Dihalogenation of *gem*-Aryl-Disubstituted Methylenecyclopropanes by DEAD, DIAD/TiX_4 or Free Halogen

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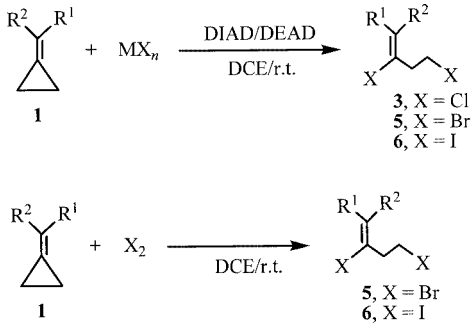
The reaction of *gem*-aryl-disubstituted methylenecyclopropanes with TiX_4/diethyl azodicarboxylate and TiX_4/diisopropyl azodicarboxylate in 1,2-dichloroethane gave the dihalogenated ring-opened product, 2,4-dihalobut-1-ene, in moderate-to-excellent yields under mild conditions. On the basis of the proposed Orton-type mechanism, we found that this reaction can also be carried out with free halogens such as bromine or iodine to give the same products in good yields.

Introduction

Methylenecyclopropanes (MCPs) **1** are highly strained but readily accessible molecules that have served as useful building blocks in organic synthesis. MCPs **1** undergo a variety of ring-opening reactions because the relief of ring strain provides a potent thermodynamic driving force.[1] Transition-metal-catalyzed (such as Pd, Rh, Ru, and Pt) reactions of MCPs **1** with various reactants have attracted much attention.[2,3] In the Lewis acid catalyzed ring-opening reactions of MCPs **1**, we have found that the propane ring of MCPs **1** can be opened with the use of alcohols and other nucleophiles by a different, novel mechanism to give the corresponding homoallylic derivatives in good yields under mild conditions.[4,5] For example, the reaction of MCPs **1** with titanium(IV) chloride ($TiCl_4$) in dichloromethane (DCM) produced the corresponding homoallylic chlorides in good yields at room temperature. This interesting result encouraged us to investigate further the Lewis acid catalyzed reactions of MCPs **1** with other reactants. Previously we reported the ring expansion of MCPs **1** in the presence of $Zr(OTf)_4$ (Lewis acid) and diethyl azodicarboxylate (DEAD) or diisopropyl azodicarboxylate (DIAD) under mild conditions.[6]

In this paper we report a new transformation of MCPs using TiX_4/DEAD or TiX_4/DIAD. In this system, the dihalogenation/ring-opening reaction of MCPs **1** in the presence of metal halides (Lewis acids) and DEAD or DIAD in 1,2-dichloroethane (DCE) occurred under mild conditions to give 2,4-dihalobut-1-enes **3** (X = Cl), **5** (X = Br) and **6** (X = I) as products in moderate-to-excellent yields (Scheme 1).[7] In addition, on the basis of the proposed Orton-type mechanism, we further found that these ring-opening reactions can also be carried out with free halogens to give the same products under mild conditions (Scheme 1).



Scheme 1

Results and Discussion

Initially we carried out the reaction of (diphenylmethylene)cyclopropane (**1a**, 0.2 mmol) with various metal halides (0.24 mmol) in the presence of DEAD (40% in toluene) (0.2 mmol) in 1,2-dichloroethane (DCE) at room temperature.

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Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

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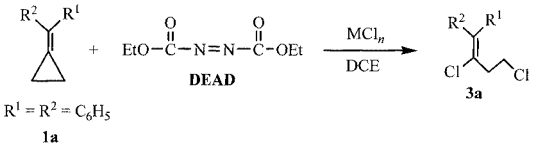
Table 1. The effects of various metal chlorides (0.24 mmol) on the dichlorination of MCP **1a** (0.2 mmol) in the presence of DEAD (0.2 mmol) in DCE



entry	Lewis acid[a]	yield (%)[b]
1	–	NR
2	$ZnCl_2$	Disordered Reaction
3	$MgCl_2$	Disordered Reaction
4	$CuCl_2$	Disordered Reaction
5	$YbCl_3$	Disordered Reaction
6	$BiCl_3$	Disordered Reaction
7	$LaCl_3$	Disordered Reaction
8	$AlCl_3$	Disordered Reaction
9	$TiCl_4$	67
10[c]	$TiCl_4$	64
11[d]	$TiCl_4$	71

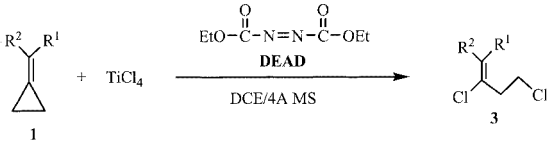
[a] 1.2 equiv. of metal chloride (Lewis acid) was used. [b] Isolated yields. [c] $TiCl_4$ (1.0 mL) in CH_2Cl_2 (1 mol·L^{-1}, 5.0 equiv.) was used as the promoter and solvent. [d] $TiCl_4$ (0.5 mL) in CH_2Cl_2 (1 mol·L^{-1}, 2.5 equiv.) was used as the promoter and solvent (0.5 mL) was added.

The results are summarized in Table 1. No major product was obtained with DEAD in the presence of metal halides such as $ZnCl_2$, $MgCl_2$, $CuCl_2$, $YbCl_3$, $BiCl_3$, $LaCl_3$ and $AlCl_3$ (Table 1, entries 2−8). The reaction only proceeded smoothly to give the corresponding 1,1-diphenyl-2,4-dichlorobut-1-ene **3a** in good yields in the presence of $TiCl_4$. Increasing the amount of $TiCl_4$ did not significantly improve the yields of **3a** (Table 1, entries 9−11).

Next, we utilized $TiCl_4$ as the Lewis acid reagent (0.24 mmol) to examine this dichlorination reaction with various MCPs **1** (0.2 mmol) in the presence of DEAD (40% in toluene) (0.2 mmol). The results are shown in Table 2. With MCPs **1b** and **1d**−**g** (both R^1 and R^2 are aromatic groups), the reactions proceeded smoothly to give the dichlorinated products **3b** and **3d**−**g** in moderate-to-good yields (Table 2, entries 1 and 3−6). With the unsymmetric MCPs **1b** and **1e**, the corresponding dichlorinated products **3b** and **3e** were obtained as mixtures of *E* and *Z* isomers (Table 2, entries 1 and 4). With MCP **1h** (R^1 is an aromatic group and R^2 is a hydrogen atom), this reaction also proceeded smoothly to give the corresponding dichlorinated product **3h** as the *Z* isomer in 15% yield (Table 2, entry 7). The identity of the *Z* isomer of **3h** was determined by ^{1}H NMR NOESY spectroscopic data (see the Supporting Information). With MCP **1c** (R^1 is an aromatic group and R^2 is a methyl group), the desired product was not obtained (Table 2, entry 2).

We found that different solvents and substituents on the benzene ring of the MCP can significantly affect the nature of the reaction products of this novel dihalogenation/ring-opening reaction. The results are summarized in Table 3. When the reaction was carried out in CH_3CN, homoallylic chloride **2** was obtained as the major product in many cases along with dichlorinated product **3** or the ring-expansion product **4**[6] (Table 3, entries 1−3). With MCP **1a** in CH_3CN, homoallylic chloride **2a** was obtained in 89% yield (Table 3, entry 1). With MCP **1d** (electron-donating substituent on the benzene ring of the MCP) in CH_3CN, the homoallylic chloride **2d** was obtained in 38% yield along with the ring-expansion product **4d** in 7% yield (Table 3, entry 2). With MCP **1f** (electron-withdrawing substituent on the benzene ring of the MCP) in CH_3CN, the dichlorinated product **3f** was obtained in 12% yield along with homoallylic chloride **2f** in 32% yield (Table 3, entry 3). When the reaction was carried out in Et_2O, the dichlorinated product **3** was obtained in low yields for all of the employed MCPs, **1a**, **1d** and **1f** (Table 3, entries 4−6). With substrate **1a** and **1d** (electron-donating substituents on the benzene ring of the MCP), the ring-expansion product **4** was obtained along with the dichlorination product **3** (Table 3, entries 4 and 5). With substrate **1f** (electron-withdrawing substituent on the benzene ring of the MCP), the

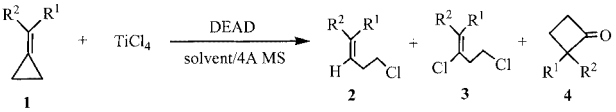
Table 2. Dichlorination of MCPs **1** (0.2 mmol) in the presence of $TiCl_4$ (0.24 mmol) and DEAD (0.2 mmol) in DCE



entry	R^1/R^2	substrate	yield (%)[a]
1	C_6H_5/*p*-$MeOC_6H_4$	**1b**	**3b**, 44 (1:1)[b]
2	*p*-$EtOC_6H_4$/Me	**1c**	Disordered reaction
3	*p*-MeC_6H_4/*p*-MeC_6H_4	**1d**	**3d**, 62
4	C_6H_5/*o*-ClC_6H_4	**1e**	**3e**, 58 (1:1)[b]
5	*p*-ClC_6H_4/*p*-ClC_6H_4	**1f**	**3f**, 77
6	*p*-FC_6H_4/*p*-FC_6H_4	**1g**	**3g**, 70
7	*p*-$MeOC_6H_4$/H	**1h**	**3h**, 15

[a] Isolated yields. [b] Mixtures of *E* and *Z* isomers were obtained.

Table 3. The effect of solvent on the dichlorination of MCPs **1** (0.2 mmol) in the presence of $TiCl_4$ (0.24 mmol) and DEAD (0.2 mmol) in DCE



entry	R^1/R^2	substrate	solvent	yield (%)[a]		
				2	**3**	**4**
1	C_6H_5/C_6H_5	**1a**	CH_3CN	**2a**, 89	–	–
2	*p*-MeC_6H_4/*p*-MeC_6H_4	**1d**	CH_3CN	**2d**, 38	–	**4d**, 7
3	*p*-ClC_6H_4/*p*-ClC_6H_4	**1f**	CH_3CN	**2f**, 32	**3f**, 12	–
4	C_6H_5/C_6H_5	**1a**	Et_2O	–	**3a**, 29	**4a**, 50
5	*p*-MeC_6H_4/*p*-MeC_6H_4	**1d**	Et_2O	–	**3d**, 26	**4d**, 40
6	*p*-ClC_6H_4/*p*-ClC_6H_4	**1f**	Et_2O	–	**3f**, 46	–

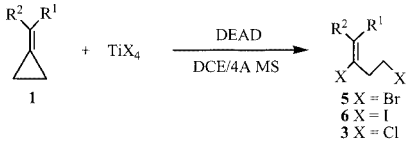
[a] Isolated yields.

dichlorinated product **3f** was obtained as the sole product in moderate yield (Table 3, entry 6). At this stage, we cannot explain such solvent and substituents effects on this reaction. However, by using Et_2O or MeCN as the solvent, the differences in the coordination of the solvent to the $TiCl_4$ promoter may affect the activity of the latter in this reaction.

In order to complete this set of dihalogenation/ring-opening reactions with MCPs **1**, we carried out the dibromination/diiodination ring-opening reactions of MCPs **1** (0.2 mmol) in the presence of DEAD (40% in toluene) (0.2 mmol). The results are shown in Table 4. With MCPs **1a**, **1d** and **1f** (both R^1 and R^2 are aromatic groups), the reactions proceeded smoothly to give the dibrominated and diiodinated products **5a**, **5d**, **5f**, **6a**, **6d** and **6f** in high-to-excellent yields (Table 4, entries 1−6). By using diisopropyl azodicarboxylate (DIAD) as the reagent under the same conditions, similar results were obtained to those obtained with DEAD. The results are also shown in Table 4. With MCPs **1a**, **1d** and **1f** (0.2 mmol) in the presence of DIAD (0.2 mmol) and $TiCl_4$ (0.24 mmol), the dichlorinated products **3a**, **3d** and **3f** were obtained in 61, 75 and 87%, respectively (Table 4, entries 7−9). The slight difference in yields may be due to the fact that the presence of toluene in the DEAD solution affects this reaction to some extent.

A plausible mechanism for the dihalogenation/ring-opening reaction of MCPs **1** promoted by TiX_4 and DEAD or DIAD, based on the Orton rearrangement mechanism, is shown in Scheme 2.[8] The Lewis acid (TiX_4) activates DEAD and an X^- anion from the Lewis acid promoter (TiX_4) attacks the N=N double bond in a manner similar to a Michael addition to give the intermediate **A**. Intramolecular attack by X^- gives X_2 and intermediate **B** which is hydrolysed to give 1,2-bis(ethoxycarbonyl)hydrazine. The formation of 1,2-bis(ethoxycarbonyl)hydrazine was confirmed by GLC and GC-MS (see Supporting Information). The ring-opening of MCPs **1** by reaction with X_2 furnishes the dihalogenated products.

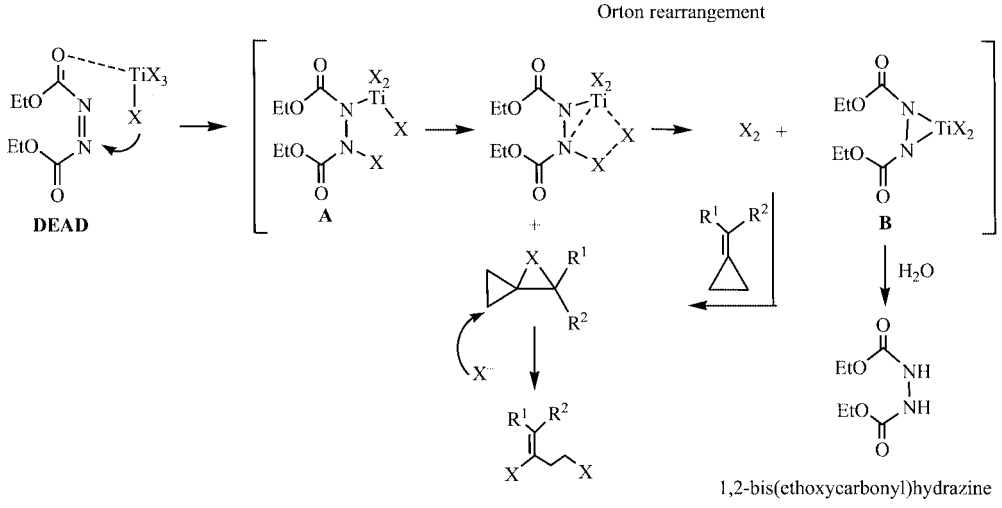
Table 4. Dihalogenation of MCPs **1** (0.2 mmol) in the presence of TiX_4 (X = Cl, Br, I) (0.24 mmol) and azo compound (0.2 mmol) in DCE



entry	R^1/R^2	halogen (X)	azo compound	yield (%)[a]
1	C_6H_5/C_6H_5 (**1a**)	Br	DEAD	**5a**, 82
2	*p*-MeC_6H_4/*p*-MeC_6H_4 (**1d**)	Br	DEAD	**5d**, 71
3	*p*-ClC_6H_4/*p*-ClC_6H_4 (**1f**)	Br	DEAD	**5f**, 83
4	C_6H_5/C_6H_5 (**1a**)	I	DEAD	**6a**, 98
5	*p*-MeC_6H_4/*p*-MeC_6H_4 (**1d**)	I	DEAD	**6d**, 99
6	*p*-ClC_6H_4/*p*-ClC_6H_4 (**1f**)	I	DEAD	**6f**, 99
7	C_6H_5/C_6H_5 (**1a**)	Cl	DIAD	**3a**, 61
8	*p*-MeC_6H_4/*p*-MeC_6H_4 (**1d**)	Cl	DIAD	**3d**, 75
9	*p*-ClC_6H_4/*p*-ClC_6H_4 (**1f**)	Cl	DIAD	**3f**, 87

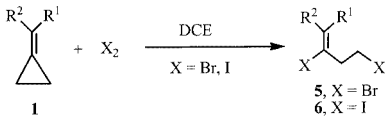
[a] Isolated yields.

In order to clarify the proposed mechanism, we attempted the dibrominated and diiodinated ring-opening reactions of some MCPs **1** (0.2 mmol) with Br_2 [9] and I_2 (0.2 mmol), respectively, under similar conditions. The results are summarized in Table 5. We found that these reactions proceeded smoothly to give the dibrominated or diiodinated product **5** or **6** in good-to-high yields (Table 5, entries 1−8). With the symmetric MCPs **1a**, **1d**, **1f** and **1i** (both R^1 and R^2 are aromatic groups), these reactions proceeded very well to give the dibrominated or diiodinated product **5** or **6** in high yields (Table 5, entries 1−4, 6−8). The electron-donating and electron-withdrawing substituents on the benzene ring of MCPs **1** had a small effect on this reaction in DCE. With the unsymmetric MCP **1c** (R^1 is an aromatic group and R^2 is an aliphatic group), the reaction also proceeded smoothly but gave the product in a somewhat lower



Scheme 2

Table 5. Dihalogenation of MCPs **1** (0.2 mmol) by Br_2 or I_2 (0.2 mmol) in DCE



entry	R^1/R^2	substrate	X	yield (%)[a]
1	C_6H_5/C_6H_5	**1a**	Br	**5a**, 83
2	*p*-MeC_6H_4/*p*-MeC_6H_4	**1d**	Br	**5d**, 93
3	*p*-ClC_6H_4/*p*-ClC_6H_4	**1f**	Br	**5f**, 66
4	C_6H_5/C_6H_5	**1a**	I	**6a**, 88
5	*p*-$EtOC_6H_4$/Me	**1c**	I	**6c**, 27
6	*p*-MeC_6H_4/*p*-MeC_6H_4	**1d**	I	**6d**, 90
7	*p*-ClC_6H_4/*p*-ClC_6H_4	**1f**	I	**6f**, 92
8	*p*-$MeOC_6H_4$/*p*-$MeOC_6H_4$	**1i**	I	**6i**, 90

[a] Isolated yields.

yield (27%) as the *E* isomer, as determined by ^{1}H NMR NOESY spectroscopy (see Supporting Information) (Table 5, entry 5). Therefore, it is clear that free halogens can indeed react with MCPs **1** to give the dihalogenated ring-opened products. This result suggests that the halogen generated in the reaction of TiX_4 and DEAD or DIAD is the real reagent for this type of dihalogenation transformation.

In conclusion, we have disclosed a new transformation of MCPs **1** in the presence of TiX_4/DEAD or TiX_4/DIAD to give the corresponding dihalogenated products in moderate-to-excellent yields. The ring-opening mode in this MCPs system is due to the influence of aryl substituents on the stability of the intermediate halogenaspiropentyl cation shown in Scheme 2. The stabilized cation readily undergoes nucleophilic attack by another halogen to give the dihalogenation/ring-opened products **3**, **5** and **6**. It is interesting that the dihalogenation of MCPs **1** is achieved in the presence of titanium(IV) halides and DEAD or DIAD under mild conditions. On the basis of the proposed Orton-type mechanism, we have also disclosed that free halogens, such as bromine and iodine, are good reagents for the ring-opening reaction of the MCPs reported in this paper and give the dihalogenated ring-opened products in good yields under mild conditions. Efforts are underway to elucidate the mechanistic details of the reaction and to disclose its scope and limitations. Work along this line is currently in progress.

Experimental Section

General Remarks: ^{1}H NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard. Infrared spectra were measured on a Perkin-Elmer 983 spectrometer. Mass spectra were recorded on a HP-5989 instrument and HRMS spectra were measured on a Finnigan MA^+ mass spectrometer. Satisfactory CHN microanalyses were obtained with a Carlo−Erba 1106 analyzer. Melting points are uncorrected. All reactions were monitored by TLC with Huanghai GF_{254} silica-gel-coated plates. Flash column chromatography was carried out using 300−400 mesh silica gel.

General Reaction Procedure for the Reaction of MCPs 1 in the Presence of TiX_4 and DEAD: Under an argon atmosphere, MCPs **1** (0.20 mmol), DEAD (0.20 mmol), Lewis acid promoter (0.24 mmol) and 1,2-dichloroethane (1.0 mL) were added to a Schlenk reaction tube. The mixture was stirred at room temperature for about 8 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2).

General Reaction Procedure for the Reaction of MCPs 1 with Bromine: Under an ambient atmosphere, MCPs **1** (0.20 mmol), bromine (0.20 mmol) and 1,2-dichloroethane (1.0 mL) were added to a Schlenk reaction tube. The mixture was stirred at room temperature for about 8 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2).

2,4-Dichloro-1,1-diphenylbut-1-ene (3a): A yellow solid; m.p. 64−67 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 3940, 3044, 2978, 2304, 1494, 1442, 1265, 739 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.89 (t, J = 6.6 Hz, 2 H), 3.77 (t, J = 6.6 Hz, 2 H), 7.19−7.32 (m, 10 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 39.0, 41.9, 127.4, 127.5, 128.0, 128.5, 128.9, 129.1, 129.2, 140.2, 140.7, 141.8 ppm. MS (%): *m*/*z* = 278 (100), 277 (26.35), 276 [M^+] (100), 227 (100), 191 (100). HRMS calcd. for $C_{16}H_{14}Cl_2$: 276.0473; found: 276.0445.

2,4-Dichloro-1-methoxyphenyl-1-phenylbut-1-ene (3b): A pale yellow solid, mixture of *E* and *Z* isomers (1:1); m.p. 73−75 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 3956, 3059, 2970, 2311, 1605, 1416, 1265, 895, 742 cm^{-1}. *E* or *Z* isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.87−2.94 (m, 2 H), 3.76−3.80 (m, 5 H, CH_2 + OCH_3), 6.84−7.12 (m, 2 H, Ar), 7.19−7.34 (m, 7 H, Ar) ppm. *Z* or *E* isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.87−2.94 (m, 2 H), 3.76−3.80 (m, 5 H, CH_2 + OCH_3), 6.84−7.12 (m, 2 H, Ar), 7.19−7.34 (m, 7 H, Ar) ppm. *E* or *Z* isomer: ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 39.2, 42.0, 55.2, 113.8, 127.5, 128.2, 128.4, 129.2, 130.7, 133.0, 141.0, 141.4, 158.9 ppm. *Z* or *E* isomer: ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 39.1, 42.0, 55.1, 113.3, 127.3, 128.0, 128.4, 129.1, 130.3, 132.5, 140.5, 141.3, 158.7 ppm. MS (%): *m*/*z* = 308 (54.71), 307 (22.56), 306 [M^+] (3.71), 257 (100), 222 (82.84). HRMS calcd. for $C_{17}H_{16}Cl_2O$: 306.0573; found: 306.0565.

2,4-Dichloro-1,1-bis(4-methylphenyl)but-1-ene (3d): A glutinous yellow liquid. IR (CH_2Cl_2): $\tilde{\nu}$ = 3941, 3054, 2978, 2304, 1422, 1265, 896, 746 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.33 (s, 6 H, $2CH_3$), 2.90 (t, J = 7.2 Hz, 2 H), 3.77 (t, J = 7.2 Hz, 2 H), 7.03−7.21 (m, 8 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 21.16, 21.23, 39.2, 42.0, 126.2, 128.1, 128.7, 128.9, 129.1, 129.3, 137.1, 137.2, 137.5, 138.0 ppm. MS (%): *m*/*z* = 306 (52.43), 305 (19.25), 304 [M^+] (81.20), 255 (86.81), 219 (100), 205 (97.66). HRMS calcd. for $C_{18}H_{18}Cl_2$: 304.0780; found: 304.0773.

2,4-Dichloro-1-(2-chlorophenyl)-1-phenylbut-1-ene (3e): A bright yellow liquid, mixture of *E* and *Z* isomers (1:1). IR (CH_2Cl_2): $\tilde{\nu}$ = 3941, 3059, 2978, 2296, 1412, 1265, 891, 739 cm^{-1}. *E* or *Z* isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.69−2.79 (m, 2 H), 3.65−3.87 (m, 2 H), 7.23−7.40 (m, 9 H, Ar) ppm. *Z* or *E* isomer: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.69−2.79 (m, 2 H), 3.65−3.87 (m, 2 H), 7.23−7.40 (m, 9 H, Ar) ppm. *E* or *Z* isomer: ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 39.4, 41.7, 126.8, 127.4, 127.8, 128.1, 128.4, 128.9, 129.5, 129.7, 130.2, 130.0, 138.1, 138.3

ppm. *Z* or *E* isomer: ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 38.2, 41.5, 126.8, 127.0, 127.6, 127.9, 128.2, 128.8, 129.2, 129.6, 129.93, 130.00, 131.2, 138.7 ppm. MS (%): *m/z* = 312 (68.98), 311 (20.55), 310 [M^+] (70.73), 225 (100). HRMS calcd. for $C_{16}H_{13}Cl_3$: 310.0077; found: 310.0064.

2,4-Dichloro-1,1-bis(4-chlorophenyl)but-1-ene (3f): A yellow liquid. IR (CH_2Cl_2): $\tilde{\nu}$ = 3941, 3052, 2993, 2311, 1490, 1416, 1265, 896, 749 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.91 (t, *J* = 6.6 Hz, 2 H), 3.81 (t, *J* = 6.6 Hz, 2 H), 7.15 (d, *J* = 11.7 Hz, 2 H, Ar), 7.27 (d, *J* = 8.4 Hz, 2 H, Ar), 7.31 (d, *J* = 6.0 Hz, 2 H, Ar), 7.33 (d, *J* = 5.7 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 38.9, 41.7, 128.4, 128.9, 130.1, 130.6, 130.7, 133.5, 133.9, 138.2, 138.6, 139.6 ppm. MS (%): *m/z* = 346 (100), 344 [M^+] (78.04), 295 (87.49). HRMS calcd. for $C_{16}H_{12}Cl_4$ (M + 2 H − 2 Cl): 276.0473; found (M + 2 H − 2 Cl): 276.0445.

2,4-Dichloro-1,1-bis(4-fluorophenyl)but-1-ene (3g): A glutinous yellow liquid. IR (CH_2Cl_2): $\tilde{\nu}$ = 3956, 3054, 2993, 1601, 1422, 1265, 896, 742 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.89 (t, *J* = 6.3 Hz, 2 H), 3.79 (t, *J* = 6.3 Hz, 2 H), 7.01−7.07 (m, 4 H, Ar), 7.16−7.26 (m, 4 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 38.8, 41.8, 115.1 (d, J_{C-F} = 21.45 Hz), 115.6 (d, J_{C-F} = 21.45 Hz), 129.6, 130.9 (d, J_{C-F} = 13.28 Hz), 131.0 (d, J_{C-F} = 13.35 Hz), 136.0 (d, J_{C-F} = 3.45 Hz), 136.4 (d, J_{C-F} = 3.30 Hz), 139.8, 161.9 (d, J_{C-F} = 246.30 Hz), 162.1 (d, J_{C-F} = 246.30 Hz) ppm. MS (%): *m/z* = 314 (37.62), 312 [M^+] (59.24), 263 (71.74), 227 (100). HRMS calcd. for $C_{16}H_{12}Cl_2F_2$: 312.0279; found: 312.0275.

1-(2,4-Dichlorobut-1-enyl)-4-methoxybenzene (3h): A colorless liquid. IR (CH_2Cl_2): $\tilde{\nu}$ = 3003, 2961, 2934, 1607, 1575, 1511, 1463, 1252, 897, 749 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.89 (t, *J* = 6.9 Hz, 2 H), 3.78 (t, *J* = 6.9 Hz, 2 H), 3.82 (s, 3 H, CH_3O), 6.51 (s, 1 H), 6.89 (d, *J* = 9.0 Hz, 2 H, Ar), 7.59 (d, *J* = 9.0 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 41.8, 44.1, 55.2, 113.6, 126.9, 127.1, 127.6, 130.4, 159.1 ppm. MS (%): *m/z* = 230 [M^+] (73.43), 181 (100). HRMS calcd. for $C_{11}H_{12}Cl_2O$: 230.0265; found: 230.0293.

1-Chloro-4,4-diphenylbut-3-ene (2a): A colorless oil. IR (neat): $\tilde{\nu}$ = 3079, 3024, 2956, 1598, 1494, 1444, 1296, 1029 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.56 (td, *J* = 7.2, 7.2 Hz, 2 H), 3.55 (t, *J* = 7.2 Hz, 2 H), 6.12 (t, *J* = 7.2 Hz, 1 H), 7.23−7.47 (m, 10 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.0, 44.4, 124.8, 127.3, 127.3, 127.4, 128.2, 128.4, 129.8, 139.7, 142.2, 144.4 ppm. MS (EI): *m/z* = 242 [M^+], 193, 180, 165, 115, 104, 91. HRMS (EI) calcd. for $C_{16}H_{15}Cl$: 242.0862; found: 242.0829.

1-Chloro-4,4-bis(4-methylphenyl)but-3-ene (2d): A colorless liquid. IR (CH_2Cl_2): $\tilde{\nu}$ = 3022, 2955, 2921, 2862, 1904, 1747, 1609, 1567, 1511, 1448, 1363, 1295, 1110, 1021 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.29 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 2.58 (q, *J* = 6.9 Hz, 2 H), 3.56 (t, *J* = 6.9 Hz, 2 H), 6.03 (t, *J* = 6.9 Hz, 1 H), 7.04−7.19 (m, 8 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 21.1, 21.2, 33.0, 44. 5, 123.7, 127.2, 127.6, 128.8, 129.0, 130.0, 136.8, 137.0, 139.5, 144.2 ppm. MS (%): *m/z* = 270 [M^+] (51.53), 221 (100). HRMS calcd. for $C_{18}H_{19}Cl$: 270.1175; found: 270.1194.

1-Chloro-4,4-bis(4-chlorophenyl)but-3-ene (2f): A colorless oil. IR (neat): $\tilde{\nu}$ = 3030, 2956, 2925, 1592, 1492, 1401, 1091 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.57 (td, *J* = 6.6, 6.6 Hz, 2 H), 3.58 (t, *J* = 6.6 Hz, 2 H), 6.11 (t, *J* = 6.6 Hz, 1 H), 7.09−7.38 (m, 8 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.0, 44.4, 126.2, 128.6, 128.8, 129.0, 131.3, 133.6, 133.7, 137.8, 140.4, 142.5 ppm. MS (EI): *m/z* = 310 [M^+], 275, 261, 226, 191, 163. HRMS (EI) calcd. for $C_{16}H_{13}Cl_3$: 310.0083; found: 310.0047.

2,2-Diphenylcyclobutanone (4a): A colorless liquid; this is a known compound. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.83 (t, *J* = 8.1 Hz, 2 H, CH_2), 3.15 (t, *J* = 8.1 Hz, 2 H, CH_2), 7.17−7.39 (m, 10 H, Ar) ppm [ref.[10] ^1H NMR ($CDCl_3$, 60 MHz, TMS): δ = 2.76 (t, *J* = 8.5 Hz, 2 H, CH_2), 3.08 (t, *J* = 8.5 Hz, 2 H, CH_2), 7.0−7.8 (m, 10 H, Ar) ppm]. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 25.5, 43.3, 76.1, 126.3, 126.9, 128.7, 142.0, 209.1 ppm. MS (%): *m/z* = 222 [M^+] (1.68), 180 (100).

2,2-Bis(4-methylphenyl)cyclobutanone (4d): A colorless liquid. IR (CH_2Cl_2): $\tilde{\nu}$ = 1781, 1510, 1266, 739 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.28 (s, 6 H, 2 CH_3), 2.78 (t, *J* = 8.7 Hz, 2 H), 3.13 (t, *J* = 8.7 Hz, 2 H), 7.10 (d, *J* = 8.7 Hz, Ar, 4 H), 7.24 (d, *J* = 8.7 Hz, 4 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 21.3, 25.9, 43.6, 75.9, 126.5, 129.6, 136.7, 139.6, 209.7 ppm. MS (%): *m/z* = 250 [M^+] (2.28), 208 (100). HRMS calcd. for $C_{18}H_{18}O$: 250.1358; found: 250.1330.

2,4-Dibromo-1,1-diphenylbut-1-ene (5a): A white solid; m.p. 74−76 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 3933, 3054, 2985, 1486, 1443, 1265, 896, 746 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.07 (t, *J* = 6.9 Hz, 2 H), 3.62 (t, *J* = 6.9 Hz, 2 H), 7.20−7.32 (m, 10 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 31.0, 40.8, 123.2, 127.4, 127.6, 128.1, 128.5, 128.7, 128.8, 140.3, 142.7, 144.9 ppm. MS (%): *m/z* = 367 (16.93), 366 [M^+] (59.88), 192 (100). HRMS calcd. for $C_{16}H_{14}Br_2$: 363.9457; found: 363.9470.

2,4-Dibromo-1,1-bis(4-methylphenyl)but-1-ene (5d): A white solid; m.p. 70−72 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 3941, 3054, 3000, 2296, 1422, 1265, 896, 739 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.33 (s, 6 H, 2 CH_3), 3.08 (t, *J* = 6.9 Hz, 2 H), 3.62 (t, *J* = 6.9 Hz, 2 H), 7.06−7.17 (m, 8 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 21.2, 21.3, 31.2, 41.0, 122.4, 128.6, 128.7, 128.8, 129.2, 137.1, 137.3, 137.6, 134.0, 144.7 ppm. MS (%): *m/z* = 295 (11.53), 294 [M^+] (54.85), 393 (7.46), 220 (100). HRMS calcd. for $C_{18}H_{18}Br_2$: 391.9770; found: 391.9778.

2,4-Dibromo-1,1-bis(4-chlorophenyl)but-1-ene (5f): A white solid; m.p. 78−80 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 3941, 3052, 2970, 2311, 1494, 1420, 1265, 896, 746 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.06 (t, *J* = 6.9 Hz, 2 H), 3.63 (t, *J* = 6.9 Hz, 2 H), 7.12−7.16 (m, 2 H, Ar), 7.19−7.21 (m, 2 H, Ar), 7.29−7.33 (m, 4 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 31.0, 40.5, 124.4, 128.4, 128.8, 130.2, 130.4, 133.6, 133.8, 138.3, 140.6, 142.6 ppm. MS (%): *m/z* = 436 (81.11), 435 (19.89), 434 [M^+] (91.07), 260 (100). HRMS calcd. for $C_{16}H_{12}Br_2Cl_2$: 431.8677; found: 431.8659.

2,4-Diiodo-1,1-diphenylbut-1-ene (6a): A yellow solid; m.p. 68−70 °C. IR (neat): $\tilde{\nu}$ = 3045, 2877, 1954, 1597, 1490, 1245 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.05 (t, *J* = 6.9 Hz, 2 H), 3.36 (t, *J* = 6.9 Hz, 2 H), 7.18−7.36 (m, 10 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 6.2, 44.3, 106.6, 127.51, 127.53, 128.48, 128.50, 128.52, 128.5, 139.9, 146.3, 150.6 ppm. MS (EI): *m/z* = 460 [M^+], 333, 254, 206, 178. HRMS (EI) calcd. for $C_{16}H_{14}I_2$: 459.9185; found: 459.9189.

1-(2,4-Diiodo-1-methylbut-1-enyl)-4-ethoxybenzene (6c): A pale red liquid. IR (CH_2Cl_2): $\tilde{\nu}$ = 3046, 2980, 2918, 2868, 1606, 1570, 1506 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.41 (t, *J* = 6.9 Hz, 3 H), 2.21 (s, 3 H, CH_3), 2.87 (t, *J* = 7.5 Hz, 2 H), 3.22 (t, *J* = 7.5 Hz, 2 H), 4.02 (q, *J* = 6.9 Hz, 2 H), 6.85 (d, *J* = 6.6 Hz, 2 H, Ar), 7.03 (d, *J* = 6.6 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 5.4, 14.8, 32.3, 44.6, 63.3, 104.6, 114.3, 128.4,

132.7, 144.4, 158.0 ppm. MS (%): *m/z* = 442 [M^+] (100), 188 (96.27). HRMS calcd. for $C_{13}H_{16}I_2O$: 441.9291; found: 441.9292.

2,4-Diiodo-1,1-bis(4-methylphenyl)but-1-ene (6d): A yellow solid; m.p. 104−106 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 3941, 3044, 2985, 1416, 1265, 742, 705 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.32 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 3.07 (t, *J* = 6.9 Hz, 2 H), 3.36 (t, *J* = 6.9 Hz, 2 H), 7.08 (t, *J* = 8.1 Hz, 2 H, Ar), 7.13 (s, 6 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 6.4, 21.2, 21.3, 44.4, 105.8, 128.39, 128.42, 128.8, 129.1, 137.15, 137.19, 143.6, 150.5 ppm. MS (%): *m/z* = 488 [M^+] (97.45), 219 (100). HRMS calcd. for $C_{18}H_{18}I_2$: 487.9492; found: 487.9485.

1,1-Bis(4-chlorophenyl)-2,4-diiodobut-1-ene (6f): A yellow solid; m.p. 68−70 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 3948, 3696, 3054, 2993, 2304, 1727, 1501, 1422, 1265, 1095, 896, 746, 705 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.03 (t, *J* = 6.6 Hz, 2 H), 3.36 (t, *J* = 6.6 Hz, 2 H), 7.12 (d, *J* = 8.4 Hz, 2 H, Ar), 7.17 (d, *J* = 8.4 Hz, 2 H, Ar), 7.308 (d, *J* = 8.4 Hz, 2 H, Ar), 7.314 (d, *J* = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 6.4, 43.9, 107.9, 128.6, 128.8, 130.0, 130.1, 133.7, 133.8, 137.9, 144.2, 148.3 ppm. MS (%): *m/z* = 530 (38.25), 528 [M^+] (60.36), 239 (100). HRMS calcd. for $C_{16}H_{12}Cl_2I_2$: 527.8400; found: 527.8418.

2,4-Diiodo-1,1-bis(4-methoxyphenyl)but-1-ene (6i): A yellow solid; m.p. 112−114 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 3046, 2954, 2833, 1605, 1508 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.08 (t, *J* = 7.2 Hz, 2 H), 3.37 (t, *J* = 7.2 Hz, 2 H), 3.80 (s, 6 H, 2 CH_3O), 6.85 (d, *J* = 6.9 Hz, 2 H, Ar), 6.86 (d, *J* = 6.9 Hz, 2 H, Ar), 7.07 (d, *J* = 6.9 Hz, 2 H, Ar), 7.16 (d, *J* = 6.9 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 6.6, 44.5, 55.1, 55.2, 105.5, 113.3, 113.8, 129.9, 130.1, 132.5, 139.0, 149.7, 158.7, 158.8 ppm. MS (%): *m/z* = 520 [M^+] (84.92), 266 (100). HRMS calcd. for $C_{18}H_{18}I_2O_2$: 519.9396; found: 519.9406.

Supporting Information Available: The spectroscopic data of the compounds shown in Tables 1−5, the NOESY spectroscopy of **3h** and **6c**, the GC and GC-MS spectroscopy for the formation of 1,2-bis(diethoxycarbonyl)hydrazine. See also the footnote on the first page of this article.

Acknowledgments

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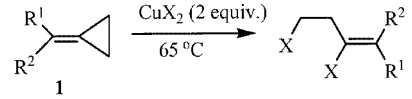

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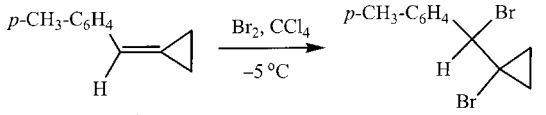

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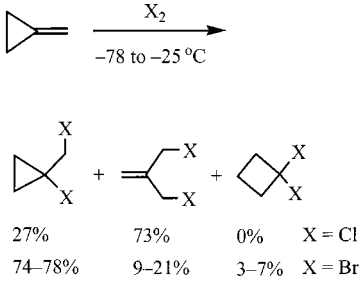

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