

carrying out some of these experiments is much appreciated. One of us (J.-P.C.) thanks the People's Republic of China for a fellowshipship.

**Registry No.** 2, 563-52-0; 3, 2190-48-9; 4, 591-97-9; 5, 503-60-6; 6 (G = *o*-tol), 106358-47-8; 6 (G = *t*-Bu), 106358-49-0; 7, 106358-45-6; 8, 106358-50-3; *t*-BuCl, 507-20-0; 9-CNFIH, 1529-40-4; PhCH<sub>2</sub>Cl, 100-44-7; 9-MeFl<sup>-</sup>·K<sup>+</sup>, 64918-34-9; 9-*o*-tolFl<sup>-</sup>·K<sup>+</sup>, 106358-46-7; 9-*t*-BuFl<sup>-</sup>·K<sup>+</sup>, 106358-48-9; 9-PhFl<sup>-</sup>·K<sup>+</sup>, 106358-43-4; 2-Cl-9-MeFl<sup>-</sup>·K<sup>+</sup>, 106358-57-0; 2,7-Br<sub>2</sub>-9-MeFl<sup>-</sup>·K<sup>+</sup>, 106358-58-1; 2-Br-9-*t*-BuFl<sup>-</sup>·K<sup>+</sup>, 106358-59-2; 2,7-Br<sub>2</sub>-9-*t*-BuFl<sup>-</sup>·K<sup>+</sup>, 106358-60-5; 9-*p*-MeSO<sub>2</sub>-*o*-tolFl<sup>-</sup>·K<sup>+</sup>, 106358-61-6; 9-*m*-ClC<sub>6</sub>H<sub>4</sub>Fl<sup>-</sup>·K<sup>+</sup>, 106358-62-7; 9-*p*-MeSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Fl<sup>-</sup>·K<sup>+</sup>, 106358-

63-8; 9-*p*-BrC<sub>6</sub>H<sub>4</sub>SFl<sup>-</sup>·K<sup>+</sup>, 106358-64-9; 2-Br-9-PhSFl<sup>-</sup>·K<sup>+</sup>, 106358-65-0; 2,7-Br<sub>2</sub>-9-PhSFl<sup>-</sup>·K<sup>+</sup>, 106358-66-1; DCH=CHCH<sub>2</sub>Cl, 89275-39-8; allyl chloride, 107-05-1; 9-phenyl-9-(2-butenyl)fluorene, 106358-44-5; 9-cyano-9-(3-methyl-2-butenyl)fluorene, 106358-51-4; potassium 9-cyanofluorenyl, 57643-25-1; potassium 9-(phenylthio)fluorenyl, 106358-52-5; 9-(phenylthio)-9-(3-methyl-2-butenyl)fluorene, 106375-42-2; potassium 9-(methoxycarbonyl)fluorenyl, 57643-28-4; 9-(methoxycarbonyl)-9-(3-methyl-2-butenyl)fluorene, 106358-53-6; 9-cyano-9-*tert*-butylfluorene, 94004-10-1; 9-methyl-9-allylfluorene, 34163-29-6; 9-phenyl-9-allyl- $\gamma$ -*d*<sub>1</sub>-fluorene, 106358-54-7; 9-cyano-9-(1,1-dimethyl-2-propenyl)fluorene, 106358-55-8; 9-(methoxycarbonyl)-9-(1,1-dimethyl-2-propyl)fluorene, 106358-56-9.

## How Does an Allene Distort to Accommodate Negative Charge? 1,1,3,3-Tetraphenylallene

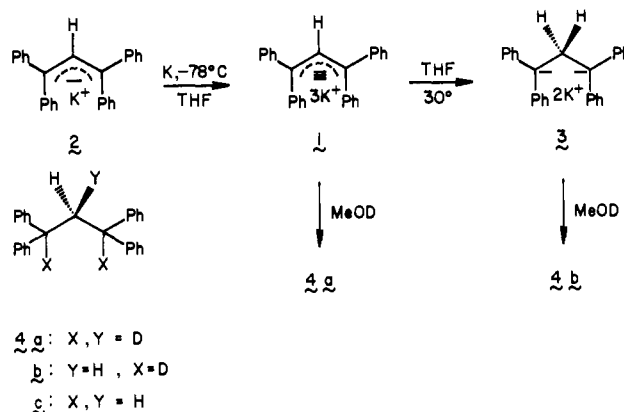
Andrzej Rajca\*<sup>1a</sup> and Laren M. Tolbert\*<sup>1b</sup>

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055. Received May 22, 1986

**Abstract:** Treatment of 1,1,3,3-tetraphenylallene with lithium at low temperature in ethereal solvents leads to a dilithium allenide which apparently consists of two equilibrating 2-lithioallyllithium structures **6a**. Reduction with sodium leads to an analogous, though less stable, species **6b**. Reduction with potassium does not allow detection of the analogous dipotassium allenide **6c**. Rather, protonation by solvent yields 1,1,3,3-tetraphenylallylpotassium (**2c**) which, in the presence of excess potassium, is further reduced to the corresponding trianion **1**. The use of <sup>13</sup>C-enriched material and <sup>13</sup>C-<sup>13</sup>C coupling constants allows a determination of the structure of the hydrocarbon framework. Even in the trianion, substantial residual  $\pi$ -bond order is evident.

With the increased availability of modern computational, crystallographic, and spectroscopic techniques, the study of carbanions or, more correctly, alkali metal derivatives of hydrocarbons has taken a more quantitative turn. We have been engaged in a study of how a three-atom system containing stabilizing groups, e.g., tetraphenylallene, distorts to accommodate excess negative charge.<sup>2</sup> To a first approximation, addition of electrons to such a system mimics the excited state, in that antibonding molecular orbitals are being populated. Thus we have reported that the *D*<sub>2d</sub> tetraphenylallene lowers its symmetry to *C*<sub>2</sub> upon formation of the dilithium derivative.<sup>2</sup> We now report that the corresponding dipotassium derivative cannot be observed directly, but it undergoes rapid protonation by solvent at low temperature to produce the 1,1,3,3-tetraphenylallyl anion. We might ask how this system in turn responds to the presence of three negative charges, i.e., the allyl "trianion" formed by reduction of the monoanion. On the one hand, the lack of degeneracy in the allyl  $\pi^*$  provides no impetus for a Jahn-Teller distortion for the trianion as it does in the allene dianion. On the other hand, population of the allyl  $\pi^*$ -orbital might be expected to result in zero bond order, thus leading to a perpendicular orientation of the benzhydryl groups. In fact, Hückel molecular orbital calculations indicate a substantial residual bond order ( $\rho > 0.4$ ) when two or more phenyl groups further delocalize the  $\pi^*$  orbital. Of course, the strong counterion dependence for the dianion cannot be ignored in the trianion. Since the one-bond <sup>13</sup>C-<sup>13</sup>C and <sup>13</sup>C-<sup>1</sup>H coupling constants are generally

**Scheme I.** Protonation of 1,1,3,3-Tetraphenylallyl Trianion



accepted as measures of the s-character in the associated atomic orbitals,<sup>3</sup> direct observation of the <sup>1</sup>H and <sup>13</sup>C NMR spectra of a <sup>13</sup>C-enriched trimetallopropane derivative appeared to be essential both for establishing the existence of the species and determining its structure. We now report (1) spectroscopic evidence indicating that 1,1,3,3-tetraphenylallyl trianion (**1**) does in fact maintain the allyl geometry insofar as the hydrocarbon framework is concerned, (2) additional low-temperature NMR data in dimethyl ether for dilithium and disodium tetraphenylallenides (**6a,b**) to confirm the previous conclusion about the geometry of the hydrocarbon framework,<sup>2</sup> and (3) full experimental details on both

(1) (a) On leave from the Technical University of Wrocław, Poland. Address correspondence to this author at the Department of Chemistry, University of California, Berkeley, CA 94720. (b) Fellow of the A. P. Sloan Foundation. Address correspondence to this author at the School of Chemistry, Georgia Institute of Technology, Atlanta, GA 30332.

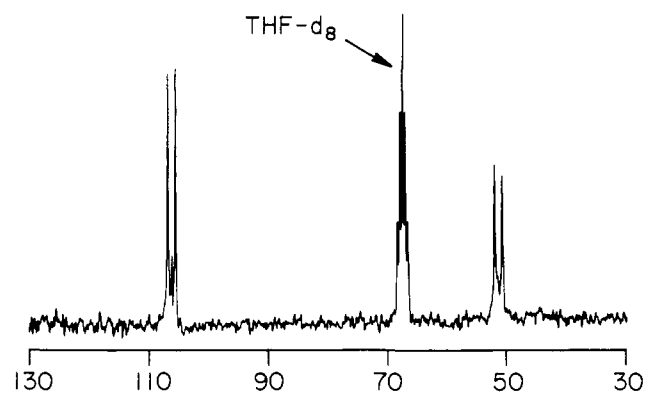
(2) (a) Rajca, A.; Tolbert, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 2969. (b) Rajca, A.; Streitwieser, A., Jr.; Tolbert, L. M. *J. Am. Chem. Soc.*, following paper in this issue.

(3) (a) Bingel, W. A.; Lüttke, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 899. (b) For examples see: Wardeiner, J.; Lüttke, W.; Bergolz, R.; Machinek, R. *Ibid.* **1982**, *21*, 872. Kamińska-Trela, K.; Biedrzycka, Z.; Machinek, T.; Kniere, B.; Lüttke, W. *Org. Magn. Reson.* **1984**, *22*, 317. (c) Wray, V. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *13*, 177.

Table I.  $^{13}\text{C}$  NMR Data (ppm) of Anions 1-4

compd <sup>a</sup>	temp, °C	C(1) <sup>b</sup>	C(2)	$^1J(\text{CC})$ , Hz	$^1J(\text{CH})$ , Hz
1- $^{13}\text{C}_2$ (and $^{13}\text{C}_3$ ) <sup>c</sup>	-82.5	106.1	51.7	64.2	139.8
2- $^{13}\text{C}_3$	-84	105.9	132.8	67.3	138.2 <sup>d</sup>
3- $^{13}\text{C}_3$	24	84.8	37.1	47.5	119.4
4c- $^{13}\text{C}_3$	24	49.8	42.3	34.2	

<sup>a</sup> 90%  $^{13}\text{C}$  enrichment at the C(1) and C(2) or C(1), C(2), and C(3) 0.02-0.1 M solutions in THF- $d_8$  or THF- $h_8$ /THF- $d_8$  mixtures. <sup>b</sup> Reference relative to  $\text{Me}_4\text{Si}$  = 0.00 ppm; THF- $d_8$ , 67.45 ppm for 1 and THF- $h_8$ , 67.96 ppm for 2, 3, and 4c. <sup>c</sup> For the triply  $^{13}\text{C}$ -labeled 1 the high-field absorption of C(2) appears as a triplet. <sup>d</sup> Obtained for 2- $^{13}\text{C}_2$  with lithium counterion at 23 °C.

Figure 1.  $^{13}\text{C}$  NMR spectrum of 1,2- $^{13}\text{C}_2$ -1,1,3,3-tetraphenylallyltripotassium in tetrahydrofuran.

allene and allyl anion reduction by the alkali metals lithium, sodium, and potassium.

## Results and Discussion

**1,1,3,3-Tetraphenylallyltripotassium (1).** Reaction of 1,1,3,3-tetraphenylallyltripotassium (2c) with potassium in tetrahydrofuran<sup>4</sup> at -78 °C for 24 h yielded, after quenching with methanol- $d_1$ , 1,1,3,3-tetraphenylpropane- $d_3$  (4a) (74%). When, prior to the quenching, part of the reaction mixture was allowed to warm to room temperature for 30 min, the tetraphenylpropane- $d_2$  (4b) (50%) was isolated. The  $^1\text{H}$  NMR spectrum at ambient temperature of the reaction mixture exhibited the characteristic five-proton doublet-triplet-triplet pattern in the aromatic region for a benzylic carbanion,<sup>5</sup> i.e., dianion 3<sup>7</sup> (see Scheme I). Moreover, ethylene ( $\delta_{\text{H}} = 5.33$ ), one of the products of base-catalyzed decomposition of the tetrahydrofuran,<sup>6</sup> could be detected in an amount exceeding 0.70 equiv. These quenching results were confirmed by  $^{13}\text{C}$  NMR spectroscopy. A tetrahydrofuran- $d_8$  solution of 1,1,3,3-tetraphenylallyltripotassium<sup>8b</sup> with added metallic potassium at 24.5 °C afforded the  $^{13}\text{C}$  NMR spectrum of 3 exclusively. NMR signals from 1 and 2 were not visible. If the same reaction mixture was subjected to further reduction for 3 h in a -74 °C ultrasonic bath, the  $^{13}\text{C}$  NMR spectrum at -82 °C

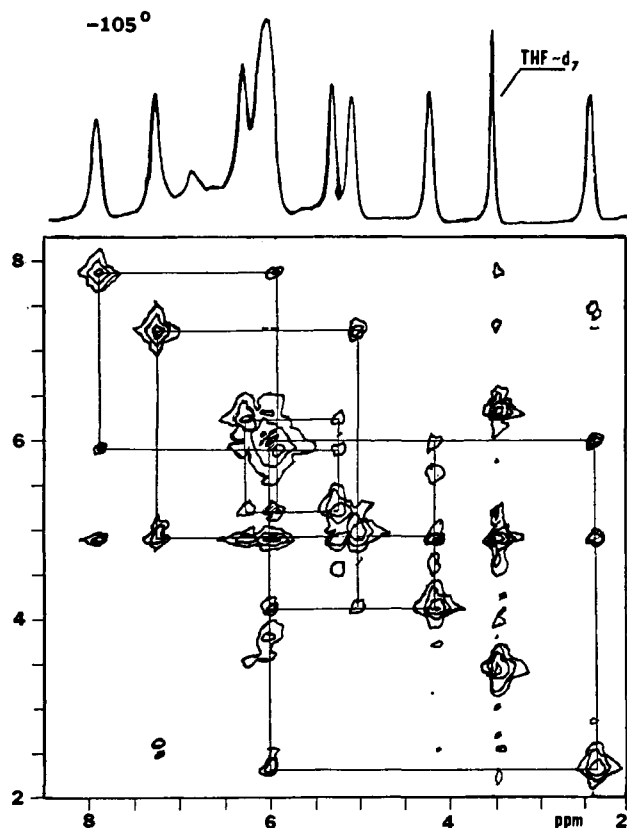
(4) (a) Boche, G.; Buckl, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 284. (b) Dowd, P. *J. Am. Chem. Soc.* **1965**, *87*, 4968. (c) Koelsch, C. F. *J. Am. Chem. Soc.* **1957**, *79*, 4439.

(5)  $^1\text{H}$  NMR (corrected  $\text{Me}_4\text{Si} = 0$  ppm based on known solvent chemical shift: THF- $d_8$ , 3.58; THF- $h_8$ , 1.75): (a) 1,  $^{13}\text{C}_2$  (THF- $d_8$ , ppm, -105 °C) 7.98 (H-9), 6.36 (H-9'), 7.32 (H-5), 2.44 (H-5'), 6.10 (H-6, H-10, H-10'), 5.36 (H-11), 5.12 (H-6'), 4.26 (H-7), H(2) absorption not visible; assignment based on a 2D-COSY experiment. (b) 2 (THF- $d_8$ , ppm, 23 °C) 6.98, d of d (H-5, H-9), 6.67, t (H-6, H-10), 6.36, t of t and s (H-2, H-7, H-11). (c) 3 (THF- $d_8$ , ppm, 34 °C) 6.91, d (ortho); 6.51 t (meta); 5.61, t (para); 3.20, s (H-2). (d) 3 (THF- $h_8$ , ppm, 34 °C) 6.92 d (ortho); 6.48, t (meta); 5.58, t (para); (allylic H(2) resonance buried under the solvent; 5.33, s (ethylene)).

(6) Lehmann, R.; Schlosser, M. *Tetrahedron Lett.* **1984**, *25*, 745.

(7) Wittig, G.; Obermann, B. *Chem. Ber.* **1934**, *67*, 2053.

(8)  $^{13}\text{C}$  NMR (natural abundance, corrected to  $\text{Me}_4\text{Si} = 0$  ppm based on solvent chemical shift: THF- $d_8$ , 67.45): (a) 1 (ppm, -82 °C) 137.1, 130.9, C(4), C(8) 133.8, 125.2, 123.9, 122.1, C(5), C(6), C(9), C(10), 109.5, 96.0, C(7), C(11) 106.1, C(1), C(3) 51.7, C(2). (b) 2 (ppm, -50 °C) 149.9, 145.2, C(4), C(8) 133.3, C(2) 129.1, 127.7, 126.8, 124.2, C(5), C(6), C(9), C(10) 119.2, 117.0, C(7), C(11) 106.4, C(1), C(3). (c) 3 (ppm, 24 °C) 146.3, C(4) 128.5, C(6) 118.5, C(10) 107.1, C(7) 85.3, C(1), C(3) 37.3, C(2).

Figure 2.  $^1\text{H}$  NMR (COSY) spectrum of "allyl trianion" 1.

indicated a mixture of 1 and 3.<sup>8a</sup> Subsequent warming to room temperature afforded the spectrum of pure 3,<sup>8c</sup> which did not change upon cooling to -105 °C.

We then turned our attention to the isotopically enriched (90%  $^{13}\text{C}$ ) 1,2- $^{13}\text{C}_2$ -1 and 1,2,3- $^{13}\text{C}_3$ -1. Although the NMR data for these isotopomers (see Table I and Figure 1) did not allow us to locate the counter cations, we were able to draw the following conclusions about the shape of the hydrocarbon framework of 1:

(i) The coupling constants [ $J(\text{CC}) = 64.2$  Hz,  $J(\text{CH}) = 139.8$  Hz] suggest that 1 possesses an  $\text{sp}^2$ -hybridized allyl framework<sup>3</sup> with a CCC valence angle similar to the monoanion 2 and support the HMO calculation indicating a significant C(1)-C(2) bond order.

(ii) The high-field absorptions of C(2) relative to C(1), C(3) indicate a  $\pi$ -charge distribution reflecting population of the antibonding allyl  $\pi^*$ -orbital, in accordance with observed protonation of 1 at the C(2). The empirical correlation between  $^{13}\text{C}$  chemical shifts<sup>8a</sup> and charge densities<sup>9</sup> yields a  $\pi$ -charge density at C(2) of -0.54 compared with the value calculated from HMO coefficients of -0.58 (see Experimental Section). This, together with the pronounced shielding of the para protons of the phenyl rings, suggests a significant charge delocalization into the phenyl rings, a fact which is again supported by the HMO calculation.

(iii) The absorption pattern of the 200-MHz  $^1\text{H}$  NMR spectrum at -105 °C, with eight distinct proton multiplets containing strongly shielded inside ortho protons and strongly deshielded outside ortho protons for the endo phenyl groups, indicates a planar  $C_{2v}$  or an approximately planar  $C_2$ - or  $C_s$ -symmetric structure for the allyl framework with the phenyl rings twisted out of the CCC plane in propeller fashion (Figure 2).<sup>5a</sup> A  $D_2$  structure with 90° twisted benzhydryl groups would have only five proton absorptions.

Thus we conclude that the geometry of the hydrocarbon framework of the allyltripotassium derivative 1 and the allyltripotassium derivative 2 are comparable.

(9) (a)  $\rho_{\text{charge}} = (\delta_{\text{C}} - 134.1)/153.7$ . See: Boche, G.; Etzrodt, H.; Marsch, M.; Thiel, W. *Angew. Chem. Suppl.* **1982**, *345*. (b) Rajca, A.; Tolbert, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 698. (c) Rajca, A.; Tolbert, L. M., in preparation.

**Table II.**  $^{13}\text{C}$  NMR Data (ppm) for  $^{13}\text{C}$ -Enriched Anions and Their Precursors

compd <sup>a</sup>	temp, °C	C(1) <sup>b</sup>	C(2)	C(3)	$J(1,2)$ , Hz	$J(2,3)$ , Hz	solvent <sup>c</sup>
<b>5</b>	-112	113.5	209.8		103.0		Me <sub>2</sub> O
<b>6a</b>	-80	118.2	203		40.0		Me <sub>2</sub> O
	-115	117.7	203.8		40.0		Me <sub>2</sub> O
<b>6b</b>	-140	117.2	<i>d</i>		40.0		Me <sub>2</sub> O
	-80	112.1	205.2		40.2		Me <sub>2</sub> O
	-111	112.3	207.0		40.0		Me <sub>2</sub> O
	-140	112.7	208.9		40.0		Me <sub>2</sub> O
<b>2b</b>	-120	105.6	113.0		67		Me <sub>2</sub> O
<b>7a</b>	-80	106.9	129.1	112.1	66	66	THF
<b>7c</b>	-80	105.7	128.1	111.7	65	67	THF
<b>9</b>	-85	80.9	45.2	61.3	47	45	THF- <i>d</i> <sub>8</sub>
<b>10-Li</b>	-80	61.9	208.2	<i>e</i>	15.3		THF- <i>d</i> <sub>8</sub>

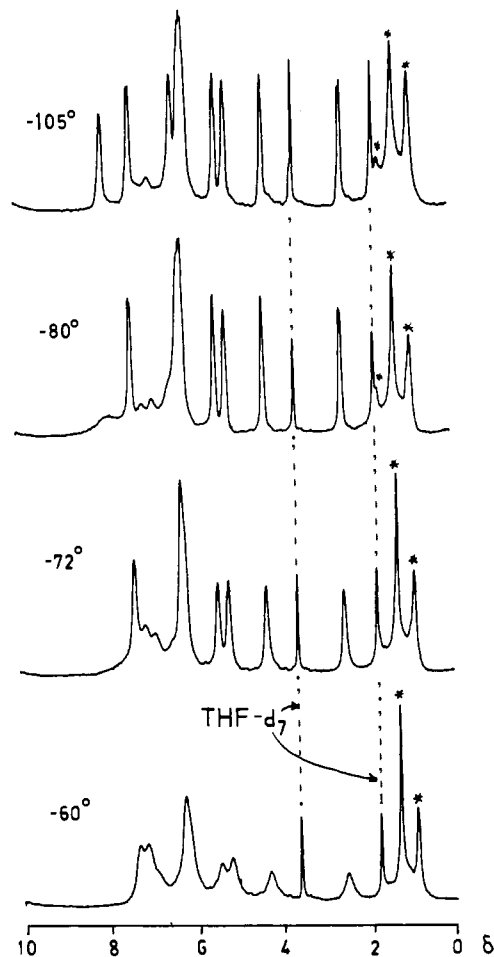
<sup>a</sup> 90%  $^{13}\text{C}$  enrichment at the C(1) and C(2) or C(1), C(2), and C(3). <sup>b</sup> Reference relative to Me<sub>4</sub>Si = 0.00 ppm; Et<sub>2</sub>O-*d*<sub>10</sub>, 14.50 ppm for Me<sub>2</sub>O solutions; THF-*h*<sub>8</sub>, 67.96 ppm for THF solutions; THF-*d*<sub>8</sub>, 67.45 ppm for THF-*d*<sub>8</sub> solutions. <sup>c</sup> The nondeuterated solvents such as Me<sub>2</sub>O and THF contained a 10–30% admixture of Et<sub>2</sub>O-*d*<sub>10</sub> and THF-*d*<sub>8</sub>, respectively. <sup>d</sup> The signal-to-noise ratio was insufficient to resolve C(2) at this temperature. <sup>e</sup>  $^{13}\text{C}$  nonenriched carbon.

The slow allylic rotation (on the NMR time scale) at temperatures up to  $-80\text{ }^\circ\text{C}$  ( $^1\text{H}$  NMR) indicates that the underlying barrier is at least 8.7 kcal/mol, reflecting considerable bond order between allylic carbons. This should be compared to 13.3 kcal/mol for 1,1,3,3-tetraphenylallyllithium (**2a**).<sup>10</sup> A quantitative measurement of the barrier for **1** is hampered by line broadening at higher temperatures ( $-60$  to  $-15\text{ }^\circ\text{C}$ ). However, it should be noted that factors other than allylic rotation must contribute to this exchange broadening, because the allylic carbon resonances broaden as well (see supplementary material). Upon recooling to  $-105\text{ }^\circ\text{C}$ , the original spectrum is recovered. Trianion **1** and the related system **2c** exhibit a remarkable stereodynamic behavior indicating a "locked" conformation on the NMR time scale for **1** at  $-105\text{ }^\circ\text{C}$ . At  $-80\text{ }^\circ\text{C}$ , the two resonances at  $\delta$  7.98 and 6.36 shift  $\delta$  0.1 toward each other and broaden, coalescing at  $-80$  to  $-72\text{ }^\circ\text{C}$ , which suggests the onset of rotation of the *exo*-phenyl groups (see Figure 3). In **2c** the *exo*-phenyl rotation cannot be halted, although the resonances did broaden nearly to base line at  $-105\text{ }^\circ\text{C}$ . Coalescence temperatures for *endo*-phenyl and allylic rotations are about  $-80$  and  $-20\text{ }^\circ\text{C}$ , respectively. All resonances are easily assigned via COSY experiments (see supplementary material). The important feature of this dynamic behavior is that the allylic resonance as measured by the rotational barrier is still significant in trianion **1**.

Interestingly, 1,1,3,3-tetraphenylallyllithium in tetrahydrofuran is not reduced even after prolonged exposure to an activated lithium metal surface ( $-74\text{ }^\circ\text{C}$  to room temperature). Conversely, 1,2,3-triphenylallyllithium in tetrahydrofuran is reduced by lithium to form the corresponding allyltrilithium derivative.<sup>4a</sup> Moreover, the trimetallo 1,2,3-triphenylallyl trianion (M = Li, Na, K, Cs) is stable in tetrahydrofuran at room temperature.<sup>4a</sup> Although this apparently greater stability may result from kinetic effects leading to an increased barrier for proton transfer, a more appealing explanation for the decisive effect of phenyl substitution at C-2 lies in the lowering of  $\pi^*$  from  $0.71|\beta|$  in 1,1,3,3-tetraphenylallyl anion to  $0.64|\beta|$  in 1,2,3-tetraphenylallyl anion, as well as a decrease in the negative charge density at C-2 from  $-0.58$  to  $-0.26$ . This effect, predicted from Hückel molecular orbital theory, is in accord with our recent studies on 1,3-diphenyl-2-arylallyl anions.<sup>11</sup>

**Dilithium and Disodium Tetraphenylallene (6a,b).** Alkali metal reductions of 1,2,3- $^{13}\text{C}_3$ -1,1,3,3-tetraphenylallene (**5**) in sealed NMR tubes afforded dilithium and disodium compounds **6a** and **6b** as blue solutions in a 90:10 mixture of dimethyl ether and diethyl-*d*<sub>10</sub> ether. In the case of the dilithium derivative reductions were performed at  $-74\text{ }^\circ\text{C}$  while **6b** had to be produced at much lower temperature ( $-105\text{ }^\circ\text{C}$ ) due to its instability.

The  $^{13}\text{C}$  NMR data for 1,2,3- $^{13}\text{C}_3$ -**6a** in Me<sub>2</sub>O/Et<sub>2</sub>O-*d*<sub>10</sub> (see Table II) are essentially identical with the previously reported data



**Figure 3.**  $^1\text{H}$  NMR spectra of allyl "trianion" **1** showing rotation of *exo*-phenyl groups. Asterisks indicate unassigned peaks and hydrocarbons from potassium hydride suspension.

in tetrahydrofuran and are indicative of a bent CCC framework.<sup>2</sup> We note that the terminal carbon resonances remained equivalent and uncoupled to  $^6\text{Li}$  even at  $-140\text{ }^\circ\text{C}$ . The C(2) resonance showed a 9 Hz line splitting due to  $^{13}\text{C}$ - $^6\text{Li}$  coupling. The  $^6\text{Li}$  NMR spectrum exhibited only a well-resolved doublet ( $J = 9\text{ Hz}$ ) at  $-115\text{ }^\circ\text{C}$  from  $^{13}\text{C}(2)$ - $^6\text{Li}$  coupling (see Figure 4), comparable to the poorly resolved spectrum reported in THF (see Figure 2, ref 2). Recalling the splitting of the C(2) resonance into a quintet because of the  $^6\text{Li}$  ( $J = 1$ ) coupling, we can reiterate our previous conclusion that **6a** possesses two equivalent lithium atoms and is monomeric.<sup>2</sup>

In an attempt to freeze out possible intramolecular lithium exchanges—note that intermolecular exchange would abolish C-Li

(10) Bauer, H.; Angrick, M.; Rewicki, D. *Org. Magn. Reson.* **1979**, *12*, 624.

(11) (a) Tolbert, L. M.; Ali, M. Z. *J. Org. Chem.* **1985**, *50*, 3288. (b) Ali, M. Z. Ph.D. Thesis, University of Kentucky, 1982.

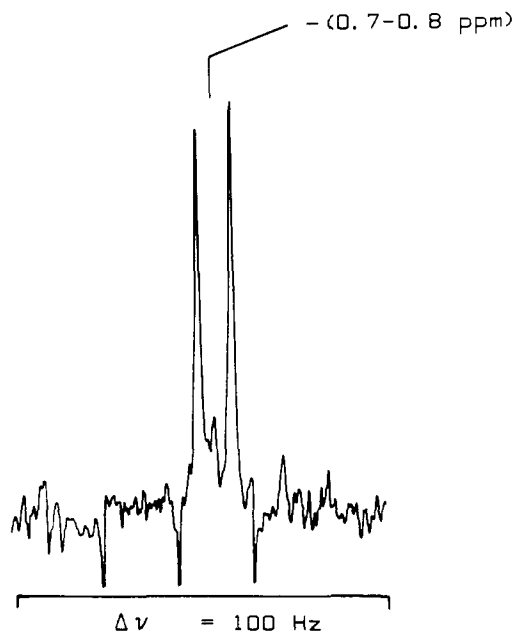


Figure 4.  ${}^6\text{Li}$  NMR spectrum of dilithium 1,2,3- $[^{13}\text{C}_3]$ -1,1,3,3-tetraphenylallene.

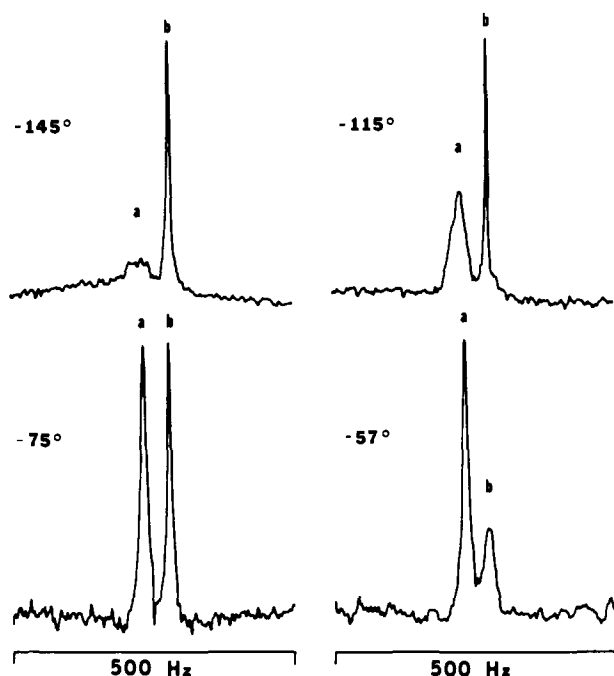


Figure 5.  ${}^7\text{Li}$  NMR spectrum of dilithium tetraphenylallene in the presence of 1,1,3,3-tetraphenylallyllithium: (a)  $-(0.8-0.7)$  ppm,  $\text{Ph}_2\text{CCPh}_2\text{-}{}^7\text{Li}_2$ ; (b)  $-(1.3-1.4)$ ,  $\text{Ph}_2\text{CCHCPh}_2\text{-}{}^7\text{Li}$ .

coupling—the reduction was performed with  ${}^7\text{Li}$  (natural abundance, 95.6%  ${}^7\text{Li}$ ) and nonenriched tetraphenylallene (**5**). A solvent containing traces of water was employed in order to obtain an approximately equimolar mixture of dianion **6a** and 1,1,3,3-tetraphenylallyllithium (**2a**). Compound **2a**, which could be assumed to exist as a solvent separated ion pair or as free ions at low temperature, served as an indicator of the limiting  ${}^7\text{Li}$  NMR resolution. The  ${}^7\text{Li}$  NMR spectrum indicated a gradual broadening of the  ${}^7\text{Li}$  resonance of **6a** upon temperature lowering, while that for **2a** remained unchanged (see Figure 5). At  $-145^\circ\text{C}$  the resonance nearly approached the base line, which made conclusions about its Lorentzian or non-Lorentzian line shape difficult, especially given the additional possibility of instrumental effects at low temperature. A Lorentzian line shape would suggest coalescence of two nonequivalent lithiums, while a non-Lorentzian would be characteristic of  $I > 1$  nuclei upon breaking the extreme narrowing

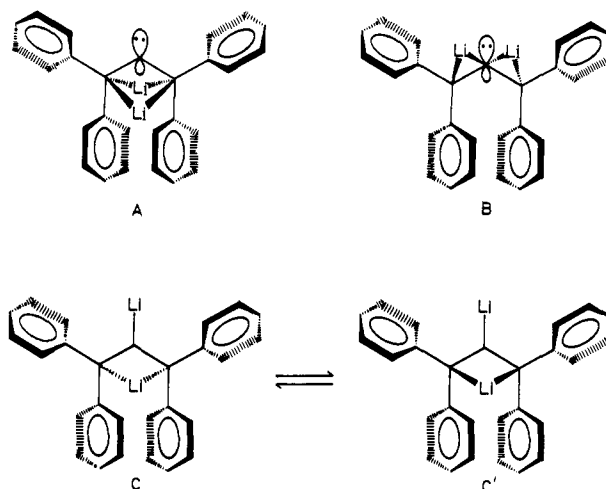


Figure 6. Possible structures for dilithium tetraphenylallene (**6a**).

approximation.<sup>12</sup> Thus we cannot rigorously distinguish between quasi- $C_2$  or  $-C_{2v}$  symmetric structures A or B and two quasi- $C_s$  symmetric structures C and C' undergoing fast exchange on the NMR time scale (see Figure 6). Ab initio calculations<sup>2b</sup> on 2,3-dilithiopropenes indicate that structures corresponding to A, B, and C are within 7 kcal/mol (HF/3-21G//3-21G) with C being the minimum of the three. Moreover, the barrier for the corresponding lithium exchange ( $C = C'$ ) via structure A is estimated to be only around 5 kcal/mol.<sup>2b</sup> The structure related to B would fit the NMR data and, provided  $sp^2$  hybridization of atoms 1 and 3 leads to zero coupling, has some precedence in the related dilithium derivative of dibenzyl ketone.<sup>13</sup> However, it has the highest energy among these three for unsubstituted 2,3-dilithiopropenes. Thus our spectroscopic results, together with the ab initio calculations on the parent system, are supportive of a fast exchange between structures C and C'.

The barrier for the allylic rotation in **6a** is less than in the corresponding allyllithium derivative **2a**, i.e., at 200 MHz  ${}^1\text{H}$  resonances for **2a** in tetrahydrofuran- $d_8$  coalesced between  $-10$  and  $-20^\circ\text{C}$ , while for **6a**, which possessed more different chemical shifts for the pairs of exchanging protons,<sup>14</sup> coalescence could not be observed even at  $-40^\circ\text{C}$ . Such a result does not necessarily imply less allylic resonance in **6a**. Boche and co-workers<sup>15</sup> documented that the more bulky the substituent at C(2) the smaller the barrier for allylic rotation in 2-alkyl-1,3-diphenylallyl anions. Since **6a-c** could be formally treated as 2-lithio-substituted **2a**, the smaller barrier for the allylic rotation in **6a** might be an artifact of the larger steric requirements for lithium vs. hydrogen.<sup>15</sup>

The  ${}^{13}\text{C}$  NMR spectrum at  $-140^\circ\text{C}$  for disodium 1,2,3- $[^{13}\text{C}_3]$ -1,1,3,3-tetraphenylallene (**6b**) showed the expected triplet and doublet at  $\delta$  208.9 and 112.7 ( $J = 40.0$  Hz, see Figure 7a). The spectrum also showed residual amounts of the allene **5** and 1,2,3- $[^{13}\text{C}_3]$ -1,1,3,3-tetraphenylallylsodium (**2b**) (upfield doublet  $\delta$  105.6,  $J = 67$ ). Although the  ${}^{13}\text{C}$ - ${}^{13}\text{C}$  coupling constant for **6b** was identical with the one for the dilithium derivative **6a**, the chemical shifts were slightly different, i.e., the C(2) resonance in **6b** was shifted downfield by 2–6 ppm and the C(1), C(3) resonance appeared upfield by ca. 6 ppm. The chemical shift of the C(2) resonance was temperature dependent (see Table II). Aside from a negligible broadening of the C(2) resonance, no

(12) (a) Hubbard, P. S. *J. Chem. Phys.* **1970**, *53*, 985. (b) For  ${}^7\text{Li}$ , which is an  $I = 3/2$  nucleus, a non-Lorentzian line shape may consist of two absorptions: one sharp and one underlying broad one (cf. Figure 5). (c) For  ${}^{23}\text{Na}$  ( $I = 3/2$ ) non-Lorentzian line shapes, see: Lerner, L.; Torchia, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 4264 and references therein.

(13) Dietrich, H.; Mahdi, W.; Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *24*, 621.

(14) Bernard, J.; Schnieders, C.; Müllen, K. *J. Chem. Soc., Chem. Commun.* **1985**, 12.

(15) (a) Boche, G.; Buckl, K.; Martens, D.; Schnieder, D. R. *Liebigs Ann. Chem.* **1980**, 1135. (b) For example, the  ${}^1\text{H}$  NMR (200 MHz) spectrum of 2-methyl-1,1,3,3-tetraphenylallyllithium in tetrahydrofuran- $d_8$  did not coalesce even at  $-40^\circ\text{C}$ .

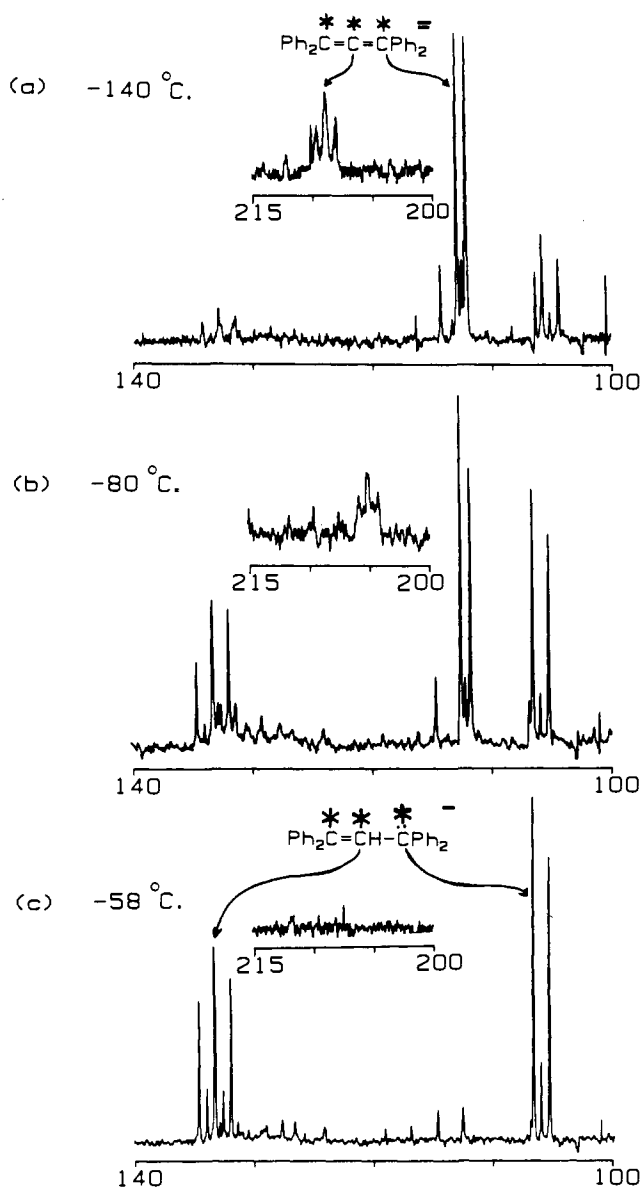
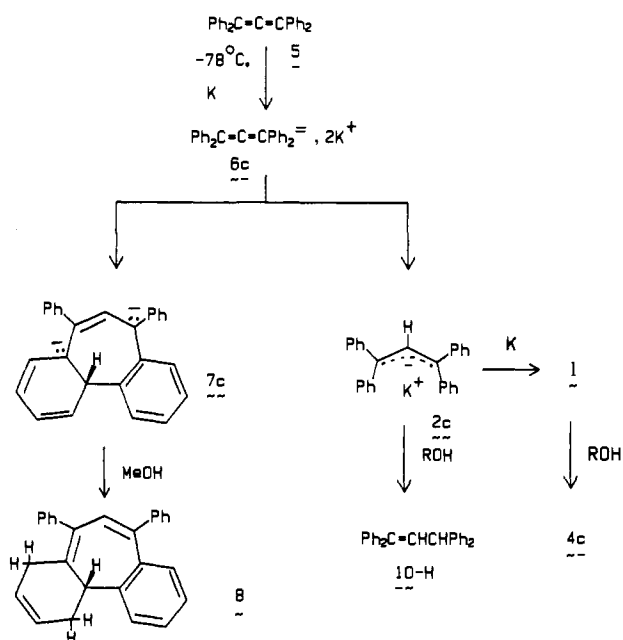


Figure 7. Evolution of  $^{13}\text{C}$  NMR spectrum of disodium tetraphenylallene (**6b**).

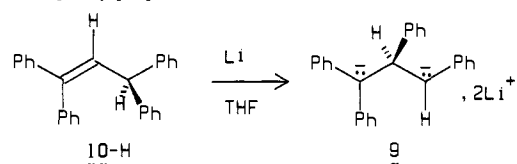
detectable  $^{13}\text{C}$ - $^{23}\text{Na}$  coupling could be observed. The large quadrupole moment, four orders of magnitude larger for  $^{23}\text{Na}$  than for  $^6\text{Li}$ , might be responsible for the effective decoupling of the carbon resonance. Other causes for lack of detectable C-Na coupling such as intermolecular exchange of sodium or the large ionicity of the C-Na bond could not be excluded. Upon warming to  $-80^\circ\text{C}$  the relative amount of monoanion **2b** increased and the C(2) resonance for dianion **6b** moved upfield (see Figure 7b). Further warming to  $-60^\circ\text{C}$  led to disappearance of dianion **6b** within 15 min. Monoanion **2b** was the sole product (see Figure 7c). The reaction mixture changed in color from blue to red. The spectrum remained unchanged upon recooling to  $-120^\circ\text{C}$ .

Bernard, Schnieders, and Müllen,<sup>14</sup> and, earlier, Dowd<sup>26</sup> reported that dianion **6a** underwent irreversible cyclization/tautomerization to **7a** at room temperature in THF- $d_8$  (compare to the potassium derivative **7c** in Scheme II). We confirmed their result using dilithium 1,2,3- $^{13}\text{C}_3$ -1,1,3,3-tetraphenylallene (**6a**) in THF (30%  $d_8$ ). The  $^{13}\text{C}$  NMR data for the resultant triply  $^{13}\text{C}$ -enriched dianion **7a**, which indicated three nonequivalent  $^{13}\text{C}$ -enriched carbons, nevertheless exhibited both  $^{13}\text{C}$  chemical shifts and CC coupling constants very similar to 1,2,3- $^{13}\text{C}_3$ -1,1,3,3-tetraphenylallyllithium (**2a**).<sup>210</sup> This agrees both with MO charges for octatetraene dianion and the previously proposed pictorial representation of **7a** as allyl and pentadienyl anions.<sup>14</sup>

### Scheme II. Reaction of Tetraphenylallene with Potassium



### Scheme III. Reductive Rearrangement of 1,1,3,3-Tetraphenylpropene



**Reaction of Tetraphenylallene with Potassium.** Reactions at  $-78$  and  $-45^\circ\text{C}$  of tetraphenylallene (**5**) with potassium in THF yielded, after MeOH quenching, 1,1,3,3-tetraphenylpropane (**4c**) and hydrocarbon **8** as the main products. In both cases 1,1,3,3-tetraphenylpropene (**10-H**) was a minor product (see Scheme II).

$^1\text{H}$  NMR examination ( $34^\circ\text{C}$ ) of the  $-78$  and  $-45^\circ\text{C}$  reaction mixtures revealed the presence of ethylene and 1,1,3,3-tetraphenylpropane-1,3-diyl dipotassium (**3**). Both dianion **3** and ethylene were presumably products of protonation of 1,1,3,3-tetraphenylallyltripotassium (**1**) by THF at room temperature. Moreover trianion **1**, which is stable at low temperature, was shown to arise as the product of reduction of 1,1,3,3-tetraphenylallyltripotassium (**2c**) with potassium in THF. Bearing in mind the propensity of disodium tetraphenylallene (**6b**) toward protonation at the C(2) by an ethereal solvent, we propose that **2c** arises similarly from dipotassium tetraphenylallene (**6c**). Dianion **6c** might decompose competitively to dianion **7c** analogously to **6a** (see Scheme II).

Again, use of  $^{13}\text{C}_3$ -labeled material allowed us to monitor the reaction by  $^{13}\text{C}$  NMR. With 1,2,3- $^{13}\text{C}_3$ -1,1,3,3-tetraphenylallene (**5**) as a substrate, reduction with potassium in THF (30%  $d_8$ ) in a sealed 10-mm NMR tube in a  $-74^\circ\text{C}$  ultrasonic bath for 3 h afforded the  $^{13}\text{C}$  NMR spectrum at  $-80^\circ\text{C}$ , which indicated the presence of dianion **7c** and monoanion **2c** (see Table II). After an additional 3 h in an ultrasonic bath, monoanion **2c** was completely replaced by trianion **1**. Upon warming the mixture to room temperature, trianion **1** was protonated at the C(2) to give dianion **3** (see supplementary material).

**1,1,2,3-Tetraphenylpropane-1,3-diyl dilithium (9).** Dianion **9** was examined as a model dianion with CC couplings between  $\text{sp}^3$ - and  $\text{sp}^2$ -hybridized carbons.

Reduction of 1,1,3,3-tetraphenylpropene (**10-H**) with lithium in THF at  $-20^\circ\text{C}$  yielded after quenching with MeOD a mixture of 1,3-dideuterio-1,1,2,3-tetraphenylpropanes. With 1,1,3,3-tetraphenyl-1,2- $^{13}\text{C}_2$ -propene and its 2,3- $^{13}\text{C}_2$  isotopomer as substrates, reduction with  $^6\text{Li}$  in THF- $d_8$  in a sealed 10-mm NMR tube in a  $-74^\circ\text{C}$  ultrasonic bath for 3 h gave a  $^{13}\text{C}$  NMR spectrum

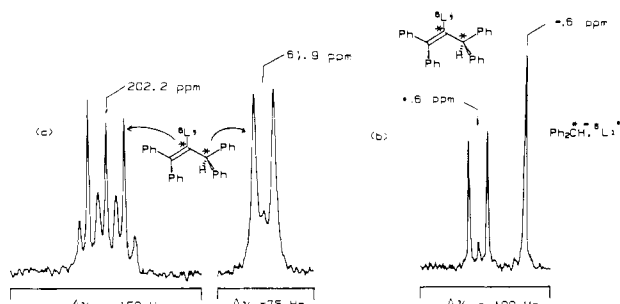
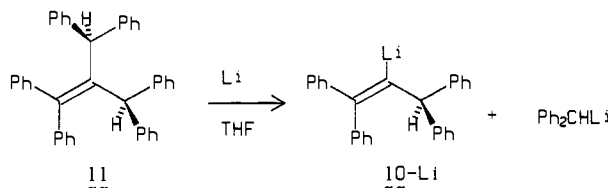


Figure 8.  $^{13}\text{C}$  NMR spectrum (a) and  $^6\text{Li}$  NMR spectrum (b) of 2-lithio-1,1,3,3-tetraphenylpropene, 50:50  $^{13}\text{C}_2$  and  $^{13}\text{C}_1$  at  $-80^\circ\text{C}$ .

**Scheme IV. Reductive Cleavage of 2-(Diphenylmethyl)-1,1,3,3-tetraphenylpropene**



which exhibited three distinct resonances with the expected coupling pattern (see Table II). The chemical shifts were slightly temperature dependent as expected for arylmethyl type of anions. The CC coupling constants were essentially temperature independent and their values were in the generally accepted range for  $\text{sp}^2\text{-sp}^3$  CC bonds. We note that the coupling constant to benzydryl anion carbon ( $J = 47$  Hz) was larger than one to benzylic anion carbon ( $J = 45$  Hz). This might be the effect of different negative charges on these carbons as well as an intermediate  $\text{sp}^2/\text{sp}^3$  hybridization in benzylic anion.<sup>16</sup>

**2-Lithio-1,1,3,3-tetraphenylpropene (10-Li).** Reduction of 2-(diphenylmethyl)-1,1,3,3-tetraphenylpropene (**11**)<sup>9b,c</sup> with lithium in tetrahydrofuran afforded a mixture of the lithium compound **10-Li** and diphenylmethyl lithium (Scheme IV).

Reduction at room temperature followed with MeOD quench after 7 h gave 2-deuterio-1,1,3,3-tetraphenylpropene (**10-D**) in 39% yield while a  $-78^\circ\text{C}$  reaction quenched with MeOH afforded a mixture of 1,1,3,3-tetraphenylpropene (**10-H**), diphenylmethane, and the unreacted substrate as sole products ( $>2\%$ ). Subsequently 2,3- $^{13}\text{C}_2$ -**11**<sup>9c</sup> and  $^6\text{Li}$  in tetrahydrofuran- $d_8$  were employed as substrates, and the resultant green-brown solution was examined by  $^{13}\text{C}$  and  $^6\text{Li}$  NMR. The  $^{13}\text{C}$  NMR spectrum at  $-80^\circ\text{C}$  showed a sharp singlet at 80.9, a doublet ( $J = 15.3$  Hz) at  $\delta$  61.9, and a downfield multiplet at  $\delta$  208.2 (Figure 7a and Table II). The  $^6\text{Li}$  NMR spectrum at  $-80^\circ\text{C}$  showed a downfield doublet ( $J = 14$  Hz) and an upfield singlet (Figure 8b). The spectra remained unchanged up to  $-20^\circ\text{C}$  although the fine structure of the carbon multiplet collapsed at room temperature ( $22^\circ\text{C}$ ). Both singlets in the spectra at  $-80^\circ\text{C}$  were assigned to diphenylmethyl lithium.<sup>17</sup> Since the splittings for both doublets are similar, i.e.,  $^1J(\text{CC}) = ^1J(\text{C}^6\text{Li})$ , the carbon multiplet can be interpreted as a triplet [ $^1J(^{13}\text{C}^6\text{Li}) = 14$  Hz,  $I = 1$  for  $^6\text{Li}$ ] and an approximately equally intense doublet [ $^1J(^{13}\text{C}^{13}\text{C}) = 15.3$  Hz] of triplets [ $^1J(^{13}\text{C}^6\text{Li}) = 14$  Hz] which appeared as a quartet ( $J = 15$  Hz). Therefore we observed a mixture of the monomeric 2- $[\text{Li}]-1,1,3,3$ -tetraphenyl-2- $^{13}\text{C}$ -propene and its 2,3- $^{13}\text{C}_2$  isotopomer. Although  $\alpha$ -hetero lithiocarbons are generally monomeric,<sup>18a-c</sup> this is the

first proof of a non-ionized hydrocarbon-lithium compound which is monomeric in solution on the NMR time scale.<sup>19</sup> We speculate that the steric hindrance of four phenyl groups contributes to this phenomenon.<sup>19b,c</sup>

The small value of the  $^{13}\text{C}$ - $^{13}\text{C}$  coupling constants (15 Hz vs. 44 Hz for the corresponding propene<sup>2</sup>) is reminiscent of that in dilithiopropene derivative **6a** ( $J = 40$  Hz vs. 67 Hz for the corresponding allyllithium compound<sup>2</sup>). The lithium-induced rehybridization of C(2) can explain these smaller values compared to the "normal"  $\text{sp}^2\text{-sp}^3$  and  $\text{sp}^2\text{-sp}^2$  CC bonds. Seebach and co-workers reported such a phenomenon for other lithium compounds as well.<sup>18</sup> The magnitude of the observed  $^{13}\text{C}$ - $^6\text{Li}$  coupling in the monomeric isotopomers of **10-Li** ( $J = 14$  Hz) was commensurate with the analogous coupling in the dilithium compound **6a** ( $J = 9$  Hz), which, although a monomer, is "effectively" dimeric (statically or dynamically on the NMR time scale) with respect to C-Li bonding.<sup>18</sup> The dramatic downfield chemical shift for C-2 in **6a,b** and **10-Li** also finds precedence in the similarly hybridized aryl- and vinyl lithium derivatives.<sup>18b,d</sup>

**Conclusions**

The dilithio adduct of tetraphenylallene adopts  $C_2$  symmetric geometry on the NMR time scale. Carbon-lithium coupling allows us to conclude that the dilithium compound **6a** is monomeric at low temperature in ethereal solvents on the NMR time scale. Disodium tetraphenylallene, which is much less stable than its dilithium analogue, possesses a similar allylic type of hydrocarbon framework. That the model compound, i.e., 2-lithio-1,1,3,3-tetraphenylpropene, is monomeric as well may suggest a role for steric hindrance in these tetraphenyl substituted  $C_3$  systems.

While the addition of two alkali metal atoms breaks the symmetry of tetraphenylallene, resulting in allylic geometry, the addition of two potassium atoms to the secondary reduction product 1,1,3,3-tetraphenylallyl potassium essentially preserves the geometry of the hydrocarbon framework. Treating the adducts as ion triplets or ion quartets<sup>20</sup> and neglecting the influence of the cations on the shape of the hydrocarbon framework, a straightforward analysis of anions can be obtained based upon an appeal to Hückel theory. We are intrigued by the one-to-one correspondence between the properties of the polyanions and the excited states of the unreduced species. Such a relationship was inferred in the past with Walsh rules or the Jahn-Teller effect.<sup>21</sup> Thus tetraphenylallene "dianion", the parent allene excited state, and by analogy the tetraphenylallene excited state adopt quasi- $C_2$  symmetry.<sup>21,22</sup> Both tetraphenylallyl trianion and the excited state of tetraphenylallyl anion undergo protonation at C(2).<sup>11b</sup> Conversely, the 1,2,3-triphenylallyl "trianion" and the 1,2,3-triphenylallyl anion excited state<sup>11a</sup> are stabilized by the C(2) substituent. Finally, the maintenance of a non-zero bond order for the tetraphenylallyl "trianion" illustrates that, unlike the parent systems, arylated olefins and their relatives maintain a significant bond order in the excited state. Of course we cannot push the analogy too far. For example, the fact that tetraphenylallene singlet excited state is preferentially protonated at C(2) can only be explained at a higher level of theory.<sup>22</sup> Nevertheless, our ability

(16) Browne, S. E.; Asher, S. E.; Cornwall, E. H.; Frisoli, J. K.; Harris, L. J.; Salot, E. A.; Sauter, E. A.; Trecocke, M. A.; Veale, P. S., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 1432. (b) McKeever, L. D.; Waack, R. *J. Organomet. Chem.* **1971**, *28*, 145. (c) Waack, R.; Doran, M. H.; Duker, E. B.; Olah, G. A. *J. Am. Chem. Soc.* **1966**, *88*, 1272.

(17) O'Brien, D. H.; Russell, G. R.; Hart, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 7427.

(18) (a) Seebach, D.; Gabriel, J.; Hassig, R. *Helv. Chim. Acta* **1984**, *67*, 1083. (b) Seebach, D.; Hassig, R.; Gabriel, J. *Ibid.* **1983**, *66*, 308. (c) Siegel, H.; Hiltbrunner, K.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 785. (d) Fraenkel, G.; Pramanik, P. *J. Chem. Soc., Chem. Commun.* **1983**, 1527.

(19) (a) Recently a monomeric phenyllithium was crystallized with pentamethyldiethylenetriamine as a ligand; this, however, does not implicate the identity of the prevailing oligomer (monomer) in solution, see: Schumann, U.; Kopf, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 215. (b) See also: Lappert, M. F.; Engelhardt, L. M.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1323. (c) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 827.

(20) (a) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353. (b) Streitwieser, A., Jr.; Swanson, J. T. *J. Am. Chem. Soc.* **1983**, *105*, 2502. (c) Schleyer, P. v. R.; Kos, A. J.; Wilhelm, D.; Clark, T.; Boche, G.; Decher, G.; Etrudt, H.; Dietrich, H.; Mahdi, W. *J. Chem. Soc., Chem. Commun.* **1984**, 1495.

(21) (a) Walsh, A. D. *J. Chem. Soc.* **1953**, 2289. (b) Buenker, R. J.; Pyrimhoff, S. D. *Chem. Rev.* **1974**, *74*, 166. (c) Buenker, R. J.; Pyrimhoff, S. D. *Theor. Chim. Acta* **1972**, *24*, 132. (d) Pearson, R. G. *Symmetry Rules for Chemical Reactions*; Wiley: New York, 1976.

(22) (a) Lam, B.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 7479. (b) Kleit, M. W.; Johnson, R. P. *Ibid.* **1985**, *107*, 3963. (c) Rafizadeh, K.; Yates, K. *J. Org. Chem.* **1984**, *49*, 1500. (d) Kleit, M. W.; Johnson, R. P. *Tetrahedron Lett.* **1983**, *24*, 1107.

to treat resonance-stabilized carbanions by straightforward molecular orbital techniques has again been affirmed.

### Experimental Section

**Materials.** Tetrahydrofuran, dimethyl ether, and diethyl ether were distilled from sodium benzophenone ketyl immediately before use. Barium carbonate (90%  $^{13}\text{C}$  enriched) and tetrahydrofuran- $d_8$  were obtained from Stohler Isotopes.

**Diphenylmethane- $^{13}\text{C}$ .** Benzophenone- $^{13}\text{C}$  (2.88 g) prepared as a crude mixture containing ca. 12% triphenylcarbinol- $^{13}\text{C}$  from phenyllithium and  $^{13}\text{CO}_2$  was subjected to sodium borohydride reduction in trifluoroacetic acid.<sup>23</sup> The resultant mixture of diphenylmethane- $^{13}\text{C}$  and triphenylmethane- $^{13}\text{C}$  was distilled to yield pure diphenylmethane- $^{13}\text{C}$  (1.62 g, 64.0% based upon  $\text{CO}_2$ ) as a colorless liquid, bp 75–78.5 °C (0.7 Torr) (lit.<sup>23</sup> bp 60–62 °C (0.35 Torr)).

The spectral data were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.95 (d,  $^1J(\text{CH}) = 126$  Hz, 2 H), 7.20 (s, 10 H); the absorption pattern was in full accord with 90%  $^{13}\text{C}$  enrichment at the  $\alpha$ -carbon.

**Diphenylacetic- $^{13}\text{C}_2$  and  $^{13}\text{C}_1$  Acid.** A tetrahydrofuran solution (22 mL) of diphenylmethane- $^{13}\text{C}$  (1.48 g, 8.74 mmol) at  $-10$  °C was treated with 4.4 mL (9.24 mmol) of 2.1 M *n*-BuLi in hexane. After 1 h, the solution was warmed to room temperature for 30 min and then cooled to  $-70$  °C, and  $^{13}\text{CO}_2$  generated from  $\text{Ba}^{13}\text{CO}_3$  (2.05 g, 10.3 mmol) and sulfuric acid (15 mL) was introduced while the temperature of the reaction mixture was raised from  $-70$  to  $-10$  °C. The organic product was isolated by water quenching and pentane extraction to yield colorless crystals (1.57 g, 84%).

The spectral data were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.12 (d of d,  $^1J(\text{CH}) = 130.5$  Hz,  $^2J(\text{CH}) = 9$  Hz), 7.33 (s), 9.2 (br);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  57.0 (d,  $^1J(\text{CC}) = 44.3$  Hz), 178.6 (d,  $^1J(\text{CC}) = 44.3$  Hz); nonenriched carbons 127.5, 128.7 (ortho, meta, para), 138.0 (d,  $^1J(\text{CC}) = 42.5$  Hz, ipso).

**Tetraphenylallene- $^{13}\text{C}_3$  (5).** Barium diphenylacetate- $^{13}\text{C}_4$  (1.33 g, 2.38 mmol) prepared from barium hydroxide and diphenylacetic- $^{13}\text{C}_2$  acid was subjected to vacuum pyrolysis at 300 °C (0.02 Torr) to yield the crude allene as a yellow crystalline material in the upper part of the trap. From the lower part of the trap crude diphenylmethane- $^{13}\text{C}_1$  (0.385 g) was recovered and reused. Recrystallization (acetone/absolute ethanol) afforded colorless crystals of tetraphenylallene (0.307 g, 37%), mp 169.5–171 (lit.<sup>24</sup> mp 170–170.5 °C).

The spectral data were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.37 (m);  $^{13}\text{C}$  NMR  $\delta$  208.5 (t,  $^1J(\text{CC}) = 103$  Hz), 112.6 (d,  $^1J(\text{CC}) = 103$  Hz), nonenriched carbons 128.5, 127.5 (ortho, meta, para), 136.4 (d,  $^1J(\text{CC}) = 58$  Hz, ipso); MS, *m/e* at 347. MS and  $^{13}\text{C}$  NMR spectral patterns were in agreement with 90%  $^{13}\text{C}$  enrichment at each allenic carbon. The  $^{13}\text{C}_1$  isotopomer (90%  $^{13}\text{C}$  enrichment at C-2) was obtained in a similar way from barium diphenylacetate- $^{13}\text{C}_2$  (1.52 g) in 36% yield.

**1,1,3,3-Tetraphenylpropene.** 1,1,3,3-Tetraphenylacetone- $^{13}\text{C}_2$  (0.117 g, 0.321 mmol) was subjected to  $\text{LiAlH}_4$  reduction (0.39 g, 10.3 mmol in 3 mL of tetrahydrofuran). The resulting 1,1,3,3-tetraphenylpropan-2-ol- $^{13}\text{C}_2$ <sup>25</sup> was obtained as a colorless oil in quantitative yield.

The spectral data for 1,1,3,3-tetraphenylpropan-2-ol- $^{13}\text{C}_2$  were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.20 (m, 20 H), 5.01 (m,  $^1J(\text{CH}) = 142.5$  Hz, 1 H), 3.90 (m,  $^1J(\text{CH}) = 125$  Hz, 2 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  76.2 (d,  $^1J(\text{CC}) = 37.6$  Hz), 54.5 (d,  $^1J(\text{CC}) = 37.6$  Hz). The previously obtained propanol- $^{13}\text{C}_2$  was acetylated with acetic anhydride (0.1 mL) in chloroform-*d* containing a small crystal of 4-(dimethylamino)pyridine. The resulting 2-acetoxy-1,1,3,3-tetraphenylpropane- $^{13}\text{C}_2$  was maintained at 400 °C for 45 min. Column chromatography ( $\text{SiO}_2$ , hexane, hexane/chloroform) afforded 92.8 mg (83% based on ketone) of colorless crystals, mp 127–129 °C (lit.<sup>24</sup> mp 125–126 °C).

The spectral data for 1,1,3,3-tetraphenylpropene- $^{13}\text{C}_2$  (first order analysis) were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.17 (m, 20 H), 6.55 (d of d,  $^1J(\text{CH}) = 154.2$  Hz,  $^3J(\text{HH}) = 10.6$  Hz, 1 H), 4.82 (m,  $^1J(\text{CH}) = 128.5$  Hz,  $^2J(\text{CH}) = 6.5$  Hz,  $^3J(\text{HH}) = 10.6$  Hz, 1 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  141.6 (d,  $^1J(\text{CC}) = 74.3$  Hz), 131.0 (d of d,  $^1J(\text{CC}) = 74.3$  Hz,  $^1J(\text{CC}) = 44.1$  Hz), 50.5 (d,  $^1J(\text{CC}) = 44.1$  Hz).

**NMR Measurements. General Procedure.** A solid hydrocarbon substrate in an NMR tube attached to a vacuum line was subjected to vacuum degassing and argon purging. A metal was added either under a stream of argon or under nitrogen in a glovebag. After addition of solvent the tube was sealed under vacuum and immersed in an ultrasonic bath at  $-105$  to  $+20$  °C. Samples prepared in this way were stable to further reaction indefinitely if stored in liquid nitrogen. The reaction

mixtures were monitored by NMR at 3-h intervals.

A Varian XL-200 spectrometer equipped with a standard variable temperature probe was employed for NMR experiments nearly exclusively. The low temperatures in the probe were maintained with a flow of dry nitrogen passed through a liquid nitrogen heat exchanger. Temperatures were calibrated to  $-90$  °C with an internal MeOH standard. Lower temperatures were calculated by extrapolation. The operating frequencies are the following:  $^1\text{H}$  200.0 MHz,  $^{13}\text{C}$  50.309 MHz,  $^6\text{Li}$  29.441 MHz,  $^7\text{Li}$  77.746 MHz.  $^1\text{H}$ -decoupled  $^{13}\text{C}$  NMR spectra were obtained with use of the MLEV16 pulse sequence.

Typically the width of the spectral window was 9–13 kHz. The data were collected with a recycling time of 1.2–2 s with 32K points. Acceptable signal-to-noise ratios were obtained for most samples with 1000 scans and 0.5–1.0-Hz exponential line broadening.

Prototype  $^6\text{Li}$  and  $^7\text{Li}$  NMR spectra were obtained with use of the standard carbon-like pulse sequence with  $^1\text{H}$  broad-band decoupling. The spectral window, acquisition memory, and recycling time were 1000 Hz, 8K, and 4 s.

**NMR Studies. A. Lithium Derivative 6a in MeOMe/Ether- $d_{10}$ .** Tetraphenylallene- $^{13}\text{C}_3$  (16.0 mg, 0.046 mmol) and  $^6\text{Li}$  (multimolar excess) were placed in a 10-mm NMR tube. Diethyl- $d_{10}$  ether (0.3 mL) was added, and the tube was immersed in a  $-74$  °C ultrasonic bath for 3 h. The solution was cooled to  $-117$  °C, dimethyl ether (2.7 mL) was introduced, and the tube was sealed under vacuum.

**B. Sodium Derivative 6b in MeOMe/Ether- $d_{10}$ .** Tetraphenylallene- $^{13}\text{C}_3$  (21.5 mg, 0.062 mmol) and sodium (multimolar excess) were placed in a 10-mm NMR tube. Diethyl- $d_{10}$  ether (0.3 mL) followed by dimethyl ether (2.2 mL) were added at  $-117$  °C. The tube was sealed and immersed in an ultrasonic bath maintained at  $-105$  °C.

**C. Lithium Derivative 6a in Tetrahydrofuran.** An NMR tube containing tetraphenylallene (15–25 mg, 0.045–0.073 mmol) and lithium (multimolar excess) was cooled to  $-78$  °C and tetrahydrofuran (1.5–2.5 mL) and tetrahydrofuran- $d_8$  (0.3–0.8 mL) were added. The sealed tube was immersed at  $-74$  °C in an ultrasonic bath.

**D. Potassium Derivative 6c in Tetrahydrofuran.** A 10-mm NMR tube containing tetraphenylallene- $^{13}\text{C}_3$  (19.5 mg, 0.056 mmol) and potassium (multimolar excess) was cooled to  $-95$  °C (acetone/liquid nitrogen). Tetrahydrofuran ( $h_8/d_8$ ) was added and the tube was sealed.

**E. 1,1,3,3-Tetraphenylallylpotassium (2c).** For  $^1\text{H}$  NMR, solutions were prepared by adding tetrahydrofuran- $d_8$  (1.35 mL) to a multimolar excess of mineral-oil-free potassium hydride and 1,1,3,3-tetraphenylpropene (34.1 mg, 0.098 mmol). After 12 h the red-wine solution was transferred (0.4 mL) via gas-tight syringe to a 5-mm NMR tube, which was then sealed. For  $^{13}\text{C}$  NMR, solutions were prepared analogously, except that a 10-mm NMR tube was attached directly to a Schlenk tube and the solution was filtered into the tube after 3 days of stirring at room temperature.

**1,1,3,3-Tetraphenylallyltripotassium (1) and Dianion 3. A. NMR Studies.** Tetrahydrofuran- $d_8$  (1.30 mL) was added to a multimolar excess of mineral-oil-free potassium hydride and 1,1,3,3-tetraphenylpropene- $^{13}\text{C}_2$  (24.7 mg, 0.071 mmol). After 12 h the red-wine solution was transferred (0.45 mL) via gas-tight syringe to a 5-mm NMR tube containing a multimolar excess of potassium at  $-78$  °C. After the tube was sealed and immersed in a  $-74$  °C ultrasonic bath, the red reaction mixture was examined by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR.

**B. Quenching Studies.** To a 3.5-mL portion of KH in mineral oil (35 wt %) washed with pentane was added 300 mg (0.866 mmol) of 1,1,3,3-tetraphenylpropene and 6 mL of tetrahydrofuran. After 12 h, 13 mL of tetrahydrofuran was added. The  $^1\text{H}$  NMR spectrum of the solution indicated the presence of 1,1,3,3-tetraphenylallylpotassium. The solution was divided into three parts. Parts B and C of the reaction mixture (11 mL) were transferred into another flask with potassium metal at  $-78$  °C. The rest of the reaction mixture (part A) was quenched with MeOD. Parts B and C were similarly allowed to react with potassium for 27 h at  $-78$  °C. The  $^1\text{H}$  NMR spectrum at 34 °C of a 0.6-mL sample showed [ $\delta$ , multiplicity (intensity)] the following: 5.33, s (14.5); 5.58, t (19); 6.48, t (44); 6.92, d (44). Part C of the reaction mixture (5 mL) was transferred into another flask at room temperature and was allowed to warm up for 30 min. Both reaction mixtures (part B, 29 h at  $-78$  °C; part C, 30 min at room temperature) were quenched with MeOD. The three fractions were subjected to ether extraction, water washing, and rotary evaporation, and the crude extracts (A, 83.8 mg; B, 85.7 mg; C, 80.2 mg) were subjected to silica gel column chromatography. The identities and yields of the isolated products were as follows.

**A:** 3-[ $^2\text{H}$ ]-1,1,3,3-tetraphenylpropene, 33.5 mg, mp 129–131 °C. The spectral data were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.20 (20 H, m) and 6.53 (1 H, s).

**B:** 1,2,3-[ $^2\text{H}_3$ ]-1,1,3,3-tetraphenylpropane, 62.8 mg, 74%, mp 142–144 °C. The spectral data were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.18 (20

(23) Gribble, G. W.; Kelly, W. J.; Emery, S. E. *Synthesis* 1978, 763.

(24) Vorlander, D.; Sieber, C. *Chem. Ber.* 1906, 39, 1024.

(25) (a) Dean, D. O.; Dickinson, W. B.; Quayle, O. R.; Lester, C. T. *J. Am. Chem. Soc.* 1950, 72, 1740. (b) Dean, D. O.; Dickinson, W. B.; Hoey, G. B.; Lester, C. T. *Ibid.* 1954, 76, 4988.

H, s), 2.77 (1 H, br s); MS,  $m/e$  at 351 indicated 89% of product to be  $d_3$ .

C: fraction 1, 3- $^{2}\text{H}$ -1,1,3,3-tetraphenylpropene, 9.7 mg. The spectral data were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.20 (20 H, m), 6.53 (1 H, s). Fraction 2, 1,3- $^{2}\text{H}_2$ -1,1,3,3-tetraphenylpropene, 40.5 mg, 51%. The spectral data were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.18 (20 H, s), 2.77 (2 H, s) for (**4b-d**); 19% of (**4b-d**); MS,  $m/e$  at 350 indicated 76% of product to be  $d_2$ .

A similarly prepared sample of 1,1,3,3-tetraphenylpropene was allowed to remain at room temperature for 48 h and then transferred at 0 °C to water. 1,1,3,3-Tetraphenylpropene was formed in 90% yield, along with 2% of 1,1,3,3-tetraphenylpropene.

The spectral data for 1,1,3,3-tetraphenylpropene were  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.17 (20 H, s), 3.77 (2 H, t), 2.77 (2 H, t).

**Dimetallo 1,1,3,3-Tetraphenylallene 6. Quenching Studies. A. Lithium Derivative 6a, Quenching with MeOH/MeOD.** Freshly cut lithium wire was added under argon to a flask containing tetraphenylallene (81.8 mg, 0.237 mmol). The flask was immersed in a  $-78$  °C bath and tetrahydrofuran (17 mL) was added. After 20 h the deep blue reaction mixture was quenched with 1.5 mL of precooled ( $-60$  °C) MeOH in 10 mL of ether. The organic residue was isolated by chloroform extraction and water washing to yield 86.7 mg of an oily yellow solid. Column chromatography ( $\text{SiO}_2$ , hexane, hexane/ $\text{CHCl}_3$ , 20:1) afforded colorless crystals (76.5 mg, 93%), mp 133 °C (lit.<sup>24</sup> mp 125–126 °C). The spectral data were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.20 (20 H, m), 6.53 (1 H, d,  $J = 10$  Hz), 4.80 (1 H, d,  $J = 10$  Hz). A sample similarly prepared and quenched with MeOD indicated the absence of the  $\delta$  6.53 and 4.80. NMR absorptions and the mass spectrum at  $m/e$  348 had isotopic intensities indicating 82% of the  $d_2$  product.

A sample identically prepared but allowed to warm to ambient temperature before quenching with MeOD afforded a colorless glass whose  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) indicated the presence of a mixture of 1,1,3,3-tetraphenylpropene- $d$  and the deuterated hydrocarbon **8-d**<sub>2</sub> (cf. Scheme II) identical with that reported by Dowd.<sup>26</sup>

Finally, quenching of a similarly prepared sample with EtOH/HCl at  $-127$  °C upon dilution with MeOMe produced the 1,1,3,3-tetraphenylpropene only.

**B. Sodium Derivative 6b, Quenching with MeOH/MeOD.** Freshly cut sodium (1.75 g, 76 mmol) was added under argon to a flask containing tetraphenylallene (1.52 g, 4.40 mmol). Diethyl ether (85 mL) was added, and the red solution was stirred at room temperature for 27 h. The reaction flask was immersed in a bath maintained at  $-78$  °C and MeOH (2.5 mL) was added. The resultant solution was separated from the accompanying white precipitate, poured into dilute HCl (100 mL) at 0 °C, and extracted with ether. Crystallization of the ether extract from hexane yielded slightly yellow crystals (1.18 g, 77%) of 1,1,3,3-tetraphenylpropene. Quenching after 6.5 h of a similar solution but prepared at  $-78$  °C with MeOD yielded 1,1,3,3-tetraphenylpropene whose  $^1\text{H}$  NMR spectrum indicated the absence of the  $\delta$  4.80 doublet. Mass spectral analysis of the peaks at  $m/e$  348 and 347 indicated that 56% of the propene was  $d_2$  and 44% was  $d_1$ , similar to the results obtained by Dowd.<sup>26</sup>

**Reaction of Tetraphenylallene with Potassium.** To a multimolar excess of freshly cut potassium under argon at  $-45$  °C was added 10 mL of tetrahydrofuran, followed by a solution of tetraphenylallene (151 mg, 0.438 mmol) in 2 mL of tetrahydrofuran. After 3 h of vigorous stirring the reaction mixture was quenched with MeOH (0.3 mL) and then transferred into 20 mL of dilute HCl at 0 °C. Ether extraction and silica gel column chromatography with hexane and 12:1 hexane/ $\text{CHCl}_3$  afforded the following products: hydrocarbon **8**, yellow oil, 62.4 mg (44%); 1,1,3,3-tetraphenylpropene (**10-H**), colorless solid, 18.0 mg (13%); 1,1,3,3-tetraphenylpropene (**4c**), colorless solid, 15.0 mg (10.5%).

The spectral data were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): **8**,  $\delta$  7.23 (14 H, m), 6.80 (1 H, d), 5.65–6.35 (2 H, m), 1.80–3.40 (5 H, m);<sup>25</sup> **10-H** and **4c**, see previous data. A similarly prepared reaction mixture maintained at  $-78$  °C yielded 1,1,3,3-tetraphenylpropene (53%) and 1,1,3,3-tetraphenylpropene (27%).

**1,1,3,3-Tetraphenylallyllithium (2a).** 1,1,3,3-Tetraphenylpropene- $^{13}\text{C}_2$  (20.0 mg, 0.058 mmol) was dissolved in a 5-mm NMR tube containing 0.6 mL of a 0.5 M solution of MeLi in tetrahydrofuran- $d_8$ . The deep-red solution was allowed to stand at room temperature for 16 h, tetrahydrofuran- $h_8$  (2.5 mL) was added, and the NMR tube was sealed under vacuum.

**Diphenylmethylithium- $^{13}\text{C}$ .** Treatment of diphenylmethane- $^{13}\text{C}$  (55.2 mg, 0.329 mmol) in the tetrahydrofuran- $d_8$  (0.4 mL) with *n*-BuLi (0.16 mL of 2.4 M hexane solution, 0.38 mmol) yielded an orange solution of diphenylmethylithium- $^{13}\text{C}$ .

**Reaction of 1,1,3,3-Tetraphenylpropene with Lithium at  $-78$  °C.** To a multimolar excess of freshly cut lithium wire under argon in 11 mL of tetrahydrofuran at  $-78$  °C was added a solution of 1,1,3,3-tetraphenylpropene (85.8 mg, 0.245 mmol) in 2 mL of tetrahydrofuran (2 mL). The brownish-red reaction mixture was allowed to warm to 20 °C and then quenched with MeOD (0.5 mL) and transferred to dilute aqueous HCl (15 mL). The residue from ether extraction and water washing was subjected to silica gel column chromatography to yield 79.8 mg (93%) of pure 1,3-dideuterio-1,1,2,3-tetraphenylpropanes.

A similarly prepared reaction mixture prepared from 125 mg (0.361 mmol) of 1,1,3,3-tetraphenylpropene and then quenched with MeOH at  $-78$  °C after 13 h at  $-78$  °C produced, after extraction and column chromatography, 1,1,3,3-tetraphenylpropene (33.0 mg, 23.5%), mp 142–144 °C (lit.<sup>27</sup> mp 135 °C), and 1,1,2,3-tetraphenylpropene (72.8 mg, 58%), mp 85 °C (lit.<sup>28</sup> mp 87–89 °C).

The mass spectral data for 1,1,3,3-tetraphenylpropene were as follows: MS at  $m/e$  348 (100), 254 (40).

The spectral data for 1,1,2,3-tetraphenylpropene were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.03 (20 H, m), 4.27 (1 H, d,  $J = 11.5$  Hz), 3.80 (1 H, t of d,  $J = 11.1$  Hz), 3.03 (1 H, d of d,  $J = 13.3, 2.9$  Hz), 2.69 (1 H, d of d,  $J = 13.3, 10.9$  Hz); MS at  $m/e$  348 (10), 257 (100).

**1,1,2,3-Tetraphenylpropene-1,3-diylidilithium (9). NMR Studies.** An equimolar mixture of 1,2- $^{13}\text{C}_2$ - and 2,3- $^{13}\text{C}_2$ -1,1,3,3-tetraphenylpropene (14.7 mg, 0.0422 mmol) and lithium (multimolar excess) were placed in a 10-mm NMR tube. Tetrahydrofuran- $d_8$  (2 mL) was added at  $-78$  °C. The sealed tube was immersed in an ultrasonic bath maintained at  $-74$  °C and then subjected to NMR analysis (see text).

**2-Lithio-1,1,3,3-tetraphenylpropene (10-Li). A. Quenching Studies.** Tetrahydrofuran (5 mL) was added to a flask containing freshly cut lithium wire and 2-(diphenylmethyl)-1,1,3,3-tetraphenylpropene (**11**) (107.7 mg, 0.210 mmol). After 7 h the mixture was quenched with 0.25 mL of MeOD. The organic residue was isolated by ether/chloroform extraction and water washing to yield 101.1 mg of a colorless oil. Silica gel column chromatography (hexane/chloroform 20:1) afforded a colorless solid (26.8 mg, 39%). The spectral data were as follows:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.20 (20 H, m), 4.90 (1 H, s); MS,  $m/e$  347. A similarly prepared mixture at  $-78$  °C from 94.7 mg (0.185 mmol) of 2-(diphenylmethyl)-1,1,3,3-tetraphenylpropene (**11**) was quenched with 0.4 mL of MeOH after 9 h. The  $^1\text{H}$  NMR spectrum of the organic residue indicated a mixture of 41% unreacted substrate, 29% 1,1,3,3-tetraphenylpropene, and 29% diphenylmethane.

**B. NMR Studies.** 2,3- $^{13}\text{C}_2$ -(Diphenylmethyl)-1,1,3,3-tetraphenylpropene (28.0 mg, 0.0545 mmol) was dissolved in 2.4 mL of tetrahydrofuran- $d_8$  in a 10-mm NMR tube containing a multimolar excess of  $^6\text{Li}$ . The tube was sealed and immersed in a  $-74$  °C ultrasonic bath.

**Molecular Orbital Calculations.** Hückel calculations were performed assuming planar geometries and constant bond lengths between all neighboring carbon atoms, using a resonance integral of  $1\beta$  (ethylene) for all nearest neighbors.

**Registry No.** **1**, 106627-01-4; **2**, 74589-99-4; **2b**, 106627-03-6; **3**, 7022-15-3; **4c**, 36171-50-3; **5**, 1674-18-6; **5- $^{13}\text{C}_3$** , 96165-48-9; **6a**, 96165-46-7; **6b**, 106627-02-5; **7a**, 106627-04-7; **7c**, 106627-05-8; **9**, 106627-06-9; **10-Li**, 106627-07-0; diphenylmethane- $^{13}\text{C}$ , 6933-21-7; diphenylacetic acid- $^{13}\text{C}_2$ , 106627-08-1; diphenylacetic acid- $^{13}\text{C}_1$ , 106627-09-2; 1,1,3,3-tetraphenylpropene, 4960-55-8.

**Supplementary Material Available:** Temperature-dependent  $^{13}\text{C}$  NMR spectra of  $^{13}\text{C}$ -enriched 1,1,3,3-tetraphenylallyltripotassium (**1**),  $^1\text{H}$  NMR spectra of 1,1,3,3-tetraphenylallylpotassium (**2c**), and  $^{13}\text{C}$  NMR spectra of  $^{13}\text{C}$ -enriched 1,1,3,3-tetraphenylallene upon reduction by potassium (12 pages). Ordering information is given on any current masthead page.

(27) Wooster, C. B.; Ryan, J. F. *J. Am. Chem. Soc.* **1934**, *56*, 1133.

(28) Bergmann, E.; Weiss, H. *Chem. Ber.* **1931**, *34*, 1485.

(29) Hoffmann, A. K.; Zweig, A. *J. Am. Chem. Soc.* **1962**, *84*, 3278.

(30) Levitt, M. H.; Freeman, R.; Frenkiel, J. *Magn. Reson.* **1982**, *47*, 328.

(31) Support by the National Science Foundation through Grant CHE-8024644 and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We are indebted to Professor A. Streitwieser, Jr., for critical remarks.