and **15** from linear dianions **5/6**. The remaining products resulted from alkylation of monoanions. A possible sequence of events leading to the formation of **10** from **9** via **5/6** is shown in Scheme I.

Protonation of dianion **9** at the carbon with greatest electron density[13] by each of the three initially formed monoanions could lead to regeneration of **9** (steps A and C) or formation of **5/6** (step B) with the concomitant formation of monoanion **22**, which could be directly metalated to give dianion **10** (steps I and J). Reaction of dianions **5/6** with each of the three initially formed monoanions would presumably occur to give the more stable pentadienyl monoanion **23** (steps D–F), with the regeneration of **5/6** (steps

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(12) Rusinko, A.; Mills, N. S.; Morse, P. *J. Org. Chem.*, in press.
(13) Bahl, J. J.; Bates, R. B.; Beavers, W. B.; Mills, N. S. *J. Org. Chem.* **1976**, *41*, 1620.

E and F) and **9** (step D). As with monoanion **22**, transmetalation of **23** by either dianion **9** or **5/6** would lead to **10** and monoanion **22** or **23**.

The intermediacy of monoanion **23** is suggested by the identification of 3-butyl-2-methyl-1,4-hexadiene and 5-methyl-2,4-decadiene in the reaction mixture, although these products could also have arisen by protonation/alkylation of dianions **5/6**. Our inability to observe products from **22** in concentrations larger than 1% of the reaction mixture probably reflects the fact that **22** is less stable and more easily metalated than **23**.

Steps A, B, and C are probably relatively slow, because the dianions are not very soluble in the hydrocarbon solvent. Steps D, E, and F are more rapid because the larger concentration of dianions **5/6** in solution allows for a faster rate of reaction. Steps A–F allow formation of "isomerized" monoanions **22** and **23** which can be deprotonated by **5/6** (fast) or **9** (slow) to yield cross-conjugated dianion **10**.

Discussion

Metalation of 2-methyl-1,5-hexadiene with either *n*-butyllithium/TMEDA or *n*-butyllithium/potassium *tert*-butoxide results in formation of cross-conjugated dianion **10** as a significant fraction of the reaction mixture. The increase in the percentage of **10** with time suggests that it is thermodynamically the most stable dianion in the reaction mixture. The proposed Scheme I for transmetalation of the dipotassioalkenes and the sequences of anion formation observable through ^{1}H NMR spectroscopy of the *n*-butyllithium/TMEDA metalation of the starting alkene both suggest that dianion **10** is formed at the expense of dianions **5/6** and **9**.

The preference for **10** over **5/6** can be explained by an examination of their relative resonance energies per atom (REPA).[14] The REPA's for **10** and **5/6**, computed in this manner,[8] are 0.065β and 0.028β, respectively. The resonance stabilization of ions can be computed by subtracting from the Hückel π energy the energy calculated for a localized reference structure. Using the resonance energy of the allylic system along with the energy of this reference structure allows computation with all bond energy terms for any localized conjugated ion. The resonance energies per atom (REPA) are then computed by

$$REPA = 1/n[E\pi_b - E(ref)]$$

where n is the number of atoms, $E\pi_b$ is the Hückel π binding energy, $E(ref)$ is the π binding energy of the localized reference structure. As mentioned earlier, the relationship between thermodynamic stability and a larger REPA for isomeric polyanions has been demonstrated for the isomeric C_4 dianions, the isobutylene dianion (REPA = 0.034β) and the butadiene dianion (REPA = −0.040β). When both are allowed to form in the same hydrocarbon system, 2-methyl-2-butene, the dianion with the larger REPA forms at the expense of the other.[3] Other acyclic polyanions which have been formed with high REPA values include the dianion of 2,3-dimethylbutadiene (REPA = 0.062β),[15] the 4-methylheptatrienyl dianion (REPA = 0.061β),[16] and the 3-vinylhexatriene dianion (REPA = 0.040β).[8] The larger REPA for dianion **10** suggests its greater stability compared with dianions **5/6** and agrees with its ease of formation.

The dianion that served as the original motivation for this study, the alkyl-substituted dianion of isobutylene, **4**, was never seen. Formation of **4** from 2-methyl-1,5-hexadiene was anticipated to be facile. In both metalating systems, monoanion **19** was implicated as the initially formed monoanion. In Lochmann's base,[11] the second proton abstraction in the majority of the reaction occurred at the disubstituted carbon to give the secondary allylic monoanion of **9**. The proton abstraction required to form dianion **4** would have to occur also at a disubstituted carbon and should have been equally favored. The preference for two allylic monoanionic systems rather than the isobutylene dianion might be

explained again by a consideration of the resonance energies involved. The REPA for each monoanion is calculated as 0.055β;[8] that for the cross-conjugated dianion is 0.046β. Metalation appears to occur in such a manner as to give the anionic system(s) with the largest REPA. Again, the species **10** whose concentration increases with time, at the expense of dianion **9**, has a larger REPA (0.065β) than **9** (0.055β for each anionic system). The formation of **5/6** might be considered as again occurring as the formation of two monoanions that might only reluctantly assume planarity and full conjugation. Bates[6] in his preparation of the parent hexatriene dianion noted that it was formed more rapidly from 1,5-hexadiene than from 1,4-hexadiene. The 1,5-dienyl system would more easily allow the formation of two "isolated" allyl anions; the 1,4-dienylic system could form initially either a pentadienyl (REPA = 0.053β)[8] or an allylic monoanion, and proton abstraction α to the pentadienyl anionic system would be expected to be retarded because the hexatriene dianion system would result immediately, forced by the planarity of the pentadienyl anion.

The same arguments hold when the metalating system is *n*-butyllithium/TMEDA. Again, the initially formed monoanion appears to be the doubly primary allylic anion **19** (REPA = 0.055β), which is then, in the majority of cases, metalated a second time to dianion **9**. Dianions **5/6** appear to be a second kinetic product of deprotonation that undergo facile transmetelation to dianion **10**, the thermodynamic product. The increased solubility of the dilithioalkadiene allows more facile isomerization to the system with the larger REPA, dianion **10**, as 86% of the dianion concentration.

In summary, the formation of dianions in 2-methylhexadiene systems suggests that cross-conjugated 2-methylenepentadienyl dianions are more stable than linear hexatriene dianions. In addition, formation of two allylic monoanions is favored over the "Y-aromatic" dianion. This unexpected preference can be rationalized by consideration of the resonance energy per atom in the respective systems. We therefore feel that the conclusion that the isobutylene dianion constitutes one member of a unique set of acyclic aromatic compounds based on its thermodynamic stability, as well as other properties, may be premature, with its thermodynamic stability reflecting a property seen in many cross-conjugated systems.

Experimental Section

General Procedures. ^{1}H NMR spectra were recorded on a Varian T-60 spectrometer. Tetramethylethylenediamine (TMEDA) and pentane were dried by distillation from the benzophenone ketyl. The alkene substrate, 2-methyl-1,5-hexadiene, was used as obtained from Pfaltz and Bauer. Potassium *tert*-butoxide and *n*-butyllithium were used as obtained from the manufacturer. A Perkin-Elmer Sigma 3B gas chromatograph, equipped with a thermal conductivity detector, was used preparatively. Helium was used as the carrier gas with a flow rate of 30 mL/min.

General Procedure for Metalation. (A) With Lochman's base. Potassium *tert*-butoxide (1.73 g, 14.3 mmol) in pentane and *n*-butyllithium (5.9 mL, 14.3 mmol) were combined in a septum-capped test tube under argon to form a beige complex. To the metalating system at 0 °C was added 2-methyl-1,5-hexadiene (1 mL, 7.13 mmol). The metalated hexadiene was quenched with *n*-butyl bromide (1.5 mL, 14.3 mmol), the solution was neutralized with 10% HCl, the layers were separated and dried, and the organic layer was flash distilled ((180 °C (10^{-1} torr)). The products were separated by temperature-programmed GC (100–150 °C, 2.7 m, 6% OV-17 column).

(B) With *n*-butyllithium/TMEDA. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) (2.1 mL, 14.3 mmol) and *n*-butyllithium (5.9 mL, 14.3 mmol) were combined in a septum-capped test tube under argon. To the metalating system was added 2-methyl-1,5-hexadiene (1 mL, 7.13 mmol) to give a deep red-brown solution. *n*-Butyl bromide (1.5 mL, 14.3 mmol) was added to the solution at 0 °C to quench the anions. The reaction mixture was extracted with 10% HCl to remove the amine, the layers were separated, and the organic layer was dried with magnesium sulfate and flash distilled. The products were isolated as described above.

(Z)-2-Pentyl-1,4-decadiene (11). Spectral data: ^{1}H NMR (CDCl$_3$) δ 0.88 (6 H, CH$_3$R), 1.30 (12 H, CH$_2$), 1.96 (4 H, CH$_2$—C═C), 2.66 (2 H, C═C—CH$_2$—C═C), 4.6 (2 H, CH$_2$═C), 5.34 (2 H, CH═CH).

(Z)-3-Butyl-5-methyl-1,4-decadiene (12). Spectral data: ^{1}H NMR (CDCl$_3$) δ 0.96 (6 H, CH$_3$R), 1.22 (12 H, CH$_2$), 1.65 (3 H, CH$_3$—C═C), 1.94 (2 H, CH$_2$—C═C), 2.8 (1 H, C═C—CH—C═C), 4.90–5.95 (4 H, HC═C, HC═CH$_2$).

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4-Butyl-2-pentyl-1,5-hexadiene (13). Spectral data: ^{1}H NMR (CDCl$_3$) δ 0.88 (6 H, CH$_3$R), 1.26 (12 H, CH$_2$), 2.01 (5 H, CH$_2$—C=C, CH—C=C), 4.62 (4 H, CH$_2$=C), 5.1–5.8 (1 H, CH=C).

(Z,Z)-6-Methyl-6,8-tetradecadiene (14) and (E,Z)-6-Methyl-6,8-tetradecadiene (15). These isomeric dienes were partially resolved by GC but had retention times that precluded isolation by GC. Spectral data: ^{1}H NMR (CDCl$_3$) δ 0.97 (6 H, CH$_3$R), 1.27 (12 H, CH$_2$), 1.77 (3 H, CH$_3$C=C), 2.07 (4 H, CH$_2$C=C), 5.08–5.98 (3 H, C=CH—CH=CH).

(Z)-3-Butyl-2-pentyl-1,4-hexadiene (16). Spectral data: ^{1}H NMR (CDCl$_3$) δ 0.91 (6 H, CH$_3$R), 1.33 (12 H, CH$_2$), 1.64 (3 H, CH$_3$C=C), 2.01 (2 H, CH$_2$C=C), 2.95 (1 H, C=C—CH—C=C), 4.81 (2 H, CH$_2$=C), 5.05–5.85 (2 H, HC=CH).

5-Pentyl-2,4-decadiene (17). Spectral data: ^{1}H NMR (CDCl$_3$) δ 0.89

(6 H, CH$_3$R), 1.28 (12 H, CH$_2$), 1.74 (3 H, CH$_3$C=C), 2.09 (4 H, CH$_2$C=C), 5.16–5.97 (3 H, C=CHCH=CH).

(E)-5-Methyl-2-pentyl-1,3-nonadiene (18). Spectral data: ^{1}H NMR (CDCl$_3$) δ 0.94 (6 H, CH$_3$R), 1.22 (12 H, CH$_2$), 2.09 (3 H, CH$_2$C=C, CHC=C), 4.73 (2 H, CH$_2$=C), 5.31–6.04 (2 H, C=CCH=CH).

Stabilization of Stibabenzene and Bismabenzene by 4-Alkyl Substituents[1]

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Abstract: Stibabenzenes and bismabenzenes are readily prepared by dehydrohalogenation of 1-chlorostibacyclohexa-2,5-dienes and 1-chlorobismacyclohexa-2,5-dienes, respectively. 4-Alkyl-substituted derivatives **16** and **19** are markedly more stable toward polymerization than the parent compounds. Stibabenzene, bismabenzene, and 4-methylbismabenzene are in mobile equilibrium with their head-to-head Diels–Alder dimers. The ^{1}H NMR spectra of stibabenzenes and bismabenzenes show very low field signals for the α-protons due to very large diamagnetic anisotropies of the Sb and Bi atoms.
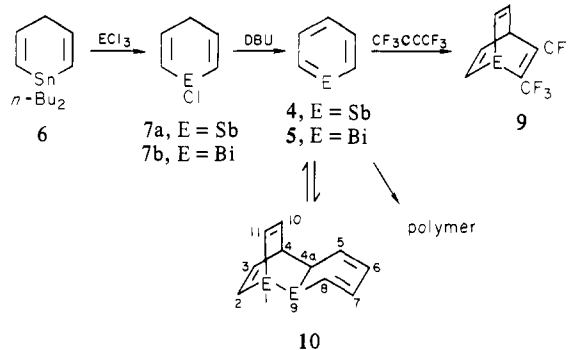
Pyridine (**1**) and its heavier homologues **2–5** comprise a unique

1   **2**   **3**   **4**   **5**
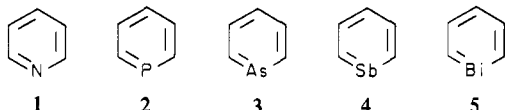
series in which elements of an entire column of the periodic table have been incorporated into aromatic rings. This series is of considerable interest for the study of aromaticity and heavier element–carbon π bonding. Detailed investigations of phosphabenzene (**2**)[2–7] and arsabenzene (**3**)[4–8] have shown that they display a high degree of aromatic character. On the other hand, stibabenzene (antimonin, **4**) and bismabenzene (bismin, **5**) have been subjected to much less work. We have made only preliminary reports of their synthesis[9–11] and spectra.[12–14] We now wish to

record in detail our observations on stibabenzene and bismabenzene.

Stibabenzene. The ease with which vinyltin compounds undergo exchange reactions with main group element halides[15] makes stannacyclohexadienes excellent precursors for antimony and bismuth heterocycles. Thus the reaction of 1,1-dibutylstannacyclohexa-2,5-diene (**6**) with a tetrahydrofuran solution of an-

6   **7a, E = Sb**   **4, E = Sb**   **9**
        7b, E = Bi   **5, E = Bi**

10   polymer

10

timony trichloride gave a mixture of dibutyltin dichloride and 1-chlorostibacyclohexa-2,5-diene (**7a**). Pure **7a** may be obtained by recrystallization from pentane. The reaction of a tetrahydrofuran solution of **7a** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) affords stibabenzene (**4**), which may be codistilled with tetrahydrofuran from the hydrochloride of the base. It is particularly convenient to treat a tetraglyme solution of the crude

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