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Y-Conjugated Dianions. A ^{13}C Nuclear Magnetic Resonance Study

Andrzej Rajca*[1a] **and Laren M. Tolbert***[1b]

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506. *Received June 8, 1987*

Abstract: Tris(diphenylmethylene)methane dianion (**1**$^{2-}$), tetraphenylacetone dianion (**2**$^{2-}$), and diphenylacetate dianion (**3**$^{2-}$) were generated in dimethyl sulfoxide or tetrahydrofuran solutions by deprotonation of the appropriate carbon acid. Chemical shifts, carbon–carbon spin coupling constants, and other spectroscopic evidence indicated an sp^2-hybridized central atom for all dianions, as well as D_3 symmetry for the all-carbon dianion. The one-bond CC spin coupling constant for **1**$^{2-}$ (62 Hz) increased upon consecutive replacements of diphenylmethylene by the groups, i.e., to 69 Hz for **2**$^{2-}$ and 76.7 Hz for **3**$^{2-}$,2K$^+$ (86.0 Hz for the Li$^+$ salt) reflecting charge localization at oxygen. An empirical model for the residual charge on phenyl-substituted resonance-stabilized carbanions that allows comparison of dissimilarly substituted carbanions was developed.

Y-Conjugated dianions and their ion pairs are ubiquitous species, represented by the dianions of carbonic and carboxylic acids, by dianions of ketones, and by the all-carbon trimethylenemethane dianion.[2-9] While linear or cyclic topology is preferred for neutral π-conjugated systems, Y-conjugated dianions and cross-conjugated polyanions in general are distinguished by their greater stability relative to other topologies.[10] A number of explanations have been advanced, especially for the all-carbon species: (1) 6π-electron aromaticity, with conjugation through the center rather than through a cycle,[11-13] (2) increased alternation of charges,[11] (3) reduced Coulombic repulsions.[14] The effect of counterions must also be considered.[15] We now report a full ^{13}C NMR analysis, including ^{13}C^{13}C coupling constants, of the tris(diphenylmethylene)methane dianion (**1**$^{2-}$) and its oxo analogues 1,1,3,3-tetraphenylacetone dianion (**2**$^{2-}$) and diphenylacetate dianion (**3**$^{2-}$). We also provide further details for our preliminary report on **1**$^{2-}$.[16]

Results

2-(Diphenylmethyl)-1,1,3,3-tetraphenylpropene (**1**-H$_2$) was prepared by the addition of (diphenylmethyl)lithium to tetraphenylallene.[16] Material labeled with ^{13}C at C(2) and C(3) was prepared by use of [[1-^{13}C]diphenylmethyl]lithium and [2-^{13}C]tetraphenylallene. Quenching of the monolithium derivative led to formation of [2,3-^{13}C]-**1**-H$_2$ without scrambling to C(1). Similarly prepared were [1,2-^{13}C]-1,1,3,3-tetraphenylacetone (**2**-H$_2$) and [1,2-^{13}C]diphenylacetic acid (**3**-H$_2$) (see Figure 1).

Dianions **1**$^{2-}$–**3**$^{2-}$ were prepared by addition of base to the appropriate carbon acids in Me$_2$SO or Me$_2$SO-d_6 or in tetrahydrofuran (THF) or tetrahydrofuran-d_8. Formation of tris(diphenylmethylene)methane dianion (**1**$^{2-}$) was accomplished with lithium or potassium (methylsulfinyl)methide ("dimsyl") and 2-(diphenylmethyl)-1,1,3,3-tetraphenylpropene (**1**-H$_2$) in either Me$_2$SO or THF. In all cases the NMR spectrum of the intermediate monanion **1**-H$^-$ could be observed. Solutions of pure **1**-H$^-$ were generated by employing such bases as potassium hydride/18-crown-6 or MeLi in THF. Use of Me$_2$SO as solvent and potassium as countercation accelerated the second deprotonation. Usually about 10 equiv of dimsyl anion was used to shorten the reaction time; with 2.5 equiv of potassium (methylsulfinyl)methide in Me$_2$SO about 2–3 days at room temperature was required for >95% conversion of the hydrocarbon **1**-H$_2$ to the dianion. Formation of the dianion was accompanied by a significant change in the ^{13}C NMR spectrum of the doubly labeled material (see Figure 2).

Treatment of 1,1,3,3-tetraphenylacetone (**2**-H$_2$) with up to 20 equiv of dimsylpotassium in Me$_2$SO-d_6 produced a red solution containing **2**-H(D)$^-$,K$^+$ as the only detectable species by ^{1}H NMR, although the red color suggested a small concentration of dianion **2**$^{2-}$. The monanion **2**-H$^-$,K$^+$(Li$^+$), yellow in Me$_2$SO, was prepared with 1.5 equiv of dimsyl anion. With n-butyllithium in THF/hexane, sequential deprotonation of **2**-H$_2$ was observed, leading to **2**-H$^-$,Li$^+$ and, finally, to **2**$^{2-}$,2Li$^+$.[16] When **2**$^{2-}$,2Li$^+$ was treated with Me$_2$SO-d_6, protonation to regenerate the monoanion occurred (see Figures 3 and 4).

Lambert[5] reported ^{13}C NMR data for diphenylacetate dianion **3**$^{2-}$,2Na$^+$ in Me$_2$SO. We prepared this dianion, using doubly labeled material, as the lithium and potassium derivatives. NMR spectra for the neutrals were recorded in CDCl$_3$. For all anions THF, Me$_2$SO, or a Me$_2$SO/THF mixture was employed. The chemical shifts and coupling constants are listed in Table I. ^{13}C–^{13}C coupling constants were obtained by using doubly ^{13}C-enriched compounds (90% ^{13}C at each carbon).

Discussion

The evidence for the formation of dianions, using **1**$^{2-}$ as an example, can be outlined as follows:

(i) While the ^{13}C$_2$ monoanion **1**-H$^-$ exhibited the two spin systems (AX and AB) expected for the two possible label distributions, the ^{13}C$_2$ dianion exhibited a single AB spin system, indicating a threefold degeneracy of the C(1) carbon on the NMR time scale, as well as the natural abundance aromatic resonances at δ 112.5 (para), 124.2 (ortho), 125.4 (meta), and 151.4 (ipso) (see Figure 5).

(ii) Quenching of solutions of the dianion **1**$^{2-}$ with water allowed recovery of the hydrocarbon substrate. While the ^{13}C$_2$ substrate

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(1) (a) Present address: Department of Chemistry, University of California, Berkeley, CA 94720. (b) Present address: School of Chemistry, Georgia Institute of Technology, Atlanta, GA 30332.

(2) Kaneti, J.; Schleyer, P. v. R.; Kos, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1014.

(3) (a) Adam, W.; Ceuto, O. *J. Org. Chem.* **1977**, *42*, 38. (b) Ivanov, D.; Vassilev, G.; Panayoto, I. *Synthesis* **1975**, 83.

(4) (a) Dietrich, H.; Mahdi, W.; Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 621. (b) Kos, A. J.; Clark, T.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 622. (c) Wilhelm, D.; Clark, T.; Schleyer, P. v. R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 915.

(5) (a) Lambert, J. B.; Wharry, S. M. *J. Am. Chem. Soc.* **1982**, *104*, 5857. (b) Lambert, J. B.; Wharry, S. M. *J. Chem. Soc., Chem. Commun.* **1978**, 172.

(6) Wilhelm, D.; Dietrich, H.; Clark, T.; Mahdi, W.; Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 7279.

(7) Wilhelm, D.; Clark, T.; Schleyer, P. v. R.; Buckl, K.; Boche, G. *Chem. Ber.* **1983**, *116*, 1669.

(8) Klein, J.; Medlik, A. *J. Chem. Soc., Chem. Commun.* **1973**, 275.

(9) (a) Mills, N. S.; Shapiro, J.; Hollingsworth, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 1263. (b) Mills, N. S. *J. Am. Chem. Soc.* **1982**, *104*, 5689.

(10) Klein, J. *Tetrahedron* **1983**, *39*, 2733.

(11) (a) Inagaki, S. *Chem. Lett.* **1982**, 709. (b) Inagaki, S.; Kawata, H.; Hirabayashi, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3724.

(12) (a) Finnegan, R. A. *Ann. N.Y. Acad. Sci.* **1969**, *152*, 242. (b) Gund, P. *J. Chem. Educ.* **1972**, *49*, 100.

(13) Agranat, I.; Skancke, A. *J. Am. Chem. Soc.* **1985**, *107*, 867.

(14) Clark, T.; Wilhelm, D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1982**, *23*, 3547.

(15) (a) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353. (b) Streitwieser, A., Jr.; Swanson, J. T. *J. Am. Chem. Soc.* **1983**, *105*, 2502.

(16) Rajca, A.; Tolbert, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 698.

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

0002-7863/88/1510-0871$01.50/0

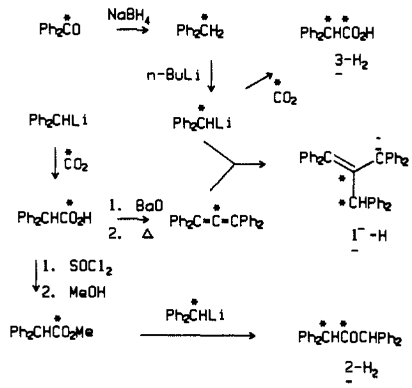

Figure 1. Synthesis of ^{13}C-labeled materials.

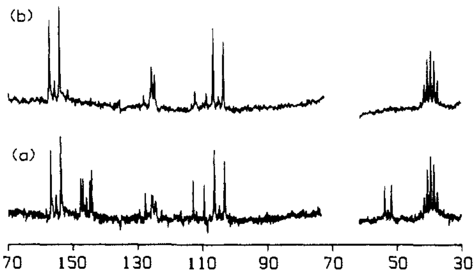

Figure 2. 20-MHz ^{13}C NMR spectrum of [^{13}C$_2$]-**1**$^{2-}$,2K$^+$ and [^{13}C$_2$]-**1**-H$^-$,K$^+$ in Me$_2$SO-d_6: (a) after 3 days; (b) after 22 days.

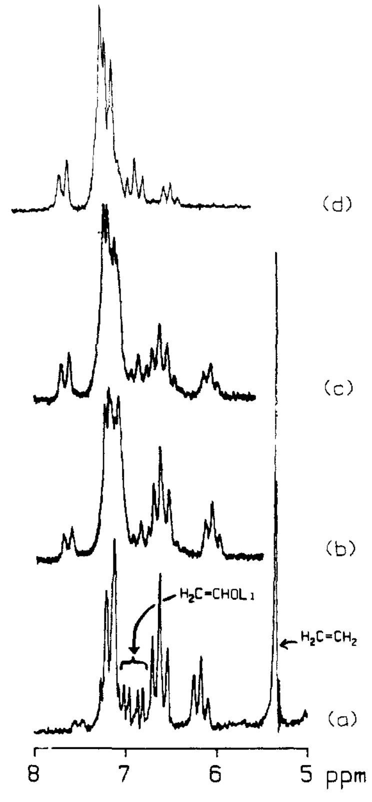

Figure 3. 90-MHz ^{1}H NMR spectrum of **2**$^{2-}$,2Li$^+$: (a) in tetrahydrofuran; (b) after addition of Me$_2$SO-d_6 containing 3 M dimsylpotassium; (c) 10 min after addition; (d) 50 min after addition.

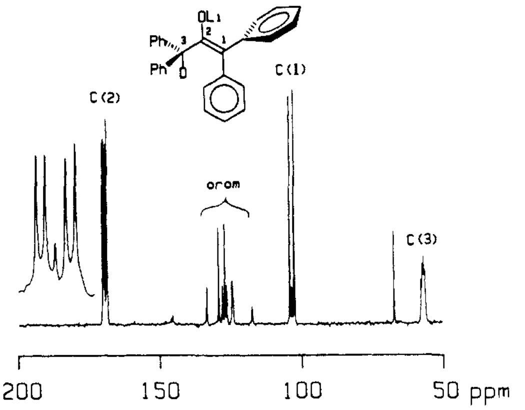

Figure 4. 50-MHz ^{13}C NMR spectrum of **2**-D$^-$,Li$^+$ in Me$_2$SO-d_6.

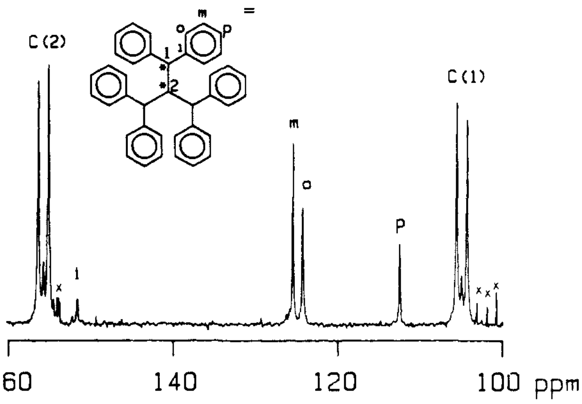

Figure 5. 50-MHz ^{13}C NMR spectrum of [^{13}C$_2$]-**1**$^{2-}$,2K$^+$ in Me$_2$SO-d_6. The peaks marked X are due to impurities.

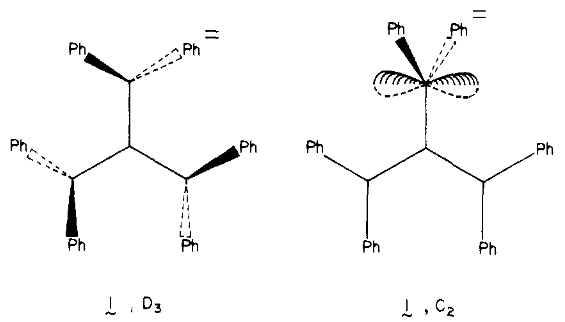

Figure 6. Possible conformation of **1**$^{2-}$.

had its ^{13}C labels exclusively at the C(2) and C(3), the one isolated after quenching had the ^{13}C label scrambled over C(1). Such scrambling did not occur when the monoanion **1**-H$^-$, formed during the synthesis of [2,3-^{13}C$_2$]-2-(diphenylmethyl)-1,1,3,3-tetraphenylpropene was quenched with water. However, the ^{13}C$_2$ anion **1**-H$^-$,Li$^+$ obtained by deprotonation of **1**-H$_2$ with CH_3SOCH_2Li exhibited ^{13}C NMR spectra consisting of nested AX and AB spin systems of approximately equal intensity (see Figure 2). Similarly, **2**-H$^-$ in Me$_2$SO-d_6 exhibited nested AX and AB systems for the two possible isotopomers (see Figure 4).

(iii) The twofold and the threefold symmetry for the monoanion **1**-H$^-$ and the dianion **1**$^{2-}$, respectively, which manifested itself in ^{13}C NMR spectra of the ^{13}C$_2$ anions (see Figure 5), was observed for the ^{1}H NMR spectra as well. In particular, the ^{1}H NMR spectrum showed the doublet, triplet, triplet pattern for the ortho, meta, and para protons characteristic for the benzene rings attached to the carbanionic center in the sterically hindered environment (see Figure 2 of ref 16). Additionally, the charge calculated from the ^{13}C NMR chemical shifts is −1.99 for the dianion **1**$^{2-}$ (see below). Thus, we conclude we have indeed generated a dianion.

Tris(diphenylmethylene)methane Dianion (1^{2-}). We now consider some relevant properties of this unique dianion.

A. Stability. As we have reported previously **1**$^{2-}$ and **3**$^{2-}$ are stable in Me$_2$SO, while **2**$^{2-}$ undergoes protonation to its conjugate acid (enolate).[16] Thus, anion **2**-H$^-$, in contrast to **1**-H$^-$ and **3**-H$^-$, is less acidic than Me$_2$SO.

B. Geometry. In order to determine whether the extraordinary stability of dianion **1**$^{2-}$,2K$^+$ is a resonance effect, we probed its geometry in THF/Me$_2$SO solution by means of ^{13}C NMR (50.3 MHz) at −80 °C. All three terminal carbon atoms remained equivalent, a result that is consistent with either a single conformer

Table I. ^{13}C NMR Data[a] for the Y-Conjugated Dianions and Their Precursors

			δ			J, Hz	
compd	solvent	temp, °C	C(1)	C(2)	C(3,4)	C(1)C(2)	C(2)C(4)
1-H$_2$	CDCl$_3$	23	54.9	139.3		78.3	42.9
1-H$^-$,Li$^+$	Me$_2$SO-d_6	40	111.7	145.8	52.5	67.9	42.0
1-H$^-$,K$^+$	Me$_2$SO	40	111.5	145.8	52.4	67.8	41.8
1-H$^-$,K$^+$	THF/Me$_2$SO-d_6	8	111.7	146.0	52.8	68.0	41.9
$\mathbf{1}^{2-}$,2K$^+$	Me$_2$SO-d_6	23	105.0	155.5		61.6	
$\mathbf{1}^{2-}$,2K$^+$	THF/Me$_2$SO-d_6	23	106.3	156.0		62.1[b]	
2-H$_2$	CDCl$_3$	23	63.6	205.3		38.5	
2-H(D)$^-$,Li$^+$	Me$_2$SO-d_6	24	103.4	169.5	55.6	77.5	41.4
2-H$^-$,K$^+$	Me$_2$SO-d_6	40	101.9	171.2	56.9	76.5	40.4
$\mathbf{2}^{2-}$,2Li$^+$	THF/THF-d_8	40	98.2	175.4		68.8	
3-H$_2$	CDCl$_3$	23	57.0	178.6		44.3	
$\mathbf{3}^{2-}$,2Li$^+$	Me$_2$SO-d_6	40	84.8	172.8		86.0	
$\mathbf{3}^{2-}$,2K$^+$	Me$_2$SO-d_6	40	84.1	175.1		76.7	

[a] Chemical shifts relative to Me$_4$Si (δ 0.00) and/or calculated from the solvent chemical shift: Me$_2$SO-d_6, δ 39.5; Me$_2$SO-h_6, δ 40.5; THF-h_8, δ 67.96. [b] ^1J(C(1)C(5)) = 60.5 Hz; ^3J(C(2)C(6)) = 2.7 Hz; ^3J(C(3)C(5)), ^2J(C(2)C(5)) < 1.5 Hz; ^2J(C(1)C(6)) < 2.3 Hz; ^3J(C(1)C(7)) < 0.8 Hz. For numbering, refer to Figure 7.

of D_3 symmetry in which the benzhydryl groups are arranged propellerlike around the central atom or equilibrating C_2 conformers in which one benzhydryl group bisects the plane of the remaining "allylic" moiety (see Figure 6). We note that conformational mobility in equivalently substituted allyl anions and "trianions", i.e., (1,1,3,3-tetraphenylallyl)lithium, (1,1,3,3-tetraphenylallyl)potassium or (1,1,3,3-tetraphenylallyl)tripotassium, could be inhibited at low temperature.[18b] A comparison of HMO 1,2 π-bond orders for the tris(diphenylmethylene)methane dianion $\mathbf{1}^{2-}$ (0.52), tetraphenylallyl anion (0.62), and tetraphenylallyl trianion (0.42) would suggest an intermediate barrier between bisected C_2 conformers for Y-conjugated dianions. Since twisting of benzhydryl groups should not change that relative order, we conclude that we should be able to observe exchange phenomena among the various C_2 conformers if they were present. The notion of threefold symmetry is further supported by MNDO calculations on the corresponding tribenzylidenemethane dianion,[7] which shows an energy minimum at the C_3 geometry with benzyl groups twisted 19° out of plane. Finally, we fail to observe a carbon-13 equilibrium isotope effect[19,20] in the ^{13}C NMR spectra of a mixture of $^{13}C_2$ and $^{13}C_1$ isotopomers of $\mathbf{1}^{2-}$. The average of the frequencies of the peaks of an AX doublet is shifted upfield by about 2 Hz both at +23 and −80 °C relative to the singlet derived from the monolabeled compound, consistent with an intrinsic isotope shift.[21] Thus, we conclude that dianion $\mathbf{1}^{2-}$ possesses D_3 symmetry, a fact that further confirms the importance of resonance stabilization in $\mathbf{1}^{2-}$.

A similar argument can be proposed in the case of [[1,2-$^{13}C_2$]-1,1,3,3-tetraphenylallyl]lithium ($\mathbf{4}^-$),[18] which exhibits an intrinsic ^{13}C isotope shift of ca. 2 Hz (δ 0.04) for the terminal carbon between +20 and −100 °C in THF. No equilibrium isotope shift could be detected, indicating a C_2-symmetric allylic geometry for **4**.

The one-bond ^{13}C^{13}C coupling constant (^1J(CC)) is generally accepted as a measure of the s-character in the associated atomic orbitals.[22-24] It depends on the bond length,[25] which, for unsaturated systems, is equivalent to π-bond order.[26] The 62-Hz C(1)C(2) coupling constant for $\mathbf{1}^{2-}$ reported in Table I indicates the expected sp^2 hybridization for the Y-conjugated framework of $\mathbf{1}^{2-}$,2K$^+$. The three-bond ^{13}C^{13}C coupling constant (^3J(CC)) has an analogous dihedral angle dependence to its proton–proton counterpart in most cases.[27] The fact that ^3J(C(2)C(6)), the coupling of the *o*-phenyl carbons to the central carbon atom, is greater than ^3J(C(3)C(5)), the coupling of the *ipso*-phenyl carbon to the distal allylic carbon, might suggest that the out-of-plane bending of the phenyl rings is less than that of the benzhydryl moieties (see Figure 7). This is in agreement with the MNDO calculations on tribenzylidenemethane dianion[7] as well as with HMO calculations on the tris(diphenylmethylene)methane dianion $\mathbf{1}^{2-}$, which, assuming planar geometries, yield a 1,2 π-bond order of 0.52 but a 1,5 π-bond order of 0.54. A tentative value of 38° for the "2156" dihedral angle was obtained from the empirical correlation for aryl-substituted ethylenes.[28] Although this number is rather provisional, it compares favorably with the value of 19° obtained for the less sterically hindered benzylic system.[7]

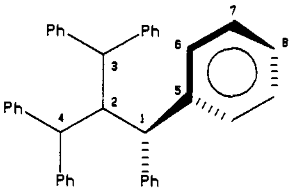

Figure 7. Out-of-plane twisting of C_3 conformation of $\mathbf{1}^{2-}$.

C. Charge Distribution. Average ^{13}C chemical shifts are known to correlate well with average charge densities.[29,30] For example, O'Brien's method[30] uses the following equation for charge densities:

$$\text{charge} = (\delta_c - 133.2)/156.3 \qquad (1)$$

A recent modification, which is fit to polyphenylmethyl anion and cation data, is nearly identical:[31]

$$\text{charge} = (\delta_c - 134.1)/153.7 \qquad (2)$$

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(18) (a) Rajca, A.; Tolbert, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 2969. (b) Rajca, A.; Tolbert, L. M. *Ibid.* **1987**, *109*, 1782.

(19) (a) Saunders, M.; Kates, M. R.; Walker, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 4623. (b) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070.

(20) Krishnamurthy, V. V.; Prakash, G. K. S.; Iyer, P. S.; Olah, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 5015.

(21) Equilibrium isotope effects, even within the harmonic approximation, may exhibit "anomalies" in their temperature dependence, particularly at the intermediate range of temperatures. See: Stern, M. J.; Spindel, W.; Monse, E. U. *J. Chem. Phys.* **1968**, *48*, 2908. This makes a definitive conclusion about the presence or the absence of the equilibrium isotope effect rather difficult, especially, when based on the NMR data at only two temperatures. We also note that the isotopic perturbation (^{13}C at the central carbon) is applied to an already unsymmetrical (^{13}C at the terminal carbon) compound and the chemical shift difference between the benzhydryl and allyl carbons in the "frozen-out" C_2-symmetric $\mathbf{1}^{2-}$–^{13}C, estimated at only δ 16.2 (810 Hz); thus, the effect may not be large enough to be observed in our experiments.

(22) Bingel, W. A.; Luttke, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 899.

(23) Wardeiner, J.; Luttke, W.; Bergholz, R.; Machinek, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 872.

(24) Kamienska-Trela, K.; Biedrzycka, Z.; Machinek, R.; Knieriem, B.; Luttke, W. *Org. Magn. Reson.* **1984**, *22*, 317.

(25) Benn, R.; Rufinska, A. *J. Organomet. Chem.* **1982**, *239*, C19.

(26) Wray, V. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *13*, 177.

(27) Severson, M. L.; Maciel, G. E. *J. Magn. Reson.* **1984**, *17*, 248. Hansen, P. E. *Org. Magn. Reson.* **1978**, *11*, 215.

(28) Hansen, P. E.; Poulsen, O. K.; Berg, A. *Org. Magn. Reson.* **1979**, *12*, 43.

(29) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468.

(30) O'Brien, D. H.; Hart, A. J.; Russel, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410.

Table II. Partition of Charge Density in Selected Carbanions and Carbodianions

parent framework	statistically corrected charge on framework (α, %)[a] for[n] phenyl gps					
	1	2	3	4	5	6
Y-conjugated	83[b]	78[d]	78[e]			77
cyclobutadiene				78[e]		
butadiene (1,4)		73				
allyl (1,3)	69	69		74[c]		
methyl	66	56	64			
benzyl	66	74				

[a] Chemical shifts from: O'Brien, D. H. In *Comprehensive Carbanion Chemistry*; Buncel, T., Durst, E., Eds.; Elsevier: New York, 1980; Vol. 5, Chapter 6 and references therein. [b] Wilhelm, D.; Schleyer, P. v. R., unpublished results. [c] For the trianion,[18b] $\alpha = 77$. [d] Reference 4c. [e] Reference 7.

The last equation seems to be more appropriate to use with dianion $\mathbf{1}^{2-}$. The charge for individual carbon atoms as calculated from eq 1 or 2 correlates very roughly with gas-phase MNDO data.[7,31] Thus, we may partition the total charge density into that fraction localized on the parent "Y" framework and that distributed into the phenyl rings. Since such partitioning involves a great deal of averaging, one may expect that the relative charges for the parent (Y) moiety and substituents calculated by means of eq 2 will be valid. Using this method, we have found an empirical relationship for the distribution of charge in the presence of a number of phenyl groups, thus allowing us to compare differentially substituted anions. With a single phenyl substituent, if the charge on the parent framework is decreased by factor α ($\alpha < 1$), the corresponding factor in the presence of n phenyl groups will be α^n. For the phenyl-substituted Y-conjugated dianions α is about 0.78. Such a relationship can be tested for other anions or substituents (Table II).

The "α" parameter is expected to be a measure of the conjugation between a "parent moiety" and the phenyl substituents and, in turn, an indicator for the importance of resonance within the parent moiety itself, ***independent of the number of phenyl groups***! Of course, the π-overlap between substituents and the parent framework must not be significantly changed due to steric congestion, ion aggregation, etc. upon moving from one system to another or varying degree of the phenyl substitution. Steric hindrance is probably the reason for the lack of a common α parameter for the series of polyphenylated methyl anions and a significant increase in the α parameter upon the introduction of the third and fourth phenyl substituent to the allyl anion (see Table II). However, the more diffuse electron clouds associated with dianions may ameliorate any effects of decreased π-overlap due to twisting of phenyl groups. This is apparently the case, since an excellent relationship for Y-conjugated systems exists ($n = 2$, 3, 6; see Table II) despite severe twisting for $n = 6$ ($\mathbf{1}^{2-}$) as indicated by $^{13}C^{13}C$ coupling constants. It is somewhat worse, however, for $n = 1$ ($\alpha = 82.5\%$ vs 78%). This might be caused either by a different state of aggregation in solution or just by "saturation" of the solitary benzene ring with a charge of $-0.175 \times 2 = -0.35e$.

Of course, we expect that topologically unequivalent sites of substitution, e.g., 1-phenylallyl anion vs 2-phenylallyl anion or 1-phenylbutadiene dianion vs 2-phenylbutadiene dianion, have different α's, which reflects the differential stabilizing ability of phenyl at various sites. Hence, with some uncertainty, we attribute the diminished magnitude of α (72.5%) for terminal substitution of butadiene dianion to poorer resonance stabilization as compared with its four-carbon Y- and cyclic conjugated isomers.

Oxycarbanions. "The Dianions" of Tetraphenylacetone and Diphenylacetic Acid. In strongly solvating media such as Me_2SO less ion–ion interaction and aggregation even for oxycarbanions is expected. Nevertheless, the extensively resonance-stabilized enolate salts of 1,1,3,3-tetraphenylacetone show a significant dependence of $^1J(CC)$ and ^{13}C chemical shifts on the counterion, even in Me_2SO. As expected, lithium cation—a hard Lewis acid—interacts much more strongly with negatively charged oxygen—a hard Lewis base—than with an α-carbon with a remnant of negative charge. The larger potassium cation interacts more weakly with oxygen, which leads to an increased charge $\delta_{C(1)}$ delocalization on the hydrocarbon framework $\delta_{C(1)}$ 103.4 for Li^+ vs $\delta_{C(1)}$ 101.9 for K^+ and a decrease in the C(1)–C(2) bond order ($^1J(CC) = 77.5$ vs 76.5 Hz). The magnitude of the $^1J(CC)$'s for both counterions indicates a normal carbon–carbon double bond between C(1) and C(2). This is confirmed by the lack of conformational mobility around this bond on the ^1H and ^{13}C NMR time scale at room temperature, to the extent that the α-phenyl groups become nonequivalent. One phenyl group shows charge delocalization into the ring, as noted by upfield proton chemical shifts (see Figure 3a), while the other presumably Z-phenyl group shows no such delocalization. We attribute this effect to steric crowding (see Figure 8). The analogue in which oxygen is replaced by a diphenylmethylene group, i.e., 1,1,3,3-tetraphenylallyl anion ($\mathbf{4}^-$), shows a significantly smaller $^1J(CC)$ (67.3 Hz) and fast allylic rotation on the ^1H and ^{13}C NMR time scale at room temperature.

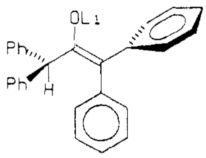

Figure 8. Predicted conformation of $\mathbf{2}$-H^-,Li^+.

The decrease in $^1J(CC)$ when going from the monoanion to the dianion of the ketone (77.5 vs 68.8 Hz) is accompanied by increased conformational mobility with respect to the C(1) and C(2) bond on the ^1H and ^{13}C NMR time scale. The $^1J(CC)$ and the free allylic rotation for the dianion are similar to the analogous all-carbon allyl anions, e.g., 2-(diphenylmethyl)-1,1,3,3-tetraphenylallyl anion ($\mathbf{1}$-H^-, $^1J(CC) = 68.0$ Hz; see Table I). The ^1H NMR spectrum exhibits equivalent phenyl resonance with the typical triplet–triplet–doublet pattern associated with benzylic carbanions. The NMR spectra of the "dianion" of diphenylacetic acid in Me_2SO are even more cation dependent. In particular, the remarkably different $^1J(CC)$'s (86.0 vs 76.7 Hz) for lithium and potassium cations suggest a drastically larger C(1)–C(2) bond order for the former cation. The $^1J(CC)$ of 86.0 Hz can be viewed as large for a carbon–carbon double bond; for instance, $^1J(CC)$ for ethylene is 67 Hz. However, an increased $^1J(CC)$ is also observed for vinyl ethers[32] and for lithium (dimethylamino)cycloheptatrienylidene methoxide ($^1J(CC) = 88.0$ Hz).[33] The latter possesses a short (1.385 Å; X-ray) exocyclic CC bond and a significant activation free energy (17.5 kcal mol^{-1}; NMR) for the barrier to rotation about this bond.[34]

Resonance, Electronegativity, and Charge Alternation. That consecutive replacements of diphenylmethylene by the oxo group leading to dianions $\mathbf{2}^{2-}$ and $\mathbf{3}^{2-}$ increase the CC coupling constants in the Y-conjugated moiety suggests enhanced CC bond orders and localization of negative charge on the oxo groups. Such a trend parallels that found in going from allyl anion to enolate and is amplified by a small countercation (Li^+). Notwithstanding the fact that structural patterns in the Y-conjugated dianions and allyl anions compared with their oxo derivatives are remarkably similar, the free energy differences relative to the neutrals do not follow these characteristics. That is, while 1,1,3,3-tetraphenylallyl anion ($\mathbf{4}^-$) is less stable than the enolate anion of 1,1,3,3-tetraphenylacetone ($\mathbf{2}$-H^-) by 8 pK_a units, i.e., ca. 12 kcal/mol,[35] the cor-

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(31) Boche, G.; Etzrodt, H.; Marsch, M.; Thiel, W. *Angew. Chem. Suppl.* **1982**, 345–354, 355–360.

(32) Krivdin, L. B.; Kushnarev, D. F.; Kalabin, G. A.; Proidakov, A. G. *Zh. Org. Khim.* **1984**, *20*, 949.

(33) Rapp, K. M.; Burgemeister, T.; Daub, J. *Tetrahedron Lett.* **1978**, 2685.

(34) (a) Bauer, W.; Laube, T.; Seebach, D. *Chem. Ber.* **1985**, *118*, 764. (b) Boche, G.; Bosold, F.; Eiben, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 797.

responding Y-conjugated dianion $\mathbf{1}^{2-}$ is more stable than $\mathbf{2}^{2-}$. Moreover, dianion $\mathbf{3}^{2-}$, which contains two oxo groups, is more stable than dianion $\mathbf{2}^{2-}$. Therefore, the electronegativity effects operate in the Y-conjugated and allylic systems in the same way; that is, the oxo group stabilizes an anion more effectively than the diphenylmethylene group does. The relative stability of $\mathbf{1}^{2-}$ compared with $\mathbf{2}^{2-}$ can be ascribed either to an extraordinary resonance stabilization (aromaticity) or to charge alternation. These are not necessarily independent. Agranat and Skancke[13] recently pointed out that trends in resonance energy per atom (REPA) parallel those in charge alternation, at least for some key dianions used by Klein[10] to emphasize importance of the charge alternation. Agranat and Skancke conclude that both effects are woven together.[13]

Dianion $\mathbf{1}^{2-}$ possesses negative charge concentrated on the terminal carbons ($\delta_{C(1)}$ 105.0) and some positive charge on the central carbon ($\delta_{C(2)}$ 155.5), in agreement with ab initio calculations for the prototype trimethylenemethane dianion and with ^{13}C NMR chemical shifts for other derivatives.[13] Introduction of oxo groups ($\mathbf{2}^{2-}$, $\mathbf{3}^{2-}$) decreases the alternation of charges within the parent four-atom framework as suggested by CC coupling constants.

Conclusion

Tris(diphenylmethylene)methane dianion ($\mathbf{1}^{2-}$) possesses a D_3-symmetric sp^2-hybridized hydrocarbon framework; the diphenylmethylenes and phenyl rings are significantly twisted in a propellerlike manner. However, sufficient resonance is realized so that the parent C_4 framework of $\mathbf{1}^{2-}$ retains a significant share of negative charge. Dianion $\mathbf{1}^{2-}$ is Y-aromatic in the sense that its unusual stability is ascribed to resonance; it is difficult to reconcile mere variations in solvation or counterion interactions in Me_2SO with such a large effect. Finally, we would like to reemphasize the utility of ^{13}C NMR spectroscopy with its chemical shifts, CC coupling constants, and isotope shifts for establishing the identity and investigation the structure of anions in solution.

Experimental Section

Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl in an argon atmosphere immediately before use. Me_2SO (h_6 and d_6) was purified by the method of Bordwell.[36] Solutions of dimsyllithium or dimsylpotassium were obtained by reaction of Me_2SO with either lithium or potassium hydride and were titrated with triphenylmethane prior to use. Solutions prepared in this manner and stored in the dark were stable for 2 weeks. The barium [^{13}C]carbonate (^{13}C, 90%) was purchased from Stohler Isotopes. Preparation of the ^{13}C-enriched (90%) substrates used here has been described elsewhere.[18]

Anions and NMR Measurements. Anions for the NMR measurements were generated directly in NMR tubes either equipped with rubber septa or sealed in vacuo after preparation unless indicated otherwise. Varian Instruments spectrometers EM-390 (^{1}H, 90 MHz), FT-80 (^{13}C, 20 MHz), and XL-200 (^{1}H, 200.0 MHz, ^{13}C, 50.3 MHz) were employed for measurements of the NMR spectra. The dianion of diphenylacetic acid was prepared according to the procedure of Lambert and Wharry.[5]

The long-range coupling constants reported in Table I were measured by use of [1,2-$^{13}C_2$]- and [1-$^{13}C_1$]-enriched anions $\mathbf{1}^{2-}$ in THF-h_8/Me_2SO-d_6 and THF-d_8/Me_2SO-d_6, respectively, at 20 °C. The couplings and line widths for the ^{13}C natural-abundance carbons were observed with the MLEV16 pulse sequence for broad-band proton decoupling. The width of the spectral window was 11 kHz. The data were collected with repetition time of 2 s with 32K points. In each case, 20 000–40 000 scans were necessary to obtain a signal-to-noise ratio sufficient for extensive resolution enhancement. The last was performed on the 64K zero-filled fid's with exponential multiplication and apodization with parameters optimized for each signal of interest from ^{13}C natural-abundance carbon.

Calculations. Hückel molecular orbital calculations were performed assuming planar geometries and constant bond lengths between all neighboring atoms, using a resonance integral of 1β (ethylene) for all nearest neighbors.

2-(Diphenylmethyl)-1,1,3,3-tetraphenylpropene (1-H_2). (Diphenylmethyl)lithium was prepared with diphenylmethane (1.75 g, 10.4 mmol) in 27 mL of THF and *n*-BuLi (5.6 mL of a 2.1 M solution in hexane, 11.8 mmol). After 1 h, the ^{1}H NMR spectrum of the orange reaction mixture indicated the presence of (diphenylmethyl)lithium, slightly contaminated with the products of solvent decomposition (the lithium enolate of acetaldehyde, and ethylene). After an additional 30 min, tetraphenylallene (1.72 g, 5.00 mmol) in THF (13 mL) was added. The black reaction mixture was stirred for 16 h at 0 °C before it was quenched with dilute hydrochloric acid. After extraction with ether (40 mL) and chloroform (2 × 30 mL) and drying over $MgSO_4$, concentration in vacuo afforded 3.52 g of a colorless solid. Washing with hexane and crystallization from acetone gave 1.16 g (45%) of colorless crystals, mp 197–198 °C. Concentration of the mother liquor and subsequent crystallizations increased the total yield to 2.13 g (83%) of product, chromatographically pure 2-(diphenylmethylene)-1,1,3,3-tetraphenylpropene. Spectral data: ^{1}H NMR ($CDCl_3$) δ 5.49 (s, 2 H), 7.01 (s, 30 H); ^{13}C NMR ($CDCl_3$) δ 145.6, 143.8, 139.3, 129.9, 127.9, 127.8, 127.4, 125.6, 125.5, 54.9; MS, *m/e* 512. Anal. Calcd. for $C_{40}H_{32}$: C, 93.71; H, 6.29. Found: C, 93.80; H, 6.36.

The $^{13}C_2$ isotopic isomer was obtained similarly, using crude [^{13}C]-diphenylmethane (0.385 g) and [^{13}C]tetraphenylallene (0.231 g, 0.670 mmol). The yield of the $^{13}C_2$ product labeled exclusively at C(2) and C(3) was 75% (0.25 g, 0.504 mmol). Spectral data: ^{1}H NMR ($CDCl_3$) δ 7.01 (s, 30 H), 5.39 (m, ^1J(CH) = 124 Hz, ^2J(C(2)H) = 7.5 Hz, ^3J(C(3)H) = 4.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 139.3 (d, ^1J(CC) = 42.9 Hz), 54.9 (d, ^1J(CC) = 42.9 Hz); MS, *m/e* at 514.

Methyl [$^{13}C_2$]Diphenylacetate. Thionyl chloride (2 mL) was added dropwise to a solution of [$^{13}C_2$]diphenylacetic acid (0.469 g, 2.19 mmol) in methanol (10 mL).[18] After 14 h the solvent was removed in vacuo. According to the ^{1}H NMR and ^{13}C NMR spectra the resultant yellow oil (0.527 g) contained methyl [1,2-$^{13}C_2$]diphenylacetate in 100% yield, along with a trace of methanol. Spectral data: ^{1}H NMR ($CDCl_3$) δ 3.70 (d, ^3J(CH) = 3.75 Hz, 3 H), 5.03 (d of d, ^1J(CH) = 130.5 Hz, ^2J(CH) = 8.70 Hz, 1 H), 7.30 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 57.3 (d, ^1J(CC) = 57.65 Hz), 173.1 (d, ^1J(CC) = 57.65 Hz). *Note*: An analogous preparation of natural-abundance material on a larger scale (10.3 g of diphenyl acetic acid, 75 mL of methanol, 20 mL of thionyl chloride) gave after a single crystallization from hexane 7.86 g (71.5%) of methyl diphenylacetate, mp 62–62.5 °C (lit.[37] mp 60 °C).

1,1,3,3-Tetraphenylacetone (2-H_2). Methyl diphenylacetate (5.11 g, 23.6 mmol) in THF (20 mL) was added over 5 min to 160 mL of a 5:1 THF/hexane solution of (diphenylmethyl)lithium (59.5 mmol) at 0 °C. The red color of (diphenylmethyl)lithium deepened to black-red. After 2 h, the reaction mixture was allowed to warm to room temperature and then quenched with dilute hydrochloric acid. The ethereal extract was washed with aqueous sodium bicarbonate and dried over $MgSO_4$. Concentration in vacuo afforded a colorless oily solid (15.7 g), which contained 1,1,3,3-tetraphenylacetone and unreacted ester in a 7:1 molar ratio, in addition to unreacted diphenylmethane (^{1}H NMR). The crude material was washed repeatedly with pentane (ca. 100 mL total) to give pure 1,1,3,3-tetraphenylacetone (5.42 g, 63%) as a colorless solid, mp 136.5–137 °C (lit.[38] mp 134 °C). Spectral data: ^{1}H NMR ($CDCl_3$) δ 7.23 (m, 20 H), 5.25, (s, 2 H); MS, *m/e* at 362.

The $^{13}C_2$ isotopic isomer was obtained from diphenylmethane (1.16 g, 6.88 mmol) and the $^{13}C_2$ ester (0.489 g, 2.14 mmol) in 44% yield after an additional crystallization from diethyl ether. Spectral data: ^{1}H NMR ($CDCl_3$) δ 7.23 (m 20 H), 5.25 (d of d and d, ^1J(CH) = 127.5 Hz, ^2J(C(carbonyl)H) = 5.7 Hz, ^3J(C(benzhydryl)H) < 1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 205.3 (d, ^1J(CC) = 38.5 Hz), 63.6 (d, ^1J(CC) = 38.5 Hz).

[2-(Diphenylmethyl)-1,1,3,3-tetraphenylallyl]potassium (1-H^-,K^+). From Potassium Hydride in THF. A 5-mL solution of 2-(diphenylmethyl)-1,1,3,3-tetraphenylpropene (0.111 g, 0.217 mmol) and 18-crown-6 (0.248 g, 0.936 mmol) in tetrahydrofuran was added to a multimolar excess of potassium hydride previously washed with pentane. The black reaction mixture was stirred vigorously for 5 h. The ^{1}H NMR spectrum indicated the absence of substrate. After an additional 14 h of stirring, the reaction mixture was withdrawn via an air-tight syringe and injected into a mixture of 1 mL of MeOD and 10 mL of pentane. Dilute aqueous hydrochloric acid was added to achieve pH <2. Extraction with chloroform (2 × 10 mL), drying the extract over $MgSO_4$, and concentration in vacuo afforded an oily yellow solid (0.129 g). The

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(35) (a) The pK_a of 2-H_2 is 17.6. See: Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; McCollum, G. J.; Van Der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* **1977**, *42*, 321. (b) The pK_a of 1,1,3,3-tetraphenylpropene is 25.8. See: Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1983**, *48*, 2216.

(36) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCallum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.

(37) *Handbook Chemistry and Physics*, 49th ed.; CRC: Cleveland, OH, p C-93.

(38) Vorlander, D.; Rack, E. *Chem. Ber.* **1923**, *56*, 1125.

^{1}H NMR spectrum indicated an equimolar mixture of the monodeuteriated substrate and 18-crown-6. Crystallization from acetone/ethanol afforded recoved 2-(diphenylmethyl)-1,1,3,3-tetraphenylpropane (60.5 mg, 54%) as colorless crystals, indistinguishable by TLC from starting material. *Note*: (1) After another crystallization the yield of the pure product increased to 68%. The actual yield was much higher, since a significant amount of the reaction mixture remained in the reaction flask. (2) The presence of 18-crown-6 was found to be essential. ^{1}H NMR examinations of the alkene substrate (0.158 g) and potassium hydride in TMF (5 mL) after 19 h of vigorous stirring at the room temperature and 4 h of reflux showed the unreacted substrate only. When 18-crown-6 (0.725 g in 0.7 mL of THF) was added the ^{1}H NMR spectrum (after 1 h) showed the anion (1-H$^-$,K$^+$) exclusively.

[2-(Diphenylmethyl)-1,1,3,3-tetraphenylallyl]potassium (1^-,K$^+$) and Tris(diphenylmethylene)methane Dianion (1^{2-},2K$^+$) in Me$_2$SO/THF (for NMR). A. For ^{1}H NMR. 2-(Diphenylmethyl)-1,1,3,3-tetraphenylpropene (27.0 mg, 0.053 mmol) was dissolved in THF (0.4 mL) in a 5-mm ^{1}H NMR tube. Dimsylpotassium (ca. 0.05 mL of a 3 M solution in Me$_2$SO-d_6) was added, and the reaction mixture became black. The ^{1}H NMR spectrum after 20 min showed a pure solution of the monoanion **1**-H$^-$. The next 0.05-mL portion of base was added, and after 16 days a solution of dianion was obtained. The reaction mixture was quenched with water, poured into dilute hydrochloric acid, extracted with methylene chloride, and dried over NaHCO$_3$/MgSO$_4$. Concentration in vacuo yielded recovered propene **1**-H$_2$.

B. For ^{13}C NMR. Dimsylpotassium (0.2 mL of 1.6 M solution in Me$_2$SO-d_6) was added to a THF (2.6 mL) solution of [^{13}C$_2$]-2-(diphenylmethyl)-1,1,3,3-tetraphenylpropene (20.3 mg, 0.039 mmol) in a 10-mm ^{13}C NMR tube, which was sealed under vacuum. After 3 days at room temperature the ^{13}C NMR spectrum taken at 8 °C indicated the pressure of a mixture of monoanion **1**-H$^-$ and dianion $\mathbf{1}^{2-}$ (approximately 1:1). After 22 days, the ^{13}C-labeled carbons displayed the AB spin system of the dianion $\mathbf{1}^{2-}$ only (Figure 2).

Tris(diphenylmethylene)methane Dianion (1^{2-},2K$^+$) in Me$_2$SO-d_6. A. For ^{1}H NMR. Dimsylpotassium (0.5 mL of 3 M in Me$_2$SO-d_6) was added to solid 2-(diphenylmethyl)-1,1,3,3-tetraphenylpropene (0.0530 g, 0.104 mmol) in a 5-mm ^{1}H NMR tube. The tube was subsequently immersed into acetone/water/ice bath (−10 °C) and sealed under vacuum. The ^{1}H NMR spectrum showed a mixture of dianion $\mathbf{1}^{2-}$ and monoanion **1**-H$^-$. The spectrum, taken after 5 min, showed greatly decreased intensities of the signals ascribed to monoanion **1**-H$^-$. After 3 h at room temperature, only dianion $\mathbf{1}^{2-}$ could be detected.

This facile formation of $\mathbf{1}^{2-}$ should be directly compared with the unsuccessful deprotonation for the ketone; only **2**-H$^-$/**2**-D$^-$ could be detected by ^{1}H NMR under comparable conditions (see the second following experiment).

B. For ^{13}C NMR. A solution of $\mathbf{1}^{2-}$,2K$^+$ in pure Me$_2$SO-d_6 was prepared by adding a dimsylpotassium solution to solid [^{13}C$_2$]-2-(diphenylmethyl)-1,1,3,3-tetraphenylpropene (48.6 mg, 0.095 mmol). After 4 days at ambient temperature, the ^{13}C NMR spectrum was taken at 23 °C with low-power ^{1}H broad-band decoupling using the MLEV16 pulse sequence (see Figure 5).[39] The reaction mixture was quenched with water (100 mL) and extracted with methylene chloride, and the extract was washed with water and dried over MgSO$_4$. Concentration in vacuo and subsequent column chromatography (SiO$_2$, chloroform/hexane, 1:4) returned recovered propene **1**-H$_2$ as a colorless solid (26.9 mg, 53%) with the labels scrambled among C(1), C(3), and C(4).

[2-(Diphenylmethyl)-1,1,3,3-tetraphenylallyl]lithium (1-H$^-$,Li$^+$) in Me$_2$SO-d_6. For ^{13}C NMR. Dimsyllithium (0.12 mL of a 1.5 M solution in Me$_2$SO-d_6) was added to a stirred suspension of [^{13}C$_2$]-2-(diphenylmethyl)-1,1,3,3-tetraphenylpropene (**1**-H$_2$; 72.5 mg, 0.141 mmol) in 2.1 mL of Me$_2$SO-d_6. After 30 min, a portion of the black reaction mixture examined by ^{1}H and ^{13}C NMR indicated the presence of the monoanion **1**-H$^-$ only. After 2 h, a second portion of dimsyllithium (0.24 mL) was added, to yield a mixture of dianion $\mathbf{1}^{2-}$ and the monoanion by ^{1}H NMR. After an additional 1 h, a third portion of dimsyllithium (0.10 mL) was added. The ^{13}C NMR spectrum (12-h acquisition time) of the previous spectrum revealed signals from the residual monoanion at 10% intensity relative to Me$_2$SO-d_6 and extremely broadened absorptions from the dianion. The spectrum at 63 °C indicated the absence of the monoanion **1**-H$^-$ and broadened signals from the dianion. The reaction mixture was quenched with water and dilute HCl. The reaction mixture was diluted with water and extracted with methylene chloride, and the extract was washed with water and dried over NaHCO$_3$ and MgSO$_4$. Concentration in vacuo yielded recovered propene **1**-H$_2$ (45.2 mg, 62%) after column chromatography (SiO$_2$, hexane, hexane/chloroform, 7:1). The ^{13}C and ^{1}H NMR spectra indicated scrambling of the ^{13}C label.

1,1,3,3-Tetraphenylacetone Anion (2-H$^-$,K$^+$) in Me$_2$SO-d_6. Dimsylpotassium (0.45 mL of a 3 M solution in Me$_2$SO-d_6) was added to solid 1,1,3,3-tetraphenylacetone (23.1 mg, 0.0639 mmol). The ^{1}H NMR spectrum of the resultant red solution indicated the presence of monoanion **2**-H$^-$. After 14 h at ambient temperature, the integration for the benzhydryl proton (δ 4.73) had decreased by 75% due to deuterium exchange. After an additional 30 min at 60 °C (^{1}H NMR at 60 °C), the signal at δ 4.73 had practically disappeared (<5%). No change in the spectrum appeared after 2 days at ambient temperature.

1,1,3,3-Tetraphenylacetone Dianion, Lithium Salt (2^{2-},2Li$^+$). Protonation by Me$_2$SO-d_6. A 0.1-mL portion of *n*-butyllithium (2.1 M solution in hexane) was added to 0.4 mL of a tetrahydrofuran solution of 1,1,3,3-tetraphenylacetone (26.0 mg, 0.072 mmol) at 0 °C. The red solution was allowed to stand for 15 min at 0 °C, and a series of ^{1}H NMR spectra were taken. After 40 min in an NMR probe maintained at 34 °C, deep red crystals were observed. The temperature of the reaction mixture was lowered to −15 °C for 15 min, the supernatant withdrawn via syringe, and the residual solvent evaporated in vacuo at ambient temperature. The deep red crystals were dissolved in 0.4 mL of Me$_2$SO-d_6, 3 M in dimsylpotassium, to produce a deep red solution. ^{1}H NMR indicated the presence of a mixture of $\mathbf{2}^{2-}$ and **2**-D$^-$, which underwent complete conversion to the monoanion **2**-D$^-$ after 40 min at ambient temperature (Figure 3). A comparable experiment, monitored by ^{13}C NMR, yielded similar results.

1,1,3,3-Tetraphenylacetone Dianion, Lithium Salt (2^{2-},2Li$^+$), in Tetrahydrofuran. A. ^{13}C Natural-Abundance Sample, for ^{13}C NMR. *n*-BuLi (0.15 mL, 2.4 M in hexane) was added to a THF-d_8 (0.5 mL) solution of 1,1,3,3-tetraphenylacetone (0.545 g, 0.150 mmol) at −10 °C in a 10-mm ^{13}C NMR tube. The reaction mixture was allowed to stand for 30 min at −10 °C, 50 min at ambient temperature, and 8 h at −78 °C. The mixture was warmed to ambient temperature, and THF-h_8 (2.2 mL) was added. After vigorous shaking a homogenious solution was obtained. A ^{13}C NMR spectrum was obtained at 24.5 °C. After 10 h, D$_2$O (1 mL) was injected into the solution, and then the mixture was poured into dilute aqueous HCl (15 mL). Extraction with ether, drying over NaHCO$_3$ and MgSO$_4$, and concentration in vacuo yielded 1,1,3,3-tetraphenylacetone-d_2 (50.5 mg, 92%) as colorless crystals, mp 134–135 °C (**2**-H$_2$, mp 136.5–137 °C).

B. ^{13}C$_2$-Enriched Sample. *n*-BuLi (0.15 mL, 2.1 M in hexane) was added to the THF-d_8 (0.6 mL) solution of [^{13}C$_2$]-1,1,3,3-tetraphenylacetone (15.6 mg, 0.043 mmol) at −10 °C in a 10-mm ^{13}C NMR tube. After 15 min, the red reaction mixture was allowed to warm to room temperature. After an additional 30 min, THF-H$_8$ (2.5 mL) was added, dissolving the precipitate. Immediate ^{13}C NMR analysis of the homogeneous solution at 40 °C indicated exclusive formation of 1,3-dilithiotetraphenylacetone ($\mathbf{2}^{2-}$,2Li$^+$). After 16 h at +40 °C, ^{1}H NMR examination of the reaction mixture indicated significant formation of lithium enolate of acetaldehyde [δ 6.94 (dd)] and ethylene [δ 5.34 (s)]. Signals from these two impurities were detectable in both (A and B) ^{13}C NMR spectra too (see below). Quenching with D$_2$O followed by addition of dilute aqueous HCl, extraction with chloroform, and keeping the extract over NaHCO$_3$ and MgSO$_4$ afforded crude [1,3-^{13}C$_2$,-1,3-^{2}H]-1,1,3,3-tetraphenylacetone: 27.2 mg; ^{1}H NMR; MS, *m/e* 366.

C. Reaction of Tetrahydrofuran with *n*-BuLi. *n*-BuLi (0.45 mL, 2.4 M in hexane) was added to the mixture of THF-d_8 (0.3 mL) and THF-h_8 (3 mL). After standing overnight at room temperature the ^{13}C NMR spectrum was recorded. The spectral data (acetaldehyde enolate, δ 159.1 and 81.6; ethylene, δ 123.2) corresponded to those obtained from 1,3-dilithio-1,1,3,3-tetraphenylacetone ($\mathbf{2}^{2-}$,2Li$^+$) (see above).

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Registry No. **1**-H$_2$, 94234-95-4; **1**-H$_2$ (^{13}C$_2$ isomer), 111975-69-0; **1**-H$^-$,Li$^+$, 111975-67-8; **1**-H$^-$,K$^+$, 111975-68-9; $\mathbf{1}^{2-}$,2K$^+$, 94234-96-5; **2**-H$_2$, 7476-11-1; **2**-H$_2$ (^{13}C$_2$ isomer), 111975-70-3; **2**-H$^-$,Li$^+$, 94234-98-7; **2**-H$^-$,K$^+$, 94235-00-4; $\mathbf{2}^{2-}$,2Li$^+$, 94234-97-6; **3**-H$_2$, 117-34-0; $\mathbf{3}^{2-}$,2Li$^+$, 60538-71-8; $\mathbf{3}^{2-}$,2K$^+$, 94235-01-5; diphenylmethane, 101-81-5; tetraphenylallene, 1674-18-6; [1,3-^{13}C$_2$,1,3-^{2}H$_2$]-1,1,3,3-tetraphenylacetone, 111975-71-4; diphenylacetic acid, 117-34-0; methyl diphenylacetate, 3469-00-9; (diphenylmethyl)lithium, 881-42-5.

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[39] Levitt, M. H.; Freeman, R.; Frenkiel, T. *J. Magn. Reson.* **1982**, *7*, 328.