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Magnesium Alkylidene Carbenoids: Generation from 1-Halovinyl Sulfoxides with Grignard Reagents and Studies on Their Property, Mechanism, and Some Synthetic Uses

Tsuyoshi Satoh,[a)]* Koji Takano,[b)] Hiroyuki Ota,[a)] Hideaki Someya,[b)] Kenji Matsuda,[b)] and Mai Koyama[b)]

[a)]Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162 and

[b)]Faculty of Pharmaceutical Sciences, Science University of Tokyo; Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162, Japan

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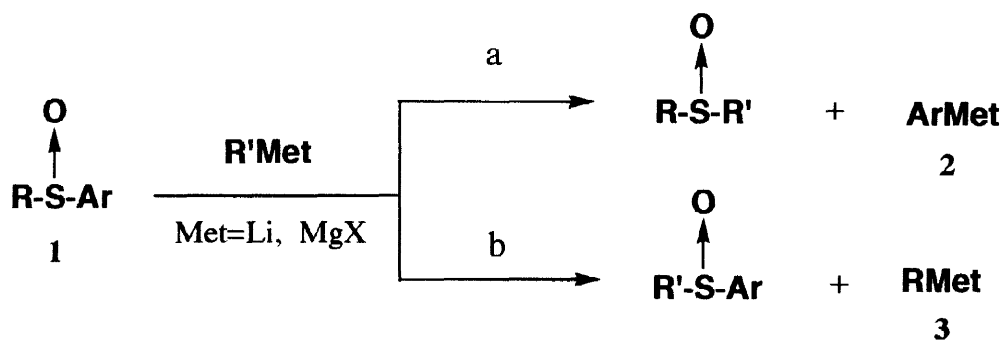
Magnesium alkylidene carbenoids were generated from 1-halovinyl sulfoxides, derived from ketones and aryl halomethyl sulfoxide, through the ligand exchange reaction of sulfoxides with Grignard reagents. The generated magnesium alkylidene carbenoids were found to be stable at -78 °C for over 30 min. The carbenoids reacted with aldehydes to give the adducts in moderate yields; however, they were found to be relatively unreactive to usual electrophiles. The generated magnesium alkylidene carbenoid exists in equilibrium between an α-halo alkenyl Grignard reagent and an alkylidene carbene-magnesium halide complex. Halogen exchange and geometrical isomerization of the alkylidene carbenoids were observed. 1-Chlorovinyl sulfoxides reacted with excess aryl Grignard reagents to give alkenyl Grignard reagents having an aryl group. These Grignard reagents reacted with several electrophiles to give tetra-substituted olefins in moderate to good yields.

It has been known that on treatment of alkyl aryl sulfoxide **1** with alkylmetal (alkyllithium or Grignard reagent) sulfur-aryl (path a) or sulfur-alkyl (path b) bond-cleavage takes place to give arylmetal **2** or alkylmetal **3**. This reaction is commonly called ligand exchange reaction of sulfoxides.[1] In the reaction, which path predominantly takes place is dependent on the structure of the sulfoxide **1**.[2] However, this dependence between the structure and the reaction path is somewhat obscure at present.[3]



Recently, the author's group extensively studied application of the ligand exchange reaction of sulfoxides in development of new synthetic methods.[4] Specifically, we found that on treatment of 1-chlorovinyl sulfoxides **4**, which was derived from **aldehydes**, with *tert*-butyllithium the sulfur-alkenyl bond was cleaved to give acetylene

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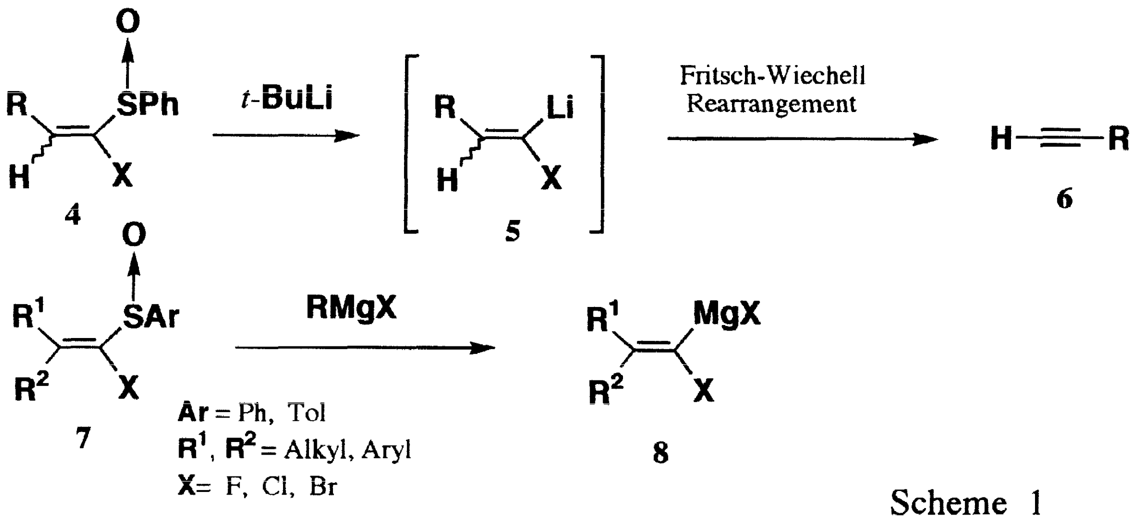
6 via lithium alkylidene carbenoid **5**.[5] In continuation of this chemistry we studied the ligand exchange reaction of 1-halovinyl sulfoxides **7**, derived from **ketones**, with alkylmetals and found that the Grignard reagent reacted well with **7** to afford relatively stable magnesium alkylidene carbenoid **8** (Scheme 1).[6]



Scheme 1

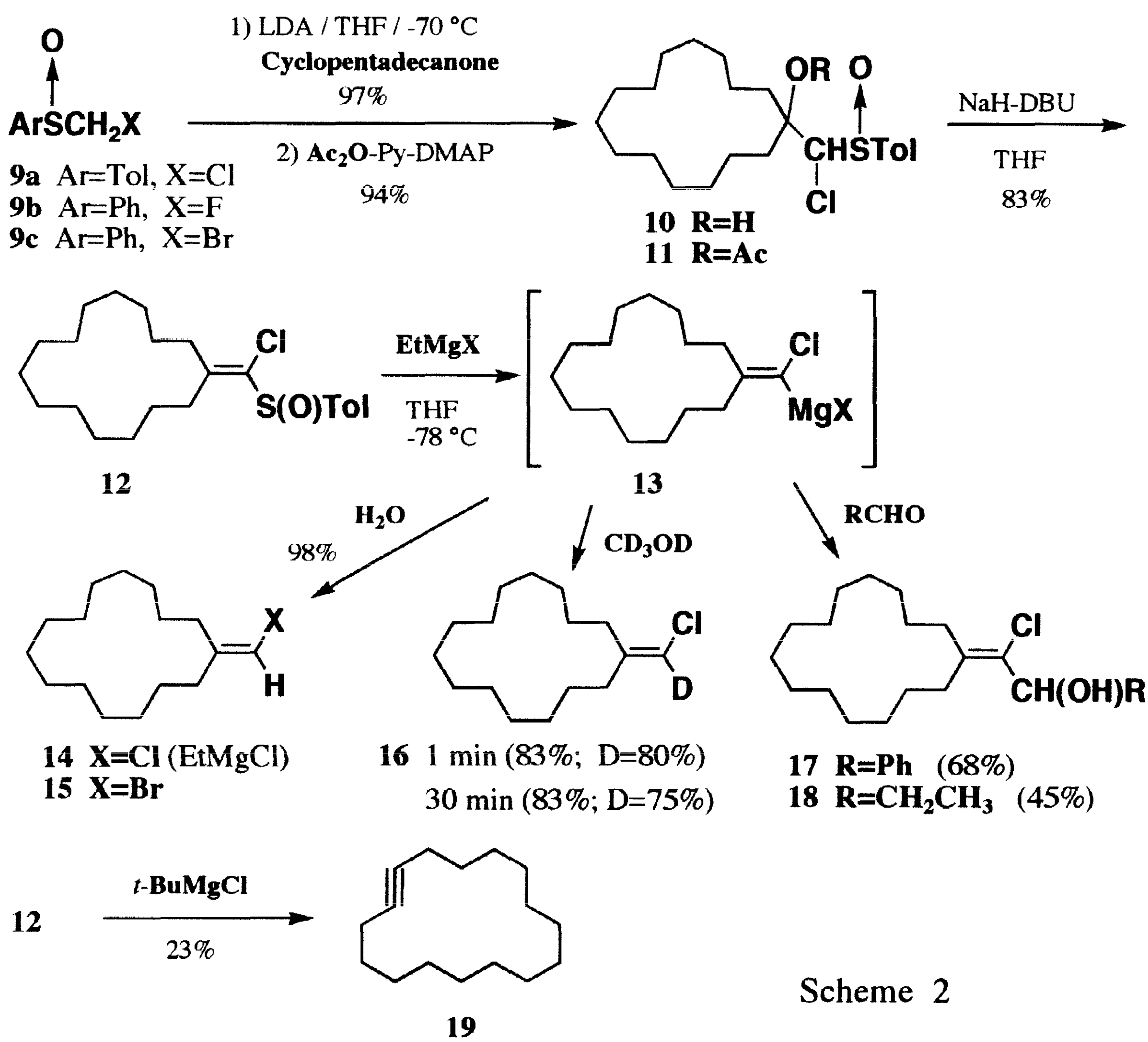
Carbenes and carbenoids are a highly reactive carbon species and frequently used as practical intermediates in organic synthesis.[7] Alkylidene carbenoids, carbenoids of olefinic carbon, are also a quite interesting, highly reactive carbon species.[8] Moreover, magnesium alkylidene carbenoid has rarely been reported.[9] We decided to continue to study the chemistry of the magnesium alkylidene carbenoids. In this paper, we report in detail the generation of magnesium alkylidene carbenoids and their property, mechanism, and application to new synthetic methods.[6]

Results and Discussion

Synthesis of 1-Halovinyl Sulfoxides from Ketones and Reaction with Alkylmetals.

First, a general method for synthesis of 1-halovinyl sulfoxides **7** from ketones was investigated (Scheme 2). Lithium carbanion of chloromethyl *p*-tolyl sulfoxide **9a** was reacted with cyclopentadecanone at -78 °C to give the adduct **10** in 97% yield. In an attempt to eliminate the hydroxyl group, **10** was acetylated with acetic anhydride in pyridine in the presence of DMAP[10] to afford acetate **11** in 94% yield. Elimination of the acetate was investigated with several kinds of bases and it was found that sodium hydride in THF in the presence of DBU at room temperature was the conditions of choice. It is interesting to note that in the absence of DBU this elimination of acetate totally failed. The elimination of acetic acid from **11** under the above-mentioned conditions gave the desired 1-chlorovinyl sulfoxide **12** in 83% yield as colorless crystals (Scheme 2).

Following the previous work[5] the ligand exchange reaction of sulfoxide of **12** was carried out with *n*-BuLi and *tert*-BuLi in THF at -78 °C. However, this reaction did not give the desired acetylenic compound **19**; instead a complex mixture was obtained. Next, **12** was treated with EtMgBr at -78 °C for 10 min. This reaction cleanly gave a single product, detected on silica gel plate, in 91% yield. Surprisingly, this product was an inseparable mixture of vinylchloride **14** and vinylbromide **15** (see in Table 1) in a ratio of 1:1.5. This very interesting result and the mechanism of this reaction are discussed later. Finally, the ligand exchange reaction of **12** was carried out with 1.5 equivalents of EtMgCl at -78 °C for 5 min to give pure vinylchloride **14** in 98% yield. Needless to say, this reaction also gave ethyl *p*-tolyl sulfoxide in quantitative yield.



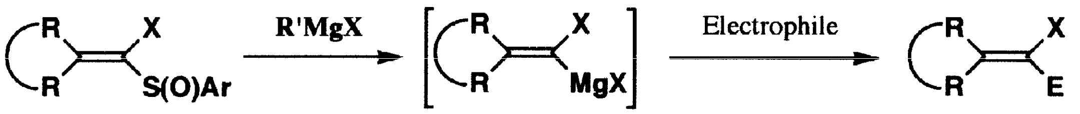
Scheme 2

It appeared obvious that the intermediate of this reaction was magnesium alkylidene carbenoid **13**. To ascertain that the intermediate was the magnesium alkylidene carbenoid, the reaction of **12** with EtMgCl at -78 °C for 1 min was quenched with deuterated methanol to give deuterated vinylchloride **16** in 83% yield with 80% deuterium incorporation. Delaying quenching the reaction for 30 min gave **16** in 83% yield with 75% deuterium incorporation. This result indicates that the magnesium alkylidene carbenoid **13** is stable at -78 °C for over 30 min. The slightly lowered deuterium incorporation was thought to be an experimental error.

The magnesium alkylidene carbenoid **13** was found to be reactive with aldehydes. For example, **13** reacted with benzaldehyde and propionaldehyde to give the adducts **17** and **18** in moderate yields, respectively. However, **13** did not react at all with ketone carbonyl group, such as acetone and cyclohexanone. 1-Chlorovinyl sulfoxide **12** did not react with *tert*-BuMgCl in THF at -78 °C; however, gradually warming the reaction mixture to room temperature gave cyclohexadecyne **19** in 23% yield. This result also indicated that the intermediate of the reaction of **12** with the Grignard reagent is a magnesium alkylidene carbenoid.

In order to know the properties of the magnesium alkylidene carbenoids, some other 1-halovinyl sulfoxides having chlorine, fluorine, and bromine **20-24** were synthesized from **9a**, fluoromethyl phenyl sulfoxide **9b**[11] and bromomethyl phenyl sulfoxide **9c**[12] with ketones and treated with Grignard reagent. The results are summarized in Table 1.

Table 1. Generation of Magnesium Alkylidene Carbenoid from 1-Halovinyl Sulfoxides and Reaction with Electrophiles



20 - 24 **25 - 37**

Entry	Ar	1-Halovinyl sulfoxide R	X	R'MgX	Temp.(°C)	Electrophile	Product Yield/%[a)]
1	Tol	$CH_3(CH_2)_4$	Cl	EtMgCl	-78	H_2O	**25** 78 (E=H)
2		**20**			-78	CD_3OD	**26** 80 (E=D; 80%[b)])
3					-78	PhCHO	**27** 50 (E=CH(OH)Ph)
4					-78 - -50	CH_3CH_2CHO	**28** 54 (E=CH(OH)Et)
5	Tol	Ph	Cl	EtMgCl	-78	H_2O	**29** 96 (E=H)
6		**21**			-78	CD_3OD	**30** 99 (E=D; 72%[b)])
7					-78 - -50	PhCHO	**31** 59(69)[c)](E=CH(OH)Ph)
8					-78 - -50	CH_3CH_2CHO	**32** 44 (E=CH(OH)Et)
9					0 (30 min)	H_2O	___[d)]
10	Ph	$-(CH_2)_{14}-$	F	EtMgCl	-100	H_2O	___[e)]
11		**22**		*t*-BuMgCl	-78 - r.t.	H_2O	___[f)]
12	Ph	Ph	F	EtMgCl	-100	H_2O	**33** 91 (E=H)
13		**23**			-100	CD_3OD	**34** 88 (E=D; 71%[b)])
14	Ph	$-(CH_2)_{14}-$	Br	EtMgBr	-100	H_2O	**15** 86 (E=H)
15		**24**			-100	CD_3OD	**35** 84 (E=D; 90%[b)])[g)]
16					-78	CD_3OD	**35** 82 (E=D; 62%[b)])
17					-78 (30 min)	CD_3OD	**35** 85 (E=D; 52%[b)])
18					-90	PhCHO	**36** 68 (E=CH(OH)Ph)[g)]

a) Unless otherwise noted, Grignard reagent (1.5 equivalents) was added to a solution of 1-halovinyl sulfoxide at the temperature and the reaction mixture was stirred for 5 min, then the electrophile was added. Isolated yield after silica gel column chromatography. b) The deuterium incorporation was measured from ^{1}H NMR. c) Conversion yield. d) A mixture of diphenylacetylene and 1,1-diphenyl-1-butene was obtained in good yield. e) See text. f) At low temperature this 1-fluorovinyl sulfoxide did not react with *t*-BuMgCl. At 0°C to room temperature this compound slowly decomposed to give a complex mixture. g) In this reaction, a solution of **24** in THF was added to a solution of 3 equivalents of EtMgBr in THF (inverse addition) and after 5 min, the electrophile was added to the reaction mixture.

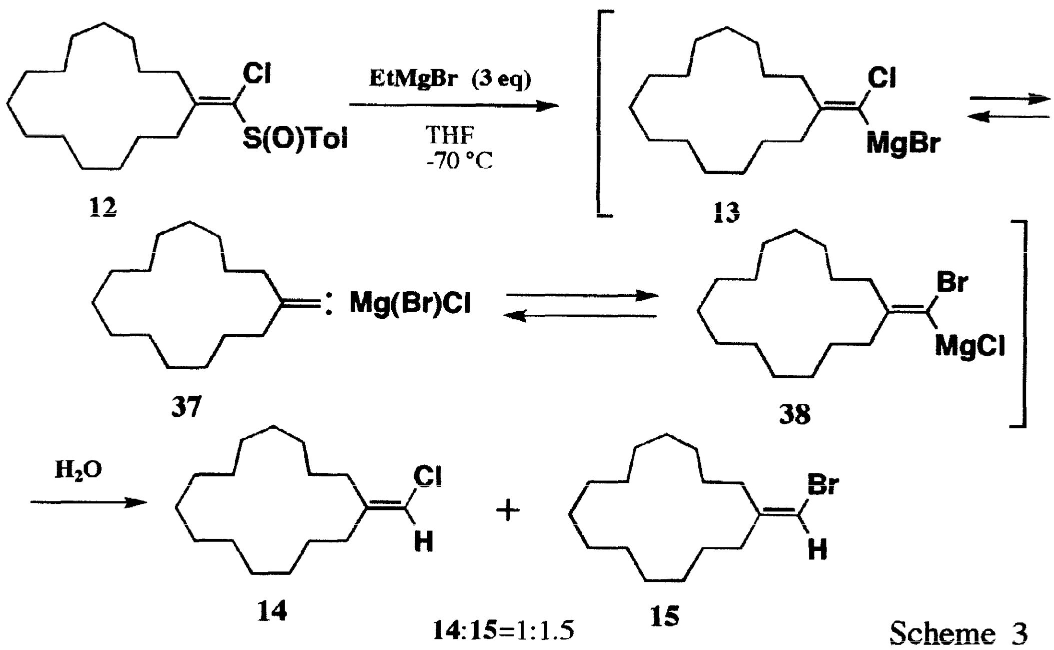
Entries 1-8 show that the reactivity of 1-chlorovinyl sulfoxide **20** and **21** with EtMgCl is quite similar to that of **12**. In the case of **21**, the magnesium alkylidene carbenoid rearranged to diphenylacetylene at around 0 °C (entry 9). Entries 14-18 show the reaction of 1-bromovinyl sulfoxide **24** with EtMgBr. The results are similar to those of the 1-chlorovinyl sulfoxides **12**, **20**, and **21**. It is important to note that the deuterium incorporation of the experiment in entries 6, 13, 16, and 17 was somewhat lower than expected. The reason is thought to be the presence of a trace of water in the solvent THF.[3] In this case inverse addition (a solution of the sulfoxide is added into a solution of the Grignard reagent) was found to be quite effective (entries 15 and 18). As shown in entries 16 and 17, the magnesium alkylidene carbenoid having bromine is also stable at -78 °C over 30 min.

The magnesium alkylidene carbenoids derived from 1-fluorovinyl sulfoxides **22** and **23** showed different results compared to those from the chlorides and bromides. Reaction of **22** with EtMgCl at -78 °C gave a complex mixture. The reaction was carried out at -100 °C (entry 10); however, this again gave a mixture of a fluorovinyl compound, chlorovinyl compound, and propylidenecyclopentadecanone (observed on ^{1}H NMR).

In contrast to **22**, 1-fluorovinyl sulfoxide **23** gave the magnesium alkylidene carbenoid having fluorine at -100 °C (entries 12 and 13). Though the carbenoids were detected as above, this carbenoid did not react with aldehyde carbonyl group.

Structure and Property of the Magnesium Alkylidene Carbenoid.

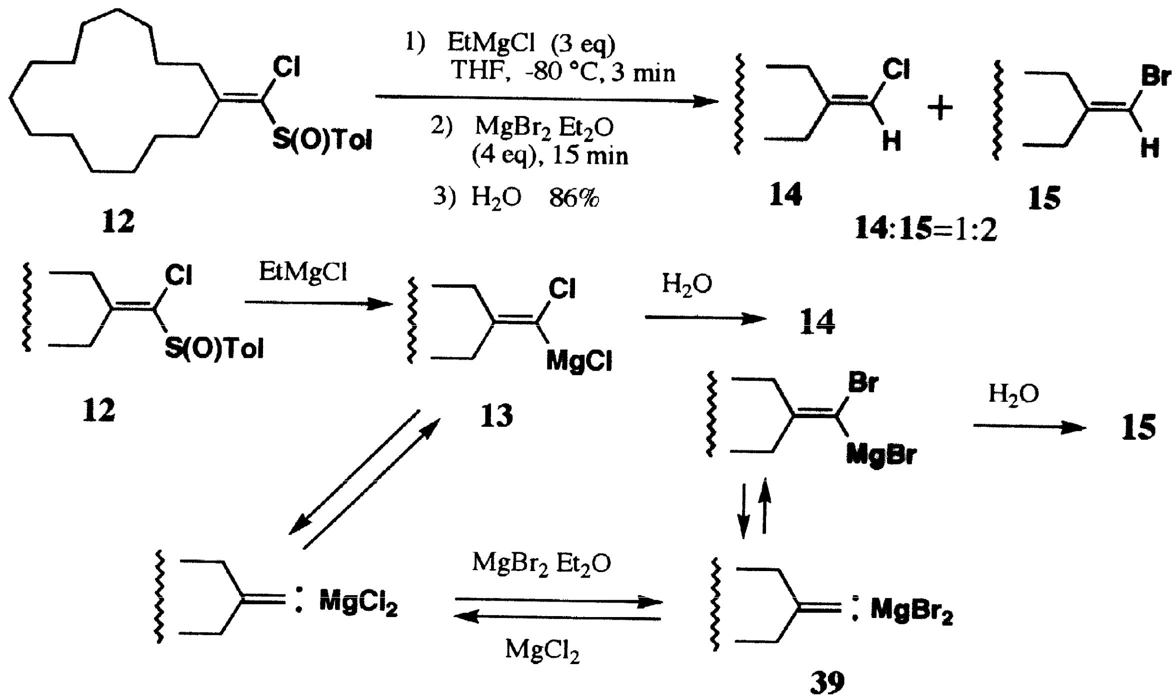
As mentioned above, 1-chlorovinyl sulfoxide **12** reacted with EtMgBr to give a mixture of chloride **14** and bromide **15** (Scheme 2). This strange result implies that the structure of the magnesium alkylidene carbenoid is not a simple vinylmagnesium compound such as **13** but in equilibrium between the alkylidene carbene-magnesium complex **37** and **13** (Scheme 3).[13] The above-mentioned result is deduced from the presence of an equilibrium between **13** and **38** through the magnesium complex **37**.



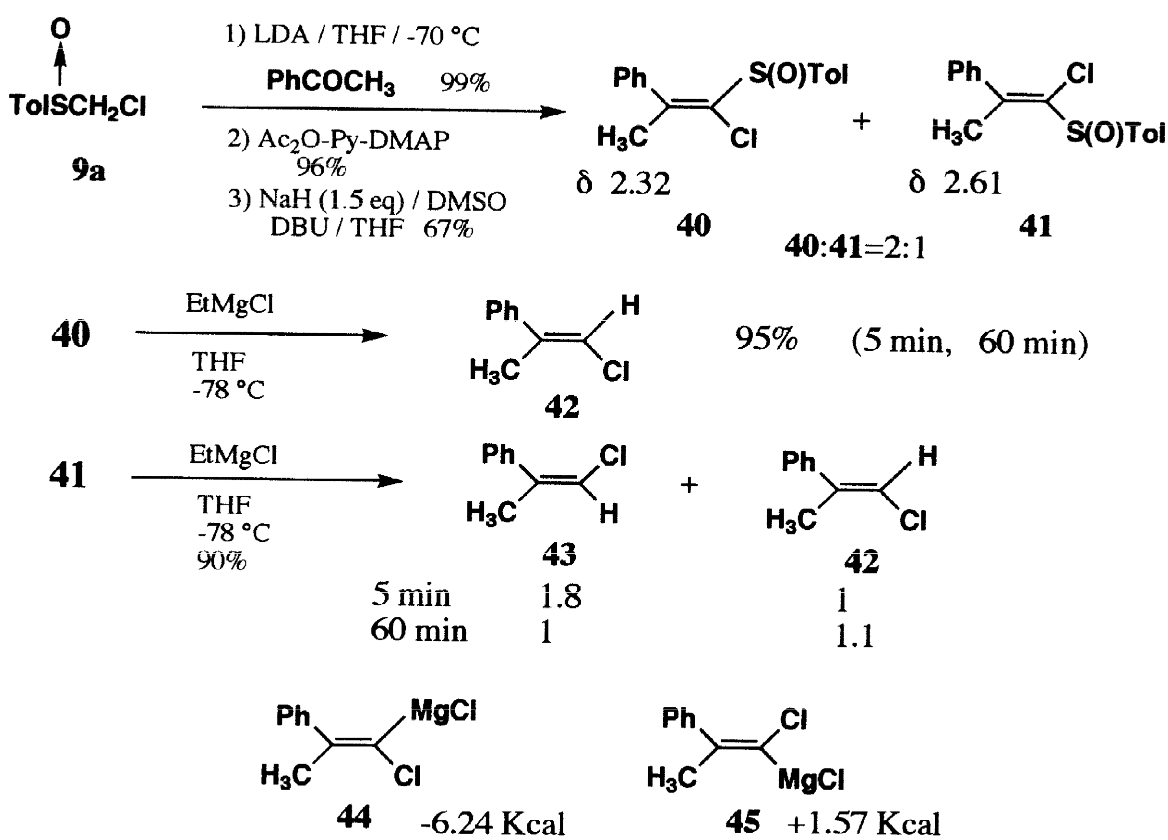
Scheme 3

Further evidence for the alkylidene carbene-magnesium complex and the presence of the equilibrium was obtained by an experiment as follows (Scheme 4). 1-Chlorovinyl sulfoxide **12** was added to a solution of

Scheme 4. Plausible Mechanism of the Halogen Exchange



Scheme 5. Geometrical Isomerization of Chlorine in the Carbenoid Reaction



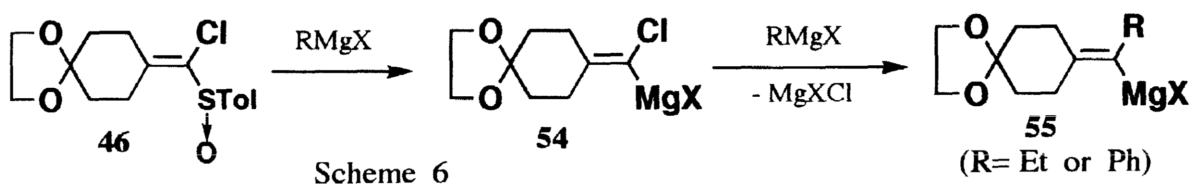
EtMgCl in THF at -80 °C and after 3 min a solution of $MgBr_2$-etherate in ether was added to the reaction mixture. The reaction mixture was stirred for 15 min and quenched to give a mixture of **14** and **15** in a ratio of 1:2 in good yield. The result also suggested that there is an equilibrium between the complex of alkylidene carbene with magnesium chloride and magnesium bromide (to give **39**) as shown in Scheme 4.[14]

If the above-mentioned equilibrium is present in these reactions, geometrical isomerization would be present when unsymmetrical halovinyl sulfoxides were reacted with the Grignard reagent. This presumption was verified as follows (Scheme 5). (*E*)-1-Chlorovinyl sulfoxide **40** and (*Z*)-isomer **41** were synthesized from acetophenone. The geometry of the two products was easily determined from the chemical shift of the methyl group.[15] First, 1-chlorovinyl sulfoxide **40** was treated with EtMgCl in THF at -78 °C for 5 min to give (*E*)-vinylchloride **42** as a single product in quantitative yield. Prolonging this reaction to 60 min gave the same result. In contrast to this result, the treatment of (*Z*)-1-chlorovinyl sulfoxide **41** for 5 min gave a mixture of (*Z*)-vinylchloride **43** and the isomer **42** in a ratio of 1.8:1. In this case, prolonging the reaction to 60 min gave a mixture of **43** and **42** in a ratio of 1:1.1. These results clearly indicated that the intermediate of this reaction, magnesium alkylidene carbenoid **45**, isomerizes to **44** via the alkylidene carbene-magnesium complex.[16] The MM2-energy value for the magnesium alkylidene carbenoid **44** was about 7.5 Kcal mol^{-1} lower than that of the isomer **45**.[17] This result strongly supports the results of the geometrical isomerization mentioned above.

Application of the Alkylidene Carbenoids to a Synthesis of Methylene Compound Having Aryl Group.

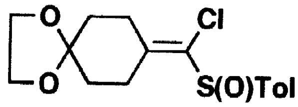
Further studies for the elucidation of reactivity of the magnesium alkylidene carbenoid were carried out using 1-chlorovinyl sulfoxide **46** and the results are summarized in Table 2. Entries 1-4 show that the reactivity of **46** with EtMgCl and the so-generated magnesium alkylidene carbenoid with methanol and aldehyde is almost the same as those of **12**, **20**, and **21**. In order to trap the magnesium alkylidene carbenoid generated from **46**, ethyl chloroformate was added (entry 5). However, this reaction did not give the desired carboxylic ester but 1,2,3-triene **50** as an isolable main product.[18] Entry 6 shows the treatment of the magnesium alkylidene carbenoid with chlorotrimethylsilane. This reaction again did not give the expected silylated compound but propylidene compound **51** as the main product. Treatment of the carbenoid with olefin did not give any adduct but 1,2,3-triene **50** as the main product (entry 7).

The result in entry 6 shows that the magnesium alkylidene carbenoid **54** reacts with the Grignard reagent to give alkenyl Grignard reagent **55** (Scheme 6).[19] In fact, treatment of **46** with large excess EtMgCl gave **51** in moderate yield (entry 8). At this stage we investigated the above-mentioned reaction with PhMgBr and it was found that the reactivity of PhMgBr to **46** was lower than that of EtMgCl; however, the yield of the benzylidene compound **52** was much higher (entry 9). In this reaction the conditions in entry 10 gave 80% yield of the benzylidene compound **53** with perfect deuteration.

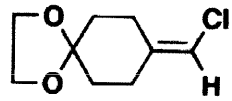
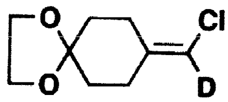
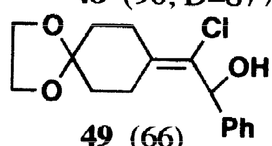
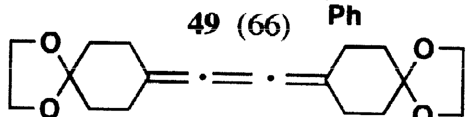
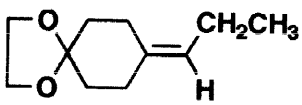
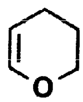
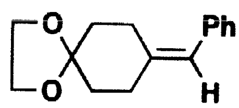
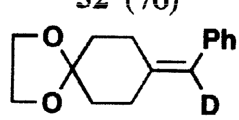


Scheme 6

Table 2. Reaction of Chlorovinyl Sulfoxide **46** with Alkylmetal Followed by Some Electrophiles



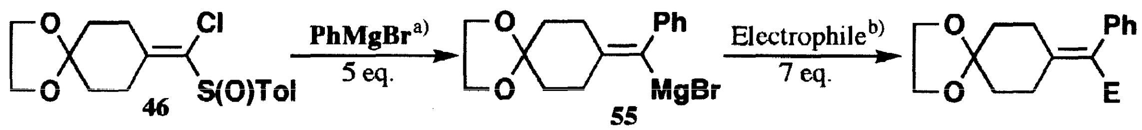
46

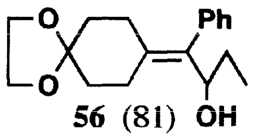
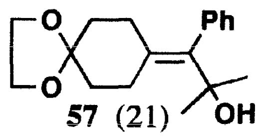
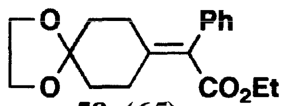
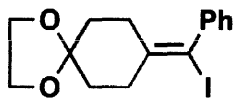
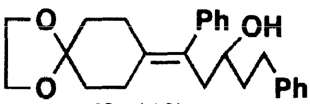
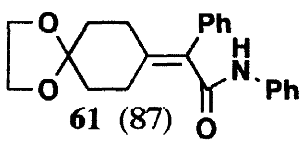
Entry	Alkylmetal[a)] (equivalents)	Temp./°C	Electrophile	Product[b)] (Yield/%)
1	EtMgCl (3)	-80	H_2O	 **47** (84)
2	*t*-BuLi (3)	-85	CD_3OD	Complex mixture
3	EtMgCl (3)	-80	CD_3OD	 **48** (90; D=87%)
4	EtMgCl (3)	-80	PhCHO	 **49** (66)
5	EtMgCl (3)	-80 ~ -30 (2 h)	ClCOOEt	 **50** (19)
6	EtMgCl (3)	-80 ~ -30 (2 h)	Me_3SiCl	 **51** (24)
7	EtMgCl (3)	-80 ~ -10 (3 h)		**50** (20)
8	EtMgCl (10)	-85 ~ -42[c)] (2 h)	H_2O	**51** (63)
9	PhMgBr (10)	-78 ~ -53[c)] (1 h)	H_2O	 **52** (76)
10	PhMgBr (5)	-85 ~ -50[c)] (2 h)	CD_3OD	 **53** (80; D=99%)

a) Unless otherwise noted, the reaction was carried out as follows: A solution of **46** in THF was added to a solution of alkylmetal and after 5 min excess amount of the electrophile was added. b) Isolated yield after silica gel column chromatography. Deuterium content was measured by ^{1}H NMR. c) A solution of **46** in THF was added to a solution of the Grignard reagent and the temperature of the reaction mixture was gradually allowed to warm to the temperature in this table. Water or deuterated methanol was then added to the reaction mixture.

In order to extend these reactions to a new synthetic method for tetrasubstituted olefinic compounds having an aryl group from 1-chlorovinyl sulfoxides, we tried to trap the intermediate alkenyl Grignard reagent **55** with several electrophiles and the results are summarized in Table 3.

Table 3. Reaction of Chlorovinyl Sulfoxide **46** with PhMgBr Followed by Some Electrophiles

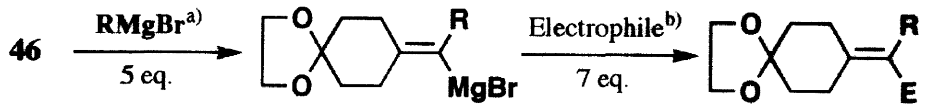


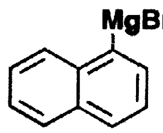
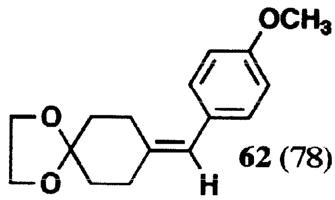
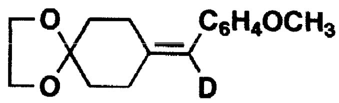
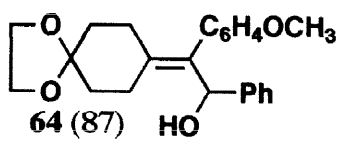
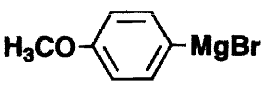
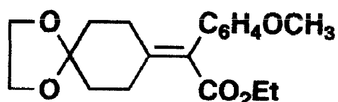
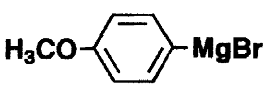
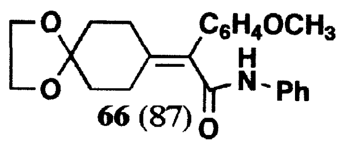
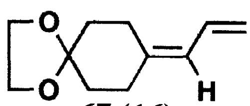
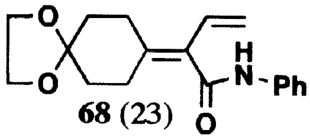
Entry	Conditions temp./°C	Electrophile	Product[c] (Yield/%)
1	-80 ~ -50 (100 min)[a] -50 ~ -45 (30 min)[b]	CH_3CH_2CHO	 **56** (81)
2	-80 ~ rt (2.5 h)[a] rt (0.5 h)[b]	CH_3COCH_3	 **57** (21) **52** (34)
3	-60 ~ rt (2 h)[a] rt (70 min)[b]	ClCOOEt	 **58** (65)
4	-80 ~ rt (3 h)[a] rt (1 h)[b]	I_2	 **59** (53)
5	-75 ~ rt (3 h)[a] rt (60 h)[b]		 **60** (42)
6	-80 ~ rt (2 h)[a] rt (40 h)[b]	PhNCO	 **61** (87)

a) A solution of **46** in THF was added to a solution of PhMgBr. The conditions for the reaction of **46** with PhMgBr to give the alkenyl Grignard reagent. b) The conditions for the reaction of electrophiles with the generated alkenyl Grignard reagent. c) Isolated yield after silica gel column chromatography. Deuterium content was measured by ^{1}H NMR.

The reaction of propionaldehyde with the alkenyl Grignard reagent **55** gave good yield of the adduct **56**; however, the reaction with acetone gave the desired adduct **57** in only low yield. The main product was the protonated product **52**. Entries 3-5 show that **55** reacts with ethyl chloroformate, iodine, and epoxide to give the corresponding products **58**-**60** in moderate yields. The best result was obtained with phenyl isocyanate to

Table 4. Reaction of Chlorovinyl Sulfoxide **46** with RMgBr Followed by Some Electrophiles



Entry	RMgBr	Conditions temp./°C	Electrophile	Product[c] (Yield/%)
1		-70 ~ rt (2.5 h)[a]	H_2O	No reaction
2		-70 ~ rt (3 h)[a]	H_2O	 **62** (78)
3		-70 ~ rt (3 h)[a] rt (10 min)[b]	CD_3OD	 **63** (78; D=91%)
4		-70 ~ rt (3 h)[a] rt (1 h)[b]	PhCHO	 **64** (87)
5		-80 ~ rt (2.5 h)[a] rt (1 h)[b]	ClCOOEt	 **65** (67)
6		-70 ~ rt (3 h)[a] rt (44 h)[b]	PhNCO	 **66** (87)
7		-78 ~ rt (100 min)[a]	H_2O	 **67** (16)
8		-70 ~ rt (3 h)[a] rt (20 h)[b]	PhNCO	 **68** (23)

a) A solution of **46** in THF was added to a solution of RMgBr. The conditions for the reaction of **46** with RMgBr to give the alkenyl Grignard reagent. b) The conditions for the reaction of electrophiles with the generated alkenyl Grignard reagent. c) Isolated yield after silica gel column chromatography. Deuterium content was measured by ^1H NMR.

afford the desired amide **61** in high yield. We also tried the reaction of **55** with chlorotrimethylsilane, diethyl chlorophosphate, and diethylcarbamoyl chloride; however, these electrophiles did not react at all with **55** and only gave the protonated **52** in 73-86% yield.

Table 4 shows the results for the reaction of **46** with α-naphthylmagnesium bromide, *p*-methoxymagnesium bromide, and vinylmagnesium bromide followed by some electrophiles. As shown in entry 1, α-naphthylmagnesium bromide did not react at all with **46** and after the workup the starting material **46** was recovered almost quantitatively. The reaction of **46** with *p*-methoxymagnesium bromide showed almost equal reactivity as phenylmagnesium bromide (entries 2-6: compare the results in Table 2, entries 9 and 10, and Table 3, entries 1, 3, and 6).

The reaction of **46** with vinylmagnesium bromide was found to be problematical. Vinylmagnesium bromide showed similar reactivity with **46** as phenylmagnesium bromide; however, the reaction gave many unknown products and the desired product (**67** and **68**) could be obtained only in low yields (entries 7 and 8).

In conclusion, we found that reaction of 1-halovinyl sulfoxides derived from ketones with Grignard reagents afforded magnesium alkylidene carbenoids. We studied the property of the generated magnesium alkylidene carbenoids. The magnesium alkylidene carbenoids are thought to have many interesting properties. We are now investigating uses of the magnesium alkylidene carbenoids in developing new synthetic methods.

Experimental Section

Mps were measured with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were measured in a $CDCl_3$ solution with JEOL GX-270 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel BW-127 ZH (Fuji-Silicia) containing 0.5% fluorescence reagent 254 and a quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry solvent, THF was distilled from diphenylketyl; DMSO was distilled from CaH_2.

[Chloro-(*p*-tolylsulfinyl)methylidene]cyclopentadecane (12). A solution of **9a** (944 mg; 5 mmol) in dry THF (2 ml) was added dropwise to a solution of LDA (6.5 mmol) in 10 ml of THF at -78 °C. The solution was stirred at -78 °C for 10 min, then a solution of cyclopentadecanone (1.24 g; 5.5 mmol) in 3 ml of THF was added. The reaction mixture was stirred for 10 min and the reaction was quenched by sat. aq. NH_4Cl. The whole was extracted with $CHCl_3$. The organic layer was washed once with sat. aq. NH_4Cl and dried over $MgSO_4$. The solvent was evaporated to leave colorless crystals. The crystals were washed with a mixture of hexane-AcOEt (10:1) to give pure chloro-alcohol **10** (2.01 g; 97%). Recystallization of the crystals from $CHCl_3$-hexane gave colorless needles, mp 162-164 °C. IR (KBr) 3350 (OH), 1043 (SO) cm^{-1}; ^{1}H NMR δ 0.8-1.6 (24H, m), 1.7-1.8 (2H, m), 1.9-2.2 (2H, m), 2.43 (3H, s), 4.32 (1H, s), 7.36, 7.47 (each 2H, d, *J*=8 Hz). Anal. Calcd for $C_{23}H_{37}ClO_2S$: C, 66.88; H, 9.03; Cl, 8.58; S, 7.76. Found: C, 66.22; H, 9.08; Cl, 9.02; S, 7.42.

4-Dimethylaminopyridine (43 mg; 0.3 mmol) was added to a suspension of **10** (290 mg; 0.7 mmol) in a mixture of acetic anhydride (2 ml) and pyridine (3 ml). The suspension was stirred at room temperature for 16 h. The suspension gradually turned to a clear solution. The acetic anhydride and pyridine were evaporated under vacuum and the residue was purified by silica gel column chromatography to give acetate **11** (299 mg; 94%) as colorless prisms; mp 103-105 °C (hexane). IR (KBr) 1724 (CO), 1238 (COC), 1093, 1063 (SO) cm^{-1}; ^{1}H NMR δ 1.2-1.4 (24H, m), 1.5-1.7 (2H, m), 2.0-2.2 (2H, m), 2.13 (3H, s), 2.41 (3H, s), 5.46 (1H, s), 7.32, 7.46 (each 2H, d, *J*=8 Hz). Anal. Calcd for $C_{25}H_{39}ClO_3S$: C, 65.98; H, 8.64; Cl, 7.79; S, 7.04. Found: C, 66.08; H, 8.71; Cl, 7.85; S, 7.09.

1,8-Diazabicyclo[5.4.0]undec-7-ene (1.1 ml; 7.2 mmol) and NaH (60% oil suspension; 360 mg; 9 mmol) were added to a solution of the acetate **11** (812 mg; 1.8 mmol) in THF (36 ml). The reaction mixture was stirred at room temperature for 3.5 h. The reaction was quenched by adding sat. aq. NH_4Cl and the whole was extracted with ether-benzene. The organic layer was washed with sat. aq. NH_4Cl and the solvent was evaporated. The residue was purified on silica gel column chromatography to afford **12** (590 mg; 83%) as colorless needles; mp 70-72 °C (hexane). IR (KBr) 1053 (SO) cm^{-1}; ^{1}H NMR δ 1.2-1.8 (24H, m), 2.32 (2H, t, *J*=7 Hz), 2.41 (3H, s), 2.70 (2H, t, *J*=7 Hz), 7.32, 7.42 (each 2H, d, *J*=8 Hz); ^{13}C NMR δ 21.40 (CH_3), 25.01, 26.09, 26.21, 26.25, 26.29, 26.34, 26.43, 26.56, 27.51, 27.63, 33.62, 34.21, 124.70, 129.70, 133.54, 138.63, 141.34, 153.00. Anal. Calcd for $C_{23}H_{35}ClOS$: C, 69.95; H, 8.93; Cl, 8.97; S, 8.12. Found: C, 69.99; H, 8.89; Cl, 9.16; S, 8.16.

Reaction of 12 with EtMgBr. A solution of EtMgBr in ether (0.6 mmol) was added to a solution of **12** (79 mg; 0.2 mmol) in 4 ml of dry THF under Ar atmosphere at -70 °C. The reaction mixture was stirred for 10 min, then the reaction was quenched with sat. aq. NH_4Cl. The usual workup followed by silica gel column chromatography gave 40 mg of a colorless oil. This product was found to be a mixture of chloride **14** and bromide **15** in a ratio of 1:1.5 by ^{1}H NMR and mass spectrum.

(Chloromethylidene)cyclopentadecane (14). A solution of EtMgCl (0.21 mmol) was added dropwise to a solution of **12** (66 mg; 0.17 mmol) in 17 ml of dry THF at -78 °C with stirring. The solution was stirred for 5 min, then the reaction was quenched by adding sat. aq. NH_4Cl. The whole was extracted with ether-hexane. The product was purified by silica gel column chromatography to afford **14** (42 mg; 98%) as a colorless oil. IR (neat) 1631, 1460 cm^{-1}; ^{1}H NMR δ 1.2-1.6 (24H, m), 2.06 (2H, t, *J*=7 Hz), 2.20 (2H, t, *J*=7Hz), 5.79 (1H, s); MS *m/z* (%) 256 (M$^+$, 57), 221 (18), 109 (50), 95 (86), 82 (100). Calcd for $C_{16}H_{29}Cl$: M, 256.1955. Found: *m/z* 256.1947.

[Chloro-(deuterio)methylidene]cyclopentadecane (16). A solution of EtMgCl (0.21 mmol) was added dropwise to a solution of **12** (54 mg; 0.14 mmol) in 14 ml of dry THF at -78 °C. The solution was stirred at -78 °C for 1 min, then CD_3OD (0.2 ml) was added. After 10 min, the reaction was quenched with sat. aq. NH_4Cl. The workup described above gave **16** (29 mg; 83%) as a colorless oil. IR (neat) 1616, 1460 cm^{-1}; ^{1}H NMR: only the signal of the vinyl hydrogen was reduced. The deuterium content was calculated by using this signal. MS *m/z* (%) 257 (M$^+$, 53), 222 (14), 109 (47), 96 (86), 83 (100). Calcd for $C_{16}H_{28}DCl$: M, 257.2018. Found: *m/z* 257.2014.

[Chloro-(α-hydroxybenzyl)methylidene]cyclopentadecane (17). A solution of EtMgCl (0.24 mmol) was added dropwise to a solution of **12** (62 mg; 0.16 mmol) in 16 ml of dry THF at -78 °C. The reaction mixture was stirred for 5 min, then benzaldehyde (0.24 mmol) was added. The solution was stirred for 30 min. The reaction was quenched with sat. aq. NH_4Cl. After the usual workup, the product was purified by silica gel column chromatography to give 39 mg (68%) of the adduct **17** as a colorless viscous oil. IR (neat) 3390 (OH) cm^{-1}; ^{1}H NMR δ 1.2-1.6 (24H, m), 2.29 (4H, t, *J*=7 Hz), 2.46 (1H, d, *J*=8 Hz, OH), 5.81 (1H, d, *J*=8 Hz), 7.2-7.5 (5H, m). MS *m/z* (%) 362 (M$^+$, 5), 344 (100). Calcd for $C_{23}H_{35}ClO$: M, 362.2374. Found: *m/z* 362.2366.

(Chloro(1-hydroxypropyl)methylidene)cyclopentadecane (18). This compound was synthesized from **12** and propionaldehyde as described above. Colorless viscous oil; IR (neat) 3370 (OH) cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, *J*=7 Hz), 1.2-1.8 (26H, m), 2.1-2.3 (4H, m), 4.52 (1H, m); MS *m/z* (%) 314 (M$^+$, 2), 296 (17), 285 (100). Calcd for $C_{19}H_{35}ClO$: M, 314.2374. Found: *m/z* 314.2386.

Cyclohexadecyne (19). *tert*-BuMgCl (0.72 mmol) was added dropwise to a solution of **12** (71 mg; 0.18 mmol) in THF (18 ml) at -78 °C. The temperature was allowed to warm to room temperature. The reaction was quenched with sat. aq. NH_4Cl and after the usual workup followed by silica gel column chromatography to give cyclohexadecyne **19** (9 mg; 23%) as a colorless oil.[4k]

1-Halovinyl Sulfoxide (20-24).

1-Chloro-2-pentyl-1-(*p*-tolylsulfinyl)-1-heptene (20). This compound was synthesized from chloromethyl *p*-tolyl sulfoxide and 6-undecanone as described for **12**. **Chloro alcohol**: 93% yield; colorless crystals; mp 87-89 °C ($CHCl_3$-hexane). IR (KBr) 3367 (OH), 1043 (SO) cm^{-1}; ^{1}H NMR δ 0.89, 0.92 (each 3H, t, *J*=7 Hz), 1.3-1.5 (12H, m), 1.7-2.1 (4H, m), 2.42 (3H, s), 4.35 (1H, s), 7.35, 7.48 (each 2H, d, *J*=8 Hz). Anal. Calcd for $C_{19}H_{31}ClO_2S$: C, 63.57; H, 8.70; Cl, 9.88; S, 8.93. Found: C, 63.53; H, 8.73; Cl, 9.81; S, 8.92. **Acetate**: 87% yield; colorless oil; IR (neat) 1732 (CO), 1236 (COC), 1093, 1066 (SO) cm^{-1}; ^{1}H NMR δ 0.88, 0.91 (each 3H, t, *J*=7 Hz), 1.2-1.6 (12H, m), 1.9-2.2 (4H, m), 2.12 (3H, s, $COCH_3$), 2.41 (3H, s), 5.33 (1H, s), 7.30, 7.48 (each 2H, d, *J*=8 Hz). **20**: 62% yield; colorless oil; IR (neat) 1087, 1061 (SO) cm^{-1}; ^{1}H NMR δ 0.88, 0.90 (each 3H, t, *J*=7 Hz), 1.2-1.8 (12H, m), 2.32 (2H, t, *J*=8 Hz), 2.40 (3H, s), 2.69 (2H, t, *J*=7 Hz), 7.30, 7.46 (each 2H, d, *J*=8 Hz). MS *m/z* (%) 340 (M$^+$, 20), 323 (100). Calcd for $C_{19}H_{29}ClOS$: M, 340.1625. Found: *m/z* 340.1622.

1-Chloro-2,2-diphenyl-1-(*p*-tolylsulfinyl)ethene (21). This compound was synthesized from chloromethyl *p*-tolyl sulfoxide and benzophenone. **Chloro alcohol**: 93% yield; colorless crystals. IR (KBr) 3568 (OH), 1090, 1053 (SO) cm^{-1}; ^{1}H NMR δ 2.41 (3H, s), 5.34 (1H, s), 7.2-7.7 (14H, m). **Acetate**: 89% yield; colorless crystals; IR (KBr) 1739 (CO), 1228 (COC), 1093, 1020 (SO) cm^{-1}; ^{1}H NMR δ 2.32 (3H, s), 2.41 (3H, s), 6.15 (1H, s), 7.3-7.6 (14H, m). **21**: 78% yield; Colorless needles; mp 139-140 °C (AcOEt-hexane). IR (KBr) 1084, 1051 (SO) cm^{-1}; ^{1}H NMR δ 2.42 (3H, s), 7.2-7.6 (14H, m). Anal. Calcd for $C_{21}H_{17}ClOS$: C, 71.48; H, 4.86; Cl, 10.05; S, 9.09. Found: C, 71.35; H, 4.78; Cl, 10.03; S, 9.10.

[Fluoro(phenylsulfinyl)methylidene]cyclopentadecane (22). This compound was synthesized from fluoromethyl phenyl sulfoxide and cyclopentadecanone. **Fluoro alcohol**: 90% yield; colorless crystals. IR (KBr) 3331 (OH), 1070, 1022 (SO) cm^{-1}; ^{1}H NMR δ 1.3-1.7 (24H, m), 1.7-2.1 (4H, m), 4.68 (1H, d, *J*=46 Hz), 7.5-7.7 (5H, m). **Acetate**: 99% yield; colorless viscous oil. IR (neat) 1732 (CO), 1244 (COC), 1093, 1049, 1022 (SO) cm^{-1}; ^{1}H NMR δ 1.2-1.6 (24H, m), 2.0-2.2 (4H, m), 2.12 (3H, s), 5.73 (1H, d, J=47 Hz), 7.5-7.7 (5H, m). **22**: 64% yield; colorless viscous oil. IR (neat) 1086, 1047 (SO) cm^{-1}; ^{1}H NMR δ 1.2-1.7 (24H, m), 2.19 (2H, m), 2.50 (2H, m), 7.4-7.7 (5H, m). MS *m/z* (%) 364 (M$^+$, 1), 347 (100). Calcd for $C_{22}H_{33}FOS$: M, 364.2235. Found: *m/z* 364.2254.

1-Fluoro-2,2-diphenyl-1-phenylsulfinylethene (23). This compound was synthesized from fluoromethyl phenyl sulfoxide and benzophenone. **Fluoro alcohol**: 96% yield; colorless crystals. IR (KBr) 3456, 3232 (OH), 1086, 1026 (SO) cm^{-1}; ^{1}H NMR δ 5.64 (1H, d, *J*=46 Hz), 7.1-7.9 (15H, m). **Acetate**: less polar acetate; 19% yield; colorless viscous oil. IR (neat) 1751 (CO), 1228 (COC), 1053 (SO) cm^{-1}; ^{1}H NMR δ 2.21 (3H, s), 6.52 (1H, d, *J*=47 Hz), 7.2-7.8 (15H, m). More polar acetate; 76% yield; colorless crystals. IR (KBr) 1736 (CO), 1236 (COC), 1099, 1051, 1018 (SO) cm^{-1}. **23**: 77% yield; colorless needles; mp 113-114 °C (AcOEt-hexane). IR (KBr) 1082, 1047 (SO) cm^{-1}; ^{1}H NMR δ 7.2-7.8 (m). Anal. Calcd for $C_{20}H_{15}FOS$: C, 74.51; H, 4.69; F, 5.89; S, 9.95. Found: C, 74.29; H, 4.67; F, 5.87; S, 9.87.

[Bromo(phenylsulfinyl)methylidene]cyclopentadecane (24). This compound was synthesized from bromomethyl phenyl sulfoxide and cyclopentadecanone. **Bromo alcohol**: 90% yield; colorless crystals; mp 161-162 °C ($CHCl_3$-hexane). IR (KBr) 3351 (OH), 1041 (SO) cm^{-1}; ^{1}H NMR δ 1.2-1.6 (24H, m), 1.7-1.9 (2H, m), 1.9-2.3 (2H, m), 4.56 (1H, s), 7.5-7.6 (5H, m). Anal. Calcd for $C_{22}H_{35}BrO_2S$: C, 59.58; H, 7.96; Br, 18.02; S, 7.23. Found: C, 59.60; H, 7.96; Br, 18.07; S, 7.28. **Acetate**: 98% yield; colorless crystals; mp 131-132 °C (AcOEt-hexane). IR (KBr) 1724 (CO), 1234 (COC), 1090, 1055 (SO) cm^{-1}; ^{1}H NMR δ 1.2-1.5 (24H, m), 1.5-1.7 (2H, m), 2.0-2.4 (2H, m), 2.13 (3H, s), 5.66 (1H, s), 7.4-7.6 (5H, m). Anal. Calcd for $C_{24}H_{37}BrO_3S$: C, 59.37; H, 7.68; Br, 16.46; S, 6.60. Found: C, 59.42; H, 7.71; Br, 16.45; S, 6.60. **24**: 83% yield; colorless viscous oil. IR (neat) 1090, 1057 (SO) cm^{-1}; ^{1}H NMR δ 1.2-1.8 (24H, m), 2.35 (2H, dd, *J*=9, 7 Hz), 2.76 (2H, t, *J*=8 Hz), 7.5-7.7 (5H, m). MS *m/z* (%) 426, 424 (M$^+$, 14), 409, 407 (100). Calcd for $C_{22}H_{33}BrOS$: M, 426.1415. Found: *m/z* 426.1438.

1-Chloro-2-pentyl-1-heptene (25). Colorless oil; IR (neat) 1632, 1460, 1265, 739 cm^{-1}; ^{1}H NMR δ 0.88, 0.90 (each 3H, t, *J*=7 Hz), 1.2-1.5 (12H, m), 2.04 (2H, dd, *J*=7.6, 6.9 Hz), 2.19 (2H, t, *J*=7 Hz), 5.76 (1H, s); MS *m/z* (%) 202 (M$^+$, 46), 137 (10), 110 (25), 97 (64), 56 (100). Calcd for $C_{12}H_{23}Cl$: M, 202.1487. Found: *m/z* 202.1487.

1-Chloro-1-deuterio-2-pentyl-1-heptene (26). Colorless oil; IR (neat) 1618, 1460 cm^{-1}; ^{1}H NMR: the signal of vinyl-H (δ 5.76) was markedly reduced; MS *m/z* (%) 203 (M$^+$, 48), 111 (37), 97 (70), 57 (100). Calcd for $C_{12}H_{22}DCl$: M, 203.1550. Found: *m/z* 203.1554.

2-Chloro-3-pentyl-1-phenyl-2-octen-1-ol (27). Colorless oil; IR (neat) 3430 (OH) cm^{-1}; ^{1}H NMR δ 0.88, 0.90 (each 3H, CH_3), 1.2-1.6 (12H, m), 2.2-2.4 (4H, m), 5.81 (1H, d, *J*=9 Hz), 7.2-7.5 (5H, m); MS *m/z* (%) 308 (M$^+$, 18), 290 (37), 273 (43), 233 (100). Calcd for $C_{19}H_{29}ClO$: M, 308.1906. Found: *m/z* 308.1916.

4-Chloro-5-pentyl-4-decen-3-ol (28). Colorless oil; IR (neat) 3380 (OH), 1460 cm^{-1}; ^{1}H NMR δ 0.8-1.0 (9H, CH_3), 1.2-1.5 (12H, m), 1.6-1.8 (2H, m), 2.1-2.3 (4H, m), 4.51 (1H, q, *J*=7 Hz); ^{13}C NMR δ 9.99 (CH_3), 13.96 (CH_3), 14.02 (CH_3), 22.46, 22.50, 27.11, 28.72, 28.75, 31.84, 31.88, 32.40, 33.86, 71.38 (CH), 131.18, 139.37. MS *m/z* (%) 260 (M$^+$, 5), 242 (10), 231 (100). Calcd for $C_{15}H_{29}ClO$: M, 260.1904. Found: *m/z* 260.1895.

2-Chloro-1,1-diphenylethene (29). Colorless oil; IR (neat) 1593, 1495, 1443 cm^{-1}; ^{1}H NMR δ 6.58 (1H, s), 7.1-7.5 (10H, m); MS *m/z* (%) 214 (M$^+$, 100), 179 (69), 178 (73). Calcd for $C_{14}H_{11}Cl$: M, 214.0549. Found: *m/z* 214.0560.

2-Chloro-2-deuterio-1,1-diphenylethene (30). Colorless oil; IR (neat) 1591, 1495, 1443 cm^{-1}; ^{1}H NMR : the signal of vinyl-H (δ 6.58) was markedly reduced; MS *m/z* (%) 215 (M$^+$, 90), 179 (100). Calcd for $C_{14}H_{10}DCl$: M, 215.0611. Found: *m/z* 215.0611.

2-Chloro-1,3,3-triphenyl-2-propen-1-ol (31). Colorless viscous oil; IR (neat) 3367, 3313 (OH), 1598, 1493 cm^{-1}; ^{1}H NMR δ 5.75 (1H, d, *J*=8 Hz), 7.2-7.5 (15H, m). MS *m/z* (%) 320 (M$^+$, 32), 285 (100). Calcd for $C_{21}H_{17}ClO$: M, 320.0967. Found: *m/z* 320.0972.

2-Chloro-1,1-diphenyl-1-penten-3-ol (32). Colorless viscous oil; IR (neat) 3390 (OH), 1599, 1491 cm^{-1}; ^{1}H NMR δ 0.90 (3H, t, *J*=7 Hz), 1.77 (2H, quintet, *J*=7 Hz), 4.42 (1H, bt, *J*=7 Hz), 7.1-7.4 (10H, m). MS *m/z* (%) 272 (M$^+$, 19), 243 (100). Calcd for $C_{17}H_{17}ClO$: M, 272.0966. Found: *m/z* 272.0958.

2-Fluoro-1,1-diphenylethene (33). Colorless oil; IR (neat) 1637, 1496, 1444 cm^{-1}; ^{1}H NMR δ 6.95 (1H, d, *J*=83 Hz), 7.2-7.4 (10H, m). MS *m/z* (%) 198 (M$^+$, 100), 196 (37), 178 (11), 165 (25). Calcd for $C_{14}H_{11}F$: M, 198.0843. Found: *m/z* 198.0837.

2-Fluoro-2-deuterio-1,1-diphenylethene (34). Colorless oil; IR (neat) 1622, 1496, 1444 cm^{-1}; ^{1}H NMR: the signal of the vinyl-H (δ 6.95) was markedly reduced. MS *m/z* (%) 199 (M$^+$, 100), 178 (16), 165 (30). Calcd for $C_{14}H_{10}DF$: M, 199.0906. Found: *m/z* 199.0905.

(Bromomethylidene)cyclopentadecane (15). Colorless oil; IR (neat) 1622, 1458 cm^{-1}; ^{1}H NMR δ 1.2-1.6 (24H, m), 2.11 (2H, t, *J*=7 Hz), 2.20 (2H, t, *J*=7 Hz), 5.89 (1H, s). MS *m/z* (%) 302, 300 (M$^+$, 29), 220 (17), 97 (79), 83 (100). Calcd for $C_{16}H_{29}Br$: M, 302.1433. Found: *m/z* 302.1424.

[Bromo(deuterio)methylidene]cyclopentadecane (35). Colorless oil; IR (neat) 1458 cm^{-1}; ^{1}H NMR: the signal of the vinyl-H (δ 5.89) was markedly reduced. MS *m/z* (%) 303, 301 (M$^+$, 31), 221 (14), 95 (73), 83 (100). Calcd for $C_{16}H_{28}DBr$: M, 301.1514. Found: *m/z* 301.1523.

[Bromo-(α-hydroxybenzyl)methylidene]cyclopentadecane (36). A solution of **24** (64 mg; 0.15 mmol) in 0.2 ml of THF was added dropwise with stirring to a solution of EtMgBr (0.45 mmol) in 3 ml of THF at -90 °C. After 5 min, benzaldehyde (0.5 mmol) was added and the reaction mixture was stirred for 1 h. The reaction was quenched by adding sat. aq. NH_4Cl and the whole was extracted with ether-benzene. The organic layer was dried over $MgSO_4$ and the solvent was evaporated. As the adduct **36** and benzaldehyde have the same Rf value on silica gel, the residue was dissolved in MeOH (5 ml), cooled in an ice bath, and $NaBH_4$ (19 mg) was added with stirring to reduce the benzaldehyde. After 10 min, the MeOH was evaporated and the residue was extracted and washed. The product was purified by silica gel column chromatography to give **36** (42 mg; 68%) and 10 mg (22%) of **15**. **36**: Colorless oil; IR (neat) 3408 (OH), 1603, 1493, 1448 cm^{-1}; ^{1}H NMR δ 1.2-1.7 (24H, m), 2.2-2.4 (4H, m), 5.69 (1H, d, *J*=9 Hz), 7.2-7.4 (5H, m). MS *m/z* (%) 408, 406 (M$^+$, 3), 390, 388 (66), 338 (51), 105 (100). Calcd for $C_{23}H_{35}BrO$: M, 408.1850. Found: *m/z* 408.1850.

Treatment of 12 with EtMgCl followed by magnesium bromide diethyl etherate. A solution of **12** (59 mg; 0.15 mmol) in 0.5 ml of THF was added dropwise with stirring to a solution of EtMgCl (0.6 mmol) in 3 ml of THF at -80 °C. The reaction mixture was stirred for 3 min, then a solution of $MgBr_2$-etherate (0.4 mmol) in 0.1 ml of dry ether was added. The solution was stirred at -80 °C for 15 min. The reaction was quenched by adding sat. aq. NH_4Cl and the whole was extracted with ether-benzene. The product was purified by silica gel column chromatography to give a colorless oil (33 mg; 86% yield). ^{1}H NMR showed that the product was a mixture of chloride **14** and bromide **15** in a ratio of 1:2.

(*E*)-1-Chloro-2-phenyl-1-(*p*-tolylsulfinyl)-1-propene (40) and (*Z*)-isomer (41). The 1-chlorovinyl sulfoxide **40** and **41** were synthesized from chloromethyl *p*-tolyl sulfoxide and acetophenone as described above. **40**: Colorless crystals; mp 64-67 °C (AcOEt-hexane). IR (KBr) 1489, 1086, 1053 (SO) cm^{-1}; ^{1}H NMR δ 2.32 (3H, s, vinyl-CH_3), 2.40 (3H, s), 7.26-7.48 (9H, m). Anal. Calcd for $C_{16}H_{15}ClOS$: C, 66.19; H, 5.21; Cl, 12.05; S, 11.04. Found: C, 66.35; H, 5.14; Cl, 12.01; S, 11.07. **41**: Colorless crystals; mp 88-90 °C (AcOEt-hexane). IR (KBr) 1491, 1088, 1057 (SO) cm^{-1}; ^{1}H NMR δ 2.43 (3H, s), 2.61 (3H, s, vinyl-CH_3), 7.23-7.58 (9H, m). Anal. Calcd for $C_{16}H_{15}ClOS$: C, 66.19; H, 5.21; Cl, 12.05; S, 11.04. Found: C, 66.28; H, 5.14; Cl, 12.00; S, 10.98.

(*E*)-1-Chloro-2-methyl-2-phenyl-1-propene (42) and (*Z*)-isomer (43). On treatment of **40** with 3 equivalents of EtMgCl in THF at -78 °C for 5 min gave **42** as colorless oil (yield 95%). IR (neat) 1626, 1601, 1493, 1443 cm^{-1}; ^1H NMR δ 2.19 (3H, d, J=1.3 Hz), 6.31 (1H, q, J=1.3 Hz), 7.32 (5H, m). MS m/z (%) 252 (100), 117 (54), 115 (73). Calcd for C_9H_9Cl: M, 152.0393. Found: m/z 152.0394.

Treatment of **41** with EtMgCl gave an inseparable mixture of **42** and **43** (^1H NMR δ 2.09 (d, J=1.7 Hz), 6.10 (q, J=1.7 Hz)).

[Chloro-(*p*-tolylsulfinyl)methylidene]-4,4-ethylenedioxycyclohexane (46). This compound was synthesized from chloromethyl *p*-tolyl sulfoxide and 1,4-cyclohexanedione *mono*-ethylene ketal in a similar way as described above. **Chloro alcohol**: 95% yield; colorless crystals; mp 216-218 °C ($CHCl_3$-hexane). IR (KBr) 3367 (OH), 1037 (SO) cm^{-1}. Anal. Calcd for $C_{16}H_{21}ClO_4S$: C, 55.73; H, 6.14; Cl, 10.28; S, 9.30. Found: 55.45; H, 6.05; Cl, 10.38; S, 9.39. **Acetate**: 94% yield; colorless prisms; mp 148-150 °C (AcOEt-hexane). IR (KBr) 1728 (CO), 1228 (COC), 1060 (SO) cm^{-1}; ^1H NMR δ 1.6-2.5 (8H, m), 2.18 (3H, s), 2.42 (3H, s), 3.97 (4H, m), 5.42 (1H, s), 7.32, 7.45 (each 2H, d, J=8 Hz). Anal. calcd for $C_{18}H_{23}ClO_5S$: C, 55.88; H, 5.99; Cl, 9.16; S, 8.29. Found: C, 56.12; H, 5.97; Cl, 9.15; S, 8.32.

The acetate (387 mg; 1 mmol) was dissolved in 7 ml of DMSO. To this was added NaH (1.15 mmol) and the suspension was stirred at room temperature for 3 h. The solution was diluted with ether (10 ml) and cooled in an ice bath. The reaction was quenched by adding a solution of acetic acid (1 ml) in 10 ml of ether. The whole was extracted with ether-benzene, washed once with half-saturated aq. NH_4Cl. The product was isolated by flash chromatography to give 235 mg (72%) of **46** as colorless crystals. Mp 124-126 °C (AcOEt-hexane); IR (KBr) 1088, 1051 (SO) cm^{-1}; ^1H NMR δ 1.7-2.0 (4H, m), 2.41 (3H, s), 2.5-2.8 (2H, m), 2.90 (1H, m), 3.10 (1H, m), 4.00 (4H, s), 7.30, 7.46 (each 2H, d, J=8 Hz). Anal. Calcd for $C_{16}H_{19}ClO_3S$: C, 58.80; H, 5.86; Cl, 10.85; S, 9.81. Found: C, 58.88; H, 5.81; Cl, 11.10; S, 9.97.

(Chloromethylidene)-4,4-ethylenedioxycyclohexane (47). Colorless oil; IR (neat) 1635, 1122, 1086 cm^{-1}; ^1H NMR δ 1.70 (4H, t, J=6.5 Hz), 2.31 (2H, t, J=6.5 Hz), 2.49 (2H, t, J=6.5 Hz), 3.97 (4H, s), 5.83 (1H, s). MS m/z (%) 188 (M^+, 23), 153 (100). Calcd for $C_9H_{13}ClO_2$: M, 188.0603. Found: m/z 188.0608.

[Chloro(deuterio)methylidene]-4,4-ethylenedioxycyclohexane (48). Colorless oil; IR (neat) 1630, 1124, 1088 cm^{-1}; ^1H NMR: the signal of the vinyl-H (δ 5.83) was markedly reduced. MS m/z (%) 189 (M^+, 31), 154 (100). Calcd for $C_9H_{12}DClO_2$: M, 189.0666. Found: m/z 189.0683.

[Chloro-(α-hydroxybenzyl)methylidene]-4,4-ethylenedioxycyclohexane (49). Colorless crystals; mp 130-133 °C (AcOEt-hexane); IR (KBr) 3404 (OH), 1122, 1080 cm^{-1}; ^1H NMR δ 1.78 (4H, m), 2.63 (4H, m), 3.99 (4H, s), 5.91 (1H, d, J=7 Hz), 7.2-7.4 (5H, m). MS m/z (%) 294 (M^+, 5), 276 (34), 258 (32), 215 (100). Calcd for $C_{16}H_{19}ClO_3$: M, 294.1023. Found: m/z 294.1017.

1,2,3-Triene (50). Colorless crystals; mp 128-130 °C (AcOEt-hexane). IR (KBr) 1117, 1082 cm^{-1}; ^1H NMR δ 1.79 (8H, t, J=7 Hz), 2.45 (8H, t, J=6 Hz), 3.98 (8H, s). MS m/z (%) 304 (M^+, 100), 259 (22). Calcd for $C_{18}H_{24}O_4$: M, 304.1674. Found: m/z 304.1686.

Propylidene-4,4-ethylenedioxycyclohexane (51). Colorless oil; IR (neat) 1122, 1103 cm^{-1}; ^1H NMR δ 0.94 (3H, t, J=7.6 Hz), 1.65 (4H, m), 2.00 (2H, quintet, J=7.6 Hz), 2.23 (4H, m), 3.96 (4H, s), 5.15 (1H, t, J=7.3 Hz). MS m/z (%) 182 (M^+, 20), 153 (19), 86 (100). Calcd for $C_{11}H_{18}O_2$: M, 182.1305. Found: m/z 182.1310.

Benzylidene-4,4-ethylenedioxycyclohexane (52). Colorless oil; IR (neat) 1120, 1084, 908 cm^{-1}: ^1H NMR δ 1.68 (2H, t, J=6.6 Hz), 1.79 (2H, t, J=6.6 Hz), 2.43 (2H, t, J=5.6 Hz), 2.52 (2H, t, J=5.6 Hz), 3.98 (4H, s), 6.31 (1H, s), 7.16-7.34 (5H, m). MS m/z (%) 230 (M^+, 100), 201 (70), 129 (43). Calcd for $C_{15}H_{18}O_2$: M, 230.1306. Found: m/z 230.1314.

[Deuterio(phenyl)methylidene]-4,4-ethylenedioxycyclohexane (53). A solution of **46** (60 mg; 0.18 mmol) in 0.5 ml of THF was added with stirring to a solution of PhMgBr (0.9 mmol) in 1 ml of THF at -85 °C. The temperature of the reaction mixture was gradually allowed to warm to -50 °C for 2 h. CD_3OD (0.4 ml) was added to the reaction mixture and then, the reaction was quenched by adding aq. sat. NH_4Cl. The whole was extracted with ether-benzene and the product was purified by silica gel column chromatography to give **53** (33 mg; 80%) as a colorless oil. IR (neat) 1120, 1088, 1034 cm^{-1}; ^1H NMR: the vinyl-H (δ 6.31) completely disappeared. MS m/z (%) 231 (M^+, 100), 202 (80), 130 (45). Calcd for $C_{15}H_{17}DO_2$: M, 231.1368. Found: m/z 231.1371.

[Phenyl-(1-hydroxypropyl)methylidene]-4,4-ethylenedioxycyclohexane (56). Colorless oil; IR (neat) 3450 (OH), 1124, 1088, 1033 cm^{-1}; ^1H NMR δ 0.92 (3H, t, J=7.6 Hz), 1.3-2.1 (8H, m), 2.52 (2H, t, J=6.3 Hz), 3.94 (4H, m), 4.68 (1H, t, J=6.9 Hz), 7.2-7.8 (5H, m). MS m/z (%) 288 (M^+, 3), 270 (59), 259 (100). Calcd for $C_{18}H_{24}O_3$: M, 288.1724. Found: m/z 288.1728.

[Phenyl-(1-hydroxy-1-methylethyl)methylidene]-4,4-ethylenedioxycyclohexane (57). Colorless crystals; mp 107-109 °C (AcOEt-hexane); IR (KBr) 3425 (OH), 1120, 1087 cm^{-1}; ^1H NMR δ 1.33 (6H, s), 1.55, 1.80, 1.87, 2.85 (each 2H, t, J=6.5 Hz), 3.95 (4H, m), 6.9-7.4 (5H, m). MS m/x (%) 288 (M^+, 3), 270 (100), 169 (100), 101 (97). Anal. Calcd for $C_{18}H_{24}O_3$: C, 75.00; H, 8.39. Found: C, 74.81; H, 8.22.

[Carboethoxy(phenyl)methylidene]-4,4-ethylenedioxycyclohexane (58). Colorless oil; IR (neat) 1745, 1713 (CO), 1254, 1185, 1090, 1036 cm^{-1}; ^1H NMR δ 1.22 (3H, t, J=7.1 Hz), 1.67 (2H, t, J=6.2 Hz), 1.84 (2H, t, J=6.3 Hz), 2.26 (2H, m), 2.71 (2H, t, J=6.6 Hz), 3.96 (4H, m), 4.16 (2H, q, J=7.1 Hz), 7.1-7.4 (5H, m). MS m/z (%) 302 (M^+, 7), 273 (21), 256 (100). Calcd for $C_{18}H_{22}O_4$: M, 302.1516. Found: m/z 302.1503.

[Iodo(phenyl)methylidene]-4,4-ethylenedioxycyclohexane (59). Colorless crystals; mp 88-90 °C ($CHCl_3$-MeOH); IR (KBr) 1119, 1086, 747, 699 cm^{-1}; ^1H NMR δ 1.57, 1.81, 2.30, 2.70 (each 2H, t, J=6.5 Hz), 3.97 (4H, m), 7.2-7.4 (5H, m). MS m/z (%) 356 (M^+, 21), 299 (100), 143 (38). Anal. Calcd for $C_{15}H_{17}O_2I$: C, 50.58; H, 4.81. Found: C, 50.33; H, 4.70.

(3-Hydroxy-1,5-diphenylpentylidene)-4,4-ethylenedioxycyclohexane (60). Colorless oil; IR (neat) 3444 (OH), 1095 cm^{-1}; ^1H NMR δ 1.6-1.8 (6H, m), 2.14 (2H, m), 2.4-2.8 (6H, m), 3.51 (1H, m), 3.96 (4H, m), 7.0-7.4 (10H, m). MS m/z (%) 378 (M^+, 5), 244 (100), 91 (58). Calcd for $C_{25}H_{30}O_3$: M, 378.2193. Found: m/z 378.2203.

[*N*-Phenylcarbamoyl(phenyl)methylidene]-4,4-ethylenedioxycyclohexane (61). Colorless crystals; mp 187-189 °C ($CHCl_3$-hexane); IR (KBr) 3421 (NH), 1649 (CO), 1439 cm^{-1}; ^1H NMR δ 1.71 (2H, t, J=6 Hz), 1.86 (2H, t, J=6.3 Hz), 2.31 (2H, t, J=6.5 Hz), 2.84 (2H, t, J=6.5 Hz), 3.96 (4H, m), 7.0-7.5 (10H, m). MS m/z (%) 349 (M^+, 92), 304 (100). Calcd for $C_{22}H_{23}O_3N$: M, 349.1678. Found: m/z 349.1677.

(4-Methoxybenzylidene)-4,4-ethylenedioxycyclohexane (62). Colorless oil; IR (neat) 1510, 1247, 1119, 1082, 1035 cm^{-1}; ^1H NMR δ 1.68 (2H, t, J=6.5 Hz), 1.78 (2H, t, J=6.5 Hz), 2.41 (2H, m), 2.51 (2H, m), 3.80 (3H, s), 3.98 (4H, m), 6.24 (1H, s), 6.87 (2H, d, J=9 Hz), 7.13 (2H, d, J=9 Hz). MS m/z (%) 260 (M^+, 100), 231 (36), 159 (27). Calcd for $C_{16}H_{20}O_3$: M, 260.1412. Found: m/z 260.1418.

[Deuterio-(4-methoxyphenyl)methylidene]-4,4-ethylenedioxycyclohexane (63). Colorless oil; IR (neat) 1509, 1244, 1121, 1084, 1035 cm^{-1}; ^1H NMR: the signal of vinyl-H (δ 6.24) was markedly reduced. MS m/z (%) 261 (M^+, 100), 232 (41), 160 (22). Calcd for $C_{16}H_{19}DO_3$: M, 261.1473. Found: m/z 261.1471.

[2-Hydroxy-1-(4-methoxyphenyl)-2-phenylethylidene]-4,4-ethylenedioxycyclohexane (64). Colorless oil; IR (neat) 3412 (OH), 1509, 1244, 1033 cm^{-1}; ^1H NMR δ 1.70, 1.79, 2.29, 2.50 (each 2H, t, J=6.5 Hz), 3.76 (3H, s), 3.95 (4H, m), 4.69 (1H, s), 6.8-8.0 (9H, m). MS m/z (%) 364 ($[M-H_2]^+$, 100), 319 (38). Calcd for $C_{23}H_{24}O_4$ ($M-H_2$): M, 364.1674. Found m/z 364.1679.

[Carboethoxy(4-methoxyphenyl)methylidene]-4,4-ethylenedioxycyclohexane (65). Colorless oil; IR (neat) 1713 (CO), 1511, 1244, 1186, 1089, 1034 cm^{-1}; ^1H NMR δ 1.23 (3H, t, J=7.1 Hz), 1.67, 1.83, 2.28, 2.67 (each 2H, t, J=6.5 Hz), 3.81 (3H, s), 3.97 (4H, m), 4.17 (2H, q, J=7.1 Hz), 6.9-7.5 (4H, m). MS m/z (%) 332 (M^+, 23), 286 (100), 259 (40). Calcd for $C_{19}H_{24}O_5$: M, 332.1624. Found: m/z 332.1627.

[4-Methoxyphenyl-(*N*-phenylcarbamoyl)methylidene]-4,4-ethylenedioxycyclohexane (66). Colorless crystals; mp 108-111 °C ($CHCl_3$-hexane); IR (KBr) 1704 (CO), 1423 cm^{-1}; ^1H NMR δ 1.70 (2H, t, J=6.5 Hz), 1.85 (2H, t, J=6.5 Hz), 2.32 (2H, t, J=6.4 Hz), 2.85 (2H, t, J=6.7 Hz), 3.83 (3H, s), 3.97 (4H, m), 6.9-7.5 (9H, m). MS m/z (%) 379 (M^+, 66), 334 (58), 259 (57), 119 (100). Calcd for $C_{23}H_{25}NO_4$: M, 379.1782. Found: m/z 379.1791.

Vinylmethylidene-4,4-ethylenedioxycyclohexane (67). Colorless oil; IR (neat) 1674, 1085, 1034; ^1H NMR (90 Mhz) δ 1.5-1.9 (4H, m), 2.2-2.6 (4H, m), 3.97 (4H, m), 4.9-5.3 (2H, m), 5.85 (1H, d, J=11 Hz), 6.3-6.8 (1H, m). MS m/z (%) 180 (M^+, 41), 167 (30), 149 (75), 99 (83), 86 (100). Calcd for $C_{11}H_{16}O_2$: M, 180.1151. Found: m/z 180.1156.

[*N*-Phenylcarbamoyl(vinyl)methylidene]-4,4-ethylenedioxycyclohexane (68). Colorless crystals; mp 171-174 °C ($CHCl_3$-hexane); IR (KBr) 3426, 3291 (NH), 1657 (CO), 1598, 1542, 1439 cm^{-1}; ^1H NMR δ 1.77 (4H, m), 2.50 (4H, m), 3.97 (4H, s), 5.28 (1H, d, *J*=11 Hz), 5.33 (1H, d, *J*=17 Hz), 6.70 (1H, dd, *J*=11, 17 Hz), 7.1-7.6 (5H, m). MS *m/z* (%) 299 (M^+, 100), 254 (74), 207 (64). Calcd for $C_{18}H_{21}O_3N$: M, 299.1520. Found: *m/z* 299.1529.

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