

studies will be reported in the full paper.

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### Dianions of 2-Methyl-2-butene: Evidence for the Stability of a "Y-Aromatic" Species

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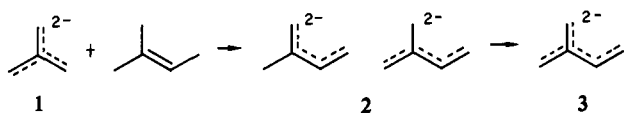
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Recently the suggestion was made that certain cross-conjugated species, such as dianion **1**,<sup>1</sup> may possess a novel aromatic character, the so-called "Y aromaticity".<sup>2,3</sup>

We wish to report that metalation of 2-methyl-2-butene with 2 equiv of base gave initial formation of the linearly conjugated dianion **2**, with facile and complete isomerization to the thermodynamically more stable cross-conjugated dianion **3**.

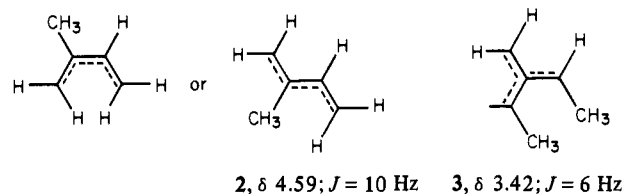


The preparation of dianions in systems in which either a linear or a cross-conjugated dianion could form allows the evaluation of the relative stabilities of each species and an estimation of the aromaticity of the cross-conjugated dianion. As further evidence, the <sup>1</sup>H NMR chemical shift of the parent anion (**1**) was measured and is in agreement with its proposed aromatic character.

Metalation was carried out by adding 1 equiv of alkene to 2 equiv of the *n*-butyllithium-tetramethylethylenediamine (TMEDA) complex<sup>4</sup> under argon at 25 °C. The reaction mixture was usually quenched after 4 days. An alternative preparation involved the addition of 1 equiv of alkene to 2 equiv of Schlosser's base mixture (*n*-butyllithium/potassium *tert*-butoxide<sup>5,6</sup>) in pentane under argon at 25 °C with quenching after 2 days. The *n*-butyllithium/TMEDA system resulted in formation of a dark reddish brown solid, while the anion prepared with Schlosser's base system was orange.

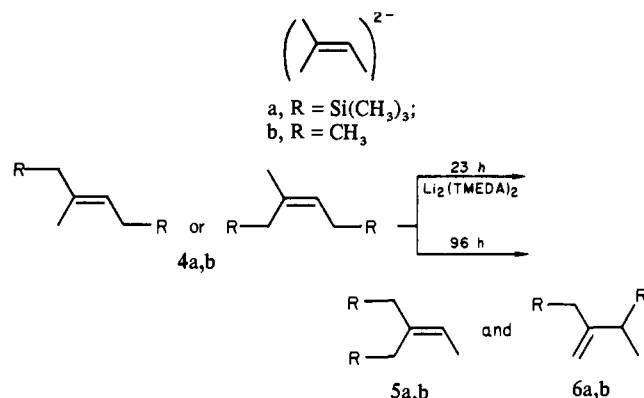
Evidence for dimetalation and the sequential formation of dianions **2** and **3** comes from <sup>1</sup>H NMR spectral observations and alkylation and silylation results. Obtaining the spectral parameters was possible only in the *n*-butyllithium/TMEDA metalating system because the dianions were moderately soluble in TMEDA. When Schlosser's base mixture was used, the dianions formed were insoluble in the pentane-based solvent and could not be observed directly. Attempts to dissolve the solid anions in dioxane resulted in immediate decomposition of solvent and anion, presumably by

proton abstraction from the solvent by the anion.<sup>7</sup> Although overlap with solvent complicated interpretation of the spectra, the following <sup>1</sup>H NMR shifts ( $\delta$ ) and coupling constants (*italics*) were deduced.



Justification of the assignment of the spectral parameters of linear dianion **2** was obtained by comparison with the butadiene dianion whose methine protons resonate at  $\delta$  4.8.<sup>1</sup> The most obvious structural feature of the spectrum of the cross-conjugated dianion is the 1:3:3:1 quartet (*J* = 6 Hz) for the vinyl proton at  $\delta$  3.42.

The linearly conjugated dianion began to appear after 10 h, reached its maximum concentration after 57 h, and disappeared by 126 h. The cross-conjugated ion appeared at 22.5 h and rapidly grew at the expense of the other dianion. Peaks from dianion **3** were still visible at 241 h, although they were beginning to be obscured by peaks from decomposition of solvent. Dianion **2** was trapped after 23 h as the bis(trimethylsilyl) derivative by quenching with (chlorotrimethyl)silane. Adducts **4a** were present as 30% of the product mixture, with the remainder due primarily to various products from monoaddition (65%) and to diaddition products from dianion **3** (5%). Trapping of dianion **3** was accomplished



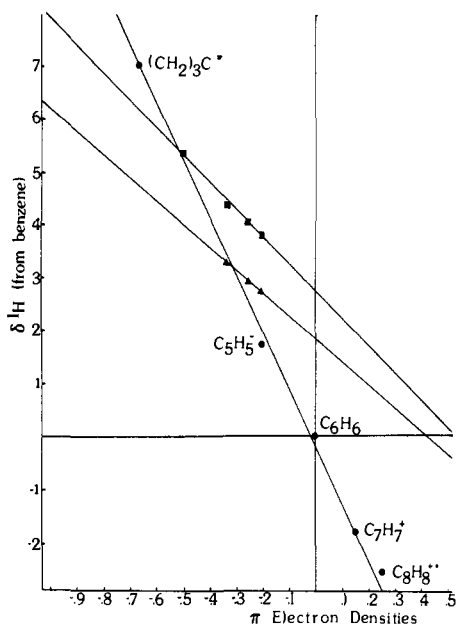
by reaction with (chlorotrimethyl)silane after 96 h to give adducts **5a** and **6a**, in 23% and 17% yield, respectively, with no formation of **4a**. Products from monoaddition comprise the remainder of the product mixture.

Interestingly, when 2-methyl-2-butene was metalated with Schlosser's base mixture and alkylated with either methyl iodide or (chlorotrimethyl)silane, the linear dianion **2** was not observed. In both cases, equal amounts of dialkylated products **5a,b** and **6a,b** formed. In an attempt to trap **2** before it isomerized to **3**, the reaction mixture from metalation with Schlosser's base system was quenched with methyl iodide at times ranging from 20 to 5760 min. There was no product from linear dianion.

For evaluation of the influence of the cation on the reaction of the dianion, we reacted 2-methyl-2-butene with Schlosser's base mixture followed by reaction with LiBr to give the dilithiated dianion.<sup>8</sup> Evidence for the success of the counterion switch comes from the color of the solution of the anion in THF. When the cation was potassium, the solution was reddish brown, while the anion in THF after treatment with LiBr was brownish black, the same color as a solution of the anion from the *n*-butyllithium/TMEDA system in THF. Reaction of the dilithiated dianion (2 days old) with chlorotrimethylsilane gave **5a** and **6a** as the only

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**Figure 1.** Correlation of  $\pi$ -electron density and  $^1\text{H}$  NMR chemical shift for aromatic ions ( $\bullet$ ),<sup>9,11</sup> the terminal protons of linear delocalized anions,  $\text{C}_3\text{H}_5\text{-C}_3\text{H}_{11}$  ( $\blacksquare$ ),<sup>12</sup> and the  $\delta$  protons of linear delocalized ions,  $\text{C}_5\text{H}_7\text{-C}_9\text{H}_{44}$  ( $\blacktriangle$ ).<sup>12</sup> The linear correlations of  $\pi$ -electron density and  $^1\text{H}$  NMR chemical shift for the terminal protons and for the  $\delta$  protons of linear anions also hold when those electron densities are calculated by the Pople method for odd linear ions,<sup>13</sup> and are significantly different from that shown by dianion **1** and the aromatic ions.

diadducts. It might be argued that in the Schlosser-prepared system the cross-conjugated dianion is in equilibrium with the linearly conjugated dianion, and the exclusive formation of product from the cross-conjugated dianion reflects only its greater reactivity. The observation that the linear dianion can be trapped when the counterions are TMEDA-chelated lithium suggests that if that dianion was present when the counterions were THF-chelated lithium it would also be trapped under the same reaction conditions.

One of the characteristics of an aromatic system is the presence of a diamagnetic ring current, present in both charged and neutral species. A plot of charge density at each carbon vs. chemical shift from benzene shows a straight-line relationship from benzene and the cyclic aromatic ions with six  $\pi$  electrons.<sup>9</sup> The trimethylenemethane dianion ( $\delta$  0.23)<sup>10</sup> shows the same linear relationship, which is significantly different from the relationship shown by the nonaromatic linear ions (Figure 1). By this method of evaluation, the trimethylenemethane dianion shows the same relationship between charge density and chemical shift as do benzene and the cyclic aromatic ions, and insofar as chemical shift is used as an indication of aromaticity, it is as aromatic as the above species. This is the first time that such a linear relationship has been reported for an acyclic system.

We are presently looking at the preference for other cross-conjugated dianions to determine if the phenomenon is a general one.

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## A New Geometrical Form for Tin. Synthesis and Structure of the Tetramethylammonium Chloride Adduct of the Spirobis(dithiastannole)

$[(\text{CH}_3)_4\text{N}]^+[(\text{C}_7\text{H}_6\text{S}_2)_2\text{SnCl}]^-$

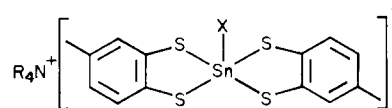
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Although pentacoordinated tin compounds are not prevalent, X-ray structural work shows that the methylstannanes  $(\text{CH}_3)_3\text{SnCl}$ ,<sup>1</sup>  $(\text{CH}_3)_2\text{SnF}_2$ ,<sup>2</sup> and  $(\text{CH}_3)_2\text{SnF}_2$ <sup>3</sup> possess intermolecular tin-halogen bonding. For (ethyl L-cysteinato-S,N)(chlorodimethyl)stannate(IV),  $(\text{CH}_3)_2\text{Sn}(\text{Cl})\text{SCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{C}_2\text{H}_5$ , an X-ray study<sup>4</sup> showed that the tin atom is pentacoordinated owing to the formation of an intramolecular donor-acceptor nitrogen-tin bond. For all of these examples, the geometry around tin is trigonal bipyramidal.

We report here the preparation and X-ray study of the first tin compound having a rectangular-pyramidal geometry. The compound, tetramethylammonium 2-chloro-5,5'-dimethyl-2,2'-spirobis(1,3,2-benzodithiastannole) (**1**), was formed by the reaction of bis(toluene-3,4-dithiolato)tin(IV),  $\text{Sn}(\text{TDT})_2$ , with 1 equiv of  $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$  in methyl cyanide at room temperature. Additional members (**2-4**) were also prepared.



- 1, X = Cl; R = Me
- 2, X = F; R = Et
- 3, X = Br; R = Et
- 4, X = I; R = Et

The structure of the monocyclic dithiastannole derivative **5**,  $[(\text{C}_2\text{H}_5)_4\text{N}][(\text{C}_7\text{H}_6\text{S}_2)\text{Ph}_2\text{SnCl}]$ , which offers an interesting comparison with **1**, was also determined by X-ray crystallography. It was prepared by treating diphenyl (toluene-3,4-dithiolato)tin,  $(\text{C}_7\text{H}_6\text{S}_2)\text{SnPh}_2$ , with 1 equiv of  $\text{Et}_4\text{N}^+\text{Cl}^-$  in methyl cyanide at 25 °C.

**Crystal Data.**  $[(\text{CH}_3)_4\text{N}]^+[(\text{C}_7\text{H}_6\text{S}_2)_2\text{SnCl}]^-$  (**1**) (bright yellow, mp 206-210 °C): monoclinic, space group  $Cc$  ( $C_2^2$ -No. 9),<sup>5a</sup> with  $a = 14.126$  (4),  $b = 11.485$  (6),  $c = 14.609$  (5) Å;  $\beta = 100.37(3)^\circ$ ;  $Z = 4$ .  $[(\text{C}_2\text{H}_5)_4\text{N}]^+[(\text{C}_7\text{H}_6\text{S}_2)\text{Ph}_2\text{SnCl}]^-$ , (**5**) (colorless, mp 156-157 °C): monoclinic, space group  $P2_1/c$  ( $C_2^2$ -No. 14),<sup>5b</sup> with  $a = 12.344$  (4),  $b = 11.975$  (5),  $c = 19.120$  (5) Å;  $\beta = 96.41$  (2)°;  $Z = 4$ .

Data for both compounds were collected on an Enraf-Nonius CAD4 automated diffractometer by using graphite monochromated  $\text{Mo K}\alpha$  radiation and the  $\theta$ - $2\theta$  scan mode, out to a maximum  $2\theta_{\text{MoK}\alpha}$  of 50. Both structures were solved by using standard Patterson and difference Fourier techniques and were refined by using full-matrix least squares<sup>6</sup> (anisotropic for non-

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