# Hydrocarbon Analogue of the Squarate Dianion. Evidence for Its Possible Aromaticity and the Examination of Its Behavior with Two Quenching Agents

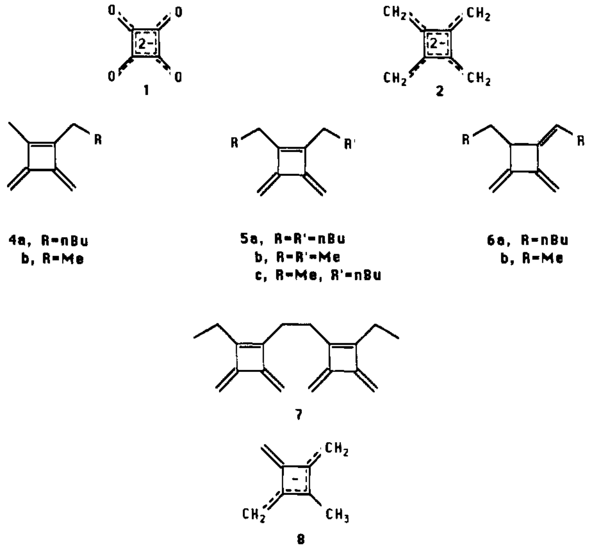
Wade T. Thorstad, Nancy S. Mills,* Daryl Q. Buckelew, and Linda S. Govea

*Department of Chemistry, Trinity University, San Antonio, Texas 78284*

*Received June 20, 1988*

The hydrocarbon analogue of the squarate dianion 2 was prepared by metalating 1,2-dimethyl-3,4-bismethylenecyclobutene with *n*-butyllithium/potassium *tert*-butoxide or *n*-butyllithium/TMEDA. The "dianion" was characterized by quench with *n*-butyl chloride or methyl iodide, which revealed a maximum concentration of dianion after 144 h when the starting alkene was metalated with *n*-butyllithium/TMEDA. The dianion was also characterized by $^1$H NMR spectroscopy, which showed a singlet at 1.71 ppm in THF. The linear relationship between charge density and chemical shift for the cyclic aromatic ions is also demonstrated by 2, suggesting its possible aromaticity. The quench with methyl iodide showed significantly more coupled products than did the quench with *n*-butyl chloride even when the counterions were lithium·TMEDA.

Chart I



The cyclic oxocarbon anions have been suggested as members of an aromatic series that is stabilized by electron delocalization of $\pi$ electrons around the ring. Squarate dianion 1, the four-carbon member of this family, possesses a square-planar structure ($D_{4h}$ symmetry) as established by vibrational spectroscopy[2] and an X-ray structure determination of potassium squarate monohydrate.[3] Because of our interest in cross-conjugated dianions[4] and novel aromatic species,[5] we prepared the hydrocarbon analogue of the squarate dianion, the dianion 2 of 1,2-dimethyl-3,4-bismethylenecyclobutene (3) (Chart I).

The reaction of 3 with 2 equiv of *n*-butyllithium/potassium *tert*-butoxide resulted in formation of the dianion 2 in less than 20 min. The dianion was identified by quench with *n*-butyl chloride or with methyl iodide. The alkylated products were separated by preparative gas chromatography and identified via their mass spectra and $^1$H NMR spectra (Table I). When the quenching agent was *n*-butyl chloride, products **4a** and **5a** were formed. The yield of **5a** and potentially of dianion **2** was relatively invarient at time periods of 3.5 h to 48 h. This undoubtedly reflects the lack of solubility of the monopotassioalkene from loss of one proton. This lack of solubility would hinder deprotonation by the second equivalent of metalating system.[5b]

Because of the difficulty of understanding the sequence of events when *n*-butyl chloride was used to quench "anions" created by metalation with *n*-butyllithium, the reaction mixture was quenched with methyl iodide. This alkylation resulted in formation of **4b** and **5b**, presumably from direct attack of the mono- or dilithiated **3** on methyl iodide although electron transfer to methyl iodide followed by coupling would give the same products. Electron transfer is not uncommon in reactions of alkyl halides with organolithium reagents.[6] Small amounts of 1-ethylidene-2,3-bismethylene-4-ethylcyclobutane (**6b**) were also observed, presumably by deprotonation of **5b** by excess base followed by reprotonation. The identification of **4a**, **5c**, and **7** also from reaction with methyl iodide is consistent with electron transfer from the mono- or dianion of **3** or from *n*-butyllithium, to give radical species followed by coupling of those radical species or with alkylation of **2** followed by electron transfer from monoanions or *n*-butyllithium to give the neutral radicals which then couple. Again, the relative amounts of mono- and dimetalated **3** are relatively invariant with time.

The heterogeneous nature of the *n*-butyllithium/potassium *tert*-butoxide metalating system makes it impossible to examine the metalation of **3** as a function of time. We therefore metalated **3** with *n*-butyllithium/*N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA), quenched the reaction mixture after varying periods of time with either methyl iodide or *n*-butyl chloride, and isolated and identified the products (Table I). When the reaction mixture was quenched with methyl iodide after 24 h, products **4a**, **4b**, **5b**, **5c**, **6b**, and **7** were observed in the reaction mixture. Table II shows the change in the composition of the reaction mixture as a function of time. There is a steady increase in products that may be formed from **2** as the reaction time increases with a concomitant decrease in monoanion **8**. Again, **4a**, **5c**, and **7** must arise from coupling of a mono- or dilithiated species with *n*-butyllithium or itself while **4b**, **5b**, and **6b** may arise by direct nucleo-

---

[1] West, R.; Powell, D. L. *J. Am. Chem. Soc.* **1963**, *85*, 2577–2579.

[2] Ito, M.; West, R. *J. Am. Chem. Soc.* **1963**, *85*, 2580–2584.

[3] MacIntyre, W. M.; Werkema, M. S. *J. Chem. Phys.* **1964**, *40*, 3563–3568.

[4] (a) Rusinko, A.; Mills, N. S.; Morse, P. *J. Org. Chem.* **1982**, *47*, 5198–5201. (b) Mills, N. S.; Rusinko, A. R. *J. Org. Chem.* **1986**, *51*, 2567–2571.

[5] (a) Mills, N. S.; Hollingsworth, M.; Shapiro, J. *J. Am. Chem. Soc.* **1981**, *103*, 1263–1264. (b) Mills, N. S. *J. Am. Chem. Soc.* **1982**, *104*, 5689–5693.

[6] Guthrie, R. D. In *Comprehensive Carbanion Chemistry: Part A*; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1980; p 197.

0022-3263/89/1954-0773$01.50/0

Table I. $^1$H NMR and GC/Mass Spectral Data for Products

| compd | $^1$H NMR spectral data[a] | GC/mass spectral data |
|---|---|---|
| **4a** | 0.89 (t, $J$ = 6.8 Hz, 3 H, 1.32 (m, 4 H), 1.56 (m, 2 H), 1.88 (s, 3 H), 2.29 (q, $J$ = 7.77 Hz, 2 H), 4.45 (s, 1 H), 4.47 (s, 1 H), 4.56 (s, 2 H) | $m/e$ 162 ($M^+$), 147 [$(M - CH_3)^+$], 105 [$(M - C_4H_9)^+$, $C_8H_9^+$] |
| **4b** | 1.15 (t, $J$ = 7.7 Hz, 3 H), 1.90 (s, 3 H), 2.33 (q, $J$ = 7.7 Hz, 2 H), 4.57 (s, 1 H), 4.60 (s, 1 H), 4.76 (s, 2 H) | $m/e$ 120 ($M^+$), 105 [$(M - CH_3)^+$, $C_8H_9^+$], 57 ($C_4H_9^+$) |
| **5a** | 0.89 (t, $J$ = 7.4 Hz, 6 H), 1.31 (m, 8 H), 1.55 (m, 4 H), 2.29 (t, $J$ = 7.4 Hz, 4 H), 4.48 (s, 2 H), 4.58 (s, 2 H) | $m/e$ 218 ($M^+$), 161 [$(M - C_4H_9)^+$], 133 [$(M - C_6H_{13})^+$], 105 ($C_8H_9^+$), 91 $(C_7H_7)^+$ |
| **5b** | 1.15 (t, $J$ = 7.6 Hz, 6 H), 2.34 (q, $J$ = 7.6 Hz, 4 H), 4.59 (s, 2 H), 4.50 (s, 2 H) | $m/e$ 134 ($M^+$), 119 [$(M - CH_3)^+$], 105 [$(M - 29)^+$, $C_8H_9^+$] |
| **5c** | 0.89 (t, $J$ = 6.8 Hz, 3 H), 1.17 (t, $J$ = 7.7 Hz, 3 H), 1.32 (m, 4 H), 1.48 (m, 2 H), 2.31 (qq, $J$ = 7.7 Hz, $J$ = 6.8 Hz, 4 H), 4.48 (s, 1 H), 4.49 (s, 1 H), 4.58 (s, 2 H) | $m/e$ 176 ($M^+$), 119 [$(M - C_4H_9)^+$], 105 ($C_8H_9^+$) |
| **6a** | see footnote 7 | $m/e$ 218 ($M^+$), 119 $(C_9H_{11})^+$, 91 $(C_7H_7)^+$ |
| **6b** | 1.12 (t, $J$ = 7.6 Hz, 3 H), 1.84 (s, 3 H), 1.83 (d, $J$ = 6.3 Hz, 3 H), 2.26 (q, $J$ = 7.6 Hz, 2 H), 4.72 (s, 1 H), 4.52 (s, 1 H), 4.92 (q, $J$ = 6.3 Hz, 1 H) | $m/e$ 134 ($M^+$), 119 [$(M - CH_3)^+$], 105, [$(M - 29)^+$, $C_8H_9^+$] |
| 7 | 1.11 (t, $J$ = 7.4 Hz, 6 H), 2.29 (q, $J$ = 7.4 Hz, 4 H), 2.55 (s, 4 H), 4.51 (s, 4 H), 4.61 (s, 4 H) | $m/e$ 238 ($M^+$), 209 [$(M - C_2H_5)^+$], 119 [$(M - C_9H_{11})^+$], 91 $(C_7H_7)^+$ |

[a] In $CDCl_3$, TMS as reference. Satisfactory elemental analyses were obtained for all compounds reported in the table.

Table II. Metalation of **3** with *n*-Butyllithium/TMEDA

| quenching agent | time, h | **3** | **4b** | **4a** | total from | **5b** | **6b** | **5c** | **7** | total from **2** |
|---|---|---|---|---|---|---|---|---|---|---|
| MeI | 24 | – | 64 | 3 | 67 | 14 | 8 | 5 | 6 | 33 |
| | 48 | – | 59 | – | 59 | 14 | 11 | – | 16 | 41 |
| | 144 | – | 34 | – | 34 | 23 | 11 | – | 32 | 66 |
| | | **3** | **4a** | | | **5a** | **6a** | | **7** | |
| *n*-BuCl | 96 | – | 77 | | 77 | 23 | – | | – | 23 |
| | 120 | – | 39 | | 39 | 54 | 6 | | – | 60 |
| | 144 | – | 30 | | 30 | 58 | 12 | | – | 70 |

philic attack of the metalated species on methyl iodide (followed by deprotonation/reprotonation in the case of **6b**) or by coupling from electron transfer to methyl iodide.

The quench with *n*-butyl chloride to give **4a**, **5a**, and **6a**[7] also showed a steady increase in the yield of products from **2** as a function of time as shown in Table II. The quench with *n*-butyl chloride was slower than that with methyl iodide. When methyl iodide was added to the test tube of metalated **2**, the loss of color from the reaction mixture occurred within 5 min at 0 °C. With *n*-butyl chloride, complete loss of color usually required 4–6 h. Because *n*-butyl chloride did coexist with the metalated alkenes, we believe that some proton abstraction by **2** from *n*-butyl chloride occurred, giving a slightly diminished yield of **5a** and **6a**, most obviously in the quench with *n*-butyl chloride at 96 h.

The presence of **6a** in the quench with *n*-butyl chloride and **6b** in the quench with methyl iodide suggests that even in the more rapid quench with methyl iodide, the alkyl halide coexists with alithiated hydrocarbon capable of abstracting a proton. *n*-Butyllithium was not present to an appreciable extent by 48 h because octane, formed by coupling of *n*-butyllithium in the presence of methyl iodide or by nucleophilic attack by *n*-butyllithium on *n*-butyl chloride, was only observed in trace amounts. The formation of **6** was greatest when the reaction mixture contained a large amount of solid, which was quenched by direct addition of alkyl halide. This solid was presumably dilithiated **3** (i.e. **2**) since monolithiated hydrocarbons in general tend to be soluble in the *n*-butyllithium/TMEDA metalating system[8] and because when the reaction mixture was quenched when there was little or no solid present, the yield of products from **8** was high and the yield of products from **2** was low. Product **6** is presumably formed at the solid/liquid interface by deprotonation of monoalkylated hydrocarbon or monolithiated–monoalkylated **3** from the localized concentration of **2** at the surface of the solid. When the solid from the reaction mixture was dissolved in THF-$d_8$ for NMR analysis, no isomerized product **6** was observed after quenching the NMR solution with *n*-butyl chloride or methyl iodide, confirming that the isomerization does not occur in solution.

The apparent coexistence of alkylating agent and lithiated **3** calls into question the formation of **2** as a discrete species. Could dialkylated products have been formed from monolithiation, alkylation, followed by a second deprotonation, and second alkylation? The $^1$H NMR spectrum confirms the formation of **2**. The starting material **3** was metalated with *n*-butyllithium/TMEDA for 144 h, the supernatant removed, and the solid dianion dissolved in THF-$d_8$ that had been dried with sodium. The $^1$H NMR spectrum showed a singlet at $\delta$ 1.71 that was assigned to **2**, as well as peaks for the anion (**8**) from monolithiated of **3**. Assignment of the peaks from **8** was made after dissolving the solid from metalation of **3** in "wet" THF-$d_8$, followed by quench with alkyl halide to confirm the absence of products from **2**. When the spectrum of the metalated solid in "wet" THF-$d_8$ was compared with the spectrum of the solid in THF-$d_8$ dried with sodium, which gave dialkylated products upon subsequent quench with alkyl halide, the peak at $\delta$ 1.71 was present only in the spectrum of the latter solution. Attempts to obtain the $^{13}$C NMR spectrum of **2** were unsucessful because the

---

(7) **6a** was identified solely on the basis of the similarity of its mass spectrum to that of **6b**, which had also been characterized by its $^1$H NMR spectrum, and by differences between its spectrum and that of **5a**. **6a**: $m/e$ 119 $(C_9H_{11})^+$, 100% relative abundance, $m/e$ 91 ($C_7H_7$), 91% relative abundance, two of the largest peaks in mass spectrum. **6b**: $m/e$ 119 $(C_9H_{11})^+$, 95% relative abundance, $m/e$ 91 $(C_7H_7)^+$, 100% relative abundance, also two largest peaks in mass spectrum. **5a**: $m/e$ 105 $(C_8H_9)^+$, 100% relative abundance; $m/e$ 119 $(C_9H_{11})^+$, 18% relative abundance, 91 $(C_7H_7)^+$, 67% relative abundance. **5b**: $m/e$ 105 ($C_8H_9$), 100% relative abundance, 119 $(C_9H_{11})^+$, 18% relative abundance, 91 $(C_7H_7)^+$, 51% relative abundance.

(8) Mills, N. S. Ph.D. Thesis, University of Arizona, 1976.

**Table III. Products from Coupled vs Noncoupled Anions[a]**

| metalating system | ratio of metalating system to **3** | time, h | from noncoupled monoanion (**4b**) | from noncoupled dianion (**5b**, **6b**) | from coupled monoanion (**4a**) | from coupled dianion (**5c**, **7**) |
|---|---|---|---|---|---|---|
| KO-*t*-Bu/*n*-BuLi | 2:1 | 22 | 24 | 27, 1 = 28 | 1 | 3, 45 = 48 |
| | 2:1 | 48 | 21 | 28, 1 = 29 | – | 1, 48 = 49 |
| | 4:1 | 22 | 23 | 24, 10 = 34 | – | 2, 41 = 43 |
| *n*-BuLi/TMEDA | 2:1 | 24 | 64 | 14, 8 = 22 | 3 | 5, 6 = 11 |
| | 2:1 | 48 | 59 | 14, 11 = 25 | – | –, 16 = 16 |
| | 2:1 | 144 | 34 | 23, 11 = 34 | – | –, 32 = 32 |

[a] Percentages reflect only products from reaction of anionic species, starting material has been excluded.

**Table IV. Coupling of Anionic Species with *n*-Butyllithium vs "Self-Coupling"**

| metalaing system | ratio of metalating system to **3** | time, h | product from coupling with *n*-butyllithium (**4a**, **5c**) | product from coupling with **2** (**7**) |
|---|---|---|---|---|
| KO-*t*-BuLi/*n*-BuLi | 2:1 | 22 | 8 | 92 |
| | 2:1 | 48 | 2 | 98 |
| | 2:1 | 144 | 5 | 95 |
| *n*-BuLi/TMEDA | 2:1 | 24 | 59 | 41 |
| | 2:1 | 48 | – | 100 |
| | 2:1 | 144 | – | 100 |

[a] Percentages reflect only products from coupling of anionic species, starting material has been excluded.

dianion reacted with the THF solvent before a sufficient number of transients could be obtained. For the same reason, the spectrum of dipotassio-**2** from metalation with *n*-butyllithium/potassium *tert*-butoxide was not attainable.

In addition to verifying the existence of **2** as a discrete entity, the $^1$H NMR spectrum gave insight into its potential aromaticity. When the chemical shift of dilithio-**2** is compared with the charge density on the terminal carbons, the dianion shows the same linear relationship as the aromatic ions,[9] the cyclopentadienyl anion, the cycloheptatrienyl cation, the trimethylenemethane dianion,[5a] and benzene. By this criterion, anion **2** is as aromatic as the previously mentioned ions. Interestingly, the relationship between charge density and chemical shift shown by **2** was more similar to that demonstrated by the 6 $\pi$-electron systems than that shown by the 10 $\pi$-electron systems, cycloheptatrienyl trianion, cyclooctatetraene dianion, and the cyclononaenyl monoanion. The chemical shift/charge density of **2** were compared with the chemical shifts/charge densities of the terminal carbons of the nonaromatic linear delocalized monoanions to determine whether the chemical shift could be due to simple delocalization rather than aromaticity. These delocalized anions also demonstrate the linear relationship between chemical shift and charge density.[5a] The correlation for **2** is much closer to the relationship shown by the aromatic ions than to that shown by the linear monoanions.

The differences in the behavior of the reaction mixture with the two quenching agents make comments on these differences appropriate. Quench with methyl iodide unquestionably gives higher yields of coupled products rather than products from direct nucleophilic attack on the alkyl halide. When the quenching agent is *n*-butyl chloride, it is impossible to differentiate between alkylation by *n*-butyl chloride and electron transfer to give ultimately coupling between radicals from *n*-butyllithium and radicals from **2**. However, no "self-coupled" products like **7** were observed from *n*-butyl chloride quench of anions from **3** with either metalating system. Since **7** is formed in 29–41% after quench with methyl iodide when the metalating system is potassium *tert*-butoxide/*n*-butyllithium and from 1 to 32% after quench with methyl iodide when the metalating system is *n*-butyllithium/TMEDA, the complete absence of **7** after quenching with *n*-butyl chloride suggests strongly the absence of electron transfer during those quenches.

Tables III and IV compare products from reaction of the metalated **3** with methyl iodide. Table III groups products that have been methylated (products that presumably were formed by nucleophilic attack rather than coupling of radical species from anions) with products that contain an additional butyl group, presumably from *n*-butyllithium, or products from self-coupling of **2**, i.e. **7**. With the potassium *tert*-butoxide/*n*-butyllithium metalating system the ratio of products from non-coupled vs coupled anions is relatively invariant with time. Since **4a**, the product from electron transfer from monoanion followed by coupling with the *n*-butyl radical, is observed only in the reaction mixture quenched after 22 h and then is present in only 1% abundance, it appears obvious that electron transfer is significantly more facile from dianion **2** than from monoanion **8**.

An alternative way to look at the coupled products is to consider the amount of coupling with *n*-butyllithium vs coupling of **2** with itself. As shown in Table IV, when the metalating system is potassium *tert*-butoxide/*n*-butyllithium, the majority of coupled products arise from electron transfer from **2** followed ultimately by coupling of two of the radical species from **2** to give **7**. After 22 h, 92% of the coupled products resulted from "self-coupling", with an increase to 98% by 48 h. The formation of such a high yield of "self-coupled" product is consistent with the insolubility of mono- and dipotassioalkenes, which would limit access to the *n*-butyllithium in solution.

An examination of Table III for the *n*-butyllithium/TMEDA metalating system shows that the yield of products from either coupled or noncoupled dianion increases at the expense of monoanion. The rate of increase in the yield of coupled product originating from **2** was slightly greater at longer periods of time than was the increase in the yield of alkylated products from **2**. As is apparent from the results in the potassium *tert*-butoxide/*n*-butyllithium metalating system, the formation of a higher yield of coupled products that originate from dianion **2** rather than coupled products from **8** suggests that electron transfer is more facile from dilithio-**2** than monolithio-**8**.

---

(9) Bates, R. B.; Hess, B. A.; Ogle, C. A.; Schaad, L. *J. Am. Chem. Soc.* **1981**, *103*, 5052–5058.

Again, an examination of the coupled products only (Table IV) from the *n*-butyllithium/TMEDA metalating system is useful. At short times, more coupled product results from reaction of radicals derived from **2** with *n*-butyllithium than from self-coupling of **2**. This presumably reflects the greater solubility of dilithio-**2** over dipotassio-**2** and its ability to encounter *n*-butyllithium/TMEDA in solution. By 48 h, the coupled product is exclusively from self-coupling of radical species derived from **2**. By this stage in the reaction, the bulk of the dianion exists as a solid at the bottom of the reaction vessel. We believe that the enhanced yield of **7** reflects the fact that election transfer from **2** and coupling occurs in the solid phase or at the solid/liquid interface, rather than in solution. Confirmation of this observation is found when dianion **2** is dissolved in THF-$d_8$ for $^1$H NMR analysis. When the dianion is dissolved and then reacted with methyl iodide, none of the product from self-coupling (**7**) is observed, although **5a** constitutes approximately 10% of the reaction mixture, showing that electron transfer in the presence of methyl iodide still occurs.

The increased yield of self-coupled products when the reaction mixture was treated with methyl iodide compared to the reaction with *n*-butyl chloride, especially when the metalating system was *n*-butyllithium/TMEDA, was curious to us. While electron-transfer reactions in the presence of methyl iodide are not unknown,[10] the dianions that undergo electron transfer are normally formed by metalation with *n*-butyl-lithium/potassium *tert*-alkoxide rather than *n*-butyllithium/TMEDA. Exceptions to this include the stilbene dianion dilithium salt. It exhibits an ESR signal in THF while the cross-conjugated dilithium salt of the tribenzylidenemethane dianion[12] does not, suggesting that charge repulsion in the 1,2-dimetalated compound is responsible for this redox behavior. One could also consider the results in terms of charge alternation, suggested by Klein,[13] which would help stabilize 1,3-dimetalated species and destabilize 1,2-dimetalated systems. Dianion **2** could be seen as a vinyligous 1,2-dimetalated system, or 1,4-dimetalated system, whose lack of charge alternation would predict the tendency for electron transfer, which we observed.[14]

The preparation of **2** by metalation of **3** with two different metalating systems has been described and **2** identified through reaction with two different quenching agents and through $^1$H NMR spectroscopy. Its proton chemical shift suggests that it may possess a novel type of aromatic character. As such, it joins the trimethylenemethane dianion as an aromatic species whose structure is not limited to cyclic delocalization.[15] In addition, in so far as one can draw conclusions for heteroatomic compounds based on the analogous hydrocarbons, the stability/aromaticity of **2** suggests the aromaticity/stability of the squarate dianion, a species whose "aromatic" character has undergone intense scrutiny.[16]

## Experimental Section

**Apparatus and Materials.** $^1$H NMR spectra were recorded in $CDCl_3$ on a Varian VXR-300 MHz nuclear magnetic resonance spectrometer. Product distribution in reaction mixtures at varying periods of time were analyzed on a methyl silicone capillary column with a Hewlett-Packard 5890A gas chromatograph. Mass spectral data were obtained with a Hewlett-Packard 5995 GC/MS. Gas chromatographic separations for NMR analysis were performed on a Perkin-Elmer Sigma 3-B gas chromatograph. Pentane was obtained from Baker and dried by distillation from phosphorus pentoxide. TMEDA, from Aldrich Chemical Co., was distilled from the sodium/benzophenone ketyl. *n*-Butyllithium (1.6 M in hexane) was obtained from Fluka Chemical Corp. 1,2-Dimethyl-3,4-bismethylenecyclobutene was prepared as reported previously.[17]

**Metalation with the Schosser/Lockman-Lim base.** Potassium *tert*-butoxide (0.112 g, 2.00 mmol) in pentane and *n*-butyllithium (1.25 mL, 2.00 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 1,2-dimethyl-3,4-bismethylenecyclobutene (0.240 mL of a 50% solution in hexane, 1.00 mmol). The reaction was quenched with methyl iodide (0.250 mL, 4.00 mmol) or with *n*-butyl chloride (0.418 mL, 4.00 mmol). Water was added to the test tube after 30 min (for the methyl iodide quench) or 24 h (for the *n*-butylchloride quench) until 2 layers were apparent. Mesitylene (24 μL, 0.173 mmol) was then added to serve as an internal standard for gas chromatographic analysis.

For gas chromatographic analysis, the water layer was extracted with pentane and the organic layers were combined and extracted with saturated ammonium chloride to remove TMEDA. Yield data was obtained on a 25-m Hewlett-Packard methyl silicone column under the following conditions: initial temperature 75 °C; initial time 5.0 min; rate 5.0°/min; final temperature 175 °C; final time 5.0 min. The internal standard showed a mass balance of 96–100% of starting material. Comparison of reaction mixtures quenched under identical conditions shows that the percent abundance of each component of the reaction mixture was reproducible to >90%. For $^1$H NMR analysis, the reaction mixture was concentrated by removal of pentane by fractional distillation and the products were separated and collected by preparative gas chromatography on a 4-m OV-17 column.

**Metalation with *n*-Butyllithium/TMEDA.** *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) (0.302 mL, 2.00 mmol) and *n*-butyllithium (1.25 mL, 2.00 mmol) were combined in a septum-capped test tube under argon. To the metalating system was added 1,2-dimethyl-3,4-bismethylenecyclobutene (0.240 mL of a 50% solution in hexane, 1.00 mmol). Methyl iodide (250 mL, 4.00 mmol) was added to the test tube at 0 °C to quench the anions. The reaction mixture was worked up as described above.

Spectral data for all compounds reported are summarized in Table I.

**Acknowledgment.** We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Welch Foundation (Grant W-794), and the National Science Foundation (Grant CHE-85-06038) for financial support of this work and Grant CHE-8619705 for partial assistance in the purchase of the Varian VXR-300 MHz nuclear magnetic resonance spectrometer.

---

(10) (a) Bates, R. B.; Ogle, C. A. *J. Org. Chem.* **1982**, *47*, 3949–3952. (b) Wilhem, A.; Clark, T.; Schleyer, P. v. R.; Courtneidge, J. L.; Davis, A. O. *J. Am. Chem. Soc.* **1984**, *106*, 361–367.

(11) Schleyer, P. v. R. *Pure Appl. Chem.* **1984**, *56*, 151–162, Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 7928–7929.

(12) Wilhelm, D.; Clark, T.; Courtneidge, J. L.; Davies, A. G. *J. Chem. Soc., Chem. Commun.* **1983**, 213.

(13) Klein, J. *Tetrahedron* **1988**, *44*, 503–518.

(14) We thank a referee for calling the Clark and Davies paper to our attention.

(15) For recent evaluations of Y-aromaticity, see: Agranat, I.; Skanche, A. *J. Am. Chem. Soc.* **1985**, *107*, 867–871. Rajca, A.; Tolbert, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 698–699.

(16) Arhara, J. *J. Am. Chem. Soc.* **1981**, *103*, 1633–1635. Jug, K. *J. Org. Chem.* **1983**, *48*, 1344–1348. Herndon, W. C. *Theochem* **1983**, *103*, 219–234.

(17) Borden, W. T.; Gold, A.; Young, S. D. *J. Org. Chem.* **1978**, *43*, 486–491.