of 1.497 (8) Å. The short C2–C3 bond (1.469 (9) Å) suggests an electronic interaction between the phosphirane ring and its neighboring C=C bond. The two P–C bonds of the phosphirane are 1.816 (6) and 1.851 (5) Å long with the P–C3 bond being the longest for hyperconjugative reasons, which is in line with the observed [1,3]-sigmatropic shift. Homolytic cleavage of the weaker P–C3 bond to yield a biradical intermediate is highly unlikely because such a species would yield either only an *anti*-phospholene with retention of configuration, when P–C fusion is faster than P-inversion or a mixture of *syn*- and *anti*-**5** (as well as *syn*-**4**), when P-inversion is faster than P–C fusion.

The observed tricyclic phospholene **5** has longer bridging P–C bonds of 1.876 (6) and 1.879 (7) Å with a larger CPC angle of 79.6 (3)° than found in the bicyclic phosphirane structure **4**. As expected for the different P-hybridizations, structure **5** has the smaller phenyl–P–$W(CO)_5$ angle of 112.7° vs 118.6° in **4**, although steric effects can not be excluded. However, if these are present, they apparently do not influence the direction (or twisting) of the P-ligands; the C1–P–C4 and phenyl–P–$W(CO)_5$ planes are orthogonal. The structural parameters of **5** are similar to those of the Cr analogue of **1**,[17] which has similar bridging P–C bonds of 1.877 and 1.878 Å with a CPC angle of 79.0°.

The ^{31}P NMR chemical shifts of δ −131.2 ppm for **4** and δ +65.7 ppm for **5** are strikingly different. The former value is typical for phosphiranes while the latter compares well with P-bridged structures.[1,18]

(17) Marinetti, A.; Mathey, F.; Fischer, J.; Mitscher, A. *J. Chem. Soc., Chem. Commun.* **1982**, 667.
(18) Verkade, J. G.; Quin, L. D. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; VCH: Deerfield Beach, FL, 1987.

Conclusions. The reaction of the carbene-like terminal phosphinidene complex Ph–P–$W(CO)_5$ with the activated cyclic diene **3** yields as primary product the bicyclic phosphirane **4** in high stereoselectivity. It is suggested that this selectivity is determined early on the reaction path and results from repulsive interactions between the *P*-phenyl and diene groups. Tricyclic phospholene **5** is not a primary (1,4-addition) product from diene **3**, but rather a secondary reaction product resulting from a [1,3]-sigmatropic shift in phosphirane **4** with complete inversion of the stereochemistry of the sterically crowded P-center.

The overall reaction involves a transfer of the phosphinidene complex **2** from the tricyclic diene reagent **1** to yield a structurally similar tricyclic olefin.

The stepwise 1,4-addition of the complexed phosphinidene to a cisoid 1,3-diene differs from recently reported direct 1,4-additions of both carbenes and alkadienylidene carbenes.

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Supplementary Material Available: Listings of bond distances and angles for coordinates of hydrogen atoms, least-squares planes, and anisotropic thermal parameters **4** and **5** (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

One-Step Spiroannulation Using 1,2-Bis(methylene)cycloalkane–Magnesium Reagents

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A one-step method for the synthesis of a wide variety of spirocyclic systems has been developed based on the reactions of bis-electrophiles with a series of new 1,3-diene–magnesium reagents, the magnesium complexes of 1,2-bis(methylene)cycloalkanes. The direct metalation of 1,2-bis(methylene)cycloalkanes with highly reactive magnesium in THF at ambient temperature generates the corresponding diene–magnesium reagents in high yields. Reactions of the diene–magnesium reagents with 1,*n*-dibromoalkanes produce a large number of spirocarbocycles containing an exocyclic double bond. The ring sizes of the accessible spiro compounds can be any combinations of four- to seven-membered rings. In most cases, the initially alkylated intermediates can be trapped by protonation, giving the corresponding bromo olefins. Significantly, treatment of the diene–magnesium reagents with bromoalkyl nitriles leads to a one-step synthesis of keto-functionalized spirocycles. The initial adduct is believed to be a Grignard reagent containing a cyano group. When a bromo nitrile containing a cyclic moiety is used as the bis-electrophile, the approach provides a direct access to dispiroenones.

Introduction

Halide-free organomagnesium compounds prepared from the direct metalation of conjugated dienes with activated magnesium represent an important advance in organomagnesium chemistry.[1] From the viewpoint of nucleophilic reactivity, these diene–magnesium reagents can be regarded as magnesium 1,3-diene dianions which allow for the formation of two bonds with electrophilic substrates in one synthetic operation. Depending upon the nature of various electrophiles, both 1,2- and 1,4-additions to the original dienes have been observed.[2,3] When two electrophilic centers reside in one substrate, the overall process provides an easy access to cyclic molecules.

However, since the first report by Ramsden[4a] in 1968, the studies on the chemistry of diene–magnesium com-

(1) For a recent review, see Dzhemilev, U. M.; Ibragimov, A. G.; Tolstikov, G. A. *J. Organomet. Chem.* **1991**, *406*, 1.

(2) (a) Herberich, G. E.; Boveleth, W.; Hessner, B.; Hostalek, M.; Koeffer, D. P. J.; Ohst, H.; Soehnen, D. *Chem. Ber.* **1986**, *119*, 420. (b) Richter, W. J. *Chem. Ber.* **1983**, *116*, 3293. (c) Salomon, R. G. *J. Org. Chem.* **1974**, *39*, 3602. (d) Richter, W. J. *J. Organomet. Chem.* **1983**, *289*, 45. (e) Richter, W. J.; Neugebauer, B. *Synthesis*, **1985**, 1059.
(3) (a) Xiong, H.; Rieke, R. D. *J. Org. Chem.* **1989**, *54*, 3247. (b) Rieke, R. D.; Xiong, H. *J. Org. Chem.* **1991**, *56*, 3109.

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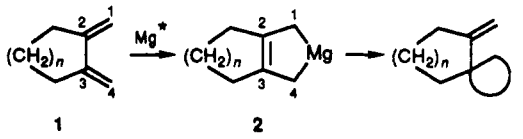
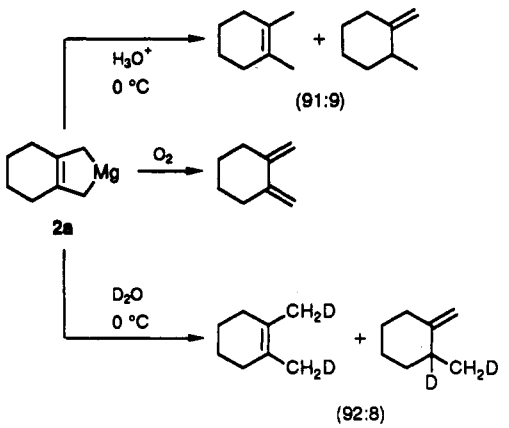
Scheme I



Scheme II



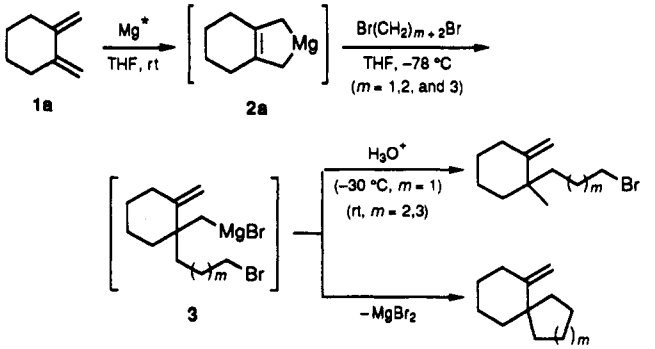
pounds have been mainly limited to the following open-chain 1,3-dienes: 1,3-butadiene, isoprene, myrcene, 2,3-dimethyl-1,3-butadiene, and (*E,E*)-1,4-diphenyl-1,3-butadiene.[1,2,4] This limited investigation was primarily due to the difficulty for the preparation of 1,3-diene–magnesium reagents caused by the limited reactivity of metallic magnesium.

We have previously shown that substituted 1,3-diene–magnesium complexes can be readily prepared by using highly reactive magnesium.[3,5] As a continuation of our studies on diene–magnesium chemistry, we have recently extended this chemistry to the corresponding exocyclic conjugated dienes,[6] providing a fundamentally new approach for a one-step spiroannulation (Scheme I).[7] In this paper, the preparation of 1,2-bis(methylene)cycloalkane–magnesium reagents and the synthesis of spiro olefin and spiroenone using the diene–magnesium reagents are described.

Results and Discussion

1,2-Bis(methylene)cycloalkane–Magnesium Reagents. The starting dienes (1,2-bis(methylene)cyclohexane (**1a**), 1,2-bis(methylene)cyclopentane (**1b**), and 1,2-bis(methylene)cycloheptane (**1c**)) required for this investigation were prepared by established procedures.[8] The preparation of the magnesium complexes of 1,2-bis(methylene)cycloalkanes was effected by using highly reactive magnesium (Mg*) which is readily generated by the reduction of anhydrous magnesium chloride in THF with either preformed lithium naphthalenide or Li in the presence of naphthalene.[5] In a typical reaction, 1,2-bis-

Scheme III



(methylene)cycloalkane was added to an excess of newly generated activated Mg* in THF (typical equivalent ratio of magnesium/diene = 2:1). After the mixture was stirred for 3–4 h at ambient temperature under argon, the corresponding diene–magnesium adduct (**2**) was formed as a soluble complex in THF. The resulting yellowish-gold THF solution of the complex was easily separated from the excess magnesium by either filtration or cannulation under argon. This freshly prepared THF solution of diene–magnesium complex was usually treated directly with the appropriate electrophiles.

The structures of 1,2-bis(methylene)cycloalkane–magnesium reagents are presumably similar to that of magnesium complexes of open-chain 1,3-dienes.[9] In THF solution **2** exists most likely as five-membered metallocycles or organometallic oligomers. The passage of pure O_2 through the THF solution of **2** gave back the original dienes. Direct hydrolysis of **2** yielded a mixture of dihydro products of the diene. For example, protonation of the magnesium complex (**2a**) of 1,2-bis(methylene)cyclohexane in THF with diluted hydrochloric acid at 0 °C produced 1,2-dimethylcyclohex-1-ene and 1-methyl-2-methylenecyclohexane in a ratio of 91:9. Treatment of **2a** with D_2O at 0 °C resulted in dideuteronation of the diene, yielding 1,2-bis(deuteromethyl)cyclohex-1-ene and 1-deutero-1-(deuteromethyl)-2-methylenecyclohexane in a ratio of 92:8 (Scheme II). Direct ^{13}C NMR analyses at room temperature for the THF solution of **2a** resulted in the observation of only four different carbons (δ 119.4, 33.7, 25.6, and 20.2), indicating that 1,2-bis(methylene)cyclohexane–magnesium reagent possesses a symmetrical structure in THF. It is also possible that some dynamic exchange process is also occurring which results in only four carbon signals.

Reactions of 1,2-Bis(methylene)cycloalkane–Magnesium Reagents with Bis-Electrophiles. On the basis of the bis-nucleophilic property of 1,3-diene–magnesium complexes, reactions of **2** with bis-electrophiles can lead to spiro or fused bicyclic molecules, depending upon the positions where cyclization occurs. It has been found that treatment of magnesium complexes of 1,2-bis(methylene)cycloalkanes with 1,*n*-dibromoalkanes resulted in overall 1,2-cyclizations of the original dienes, giving spirocarbocycles in good to excellent yields. The results are summarized in Table I.

Scheme III illustrates the reaction pathways of **2a** with 1,*n*-dibromoalkanes. In general, 1,*n*-dibromoalkane is added to the THF solution of **2a** at −78 °C, producing a Grignard intermediate containing a bromo group (**3**). This intermediate can be trapped by protonation at an appropriate temperature, yielding the corresponding bromo

(4) (a) Ramsden, H. E. US 3,388,179, 1698; *Chem. Abstr.* **1968**, *69*, 67563d. (b) Fujita, K.; Ohnuma, Y.; Yasuda, H.; Tani, H. *J. Organomet. Chem.* **1976**, *113*, 201. (c) Yang, M.; Yamamoto, K.; Otake, N.; Ando, M.; Takase, K. *Tetrahedron Lett.* **1970**, 3843. (d) Baker, R.; Cookson, R. C.; Saunders, A. D. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1815. (e) Akutagawa, S.; Otsuka, S. *J. Am. Chem. Soc.* **1976**, *98*, 7420.

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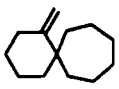
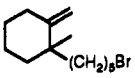
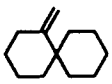
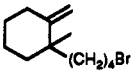
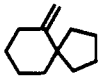
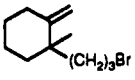
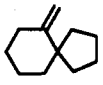
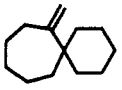
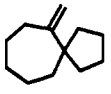
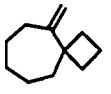
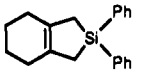
(7) The numbering system shown in Scheme I was chosen for convenience. It is not based on formal IUPAC nomenclature.

(8) (a) van Straten, J. W.; van Norden, J. J.; van Schaik, T. A. M.; Franke, G. Th.; de Wolf, W. H.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1978**, *94*, 105. (b) Le, N. A.; Jones, M. Jr.; Bickelhaupt, F.; de Wolf, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 8491.

(9) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Yasuda, H.; Nakamura, A. *Chem. Lett.* **1982**, 1277.

Table I. Reactions of Magnesium Complexes of 1,2-Bis(methylene)cycloalkanes with Bis-electrophiles

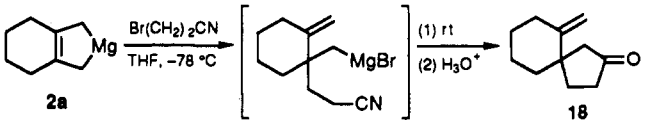
entry	diene[a]	electrophile	product	% yield[b]	note[c]
1	1a	$Br(CH_2)_5Br$		45	A
2	1a	$Br(CH_2)_5Br$		79	B
3	1a	$Br(CH_2)_4Br$		75 (81)	C
4	1a	$Br(CH_2)_4Br$		81	B
5	1a	$Br(CH_2)_3Br$		75 (87)	D
6	1a	$Br(CH_2)_3Br$		78	E
7	1a	$Cl(CH_2)_3Cl$		- (78)	F
8	1a	$Br(CH_2)_2Br$		- (15)	B
9	1a	$Cl(CH_2)_2Cl$		- (40)	B
10	1a	$(TsOCH_2)_2$		52 (67)	B
11	1b	$Br(CH_2)_3Br$		60 (70)	D
12	1c	$Br(CH_2)_4Br$		73	C
13	1c	$Br(CH_2)_3Br$		77 (86)	D
14	1c	$(TsOCH_2)_2$		46 (59)	B
15	1a	Ph_2SiCl_2		89	B

[a] 1a: 1,2-Bis(methylene)cyclohexane; 1b: 1,2-bis(methylene)-cyclopentane; 1c: 1,2-bis(methylene)cycloheptane. [b] Isolated overall yields were based on 1,2-bis(methylene)cycloalkanes. GC yields are shown in parentheses. [c] Bis-electrophiles were added to the THF solution of the diene–magnesium reagent at −78 °C. The reaction mixture was then stirred at −78 °C for 1 h prior to warming to the specified temperature. A: reflux (15 h); B: room temperature (30 min); C: reflux (10 h); D: room temperature (10 h); E: −30 °C; F: room temperature (30 h).

olefin. On the other hand, cyclization occurs upon warming, affording a spirocarbocycle containing an exocyclic double bond.

The temperature required for cyclizations varied with the chain length of 1,*n*-dibromoalkanes. For example, cyclization took place at room temperature when **2a** was treated with 1,3-dibromopropane, producing 6-methylenespiro[4.5]decane (**8**) (Table I, entry 5). In the cases of reactions of **2a** with 1,4-dibromobutane and 1,5-dibromopentane, refluxing conditions were required in order to obtain the spirocarbocycles (Table I, entries 1 and 3).

Scheme IV



2a **16** **18**

The position where the initial alkylation occurred was established by the protonation of the intermediate at low temperatures. For the reaction of **2a** with 1,3-dibromopropane, acidic hydrolysis at −30 °C resulted in monoalkylation, yielding the corresponding bromo olefin containing a quaternary center (Table I, entry 6). On the other hand, the monoalkylated intermediates derived from the treatment of 1,4-dibromobutane and 1,5-dibromopentane with **2a** were protonated at room temperature, yielding the corresponding uncyclized products (Table I, entries 2 and 4).

Attempts to generate a four-membered ring by treating **2a** with 1,2-dibromoethane or 1,2-dichloroethane gave only low yields of 5-methylenespiro[3.5]nonane (**10**) (Table I, entries 8 and 9). However, this spirocarbocycle was prepared in good yield by the reaction of **2a** with ethylene glycol di-*p*-tosylate in THF at −78 °C followed by warming to room temperature (Table I, entry 10).

Significantly, the spiroannulation approach has been easily extended to the analogous 1,2-bis(methylene)-cycloalkanes. A wide variety of spirocarbocycles have been synthesized from the reactions of magnesium complexes of 1,2-bis(methylene)cyclopentane and 1,2-bis(methylene)cycloheptane with 1,*n*-dibromoalkanes (Table I, entries 11–14). Therefore, this new spiroannulation method provides a very general approach to a large number of spirocarbocycles with different combinations of ring sizes.

In contrast to the general 1,2-cyclizations with 1,*n*-dibromoalkanes, treatment of dichlorodiphenylsilane with **2a** resulted in overall 1,4-cyclization to give 2,2-diphenyl-2,3,4,5,6,7-hexahydro-2-sila-1*H*-indene (**15**) (Table I, entry 15). This example represents a facile approach to silicon-containing fused bicyclic rings.

Reactions of 1,2-Bis(methylene)cycloalkane–Magnesium Reagents with Bromoalkyl Nitriles. Reactions of Grignard reagents with nitriles represent a classic method of preparing ketones.[10] Since one of the significant differences between an ordinary Grignard reagent and a magnesium complex of a 1,3-diene is that the latter contains two formal Mg–C bonds and therefore offers the possibility of ring annulation. We have previously found that treatment of (2,3-dimethyl-2-butene-1,4-diyl)magnesium reagent with bromoalkyl nitriles afforded cyclic ketones.[3b] Current studies demonstrated that the approach for the formation of cyclic ketones can be extended to the 1,2-bis(methylene)cycloalkane–magnesium reagents. Thus, the reactions of **2** with bromoalkyl nitriles resulted in the generation of keto-functionalized spirocycles. Table II summarizes the results of these studies.

For example, addition of 3-bromopropionitrile to a magnesium complex of 1,2-bis(methylene)cyclohexane (**2a**) at −78 °C yielded a Grignard containing a cyano group (**2**). This intermediate began to cyclize even at −78 °C, preventing the trapping of the monoalkylated adduct. Hy-

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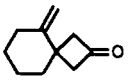
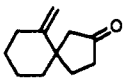
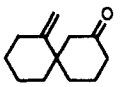
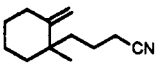
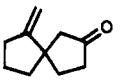
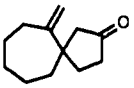
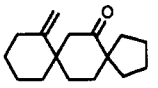
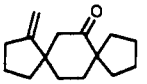
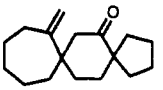
Table II. Reactions of Magnesium Complexes of 1,2-Bis(methylene)cycloalkanes with Bromoalkyl Nitriles

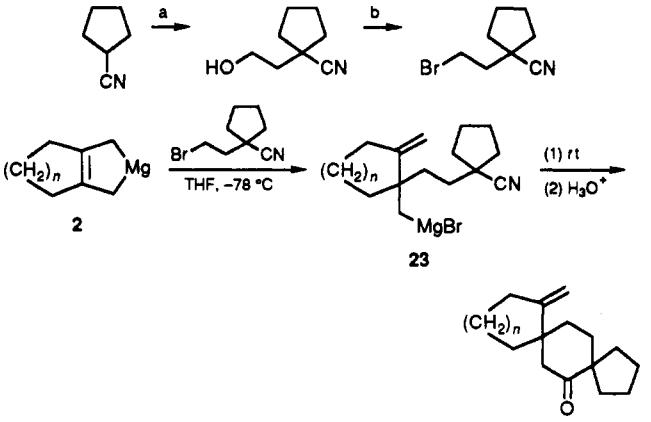
entry	diene[a]	bromo nitrile[b]	product[c]	% yield[d]
1	1a	$BrCH_2CN$		46
2	1a	$Br(CH_2)_2CN$		51
3	1a	$Br(CH_2)_3CN$		13
4	1a	$Br(CH_2)_3CN$		61[e]
5	1b	$Br(CH_2)_2CN$		40
6	1c	$Br(CH_2)_2CN$		54
7	1a	BrC_2H_4CpCN[f]		74
8	1b	BrC_2H_4CpCN[f]		46
9	1c	BrC_2H_4CpCN[f]		52

[a] 1a: 1,2-Bis(methylene)cyclohexane; 1b: 1,2-bis(methylene)-cyclopentane; 1c: 1,2-bis(methylene)cycloheptane. [b] Bromo nitriles were added to the THF solution of the magnesium complexes of 1,2-bis(methylene)cycloalkanes at −78 °C. The reaction mixture was then stirred at −78 °C for 30 min prior to warming to room temperature followed by workup. [c] All compounds have been completely characterized spectroscopically. [d] Percentage isolated yields. [e] Protonation at −40 °C resulted in the survival of the cyano group. [f] BrC_2H_4CpCN = 1-(2-bromoethyl)cyclopentanecarbonitrile.

drolysis at room temperature followed by workup yielded 6-methylenespiro[4.5]decan-2-one (18) in 51% isolated yield (Scheme IV) (Table II, entry 2). Similarly, the reactions of magnesium complexes of 1,2-bis(methylene)-cyclopentane and 1,2-bis(methylene)cycloheptane with 3-bromopropionitrile gave the corresponding spiroenones (Table II, entries 5 and 6). Surprisingly, treatment of bromoacetonitrile with **2a** at −78 °C afforded 5-methylenespiro[3.5]nonan-2-one (17) (Table II, entry 1). Reaction of 1,2-bis(methylene)cyclohexane–magnesium reagent with 4-bromobutyronitrile and trapping of the intermediate by protonation at −40 °C afforded the monoalkylated product of the original diene, establishing where the initial attack occurred (Table II, entry 4).

Remarkably, double spiroannulation can also be accomplished in one step by using a bromo nitrile containing a cyclic moiety as the bis-electrophile. The cyclic bromo nitrile can be readily prepared from the corresponding cyclic carbonitrile by established methods.[11] Scheme V describes the strategy of the dispiroannulation using 1,2-bis(methylene)cycloalkane–magnesium reagents. Basically, **2** was treated with 1-(2-bromoethyl)cyclopentanecarbonitrile at −78 °C, producing presumably a Grignard reagent containing a cyano group (**23**). Upon warming to room

Scheme V



temperature, cyclization took place. Workup gave dispirocycles (Table II, entries 7, 8, and 9). In this process, two cyclic species were used to construct a complex molecule in one synthetic operation, with the generation of a new six-membered ring and formation of two spirocenters. It is obvious that the ring size of the electrophile can be varied and thus the strategy described in Scheme V represents a general approach to a variety of dispirocycles.

A major advantage of the present spiroannulation method is that the generation of a quaternary carbon center and formation of a ring are achieved in one synthetic operation. Alternative methods to accomplish this overall process usually require two or more separate steps.[12,13] One of the useful one-step methods is based on the treatment of cycloalkanones with 1,*n*-dihaloalkanes in the presence of 2 equiv of base.[14] This approach has been used for the synthesis of β-vetivone by Stork, Danheiser, and Ganem.[15] Another efficient one-step method suitable for the preparation of general spirocyclic systems has been developed by Wender, White, and Eck.[16] The method involves the reactions of organobis(cuprates) with β-halocycloalkenones. The bis(cuprates) can be prepared by transmetalation from the corresponding dilithium reagents.

While significant progress has been made, the use of 1,2-bis(methylene)cycloalkane–magnesium reagents provides not only a simple approach for spiroannulation but also an efficient access to various spirocarbocycles. Several spirocyclic systems, such as spiro[3.5]nonane, spiro[4.5]-decane, spiro[5.5]undecane, and even spiro[5.6]dodecane bicyclic rings, can be synthesized by this method. Furthermore, spirocycles prepared by this approach contain functional groups such as the exocyclic double bond or keto group in one of the rings which could be used for further elaboration of these molecules.

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Conclusions

A series of new conjugated diene–magnesium reagents has been prepared by the reactions of bis(methylene)-cycloalkanes with highly reactive magnesium. Reactions of these diene–magnesium reagents with bis-electrophiles provide a general and efficient method for the synthesis of commonly encountered spirocyclic systems. A wide variety of spirocarbocycles containing an exocyclic double bond has been synthesized by the reactions 1,2-bis(methylene)cycloalkane–magnesium reagents with 1,*n*-dibromoalkanes. The ring sizes of accessible spirocycles can be any combinations of four- to seven-membered rings. In most cases, the monoalkylated adducts can be trapped by protonation, producing the corresponding bromo olefins. Significantly, treatment of the diene–magnesium reagents with bromoalkyl nitriles leads to the generation of keto-functionalized spirocarbocycles. This approach can be extended to the preparation of dispiroenones by using cyclic bromo nitriles as the bis-electrophiles.

Experimental Section

All manipulations were carried out under an atmosphere of argon on a dual manifold vacuum/argon system. The Linde prepurified grade argon was further purified by passage over a BASF R3-11 catalyst column at 150 °C, a phosphorous pentoxide column, and a column of granular potassium hydroxide. Lithium, naphthalene, and $MgCl_2$ were weighed out and charged into reaction flasks under argon in a dry box (Vacuum Atmospheres Co.). Tetrahydrofuran was distilled from Na/K alloy under an atmosphere of argon immediately before use.

Gas chromatographic analyses were done on a Hewlett-Packard 5890A chromatograph equipped with stainless steel columns (12 ft × $^1/_8$ in.) packed with SP-2250 (10%) on 100/120 Supelcoport or SP-2100 (10%) on 100/120 Supelcoport and interfaced with a Perkin-Elmer LCI-100 integrator. GC yields were quantified by determining response factors for pure samples and calculating the yield relative to an internal standard. Product purification was typically performed by column chromatography using glass columns packed with Merck flash silica gel 60 (230–400 mesh). Fractions were monitored with analytical thin-layer chromatography using Merck 5735 indicating plates precoated with silica gel 60 F254 (layer thickness 0.2 mm). The product spots were visualized by developing the thin-layer plates in an iodine chamber or with vanillin solution.[17]

^{1}H NMR (360 MHz) spectra were recorded in $CDCl_3$ solution unless specified. All chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. Fully decoupled ^{13}C NMR (50 MHz) spectra were recorded in $CDCl_3$ solution. The center peak of $CDCl_3$ (77.0 ppm) was used as the internal reference. FTIR spectra are reported as cm^{-1}. Mass spectra were performed by the Midwest Regional Center for Mass Spectrometry at the University of Nebraska—Lincoln. Elemental analyses were done by Oneida Research Services, Inc., Whitesboro, NY or Desert Analytics, Tucson, AZ.

Preparation of Activated Magnesium (Mg*). Activated magnesium was prepared by the reduction of anhydrous magnesium chloride with either lithium using naphthalene as an electron carrier or preformed lithium naphthalenide. Both reduction procedures were described previously.[3b,5b]

Typical Preparation of Spiro Olefin: 6-Methylenespiro[4.5]decane[18] (8). 1,2-Bis(methylene)cyclohexane (0.199 g, 1.84 mmol) was added via a disposable syringe to the activated magnesium (3.66 mmol) in THF (15 mL). *n*-Nonane was added as an internal standard. After being stirred at room temperature for 4 h, the reaction mixture was allowed to stand until the solution became transparent (ca. 2 h). The yellowish-gold THF solution of the complex was then separated from the excess magnesium by cannulating the solution to another flask under argon. The THF solution of newly formed magnesium complex of 1,2-bis(methylene)cyclohexane was cooled to −78 °C using a dry ice/acetone bath, and 1,3-dibromopropane (0.461 g, 2.28 mmol) was added via a disposable syringe. The mixture was stirred at −78 °C for 1 h, then gradually warmed to room temperature, and stirred overnight at room temperature. An aqueous solution of 1.5 N HCl (10 mL) was added at 0 °C. The reaction mixture was washed with diethyl ether (20 mL). The aqueous layer was extracted with diethyl ether (2 × 15 mL), and the combined organic phases were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and water (20 mL) and dried over anhydrous $MgSO_4$. Removal of solvents and flash column chromatography (eluted by hexanes) gave 6-methylenespiro[4.5]decane (8) (0.208 g, 75% (87% GC) yield). 8 was also prepared from **2a** and 1,3-dichloropropane in 78% GC yield: ^{1}H NMR δ 4.62 (m, 1 H), 4.59 (d, J = 1.9 Hz, 1 H), 2.17 (t, J = 5.7 Hz, 2 H), 1.80–1.70 (m, 2 H), 1.66–1.47 (m, 8 H), 1.46–1.37 (m, 4 H); ^{13}C NMR δ 155.5, 104.2, 49.1, 39.7, 36.4, 34.5, 28.9, 23.9, 23.7; FTIR (neat) 3801, 2954, 2929, 2856, 1639, 1446, 887 cm^{-1}; EIMS m/z (rel intens) 150 ($M^{\bullet+}$, 22), 135 (20), 121 (20), 109 (53), 93 (57), 67 (100); HRMS calcd for $C_{11}H_{18}$ 150.1409, found 150.1410.

1-Methylenespiro[5.6]dodecane (4): 45% yield; ^{1}H NMR δ 4.67 (m, 1 H), 4.62 (d, J = 1.8 Hz, 1 H), 2.15 (t, J = 5.8 Hz, 2 H), 1.77–1.65 (m, 2 H), 1.60–1.41 (m, 14 H), 1.37–1.32 (m, 2 H); ^{13}C NMR δ 157.2, 105.4, 42.4, 39.6, 37.2, 33.6, 30.9, 28.9, 22.9, 22.1; FTIR (neat) 3083, 2923, 2854, 1635, 1465, 1448, 892 cm^{-1}; EIMS m/z (rel inten) 178 ($M^{\bullet+}$, 37), 163 (10), 149 (24), 135 (42), 121 (65), 108 (45), 95 (82), 81 (100), 67 (68); HRMS calcd for $C_{13}H_{22}$ 178.1722, found 178.1727.

1-(5-Bromo-*n*-pentyl)-1-methyl-2-methylenecyclohexane (5): 79% yield; ^{1}H NMR δ 4.69 (s, 1 H), 4.58 (s, 1 H), 3.40 (t, J = 6.9 Hz, 2 H), 2.19–2.04 (m, 2 H), 1.86 (m, 2 H), 1.75–1.00 (m, 12 H), 1.00 (s, 3 H); ^{13}C NMR δ 155.2, 106.6, 40.5, 39.3, 37.1, 34.0, 33.2, 32.9, 29.0, 28.6, 25.6, 23.1, 22.0; FTIR (neat) 3081, 2931, 2854, 1635, 1450, 1371, 1249, 887 cm^{-1}; EIMS m/z (rel inten) 260 ($[M+2]^{\bullet+}$, 0.8), 258 ($M^{\bullet+}$, 0.4), 123 (7), 109 (100), 95 (25), 81 (28), 67 (37); HRMS calcd for $C_{13}H_{23}{}^{79}Br$ and $C_{13}H_{23}{}^{81}Br$ 258.0983 and 260.0963, found 258.0983 and 260.0956. Anal. Calcd: C, 60.23; H, 8.94. Found: C, 60.59; H, 8.96.

1-Methylenespiro[5.5]undecane[18a] (6): 75% (81% GC) yield; ^{1}H NMR δ 4.70 (m, 1 H), 4.63 (d, J = 2.0 Hz, 1 H), 2.17 (m, 2 H), 1.60–1.25 (m, 16 H); ^{13}C NMR δ 157.1, 105.7, 39.2, 37.3, 35.1, 33.2, 29.3, 27.0, 21.9, 21.6; FTIR (neat) 3083, 2925, 2852, 1635, 1458, 1446, 895, 883 cm^{-1}; EIMS m/z (rel inten) 164 ($M^{\bullet+}$, 47), 149 (15), 135 (28), 121 (47), 108 (36), 93 (53), 82 (97), 67 (100); HRMS calcd for $C_{12}H_{20}$ 164.1565, found 164.1561.

1-(4-Bromo-*n*-butyl)-1-methyl-2-methylenecyclohexane (7): 81% yield; ^{1}H NMR δ 4.71 (s, 1 H), 4.58 (s, 1 H), 3.40 (t, J = 6.9 Hz, 2 H), 2.20–2.05 (m, 2 H), 1.83 (m, 2 H), 1.75–1.10 (m, 10 H), 1.02 (s, 3 H); ^{13}C NMR δ 154.9, 106.8, 40.4, 39.2, 36.4, 33.7, 33.6, 33.2, 28.5, 25.5, 22.7, 22.0; FTIR (neat) 3079, 2931, 2852, 1635, 1448, 1371, 1265, 1253, 1238, 1205, 889 cm^{-1}; EIMS m/z (rel inten) 123 (2), 109 (100), 95 (12), 81 (19), 67 (28); HRMS (peak match) calcd for $C_{12}H_{21}{}^{79}Br$ and $C_{12}H_{21}{}^{81}Br$ 244.0827 and 246.0807, found 244.0834 and 246.0814. Anal. Calcd: C, 58.78; H, 8.63. Found: C, 59.12; H, 8.51.

1-(3-Bromo-*n*-propyl)-1-methyl-2-methylenecyclohexane (9): 78% yield; ^{1}H NMR δ 4.72 (s, 1 H), 4.59 (s, 1 H), 3.40 (t, J = 6.5 Hz, 2 H), 2.20–2.05 (m, 2 H), 1.88–1.47 (m, 7 H), 1.39–1.22 (m, 3 H), 1.02 (s, 3 H); ^{13}C NMR δ 154.5, 107.1, 40.6, 39.1, 35.9, 34.9, 33.1, 28.5, 27.8, 25.6, 22.0; FTIR (neat) 3079, 2956, 2927, 2854, 1635, 1448, 1436, 1259, 1245, 889 cm^{-1}; EIMS m/z (rel inten) 232 ($[M+2]^{\bullet+}$, 0.3), 230 ($M^{\bullet+}$, 0.3), 151 (1.7), 109 (100), 95 (13), 81 (19), 67 (33); HRMS calcd for $C_{11}H_{19}{}^{79}Br$ and $C_{11}H_{19}{}^{81}Br$ 230.0670 and 232.0650, found 230.0674 and 232.0652.

5-Methylenespiro[3.5]nonane (10): 15% GC yield from **2a** and 1,2-dibromoethane; 40% GC yield from **2a** and 1,2-dichloroethane; 52% (67% GC) yield from **2a** and ethylene glycol di-*p*-tosylate; ^{1}H NMR δ 4.66 (m, 1 H), 4.61 (d, J = 1.9 Hz, 1 H), 2.12–2.00 (m, 4 H), 1.96–1.81 (m, 1 H), 1.80–1.68 (m, 3 H), 1.65–1.58 (m, 2 H), 1.58–1.43 (m, 4 H); ^{13}C NMR δ 155.6, 103.4, 45.5, 39.6, 32.6, 30.9, 28.4, 22.9, 15.1; FTIR (neat) 3076, 2974, 2929, 2854, 1643, 1444, 883 cm^{-1}; EIMS m/z (rel inten) 136 ($M^{\bullet+}$, 17), 121 (18), 108 (45), 93 (59), 81 (49), 69 (100); HRMS calcd for $C_{10}H_{16}$ 136.1252, found 136.1254.

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1-Methylenespiro[4.4]nonane[19] **(11)**: 60% (70% GC) yield; ^{1}H NMR δ 4.80 (s, 1 H), 4.76 (m, 1 H), 2.39 (tt, J = 7.2, 2.1 Hz, 2 H), 1.78–1.48 (m, 12 H); ^{13}C NMR δ 161.4, 102.2, 53.7, 40.8, 40.2, 33.4, 24.9, 23.1; FTIR (neat) 3070, 2956, 2871, 1649, 1448, 1433, 875 cm^{-1}; EIMS m/z (rel inten) 136 (M$^{\bullet+}$, 28), 121 (46), 107 (31), 95 (97), 79 (100), 67 (44); HRMS calcd for $C_{10}H_{16}$ 136.1252, found 136.1252.

7-Methylenespiro[5.6]dodecane (12): 73% yield; ^{1}H NMR δ 4.83 (s, 1 H), 4.81 (s, 1 H), 2.17 (m, 2 H), 1.62–1.20 (m, 18 H); ^{13}C NMR δ 159.8, 109.6, 41.6, 36.6, 36.4, 33.2, 31.5, 30.1, 26.5, 23.9, 22.3; FTIR (neat) 3085, 2938, 2854, 1629, 1452, 885 cm^{-1}; EIMS m/z (rel inten) 178 (M$^{\bullet+}$, 47), 135 (45), 121 (24), 107 (26), 97 (90), 81 (100), 67 (97); HRMS calcd for $C_{13}H_{22}$ 178.1721, found 178.1719.

6-Methylenespiro[4.6]undecane (13): 77% (86% GC) yield; ^{1}H NMR δ 4.76 (s, 1 H), 4.73 (d, J = 1.6 Hz, 1 H), 2.20 (m, 2 H), 1.72–1.38 (m, 16 H); ^{13}C NMR δ 159.3, 109.1, 51.9, 41.0, 39.1, 34.7, 31.2, 29.9, 25.3, 24.2; FTIR (neat) 3079, 2923, 2852, 1629, 1444, 887 cm^{-1}; EIMS m/z (rel inten) 164 (M$^{\bullet+}$, 23), 149 (6), 135 (17), 121 (33), 107 (23), 93 (50), 81 (72), 67 (100); HRMS calcd for $C_{12}H_{20}$ 164.1565, found 164.1570.

5-Methylenespiro[3.6]decane (14): 46% (59% GC) yield; ^{1}H NMR δ 4.75 (m, 2 H), 2.18 (m, 2), 2.15–2.05 (m, 2 H), 1.95–1.65 (m, 6 H), 1.55–1.40 (m, 6 H); ^{13}C NMR δ 158.7, 108.4, 47.6, 41.8, 33.1, 32.5, 27.9, 27.5, 25.1, 15.0; FTIR (neat) 3073, 2975, 2927, 2852, 1631, 1444, 885 cm^{-1}; EIMS m/z (rel inten) 150 (M$^{\bullet+}$, 10), 135 (23), 122 (63), 107 (87), 93 (100), 79 (92), 67 (50); HRMS calcd for $C_{11}H_{18}$ 150.1409, found 150.1414.

2,2-Diphenyl-2,3,4,5,6,7-hexahydro-2-sila-1*H*-indene (15): 89% yield; ^{1}H NMR δ 7.58–7.53 (m, 4 H), 7.40–7.30 (m, 6 H), 2.05 (s, 4 H), 1.80 (s, 4 H), 1.62 (m, 4 H); ^{13}C NMR δ 136.6, 134.7, 133.2, 129.3, 127.9, 31.2, 23.5, 22.6; FTIR (neat) 3066, 3008, 2921, 2827, 1652, 1427, 1394, 1168, 1114, 875, 773, 728, 698 cm^{-1}; EIMS m/z (rel inten) 290 (M$^{\bullet+}$, 100), 212 (84), 183 (86), 134 (40), 105 (68), 73 (18); HRMS calcd for $C_{20}H_{22}Si$ 290.1491, found 290.1486.

Typical Preparation of Spiroenone: 6-Methylenespiro[4.5]decan-2-one[20] **(18)**. Newly formed magnesium complex **2a**, prepared from 1,2-dimethylenecyclohexane (0.217 g, 2.00 mmol) and activated magnesium (4.01 mmol), in THF (15 mL) was cooled to −78 °C. 3-Bromopropionitrile was added via a disposable syringe. The reaction mixture was stirred at −78 °C for 30 min and then gradually warmed to room temperature. Stirring was continued for 2 h at room temperature. The reaction mixture was hydrolyzed at room temperature by adding an aqueous solution of HCl (3 N, 10 mL) and stirring for 2 h. The mixture was washed with diethyl ether (20 mL). The aqueous layer was extracted with diethyl ether (3 × 15 mL) and the combined organic portions were washed with saturated aqueous solution of $NaHCO_3$ (2 × 20 mL) and brine (20 mL) and then dried over anhydrous $MgSO_4$. Evaporation of solvents and flash column chromatography (eluted with hexanes/Et_2O = 100:4, v/v) gave 6-methylenespiro[4.5]decan-2-one: 0.168 g, 51% yield; ^{1}H NMR δ 4.75 (s, 1 H), 4.59 (s, 1 H), 2.46 (d, J = 17.7 Hz, 1 H), 2.32–2.15 (m, 5 H), 2.13 (d, J = 17.7 Hz, 1 H), 1.90–1.79 (m, 1 H), 1.72–1.45 (m, 6 H); ^{13}C NMR δ 218.8, 152.4, 106.5, 50.4, 45.9, 39.2, 36.2, 33.5, 32.1, 28.2, 22.9; FTIR (neat) 3080, 2929, 2856, 1745, 1639, 1446, 1404, 1161, 891 cm^{-1}; EIMS m/z (rel inten) 164 (M$^{\bullet+}$, 90), 149 (15), 135 (13), 122 (36), 108 (94), 93 (100), 79 (84), 67 (35); HRMS calcd for $C_{11}H_{16}O$ 164.1201, found 164.1202.

5-Methylenespiro[3.5]nonan-2-one[21] **(17)**: 46% yield; ^{1}H NMR δ 4.81 (s, 1 H), 4.72 (s, 1 H), 3.10 (m, 2 H), 2.75 (m, 2 H), 2.20 (m, 2 H), 1.76–1.68 (m, 2 H), 1.68–1.56 (m, 4 H); ^{13}C NMR δ 207.3 151.7, 105.6, 55.5, 39.4, 36.0, 33.5, 27.9, 23.9; FTIR (neat) 3080, 2929, 2854, 1788, 1644, 1444, 1383, 1122, 885 cm^{-1}; EIMS m/z (rel inten) 150 (M$^{\bullet+}$, 3), 122 (24), 108 (100), 93 (88), 79 (50), 67 (13); HRMS calcd for $C_{10}H_{14}O$ 150.1045, found 150.1042.

7-Methylenespiro[5.5]undecan-2-one[16a] **(19)**: 13% yield; ^{1}H NMR (200 MHz) δ 4.80 (s, 1 H), 4.59 (s, 1 H), 2.51 (m, 1 H), 2.42–2.06 (m, 6 H), 1.93–1.48 (m, 7 H), 1.47–1.24 (m, 2 H); ^{13}C NMR δ 212.1, 153.3, 109.0, 52.8, 44.5, 41.2, 39.7, 32.9, 32.3, 28.3, 21.6, 21.1; FTIR (neat) 3085, 2929, 2856, 1712, 1637, 1440, 1226, 900 cm^{-1}; EIMS m/z (rel inten) 178 (M$^{\bullet+}$, 100), 163 (20), 149 (20), 137 (23), 120 (32), 108 (29), 93 (60), 79 (58), 67 (54); HRMS calcd for $C_{12}H_{18}O$ 178.1358, found 178.1354.

4-(1-Methyl-2-methylenecyclohexyl)butyronitrile (20): 61% yield; ^{1}H NMR δ 4.74 (s, 1 H), 4.60 (s, 1 H), 2.32 (t, J = 7.0 Hz, 2 H), 2.21–2.04 (m, 2 H), 1.85 (td, J = 12.6, 4.2 Hz, 1 H), 1.78–1.68 (m, 1 H), 1.66–1.23 (m, 8 H), 1.03 (s, 3 H); ^{13}C NMR δ 154.0, 119.8, 107.4, 40.6, 39.1, 36.3, 33.1, 28.3, 25.4, 21.9, 20.4, 17.8; FTIR (neat) 3084, 2931, 2856, 2245, 1637, 1450, 893 cm^{-1}; EIMS m/z (rel inten) 177 (M$^{\bullet+}$, 1.9), 162 (7), 148 (5), 134 (9), 109 (100), 95 (8), 81 (25), 67 (60); HRMS calcd for $C_{12}H_{19}N$ 177.1518, found 177.1520.

6-Methylenespiro[4.4]nonan-2-one (21): 40% yield; ^{1}H NMR δ 4.92 (t, J = 2.1 Hz, 1 H), 4.81 (t, J = 2.3 Hz, 1 H), 2.55–2.19 (m, 6 H), 2.07–1.85 (m, 2 H), 1.82–1.62 (m, 4 H); ^{13}C NMR δ 219.1, 158.1, 104.2, 51.6, 50.1, 39.4, 37.5, 35.5, 32.7, 22.4; FTIR (neat) 3068, 2954, 2873, 1743, 1649, 1404, 1144, 879 cm^{-1}; EIMS m/z (rel inten) 150 (M$^{\bullet+}$, 49), 108 (26), 94 (100), 79 (97); HRMS calcd for $C_{10}H_{14}O$ 150.1045, found 150.1045.

6-Methylenespiro[4.6]undecan-2-one (22): 54% yield; ^{1}H NMR δ 4.86 (s, 1 H), 4.68 (s, 1 H), 2.52 (d, J = 17.8 Hz, 1 H), 2.40–2.13 (m, 4 H), 2.10 (d, J = 17.8 Hz, 1 H), 2.05–1.95 (m, 1 H), 1.90–1.76 (m, 2 H), 1.75–1.55 (m, 4 H), 1.50–1.20 (m, 3 H); ^{13}C NMR δ 219.6, 156.1, 111.0, 52.1, 48.3, 41.0, 36.2, 34.6, 33.7, 31.3, 29.9, 24.7; FTIR (neat) 3078, 2924, 2852, 1745, 1629, 1444, 1405, 1153, 893 cm^{-1}; EIMS m/z (rel inten) 178 (M$^{\bullet+}$, 18), 136 (9), 122 (21), 107 (37), 96 (100), 79 (58), 67 (36); HRMS calcd for $C_{12}H_{18}O$ 178.1358, found 178.1357.

9-Methylenedispiro[4.2.5.2]pentadecan-6-one (24): 74% yield; ^{1}H NMR δ 4.76 (s, 1 H), 4.58 (s, 1 H), 2.52 (dd, J = 14.3, 1.7 Hz, 1 H), 2.30 (d, J = 14.3 Hz, 1 H), 2.25–1.98 (m, 5 H), 1.97–1.88 (m, 1 H), 1.75–1.42 (m, 11 H), 1.40–1.25 (m, 3 H); ^{13}C NMR δ 214.5, 153.5, 108.4, 55.8, 50.1, 44.6, 39.2, 36.1, 35.3, 34.4, 32.8, 30.2, 28.3, 25.3, 25.2, 21.5; FTIR (neat) 3085, 2929, 2859, 1700, 1637, 1440, 1130, 902, 892 cm^{-1}; EIMS m/z (rel inten) 232 (M$^{\bullet+}$, 46), 204 (27), 151 (28), 121 (27), 109 (83), 95 (87), 81 (100), 67 (84); HRMS calcd for $C_{16}H_{24}O$ 232.1827, found 232.1831. Anal. Calcd: C, 82.70; H, 10.41. Found: C, 82.69; H, 10.49.

1-Methylenedispiro[4.2.4.2]tetradecan-7-one (25): 46% yield; mp 49–50 °C; ^{1}H NMR δ 4.93 (t, J = 2.0 Hz, 1 H), 4.79 (t, J = 2.3 Hz, 1 H), 2.48 (d, J = 13.8 Hz, 1 H), 2.42–2.25 (m, 3 H), 2.20 (dd, J = 13.8, 2.0 Hz, 1 H); 1.92–1.45 (m, 14 H), 1.23–1.14 (m, 1 H); ^{13}C NMR δ 213.8, 159.1, 104.8, 55.9, 49.8, 49.7, 37.0, 36.2, 36.1, 34.3, 33.9, 32.7, 25.4, 25.1, 22.1; FTIR (KBr) 3070, 2946, 2863, 2827, 1695, 1650, 1442, 1427, 1419, 1344, 1292, 1197, 1147, 890 cm^{-1}; EIMS m/z (rel inten) 218 (M$^{\bullet+}$, 39), 190 (13), 177 (27), 149 (7), 121 (27), 108 (20), 95 (100), 79 (37); HRMS calcd for $C_{15}H_{22}O$ 218.1671, found 218.1669.

9-Methylenedispiro[4.2.6.2]hexadecan-6-one (26): 52% yield; ^{1}H NMR δ 4.89 (s, 1 H), 4.74 (s, 1 H), 2.65 (d, J = 14.0 Hz, 1 H), 2.22 (d, J = 14.0 Hz, 1 H), 2.24–2.17 (m, 1 H), 2.10–1.95 (m, 3 H), 1.83–1.18 (m, 18 H); ^{13}C NMR δ 215.0, 156.9, 112.0, 55.7, 49.8, 47.0, 39.2, 35.8, 35.7, 34.8, 33.9, 33.1, 31.8, 30.4, 25.4, 25.3, 23.2; FTIR (neat) 3085, 2927, 2856, 1700, 1633, 1444, 1197, 1143, 896 cm^{-1}; EIMS m/z (rel inten) 246 (M$^{\bullet+}$, 40), 164 (52), 151 (71), 135 (25), 121 (48), 107 (40), 95 (91), 81 (100), 67 (98); HRMS calcd for $C_{17}H_{26}O$ 246.1984, found 246.1985. Anal. Calcd: C, 82.87; H, 10.64. Found: C, 82.41; H, 10.74.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of **4**, **9**, **10**, **12–15**, **20–22**, and **25** (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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