Ultrasound-Assisted Preparation of Di-*tert*-Butyl-,Di-1,1'Adamantyl- and (1-Adamantyl)-*tert*-Butylketenes[1]

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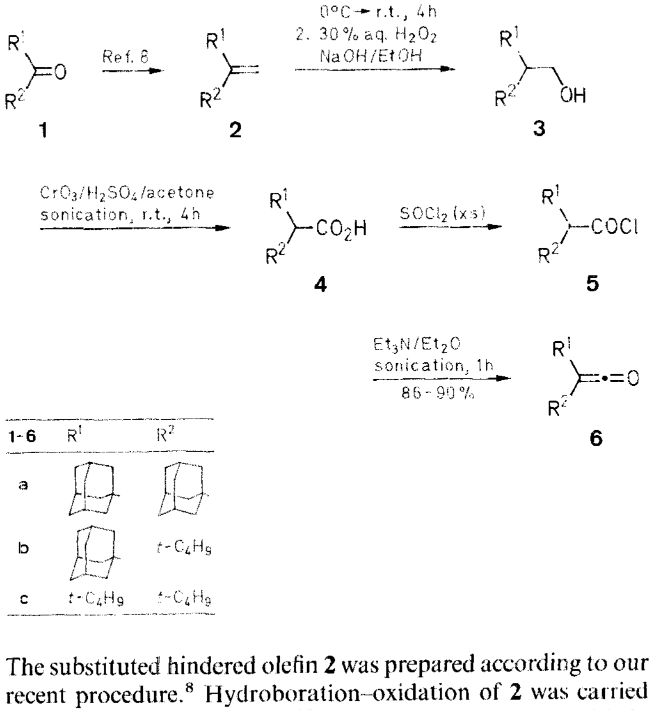
Di-*tert*-butyl-, di(1-adamantyl)- and (1-adamantyl)-*tert*-butylketenes were prepared in excellent yield from their corresponding acetyl chlorides with triethylamine under ultrasonic irradiation, showing a dramatic improvement over attempted conventional dehydrochlorination.

Standard methods[2] for the preparation of ketenes include the dehydrohalogenation of appropriately substituted acetyl halides or dehalogenation of α-haloacetyl halides.[3] Several improved methods using *p*-toluenesulfonyl chloride[4] and Mukaiyama's reagent[5] have also been reported.[6]

In the course of our studies we needed stable ketenes substituted with bulky groups such as *tert*-butyl of 1-adamantyl. Di-*tert*-butylketene was prepared by Newman et al.,[7] as the first distillable aliphatic ketene that is stable in its monomeric form (the bulky *tert*-butyl groups prevent dimerization or oligomerization). We wish to report now the improved preparation of *tert*-butyl and 1-adamantyl substituted hindered stable ketenes by ultrasound-assisted[14] dehydrohalogenation of their corresponding disubstituted acetyl chlorides with triethylamine.

When a mixture of a solution of bis-(1-adamantyl)acetyl chloride in dry ether and triethylamine was subjected to ultrasound for ca. one hour and then filtered, bis(1-adamantyl)ketene was obtained in 90% yield. Applying the same procedure to (1-adamantyl)-*tert*-butylacetyl chloride prepared by the pathway shown in the Scheme, (1-adamantyl)-*tert*-butylketene was obtained in comparably yield.



The substituted hindered olefin **2** was prepared according to our recent procedure.[8] Hydroboration–oxidation of **2** was carried out via $BH_3 \cdot THF$ complex[10] and 30% hydrogen peroxide in basic media to give a high yield of the corresponding alcohol **3**. Jones' oxidation of **3** with ultrasound irradiation has significantly improved the yield of desired substituted acetic acid **4** and shortened the reaction time.[10] Probably, the application of ultrasound prevents the precipitatio of the undesired aldehydes from the media and accelerated the formation of the desired carboxylic acid **4**. Subsequently, treatment of thionyl chloride affords the corresponding carboxylic acid chloride **5**. Dehydrochlorination of the substituted acetyl chloride **5** carried out with triethylamine, under magnetic stirring, led to very low (< 10%) yield of the corresponding ketene **6**, with $Et_3N^+HCl^-$ precipitating from the ethereal solution. However, the application of ultrasound[11] led to dramatic improvement of the yield of ketene **6** formation (Table).

Table. Dehydrochlorination of Crowded Substituted Acetyl Chlorides 5

acetyl chloride	ketene	Yield (%)		bp °C/Torr	
		with ultrasound[a]	with magnetic stirring alone[b]	found	Lit.
5a	**6a**	90	< 10	71/0.5	
5b	**6b**	89	< 10	102/0.5	
5c	**6c**	86	< 10	58/15.0	73/45.0[7]

[a] Reaction was carried out in a water bath maintained at room temperature.

[b] Reaction was carried out in ethereal solution for 24 h at ambient temperature.

Di-*tert*-butylketene was the first aliphatic ketene made that is stable as a monomer.[12] Newly prepared ketenes **6a** and **6b** have a stable similar to di-*tert*-butylketene. For example, they only react slowly with water (in aqueous dioxane solution), and no reaction occurs with liquid ammonia in ether solution.

1,1'-Diadamantyl ketone (**1a**) was prepared according to literature procedure.[13] 1-Adamantyl *tert*-butyl ketone (**1b**), 1,1-bis(1-adamantyl)ethylene (**2a**) and 1-(1-adamantyl)-1-*tert*-butylethylene (**2b**) were prepared according to our recent procedure. Di-*tert*-butyl ketone (**1c**) is commercially available (Aldrich). Tetrahydrofuran (THF) and diethyl ether were dried over sodium under reflux.

Gas chromatographic analysis was carried out on a Varian (Model 3700) Gas Chromatograph using a quarz–silica capillary column ciated with CB-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. Ultrasound-assisted reactions were carried out via the application of an Ultrasonic Processor Model W-385 (Heat System-Ultrasonics) the water bath was maintained at r.t., cooling occasionally when necessary.

2,2-Bis(1-adamantyl)ethanol (3a):

To a solution of 1,1-bis(1-adamantyl)ethylene (**2a**; 2.096 g, 10.0 mmol) and dry THF (20 mL) is added $BH_3 \cdot THF$ (1.0 M in THF; 20 ml; 20 mmol) dropwise with stirring under nitrogen at 0°C via application of an external ice cold bath. Then the ice cold bath is removed, and the reaction mixture is stirred at ambient temperature under nitrogen for an additional 4 h. Water (30 mL) is slowly added to the reaction mixture; the mixture is extracted with ether (3 × 50 mL). The combined ethereal layer is dried ($MgSO_4$). Filtration and evaporation *in vacuo* affords the corresponding alkylborate as a colorless liquid. To a solution of alkylborate in EtOH (20 mL), containing NaOH (1.0 g) is added H_2O_2 (30% in H_2O; 8.0 g) with stirring at a rate sufficient to maintain gentle reflux. Then the reaction mixture is stirred at ambient temperature for 1 h, after which H_2O (35 mL) is added. An analytical sample is obtained via column chromatography on silica gel (30% EtOAc/hexane eluent) to afford the **3a** as a colorless liquid; yield: 2.96 g (94% from **2a**); bp 146–147°C/0.7 Torr.

$C_{22}H_{34}O$	C 84.08	H 10.83
(314.5)	83.79	10.68

IR (neat): $\nu = 3390\ cm^{-1}$ (broad).

^{13}C-NMR (25 MHz, $CDCl_3$): $\delta = 62.24$ (t), 48.43 (d), 41.83 (t), 40.16 (s); 37.36 (t), 31.43 (d).

GC/MS (70 eV): $m/z = 314$ (M^+, 0.9), 296 (1.6), 135 (100.0).

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2-(1-Adamantyl)-3,3-dimethyl-1-butanol (3b):
The above procedure (hydroboration–oxidation) is carried out on **2b** (2.18 g, 10 mmol) to afford **3b** as a colorless liquid; yield: 2.15 g, (91 % from **2b**); bp 102–103 °C/0.6 Torr.

$C_{16}H_{28}O$	C 81.36	H 11.86
(236.4)	81.06	11.81

IR (neat): $\nu = 3400\ cm^{-1}$ (broad).

^{13}C-NMR (25 MHZ; $CDCl_3$): $\delta = 62.06$ (t), 48.13 (d), 41.72 (t), 40.08 (s), 37.06 (t), 31.25 (d), 29.05 (s), 28.90 (q).

GC/MS (70 eV): $m/z = 236$ (M^+, 0.2)., 218 (0.2), 152 (47.1), 135 (100.0), 57 (26.7).

2-*tert*-Butyl-3,3-dimethyl-1-butanol (3c):
The above procedure (hydroboration–oxidation) is carried out on **2c** (1.4 g, 10 mmol) to afford **3c** as a colorless solid; yield: 1.42 g (90 % from **2c**); mp 55 °C (Lit.[7] mp 52 °C). All spectral data were consistent with those given for **3c** in previous literature.

Bis(1-adamantyl)acetic acid (4a):
To a sonicated solution of 2,2-bis(1-adamantyl)ethanol (**3a**; 3.14 g; 10.0 mmol) in acetone (20 mL; fresh distilled over $KMnO_4$) is added dropwise Jones' oxidation reagent[14] (ca. 8 N) until the solution became reddish brown, and then an additional 10 mL) is added. The reaction is continued under ultrasound irradiation at ambient temperature for another 4 h and sat. aq Na_2CO_3 (50 mL) was added. Extraction is carried out with ether 3 × 50 mL). The ethereal layer is dried ($MgSO_4$), filtered, and evaporated *in vacuo* to afford the **4a** as a colorless solid; yield: 2.96 g (90 % from **3a**); mp 152–153 °C. An analytical sample is obtained via column chromatography on silica gel (ether eluent).

$C_{22}H_{32}O_2$	C 80.49	H 9.76
(328.5)	80.20	9.63

IR (KBr): $\nu = 1705\ cm^{-1}$.

^{13}C-NMR (25 MHz; $CDCl_3$): $\delta = 180.65$ (s), 65.98 (d), 41.73 (t), 39.65 (s), 36.69 (t), 30.92 (d).

GC/MS (70 eV): $m/z = 328$ (M^+; 0.4), 310 (0.6), 135 (100.0).

2-(1-adamantyl)-3,3-dimethylbutanoic acid (4b):
The above sonicated oxidation procedure is carried out on **3b** (2.36 g, 10 mmol) to afford **4b** as a colorless solid; yield: 2.20 g (88 % from **3b**); mp 128–129 °C. An analytical sample is obtained via column chromatography on silica gel (ether eluent).

$C_{16}H_{26}O_2$	C 76.80	H 10.40
(250.4)	77.12	10.62

IR (KBr): $\nu = 1700\ cm^{-1}$.

^{13}C-NMR (25 MHz, $CDCl_3$): $\delta = 180.64$ (s), 66.50 (d), 41.78 (t), 37.09 (s), 36.82 (t), 34.57 (s), 31.00 (d), 28.89 (q).

GC/MS (70 eV): $m/z = 250$ (M^+, 02.), 232 (0.2), 194 (2.6), 135 (100.0), 57 (10.2).

2-*tert*-Butyl-3,3-dimethylbutanoic Acid (4c):
The above sonicated oxidation procedure is carried out on **3c** (1.58 g, 10 mmol) to afford **4c** as a colourless solid; yield: 1.46 g (85 % from **3c**); mp 74 °C (Lit.[7] mp 72–74 °C). All spectral data were consistent with those given for **4c** in previous literature.

Bis(1-adamantyl)acetyl Chloride (5a):
A solution of bis(1-adamantyl)acetic acid (**4a**; 3.28 g, 10.0 mmol) in fresh distilled $SOCl_2$ (25 mL) is warmed at 60–65 °C via application of an external oil bath with stirring under nitrogen atmosphere for 1 h. Excess $SOCl_2$ is removed *in vacuo* to afford crude material, which could be distilled at 146–147 °C/0.3 Torr to give **5a** as a colorless liquid; yield: 3.25 g (94 %).

IR (neat): $\nu = 1805\ cm^{-1}$.

^{13}C-NMR (25 MHz, $CDCl_3$): $\delta = 174.30$ (s), 78.62 (d), 41.42 (t), 40.03 (s), 36.43 (t), 30.94 (d).

GC/MS (70 eV): $m/z = 346$ (M^+, 0.4), 310 (9.6), 135 (100.0).

2-(1-Adamantyl)-3,3-dimethylbutanoyl Chloride (5b):
The above procedure is carried out on **4b** (2.5 g; 10 mmol) to **5b** as a colorless liquid after distillation; yield: 2.52 g (94 %); bp 122–123 °C/0.2 Torr.

IR (neat): $\nu = 1800\ cm^{-1}$.

^{13}C-NMR (25 MHz; $CDCl_3$): $\delta = 174.41$ (s), 79.86 (d), 41.71 (t), 40.14 (s), 36.65 (t), 32.04 (s), 31.03 (d), 28.75 (q).

GC/MS (70 eV): $m/z = 268$ (M^+, 0.1), 232 (10.6), 135 (100.0), 57 (9.6).

2-*tert*-Butyl-3,3-dimethylbutanoyl Chloride (5c):
The above procedure is carried out on **4c** (1.72 g, 10 mmol) to give **5c** as a colorless liquid after distillation; yield: 1.64 g (86 % from **4c**); bp 186 °C (Lit.[7] bp 186 °C).

Bis(1-adamantyl)ketene (6a):
To a solution of bis(1-adamantyl)acetyl chlorice (**5a**; 3.46 g, 10.0 mmol) in dry ether (30 mL) is added dropwise fresh distilled Et_3N (1.5 g, 15 mmol) with ultrasound under N_2 over a period of 5 min. Then the reaction mixture is sonicated for another 1 h and filtered. The filtrate is concentrated *in vacuo* affording **6a** as a bright yellow liquid; yield: 2.79 g (90 %) (see Table).

$C_{22}H_{30}O$	calc.	C 85.16	H 9.68
(310.5)	found	84.89	9.64

IR (neat): $\nu = 2095\ cm^{-1}$.

^{13}C-NMR (25 MHz; $CDCl_3$): $\delta = 203.46$ (s), 52.96 (s), 43.19 (t), 36.02 (t), 32.86 (s), 32.01 (d).

GC/MS (70 eV): $m/z = 310$ (M^+, 0.6), 282 (4.3), 135 (100.0).

(1-Adamantyl)-*tert*-butylketene (6b):
The above procedure is carried out on **5b** (2.69 g, 10 mmol) to give **6b** as a bright yellow liquid; yield: 2.06 g (89 %) (see Table).

$C_{16}H_{24}$	calc.	C 82.76	10.34
(232.4)	found	82.44	10.36

IR (neat): $\nu = 2095\ cm^{-1}$.

^{13}C-NMR (25 MHz; $CDCl_3$): $\delta = 203.23$ (s), 53.15 (q); 43.39 (t), 36.09 (t), 32.96 (s), 32.07 (d), 30.73 (s), 28.52 (q).

GC/MS (70 eV): $m/z = 232$ (M^+, 9.0), 217 (44.1), 204 (6.2), 135 (100.0), 57 (12.0).

Di-*tert*.-butylketene (6c):
The above procedure is carried out on **5c** (1.91 g, 10 mmol) to **6c** as a bright yellow liquid after distillation; yield: 1.32 g (86 %) (see Table).

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