Pergamon

Tetrahedron, Vol. 52, No. 3, pp. 825-832, 1996

0040-4020/96 $15.00 + 0.00

0040-4020(95)00934-5

Synthesis of (Z)- and (*E*)-1,2-Di(1-adamantyl)ethene and Their Respective Reactions with Dichlorocarbene[1]

Alan P. Marchand*, Dongxia Xing, and Simon G. Bott*

Department of Chemistry, University of North Texas, Denton, Texas 76203-0068

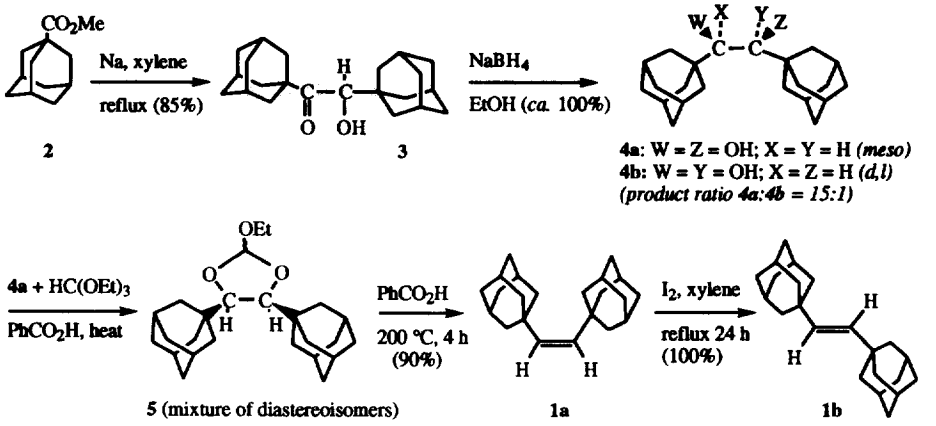
Keywords: (Z)- and (E)-1,2-Di(1-adamantyl)ethene; dichlorocarbene, carbon-hydrogen bond insertion

Abstract. The synthesis of (*Z*)- and (*E*)-1,2-di(1-adamantyl)ethene (**1a** and **1b**, respectively) is reported. Compound **1a** reacts with dichlorocarbene to afford (*Z*)-1-[3-(dichloromethyl)-1-adamantyl],2-(1-adamantyl)ethene (**2**, 27%), (*Z*)-2,3-dichloro-1,3-di(1-adamantyl)propene (**3**, 20%) and 1,1,2-trichloro-2-(1-adamantyl)chloromethyl-3-(1-adamantyl)cyclopropane (**4**, 21%). The corresponding reaction of **1b** produced (*E*)-1-[3-(dichloromethyl)-1-adamantyl],2-(1-adamantyl)ethene (**5**, 34%) and (*E*)-1,2-di[3-(dichloromethyl)-1-adamantyl]ethene (**6**, 5%). The structures of **6**, **7**, and **10** were established unequivocally via application of X-ray crystallographic methods.

Recently, we communicated the syntheses of (*Z*)- and (*E*)-1,2-di(1-adamantyl)ethenes (**1a** and **1b**, respectively) along with some features of their respective X-ray crystal structures.[1] These unusual alkenes are highly congested in the vicinity of the carbon-carbon double bond. In order to gain insight into structure-reactivity properties of these systems, it was of interest to examine their reactivity toward a variety of electrophilic reagents. As part of a continuing study of reactions of electrophiles with polycarbocyclic alkenes,[2] we have undertaken a detailed study of the behavior of **1a** and **1b** toward dichlorocarbene generated under phase-transfer conditions.[3]

Results and Discussion. The method used to synthesize **1a** and **1b** is shown in Scheme 1,[1] and the results obtained for each of the corresponding reactions of these unusual alkenes with $:CCl_2$ are summarized in Scheme 2. In each case, a significant quantity of starting material was recovered. It is particularly noteworthy that *neither* reaction afforded a simple cycloadduct (i.e., a *gem*-dichlorocyclopropane that might have been expected to result via direct cycloaddition of the carbene to the carbon-carbon double bond in the alkene substrate). Instead, the predominant reaction products in each case (i.e., **6** from **1a** + $:CCl_2$, **9** and **10** from **1b** + $:CCl_2$, respectively) appear to have been formed via insertion of $:CCl_2$ into a bridghead carbon-hydrogen bond in one (or both) of the adamantyl moities in the substrate. In addition, the reaction of **1a** with $:CCl_2$ afforded two "rearranged" products (i.e., **7** and **8**, *vide infra*). The structures of **6**, **7**, and **10** were established unequivocally via application of X-ray crystallographic methods.

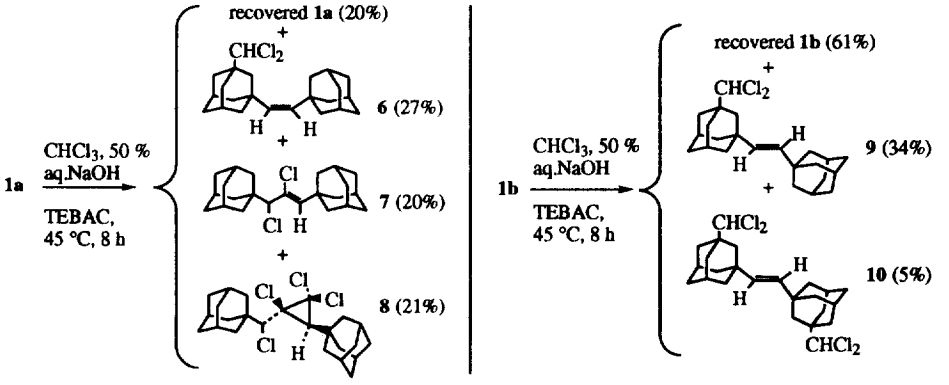
Scheme 1



The structure of **8** was arrived at via analysis of its one- and two-dimensional ^{1}H and ^{13}C NMR spectra and on the basis of mechanistic arguments. Signals at δ 1.55 and 3.58 in the ^{1}H NMR spectrum of **8** were assigned to cyclopropyl (C*H*Ad, where Ad = 1-adamantyl) and AdC*H*Cl protons, respectively. The two-dimensional ^{1}H-^{13}C heteronuclear shift-correlated NMR spectrum of **8** reveals the existence of correlations between the proton signals at δ 1.55 and 3.58 and the corresponding ^{13}C signals at δ 51.91 and 78.72, respectively. This observation permits assignment of these two ^{13}C NMR signals to be made with confidence.

The remaining cyclopropane ring carbon atoms in the ^{13}C NMR spectrum of **8** were assigned by comparison with the corresponding ^{13}C chemical shifts in two model compounds, **11** and **12** (Figure 1).[4] Finally, it should be noted that the measured value of $^{1}J_{CH}$ = 152 Hz for the cyclopropane CH in **8** compares favorably with the value of 161 Hz that has been reported previously for the corresponding $^{1}J_{CH}$ coupling constant in the parent hydrocarbon, cyclopropane.[5]

Scheme 2



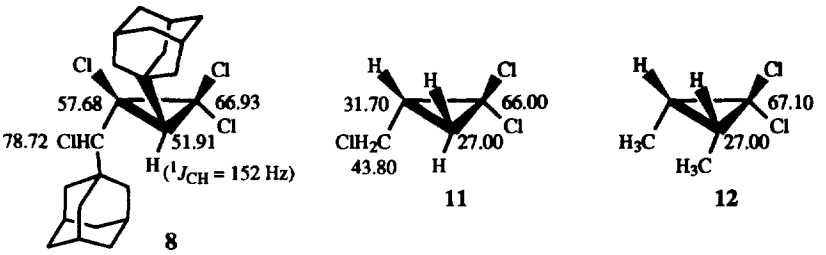
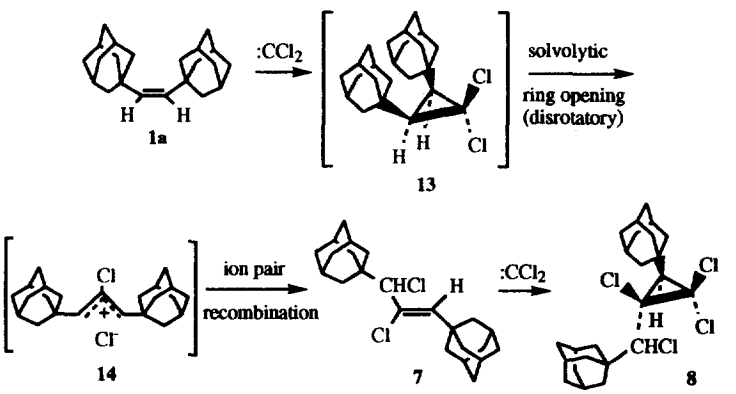


Figure 1. ^{13}C NMR chemical shifts in **8** and in two model compounds (**11** and **12**)[4]

The formation of **6** via reaction of **1a** with $:CCl_2$ can be rationalized in terms of electrophilic insertion of the carbene into a bridghead C-H bond in one of the adamantyl moieties in the substrate. Although it is well known that $:CCl_2$ is capable of undergoing insertion into C-H bonds in cycloalkanes,[6] this nevertheless is an unusual reaction, particularly in view of the fact that **1a** contains a carbon-carbon double bond!

The mechanism of formation of the remaining two products, **7** and **8**, which arise via the reaction of $:CCl_2$ with **1a** is less straightforward. In order to account for the formation of **7** and **8** in this reaction, we suggest that an intermediate *gem*-dichlorocyclopropane (**13**, Scheme 3) may be produced by initial cycloaddition of $:CCl_2$ to the carbon-carbon double bond in **1a**. If this is indeed the case, then **13**, once formed, appears to be unstable to the reaction conditions. Thus, **13** can undergo subsequent thermal (or solvolytic) ring opening via a cationic two-electron electrocyclic process, which occurs with disrotatory ring opening of the cyclopropyl moiety, thereby affording the corresponding allylic carbocation, **14**.[7] Finally, ion pair recombination affords **7**, one of the observed reaction products. The carbon-carbon double bond in **7** is significantly less hindered than the corresponding double bond in **1a**. Thus, subsequent capture of **7** by excess $:CCl_2$ produces **8**, the last of the three products formed in the reaction of **1a** with dichlorocarbene. The assignment of (*Z*)- stereochemistry for **8** is based upon the expectation that this compound resulted via stereospecific *cis* addition of $:CCl_2$ to **7**.[8]

Scheme 3



In contrast to the behavior of **1a** toward $:CCl_2$, the corresponding reaction of **1b** with this carbene afforded only C-H insertion products (i.e., **9** and **10**, Scheme 2). Inspection of space-filled molecular models reveals

that virtually any path of approach to the carbon-carbon double bond in **1b** is sterically hindered by the adjoining adamantyl moieties. Thus, this C=C double bond is effectively shielded from attack by the approaching carbene. Accordingly, the only reactive sites which remain accessible to the electrophilic carbene are the bridgehead C-H bonds in the adamantyl moieties.[6]

Experimental Section

Melting points are uncorrected. Elemental microanalytical data was obtained by personnel at M-H-W Laboratories, Phoenix, AZ.

Methyl 1-adamantanecarboxylate (2). To a solution of 1-adamantanecarboxylic acid (5.0 mg, 27.7 mmol) in MeOH (25 mL, excess) under argon was added concentrated H_2SO_4 (1.5 mL, catalytic amount), and the resulting mixture was refluxed for 2 h. The reaction mixture was cooled to room temperature, and water (30 mL) was added. The resulting mixture was extracted with Et_2O (3 x 40 mL), and the combined ether extracts were washed sequentially with saturated aqueous $NaHCO_3$ (30 mL) and water (2 x 30 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 5% EtOAc in hexane. Pure **2** (5.1 mg, 95%) was thereby obtained as a colorless microcrystalline solid: mp 34.8-35.3 °C (lit.[9] mp 38-39 °C); IR (KBr) 2922 (s), 2894 (s), 2849 (s), 1724 (s), 1445 (m), 1418 (w), 1319 (w), 1244 (s), 1172 (m), 1007 (s), 959 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.60 (s, 6 H), 1.75 (d, J = 3.6 Hz, 6 H), 1.82-1.94 (m, 3 H), 3.52 (br s, 3H); ^{13}C NMR ($CDCl_3$) δ 27.72 (d), 36.25 (t), 38.58 (t), 40.38 (s), 51.04 (q), 177.6 (s).

1,2-Di(1-adamantyl)-2-hydroxyethanone (3). To a suspension of Na (1.26 g, 6.49 mg-atom) in dry xylene (50 mL) under argon was added dropwise with stirring a solution of **2** (4.90 g, 25.6 mmol) in dry xylene (10 mL). The reaction mixture was refluxed for 1 h and then allowed to cool to room temperature. An external ice-water bath then was applied, and the reaction mixture was further cooled to 0 °C. To the cooled reaction mixture was added with stirring a solution of concentrated H_2SO_4 (2.4 mL) in water (12 mL). Water (100 mL) then was added, and the resulting mixture was extracted with xylene (3 x 80 mL). The combined extracts were washed with H_2O (50 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. Compound **3** (726 mg, 85%) was thereby obtained as a colorless microcrystalline solid: mp 224-225 °C (lit.[10] mp 224-225 °C); IR (KBr) 3481 (m), 3441 (m), 2900 (s), 2841 (m), 1685 (m), 1438 (w), 1338 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.40-1.46 (m, 3 H), 1.60-1.78 (m, 14 H), 1.78-1.92 (m, 6 H), 1.92-2.12 (m, 7 H), 2.20 (d, J = 11.6 Hz, 1H), 4.05 (d, J = 11.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.84 (d), 28.19 (d), 36.45 (t), 36.96 (t), 37.38 (s), 37.91 (t), 38.11 (t), 46.37 (s), 76.93 (d), 218.7 (s).

***meso*-1,2-Di(1-adamantyl)ethane-1,2-diol (4a).** A solution of **3** (2.00 g, 6.09 mmol) in EtOH (30 mL) under argon was cooled *via* application of an external ice bath. To this cooled solution was added with stirring $NaBH_4$ (345.6 mg, 9.14 mmol). After all of the reducing agent had been added, the reaction mixture was allowed to warm gradually to room temperature with continuous stirring for 4 h. The reaction mixture then was quenched *via* sequential addition of water (50 mL) and 10% aqueous HCl (5 mL). The resulting mixture was extracted with CH_2Cl_2 (3 x 150 mL), and the combined organic layers were washed with water until the aqueous layer reached *ca.* pH 6. The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo* to afford a mixture of **4a** and **4b** (ratio **4a**:**4b** = 15:1). The mixture was purified via column chromatography on silica gel by eluting with 2% EtOAc-hexane, thereby affording **4a** as a colorless microcrystalline solid (1.88 g, 93%): mp 273.5-274.0 °C; IR (KBr) 3528 (w), 3455 (br, m), 2899 (s), 2846 (m), 1438 (w), 1212 (br, w), 992 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.64-1.80 (m, 26 H), 1.92-2.05 (m, 6 H), 3.10-3.15 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.53 (d), 37.33 (t), 37.67 (s), 38.24 (t), 79.73 (d); Anal. Calcd for $C_{22}H_{34}O_2$: C, 79.95; H, 10.37. Found: C, 80.02; H, 10.16.

Compound **4b**, the minor product formed via $NaBH_4$ promoted reduction of **3**, was characterized unequivocally via X-ray crystallographic analysis of a solid derivative, i. e., *threo*-1-(3',5'-dinitrobenzoyloxy)-2-acetoxy-1,2-di(1-adamantyl)ethane, **15b**.[1] Compound **15b** was synthesized via the following reaction sequence: Sodium borohydride promoted reduction of 2-oxo-1,2-di(1'-adamantyl)ethyl acetate (**16**)[11] produced a mixture of *erythro* and *threo* hydroxyacetates (**17a** and **17b**, respectively) which subsequently was converted into a mixture of the corresponding *O*-(3,5-dinitrobenzoyl) derivatives, **15a** and **15b**. The resulting mixture of

isomers was separated by careful column chromatography followed by fractional recrystallization. The relevant procedures that were thus employed to prepare **15b** are described below.

***erythro*- and *threo*-2-Hydroxy-1,2-di(1-adamantyl)ethyl acetate (17a and 17b).** A solution of **16**[11] (20 mg, 0.054 mmol) in EtOH (5 mL) under argon was cooled via application of an external ice bath. To this cooled solution was added with stirring $NaBH_4$ (50 mg, excess). After all of the reducing agent had been added, the reaction mixture was allowed to warm gradually to room temperature with continuous stirring for 12 h. The reaction mixture then was quenched via addition of water (20 mL). The resulting mixture was extracted with CH_2Cl_2 (3 x 20 mL), and the combined organic layers were washed with water (2 x 30 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 5% EtOAc-hexane, thereby affording a mixture of **17a** and **17b** (ratio 1.5:1, 16 mg, 80%) as a colorless microcrystalline solid. Separation of **17a** from **17b** was performed via careful column chromatography on silica gel (400 mesh) by eluting with 3% EtOAc-hexane. Isomerically pure **17b** (6.4 mg, 32%) was thereby obtained as a colorless microcrystalline solid: mp 187.0-187.5 °C; IR (KBr) 3587 (w), 2896 (s), 2844(m), 1734 (m), 1443 (w), 1359 (w), 1230 (m), 1211 (m), 1017 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.45-1.85 (m, 25 H), 1.90-2.04 (m, 6 H), 2.09 (s, 3 H), 3.26 (d, J = 10.0 Hz, 1 H), 4.75 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.27 (q), 28.13 (d), 28.19 (d), 36.90 (t), 37.02 (t), 37.62 (t), 38.27 (t), 74.91 (d), 75.71 (d), 169.85 (s). Anal. Calcd for $C_{24}H_{36}O_3$: C, 77.38; H, 9.57. Found: C, 77.21; H, 9.57.

Continued elution of the chromatography column afforded isomerically pure **17a** (9.6 mg, 48%) as a colorless microcrystalline solid: mp 195.5-196.5 °C; IR (KBr) 3548 (br m), 3464 (br m), 2896 (s), 2838 (m), 1734 (m), 1714 (m), 1437 (w), 1359 (w), 1230 (m), 1010 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.47-1.75 (m, 25 H), 1.90-2.02 (m, 6 H), 2.07 (s, 3 H), 3.32 (d, J = 7.2 Hz, 1 H), 4.62 (d, J = 7.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.60 (q), 28.34 (d), 37.06 (t), 37 20 (t), 37.80 (t), 38.17 (t), 77.57 (d), 80.76 (d), 170.51 (s). Anal. Calcd for $C_{24}H_{36}O_3$: C, 77.38; H, 9.57. Found: C, 77.54; H, 9.72.

***erythro*- and *threo*-1-(3',5'-Dinitrobenzoyloxy)-2-acetoxy-1,2-di(1-adamantyl)ethane (15a and 15b).** To a solution of a 1.5:1 mixture of **17a** and **17b** (50 mg, 0.13 mmol, *vide supra*) in CH_2Cl_2 (3 mL) under argon at ambient temperature was added Et_3N (0.8 mL, excess), 3,5-dinitrobenzoyl chloride (80 mg, 0.41 mmol), and 4-dimethylaminopyridine (DMAP, 10 mg, catalytic amount), and the reaction mixture was stirred at room temperature for 20 h. Dichloromethane (80 mL) was added, and the resulting mixture was washed sequentially with cold 3% aqueous HCl (20 mL) and water (2 x 30 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 2% EtOAc-hexane. Isomerically pure **15b** (21 mg, 28%) was thereby obtained as a colorless microcrystalline solid: mp 195-196 °C; IR (KBr) 3099 (w), 2908 (s), 2845 (m), 1733 (m), 1724 (m), 1621 (w), 1542 (s), 1455 (w), 1339 (m), 1276 (m), 1258 (m), 1239 (m), 1164 (m), 716 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.30–1.45 (m, 3 H), 1.45-1.74 (m, 21 H), 1.85-2.02 (m, 6 H), 2.26 (s, 3 H), 5.01 (s, 1 H), 5.08 (s, 1 H), 9.20-9.27 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 21.18 (q), 27.91 (2 C, d), 36.58 (t), 36.60 (t), 37.27 (s), 37.56 (t), 37.72 (t), 37.78 (t), 74.85 (d), 77.84 (d), 122.4 (d), 129.6 (2 C, d), 134.4 (s), 148.8 (s), 161.9 (s), 170.4 (s). Anal. Calcd for $C_{31}H_{38}N_2O_8$: C, 65.71; H, 6.76. Found: C, 65.75; H, 6.59. The structure of **15b** was established unequivocally via single crystal X-ray structural analysis.

Continued elution of the chromatography column afforded isomerically pure **15a** (30 mg, 40%) as a colorless microcrystalline solid: mp 170-171 °C; IR (KBr) 3101 (w), 2980 (w), 2906 (s), 2845 (m), 1733 (m), 1720 (s), 1625 (w), 1544 (m), 1450 (w), 1335 (s), 1268 (m), 1255 (m), 1228 (m), 1153 (m), 722 (w), 709 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.40–1.86 (m, 24 H), 1.86-2.02 (m, 6 H), 2.16 (s, 3 H), 5.01 (*AB*, J_{AB} = 5.6 Hz, 1 H), 5.20 (*AB*, J_{AB} = 5.6 Hz, 1 H), 9.15-9.20 (m, 2 H), 9.22-9.27 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.46 (q), 28.04 (2 C, d), 36.76 (t), 36.81 (t), 37.89 (t), 38.05 (t), 38.53 (s), 79.08 (d), 81.57 (d), 122.6 (d), 129.5 (2 C, d), 133.9 (s), 148.8 (s), 161.8 (s), 170.1 (s). Anal. Calcd for $C_{31}H_{38}N_2O_8$: C, 65.71; H, 6.76. Found: C, 65.79; H, 6.69.

***Z*-1,2-Di(1-adamantyl)ethylene (1a).**[12] A mixture of *meso*-diol **4a** (164 mg, 0.50 mmol), triethyl orthoformate (5 mL, excess) and benzoic acid (5 mg, catalytic amount) was heated at 165 °C for 3 h. The reaction mixture was allowed to cool to room temperature. The reaction mixture was stirred with 10% aqueous Na_2CO_3 (10 mL) and then extracted with EtOAc (3 x 50 mL). The combined organic layers were washed sequentially with water (20 mL) and brine (20 mL), dried ($MgSO_4$), and filtered. The filtrate was concentrated *in vacuo*,

thereby affording **5** (mixture of isomers, 179 mg, 94%); IR (film) 2896 (s), 2844 (m), 1172 (w), 1127 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.30 (t, J = 6.6 Hz, 3 H), 1.69 (br s, 12 H), 1.82 (br s, 12 H), 1.93-2.06 (m, 6 H), 3.98 (s, 2 H), 3.74 (q, J = 14.0, 6.6 Hz, 2 H), 5.60 (s, 1 H). This material was used as obtained in the next synthetic step without further purification.

The crude product was concentrated *in vacuo* to remove any remaining triethyl orthoformate and the residue was heated under argon at 200 °C for 4 h. The reaction mixture was cooled to room temperature, quenched by addition of 10% aqueous Na_2CO_3 (30 mL), and the resulting aqueous suspension extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were washed sequentially with water (2 x 30 mL) and brine (30 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified *via* column chromatography on silica gel by eluting with hexane. Pure **1a** (133 mg, 90%) was thereby obtained as a colorless microcrystalline solid: mp 141-142 °C; IR (KBr) 2902 (s), 2894 (s), 2890 (s), 2843 (m), 1442 (w), 1335 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.62-1.72 (m, 12 H), 1.75-1.82 (m, 12 H), 1.95 (br s, 6 H), 4.95 (s, J = 15.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.92 (d), 35.11 (s), 36.74 (t), 44.00 (t), 140.4 (d). Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 88.85; H, 10.86.

***E*-1,2-Di(1-adamantyl)ethylene (1b).**[13] To a solution of **1a** (120 mg, 0.40 mmol) in xylene (8 mL) was added a few crystals of I_2, and the resulting mixture was refluxed for 24 h. The reaction mixture then was cooled and concentrated *in vacuo*. Hexane (50 mL) was added to the residue, and the resulting mixture was washed sequentially with saturated $Na_2S_2O_3$ (3 x 30 mL) and water (2 x 30 mL), dried ($MgSO_4$), and filtered. The filtrate was concentrated *in vacuo*, thereby affording **1b** (120 mg, 100%) as a colorless microcrystalline solid: mp >278 °C dec. (lit.[14] mp: >260 °C subl.); IR (KBr) 2906 (s), 2844 (m), 1448 (w), 1342 (w), 1305 (w), 1092 (w), 969 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.49-1.55 (m, 13 H), 1.58 (t, J = 3.2 Hz, 1 H), 1.62-1.72 (m, 9 H), 1.74 (t, J = 3.2 Hz, 1 H), 1.96 (br s, 6 H), 5.10 (s, J = 16.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.68 (d), 34.12 (s), 37.03 (t), 42.73 (t), 136.3 (d). Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 89.08; H, 10.63.

Dichlorocarbene Addition to *Z*-1,2-Di(1-adamantyl)ethene (1a). To a stirred solution of **1a** (200 mg, 0.67 mmol) in $CHCl_3$ (40 mL) was added sequentially triethylbenzeneamonium chloride (TEBAC, 80 mg) and 50% aqueous NaOH (16 mL), and the resulting mixture was heated with stirring at 45 °C for 8 h. Water (200 mL) was added, and the layers were separated. The aqueous layer was washed with $CHCl_3$ (3 x 60 mL). The combined organic layers were washed sequentially with 1% aqueous HCl (50 mL), water (2 x 200 mL), and brine (200 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with pentane. Workup of the individual chromatography fractions afforded recovered (unreacted) **1a** (40 mg, 20%) along with three reaction products (**6**, **7**, and **8**, respectively).

Thus, **6** (70 mg, 27%) was obtained as a colorless microcrystalline solid: mp 100.5-101.5 °C; IR (nujol) 2942 (vs), 2896 (s), 2856 (vs), 1458 (m), 1452 (m), 1378 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.50-1.82 (m, 24 H), 1.90-2.00 (3 H), 2.08-2.18 (m, 2 H), 4.98 (s, 2 H), 5.43 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 28.75 (d), 28.89 (d), 35.25 (s), 35.56 (s), 35.62 (t), 36.70 (t), 41.89 (s), 43.02 (t), 43.54 (t), 44.00 (t), 83.73 (d), 138.6 (d), 141.4 (d). Anal. Calcd for $C_{23}H_{32}Cl_2$: C, 72.81; H, 8.50. Found: C, 72.61; H, 8.38.

Compound **7** (50 mg, 20%) was obtained as a colorless microcrystalline solid: mp 138-139 °C; IR (nujol) 2929 (vs), 2856 (s), 1458 (m), 1452 (m), 1378 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.50-1.74 (m, 16 H), 1.74-1.88 (m, 3 H), 1.88-2.07 (m, 11 H), 4.03 (s, 1 H), 5.48 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 28.50 (d), 28.55 (d), 35.48 (s), 36.75 (t), 38.24 (s), 39.46 (t), 40.98 (t), 77.76 (d), 128.9 (s), 139.9 (d); Anal. Calcd for $C_{23}H_{32}Cl_2$: C, 72.81; H, 8.50. Found: C, 72.79; H, 8.35.

Compound **8** (64 mg, 21%) was also obtained as a colorless microcrystalline solid: mp 196-197 °C; IR (nujol) 2922 (vs), 2856 (s), 1458 (m), 1452 (m), 1378 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.51 (s, 1 H), 1.64-1.74 (m, 13 H), 1.74-1.82 (m, 2 H), 1.91-2.08 (m, 15 H), 3.58 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 28.38 (d), 28.57 (d), 36.68 (t), 38.47 (s), 39.94 (s), 40.25 (t), 41.39 (t), 51.91 (d), 57.68 (s), 66.93 (s), 78.72 (d), Anal. Calcd for $C_{24}H_{32}Cl_4$: C, 62.35; H, 6.98. Found: C, 62.35; H, 6.97. The structures of **6** and **7** were established unequi-vocally *via* single crystal X-ray structural analysis.

Dichlorocarbene Addition to *E*-1,2-Di(1-adamantyl)ethene (1b). To a stirred solution of **1b** (150 mg, 0.51 mmol) in $CHCl_3$ (30 mL) were added sequentially TEBAC (60 mg) and 50% aqueous NaOH (12 mL), and the resulting mixture was heated with stirring at 45 °C for 8 h. Water (150 mL) was added, and the layers were separated. The aqueous layer was washed with $CHCl_3$ (3 x 40 mL). The combined organic layers were washed sequentially with 1% aqueous HCl (30 mL), water (2 x 150 mL), and brine (150 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with pentane. Workup of the individual chromatography fractions afforded recovered (unreacted) **1b** (92 mg, 61%) along with two reaction products (**9** and **10**, respectively).

Thus, **9** (65 mg, 34%) was obtained as a colorless microcrystalline solid: mp 122-122.5 °C; IR (nujol) 2929 (vs), 2856 (s), 1458 (m), 1451 (m), 1378 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.43-1.76 (m, 25 H), 1.88-2.01 (m, 3 H), 2.08-2.20 (m, 2 H), 5.13 (s, 1 H), 5.42 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 28.53 (d), 28.62 (d), 34.27 (s), 34.81 (s), 35.87 (t), 36.99 (t), 37.23 (t), 41.70 (t), 41.77 (s), 42.64 (t), 42.69 (t), 83.76 (d), 134.8 (d), 137.3 (d). Anal. Calcd for $C_{23}H_{32}Cl_2$: C, 72.81; H, 8.50. Found: C, 72.92; H, 8.44.

Compound **10** (12 mg, 5%) was also obtained as a colorless microcrystalline solid: mp 172-173 °C; IR (nujol) 2929 (vs), 2856 (s), 1458 (m), 1452 (m), 1378 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 1.43-1.52 (m, 11 H), 1.53-1.69 (15 H), 2.09-2.18 (m, 4 H), 5.18 (s, 2 H), 5.42 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.94 (d), 35.39 (s), 36.28 (t), 37.69 (t), 42.07 (t), 42.20 (s), 42.97 (t), 84.16 (d), 136.3 (d). Anal. Calcd for $C_{24}H_{32}Cl_4$: C, 62.35; H, 6.98. Found: C, 62.10; H, 6.85. The structure of **10** was identified *via* single crystal X-ray structural analysis.

X-ray Structure Analysis of 6, 7, 10, and 15b. X-ray structure data for **6, 7, 10,** and **15b** are presented in Table 1. X-ray structure data for **6, 7,** and **10** were collected on an Enraf-Nonius CAD-4 diffractometer by using the ω -2θ scan technique, Mo Kα radiation (λ = 0.71073 Å), and a graphite monochromator. All data for **15b** were collected on an Enraf-Nonius CAD-4 diffractometer by using the ω scan technique, Mo Kα radiation (λ = 0.71073 Å), and a graphite monochromator. Standard procedures used in our laboratory have been described previously.[15] Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods [SHELX86[16] (**15b**) and SIR[17] (**6, 7,** and **10**)], and the model was refined by using full-matrix least squares techniques. The treatment of thermal parameters was based upon the number of observed data. Anisotropic parameters were incorporated for the Cl atoms in **6**, whereas sufficient data were available for **7** and **10** to enable anisotropic treatment of all non-hydrogen atoms. Due to a lack of data for **15b**, only the oxygen atoms were refined with anisotropic thermal parameters. The remaining non-hydrogen atoms in this molecule were refined with isotropic thermal parameters. In all cases, hydrogen atoms were located on difference maps and then included in the model in idealized positions [U(H) = 1.3 B_{eq}(C)]. All computations other than those specified were performed by using MolEN.[18] Scattering factors were taken from the usual sources.[19]

Acknowledgment. We thank the Office of Naval Research (Grant N00014-94-1-1039 to A. P. M.), the United States Air Force (Contract F29601-92-K-0018 to A. P. M.), the Robert A. Welch Foundation (Grants B-963 to A. P. M., B-1202 to S. G. B.), and the University of North Texas Faculty Research Committee (S. G. B.) for financial support of this study.

References and Footnotes

1. A portion of this study has been communicated previously; see: Marchand, A. P.; Xing, D.; Bott, S. G.; Ogawa, K.; Harada, J. *Tetrahedron Lett.* **1994**, *35*, 8935.
2. (a) Bellucci, G.; Bianchini, R.; Chiappe, C.; Gadgil, V. R.; Marchand, A. P. *J. Org. Chem.* **1993**, *58*, 3575. (b) Marchand, A. P.; Sorokin, V. D.; Rajagopal, D.; Bott, S. G. *Tetrahedron* **1994**, *50*, 9933.
3. (a) Makosza, M. *Tetrahedron Lett.* **1969**, 673, 677. (b) Makosza, M.; Wawrzyniewicz, M. *Tetrahedron Lett.* **1969**, 4659.
4. Rol, N. C.; Clague, A. D. H. *Org. Magn. Reson.* **1981**, *16*, 187.
5. Burke, J. J.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1964**, *86*, 1870.
6. (a) Likhotvorik, I. R.; Yuan, K.; Brown, D. W.; Krasutskii, P. A.; Smyth, N.; Jones, M., Jr. *Tetrahedron Lett.* **1992**, *33*, 911. b) Tabushi, I.; Yoshida, Z.-i.; Takahashi, N. *J. Am. Chem. Soc.* **1970**, *92*, 6670. (c) Dehmlow, E. V. *Tetrahedron* **1971**, *27*, 4071. (d) Paquette, L. A.; Kobayashi, T.; Gallucci, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 1305.

7. See: Schleyer, P. von R.; Sliwinski, W. F.; Van Dine, G. W.; Schöllkopf, U.; Paust, J.; Fellenberger, K. *J. Am. Chem. Soc.* **1972**, *94*, 125 and references cited therein.
8. See: (a) Closs, G. L. *Top. Stereochem.* **1968**, *3*, 193. (b) Zefirov, N. S.; Kazimirchik, I. V.; Lukin, K. A. *Cycloaddition of Dichlorocarbene to Olefins*, Nauka: Moscow, 1985.
9. Hallis, G. *J. Chem. Soc. B* **1967**, 91.
10. Stetter, H.; Rauscher, E. *Chem. Ber.* **1960**, *93*, 1161.
11. Bott, S. G.; Marchand, A. P.; McGuffey, A. R.; Xing, D. *J. Chemical Crystallography* **1995**, *25*, 291.
12. (a) Crank, G.; Eastwood, F. W. *Aust. J. Chem.* **1964**, *17*, 1392. (b) Block, E. In: Organic Reactions, Dauben, W. G., Ed., John Wiley & Sons: New York, 1984, Vol. 30, pp. 457-482.
13. Deter, D. F.; Chu, Y. W. *J. Am. Chem. Soc.* **1955**, *77*, 4410.
14. Adam, W.; Martinez, G.; Thompson, J. *J. Org. Chem.* **1981**, *46*, 3359.
15. Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.
16. Sheldrick, G. M. In *Crystallographic Computing*, Sheldrick, G. M.; Krüger, C.; Goddard, R., Eds., Oxford University Press, 1985, pp. 184-189.
17. Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Cryst.* **1989**, *22*, 389.
18. *MolEN, An Interactive Structure Solution Program*; Enraf-Nonius: Delft, The Netherlands; 1990.
19. Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham; 1974; Vol. IV, Table 2.

Table 1. X-ray structure data for **6**, **7**, **10**.and **15b**

Compound	**6**	**7**	**10**	**15b**
Formula	$C_{23}H_{32}Cl_2$	$C_{23}H_{32}Cl_2$	$C_{24}H_{32}Cl_4$	$C_{31}H_{38}N_2O_8$
Size (mm)	0.22 × 0.22 × 0.24	0.08 × 0.09 × 0.56	0.31 × 0.38 × 0.44	0.08 × 0.05 × 0.21
Space Group	P-1 bar	P-1 bar	$P2_1/c$	$P2_1/c$
a (Å)	6.6701 (6)	6.4800 (5)	10.0991 (7)	15.060 (2)
b (Å)	11.7448 (8)	11.147 (1)	7.2903 (7)	10.260 (2)
c (Å)	13.553 (1)	14.066 (1)	15.254 (1)	20.203 (2)
α (°)	106.638 (7)	80.104 (8)		
β (°)	98.745 (7)	89.352 (7)	99.917 (6)	111.79 (1)
γ (°)	98.968 (7)	83.742 (7)		
V (Å^3)	982.9 (2)	994.9 (2)	1106.3 (2)	2898.6 (6)
Z	2	2	2	4
D_c (g-cm^{-3})	1.282	1.266	1.388	1.298
μ (cm^{-1})	3.33	3.29	5.46	0.88
$(2\theta_{max})$	44	44	44	44
Total refl.	2399	2419	1573	5205
Unique refl.	2399	2419	1489	3556
R_{int}	- -	- -	0.027	0.041
$I \geq 3\sigma(I)$	1677	1062	982	954
Parameters	226	111	127	205
R, wR	0.0470, 0.0472	0.0482, 0.0701	0.0409, 0.0417	0.0636, 0.0638
$(\Delta/\sigma)_{max}$	<0.01	<0.01	<0.01	<0.01
ρ_{min}; ρ_{max}	0.36, -0.32	0.23, -0.30	0.28, -0.30	0.29, -0.26

(*Received in USA* 20 *July* 1995; *accepted* 20 *October* 1995)