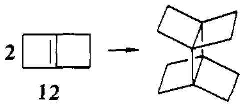
It is known that single determinant Hartree–Fock calculations do not correctly represent bond breaking and lead to large energies for this process.[47] It was possible that **6** is not a discrete species but would be found to dissociate to **7** without a potential barrier if this problem could be eliminated. Here, the generalized valence bond (GVB)[48] formalism appeared to be particularly useful, since it assigns a wave function to each electron in the specified bonds and leads to correct dissociation. Thus, a geometry optimization was carried out with the GVB perfect pairing approximation for the central bond and the 4-31G basis. The results are shown in Table II. The central bond now is somewhat longer, but the species still represents a minimum in the potential energy surface. We shall at a later time attempt to estimate the activation energy for the conversion of **6** to **7**.

Finally, we may examine the energy of bicyclo[2.2.0]-1(4)-hexene (**12**). The enthalpy of hydrogenation is calculated to be 65 kcal/mol (Table V), which may be compared with 54 kcal/mol for the hydrogenation of cyclopropene (**9**). It is clear that **12** has a considerably higher strain energy than **9**. This is in good accord with its remarkable chemical reactivity.[27] The dimerization to the highly strained propellane **13** is estimated to be exothermic by 88 kcal/mol!



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13

The preceding discussion has been concerned largely with the geometries and energies derived from the calculations. The wave functions potentially contain much information concerning intramolecular interactions, changes in electron density distribution with changes in structure, etc. A quantum topological[49] analysis of the wave functions will be presented at a later time.

Acknowledgment. This investigation was supported at Yale by the National Science Foundation (Grant CHM078-24880). This research was supported in part by the National Resource for Computation in Chemistry under a grant from the National Science Foundation and the Basic Energy Sciences Division of the U.S. Department of Energy (Contract W-7405-ENG-48).

Registry No. 1, 311-75-1; **2**, 185-94-4; **3**, 591-93-5; **4**, 285-86-9; **7**, 592-42-7; **8**, 40220-30-2; **9**, 2781-85-3; **10**, 822-35-5; **11**, 542-92-7; **12**, 30830-20-7; hydrogen, 1333-74-0; methane, 74-82-8; ethane, 74-84-0; ethylene, 74-85-1; acetylene, 74-86-2; cyclopropane, 75-19-4; bicyclo[2.2.0]hexane, 186-04-9.

Supplementary Material Available: Tables of atomic coordinates and thermodynamic data for compounds **1–12** (10 pages). Ordering information is given on any current masthead page.

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CIDNP Studies of Photoinitated Electron-Transfer Reactions. Sensitized Isomerization of an Electron Acceptor Norbornadiene

Wolfgang Schwarz,[†] Karl-Michael Dangel,[†] Guilford Jones, II,[‡] and Joachim Bargon*[†]

Contribution from the IBM Research Laboratory, San Jose, California 95193, and the Department of Chemistry, Boston University, Boston, Massachusetts 02215.

Received December 2, 1981

Abstract: Chemically induced dynamic nuclear polarization (CIDNP) has been observed on irradiation of dimethylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**3**) in the presence of aromatic electron-donor sensitizers in acetonitrile. Nuclear polarization is detected for selected protons of **3** (emission) and its quadricyclene valence isomer **4** (enhanced absorption). The complementary CIDNP effects are rationalized in terms of the quenching of hydrocarbon singlests via electron transfer, intersystem crossing between resultant singlet and triplet radical-ion pairs, and competition between singlet and triplet ion recombination. The energetics of recombination allow that triplets of either **3** or the sensitizers may be populated. A distinction is made between pairs in which the sensitizer triplet level is above or below that of **3**. The CIDNP effects are discussed in terms of other photochemical results regarding the electron-transfer photosensitized isomerization, **3** → **4**.

The photochemical interconversion of norbornadiene (**1**) and its valence isomer, quadricyclene (**2**), has been known for some time.[1] For the forward reaction the mechanism involving triplet–triplet energy transfer is well understood and has recently attracted attention as a relatively efficient means for driving a photochemical energy storage system.[2] Due to the unusual electron donor properties of the strained isomer **2**, the back reaction can also be photoinduced by using electron acceptors as sensitizing agents[3] to promote electron transfer. A new mechanism for the **1** → **2** isomerization was recently proposed,[4] also involving electron transfer which was based on the observation of chemically induced dynamic nuclear polarization (CIDNP) effects on irradiation of **1** in the presence of a singlet sensitizer, 1-cyanonaphthalene. An examination of ion-pair energies suggested the role of electron donor for **1** in the quenching of cyanonaphthalene fluorescence in acetonitrile. The data further provided that geminate ion pairs once formed as singlets may intersystem cross to triplet ion pairs of sufficient energy to populate, through back electron transfer, the triplet state of either reactant. Deposition of excitation energy in **1** through triplet recombination[5] finally leads to isomerization as expected. The different options offered to singlet vs. triplet ion pairs are responsible for opposite nuclear spin polarization in reactant and product isomers.[4]

In a separate paper[6] we have reported that the isomerization of the norbornadiene derivative **3** can be successfully carried to

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[†] IBM Research Laboratory.

[‡] Boston University.

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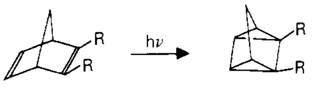

1 R = H 2
3 R = CO_2CH_3 4

high conversion in the electron-transfer photosensitization mode. This system departs from the parent norbornadiene/quadricyclene system (**1**/**2**) in that **3** is now a good electron acceptor and isomer **4** is no longer a powerful donor (or acceptor) capable of intercepting the sensitizer. We report here novel aspects of the CIDNP portion of our study involving isomerization, **3** → **4**, photoinitiated by electron transfer from donor sensitizers.

The CIDNP method has proved to be a valuable tool for the investigation of photoinduced isomerizations that proceed via electron-transfer and radical-ion intermediates. For olefin systems capable of isomerization, two types of polarization mechanism have been distinguished.[7] In the first, a competition is set up between recombination of an initial radical ion pair (with or without intersystem crossing) and diffusive separation. Olefin-radical ions, especially the cations, having left the solvent cage are endowed with sufficient lifetime to rearrange before eventual capture. The polarization observed on irradiation of 1-phenylpropene[8] or quadricyclene[4] in the presence of an acceptor sensitizer is consistent with this mechanism involving rearranging radical cations.

Another family of reactions, in which isomerizable electron-deficient olefins are combined with donor sensitizers, proceeds by the alternative triplet recombination mechanism described above. For simple olefins, the different behavior of the electron-rich relative to the electron-donor olefins seems to stem from a relatively high barrier to (geometrical) isomerization in radical anions[9] as opposed to that in radical cations. Therefore, mere generation of radical cations from donor olefins may already lead to isomerization, whereas after generation of radical anions from acceptor-type olefins, isomerization requires subsequent population of their triplet state, a process which is facilitated by the uniformly low triplet excitation energies found for the olefin acceptors. Our evidence shows that norbornadiene **3** falls into this latter category for isomerization under electron-transfer conditions.

Results

Solutions of **3** (0.02–0.10 M in CD_3CN) were irradiated in the probe of a CW NMR spectrometer in the presence of sensitizers (Table I) that absorbed readily in the region of illumination (290–360 nm). Characteristic CIDNP signals were observed. Protons of the methyl ester group as well as bridgehead and olefinic protons of **3** were observed in emission (*E*). The corresponding protons of the photoisomer **4** exhibited a complementary polarization, namely enhanced absorption (A) (Figure 1).

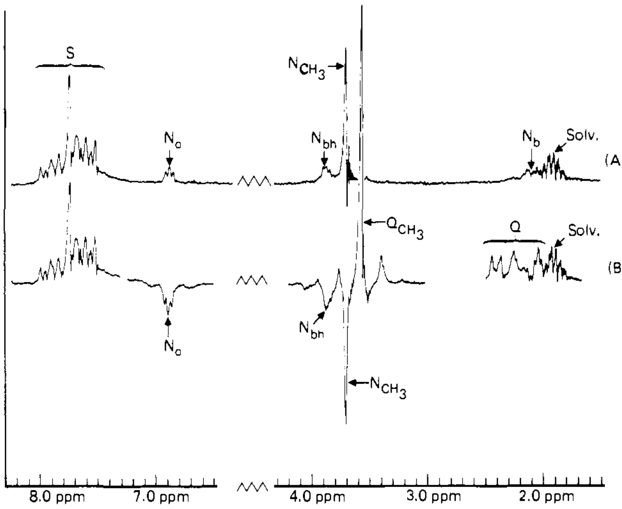

Figure 1. (a) "Dark" ^{1}H NMR (60 MHz) spectrum of a 0.02 M solution of **3** and 0.001 M phenanthrene in acetonitrile-d_3. (b) ^{1}H CIDNP spectrum of the same sample during irradiation. The resonances of **3** and **4** are denoted with N and Q, respectively; the indices refer to the protons in olefinic (o), bridgehead (bh), bridge (b), and methyl ester (CH_3) positions.

Table I. Excitation Energies for Sensitizers, *g* Values for Sensitizer Radical Cations, and Ion-Pair Energies for Sensitizers/**3**[a]

sensitizer	*g* value	$E(S_1)$	$E(T_1)$	$\Delta G(S^+,3^-)$
fluorene	2.0026[b]	95.0	68.4	74.2
triphenylene	2.0026[b]	83.4	66.5	72.7
4,4′-dimethoxybiphenyl	2.0031[c,d]	91.1[g]	62.9[h]	67.2
phenanthrene	2.0026[b,e]	82.8	62.1	71.8
naphthalene-d_8	2.0026[b]	91.0	61.0	76.9
2-methoxynaphthalene	2.0030[c]	90.0	59.9[j]	80.0
pyrene	2.0026[b]	77.0	48.5	64.0
anthracene	2.002565[f]	75.5	42.7	62.4

[a] All energies in kcal/mol. Excitation energies were taken from ref 10 and 11 or estimated from absorption and emission spectra. Ion-pair energies were calculated from polarographic half-wave potentials ($\Delta G = E(1/2)_{ox} - E(1/2)_{red} - e^2/\epsilon r$) with correction (1.4 kcal/mol for the Coulomb interaction in acetonitrile (ref 12a)). Oxidation potential values were taken from the literature (ref 12b) and the reduction potential for **3** was measured by cyclic voltammetry: $E_{pa} + E_{pc}/2 = -1.67$ V vs sce (TBAP, CH_3CN, Ag wire) (ref 13). [b] Assumed to be in the range for unsubstituted aromatic hydrocarbon radical cations (ref 14). [c] Determined by CIDNP (ref 16). [d] Reference 14d,e. [e] Reference 14c. [f] Reference 14f. [g] Reference 15a. [h] Reference 15b. [i] Reference 15c. [j] Reference 15d.

No nuclear polarization could be detected for the bridge protons (position 7) of either **3** or **4** or for the protons of the sensitizers. CIDNP was also not observed during the irradiation of solutions of various sensitizers in the presence of **4**. This finding is not surprising, since the valence isomer **4** fails to quench sensitizer fluorescence at moderate concentrations,[5b,6] and, therefore, acts as an acceptor inferior to **3**. Purging of solutions with argon did not result in detectable changes in the CIDNP spectra. Irradiation of **3** in the absence of a donor sensitizer resulted in slow photoisomerization to **4**; however, under these conditions, no CIDNP was observed. Photolysis in the presence of conventional triplet photosensitizers (benzophenone and acetophenone) brought about

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(9) (a) Ab initio calculations for 1,2-dicyanoethylene (DCNE), its anion $(DCNE)^-$, and its triplet state ^{3}(DCNE), all considered to be characteristic models for 1,2-acceptor substituted olefins, have revealed the following results: The most stable conformation of DCNE is the trans isomer, which is ~1 kcal/mol more stable than the cis isomer. The most stable conformation of $DCNE^-$ has planar trans geometry as well, with the lone electron in a π^* orbital. The cis isomer of $DCNE^-$ lies 2.7 kcal/mol above. The barrier to trans/cis isomerization was found to be 37 kcal/mol above the energy of the trans conformation. The minimum energy of the π–π^* triplet state of ^{3}DCNE was found to occur at a perpendicular conformation, as in ethylene. This minimum lies about 27 kcal/mol above the calculated ground-state minimum, i.e., above *trans*-DCNE. The planar trans and cis conformations of ^{3}DCNE are local maxima, and lie 8.6 and 9.9 kcal/mol above the perpendicular ^{3}DCNE minimum, respectively. The energy differences, though not considered to be of high quantitative accuracy, are believed to reflect the shape of the potential curves and the relative energies of isomers of a given multiplicity correctly. The single determinant wavefunction used for this calculation does not property describe the cis-trans isomerization of the π bond in the –C=C– fragment of DCNE; therefore, no rotational barrier of the ground state was calculated. The C–CN bond was shown to have π character as in any π-conjugated system. More work is in progress. Details of this and more advanced calculations as well as the optimized geometries of the different states and their isomers will be published elsewhere (B. Lui, M. Dupuis and J. Bargon, unpublished results). (b) The rate constants for isomerization of the radical anion of *cis*-4,4′-diphenylstilbene into its trans form has been estimated to be smaller than 10^4 s^{-1} (C. K. Chien, H. C. Wang, M. Szwarc, A. J. Bard, and K. Itaya, *J. Am. Chem. Soc.*, **102**, 3100 (1980).

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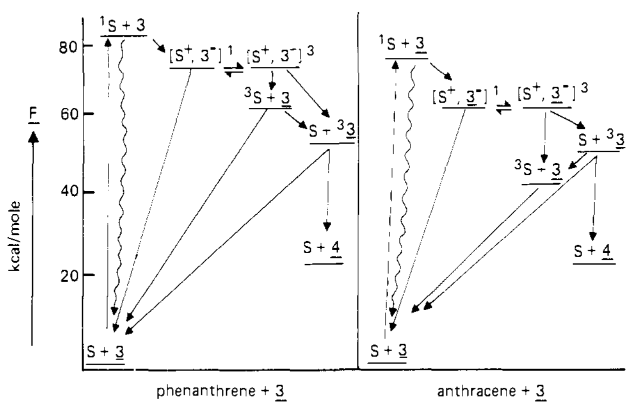


Information for the diagram:

$^1S + 3$	:	87.8 kcal/mol	$^1S + 3$	75.5 kcal/mol
$[S^+3^-]$	:	71.8 "	$[S^+3^-]$	62.4 "
$^3S + 3$	:	62.1	$S + {}^33$	53
$S + {}^33$	:	53	$^3S + 3$	42.7
$S + 4$	:	19	$S + 4$	19
↑ phenanthrene			↑ anthracene	

Figure 2. Energies of excited states and ion pairs of sensitizers in combination with norbornadiene 3.

efficient isomerization,[2b,c] but again no nuclear polarization.

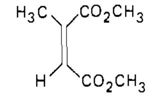
The intensities of the CIDNP signals showed a significant dependence on the identity of the sensitizer: When anthracene and pyrene were used as electron donors, signals were barely detectable and some 300–500 times smaller than CIDNP resonances found for the other sensitizers. For this comparison lamp intensities were assumed similar for all irradiations, and optical densities were high for all sensitizers at 290–360 nm.

Discussion

An examination of singlet excitation energies and ion-pair energies, obtained from redox potentials (Table I), shows that photoinduced electron transfer from the donor sensitizers to **3** is exothermic and should be relatively efficient.[12] The rate constants for quenching hydrocarbon fluorescence in acetonitrile approach the diffusion-controlled limit ($k_q \sim 10^{10}$ M^{-1} s^{-1}).[6] Reverse electron transfer in the initially formed singlet-ion pair will regenerate reactants in competition with intersystem crossing to ion pairs of triplet spin multiplicity.

Our working hypothesis is the triplet recombination mechanism. It involves a partitioning in which singlet ion pairs favor regeneration of norbornadiene **3** and triplet pairs on recombination lead predominantly to the valence isomer **4**. Energetics again provide the basis for such a mechanism (Figure 2) in that ion-pair energies (Table I) are uniformly above the value required for exothermic population of the triplet state of **3** (its energy is estimated to be about 53 kcal/mol from the quantum yields of sensitized isomerization by using triplet sensitizers of varying energy).[2b,c] The decay of the triplet state of **3** to isomer **4** is known to be efficient (~60%).[2b,c] Accordingly, the situation found here resembles that outlined in further detail elsewhere in the literature.[6,19]

The results of our CIDNP experiments are consistent with the triplet recombination mechanism. According to the well-known CIDNP phase rules,[17] and recent amendments thereto,[19] the net effect depends on five parameters: the initial spin multiplicity of the radical pair (μ), the mode of product formation (ϵ), the sign of the difference between isotropic g factors of the individual radicals (Δg), the sign of the hyperfine coupling constant (a) (hfc) for the magnetic nucleus under observation, and the "exit channel" factor (γ).[19b] According to Figure 2, which is based upon the results obtained from fluorescence quenching and quantum efficiency studies,[6] the initial ion pairs are of singlet origin ($\mu < 0$). All products are expected to be formed within the cage ($\epsilon < 0$). The g factors for the hydrocarbon radical cations are expected to be smaller than the value for $\mathbf{3}^-$ which bears electron-withdrawing substituents ($\Delta g > 0$). The signs for the proton hfc for the radical anion of **3** are not known, but all seem to have the same sign and must, therefore, be positive ($a > 0$) by comparison with results obtained in CIDNP experiments for analogous radical ions from the dimethyl esters of citraconic (**5**), 1,2-dimethylmaleic (**6**), and maleic acids.[20]



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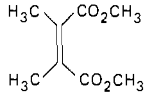

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Γ_{net}	=	μ	ϵ	Δg	a	γ		
for reactant 3 (singlet exit)	=	−	+	+	+	+	=	(emission)
for product 4 (triplet exit)	=	−	+	+	+	−	=	(enhanced absorption)

According to our results, the *olefinic* protons of $\mathbf{3}^-$ must experience a *positive* hfc together with the bridgehead and methyl ester protons. We are not aware of any precedent for this type of hyperfine interaction and the associated positive sign as observed here in the norbornadiene radical anion. An Overhauser-type mechanism[24] as a source of CIDNP seems unlikely, due to the relative intensities of the polarized protons. A triplet mechanism in turn can also be excluded, since the system is not particularly sensitive to the presence of molecular oxygen.[25] We are currently conducting a quantum chemical calculation on the hyperfine coupling mechanism in norbornadiene-type radical anions, the details of which will be published elsewhere.

Assuming that the spin-lattice relaxation rates of the methyl ester protons of **3** and **4** do not differ markedly, the near equal intensities of the CIDNP signals for reactant **3** and isomer **4** do not support a mechanism involving rearranging ions. One would otherwise expect the product resulting from the rearranged anion to show a significantly lower CIDNP intensity, assuming that escaped anions will lose some of their polarization due to spin-lattice relaxation.[7] Furthermore, if the behavior[4] of the radical cations of **1** and **2** serves as a guide, the conversion **7** → **8** should be endothermic (**7** and **8** represent only one of the several mesomeric forms).

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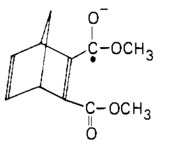

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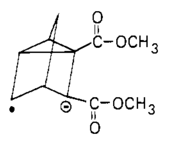

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Energetic considerations favor the triplet recombination mechanism as well. Two sets of circumstances have to be distinguished: In the first case, the triplet energies of the sensitizers lie below the ion-pair energies but above the triplet level of **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(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 ^{3}S to ^{3}**3** would populate the triplet state of **3** in competition with direct population of ^{3}**3** from the ion pair. Therefore, isomerization of ^{3}**3** 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.

Acknowledgment. The support of this research at Boston University by the Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged, including thanks for support for W.S. during a postdoctoral appointment at Boston University.

Registry No. 3, 947-57-9; **4**, 714-53-4; fluorene, 86-73-7; triphenylene, 217-59-4; 4,4'-dimethoxybiphenyl, 2132-80-1; phenanthrene, 85-01-8; naphthalene-d_8, 1146-65-2; 2-methoxynaphthalene, 93-04-9; pyrene, 129-00-0; anthracine, 120-12-7.

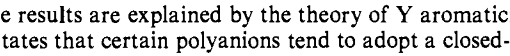
Dianions of 2-Methyl-1,5-hexadiene: Evidence against Y Aromaticity

Nancy S. Mills

Contribution from the Chemistry Department, Trinity University, San Antonio, Texas 78284.
Received February 9, 1982

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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(2) Bates, R. B. In "Comprehensive Carbanion Chemistry Part A: Structure and Reactivity"; Buncel, E., Durst, T., *eds.*; Elsevier: New York, 1981; p 1.

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(5) Finnigan, R. A. *Ann. N.Y. Acad. Sci.* **1969**, *152*, 242.

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