centrated, and the residue was crystallized from hexane/ethyl acetate to give (2S)-methyl 2-[N-(p-methoxybenzoyl)amino]-3-phenyl-1-propanoate (10.3 g, 75% yield) as white crystals: ^{1}H NMR δ 7.73–7.68 (m, 2 H), 7.33–7.25 (m, 3 H), 7.15–7.12 (m, 2 H), 6.93–6.88 (m, 2 H), 6.54 (d, J = 7.7 Hz, 1 H), 5.11–5.05 (m, 1 H), 3.84 (s, 3 H), 3.76 (s, 3 H), 3.28 (dd, J = 5.7, 13.8 Hz, 1 H), 3.21 (dd, J = 5.5, 13.8 Hz, 1 H); ^{13}C NMR δ 172.5, 166.6, 162.7, 136.1, 129.5, 129.0, 128.7, 127.3, 126.3, 113.9, 55.3, 53.3, 52.2, 37.8; MS, exact mass calcd for $C_{18}H_{20}NO_4$ (MH^+) 314.1393, found 314.1392.

(2S)-2-[N-(p-Methoxybenzyl)amino]-3-phenyl-1-propanol (2). To a 0 °C suspension of lithium aluminum hydride (3.08 g, 81.2 mmol) in THF (75 mL) was added dropwise (2S)-methyl 2-[N-(p-methoxybenzoyl)amino]-3-phenyl-1-propanoate (10.2 g, 32.6 mmol) in THF (60 mL). The reaction mixture was refluxed for 18 h and then cooled to 0 °C. The excess hydride was destroyed with 0.4 N KOH (3 mL), and the mixture was stirred at 0 °C for 5 min. Following the addition of water (ca. 10 mL), the mixture was heated at reflux for 20 min and filtered (hot) through Celite. The precipitate was rinsed four times with CH_2Cl_2, and the filtrates were combined, dried (Na_2SO_4), and concentrated. Recrystallization of the residue from hexane/ethyl acetate gave (2S)-2-[N-(p-methoxybenzyl)amino]-3-phenyl-1-propanol (8.66 g, 98% yield) as a pale-green solid: ^{1}H NMR δ 7.31–7.09 (m, 7 H), 6.82 (d, J = 8.6, 2 H), 3.77 (s, 3 H), 3.68 (s, 2 H), 3.61 (dd, J = 3.8, 10.8 Hz, 1 H), 3.32 (dd, J =5.3, 10.8 Hz, 1 H), 2.96–2.89 (m, 1 H), 2.83–2.69 (m, 2 H); ^{13}C NMR δ 158.6, 138.4, 132.0, 129.1, 128.5, 126.3, 113.8, 62.4, 59.2, 55.2, 50.4, 38.0; MS, exact mass calcd for $C_{17}H_{22}NO_2$ (MH^+) 272.1652, found 272.1650.

(4S)-4-Benzyl-3-(p-methoxybenzyl)-1,2,3-oxothiazolidine S-Oxide (6). To a mixture of (2S)-2-[N-(p-methoxybenzyl)-amino]-3-phenyl-1-propanol (6.38 g, 23.5 mmol) and triethylamine (4.76 g, 47 mmol) in CH_2Cl_2 (60 mL) at −15 °C was added dropwise thionyl chloride (3.1 g, 26 mmol) in CH_2Cl_2 (10 mL), followed by triethylamine (4.76 g, 47 mmol) in CH_2Cl_2 (10 mL). After 24 h at −15 °C, the reaction mixture was concentrated and the residue was chromatographed on silica gel (25% ethyl acetate/hexane) to give a diastereomeric mixture of (4S)-4-benzyl-3-(p-methoxybenzyl)-1,2,3-oxothiazolidine S-oxide (6.47 g, 82% yield) as a colorless oil: MS, exact mass calcd for $C_{17}H_{20}NO_3S$ (MH^+) 318.1165, found 318.1155.

(4S)-4-Benzyl-3-(p-methoxybenzyl)-1,2,3-oxothiazolidine S,S-Dioxide (7). To a solution of (4S)-4-benzyl-3-(p-methoxybenzyl)-1,2,3-oxothiazolidine S-oxide (1.98 g, 6.2 mmol) in acetonitrile (9 mL) at 0 °C was added sequentially ruthenium(III) chloride hydrate (ca. 2 mg), sodium periodate (1.97 g, 9.2 mmol), and water (9 mL), and the reaction mixture was warmed to room temperature. After 3 h, the mixture was extracted twice with ether. The organic extracts were combined, washed with water and brine, dried (Na_2SO_4), and concentrated, and the residue was chromatographed on silica gel (22% ethyl acetate/hexane) to give (4S)-4-benzyl-3-(p-methoxybenzyl)-1,2,3-oxothiazolidine S,S-dioxide (1.74 g, 84% yield) as a white solid. This white solid could be recrystallized from ethyl ether/hexane to give white crystals, mp 64–65 °C: ^{1}H NMR δ 7.33–7.25 (m, 5 H), 7.06–7.03 (m, 2 H), 6.92–6.87 (m, 2 H), 4.32–4.19 (m, 4 H), 3.82 (s, 3 H), 3.76–3.71 (m, 1 H), 3.02 (dd, J = 5.6, 13.6 Hz, 1 H), 2.73 (dd, J = 9.4, 13.6 Hz, 1 H); ^{13}C NMR δ 160.0, 135.5, 130.5, 129.3, 129.1, 127.6, 126.5, 114.3, 70.3, 59.6, 55.2, 50.1, 38.2; MS, exact mass calcd for $C_{17}H_{19}NO_4S$ (M^+) 333.1036, found 333.1049. Anal. Calcd for $C_{17}H_{19}NO_4S$: C, 61.24; H, 5.74; N, 4.20. Found: C, 61.39; H, 5.88; N, 4.19.

(2S)-1-Fluoro-2-[N-(p-methoxybenzyl)amino]-3-phenylpropane (3). To a solution of (4S)-4-benzyl-3-(p-methoxybenzyl)-1,2,3-oxothiazolidine S,S-dioxide (104 mg, 0.31 mmol) in THF was added tetrabutylammonium fluoride (0.62 mL, 1.0 M in THF), and the mixture was stirred at room temperature for 1.5 h. The reaction mixture was concentrated, and to the residue were added ether (1.0 mL) and 20% H_2SO_4 (1.0 mL). After being stirred at room temperature for 2 h, the mixture was neutralized with $NaHCO_3$(s) and extracted once with ether and twice with CH_2Cl_2. The organic extracts were combined, dried (Na_2SO_4), and concentrated, and the residue was chromatographed on silica gel (25% ethyl acetate/hexane) to give (2S)-1-fluoro-2-[N-(p-methoxybenzyl)amino]-3-phenylpropane (51.9 mg, 61% yield) as a colorless oil: ^{1}H NMR δ 7.32–7.12 (m, 7 H), 6.82 (d, J = 8.5 Hz, 2 H), 4.74–4.37 (m, 1 H), 4.32–4.21 (m, 1 H), 3.82–3.72 (m, 2 H), 3.78 (s, 3 H), 3.13–2.98 (m, 1 H), 2.79 (d, J = 6.8 Hz, 2 H), 1.63 (bs, 1 H); ^{13}C NMR δ 158.9, 138.3, 132.3, 129.4, 129.3, 128.7, 126.6, 113.9, 84.4 (J_{CF} = 170.6), 57.7 (J_{CCF} = 19.1), 55.1, 50.7, 36.9 (J_{CCCF} = 5.5); MS, exact mass calcd for $C_{17}H_{20}FNO$ (M^+) 273.1530, found 273.1515.

(2S)-1-Azido-2-[N-(p-methoxybenzyl)amino]-3-phenylpropane (4). To a solution of (4S)-4-benzyl-3-(p-methoxybenzyl)-1,2,3-oxathiazolidine S,S-dioxide (96.5 mg, 0.29 mmol) in DMF (1.0 mL) was added sodium azide (99.9 mg, 1.5 mmol), and the mixture was stirred at room temperature for 4 h. The reaction mixture was concentrated, and to the residue were added ether (2 mL) and 20% H_2SO_4 (1.5 mL). After being stirred at room temperature for 5 h, the mixture was neutralized with $NaHCO_3$(s) and extracted three times with $CHCl_3$. The combined organic extracts were dried (Na_2SO_4) and concentrated, and the residue was chromatographed on silica gel (20% ethyl acetate/hexane) to give (2S)-1-azido-2-[N-(p-methoxybenzyl)amino]-3-phenylpropane (67.9 mg, 79% yield) as a colorless oil: ^{1}H NMR δ 7.32–7.14 (m, 7 H), 6.85–6.82 (m, 2 H), 3.79 (s, 3 H), 3.79 (d, J = 12.9 Hz, 1 H), 3.72 (d, J = 13.0 Hz, 1 H), 3.36 (dd, J = 4.5, 12.3 Hz, 1 H), 3.19 (dd, J = 5.3, 12.4 Hz, 1 H), 3.01–2.93 (m, 1 H), 2.82 (dd, J = 6.6, 13.5 Hz, 1 H), 2.74 (dd, J = 7.2, 13.6 Hz, 1 H), 1.50 (bs, 1 H); ^{13}C NMR δ 159.0, 138.4, 132.3, 129.4, 129.3, 128.7, 126.7, 114.0, 57.8, 55.2, 53.5, 50.7, 38.5; MS, exact mass calcd for $C_{17}H_{21}N_4O$ (MH^+) 297.1702, found 297.1723.

(3S)-3-[N-(p-Methoxybenzyl)amino]-4-phenylbutyronitrile (5). To a solution of (4S)-4-benzyl-3-(p-methoxybenzyl)-1,2,3-oxathiazolidine S,S-dioxide (103 mg, 0.31 mmol) in DMF (1.0 mL) was added sodium cyanide (73 mg, 1.5 mmol), and the mixture was stirred at room temperature for 4 h. The reaction mixture was concentrated, and to the residue were added ether (2 mL) and 20% H_2SO_4 (1.5 mL). After being stirred at room temperature for 5 h, the mixture was neutralized with $NaHCO_3$(s) and extracted three times with $CHCl_3$. The combined organic extracts were dried (Na_2SO_4) and concentrated, and the residue was chromatographed on silica gel (25% ethyl acetate/hexane) to give (3S)-3-[N-(p-methoxybenzyl)amino]-4-phenylbutyronitrile (74 mg, 86% yield) as a colorless oil: ^{1}H NMR δ 7.35–7.15 (m, 7 H), 6.86–6.83 (m, 2 H), 3.8 (d, coupling constant obscured by overlap with singlet, 1 H), 3.80 (s, 3 H), 3.72 (d, J = 13.2 Hz, 1 H), 3.16–3.08 (m, 1 H), 2.93 (dd, J = 6.7, 13.6 Hz, 1 H), 2.83 (dd, J = 7.2, 13.7 Hz, 1 H), 2.48 (dd, J = 5.6, 16.8 Hz, 1 H), 2.35 (dd, J = 4.7, 16.8 Hz, 1 H), 1.55 (bs, 1 H); ^{13}C NMR δ 159.0, 137.4, 131.7, 129.3, 129.26, 128.9, 127.0, 118.1, 114.0, 55.1, 54.6, 50.4, 40.2, 22.2; MS, exact mass calcd for $C_{18}H_{21}N_2O$ (MH^+) 281.1655, found 281.1642.

Registry No. 1, 59490-36-7; 2, 91373-74-9; 3, 132207-10-4; 4, 132207-11-5; 5, 132207-12-6; 6 (isomer 1), 132207-13-7; 6 (isomer 2), 132295-79-5; 7, 132233-11-5; $NaIO_4$, 7790-28-5; $Na(N_3)$, 26628-22-8; Na(CN), 143-33-9; L-phenylalanine methyl ester hydrochloride, 7524-50-7; p-anisoyl chloride, 100-07-2; thionyl chloride, 7719-09-7; ruthenium(III) chloride hydrate, 13815-94-6; tetrabutylammonium fluoride, 429-41-4.

Supplementary Material Available: ^{13}C NMR spectra for compounds 1–7 (7 pages). Ordering information is given on any current masthead page.

An Unusual Stereoelectronic Reversal of Reactivities in 2,2,4,4-Tetramethylcyclobutanedione Derivatives[1]

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In the course of our studies into the preparation and reactions of extremely sterically hindered molecules in the

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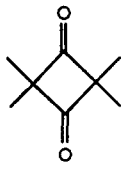
attempted synthesis of tetra-*tert*-butylethylene, we have investigated a number of tied-back derivatives as synthetic intermediates in 2-fold extrusion reactions.[2,3] One such hindered tied-back molecule that appeared to be particularly promising was the commercially available 2,2,4,4-tetramethylcyclobutanedione. Conversion of this compound to the corresponding selone and 2-fold extrusion reactions with hindered diazo compounds would afford derivatives that could be further transformed into di-*tert*-butylmethylene- or *tert*-butylisopropylmethylene groups.



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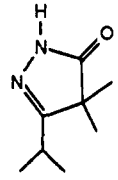
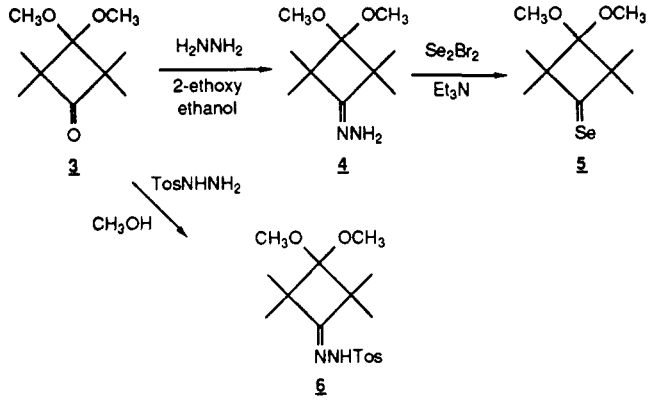


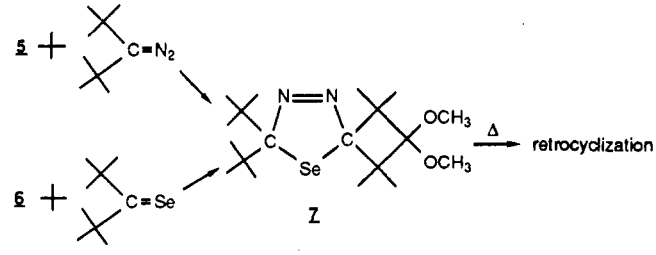
2

Selones are most easily prepared by treatment of a hydrazone with selenium(I) bromide in the presence of a tertiary amine.[4] Unfortunately, direct treatment of 2,2,4,4-tetramethylcyclobutanedione with hydrazine under a variety of conditions did not afford the desired hydrazone but only 3-isopropyl-4,4-dimethyl-2-pyrazolin-5-one (2) presumably via an initial ring opening to the corresponding enolate and intramolecular attack of the hydrazide on the resulting carbonyl group.[5] To avoid this initial ring opening, it was decided to convert the diketone 1 to the corresponding dimethyl ketal 3, which would be less prone to nucleophilic cleavage. This transformation only occurred very sluggishly using an acid-catalyzed reaction of 1 with trimethyl orthoformate in refluxing methanol. This very slow reaction was not unexpected because of the steric effect of the four methyl groups flanking the reacting carbonyl moiety.

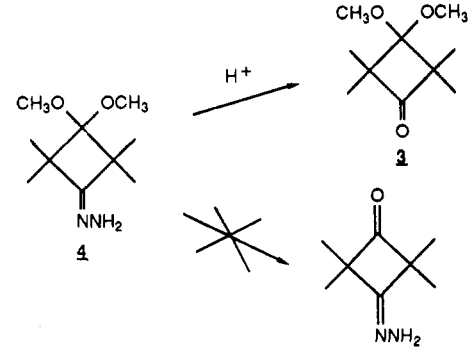
Treatment of ketal 3 with anhydrous hydrazine in refluxing 2-ethoxyethanol afforded the desired hydrazone 4 in 31% yield. This hydrazone could be converted to the corresponding selone 5 by treatment with selenium(I) bromide–triethylamine.[4] Tosylhydrazone 6 could be prepared from ketone 3 and *p*-toluenesulfonyl hydrazine.



Reaction of selone 5 with di-*tert*-butyldiazomethane afforded the desired dihydro-1,3,4-selenadiazole 7. Alternatively, 7 could be prepared from the reaction of di-*tert*-butyl selone with the tosylhydrazone 6 in the presence of sodium hydride. Unfortunately upon attempted pyrolysis of 7 no extrusion of nitrogen occurred; only retrocyclization to selone and diazo alkane was observed. Presumably this retrocyclization occurred due to steric reasons. With increasingly sterically hindered groups on the heterocyclic system, retrocyclization becomes the main reaction course in selenadiazole thermolysis.[2]



Hydrolysis of the ketal hydrazone 4 was attempted to decrease these steric interactions. Remarkably, acid hydrolysis of 4 led only to formation of monoketal 3 via cleavage of the hydrazone and retention of the ketal moiety. Why did this reversal of normal hydrolytic reactivity take place? Attempted acid hydrolysis of monoketal 3 to the corresponding diketone was unsuccessful even after 13 days of stirring at room temperature. Similar lack of hydrolytic reactivity was noted for ketal 5. This result suggests that the reactivity reversal was due to very unreactive ketal moieties in 3 and 5. This is especially surprising since severe steric interactions between the ketal methoxy groups and the flanking methyl groups would be eliminated upon cleavage of the ketal group.



The reactivity of many types of organic molecules depends to a large extent on stereoelectronic effects. The relative stereochemistry of electron pairs, both bonded and nonbonded, has been used, particularly by Deslongchamps, to explain reactivity in acetal and ketal systems.[5] We believe that the combination of stereoelectronic and steric effects in 3–5 contributes to their lowered ketal hydrolytic reactivity.

The rate-determining step in the acid-catalyzed hydrolysis of a ketal is likely to be oxonium ion formation via cleavage of a carbon–oxygen bond.[6] Loss of a protonated alkoxy group involves participation of an electron pair on the geminal alkoxy moiety. For one of the electron pairs to align in a stereoelectronically required antiperiplanar sense with the protonated leaving group, rotation about the C–O bond must take place. Normally such alignment would not be difficult; however, in the tetramethylcyclobutanone case severe steric interactions would make such an alignment unfavorable (Figure 1).

The hydrazone moiety is normally quite hydrolytically stable compared with a ketal. Nucleophilic attack at the

(1) This work is taken in part from the Ph.D. Dissertation of L.J.S., NMSU, 1988. Presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec 1989.

(2) Guziec, F. S., Jr.; Murphy, C. J.; Cullen, E. R. *J. Chem. Soc., Perkin Tran. I* **1985**, 107.

(3) Guziec, F. S., Jr.; SanFilippo, L. J.; Murphy, C. J.; Moustakis, C. A.; Cullen, E. R. *Tetrahedron* **1985**, *41*, 4843 (and references).

(4) Guziec, F. S., Jr.; Moustakis, C. A. *J. Org. Chem.* **1984**, *49*, 189.

(5) Hasek, R.; Elam, E.; Martin, J. *J. Org. Chem.* **1961**, *26*, 4340.

(6) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: Oxford, 1983; pp 1–53.

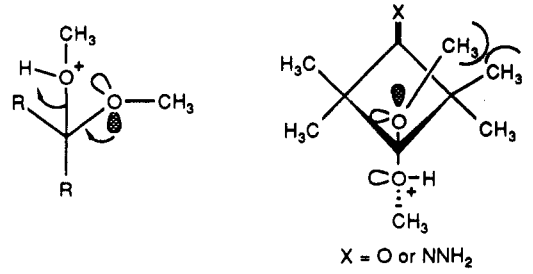


Figure 1.

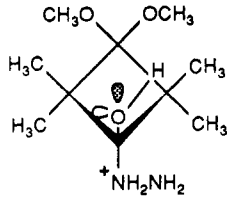


Figure 2.

carbon of the hydrazone moiety in this case also will be slowed due to steric hindrance. Because of stereoelectronic considerations, however, hydrazone cleavage would be expected to be more favorable than cleavage of the ketal. The tetrahedral intermediate formed upon nucleophilic attack by water would readily cleave, relieving steric hindrance. Note, there is much less steric interaction in the transition state for C–N bond cleavage between the proton and the flanking methyls than would occur in the methyl–methyl interactions of the ketal transition state (Figure 2). The powerful combination of steric and stereoelectronic effects therefore combine to reverse the expected relative reactivities of functionalities in the tetramethylcyclobutanone system.

Experimental Section

General experimental procedures were described in ref 2.

3,3-Dimethoxy-2,2,4,4-tetramethylcyclobutanone (3). The ketal was prepared by a modification of an unpublished procedure described by E. U. Elam [Eastman Chemical Products, Technical Data Report, TDR-X-133 (1960)]. A mixture of 2,2,4,4-tetramethylcyclobutanedione (1) (14.0 g), trimethyl orthoformate (10.6 g), and the acid form of a strong acid ion exchange resin (Dowex 50-8X) (6.0 g) was heated under reflux in absolute methanol (50 mL) under positive nitrogen pressure for 3 days. The mixture was filtered, cooled, treated with 2 N sodium hydroxide (50 mL), and heated to reflux for 2 h (in order to convert unreacted starting material to diisopropyl ketone). After cooling, the mixture was extracted with dichloromethane, and the extract was washed with 2 N sodium hydroxide and brine and dried over sodium sulfate. Careful removal of solvent and diisopropyl ketone (bp 125 °C) under reduced pressure afforded the crude ketal as a colorless solid. The solid could be distilled at 83 °C (14 Torr), affording colorless crystals with a camphoraceous odor, mp 41–42 °C, 6.2 g (30% yield): IR(neat) 1790 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.37 (s, 6 H), 1.25 (s, 12 H). Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.5; H, 9.7. Found: C, 64.4; H, 9.7.

3,3-Dimethoxy-2,2,4,4-tetramethylcyclobutanone Hydrazone (4). Ketal 3 (5.2 g), anhydrous hydrazine (3 mL), and sodium carbonate (0.5 g) in ethoxyethanol (35 mL) were heated to reflux 2 weeks under positive nitrogen pressure. The mixture was cooled, filtered, poured into an equal volume of water, and extracted with ether. The organic extract was washed with water and dried over sodium sulfate and the solvent was removed, affording a pale yellow oil, 1.91 g (34% yield): IR (neat) 3390, 2950 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.0–4.8 (bs, 2 H), 3.32 (s, 6 H), 1.24 (s, 6 H), 1.43 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 162.1, 104.1, 54.6, 53.3, 51.9, 22.7, 20.0; MS, m/z 170 (16.4), 123 (56), 102 [$(M - C_5H_{10}O_2)^+$, 100], 75 (61).

Hydrazone 4 is very prone to azine formation. Upon attempted Kugelrohr distillation purification or even upon standing at room temperature the corresponding azine [mp 101–102 °C; IR 2986, 1689, 1466 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.31 (s, 12 H), 1.35 (s, 12 H), 1.28 (s, 12 H); MS, m/z 368 (M^+, 1.1), 115 (100)] is formed almost quantitatively.

3,3-Dimethoxy-2,2,4,4-tetramethylcyclobutaneselone (5). Hydrazone 4 (283 mg) in dry dichloromethane (10 mL) and selenium(I) bromide (445 mg) in dry dichloromethane (10 mL) were added dropwise simultaneously to a ice-bath-cooled solution of triethylamine (0.5 mL) in dichloromethane (10 mL). After the addition was complete, the mixture was allowed to come to room temperature and stirred an additional 30 min. After filtration through Celite the solution was quickly washed with water, filtered through potassium carbonate (2 g), and dried over sodium sulfate. Removal of solvent and pyrolytic distillation under reduced pressure afforded the selone as a blue liquid in 35% yield: IR (neat) 1465, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.37 (s, 6 H), 1.33 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 22.96, 51.81, 74.00, 106.95, 295.58; MS m/z 250 (M^+, 0.2, ^{80}Se), 248 (0.2), 69 (41), 50 (100).

3,3-Dimethoxy-2,2,4,4-tetramethylcyclobutanone Tosylhydrazone (6). Ketal 3 (1.0, 5.38 mmol), *p*-toluenesulfonyl hydrazine (1.0, 5.38 mmol), and methanol (20 mL) were heated to reflux overnight under nitrogen. The mixture was cooled and then placed in a freezer (–26 °C) overnight. The resulting crystals were filtered via suction and recrystallized from methanol, affording colorless crystals, mp 153–154 °C, 58% yield: IR ($CHCl_3$) 3295, 2966, 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (s, 6 H), 1.24 (s, 6 H), 2.44 (s, 3 H), 3.25 (s, 6 H), 7.07 (bs, 1 H), 7.32 (d, 2 H), 7.81 (d, 2 H); ^{13}C NMR δ 19.99, 21.57, 22.24, 51.83, 53.93, 54.76, 103.42, 127.85, 129.32, 134.93, 143.87, 170.03. Anal. Calcd for $C_{17}H_{26}N_2O_4S$ (354.47): C, 57.60; H, 7.39; N, 7.91. Found C, 57.33; H, 7.39; N, 7.86.

2,2-Di-*tert*-butyl-2,5-dihydro[1,3,4]selenadiazole-5-spiro-3′,3′-dimethoxy-2′,2′,4′,4′-tetramethylcyclobutane (7). a. Sodium hydride (74 mg, 3.09 mmol) was added to a solution of tosylhydrazone 6 (806 mg, 2.27 mmol) in freshly distilled tetrahydrofuran (15 mL). After gas evolution ceased, a solution of di-*tert*-butyl selenoketone[4] (422 mg, 2.06 mmol) in tetrahydrofuran (10 mL) was added dropwise, and the resulting mixture was heated to reflux overnight under nitrogen. The mixture was cooled, poured into water, and extracted with ether. The organic layer was washed with brine, dried over sodium sulfate, and concentrated, affording a green solid. Flash chromatography (silica: chloroform) and recrystallization from methanol afforded colorless crystals, mp 110 °C, 31% yield; IR ($CHCl_3$) 2966, 1584 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13–1.26 (bs, 24 H), 1.30 (s, 6 H), 3.33 (s, 3 H), 3.45 (s, 3 H); ^{13}C NMR δ 21.46, 26.54, 31.97, 43.04, 51.85, 51.92, 55.29, 105.07, 116.55, 113.16. Anal. Calcd for $C_{19}H_{36}N_2O_2Se$ (403.46): C, 56.56; H, 8.99; N, 6.94. Found: C, 56.85; H, 9.20; N, 7.04.

b. Di-*tert*-butyldiazomethane[7] (31 mg) in tetrahydrofuran (5 mL) was added to selone 5 (46 mg) in tetrahydrofuran (5 mL). The blue selone color faded upon addition. Removal of solvent afforded the selenadiazoline as a slightly pink oil, with spectra identical with those described in *a*.

Attempted pyrolysis of this selenadiazole at 120 °C for 1 h afforded selone 5 as the only characterizable product.

Hydrolysis of 3,3-Dimethoxy-2,2,4,4-tetramethylcyclobutanone Hydrazone (4). Ketal hydrazone 4 (368 mg) was dissolved in 2 M HCl (3 mL) and THF (10 mL). After 6 days, treatment with excess dilute sodium bicarbonate solution, ether extraction, and GLC analysis showed complete conversion of 4 into ketal 3. The ketal, 213 mg, (62% yield) could be isolated upon concentration of the dried ether extract under reduced pressure.

Attempted Hydrolyses of Ketals 3 and 5. Treatment of ketal 3 (90 mg) with 2 M HCl (3 mL) and THF (10 mL) led to a homogeneous solution. After 13 days at room temperature, the ketal could be recovered nearly quantitatively. No dione 1 could be observed at this time. Similar treatment of ketal 5 for 10 days at room temperature also led to recovery of starting ketal.

Acknowledgment. We gratefully acknowledge the assistance of Professor S. Hünig for providing details of

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unpublished work on tetramethylcyclobutanedione ketalizations.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for compounds 4 - 5 (5 pages). Ordering information is given on any current masthead page.

Nature of Short Li•••H–C Contact Interactions in Organolithium Compounds and Its Implication

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Structures of organolithium compounds seldom follow classical bonding patterns and therefore have been a subject of extensive experimental[1-3] and theoretical[4] studies. One of the striking features of organolithium compounds is short H···Li contacts involving their C–H bonds.[2,3] This is particularly noteworthy in view of the ease of C–H bond activation to remove LiH from organolithium compounds.[2a,c] The H···Li contacts are comparable in length to the Li–H distance [2.043 (1) Å] found in solid lithium hydride.[5a] In gas-phase LiH, the Li–H distance is 1.596 Å.[5b] So far the shortest known D···Li distance is 1.72 (3) Å, which is found in solid CD_2Li_2.[2c] This solid also has a short Li···Li contact, i.e., 2.26 (2) Å, which is the average of the covalent radii sum 2.68 Å and the ionic radii sum 1.80 Å. In solid CD_2Li_2, each CD_2 unit is contained in a distorted cube of Li atoms as shown in the stereodiagram of Figure 1, where the large, medium, and small circles represent C, Li, and D atoms, respectively. The solid lines represent the C–D bonds [C–D(1) = 1.09 (1) Å, C–D(2) = 1.18 (1) Å] and the C–Li bonds [2 × 2.17 (1) Å]. Note that one C–D bond is normal, but the other one is unusually long. The "molecular unit" CD_2Li_2 is neither planar nor tetrahedral in shape, which is not surprising since planar *cis*-CH_2Li_2 is calculated to be only slightly less stable than tetrahedral CH_2Li_2 (by ~8 kcal/mol).[4b] The dashed lines of Figure 1 show the D···Li contacts less than 2.90 Å [i.e., Li···D(1) = 1.72 (3), 2.03 (3), 2.15 (3), 2.28 (1), 2.36 (2) Å; Li···D(2) = 1.99 (3), 2.06 (2), 2.16 (2), 2.38 (2) Å] as well as the Li···Li contact less than 2.70 Å [i.e., Li···Li = 2.26 (2) Å]. As shown in 1, the shortest Li···D and the shortest Li···Li contacts in CD_2Li_2 involve a common Li atom: With a CD_2 unit, one Li makes a monobridged Li···D–C contact and the other Li makes a dibridged Li···D–C contact. The D(1) and D(2) atoms of each CD_2

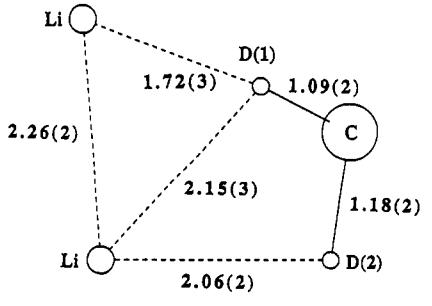

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Table I. Optimum Li•••H Distances r_{opt} and Binding Energies ΔE Calculated for the Li•••H–C Contacts in $(CH_2Li_2)_2$ and $(LiH)(CH_nLi_{4-n})$ (n = 1-4) with the 6-31G Basis Set**

system	symmetry of arrangement	r_{opt}, Å	ΔE, kcal/mol
H_2LiC–Li···H–$CHLi_2$	C_s	1.794	11.4
HLi···H–CLi_3	C_{3v}	1.699	18.6 (19.4)[a]
HLi···H–$CHLi_2$ (θ = 0°, 3)	C_s	1.733	16.8 (16.7)[a]
HLi···H–$CHLi_2$ (θ = 71.8°, 3)	C_s	1.733	25.7
HLi···H–CH_2Li	C_1	1.840	10.4 (8.10)[a]
HLi···H–CH_3	C_{3v}	2.510	0.50 (0.53)[a]

[a] Calculated with the 6-31++G* basis set using the geometries obtained with the 6-31G** basis set.

unit have distorted square-pyramidal and distorted square-planar coordinations of Li atoms, respectively. It is the D(2) atom that is associated with the unusually long C–D bond. In the present work, we examine the two striking structural features of solid CD_2Li_2, i.e., the short D···Li contacts and the long C–D bond, by carrying out ab initio SCF-MO calculations on molecular model systems H–Li···H–CH_nLi_{3-n} (n = 0–3), LiH_2C–Li···H–$CHLi_2$, and $(H–Li)_3$···H–$CHLi_2$ and consider important implications of our results.

Computational Details

Our SCF-MO calculations are carried out by using the GAUSSIAN 86 program.[6] The geometries of CH_nLi_{4-n} (n = 0–4) and LiH are optimized by SCF-MO calculations using the 6-31G** basis set.[7] In our calculations on H–Li···H–CH_nLi_{3-n} (n = 0–3), LiH_2C–Li···H–$CHLi_2$, and $(H–Li)_3$···H–$CHLi_2$, all fragment geometries are taken to be frozen unless mentioned otherwise. The global minimum energy structures of those systems are not examined, because our objective is to examine the short Li···D–C contacts and the unusually long C–D bond present in solid CD_2Li_2. The global minimum energy structures of stoichiometry CH_2Li_4 and CH_5Li have been reported in the literature.[8]

In our SCF-MO calculations on H–Li···H–CH_nLi_{3-n} (n = 0–3) with a collinear H–Li···H–C arrangement, the interaction energies

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