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Beyond the Corey Reaction II: Dimethylenation of Sterically Congested Ketones§

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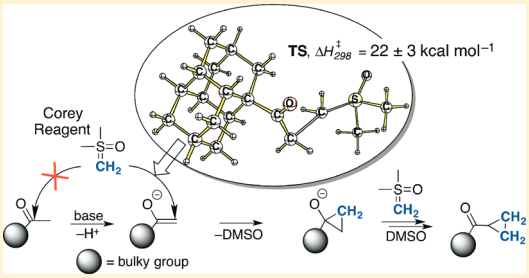
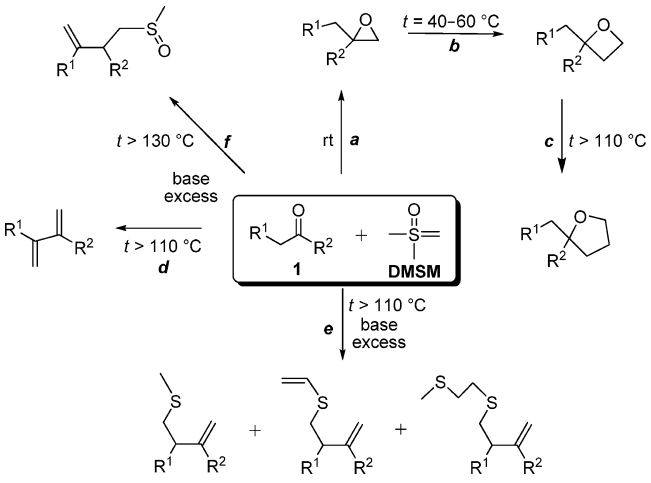
Supporting Information

ABSTRACT: Bulky methyl ketones show significantly decreased reactivities toward the Corey-Chaykovsky methylenation reagent dimethylsulfoxonium methylide (DMSM). The excess of base and temperature increase opens an alternative reaction channel that instead leads to the corresponding cyclopropyl ketones. Computations suggest that the initial reaction step involves the methylene group transfer from DMSM on the ketone enolate followed by the intramolecular cyclization. The key step is associated with a barrier of 22 ± 3 kcal mol^{-1} and is driven by exothermic elimination of DMSO.



The Corey-Chaykovsky reaction utilizes dimethylsulfoxonium methylide (DMSM) for the preparation of oxiranes from carbonyl compounds in DMSO (*a*, Scheme 1).[1] At elevated temperatures and with excess ylide further ring expansion to oxetanes[2] (*b*) and even to oxolanes (*c*) takes place.[3] At higher temperatures and with excess of base ketones can be transformed directly to 1,3-dienes (diolefination, *d*)[4−6] as well as to unsaturated sulfoxides (*f*) and sulfides (*e*), whose ratios depend on the amounts of DMSO employed. Steric factors influence the high-temperature reactions (paths *d* and *e*) substantially. For example, the yields of the diolefination (path *d*) drop considerably for bulky ketones (to ca. 20% for 1-adamantyl methyl ketone (**1**, R^1 = H; R^2 = adamantyl).[6,7] At the same time the classic Corey-Chaykovsky methylenation of **1** with DMSM, which is known to proceed through the same betaine intermediate,[3,8] still occurs through path *a* readily at room temperature to give the corresponding oxirane in up to 88% yield.[9]

Scheme 1. Reaction of Ketones (1) with Dimethylsulfoxonium Methylide (DMSM)



Hence, the experiments suggest that base excess and high temperatures may decrease the yield of the reaction of bulky ketones with sulfur ylides and may be associated with the competitive yet unknown reactions. These are the focus of the present work, where we first carefully analyzed the reaction of bulky **1** at 130 °C with DMSM in DMSO with an excess of base (Scheme 2). As expected,[4−6,10] 2-(1-adamantyl)butadiene-1,3 (**2**) forms in a 17% yield as the main product together with a mixture of sulfur-containing compounds (**3**) similar to those described earlier for cyclic ketones.[10]

Unexpectedly, 1-adamantyl cyclopropyl ketone (**4**) was also isolated in 13% yield. Such formal α-dimethylenation of the methyl group of **1** has, to the best of our knowledge, not been observed before in the reactions of methylketones with ylides. Evidently, the adamantyl group hinders the attack of the reagent on the carbonyl group as this group remains unchanged in the reaction of **1** to **4**. We next studied the reactivity of sterically congested diamantyl ketones **5** and **6** that are structurally closely related to **1** (Scheme 3). While the steric demand of the cage moiety in **5** is similar to that in **1**, medial ketone **6** is even more hindered due to the presence of hydrogens in the positions C^{13} and C^3. Unsurprisingly, 4-diamantyl methyl ketone (**5**) with DMSM gives the same product distribution as **1** under the same reaction conditions. In contrast, 1-diamantyl methyl ketone (**6**) gives 1-diamantyl

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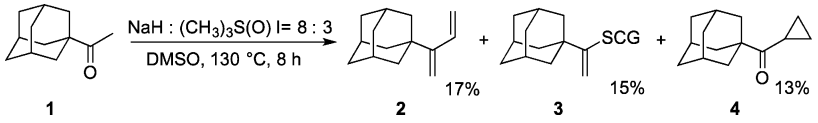
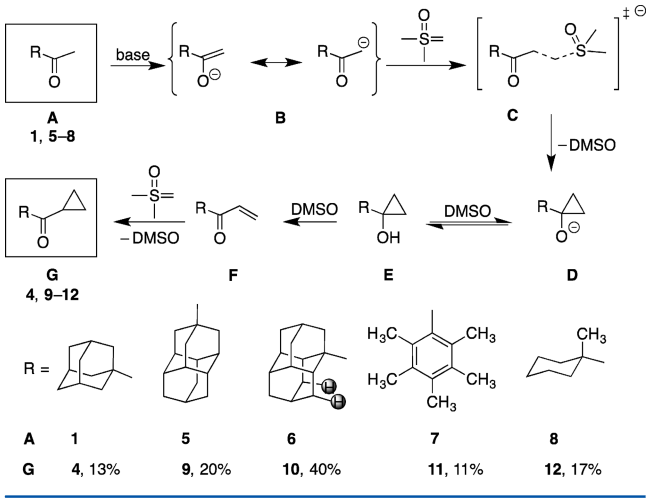
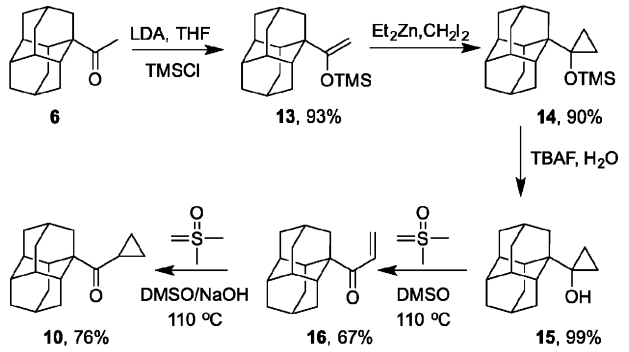
Scheme 2. Reaction of 1-Adamantyl Methyl Ketone (1) with Dimethylsulfoxonium Methylide in the Presence of Base Excess in DMSO (SCG = Sulfur Containing Group)



Scheme 3. Direct α-Dimethylenation of Sterically Congested Ketones (Yields Are Preparative)



Scheme 4. Preparation and Transformations of Intermediate 15 under the α-Dimethylenation Conditions (Yields Are Preparative)



cyclopropyl ketone (**10**) exclusively. In addition, we found that a number of other sterically congested ketones, namely 2′,3′,4′,5′,6′-pentamethyl acetophenone (**7**) and 1-(1-methylcyclohexyl)ethanone (**8**), undergo formal α-dimethylenation to give the corresponding cyclopropyl ketones (**11** and **12**, see Experimental Section for details). Apparently, the attack of DMSM on the carbonyl group and subsequent formation of the tetrahedral intermediate is hampered for such bulky ketones. Indeed, for highly sterically congested ketones such as **6** and **7**, only the methyl group of the acetyl function is involved in the transformations with DMSM. These ketones are completely inert under Corey-Chaykovsky conditions without base excess: only the starting material was isolated quantitatively from the reaction mixtures even under prolonged heating.

A rational explanation of these experimental facts begins with simple base-catalyzed enolization of ketone **A** to **B** that opens an alternative reaction channel. The formal attack of DMSM onto the enolate anion **B** through transition structure **C** results in the formation of cyclopropane alcoholate anion **D** that gives alcohol **E** in DMSO (Scheme 3).

Further oxidative fragmentation of **E** to **F** is well-established in the literature for various cyclopropanols[11] and also was shown for the transformation of independently prepared intermediate **E** (R = 1-diamantyl, **15**), under the same reaction conditions (Scheme 4). Alcohol **15** was prepared from **6** through TMS-derivative **13**, its cyclopropanation via a modified Simmons-Smith procedure[12] (see Experimental Section for details) followed by hydrolysis of thus formed **14** with tetrabutyl ammonium fluoride hydrate. We have found that at elevated temperatures, **15** forms 1-diamantyl vinyl ketone (**16**), confirming the possibility of the oxidative fragmentation of hydroxyl cyclopropanes in the DMSO/DMSM system. Subsequent cyclopropanation of **16** with DMSM involves the well-known methylenation of vinyl ketones to cyclopropyl ketones with DMSM in DMSO,[13,14] giving **10** in high yield (modeling the final step **F** → **G** in Scheme 3).

Obviously, the bottleneck step **B** → **D** (Scheme 3) requires careful scrutiny, as it involves interaction of two electron-rich species. To probe this hypothesis, we modeled the acetone enolate anion (**B**, R = CH_3) reaction with DMSM computationally (Figure 1). In order to account for dispersion interactions in the common B3LYP functional, which does not fully include noncovalent interactions,[15−17] we utilized the functionals B3PW91,[18] B3LYP-D3,[19] as well as the B3LYP-

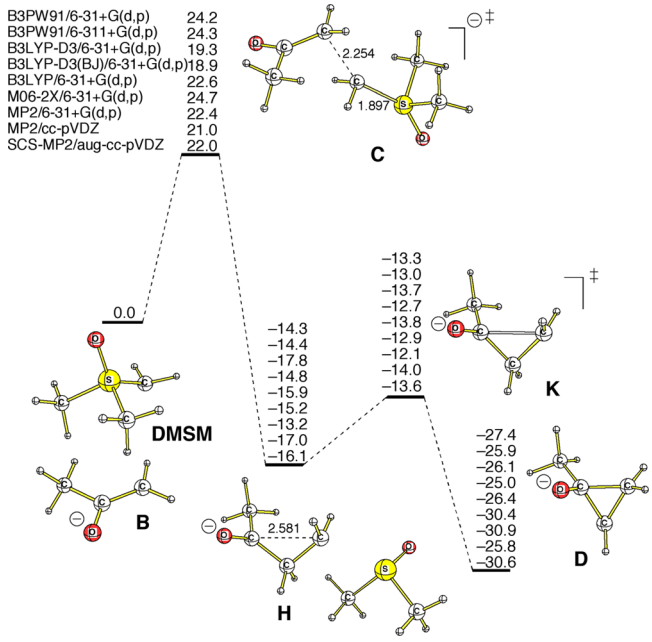


Figure 1. Relative enthalpy for the reaction of acetone enolate anion (**B**, R = CH_3) with dimethylsulfoxonium methylide (**DMSM**) computed at different levels of theory [PCM (DMSO), relative ΔH_{298} in kcal mol^{-1}, critical interatomic distances in angstroms, B3PW91/6-31+G(d,p)].

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D3(BJ) with Becke-Johnson damping,[20] which partially addresses such effects, and the highly parametrized M06-2X functional,[21] which accounts for medium-range correlation. For comparison, the MP2 as well as spin-component-scaled MP2 (SCS-MP2)[22,23] *ab initio* methods were employed. Since conventional gas-phase computations overestimate the energies of highly polarized structures, we employed a polarizable continuum model (PCM) to account for solvent effects.[24] This solvation model was previously successfully used to model reaction of sulfur ylides with ketones.[2,10] The direct attack of DMSM on the acetone enolate anion (**B**) computed at different levels of theory requires 22 ± 3 kcal mol^{-1} through the transition structure (TS) **C** that is best viewed as the nucleophilic substitution at the CH_2 group of the ylide with DMSO as the leaving group (Figure 1).

The DFT and *ab initio* barriers heights are consistent with the experimental result that the reaction requires heating. The relatively high thermodynamic stability of the leaving group (DMSO) leads to an exothermic first step (−15 ± 3 kcal mol^{-1}) to give minimum **H**. Further transformation of the anionic part of **H** through TS **K** is virtually barrierless and exothermically yields the cyclopropanol anion (**D**) that additionally releases 13 ± 2 kcal mol^{-1}. Note the reaction is only slightly sensitive to steric hindrance as the transition structure **L** (Figure 2) for the attack of DMSM on the sterically

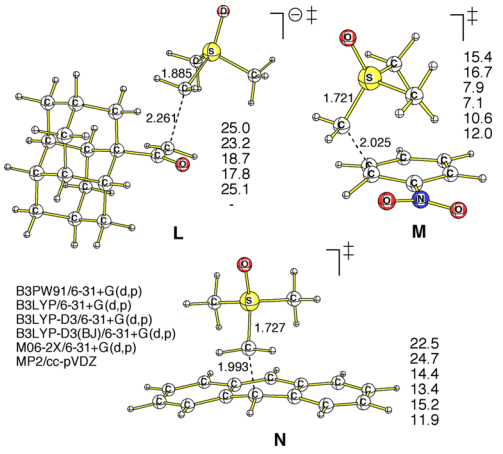

Figure 2. Transition structures for the attack of DMSM on 1-diamantyl methyl enolate (**L**), nitrobenzene (**M**), and anthracene (**N**) computed at different levels of theory [PCM (DMSO), relative $\Delta H_0^{\ddagger}$ in kcal mol^{-1} and critical interatomic distances in angstroms].

congested ketone **6** enolate anion is close structurally and energetically to **C** (Figures 1 and 2).[25] However, as diamantyl ketone **6** is more polarizable (owing to its size), it is more sensitive to the method employed; while the B3PW91, M06-2X and B3LYP computations give barriers within the 23−25 kcal mol^{-1}, the B3LYP-D3 and B3LYP-D3(BJ) methods lower the barrier by ca. 5 kcal mol^{-1}, reflecting the growing contributions from stabilizing dispersion interactions. We thus compared this reaction with other known examples of direct attacks of DMSM onto the electron-rich species such as aromatic compounds[26,27] (vicarious nucleophilic substitution[28]), where the contributions from the noncovalent interactions are expected to be substantial due to the presence of effective dispersion energy π-donors.[29]

The experimentally known C-methylenations of nitrobenzene[27,30] and anthracene[26] with DMSM (TSs **M** and **N**, Figure 2) were engaged for comparative analysis. Due to the $\sigma-\pi$ attractions between the methyl groups of DMSM and the aromatic rings, the barriers for the methylenation strongly depend on computational method (Figure 2). Unsurprisingly, the barrier of 10.6 kcal mol^{-1} for the methylenation of nitrobenzene through TS **M** at M06-2X, which is typically successful in describing the $\sigma-\pi$ interactions, is very close to the a priori dispersion-sensitive MP2 value (12.0 kcal mol^{-1}) and is consistent with the experimental data that this reaction proceeds smoothly already at room temperature.[27] While the B3LYP-D3 and B3LYP-D3(BJ) barriers are close to the above values, the barriers computed with the B3LYP and B3PW91 functionals are substantially higher (15−17 kcal mol^{-1}). The dispersion interactions stabilize the TS **N** for the methylenation of anthracene even more (by ca. 10 kcal mol^{-1}). However, the absolute barriers computed for this reaction generally are 5−7 kcal mol^{-1} higher than that for the methylenation of nitrobenzene. This agrees nicely with the experiment where the methylenation of anthracene with DMSM proceeds at 100 °C.[26]

Our computations show that the C-methylenations of enolate anions and aromatic substrates are related mechanistically and best viewed as the S_N2 substitution at the methylene group of DMSM. Remarkably, the barriers for methylene transfer from DMSM to negatively charged enolate anions (TS **L**) and uncharged anthracene (TS **N**) are comparable. The key geometrical parameters differ only slightly (TS **L** is slightly less tightly bound, Figure 2).

We conclude that high temperature and excess of base are two key factors that can drastically alter the course of the classic Corey-Chaykovsky reaction, resulting in the methylenation of enolate anions with DMSM. The driving force of the reaction between these two electron-rich species is provided by the high exothermicity of the elimination of DMSO that serves as a good leaving group in the S_N2-type reaction. This reaction parallels the well-established electrophilic methylenation of aromatic compounds with sulfur ylides but has never been observed before for carbonyl compounds. In the presence of base excess, bulky methyl ketones may follow either diolefination or dimethylenation paths, while the Corey-Chaykovsky reaction is completely suppressed under these conditions.

EXPERIMENTAL SECTION

General Information. NMR spectra were recorded at 400 MHz (^{1}H) spectrometer with TMS as the internal standard. High-resolution mass spectra (HRMS) were recorded using electron impact ionization on a double-focusing sector-field mass spectrometer. Products were purified by chromatography on 100−160 mesh silica gel. Commercially available reagents and solvents were used without further purification.

General Procedure for α-Dimethylenation of Sterically Congested Methyl Ketones. To dry NaOH (0.384 g, 9.6 mmol), dry DMSO (4 mL) was added, stirred for 15 min and then trimethylsulfoxonium iodide (0.694 g, 3.2 mmol) was added. The mixture was heated to 90−130 °C, and a solution of ketone (1.6 mmol) in DMSO (2 mL) was added. The mixture was stirred under argon atmosphere for 1−24 h, diluted with water, and extracted with hexane (3 × 15 mL). The combined organic layers were washed with water and brine and were concentrated under reduced pressure to give the crude product. Purification with column chromatography (SiO_2, hexane-ether, 95:5) gave the starting ketone together with the pure cyclopropyl ketones **4** and **9**−**12** in 11−40% preparative yields.

1-Adamantyl Cyclopropyl Ketone (**4**) was synthesized at 130 °C, during 23 h and isolated in 13% (0.035 g) preparative yield as colorless solid, mp 61−62 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.68−0.77

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(m, 2 H), 0.83−0.89 (m, 2 H), 1.60−1.75 (m, 6 H), 1.78−1.87 (m, 6 H), 2.00 (bs, 3 H), 2.07−2.16 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.6 (CH_2), 15.0 (CH), 28.0 (CH), 36.7 (CH_2), 38.2 (CH_2), 46.4 (C), 215.2 (C). HRMS: calcd for $C_{14}H_{20}O$, 204.1514; found, 204.1521.

4-Diamantyl Cyclopropyl Ketone (**9**) was synthesized at 130 °C, during 23 h and isolated in 20% (0.04 g) preparative yield as colorless solid, mp 82−83 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.76−0.83 (m, 2 H), 0.91−0.96 (m, 2 H), 1.69−1.78 (m, 10 H), 1.79−1.87 (m, 7 H), 1.88−1.93 (m, 2 H), 2.15−2.23 m (1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.6 (CH_2), 15.3 (CH), 25.6 (CH), 36.7 (CH), 37.3 (CH), 37.7 (CH_2), 39.1 (CH_2), 44.7(C), 215.4 (C). HRMS: calcd for $C_{18}H_{24}O$, 256.1827; found, 256.1819. MS, *m*/*z* (I_{rel}, %): 256 (100) $[M]^+$, 199 (7), 187 (12), 157 (15), 131 (10), 105 (16), 91 (20).

1-Diamantyl Cyclopropyl Ketone (**10**) was synthesized at 130 °C, during 21 h and isolated in 40% (0.023 g) preparative yield as colorless solid, mp 60−61 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.76−0.84 (m, 2 H), 0.94−0.98 (m, 2 H), 1.52−1.58 (m, 2 H), 1.62−1.68 (m, 4 H), 1.69−1.80 (m, 8 H), 1.85−1.90 (bs, 2 H), 1.92−1.98 (m, 1 H), 2.15−2.23 (m, 1 H), 2.25−2.31 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.7 (CH_2), 14.7 (CH), 25.5 (CH), 26.4 (CH), 35.1 (CH_2), 36.9 (CH), 37.2 (CH), 37.7 (CH_2), 37.8 (CH), 38.0 (CH_2), 40.8 (CH_2), 52.5 (C), 215.2 (C). HRMS: calcd for $C_{18}H_{24}O$, 256.1827; found, 256.1832. Mass Spectra, *m*/*z* (I_{rel}, %): 256 (100) $[M]^+$, 199 (7), 187 (12), 157 (15), 131 (10), 105 (16), 91 (20).

2′,3′,4′,5′,6′-Pentamethylphenyl Cyclopropyl Ketone (**11**) was synthesized at 90 °C, during 21 h and isolated in 11% (0.04 g) preparative yield as colorless solid, mp 68−70 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03−1.11 (m, 2 H), 1.24−1.32 (m, 2 H), 2.15−2.25 (m, 1 H), 2.18 (s, 6 H), 2.2 (s, 6 H), 2.25 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.2 (CH_2), 16.0 (CH_3), 16.7 (CH_3), 17.5 (CH_3), 23.7 (CH), 127.8 (C), 133.0 (C), 135.4 (C), 141.0 (C), 212.1 (C). HRMS: calcd for $C_{15}H_{20}O$, 216.1514; found, 216.1511.

Cyclopropyl (1-Methyl)-cyclohexyl Ketone (**12**) was synthesized at 100 °C, during 26 h and isolated in 17% (0.113 g) preparative yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.78−0.86 (m, 2 H), 0.92−1.00 (m, 2 H), 1.15 (s, 3 H), 1.23−1.60 (m, 8 H), 1.99−2.01 (m, 2 H), 2.12−2.23 m (1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.6 (CH_2), 15.7 (CH_3), 23.0 (CH_2), 24.9 (CH), 26.0 (CH_2), 34.9 (CH_2), 48.2 (C), 214.4 (C). HRMS: calcd for $C_{11}H_{18}O$, 166.1358; found, 166.1345.

1-(1-Diamantyl)-1-(trimethylsiloxy)ethene (**13**). To diisopropylamine (3.11 mL, 0.022 mol) dry THF (54 mL) was added, cooled to −10 °C, and *n*-BuLi (9.1 mL 2.5 M, 0.022 mol) was added dropwise via a syringe. After stirring for 30 min, 1-diamantyl methyl ketone (**2d**) (4 g, 0.017 mol) in dry THF (17.5 mL) was added dropwise. Reaction mixture was stirred additionally for 1 h, and chlorotrimethylsilane (4.08 mL, 0.032 mol) was added in one portion while stirring. The resulting mixture was stirred at room temperature for 1 h and then partitioned between hexane and cold aqueous $NaHCO_3$ (1:1). The organic layer was dried and concentrated to leave residual liquid (7.2 g) containing the crude silyl ether **7**. Chromatographic purification (neutral Al_2O_3, hexane-ether, 9:1) gave white crystals of silyl ether **7** (4.88 g, 93%), mp 53−54 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.24 (s, 9 H), 1.40 (d, 2 H, *J* = 12.5 Hz), 1.57−1.77 (m, 10 H), 1.80−1.90 (m, 3 H), 1.95 (bs, 2 H), 2.07 (d, 2 H, *J* = 12.5 Hz), 4.08 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.2 (CH_3), 25.8 (CH), 27.3 (CH), 33.9 (CH_2), 37.2 (CH), 37.3 (CH), 38.0 (CH_2), 38.1 (CH), 38.5 (CH_2), 43.9 (C), 44.4 (CH_2), 86.9 (CH_2), 164.8 (C). HRMS: calcd for $C_{19}H_{30}OSi$, 302.2066; found, 302.2060.

1-(1-Diamantyl)-1-(trimethylsiloxy)cyclopropane (**14**). In a flame-dried two-neck round-bottom flask, 1-(1-diamantyl)(trimethylsiloxy)-ethene (**7**) (2 g, 0.0066 mol) was dissolved in hexane (12 mL), cooled to −10 °C, and diiodomethane (21.13 g, 0.08 mol) was added. After 5 min diethylzinc solution in hexane (79.5 mL, 1 M, 0.08 mol) was added dropwise over 1 h 20 min. The reaction mixture was allowed to warm to room temperature and was stirred additionally for 14 h, partitioned between diethyl ether and cold aqueous NH_4Cl (1:1). The mixture was extracted three times with diethyl ether (3 × 50 mL). The combined organic layers were washed with a saturated solution of NH_4Cl and brine, dried over anhydrous $NaSO_4$ and concentrated in vacuo to give 1-(1-diamantyl)(trimethylsiloxy)cyclopropane (**14**) (2.13 g). Purification by chromatography (SiO_2, hexane) gave analytically pure 1-(1-diamantyl)(trimethylsiloxy)cyclopropane (**14**) (1.88 g, 90%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.08 (s, 9 H), 0.68−0.72 (m, 2 H), 0.72−0.82 (m, 2 H), 1.36 (d, 2 H, *J* = 12.8 Hz), 1.54 (bs, 2 H), 1.58−1.71 (m, 9 H), 1.71−1.83 (m, 3 H), 1.84−1.90 (m, 1 H), 2.20 (d, 2 H, *J* = 12.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 1.7 (CH_3), 12.8 (CH_2), 25.7 (CH), 27.5 (CH), 34.3 (CH_2), 37.2 (CH), 38.0 (CH), 38.0 (CH_2), 39.0 (CH_2), 39.3 (CH), 39.6 (C), 41.9 (CH_2), 62.6 (C). HRMS: calcd for $C_{20}H_{32}OSi$, 316.2222; found, 316.2220.

1-(1-Diamantyl)cyclopropanol (**15**). To 1-(1-diamantyl)-(trimethylsiloxy)cyclopropane (**14**) (1 g, 0.003 mol), a solution of TBAF × $3H_2O$ (1.196 g, 0.0037 mol) in diethyl ether (5 mL) was added, stirred for 1 h at room temperature, and partitioned between diethyl ether and water (1:1). The mixture was extracted three times with diethyl ether (3 × 5 mL). The combined organic layers were washed with a saturated solution of NH_4Cl and brine, dried over anhydrous $NaSO_4$, and concentrated in vacuo to give 1-(1-diamantyl)-cyclopropanol (**15**) (0.76 g, 99%) as white crystals, mp 105−107 °C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.68−0.75 (m, 2 H), 0.75−0.82 (m, 2 H), 1.43 (d, 2 H, J= 12.8 Hz), 1.59 (bs, 2 H), 1.63−1.73 (m, 9 H), 1.75−1.87 (m, 4 H), 1.87−1.93 (m, 1 H), 2.15 (d, 2 H, *J* = 12.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (CH_2), 25.7 (CH), 27.3 (CH), 34.3 (CH_2), 37.0 (CH), 37.1 (C), 37.8 (CH), 37.9 (CH_2), 38.8 (CH_2), 39.0 (CH), 41.8 (CH_2), 60.6 (C). HRMS calcd for $C_{17}H_{24}O$, 244.1827; found, 244.1834.

1-Diamantyl Vinyl Ketone (**16**). To NaH (0.295 g, 12.3 mmol), DMSO (16 mL) was added and stirred at 80 °C for 15 min. Then trimethylsulfoxonium iodide (2.705 g, 12.3 mmol) was added, heated to 110 °C and a solution of 1-(1-diamantyl)cyclopropanol (**15**) (0.3 g, 1.2 mmol) in DMSO (8 mL) was added. The mixture stirred for 21 h, diluted with water, and extracted with hexane (3 × 15 mL). The combined organic layers were washed with water, brine, and concentrated under reduced pressure to give crude 1-diamantyl vinyl ketone (**16**) (0.29 g). After column chromatography (SiO_2, hexane) and crystallization (hexane), white crystals (0.21 g, 67%) were obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.48−1.60 (m, 4 H), 1.62−1.67 (m, 2 H), 1.67−1.80 (m, 8 H), 1.87 (bs, 2 H), 1.92−1.98 (m, 1 H), 2.22 (bs, 2 H), 5.64 (dd, 1 H, *J* = 11 Hz, *J* = 2 Hz), 6.38 (dd, 1 H, *J* = 17.2 Hz, *J* = 2 Hz), 6.86 (dd, 1 H, *J* = 17.2 Hz, *J* = 11 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.4 (CH), 26.3 (CH), 34.8 (CH_2), 36.7 (CH), 37.5 (CH), 37.6 (CH_2), 37.8 (CH_2), 40.4 (CH_2), 51.1 (C), 77.24 (CH), 128.4 (CH_2), 130.3 (CH), 204.3 (C). HRMS calcd for $C_{17}H_{22}O$, 242.1671; found, 242.1669.

1-Diamantyl Cyclopropyl Ketone (10) from 1-Diamantyl Vinyl Ketone (16). To NaOH (0.068 g, 1.24 mmol), trimethylsulfoxonium iodide (0.09g, 0.4 mmol) and DMSO (2 mL) were added. The mixture was heated to 110 °C, and a solution of 1-diamantyl vinyl ketone (**16**) (0.05 g, 0.2 mmol) in DMSO (1 mL) was added. The mixture was stirred for 3 h, diluted with water, and extracted with hexane (3 × 15 mL). The combined organic layers were washed with water and brine and were concentrated under reduced pressure to give 1-diamantyl cyclopropyl ketone (**10**) (0.04 g, 76%) identical to the sample obtained earlier.

■ ASSOCIATED CONTENT

Supporting Information

Computational details, copies of NMR spectra, and *xyz*-coordinates of optimized species. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.
[§]For Part 1 see ref 10.

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(25) We also computed the alternative "normal" Corey-Chaykovsky reaction path for **6** (i.e., the attack of DMSM on the carbonyl group with formation of the corresponding oxirane. The formation of the tetrahedral intermediate (betaine) requires a barrier of only 8 kcal mol^{-1} for **6** [M06-2X-PCM/6-31G(d,p)], in accordance with the previously found barriers for the methylenation of sterically unhindered ketones [Aggarwal, V. K.; Harvey, J. N.; Richardson, J. *J. Am. Chem. Soc.* **2002**, *124*, 5747] However, subsequent DMSO loss and formation of the oxirane requires ca. 18 kcal mol^{-1}, which is comparable with the computed for the direct attack of DMSM on the enolate anion of **6**.
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