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Synthesis, Characterization, and Reaction of a Ketone-Derived 1,4-Dienolate Compound

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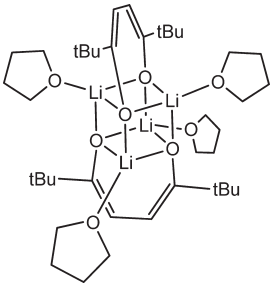


The tetrahydrofuran tetrasolvated dimeric lithium dienolate derived from 2,2,7,7-tetramethyloctan-3,6-dione is characterized in the solid state by X-ray diffraction analysis and in solution by diffusion NMR. This dienolate was reacted with tropanone to yield two new products that are also described.

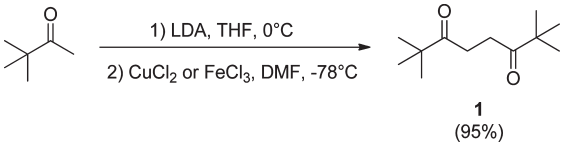
Introduction

Ketone derived enolate chemistry has long been a well-known and synthetically useful technique for carbon−carbon bond formation.[1] Lithium dienolates derived from diesters and diamides have been successfully used in synthesis.[2] Unsubstituted vinylogous dienolates derived from aldehydes, ketones, carboxylic acids, esters, amides, and imides, as well as β-substituted enolates, are known and have been successfully employed in vinylogous aldol reactions, affording complex chiral products.[3] However, 1,4-dienolates derived from ketones are not well-known. We theorized on the basis of previously reported enolates of pinacolone that pinacolone could be joined at the α-carbon to form a 1,4-diketone **1**, which could be enolized to yield the corresponding 1,4-dienolate **2**.[4] Such compounds may allow introduction of a variety of four-carbon building blocks.

Results and Discussion

Synthesis of 1,4-Diketone and Formation of 1,4-Dienolate. We synthesized the 1,4-diketone **1** from pinacolone using literature methods (Scheme 1).[5] Lithium diisopropylamide (LDA) enolizes pinacolone to form the enolate. Addition of anhydrous copper(II) chloride or iron(III) chloride forms α-chloropinacolone *in situ*, which reacts immediately with the remaining enolate to form the 1,4-diketone in good yield.

SCHEME 1. Synthesis of 1,4-Diketone 1 from Pinacolone



In order to generate the 1,4-dienolate, lithium hexamethyldisilazane (LiHMDS) was employed to enolize the 1,4-diketone **1** to the 1,4-dienolate **2**. Following the enolization of **1** to form an enolate aggregate **2**, 2 equiv of tetrahydrofuran (THF) was added (1 THF per lithium). THF tightly solvated lithium

(1) (a) Juaristi, E.; Beck, A. K.; Hansen, J.; Matt, T.; Mukhopadhyay, T.; Simson, M.; Seebach, D. *Synthesis* **1993**, *1993* (12), 1271–1290. (b) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27* (12), 1624–1654.

(2) (a) Garratt, P. J.; Pielke, M.; Porter, J. R. *Tetrahedron Lett.* **1987**, *28* (5), 589–592. (b) Doecke, C. W.; Garratt, P. J.; Shahriari-Zavareh, H.; Zahler, R. *J. Org. Chem.* **1984**, *49* (8), 1412–1417. (c) Mahalanabis, K. K.; Mumtaz, M.; Snieckus, V. *Tetrahedron Lett.* **1982**, *23* (39), 3971–3974. (d) Girard, C.; Bloch, R. *Tetrahedron Lett.* **1982**, *23* (36), 3683–3686. (e) Long, N. R.; Rathke, M. W. *Synth. Commun.* **1981**, *11* (9), 687–696.

(3) Casiraghi, G.; Zanardi, F.; Appendino, G.; Rassu, G. *Chem. Rev.* **2000**, *100* (6), 1929–1972.

(4) (a) Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1986**, *108* (3), 462–8. (b) Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1985**, *107* (11), 3345–6.

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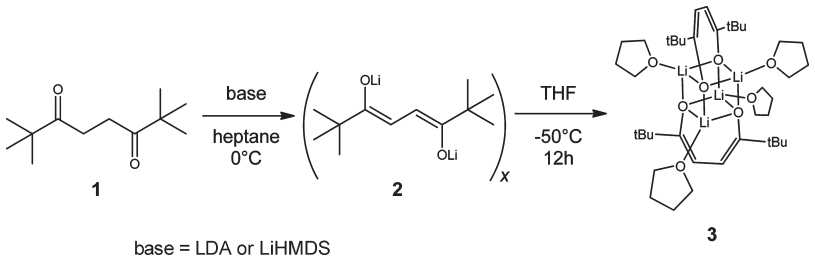
SCHEME 2. Generation of 3 from 1, Base, and THF



to form the aggregate **3**, determined by X-ray crystal diffraction analysis (Scheme 2).

The tetrasolvated dimeric aggregate of the 1,4-dienolate **3** was studied both by X-ray diffraction analysis and nuclear magnetic resonance (NMR) spectroscopy. It was found that **3** exists as the tetrasolvated dimeric aggregate in both the solid state and the solution state.

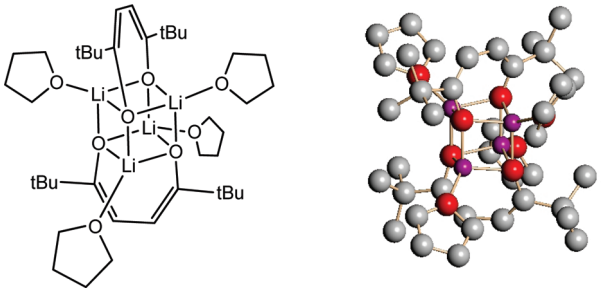


FIGURE 1. X-ray crystal structure of **3**.

Identification of 1,4-Dienolate 3 by X-ray Diffractometry Studies. X-ray analysis of crystals of **3** support the structure of **3** as a tetrasolvated dimer in the solid state.[6] The crystal contains two dienolate subunits in a distorted cubic core with 4 lithium atoms. Each lithium is solvated by a single THF molecule. This crystal structure is very similar to that of the THF solvated enolate of pinacolone with each pair of pinacolone subunits joined at the α carbon (Figure 1).[4a] A table of crystallographic data, including bond lengths, is available in the Supporting Information.

Identification of 1,4-Dienolate 3 in Solution by NMR Studies. Complex **3** was generated directly in the NMR tube in toluene-d_8 for NMR studies. Beginning with a sample of freshly prepared ^{6}LiHMDS crystals dissolved in toluene-d_8, **1** was titrated to form the unsolvated 1,4-dienolate **2**. THF was then added to form tetrasolvated complex **3**. The titration was monitored by ^{1}H and ^{6}Li NMR (Figures 2 and 3).

Formation of **2** is confirmed in the ^{1}H NMR with formation of the signature enolate peak at δ ~4.8. Following formation of **2**, complex **3** was generated by titration of 2 equiv of THF into the NMR tube. Two new peaks corresponding to **3** are apparent, as well as two peaks corresponding to THF, while the peaks of **2** are greatly diminished (Figure 2c).

In ^{6}Li NMR in toluene-d_8, ^{6}LiHMDS has a single peak at δ ~1.4. All ^{6}LiHMDS is consumed after the addition of **1** due to formation of the unsolvated 1,4-dienolate **2** at δ ~−0.5 (Figure 3b). Following the formation of **2**, addition of THF resulted in the formation of a peak from complex **3** at δ 0.19 and the corresponding decreasing intensity of the peak of **2**. Further titration of THF leads to complete disappearance of the peak of **2**, resulting in a sole peak in the ^{6}Li NMR due to (Figure 3c). It should be noted that these experiments were performed at room temperature. Though the above data are consistent with a single species, it may be possible that multiple rapidly exchanging species are present and the observation is that of the time averaged data.

Complex **3** was characterized by 1D ^{1}H, ^{13}C, and ^{6}Li NMR spectroscopy, 2D COSY, HSQC, HMBC, HMQC and NOESY

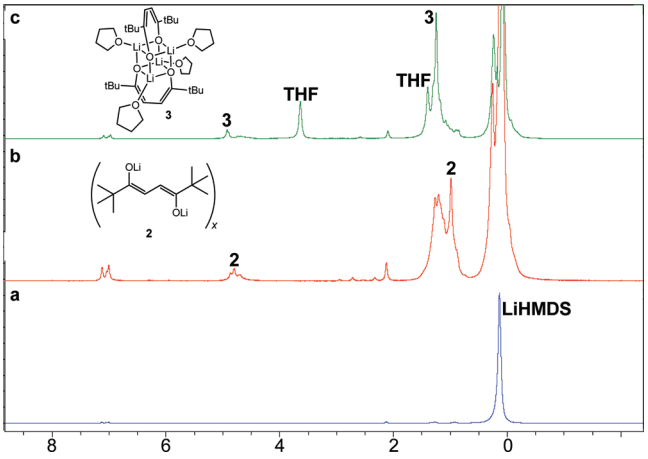


FIGURE 2. (a) ^{1}H NMR of ^{6}LiHMDS crystal in toluene-d_8. (b) ^{1}H NMR of unsolvated 1,4-dienolate **2**. (c) ^{1}H NMR of THF tetra-solvated 1,4-dienolate **3**.

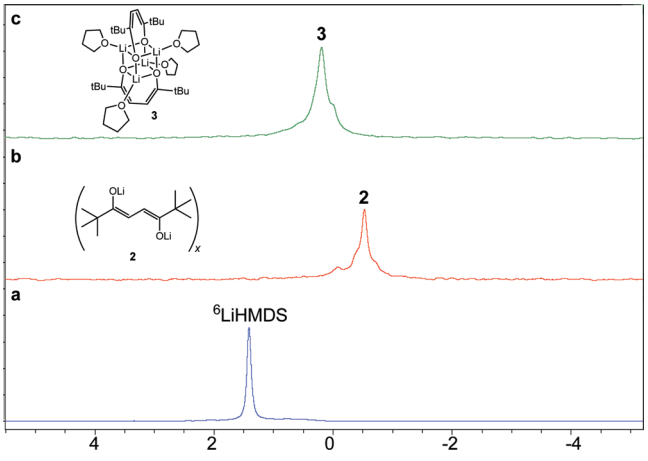


FIGURE 3. (a) ^{6}Li NMR of ^{6}LiHMDS crystal in toluene-d_8. (b) ^{6}Li NMR of unsolvated 1,4-dienolate **2**. (c) ^{6}Li NMR of THF tetra-solvated 1,4-dienolate **3**.

(6) CCDC 787357 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

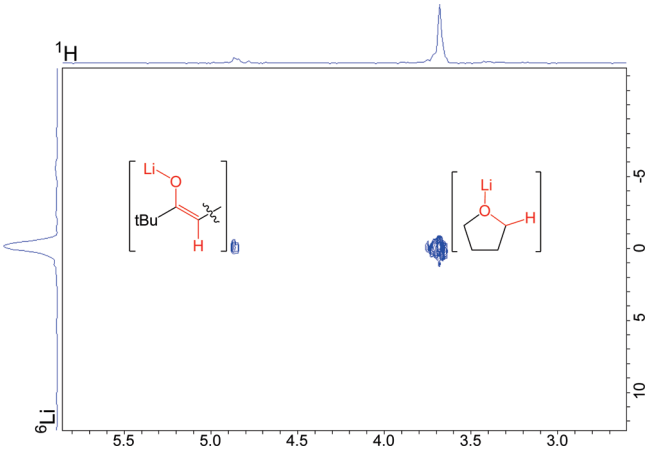


FIGURE 4. ^{1}H{^{6}Li} HMBC of **3** in toluene-d_8.

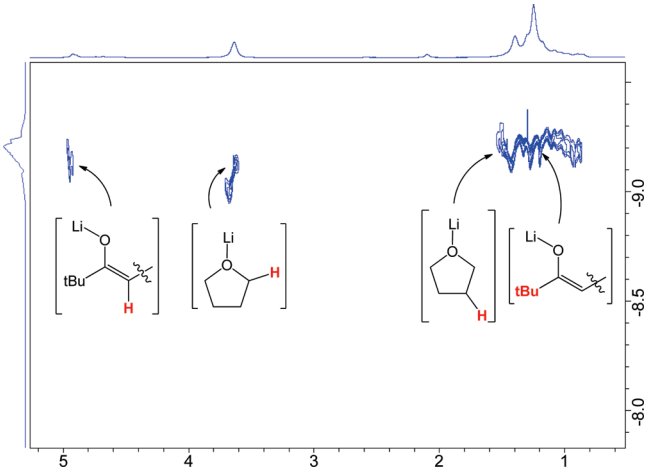


FIGURE 5. ^{1}H DOSY of **3** in toluene-d_8.

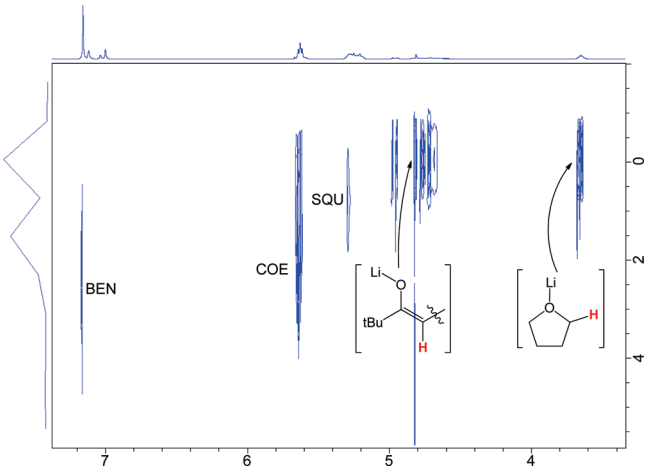


FIGURE 6. ^{1}H DOSY of **3** in toluene-d_8 with internal references benzene (BEN, 78.11 g mol^{-1}), cyclooctene (COE, 110.20 g mol^{-1}), and squalene (SQU, 410.72 g mol^{-1}).

NMR spectroscopy, as well as ^{1}H and ^{6}Li diffusion-ordered spectroscopy (DOSY). ^{1}H DOSY and ^{6}Li DOSY data were correlated though ^{1}H{^{6}Li} HMBC.[7]

The enolate peak is readily apparent in the ^{1}H NMR (δ 4.92), as are the THF peaks (δ 3.63 and 1.39), and the peak from the *tert*-butyl protons (δ 1.25). The ^{13}C NMR is similarly clear, showing the enolate carbonyl (δ 163.78), the enolate methine (δ 95.59), the quaternary carbon of the *tert*-butyl group (δ 38.10), the *tert*-butyl methyl carbons (δ 30.31), and the carbons in THF (δ 69.04 and 25.83). ^{6}Li NMR revealed only a single resonance for all lithium atoms in the aggregate (δ 0.19), as expected for a solution of **3**. ^{1}H{^{6}Li} HMBC showed strong correlation though oxygen from lithium to both the enolate proton and the downfield protons of THF, confirming that THF is indeed bound to lithium in solution under experimental conditions (Figure 4).

Diffusion-ordered NMR spectroscopy has been previously established as an efficient and important means for the identification of molecular size and formula weights of compounds in solution.[8] Our group has successfully developed internal references for ^{1}H, ^{13}C, and ^{31}P DOSY, as well as diffusion coefficient-formula weight (*D*-fw) correlation analysis for solution state structural identification of solution state aggregates.[7,9] According to our empirical equation log $D = A$ log fw $+ C$, plotting the logarithm of the diffusion coefficient against the logarithm of the formula weights of internal references gives a plot which can be used to interpolate or extrapolate formula weight data for complexes based on their experimentally determined diffusion coefficients. This noninvasive method allows investigation of aggregation states of air and moisture sensitive complexes such as **3**. These are difficult to characterize in solution by conventional means (i.e., LC- or GC-MS).

The ^{1}H DOSY spectrum of a solution of complex **3** in toluene-d_8 shows the resonances from the dienolate and THF diffusing at very similar rates, which is indicative of complexation between the two (Figure 5).

Addition of internal references benzene (BEN, 78.11 g mol^{-1}), cyclooctene (COE, 110.20 g mol^{-1}), and squalene (SQU, 410.72 g mol^{-1}) allowed examination by *D*-fw correlation analysis. Plotting the logarithm of the diffusion data of the references against the logarithm of their formula weights resulted in a plot with a very good correlation ($r^2 = 0.99$), from which the formula weight of **3** was extrapolated (Figures 6 and 7, Table 1). The DOSY *D*-fw analysis suggests that compound **3** remains a THF tetrasolvated dimer in solution under experimental conditions. The predicted formula weight (fw*) of complex **3** derived from the diffusion coefficient of

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TABLE 1. ***D*-fw Correlation Analysis of the ^{1}H DOSY of 3 with Internal References Benzene (BEN, 78.11 g mol^{-1}), Cyclooctene (COE, 110.20 g mol^{-1}), and Squalene (SQU, 410.72 g mol^{-1})**

cmpd	fw (g mol^{-1})	$D \times 10^{-10}$ (m^2 s^{-1})	log fw	log D	fw* (g mol^{-1})	% error
benzene	78.1	22.94	1.893	−8.639	79	−0.7
cyclooctene	110.2	19.15	2.042	−8.718	109	0.9
squalene	410.7	9.229	2.614	−9.035	411	−0.2
3 (enolate)	708.8	6.904	2.851	−9.161	697	1.6
3 (THF)	708.8	7.044	2.851	−9.152	672	5.1

TABLE 2. ***D*-fw Correlation Analysis of the ^{1}H DOSY of 3 with Internal References Benzene (BEN, 78.11 g mol^{-1}), Cyclooctene (COE, 110.20 g mol^{-1}), and Squalene (SQU, 410.72 g mol^{-1}) with Excess THF**

cmpd.	fw (g mol^{-1})	$D \times 10^{-10}$ (m^2 s^{-1})	log fw	log D	fw* (g mol^{-1})	% error
benzene	78.1	21.04	1.893	−8.677	75	3.7
cyclooctene	110.2	16.50	2.042	−8.783	116	−4.9
squalene	410.7	8.093	2.614	−9.092	407	1.0
3 (enolate)	708.8	5.727	2.851	−9.242	749	−5.7
THF	708.8	9.165	2.851	−9.038	326	53.9

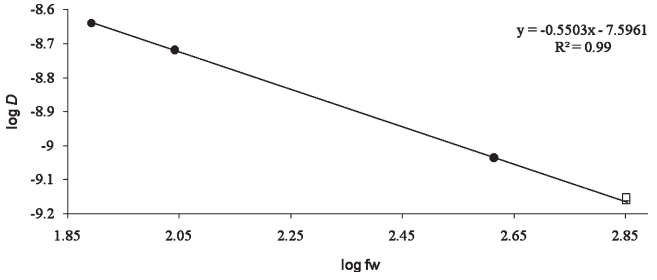


FIGURE 7. *D*-fw correlation analysis of the ^{1}H DOSY of **3** with internal references benzene (BEN, 78.11 g mol^{-1}), cyclooctene (COE, 110.20 g mol^{-1}), and squalene (SQU, 410.72 g mol^{-1}).

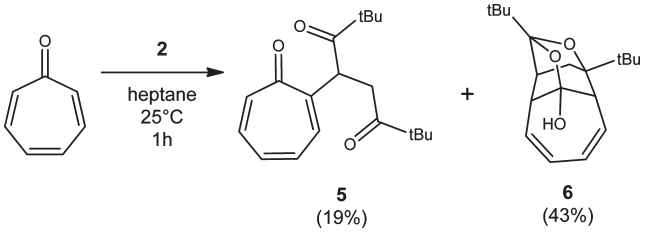
the enolate resonance is 697 g mol^{-1}, a 1.6% difference from its calculated formula weight. The fw* calculated from the diffusion coefficient of the THF resonance is 672 g mol^{-1}, a 5.1% difference from that of complex **3**. These data strongly suggest the aggregation state of complex **3** as having two dienolates and four solvating THF molecules. ^{6}Li DOSY experiments show only a single diffusion coefficient, as there is only one type of lithium present in **3**.

Excess THF was added to confirm the solvation number. With more than 2 equiv of THF, the signals of THF diffuse more quickly. The fw* calculated from the THF resonance is 326 g mol^{-1}, suggesting a portion of THF is bound to the enolate and the excess of THF is free in solution, as the experimentally observed diffusion coefficient of THF is an average of the two. However, the fw* extrapolated from the enolate resonance of **3** does not change significantly in the presence of excess THF (fw* 749 g mol^{-1}, −5.7% error) (Table 2).[10] Correlation was quite good, with $r^2 = 0.99$. This supports that in **3** the solvation number of THF is four, as observed in the crystal structure.

Taken together, the NMR data provide a clear picture of compound **3** in solution. 1D NMR and 2D correlation spectroscopy provide evidence for the bonding structure of the aggregate subunit, while DOSY NMR and subsequent *D*-fw correlation analysis provide evidence of the aggregation number, which all support the proposed structure of **3** in solution as a tetrasolvated dimer.

Reactivity. We expected **2** to react as a 1,3-diene in either [4 + 2] or [6 + 4] cycloaddition reactions; however, reaction with a variety of dienophiles yielded no products and recovery of **1**. In an attempt to react **2** with tropone, two major products were obtained, indicating reaction of **2** as a nucleophile.[11] Addition of tropone gave 2 products **5** and **6** (Scheme 3).

SCHEME 3. Reaction of Tropone As a Nucleophile with 2 To Yield 5 and 6



All tropone was consumed after 1 h and two products were present (GC−MS). The minor product **5** (19%) is from addition of **2** adding to the α-carbon of tropone in a typical fashion.[12] Though the dehydrogenated product **5** is not the intuitive product, previously reported works have shown that autoxidation can occur to convert the post-nucleophile addition α,*β*,*γ*,*δ*-unsaturated carbonyl system to the aromatic-like tropone core, especially in basic solutions.[13]

The major product **6** (43%) gave a nontrivial NMR spectrum but was crystallized from hexanes with a drop of ethanol allowing X-ray diffraction analysis (Figure 8).[14]

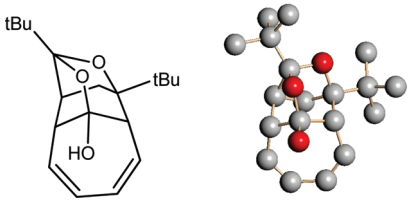


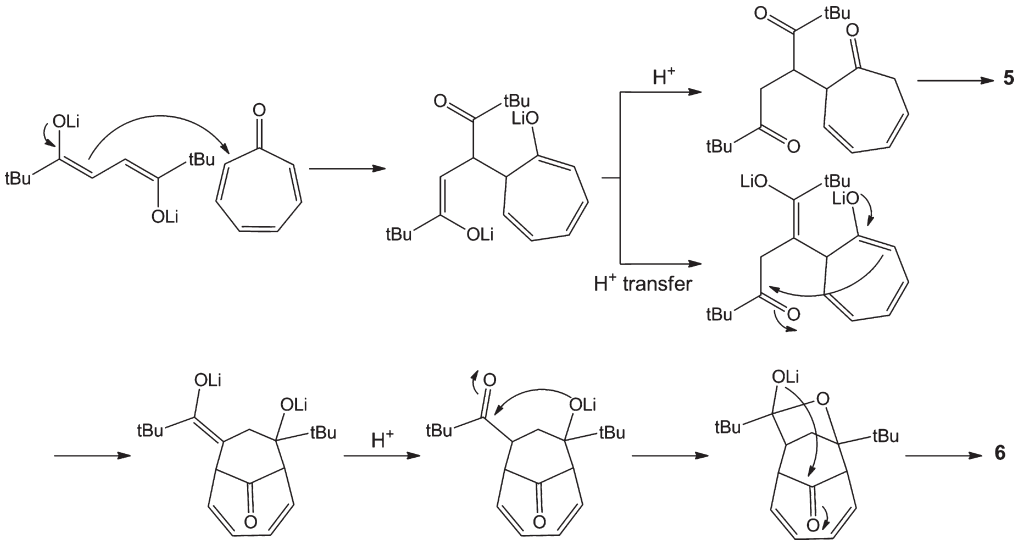
FIGURE 8. X-ray crystal structure of **6**.

Although at first glance **6** appears to be the product of [6 + 4] addition, it is actually a product of nucleophilic addition of the dienolate to tropone. The formation of both **5** and **6** can be explained by a nucleophilic addition mechanism where

(10) Typical accuracy in a DOSY *D*-fw experiment is ±10%. Differences less than this are possible due to expeimental error rather than any explicit change in diffusion.

(11) (a) Rigby, J. H.; Cuisiat, S. V. *J. Org. Chem.* **1993**, *58* (23), 6286–6291. (b) Rigby, J. H.; Rege, S. D.; Sandanayaka, V. P.; Kirova, M. *J. Org. Chem.* **1996**, *61* (3), 842–850.

SCHEME 4. Proposed Mechanism for the Generation of 5 and 6



one-half of the enolate adds to the α-carbon of tropone. Autoxidation leads to **5**, forming the thermodynamically favored conjugated π-system. Proton transfer leads to addition of the tropone back to the dienolate moiety in a 6-*exo*-*trig* fashion. Proton transfer and two 5-*exo*-*trig* closures lead to **6**, forming four stereocenters in the process (Scheme 4).

Conclusion

A new THF solvated 1,4-dienolate complex was generated easily from a synthetically accessible 1,4-diketone, expanding the scope of known dienolate compounds. Its solid-state and solution-state structures were examined and confirmed by X-ray diffractometry and NMR techniques. Its reactivity was probed with a variety of compounds, and although the expected cycloadditions did not occur, an interesting nucleophilic addition occurred, yielding an unexpected tetracyclic compound with four newly formed stereocenters. This expands the potential applicability of 1,4-diketones as precursors to 1,4-dienolates as synthetic intermediates to form complex structures from simple starting materials.

Experimental Section

General Procedures for NMR Experiments. NMR samples were prepared in tubes sealed with serum septa and Parafilm. Tubes were evacuated *in vacuo*, flame-dried, and filled with argon. Samples were prepared with ca. 50 mg of compound in 600 μL of toluene-d_8. NMR experiments were performed at 25 °C. ^{1}H chemical shifts were referenced to toluene-d_8 at δ 7.09 or benzene at δ 7.16. Experiments were performed on a 400 MHz spectrometer equipped with an *z*-axis gradient amplifier and a probe with a *z*-axis gradient coil. Maximum gradient strength was 0.214 T/m. For ^{1}H DOSY experiments, the standard pulse program, stebpgp1s19, employing stimulated echo, bipolar gradient pulses, and one spoil gradient with 3-9-19 pulse sequence solvent suppression to suppress the hexamethyldisilazane (HMDS) signal was used. Diffusion time was 200 ms. The gradient recovery delay was 200 μs. Gradient pulse duration was 1000 μs. For ^{6}Li DOSY experiments, the standard pulse program, dstebpgp3s, employing double stimulated echo, bipolar gradient pulses, and three spoil gradients was used. Diffusion time was 250 ms. The gradient recovery delay was 200 μs. Gradient pulse duration was 3000 μs. Individual rows of the quasi-2-D diffusion databases were phased and baseline corrected.

Synthesis of *n*-Bu^{6}Li. About 1.0 g (166 mmol) of finely cut ^{6}Li metal was placed into a flame-dried flask flushed with argon. The flask was fitted with a serum septum and sealed with Parafilm. The metal was washed with dry pentane by adding 10 mL of pentane to the flask via syringe. The flask was then placed in ultrasound for 5 min. Pentane was then removed via syringe. This was repeated until the washings were clear, with no white solid suspended in the wash (3 times). Dry heptane (15 mL) was added to the flask, followed by 10.9 mL (9.6 g, 104 mmol) of 1-chlorobutane, dropwise. This mixture was kept under ultrasound overnight at room temperature, after which a purple slurry was obtained. The suspension was transferred via syringe to a clean, flame-dried vial flushed with argon and fitted with a serum septum. The vial was centrifuged until the solid was separated. The supernatant was transferred to a second identical vial and centrifuged again. The supernatant was transferred to a third identical vial. This *n*-Bu^{6}Li solution in heptane was titrated using 2,2-diphenylacetic acid in tetrahydrofuran and found to be 1.04 M.

Synthesis of ^{6}LiHMDS. Crystals of ^{6}LiHMDS were prepared from HMDS and *n*-Bu^{6}Li by cooling a flame-dried and argon-filled microwave tube equipped with a stir bar to 0 °C in an ice bath and adding of 221 μL of HMDS (168 mg, 1.04 mmol). To this was added dropwise 1.00 mL of *n*-Bu^{6}Li (1.04 M in heptane, 1.04 mmol). The solution became cloudy within minutes and then cleared. The solution was stirred for 5 min and then placed in a −50 °C freezer for 4 h, after which clear crystals were obtained. These were washed twice with dry −50 °C pentane and then dissolved in ∼800 μL of toluene-d_8. A fraction of this solution was required for NMR experiments.

Synthesis of 2,2,7,7-Tetramethyloctane-3,6-dione 1. Compound **1** was synthesized in two steps from pinacolone. LDA

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was first freshly prepared in 20 mL of THF from *n*-BuLi by dropwise addition of 8.0 mL of *n*-BuLi (2.5 M in hexanes, 20 mmol) to 2.82 mL of diisopropylamide (DIPA, 2.02 g, 20 mmol) over 5 min in a dry, argon-flushed round-bottom flask. After stirring for 15 min, slow addition of 2.25 mL of pinacolone (1.8 g, 18 mmol) at 0 °C over 30 min afforded a solution of pinacolone enolate. After 15 min, 2.69 g of anhydrous copper-(II) chloride (20 mmol) as a solution in 20 mL of dimethylformamide (DMF) was directly added at −78 °C. The mixture was allowed to stir overnight. The compound **1** was obtained in 95% yield after workup and distillation of excess pinacolone, followed by vacuum distillation of the product (Scheme 1). Anhydrous iron(III) chloride was also used in an identical manner to good effect. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.74 (4H, s), 1.15 (18H, s) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 215.0, 44.2, 30.7, 26.8 ppm.

Synthesis of THF Solvated Dienolate 3. Compound **3** was crystallized from **1** using LiHMDS. *n*-BuLi (1.1 mL, 2.5 M, 2.75 mmol) was added to a dry, argon-flushed Schlenk tube containing 1.1 equiv of HMDS as well as 1 mL of dry heptanes at 0 °C. After 5 min of stirring, this was followed by the addition of 0.26 g (1.30 mmol) of **1** as a solution in 1 mL of heptane via syringe over 15 min. Unsolvated enolate **2** precipitated as a white solid during addition and remained upon warming of the solution to room temperature. Dry THF was added dropwise until all of the solid dissolved (∼0.24 mL, 2.75 mmol). Placement of the Schlenk tube in a −50 °C freezer overnight yielded clear crystals of **3** suitable for X-ray diffraction analysis (Scheme 3). ^{6}Li-enriched samples of **3** were generated directly in the NMR tube from ^{6}LiHMDS, which was synthesized from HMDS and *n*-Bu^{6}Li. The 1,4-dieketone **1** was titrated into ^{6}LiHMDS in the NMR tube, followed by the addition of dry THF. ^{1}H NMR (toluene-d_8, 400 MHz) δ 4.92 (4H, d), 3.63 (8H, m), 1.39 (8H, m), 1.25 (18H, s) ppm. ^{13}C NMR (toluene-d_8, 100 MHz) δ 163.8, 95.6, 69.0, 38.1, 30.3, 25.8 ppm. ^{6}Li NMR (toluene-d_8, 59 MHz) δ 1.93 ppm.

Synthesis of Tropone Addition Products 5 and 6. A quantity of 1.3 mmol of **2** was prepared according to the above using LDA to perform the enolization in a dry, argon-flushed Schlenk tube. To the tube was added 0.127 mL of tropone (1.31 mmol) over 5 min, and the mixture was allowed to stir at 25 °C for 1 h. The reaction mixture was quenched by 2 mL of saturated aqueous ammonium chloride. The organic layer was diluted with diethyl ether, washed with water, and dried over magnesium sulfate. GC−MS analysis showed complete disappearance of tropone after 1 h and the formation of two products, identified after separation by gel chromatography as **5** and **6**.

Data for 5: deep red solid; mp 95−100 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.13−6.95 (5H, m), 5.17 (1H, dd), 3.18 (1H, dd), 2.54 (1H, dd), 1.10 (9H, s), 1.09 (9H, s) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 216.0, 213.3, 185.4, 151.6, 141.1, 136.0, 134.6, 134.0, 133.5, 45.3, 44.0, 43.1, 41.60, 27.4, 26.8 ppm; IR (KBr) ν 2971 (m), 1712 (m), 1480 (s), 1365 (s) 1060 (s), 747 (s) cm^{-1}.

Data for 6: yellow crystals; mp 158−159.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.00 (1H, q), 5.86 (1H, q), 5.70 (1H, q), 5.54 (1H, q), 2.85 (2H, m), 2.69 (1H, m), 1.77 (1H, d), 1.53 (1H, m), 0.98 (18H, s) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 129.0, 128.2, 127.9, 126.3, 114.5, 99.7, 95.7, 54.4, 52.0, 47.7, 36.2, 35.5, 31.2, 26.9, 24.9 ppm; IR (KBr) ν 3384 (w), 3024 (s), 2952 (m), 1608 (s), 1481 (s), 1393 (s), 1365 (s), 1320 (s), 1281 (s), 1260 (s) cm^{-1}; HRMS (FAB+) m/z 327.1948 (M − Na)$^+$. Anal. Calcd: C, 74.96; H, 9.27; O, 15.77. Found: C, 74.73; H, 9.40; O, 16.52.

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Supporting Information Available: Reproductions of NMR, mass spectral and IR data, including CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.