38 half-lives for hetaryl bromide under the same conditions. Any liberated 2-thiopyridone would have been detected at this wavelength of maximum absorbance. This sulfide has a maximum absorbance at 243 nm with a shoulder at 275 nm and no significant absorbance at 340 nm.

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Registry No. 1, 106500-26-9; 5, 2637-34-5.

One-Pot Preparation of Crowded Olefins from Hindered Ketones with Alkyllithiums and Thionyl Chloride[1]

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A series of crowded olefins were prepared in high yield by the one-pot reaction of in situ generated lithium alkoxides, formed from hindered ketones and alkyllithiums, with thionyl chloride. The prepared olefins are generally inaccessible by either the Wittig reaction or using Grignard reagents because of predominant electron-transfer reduction of the hindered ketones.

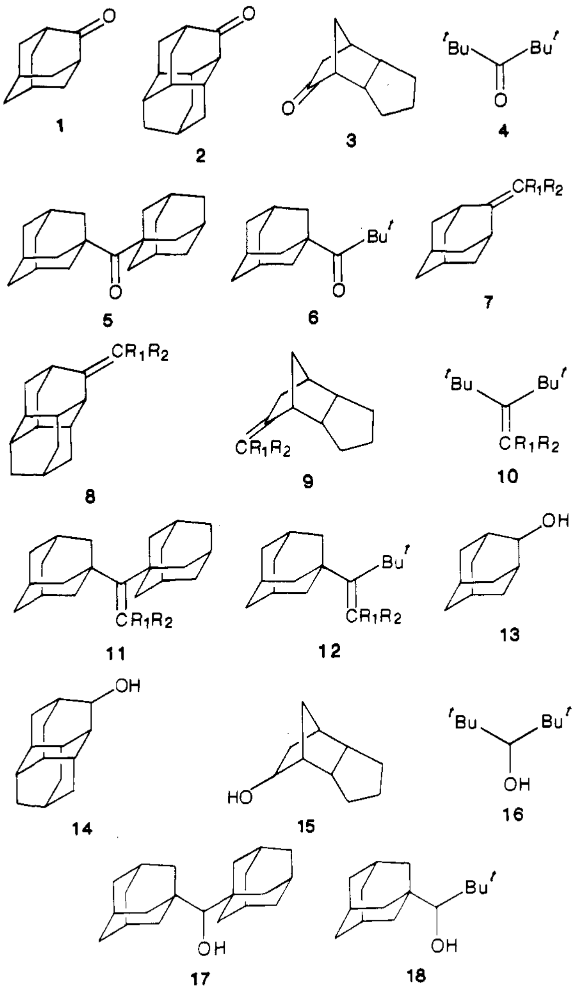
Introduction

Preparation of olefins can be accomplished in addition to dehydrogenation, dehydration, and dehydrohalogenation by a great variety of methods[2] from various functional groups such as carboxylic acids, vicinal dicarboxylic acids, alkyl halides and vicinal dihalides, halohydrins, β-hydroxy sulfonamides, amines, etc. The most widely used olefin synthesis from carbonyl compounds is the Wittig reaction.[3] A host of substituted olefins are also prepared, among other methods, by Perkin,[4] Stobbe,[5] and Darzenes'[6] reactions from carbonyl compounds.

When the Wittig reaction between alkylidenephosphorane and an enolizable ketone is sterically hindered, the enolate of the ketone is formed, together with phosphonium salt and the products of self-condensation of ketone.[7] With a nonenolizable ketone (or one that enolizes with great difficulty), no reaction under usual Wittig conditions between alkylidenephosphoranes and ketones is observed.[8] Our previous studies of preparing hindered olefins from nonenolizable ketones 2-adamantanones (1)[9,10] and 3-diamantanones (2)[10] with hindered alkylidenephosphoranes were unsuccessful, and instead we observed electron-transfer reduction.

For dehydration of alcohols to olefins among other dehydrating agents, thionyl chloride in combination with excess pyridine has been widely used.[11] Thionyl chloride, otherwise, is a chlorinating agent[12] for alcohols, reacting through intermediate chlorosulfite derivatives[13] in an S_N1 type reaction.[14] In the absence of pyridine, use of thionyl chloride as dehydrating agent for alcohols to olefins has

Scheme I[a]



[a] **a**, $R_1 = R_2 = H$; **b**, $R_1 = R_2 = CH_3$; **c**, $R_1 = CH_3$, $R_2 = CH_2CH_3$.

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Table I. Olefin Formation from Hindered Ketones with Alkyllithiums and Thionyl Chloride

	olefins (% yield)[a]		
ketone	via methyllithium	via isopropyllithium	via *sec*-butyllithium
1	**7a** (94)	**7b** (94)	**7c** (95)
2	**8a** (92)	**8b** (91)	**8c** (96)
3	**9a** (93)	**9b** (90)	**9c** (88)
4	**10a** (82)	**10b** (82)	**10c** (83)
5	**11a** (96)	**11b** (95)	**11c** (96)
6	**12a** (96)	**12b** (93)	**12c** (90), *E* + *Z*

[a] Isolated yield.

been sporadically reported. Thus, in steroid chemistry, treatment of 5α-cholestan-1α-ol and 5α-cholestan-1β-ol with thionyl chloride gives an isomeric mixture of olefins and a single ring-homologated olefin, respectively.[15]

Continuing our study of the synthesis of hindered olefins led us to the development of a convenient one-pot method of reacting hindered ketones with alkyllithium and thionyl chloride, and herein we report our results.

Results and Discussion

Six readily available hindered ketones **1**–**6** (Scheme I) have been chosen for our study: 2-adamantanone (**1**), 3-diamantanone (**2**),[16] 8-tricyclo[5.2.1.0^{2,6}]decanone (**3**), 2,2,4,4-tetramethyl-3-pentanone (**4**), 1,1′-diadamantanyl ketone (**5**),[17] and 1-adamantyl *tert*-butyl ketone (**6**). The hindered ketones were reacted in ethereal solution with alkyllithiums, forming in situ the corresponding lithium alkoxides, which then without separation were found to react with thionyl chloride in the ether solution to give the corresponding crowded olefins in high yields.

To a well-stirred solution of 2-adamantanone (**1**) (Scheme I) in diethyl ether cooled to −78 °C was added isopropyllithium (in pentane) dropwise under dry nitrogen, and the corresponding lithium alkoxide was formed in situ. When thionyl chloride was added very slowly to this well-stirred reaction mixture at −78 °C and the reaction mixture gradually allowed to warm to room temperature, isopropylideneadamantane (**7b**) was obtained in 94% yield after the usual workup (see Experimental Section). When *sec*-butyllithium was used under identical reaction conditions, isobutylideneadamantane (**7c**) was obtained in similar yields (Table I).

The procedure allowed a variety of hindered olefins to be prepared in high yield when applied to other nonenolizable ketones (Table I) using appropriate alkyllithium reagents.

The reaction of thionyl chloride with in situ generated lithium alkoxides is extremely exothermic (**CAUTION**: $SOCl_2$ must be added very slowly at −78 °C). Thionyl chloride reacts with the in situ generated lithium alkoxide to form the corresponding alkyl chlorosulfites, which upon warming of the reaction mixture cleave to give SO_2 and the desired olefin. Formation of olefin, therefore, involves a concerted elimination mechanism similar to the one involved in the reaction of alcohols with thionyl chloride in the presence of pyridine. No tertiary alkyl chlorides were observed to be formed. The mechanism is depicted in Scheme II.

Scheme II

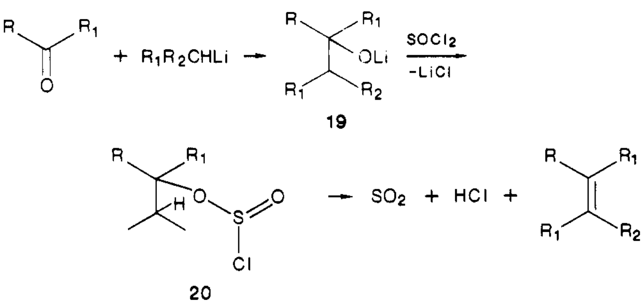


Table II. Attempted Wittig Reaction of Hindered Ketones

	product (% yield)[a]	
ketone	via $CH_2{=}PPh_3$	via $(CH_3)_2C{=}PPh_3$
1[b]	**7a** (80) + **13** (20)	**7b** (0) + **13** (20)
2	**8a** (62) + **14** (29)	**8b** (0) + **14** (40)
3	**9a** (60) + **15** (32)	**9b** (0) + **15** (36)
4	**10a** (0) + **16** (0)	**11b** (0) + **16** (0)
5	**11a** (0) + **17** (0)	**11b** (0) + **17** (0)
6	**12a** (0) + **18** (0)	**12b** (0) + **18** (0)

[a] Isolated yield. [b] Reference 9.

Table III. Reaction of Hindered Ketones with Grignard Reagents and Thionyl Chloride

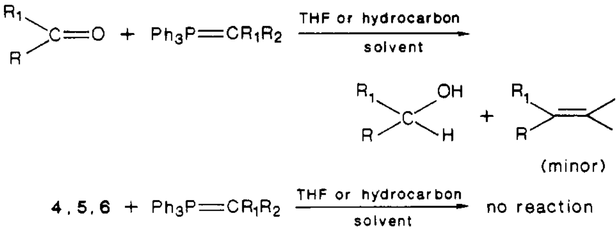
	product (% yield)[a]		
ketone	via CH_3MgI	via $(CH_3)_2CHMgBr$	via $CH_3CH_2(CH_3)$-$CHMgBr$
1	**7a** (10) + **13** (86)	**7b** (6) + **13** (70)	**7c** (8) + **13** (76)
2	**8e** (10) + **14** (69)	**8b** (12) + **14** (77)	**8c** (9) + **14** (72)
3	**9a** (12) + **15** (88)	**9b** (5) + **15** (87)	**9c** (5) + **15** (88)
4	**10a** (0) + **16** (20)	**10b** (0) + **16** (10)	**10c** (0) + **16** (10)
5	**11a** (0) + **17** (16)	**11b** (0) + **17** (6)	**11c** (0) + **17** (9)
6	**12a** (0) + **18** (16)	**12b** (0) + **18** (12)	**12c** (0) + **18** (10)

[a] Isolated yield.

In the dehydration reaction of alcohols using $SOCl_2$/pyridine, initial reaction of alcohol with $SOCl_2$/pyridine allows the formation of **20**. However, the procedure necessitates use of an isolated alcohol together with an excess of pyridine and thus involves an additional step. In the procedure presently developed, no pyridine assistance is required.

None of the discussed crowded olefins could be satisfactorily prepared from their ketone precursors by the usual Wittig reaction. It was found that one-electron transfer dominates as a competing pathway in the attempted Wittig reaction of sterically hindered systems and reduction products are predominantly observed over olefin formation.[9] 2-Adamantanone[9] and 3-diamantanone[10] react with hindered alkylidenephosphoranes to give 30–50% and 60–90% reduction products (Table II) **13** and **14**, respectively, in hydrocarbon solvents.

In ether solution, no reaction leading to olefin formation was observed.



The preparation of the discussed olefins can be accomplished only with organolithium reagents. Attempted re-

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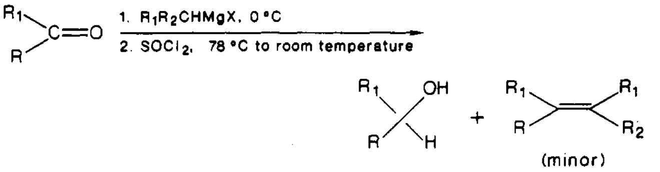
actions with Grignard reagent gave mainly reduction products[18] (Table III).



Thus, with 8-tricyclo[5.2.1.$0^{2,6}$]decanone (**3**) only 5% of the desired olefin could be obtained with isopropylmagnesium bromide. Similarly, **1**–**3** reacted with alkylmagnesium halide to give considerable amounts of reduction products (Table III). No reaction is observed with **4**–**6** and Grignard reagents.

The reported one-pot preparation of crowded olefins from their sterically hindered ketone precursors with alkyllithium and thionyl chloride in ether solution complements the Wittig reaction and related methods, which with these hindered systems tend to give primarily reduction products via electron-transfer processes.

Experimental Section

2-Adamantanone (**1**), 8-tricyclo[5.2.1.$0^{2,6}$]decanone (**3**), and 2,2,4,4-tetramethyl-3-pentanone (**4**) were commercially available (Aldrich) and were used as such. 3-Diamantanone (**2**)[16] and 1,1′-diadamantanyl ketone (**5**)[17] were prepared according to the literature procedure. Methyllithium and *sec*-butyllithium are commercially available (Aldrich), and isopropyllithium was prepared according to the literature procedure[19] and standardized[20] prior to use. Thionyl chloride was commercially available (Aldrich) and distilled prior to use. Diethyl ether was dried over metallic sodium under reflux conditions.

Gas chromatographic analysis was carried out on a Varian (Model 3700) gas chromatograph using a quartz-silica capillary column coated with DB-1. Mass spectroscopic analysis was performed on a Finnigan Mat Model 700 GC/MS spectrometer. NMR spectra were recorded on a Varian 200-MHz (VXR-200) superconducting NMR spectrometer.

Preparation of 1-Adamantyl *tert*-Butyl Ketone (6). To a solution of 1-adamantanecarboxylic acid (3.6 g; 20.0 mmol) and dry pentane (20 mL) was added *tert*-butyllithium (1.7 M in pentane; 25 mL; 42.5 mmol) via a syringe dropwise at −78 °C via application of an external dry ice/acetone cold bath with stirring under nitrogen atmosphere during a period of 10 min. After the addition of *tert*-butyllithium had been completed, the reaction mixture was stirred for another 30 min at −78 °C under nitrogen atmosphere, then the dry ice/acetone cold bath was removed, and the reaction mixture was warmed to ambient temperature. The reaction mixture was then maintained with stirring at ambient temperature for another 2 h and then quenched by water. The usual workup and extraction were carried out with ether, and the combination of organic layers was dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo to give the corresponding ketone, which can be recrystallized from ethanol, mp 42 °C as colorless microcrystals (4.1 g; 18.66 mmol; 93% yield from 1-adamantanecarboxylic acid). IR (KBr): 1720 (s) cm^{-1}. ^{13}C NMR (50 MHz, $CDCl_3$): 217.31 (s), 48.70 (s), 45.38 (s), 39.53 (t), 36.66 (t), 29.83 (d), 28.29 (q). GC/MS (70 eV): *m/e* 220 (M^+, 1.0), 163 (10.2), 135 (100.0), 107 (14.5), 93 (28.4), 57 (12.2). Anal. Calcd for $C_{15}H_{24}O$: C, 81.82; H, 10.91; O, 7.27. Found: C, 82.01; H, 10.99; O, 7.34.

General Procedure for Preparation of Olefins. To an ethereal solution of ketone (10 mmol) and dry ether (20 mL) was added dropwise alkyllithium (11–15 mmol) at −78 °C via application of an external dry ice/acetone cold bath with stirring under nitrogen atmosphere during a period of 5 min. After the addition of alkyllithium had been completed, the reaction mixture was stirred at −78 °C for another 30 min and freshly distilled thionyl chloride (1.78 g, 15 mmol) was added dropwise with good stirring at −78 °C during a period of 5 min. After the addition of thionyl chloride had been completed, the reaction mixture was stirred at −78 °C for another 5 min, and then the dry ice/acetone cold bath was removed. The reaction mixture was slowly warmed to ambient temperature. The reaction mixture was maintained with stirring at ambient temperature for another 30 min and then poured onto a separatory funnel charged with ice (50 g). Extraction was carried out with ether (50 mL × 3). The combination of ethereal layers was dried over anhydrous magnesium sulfate, filtered, and evaporated. The residue was purified via column chromatography on silica gel (hexane eluent) to afford the corresponding olefin.

2-Methyleneadamantane (7a). From the reaction of 2-adamantanone (**1**; 1.50 g; 10 mmol) with methyllithium (1.4 M in diethyl ether; 8.0 mL; 11.2 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 2-methyleneadamantane (**7a**; 1.39 g; 9.4 mmol; 94% from **1**). All spectral data were consistent with those given for **7a** in the previous report.[21]

2-Isopropylideneadamantane (7b). From the reaction of 2-adamantanone (**1**; 1.50 g; 10.0 mmol) with isopropyllithium (1.0 M in pentane; 12 mL; 12.0 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 2-isopropylideneadamantane (**7b**; 1.65 g; 9.4 mmol; 94% yield from **1**) as colorless microcrystals, mp 120–121 °C. IR (KBr): 1610 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 139.58 (s), 116.07 (s), 39.13 (t), 37.57 (d), 33.12 (t), 28.51 (d), 19.46 (q). GC/MS (70 eV): *m/e* 176 (M^+, 100.0), 161 (14.2), 133 (36.2), 119 (46.3), 91 (75.2). Anal. Calcd for $C_{13}H_{20}$: C, 88.64; H, 11.36. Found: C, 88.89; H, 11.30.

2-Isobutylideneadamantane (7c). From the reaction of 2-adamantanone (**1**; 1.50 g; 10.0 mmol) with *sec*-butyllithium (1.3 M in cyclohexane; 10.0 mL; 13.0 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 2-isobutylideneadamantane (**7c**; 1.81 g; 9.5 mmol; 95% yield from **1**) as a colorless liquid, bp 146–147 °C (1.0 mm). IR (neat): 1605 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 139.33 (s), 122.36 (s), 39.35 (t), 38.93 (t), 37.35 (t), 32.91 (d), 32.63 (d), 28.28 (d), 26.71 (t), 17.00 (q), 13.61 (q). GC/MS (70 eV): *m/e* 190 (M^+, 80.4), 175 (59.9), 161 (29.4), 133 (30.8), 119 (38.5), 105 (57.1), 91 (100.0). Anal. Calcd for $C_{14}H_{22}$: C, 88.42; H, 11.58. Found: C, 88.16; H, 11.46.

3-Methylenediamantane (8a). From the reaction of 3-diamantanone (**2**; 2.02 g; 10.0 mmol) and methyllithium (1.4 M in diethyl ether; 8.0 mL; 11.2 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 3-methylenediamantane (**8a**; 1.84 g; 9.2 mmol; 92% yield from **2**) as colorless microcrystals, mp 120–121 °C. IR (KBr): 3010 (w), 1610 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 158.72 (s), 100.87 (t), 38.63 (t), 37.47 (t), 36.35 (d), 35.31 (d), 35.14 (d), 34.88 (t), 33.34 (d), 29.87 (d), 25.63 (d). GC/MS (70 eV): *m/e* 200 (M^+, 100.0), 143 (24.5), 129 (17.6), 106 (26.8), 91 (55.7), 79 (32.0). Anal. Calcd for $C_{15}H_{20}$: C, 90.00; H, 10.00. Found: C, 90.21; H, 10.06.

3-Isopropylidenediamantane (8b). From the reaction of 3-diamantanone (**2**; 2.02 g; 10.0 mmol) with isopropyllithium (1.0 M in pentane; 12 mL; 12.0 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 3-isopropylidenediamantane (**8b**; 2.07 g; 9.1 mmol; 91% yield from **2**) as colorless microcrystals, mp 96–97 °C. IR (KBr): 1605 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 140.02 (s), 116.17 (s), 42.43 (d), 39.17 (t), 38.63 (d), 38.22 (d), 38.01 (d), 37.52 (t), 37.18 (t), 30.28 (d), 26.04 (d), 19.65 (q), 19.44 (q). GC/MS (70 eV): *m/e* 228 (M^+, 100.0), 213 (18.4), 143 (12.0), 105 (33.5), 91 (62.6). Anal. Calcd for $C_{17}H_{24}$: C, 89.47; H, 10.53. Found: C, 89.29; H, 10.66.

3-Isobutylidenediamantane (8c). From the reaction of 3-diamantanone (**2**; 2.02 g; 10.0 mmol) with *sec*-butyllithium (1.3 M in cyclohexane; 10.0 mL; 13.0 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 3-isobutylidenediamantane (**8c** mixture of 50:50 *E* and

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Z isomers; 2.32 g; 9.6 mmol; 96% yield from **2**) as a colorless liquid, bp 102–103 °C (0.5 mm). IR (neat): 1610 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 138.82 (s), 122.60 (s), 42.21 (d), 39.59 (t), 39.11 (d), 38.65 (d), 38.21 (d), 37.55 (t), 37.18 (t), 30.01 (d), 26.73 (d), 26.03 (t), 17.22 (q), 13.73 (q). GC/MS (70 eV): *m/e* 242 (M$^+$, 100.0), 227 (67.9), 213 (38.2), 131 (33.9), 105 (47.8), 91 (85.4). Anal. Calcd for $C_{18}H_{26}$: C, 89.26; H, 10.74. Found: C, 89.46; H, 10.96.

8-Methylenetricyclo[5.2.1.0^{2,6}]decane (9a). From the reaction of 8-tricyclo[5.2.1.0^{2,6}]decanone (**3**; 1.50 g; 10.0 mmol) with methyllithium (1.4 M in diethyl ether; 8.0 mL; 11.2 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 8-methylenetricyclo[5.2.1.0^{2,6}]decane (**9a**; 1.38 g; 9.3 mmol; 93% yield from **3**) as a colorless liquid, bp 62–63 °C (2.0 mm). IR (neat): 3050 (w), 1600 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 155.14 (s), 101.88 (t), 49.91 (d), 47.85 (d), 47.57 (d), 41.40 (d), 37.54 (t), 32.82 (t), 32.47 (t), 31.79 (t), 27.63 (t). GC/MS (70 eV): *m/e* 148 (M$^+$, 26.4), 133 (15.2), 119 (12.5), 105 (24.5), 91 (45.0), 79 (100.0). Anal. Calcd for $C_{11}H_{16}$: C, 89.19; H, 10.81. Found: C, 89.26; H, 10.93.

8-Isopropylidenetricyclo[5.2.1.0^{2,6}]decane (9b). From the reaction of 8-tricyclo[5.2.1.0^{2,6}]decanone (**3**; 1.50 g; 10.0 mmol) with isopropyllithium (1.0 M in pentane; 12.0 mL; 12.0 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 8-isopropylidenetricyclo[5.2.1.0^{2,6}]decane (**9b**; 1.58 g; 9.0 mmol; 90% yield from **3**) as a colorless liquid, bp 91–92 °C (2.0 mm). IR (neat): 1615 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 139.62 (s), 125.30 (s), 47.83 (t), 44.99 (d), 42.00 (d), 37.02 (d), 36.33 (d), 33.40 (t), 33.00 (t), 32.24 (t), 28.00 (t), 19.85 (q), 19.66 (q). GC/MS (70 eV): *m/e* 176 (M$^+$, 11.9), 107 (100.0), 91 (20.9), 79 (10.3). Anal. Calcd for $C_{13}H_{20}$: C, 88.64; H, 11.36. Found: C, 88.90; H, 11.62.

8-Isobutylidenetricyclo[5.2.1.0^{2,6}]decane (9c). From the reaction of 8-tricyclo[5.2.1.0^{2,6}]decanone (**3**, 1.50 g; 10.0 mmol) with *sec*-butyllithium (1.3 M in cyclohexane; 10.0 mL; 13.0 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 8-isobutylidenetricyclo[5.2.1.0^{2,6}]decane (**9c** mixture of 50:50 *E* and *Z* isomers; 1.67 g; 8.8 mmol; 88% yield from **3**) as a colorless liquid, bp 98–99 °C (2.0 mm). IR (neat): 1605 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 137.53 (s), 123.82 (s), 47.73 (t), 44.85 (d), 41.29 (d), 36.63 (d), 35.92 (d), 32.99 (t), 32.55 (t), 31.90 (t), 27.84 (t), 27.55 (t), 17.47 (q), 13.35 (q). GC/MS (70 eV): *m/e* 190 (M$^+$, 21.5), 161 (9.4), 121 (100.0), 105 (22.8), 91 (51.8), 79 (45.2). Anal. Calcd for $C_{14}H_{22}$: C, 88.42; H, 11.58. Found: C, 88.78; H, 11.60.

1,1-Di-*tert*-butylethylene (10a). From the reaction of 2,2,4,4-tetramethyl-3-pentanone (**4**; 1.42 g; 10.0 mmol) with methyllithium (1.4 M in diethyl ether; 8.0 mL; 11.2 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 1,1-di-*tert*-butylethylene (**10a**; 1.14 g; 8.2 mmol; 82% yield from **4**) as a colorless liquid, bp 62–63 °C (18.0 mm) (lit.[18] bp 146–150 °C). All spectral data were consistent with those given for **10a** in the previous report.[22]

3-*tert*-Butyl-2,4,4-trimethyl-2-pentene (10b). From the reaction of 2,2,4,4-tetramethyl-3-pentanone (**4**; 1.42 g; 10.0 mmol) with isopropyllithium (1.0 M; 12.0 mL; 12.0 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 3-*tert*-butyl-2,4,4-trimethyl-2-pentene (**10b**; 1.38 g; 8.2 mmol; 82% yield from **4**) as a colorless liquid, bp 60–62 °C (12.0 mm). IR (neat): 1610 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 151.72 (s), 112.22 (s), 48.85 (s), 28.79 (q), 19.82 (q). GC/MS (70 eV): *m/e* 168 (M$^+$, 0.5), 125 (3.5), 112 (40.4), 97 (97.6), 83 (26.6), 69 (83.5), 57 (70.8), 55 (61.5), 41 (100.0). Anal. Calcd for $C_{12}H_{24}$: C, 85.71; H, 14.29. Found: C, 85.59; H, 14.42.

4-*tert*-Butyl-3,5,5-trimethyl-3-hexene (10c). From the reaction of 2,2,4,4-tetramethyl-3-pentanone (**4**; 1.42 g; 10.0 mmol) with *sec*-butyllithium (1.3 M in cyclohexane; 10.0 mL; 13.0 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 4-*tert*-butyl-3,5,5-trimethyl-3-hexene (**10c**; 1.51 g; 8.3 mmol; 83% yield from **4**) as a colorless liquid, bp 96–97 °C (12.0 mm). IR (neat): 1600 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 151.96 (s), 112.37 (s), 49.88 (s), 49.66 (s), 29.51 (q), 28.82 (q), 25.60 (t), 21.85 (q), 15.52 (q). GC/MS (70 eV): *m/e* 182 (0.2), 126 (25.9), 111 (11.5), 97 (100.0), 69 (90.3), 57 (62.7), 41 (99.2). Anal. Calcd for $C_{13}H_{26}$: C, 85.71; H, 14.29. Found: C, 85.59; H, 14.40.

1,1-Di-1′-adamantylethylene (11a). From the reaction of 1,1′-diadamantyl ketone (**5**; 2.98 g; 10.0 mmol) with methyllithium (1.4 M in diethyl ether; 8.0 mL; 11.2 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 1,1-di-1′-adamantylethylene (**11a**; 2.84 g; 9.6 mmol; 96% yield from **5**) as colorless microcrystals, mp 112–113 °C. IR (KBr): 3040 (w), 1600 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 166.4 (s), 108.38 (t), 43.46 (t), 40.74 (s), 37.30 (t), 29.34 (d). GC/MS (70 eV): *m/e* 296 (M$^+$, 9.0), 135 (100.0), 93 (16.9), 79 (22.2). Anal. Calcd for $C_{22}H_{32}$: C, 89.19; H, 10.81. Found: C, 89.02; H, 10.92.

1,1-Di-1′-adamantyl-2-methylpropene (11b). From the reaction of 1,1′-diadamantyl ketone (**5**; 2.98 g; 10.0 mmol) with isopropyllithium (1.0 M; 12.0 mL; 12.0 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 1,1-di-1′-adamantyl-2-methylpropene (**11b**; 3.08 g; 9.5 mmol; 95% yield from **5**) as colorless microcrystals, mp 130–131 °C. IR (KBr): 1610 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 151.96 (s), 126.76 (s), 49.45 (s), 40.42 (t), 37.01 (t), 29.70 (d), 25.11 (q). GC/MS (70 eV): *m/e* 324 (M$^+$, 0.2), 135 (100.0), 93 (12.0). Anal. Calcd for $C_{24}H_{36}$: C, 88.89; H, 11.11. Found: C, 89.02; H, 11.01.

1,1-Di-1′-adamantyl-2-methylbutene (11c). From the reaction of 1,1′-diadamantyl ketone (**5**; 2.98 g; 10.0 mmol) with *sec*-butyllithium (1.3 M in cyclohexane; 10.0 mL; 13.0 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 1,1-di-1′-adamantyl-2-methylbutene (**11c**; 3.24 g; 9.6 mmol; 96% yield from **5**) as colorless microcrystals, mp 126–127 °C. IR (KBr): 1610 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 158.31 (s), 125.99 (s), 43.65 (s), 42.75 (s), 41.44 (t), 39.23 (t), 37.25 (t), 36.91 (t), 29.67 (d), 29.39 (d), 29.00 (t), 22.71 (q), 14.10 (q). GC/MS (70 eV): *m/e* 338 (M$^+$, 0.2), 299 (8.2), 221 (10.3), 135 (100.0), 93 (12.7). Anal. Calcd for $C_{25}H_{38}$: C, 88.76; H, 11.24. Found: C, 88.89; H, 11.21.

2-1′-Adamantyl-3,3-dimethylbutene (12a). From the reaction of 1-adamantyl *tert*-butyl ketone (**6**; 2.20 g; 10.0 mmol) with methyllithium (1.4 M in diethyl ether; 8.0 mL; 11.2 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 2-1′-adamantyl-3,3-dimethylbutene (**12a**; 2.09 g; 9.6 mmol; 96% from **6**) as colorless microcrystals, mp 40–41 °C. IR (KBr): 3040 (w), 1610 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 165.34 (s), 108.43 (t), 43.31 (t), 40.36 (s), 37.35 (s), 37.06 (t), 33.00 (d), 29.37 (q). GC/MS (70 eV): *m/e* 218 (M$^+$, 2.1), 203 (1.7), 147 (2.0), 135 (100.0), 107 (23.3), 93 (46.1). Anal. Calcd for $C_{16}H_{26}$: C, 88.07; H, 11.93. Found: C, 88.26; H, 11.81.

3-1′-Adamantyl-2,4,4-trimethyl-2-pentene (12b). From the reaction of 1-adamantyl *tert*-butyl ketone (**6**; 2.20 g; 10.0 mmol) with isopropyllithium (1.0 M in pentane; 12.0 mL; 12.0 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 3-1′-adamantyl-2,4,4-trimethyl-2-pentene (**12b**; 2.29 g; 9.3 mmol; 93% yield from **6**) as a colorless solid, mp 50–51 °C IR (KBr): 1630 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 151.02 (s), 116.21 (s), 47.33 (s), 42.03 (s), 40.44 (t), 37.03 (t), 30.31 (d), 28.66 (q), 28.40 (q). GC/MS (70 eV): *m/e* 246 (M$^+$, 0.6), 189 (0.8), 135 (100.0), 107 (25.0), 93 (44.6), 57 (33.3). Anal. Calcd for $C_{18}H_{30}$: C, 87.80; H, 12.20. Found: C, 88.02; H, 12.00.

3-1′-Adamantyl-2,2,4-trimethyl-3-hexene (12c). From the reaction of 1-adamantyl *tert*-butyl ketone (**6**; 2.20 g; 10.0 mmol) with *sec*-butyllithium (1.3 M in cyclohexane; 10.0 mL; 13.0 mmol) and subsequent treatment with freshly distilled thionyl chloride (1.78 g; 15.0 mmol) was obtained 3-1′-adamantyl-2,2,4-trimethyl-3-hexene (**12c**; mixture of 50:50 *E* and *Z* isomers; 2.34 g; 9.0 mmol; 90% yield from **6**) as a colorless liquid, bp 92–93 °C (1.5 mm). IR (neat): 1620 (m) cm^{-1}. ^{13}C NMR (50 MHz; $CDCl_3$): 151.13 (s), 115.53 (s), 48.62 (s), 45.32 (s), 40.31 (t), 36.98 (t), 30.49 (d), 28.43 (t), 28.32 (q), 24.32 (q), 17.30 (q). GC/MS (70 eV): *m/e* 260 (M$^+$, 0.8), 203 (1.3), 135 (100.0), 107 (16.1), 93 (30.1), 57 (9.6). Anal. Calcd for $C_{19}H_{32}$: C, 87.69; H, 12.31. Found: C, 87.44; H, 12.44.

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[22] Newman, M. S.; Arkell, A.; Fukunaga, T. *J. Am. Chem. Soc.* **1960**, *82*, 2498.