Preparation of Crowded Olefins. Alkylidenation of Polycycloalkanones by Corey Homologative Epoxidation Followed by Reaction with Lithium Dialkylcuprates and with Thionyl Chloride[1]

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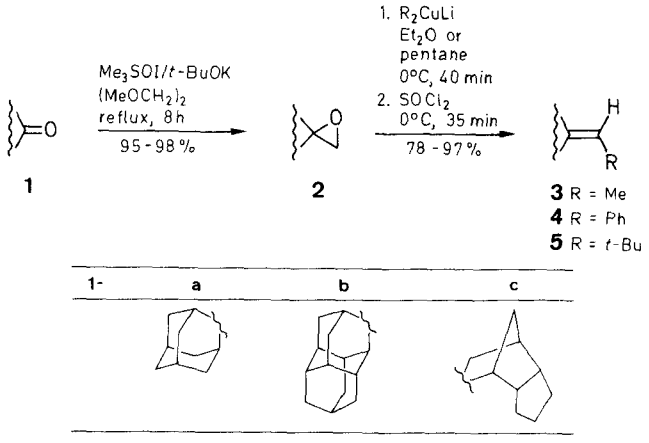
Preparation of crowded olefins from polycycloalkanones via Corey homologative epoxidation by trimethylsulfoxonium iodide/potassium *tert*-butoxide followed by reaction with lithium dialkylcuprates and thionyl chloride giving the corresponding alkylidenepolycycloalkanes is reported.

In our studies continued need arose for the conversion of hindered ketones into their related alkylidenealkanes. Carbocationic eliminations[2] from tertiary alkyl systems can give polysubstituted hindered olefins.[3] Among traditional olefinations, Wittig's[4] and Grignard's[5] methods are the most widely used. However, in our previous study both methods were shown to be unsatisfactory for the alkenylation of crowded ketones[6] as reduction products are predominantly formed via electron-transfer processes.[7] Previously, we developed a convenient methodology for the synthesis of neopentylidenepolycycloalkanes via reaction of their (dibromomethylene)polycycloalkane precursors with *tert*-butyllithium.[1]

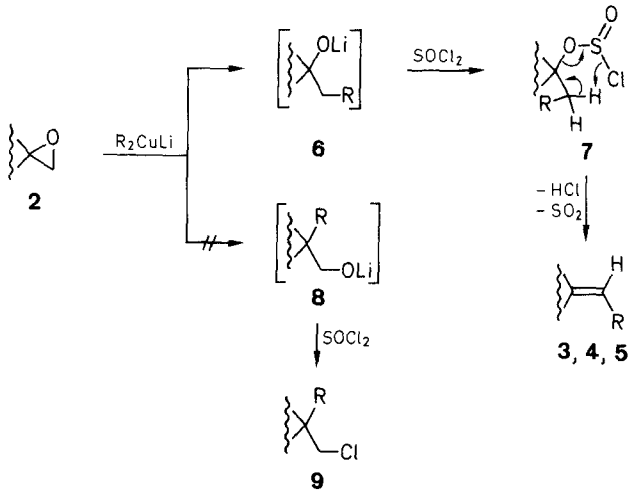
We report now an alternative effective methodology of alkylidenation (i.e., ethylidenation, benzylidenation and neopentylidenation) of polycycloalkanones based on first preparing the corresponding homologated epoxides by Corey's method[8] and then treating them with lithium dialkylcuprate followed by thionyl chloride (Scheme **A**).



Scheme **A**

The polycycloalkanones **1a–c** were chosen for our study. The first step of the conversion, i.e. homologative epoxidation to form the methylenepolycycloalkane epoxides **2a–c** was conveniently accomplished in nearly quantitative yield by Corey's method,[8] which involves treating the ketones with trimethylsulfoxonium iodide and potassium *tert*-butoxide in 1,2-dimethoxyethane (DME) solution.

High yield transformation of methylenepolycycloalkane epoxides, **2a–c**, into the corresponding alkylidenealkanes **3a–c**, **4a–c**, and **5a–c** was carried out in diethyl ether or pentane solution at 0 °C with lithium dialkylcuprate,[9] prepared *in situ* from alkyllithium and copper(I) iodide, and subsequent reaction with thionyl chloride. Lithium dialkylcuprate reacts with the methylenealkane epoxide to give the corresponding lithium *tert*-alkoxide, which subsequently gives with thionyl chloride in a one-flask reaction the corresponding olefin (Scheme **B**).



Scheme **B**

Interestingly, S_N2-like nucleophilic substitution of **2** with lithium dialkylcuprate demonstrates significant stereoselectivity, i.e. the reaction only happens on the sterically less hindered methylene carbon and leads to the formation of lithium *tert*-alkoxide **6**. Subsequent reaction with thionyl chloride gives the alkylidenealkane. No primary alkyl chloride **9** has been observed and the olefin is the only product.

The reported procedure represents an alternative preparation of (alkylidene)polycycloalkanes from the readily available corresponding ketones in good overall yields, in cases where Grignard or Wittig methods are not adaptable.

Et_2O, pentane and DME were distilled from sodium metal prior to use. 2-Adamantanone (**1a**) and 2-tricyclo[5.2.1.$0^{2,6}$]decanone (**1c**) were commercially available and used as such. 3-Diamantanone **1b**, was prepared according to the literature procedure.[10] Gas chromatographic analyses were carried out on a Varian Model 3700 Gas Chromatograph using a quartz–silica capillary column coated with DB-1. Mass spectroscopic analyses were performed on a Finnigan Mat Model 700 GC-MS spectrometer. NMR spectra were recorded on a Varian XVR-200 superconducting NMR spectrometer.

2-Methyleneadamantane epoxide (2a):
A mixture of 2-adamantanone (**1a**; 1.50 g, 10.0 mmol), Me_3SOI (2.20 g, 10.0 mmol) and *t*-BuOK (97%; 1.15 g, 10.0 mmol) in dry DME (50 mL) is refluxed with good stirring under a N_2 atmosphere for 8 h. After being quenched with H_2O, the mixture is

extracted with Et_2O (3 × 50 mL). The extract is dried, filtered and evaporated *in vacuo* to afford **2a** as colorless crystals; yield: 1.57 g (96%); mp 176°C (Lit.[13] 179°C). All the spectral data are consistent with those reported for **2a**.[11]

3-Methylenediamantane epoxide (2b):
The same procedure is used starting from 3-diamantanone (**1b**; 2.02 g, 10.0 mmol), Me_3SOI (220 g, 10.0 mmol) and *t*-BuOK (*1.15 g, 10.0* mmol) to afford **2b** as colorless crystals; yield: 2.12 g (98%); mp 181°C.

$C_{15}H_{20}O$ (216.3) calc. C 83.33 H 9.26
found 83.69 9.20

IR (KBr): $\nu = 3020\ cm^{-1}$.

^{13}C-NMR (50 MHz; $CDCl_3$/TMS): δ = 27.39 (d), 36.03 (d), 36.21 (t), 36.54 (d), 37.00 (t), 38.38 (t), 39.44 (d), 43.65 (d), 51.33 (d), 71.64 (t), 79.89 (s).

GC/MS (70 eV): *m/z* (%) = 216 (M^+, 19.6), 187 (38.4), 174 (66.3), 105 (21.9), 91 (86.5).

8-Methylenetricyclo[5.2.1.0^{2,6}]decane epoxide (2c):
Using the previous procedure for the reaction of tricyclo[5.2.1.0.^{2,6}]decan-8-one (**1c**; 1.50 g, 10.0 mmol), Me_3SOI (2.20 g, 10.0 mmol) and *t*-BuOK (1.15 g, 10.0 mmol) compound **2c** is obtained as a colorless liquid (mixture of the *endo/exo* isomers); yield: 1.56 g (95%); bp 72°C/1.3 Torr.

$C_{11}H_{16}O$ (164.25) calc. C 80.44 H 9.83
found 80.39 9.96

IR (neat): $\nu = 3020\ cm^{-1}$.

^{13}C-NMR ($CDCl_3$/TMS): δ = 27.07 (t), 31.18 (t), 31.85 (t), 36.63 (t), 41.27 (d), 45.91 (d), 46.71 (d), 54.59 (t), 58.64 (d), 71.46 (t), 79.23 (s).

GC/MS (70 eV): *m/z* (%) = 164 (M^+, 28.8), 149 (38.5), 135 (38.6), 120 (76.3), 91 (87.3).

2-Ethylideneadamantane (3a):
An ethereal solution of Me_2CuLi is prepared a 0°C (ice bath) from CuI (1.90 g, 10.0 mmol) and MeLi (1.4 M in Et_2O; 14.0 mL, 19.6 mmol). To this solution is dropwise added with good stirring under a N_2 atmosphere for a period of 10 min at 0°C 2-methyleneadamantane epoxide (**2a**; 0.4 g, 2.44 mmol) in dry Et_2O (5.0 mL). After complete addition of **2a**, the mixture is stirred at 0°C for another 30 min, and then freshly distilled $SOCl_2$ (2.40 g, 20 mmol) is added with caution within 5 min. After complete addition of $SOCl_2$ stirring is continued for another 30 min. After being quenched with H_2O, the mixture is extracted with Et_2O (3 × 50 mL), and the combined ethereal layers are dried ($MgSO_4$), filtered and the solvent evaporated. Column chromatography on silica gel (pentane eluent) give **3a** as colorless crystals; yield: 0.32 g (81%); mp 83°C.

$C_{12}H_{18}$ (162.3) calc. C 88.89 H 11.11
found 89.06 10.98

IR (KBr): $\nu = 1610\ cm^{-1}$.

^{13}C-NMR (50 MHz; $CDCl_3$/TMS): δ = 25.80 (q), 28.31 (d), 32.81 (d), 37.22 (t), 38.33 (t), 40.05 (t), 42.00 (d), 129.33 (d), 148.23 (s).

GC/MS (70 eV): *m/z* (%) = 162 (M^+, 100.0), 119 (22.6), 105 (41.2), 91 (56.0).

3-Ethylidenediamantane (3b):
From 3-methylenediamantane epoxide (**2b**; 0.53 g, 2.45 mmol) CuI (1.90 g, 10.0 mmol), MeLi (19.6 mmol) and subsequent reaction with $SOCl_2$ (2.40 g, 20 mmol) compound **3b** (mixture of *E/Z* isomers 46:54) is obtained yield: 0.42 g (80%); bp 112°C/2.0 Torr.

$C_{16}H_{22}$ (214.35) calc. C 89.72 H 10.28
found 89.39 10.06

IR (neat): $\nu = 1620\ cm^{-1}$.

^{13}C-NMR (50 MHz; $CDCl_3$/TMS): δ = 26.03 (q), 26.73 (d), 30.01 (d), 37.18 (t), 37.55 (t), 38.21 (d), 38.65 (d), 39.11 (d), 39.59 (t), 42.21 (d), 123.31 (d), 148.33 (s).

GC/MS (70 eV): *m/z* (%) = 214 (M^+, 100.0), 131 (33.9), 105 (47.8), 91 (85.4).

8-Ethylidenetricyclo[5.2.1.0^{2,6}]decane (3c):
From 8-methylenetricyclo[5.2.1.0^{2,6}]undecane epoxide (**2c**; 0.4 g, 2.44 mmol), CuI (1.90 g, 10.0 mmol), MeLi (19.6 mmol) and subsequent reaction with $SOCl_2$ (2.40 g, 20 mmol) the compound **3c** (mixture of *E/Z* isomers 42:58) is obtained; yield: 0.31 g (78%); bp 90°C/1.2 Torr.

$C_{12}H_{18}$ (162.3) calc. C 88.89 H 11.11
found 89.21 10.99

IR (neat): $\nu = 1610\ cm^{-1}$.

^{13}C-NMR: δ = 25.33 (q), 27.35 (t), 31.69 (t), 34.48 (t), 38.58 (t), 40.89 (d), 45.90 (d), 46.76 (d), 47.88 (t), 49.36 (d), 110.90 (d), 146.16 (s).

GC/MS (70 eV): *m/z* (%) = 162 (M^+, 20.4), 133 (12.3), 93 (100.0), 79 (26.3).

2-Benzylideneadamantane (4a):
An ethereal solution of Ph_2CuLi is prepared at 0°C (ice bath) from CuI (1.90 g, 10.0 mmol) and PhLi (2.0 M in Et_2O; 10.0 mL, 20.0 mmol). To this solution is dropwise added with good stirring under N_2 atmosphere over a period of 10 min at 0°C **2a** (0.40 g, 2.44 mmol) in dry Et_2O (5.0 mL). After complete addition of **2a** stirring is, continued at 0°C for another 30 min. Then freshly distilled $SOCl_2$ (2.40 g, 20 mmol) is added with caution within 5 min. After complete addition of $SOCl_2$ stirring is continued for another 30 min. After quenching with H_2O and extraction with Et_2O (3 × 50 mL) the combined ethereal layers are dried ($MgSO_4$), filtered and evaporated. Column chromatography on silica gel (pentane eluent) give **4a** as colorless crystals; yield: 0.45 g (82%); mp 102°C.

$C_{17}H_{20}$ (224.35) calc. C 91.07 H 8.93
found 91.14 8.90

IR (KBr): $\nu = 1610\ cm^{-1}$.

^{13}C-NMR (50 MHz; $CDCl_3$/TMS): δ = 28.06 (d), 32.57 (d), 36.98 (t), 38.02 (t), 39.33 (t), 41.36 (d), 121.39 (d), 127.03 (d), 127.88 (d), 128.26 (d), 141.30 (s), 148.22 (s).

GC/MS (70 eV): *m/z* (%) = 224 (M^+, 100.0), 181 (12.9), 167 (27.1), 129 (24.2), 91 (61.4).

3-Benzylidenediamantane (4b):
From the reaction of 3-methylenediamantane epoxide (**2b**; 0.53 g, 2.45 mmol) CuI (1.90 g, 10.0 mmol), PhLi (20.0 mmol) and $SOCl_2$ (2.40 g, 20.2 mmol) compound **4b** (mixture of *E/Z* isomers 52:48) is obtained; yield: 0.59 g (87%); bp 142°C/Torr.

$C_{21}H_{24}$ (276.4) calc. C 91.30 H 8.70
found 91.50 8.52

IR (neat): $\nu = 1620\ cm^{-1}$.

^{13}C-NMR (50 MHz, $CDCl_3$/TMS): δ = 27.00 (d), 30.22 (d), 37.20 (t), 37.89 (t), 38.60 (d), 38.83 (d), 39.29 (d), 39.93 (t), 43.02 (d), 124.33 (d), 125.86 (d), 126.21 (d), 127.32 (d), 142.31 (s), 148.32 (s).

GC/MS (70 eV): *m/z* (%) = 276 (M^+, 100.0), 197 (33.2), 141 (12.3) 91 (33.9).

8-Benzylidenetricyclo[5.2.1.0^{2,6}]decane (4c):
From the reaction of 8-methylenetricyclo[5.2.1.0^{2,6}]decane epoxide (**2c**; 0.4 g, 2.44 mmol), CuI (1.90 g, 10.0 mmol), PhLi (20.0 mmol) and $SOCl_2$ (2.40 g, 20.2 mmol) compound **4c** (mixture of *E/Z* isomers 51:49) is obtained; yield: 0.43 g (79%); bp 132°C/1.7 Torr.

$C_{17}H_{20}$ (224.35) calc. C 91.07 H 8.93
found 91.01 9.05

IR (neat): $\nu = 1610\ cm^{-1}$.

^{13}C-NMR (50 MHz; $CDCl_3$/TMS): δ = 27.99 (t), 32.09 (t), 35.06 (t), 39.62 (t), 41.70 (d), 46.32 (d), 47.41 (d), 48.39 (t), 50.35 (d), 116.85 (d), 126.63 (d), 127.98 (d), 128.35 (d), 137.23 (s), 149.62 (s).

GC/MS (70 eV): *m/z* (%) = 224 (M^+, 16.1), 155 (100.0), 115 (11.3), 91 (16.5).

2-Neopentylideneadamantane (5a):
A pentane solution of (*t*-Bu)$_2$CuLi is prepared at 0°C (ice bath) from CuI (1.90 g, 10.0 mmol) and *t*-BuLi (1.7 M in pentane;

11.5 mL, 19.6 mmol). To this solution is dropwise added with good stirring under N_2 atmosphere 2-methyleneadamantane epoxide (**2a**; 0.4 g, 2.44 mmol) in dry pentane (5.0 mL) within 10 min at 0 °C. After complete addition of **2a**, stirring is continued at 0 °C for another 30 min. Then freshly distilled $SOCl_2$ (2.40 g, 20 mmol) is cautiously added within 5 min. After complete addition of $SOCl_2$, stirring is continued for 30 min. After quenching with H_2O and extraction with Et_2O (3 × 50 mL) the combined ethereal layers are dried ($MgSO_4$), filtered and evaporated. Column chromatography on silica gel (pentane eluent) give **5a** as colorless crystals; yield: 0.42 g (84%); mp 60 °C. All the spectral data are consistent with those reported for **5a**.[1]

3-Neopentylidenediamantane (5b):
From the reaction of 3-methylenediamantane epoxide **2b**; 0.53 g, 2.45 mmol) CuI (1.90 g, 10.0 mmol), *t*-BuLi (1.7 M in pentane; 11.5 mL, 19.6 mmol) and $SOCl_2$ (2.40 g, 20.2 mmol) compound **5b** is obtained as colorless crystals; yield: 0.50 g (80%); mp 105 °C. All the spectral data are consistent with those reported for **5b**.[1]

8-Neopentylidenetricyclo[5.2.1.0^{2,6}]decane (5c):
From the reaction of 8-methylenetricyclo[5.2.1.0^{2,6}]decane epoxide (**2c**; 0.40 g, 2.44 mmol), CuI (1.90 g, 10.0 mmol), *t*-BuLi (1.7 M in pentane; 11.5 mL, 19.6 mmol) and $SOCl_2$ (2.40 g, 20.2 mmol) compound **5c** is obtained; yield: 0.38 g (76%); bp 92 °C/3.0 Torr. All the spectral data are consistent with those reported for **5c**.[1]

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