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Synthesis of Spiro[2.2]pentanes and Spiro[2.3]hexanes Employing the Me_3Al/CH_2I_2 Reagent

Ilfir R. Ramazanov,*[a] Rita N. Kadikova,[a] Tat'yana P. Zosim,[a] Usein M. Dzhemilev[a] and Armin de Meijere [b]

Abstract: Substituted alkylidenecyclopropanes reacted with 5 equivalents each of Me_3Al and CH_2I_2 at room temperature in hexane to give 1-mono- and 1,1-disubstituted spiro[2.2]pentanes in high yields. Surprisingly, the same reaction with substituted alkylidenecyclopropanes in CH_2Cl_2 afforded exclusively 1,1-disubstituted spiro[2.3]hexanes. The transformation of 1,1-diphenylspiro[2.2]pentane into 1,1-diphenylspiro[2.3]hexane was studied with the use of CD_2I_2 and a plausible mechanism was suggested. The reaction of substituted alkylidenecyclobutanes with the Me_3Al/CH_2I_2 reagent in CH_2Cl_2 gave only 1,1-disubstituted spiro[2.3]hexanes.

Introduction

The pioneering works of Simmons and Smith have revealed the rich potential of zinc carbenoids in the synthesis of cyclopropane compounds and gave a powerful impetus to the development of new cyclopropanating agents.[1–11] Due to the use of readily available precursors and reagents as well as the simplicity of the procedure, the so-called Simmons-Smith reaction and its analogues became extremely popular. However, it turned out that carbenoids of other metals can also be useful. Samarium(III) carbenoids can react with α-haloketones and 1,4-diketones,[12–14] enolates,[15] esters[14,16] to give cyclopropanols. The reaction of carbonyl compounds with Sm/CH_2I_2 gave iodohydrins in good yields.[12,13,17] Samarium(III) carbenoids are effective agents for the cyclopropanation of substituted allyl and allenyl alcohols which proceed under mild conditions with high diastereoselectivities.[18–21] Indium can insert into a carbon-halogen bond of dibromosubstituted carbonyl compounds or nitriles to give indium carbenoids that react with alkenes to afford substituted cyclopropanes.[22,23] Aluminum carbenoids can transform alkynes into substituted cyclopropanes in one step.[24,25] As can be seen, each metal offers unique synthetic possibilities. Previously we have noticed that aluminum carbenoids can easily form spiropentanes from substituted allenes with high steric demand.[26] Thus the twofold cyclopropanation of 1,2-cyclononadiene afforded the spiropentane-annelated cyclononane in 95% yield in one step with the Et_3Al/CH_2I_2 reagent. In contrast, the cyclopropanation of 1,2-cyclononadiene with CH_2N_2 in the presence of a palladium catalyst involved only one double bond to give bicyclo[7.1.0]dec-1-ene in 70% yield.[27,28] Repeated treatment of the latter with $CH_2N_2/[Pd(acac)_2]$ gave the tricyclic spiropentane derivative in a yield of only 15%. The reaction of phenylallene with $CH_2N_2/[Pd(OAc)_2]$ gave only benzylidenecyclopropane in a yield of 50%.[28] The use of Et_3Al/CH_2I_2 allows one to prepare 1-phenylspiro[2.2]pentane in quantitative yield. Accordingly, aluminum carbenoids can be assumed to be active enough to react with intermediately formed cyclopropylidene derivatives. It is known that the relatively bulky zinc carbenoid impedes the cyclopropanation of sterically hindered alkenes. Bicyclopropylidenes and bicyclobutylidenes showed low reactivity towards zinc carbenoids.[29,30] [3]Triangulane was obtained in 5-15% yield using Zn/Cu and Zn/Ag couple from vinylidenecyclopropane.[31] Thus, the cyclopropanation of sterically congested alkenes with zinc carbenoids appears to be problematic. Therefore it was of interest to examine aluminum carbenoids in the reaction with alkylidenecyclopropanes and -cyclobutanes.

Results and Discussion

The experimental tests showed that substituted alkylidenecyclopropanes **1a-i** upon treatment with 5 equivalents each of Me_3Al and CH_2I_2 in hexane at room temperature for 18 h furnish the corresponding spiropentanes **2a-i** with high selectivities in yields ranging from 62 to 82% (Scheme 1).

With smaller amounts of Me_3Al and CH_2I_2 the conversion of the alkylidenecyclopropanes decreases, e.g. (diphenylmethylene)cyclopropane (**1a**) with 2 equivalents each of Me_3Al and CH_2I_2 within 18 h gave 1,1-diphenylspiro[2.2]pentane (**2a**) in 48% yield. This indicates a lower reactivity of alkylidenecyclopropanes compared to less substituted ethylenes.[32] According to RHF/6-31G(d,p) calculations, the global index of nucleophilicity decreases in the series: 2,3-dimethylbut-2-ene (10.2) > 2-methylprop-1-ene (6.9) > propan-2-ylidenecyclopropane (6.8) > 1-octene (5.9) > propan-2-ylidenecyclobutane (5.5) > 1,1'-bi(cyclopropylidene) (4.9) > styrene (4.3). The global index of nucleophilicity was calculated as 1/(the global index of electrophilicity).[33] The given order of alkenes correctly reflects our understanding of the electronic effects of substituents. However, according to B3LYP/6-31G(d) computations, the calculated free activation energy for the cyclopropanation with Me_2AlCH_2I increased in the order: 2-

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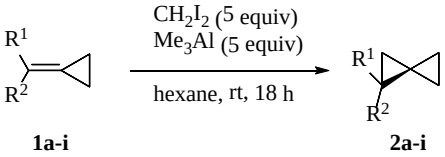
methylprop-1-ene (21.4 kcal/mol) < prop-1-ene (22.2 kcal/mol) < 2,3-dimethylbut-2-ene (24.7 kcal/mol) ≈ propan-2-ylidenecyclopropane (24.7 kcal/mol) < 1,1'-bi(cyclopropylidene) (25.4 kcal/mol). Apparently, the reactivity of unsaturated substrates in the reaction is largely determined by steric constraints arising in the transition state. Indeed, the analysis of the geometry of the transition state shows that the plane of the π-bond and the plane passing through the Al-C(H_2)-I atoms of the aluminum carbenoid are not parallel in the case of tetrasubstituted alkenes (Figure 1). This deviation results in an increase of the activation energy of the cyclopropanation reaction.



1a-i **2a-i**

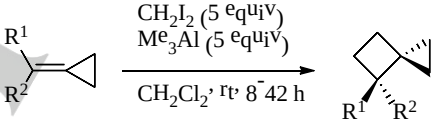
2	R¹	R²	%
a	Ph	Ph	80
b	*n*-Bu	*n*-Bu	75
c	Me	Ph	81
d	H	*n*-Hept	73
e	H	*p*-$MeOC_6H_4$	67
f	-$(CH_2)_2$-		62
g	-$(CH_2)_4$-		77
h	-$(CH_2)_5$-		82
i	2-adamantylidene		76

Scheme 1. Cyclopropanation of alkylidenecyclopropanes with Me_3Al and CH_2I_2 in hexane.

Figure 1. The transition state of the cyclopropanation reaction of tetrasubstituted ethylenes.

The Me_3Al/CH_2I_2 reagent showed a higher reactivity than the Simmons-Smith reagent Zn(Cu)/CH_2I_2 in the cyclopropanation of 1,1'-bi(cyclopropylidene). It can be linked to a lower activation energy for the reaction of the alkene with an aluminum carbenoid than with a zinc carbenoid. According to B3LYP/6-311G(d,p) calculations, the activation energy of the reaction of ethylene with Me_2AlCH_2I is 12.8 kcal/mol and that with $IZnCH_2I$ is 21.2 kcal/mol.[34] In addition, the lower activity of zinc carbenoids may be associated with its greater bulkiness since the coordination number of Zn in RZnX structures reaches six[35] compared to four in organoaluminum compounds. Moreover, the Zn atom is coordinated by bulky ether molecules of the solvent.

It is known that the use of chlorinated solvents, e.g. dichloromethane, increases the stability of intermediate aluminum carbenoids[32] that might allow one to decrease the amount of the organometallic reagent. Surprisingly, when dichloromethane was used as a solvent instead of hexane, treatment of (diphenylmethylene)cyclopropane **1a** with 5 equivalents each of Me_3Al and CH_2I_2 within 8 h unexpectedly led to 4,4-diphenylspiro[2.3]hexane (**3a**) in 78% yield (Scheme 2). The conversion of the starting material **1a** was more than 90% after 3 h. According to GC analysis of the reaction mixture, the yield of the products **2a** and **3a** was 82 and 11%, respectively. However the content of the spiro[2.3]hexane **3a** in the reaction mixture after 8 h was 85% (by GC). The conversion of the alkylidenecyclopropane **1b** into the spiro[2.3]hexane **3b** proceeds much more slowly than that to the spiro[2.2]pentane **2b** in hexane. The content of **3b** reached 77% (by GC) only in 2 days. Cycloalkylidenecyclopropanes **1g-i** showed a similar reactivity. However, alkylidenecyclopropane **1c** was reactive enough to afford spiro[2.3]hexane **3c** in 79% isolated yield within 18 h. Contrary to our expectations, monosubstituted alkylidenecyclopropanes **1d,e** and 1,1'-bi(cyclopropylidene) **1f** gave only the spiro[2.2]pentanes **2d-f** in 52-78% yield.

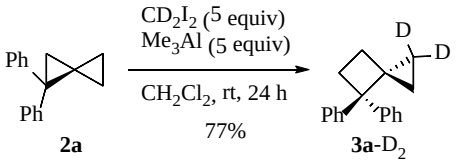


1 **3**

3	R¹	R²	Time, h	%
a	Ph	Ph	8	78
b	*n*-Bu	*n*-Bu	42	69
c	Me	Ph	18	79
g	-$(CH_2)_4$-		42	81
h	-$(CH_2)_5$-		42	68
i	2-adamantylidene		42	83

Scheme 2. Cyclopropanation of alkylidenecyclopropanes with Me_3Al and CH_2I_2 in hexane.

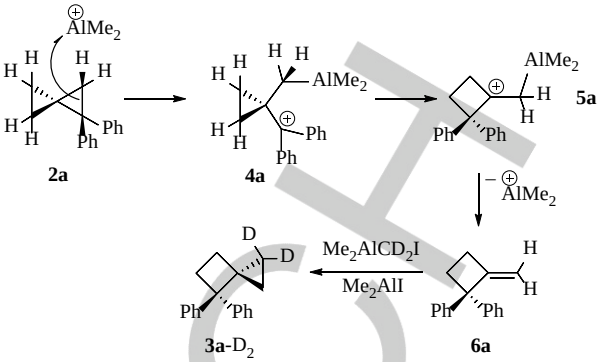
Doering et al. have shown that methylene, generated by irradiation of diazomethane, does not insert into the carbon-carbon bonds of spiro[2.2]pentane, but only leads to 1-methylspiro[2.2]pentane by carbon-hydrogen bond insertion.[36] In order to learn more about the mechanism of the above reaction leading to spiro[2.3]hexanes we used dideuteriodiiodomethane in connection with trimethylaluminum to react with 1,1-diphenylspiro[2.2]pentane **2a.** Surprisingly, the deuterium labels showed up on the cyclopropane ring of the product 4,4-diphenylspiro[2.3]hexane-1,1-d_2 (**3a**-D_2) (Scheme 3).



2a **3a**-D_2

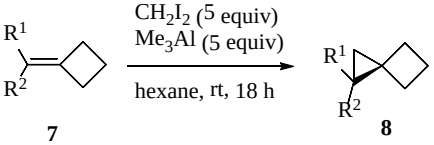
Scheme 3. Reaction of 1,1-diphenylspiro[2.2]pentane **2a** with Me_3Al/CD_2I_2 reagent.

The observed dependence of the reaction rate on the character of the substituents on the methylenecyclopropanes suggests an ionic reaction mechanism. The carbon-carbon double bond cyclopropanation is accompanied by the release of an equimolar amount of dimethylaluminum iodide which can trigger a subsequent transformation of the initially formed spiro[2.2]pentanes **2**. Dimethylaluminum iodide can also be formed by a thermal decomposition of the aluminum carbenoid. The degree of dissociation of the aluminum iodide should be higher in a more polar solvent. Fukui indices were used to estimate local nucleophilicities in 1,1-dimethylspiro[2.2]pentane.[37] According to B3LYP/6-31G(d,p) computations there are two potential sites for electrophilic attack located at the dimethyl-substituted cyclopropane ring. We supposed that the electrophilic attack of the Me_2Al^+ species will preferably occur at the methylene carbon atom of the diphenyl-substituted cyclopropane ring in **2a** to give an intermediate carbocation **4a** stabilized by a cyclopropyl and two phenyl groups (Scheme 4). It is well known that a cyclopropyl group significantly stabilizes a carbenium ion and in this respect is even more efficient than a phenyl substituent.[38] Subsequent ring-enlarging rearrangement gives the trisubstituted cyclobutyl cation **5a** which can cleave off the Me_2Al^+ cation with the aid of a nucleophilic iodide ion to yield 2,2-diphenylmethylenecyclobutane **6a.** Reaction of the latter with the aluminum carbenoid then affords the product **3a**-D_2. It should be noted that the ring-enlarging rearrangement of (1-methylcyclopropyl)carbinyl to 1-methylcyclobutyl cation is well documented.[39] Moreover, the mechanism proposed in Scheme 4 is in accord with a study on the gas-phase protonation of spiropentane which leads to the formation of (1-methylcyclopropyl)carbinyl cation and its rearrangement into 1-methylcyclobutyl cation.[40] Thus, the factors contributing to the stabilization of the carbocation center in the intermediate **4a** accelerate the transformation of spiro[2.2]pentanes into spiro[2.3]hexanes. It also explains the lack of reactivity of the spiro[2.2]pentanes **2d-f** because the attack of the dimethylaluminum cation would lead to the secondary cations in the case of **2d,e** as well as a cyclopropyl cation from **2f**, and all these would be less stable than the tertiary cations formed from **2a-c** and **2g-i**. In fact, the activation energy for the formation of an intermediate secondary cyclopropyl cation is the highest of all for cycloalkyl cations from the corresponding *p*-toluenesulfonates in S_N1 solvolysis reaction.[41]



Scheme 4. Proposed mechanism for the transformation of spiro[2.2]pentanes into spiro[2.3]hexanes.

The newly discovered virtual ring expansion of one of the cyclopropane rings in spiro[2.2]pentanes *in situ* formed from alkylidenecyclopropanes prompted us to subject the homologous disubstituted methylenecyclobutanes **7** to the same conditions. Yet, treatment of 1',1'-diphenylmethylenecyclobutane (**7a**) with 5 equivalents each of Me_3Al and CH_2I_2 in CH_2Cl_2 for 18 h cleanly led to 1,1-diphenylspiro[2.3]hexane (**8a**) in 79% yield (Scheme 5). It is remarkable that according to a qualitative kinetic study, the alkylidenecyclobutane **7a** is ~6 times less reactive than the corresponding alkylidenecyclopropane **1a**. No traces of byproducts could be detected in the reaction mixture of **7a**. Although the strain energy of **8a** is not much lower than that of **2a** and the nucleophilicities of the diphenylcyclopropyl groups in **8a** and in **2a** should also be very similar, the reactivity of **8a** towards the Me_3Al/CH_2I_2 reagent apparently is much lower. This cannot be due to steric effects, as the Me_3Al/CH_2I_2 reagent is effective for the cyclopropanation of even sterically congested alkylidenecyclobutanes, such as the adamantylidene derivative **7i**. This is understandable, because a cyclobutyl instead of a cyclopropyl group in a carbocationic intermediate of type **4a** does far less efficiently delocalize the adjacent charge.[42] Therefore, such a cyclobutylcarbinyl intermediate would not be as easily formed from the spiro[2.3]hexane **8a** as **4a** is formed from the spiro[2.2]pentane **2a**. This prevents the substituted spiro[2.3]hexane **8a** from undergoing a ring enlargement reaction.



7 **8**

8	R^1	R^2	%
a	Ph	Ph	79
c	Me	Ph	67
h	-$(CH_2)_5$-		76
i	2-adamantylidene		82
j	-$(CH_2)_3$-		86

Scheme 5. Cyclopropanation of alkylidenecyclobutanes with Me_3Al and CH_2I_2.

The observed formal homologation of spiro[2.2]pentanes into spiro[2.3]hexanes represents the first example of a non-transition metal-catalyzed cleavage of a carbon-carbon bond in spiropentanes. To recognize distinctive features of aluminum salts, we computed the cationic complexes $Me_2Al(+)*ClCH_2Cl$, $MeMg(+)*Me_2O$ and $MeZn(+)*Me_2O$ at the RHF/6-31G(d,p) level of theory. The NBO charge of the metal atom decreased in the following order: $Me_2Al(+)*ClCH_2Cl$ (+1.91 au) > $MeMg(+)*Me_2O$ (+1.57 au) > $MeZn(+)*Me_2O$ (+1.43 au). It is possible that a higher charge on the aluminum atom promotes the cleavage of the carbon-carbon bond. The main factors contributing to the transformation of spiro[2.2]pentanes into spiro[2.3]hexanes are: i) the reaction between the $Me_2Al(+)$ cation and spiro[2.2]pentane is facilitated by favorable charge stabilizations; ii) the (1-methylcyclopropyl)carbinyl to 1-methylcyclobutyl cation rearrangement has a low activation barrier.

Conclusions

Thus, we report an efficient method for the preparation of substituted spiro[2.2]pentanes and spiro[2.3]hexanes from substituted alkylidene-cyclopropanes and alkylidenecyclobutanes under the action of CH_2I_2 and Me_3Al.

Experimental Section

General remarks

The reagents were purchased from Sigma-Aldrich or Acros. Dichloromethane and hexane were distilled over P_2O_5. Cyclopropylidenealkanes **1a-i** were prepared by Wittig olefination reactions of the corresponding aldehydes and ketones upon treatment with 3-bromopropyltriphenylphosphonium bromide and *t*-BuOK.[43] Cyclobutylidenealkanes **7a**, **7c**, **7h**, **7i** were prepared in an analogous manner from the corresponding ketones, 4-bromobutyltriphenylphosphonium bromide and *t*-BuOK. 1,1'-Bi(cyclobutylidene) **7j** was prepared from 3-bromopropyltriphenylphosphonium bromide and *t*-BuOK in 50% yield.[44] Nuclear Magnetic Resonance spectroscopy was performed on a Bruker Avance 400 instrument. The ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$. The chemical shifts are reported in parts per million relative to tetramethylsilane (TMS) as the internal standard. The numbering of atoms in the ^{13}C- and ^{1}H-NMR spectra of the compounds **2a**-**2i**, **3a**-**3c, 3g-3i**, **8a**, **8c** and **8h-8j.** are shown in Figures 2, 3 and 4. Elemental analyses were performed using a Carlo-Erba CHN 1106 elemental analyser. Mass spectra were recorded on a Finnigan 4021 instrument. The yields were calculated from the isolated amount of substituted spiro[2.2]pentanes and spiro[2.3]hexanes obtained from starting substituted alkylidenecyclopropanes and alkylidenecyclobutanes. All quantum chemical calculations were performed using the B3LYP/6-31G(d) basis set as implemented in the Gaussian 09 software.[45]

Synthesis of substituted spiro[2.2]pentanes

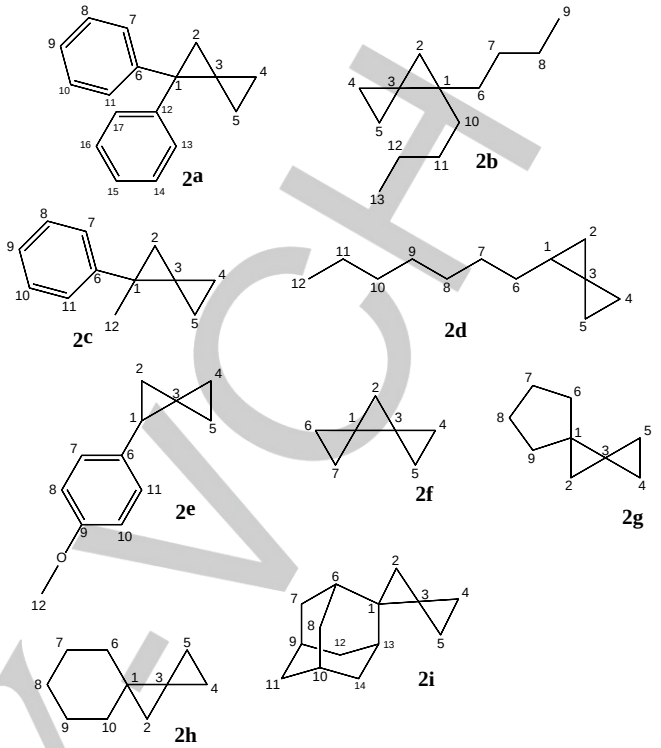


Figure 2. Numbering of atoms in the reported ^{13}C- and ^{1}H-NMR spectral data of the compounds **2a**-**2i**.

*1,1-Diphenylspiro[2.2]pentane (**2a**).*[46] To a solution of 0.413 g (2 mmol) of (diphenylmethylene)cyclopropane and 0.80 mL (10 mmol) of CH_2I_2 in hexane (8 mL), was added 1 mL (10 mmol) of Me_3Al (caution: organoaluminums are pyrophoric and can ignite on contact with air, water or any oxidizer) at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 18 hours. Then, the reaction mixture was diluted with 5 mL of CH_2Cl_2, and 3 mL of water was added dropwise while cooling the flask in an ice bath. The precipitate was collected on a filter paper. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $CaCl_2$ and concentrated in vacuo to give the crude product as a colorless oil. The residue was distilled through a micro column at a pressure of 1 mm Hg to give **2a** (0.35 g, 80%) as a colorless oil. b.p. 121-122 °C (1 mm Hg). ^{1}H NMR (δ, ppm): 1.00-1.08 (m, 2 H, $C(4)H_A$,$C(5)H_A$), 1.08-1.15 (m, 2 H, $C(4)H_B$, $C(5)H_B$), 1.78 (s, 2 H, $C(2)H_2$), 7.00-7.53 (m, 10 H, Ph). ^{13}C NMR (δ, ppm): 7.0 (2 C, C(4,5)), 24.8 (C(3)), 25.0 (C(2)), 33.1 (C(1)), 125.8 (2 C, C(9,15)), 128.1 and 128.5 (4 C and 4 C, C(7,11,13,17) and C(8,10,14,16)), 144.7 (2 C, C(6,12)). Mass *m/z* (%): 220 (20) $[M]^+$, 205 (87), 191 (100), 165 (53), 142 (19), 129 (74), 115 (45), 91 (6).

*1,1-Dibutylspiro[2.2]pentane (**2b**).* Using the procedure described above, 0.332 g (2 mmol) of nonan-5-ylidenecyclopropane gave a crude product that was distilled through a micro column at 5 mm Hg to afford **2b** (0.27 g, 75%) as a colorless oil. b.p. 80-83 °C (5 mm Hg). ^{1}H NMR (δ, ppm, *J*/Hz): 0.55 (br.s., 2 H, $C(2)H_2$), 0.60-0.67 (m, 2 H, $C(4)H_A$, $C(5)H_A$), 0.67-0.75 (m, 2 H, $C(4)H_B$, $C(5)H_B$), 0.91 (t, *J* = 6.7, 6 H, $C(9,13)H_3$), 1.05-1.55 (m, 12 H, $C(6\text{-}8,10\text{-}12)H_2$). ^{13}C NMR (δ, ppm): 4.3 (2 C, C(4,5)), 14.2 (2 C, C(9,13)), 18.6 (C(2)), 23.2 (2 C, C(8,12)), 28.6 (2 C, C(7,11)), 34.5 (2 C, C(6,10)), 20.9 (C(3)), 23.1 (C(1)). Mass *m/z* (%): 180 (<1) $[M]^+$, 165 (1), 151 (13), 137 (6), 123 (35), 109 (36), 95 (100), 81 (96), 67 (68), 55 (52). Anal. calcd for $C_{13}H_{24}$, %: C, 86.6; H, 13.4. Found, %: C, 86.5; H, 13.2.

(1-Methylspiro[2.2]pentan-1-yl)benzene (***2c***).[47] Using the procedure described above, 0.29 g (2 mmol) of (1-cyclopropylideneethyl)benzene gave a crude product that was distilled through a micro column at 5 mm Hg to afford **2c** (0.26 g, 81%) as a colorless oil. b.p. 86-88 °C (5 mm Hg). ^{1}H NMR (δ, ppm, *J*/Hz): 0.78-0.87 (m, 2 H, C(4)H_A, C(5)H_A), 0.90-0.98 (m, 2 H, C(4)H_B, C(5)H_B), 1.19 (d, *J* = 4.0, 1 H, C(2)H_A), 1.30 (d, *J* = 4.0, 1 H, C(2)H_B), 1.51 (s, 3 H, C(12)H_3), 7.14-7.39 (m, 5 H, Ph). ^{13}C NMR (δ, ppm): 5.4 and 6.4 (C(4) and (5)), 22.4 (C(2)), 22.9 (C(3)), 23.0 (C(12)), 24.4 (C(1)), 125.0 (C(9)), 126.0 (2 C, C(8,10)), 128.0 (2 C, C(7,11)), 146.1 (C(6)). Mass *m/z* (%): 158 (3) $[M]^+$, 143 (100), 129 (79), 115 (72), 103 (20), 91 (18), 77 (28), 63 (10).

1-Heptylspiro[2.2]pentane (***2d***). Using the procedure described above, 0.304 g (2 mmol) of octylidenecyclopropane gave a crude product that was distilled through a micro column at 5 mm Hg to afford **2d** (0.24 g, 73%) as a colorless oil. b.p. 73-75 °C (5 mm Hg). ^{1}H NMR (δ, ppm, *J*/Hz): 0.40-0.44 (m, 1 H, C(2)H_A), 0.85-0.90 (m, 1 H, C(2)H_B), 0.60-0.68 and 0.70-0.78 ((m, 1 H, C(4)H_A) and (m, 1 H, C(5)H_A)), 0.70-0.78 and 0.95-1.00 ((m, 1 H, C(4)H_B) and (m, 1 H, C(5)H_B)), 0.91 (t, *J* = 5.6, 3 H, C(12)H_3), 1.00-1.05 (m, 1 H, C(1)H), 1.20-1.45 (m, 12 H, C(6-11)H_2). ^{13}C NMR (δ, ppm): 3.5 and 6.2 (2 C, C(4,5)), 12.4 (C(2)), 14.1 (C(12)), 14.5 (C(3)), 17.6 (C(1)), 22.7 (C(11)), 29.3 and 29.4 and 29.6 and 31.9 (C(7-10)), 32.8 (C(6)). Mass *m/z* (%): 152 (<1), 137 (2), 123 (3), 109 (17), 95 (55), 81 (100), 67 (96), 55 (62), 41 (82). Anal. calcd for $C_{12}H_{22}$, %: C, 86.7; H, 13.3. Found, %: C, 86.5; H, 13.3.

1-Methoxy-4-(spiro[2.2]pentan-1-yl)benzene (***2e***). Using the procedure described above, 0.32 g (2 mmol) of 1-(cyclopropylidenemethyl)-4-methoxybenzene gave a crude product that was distilled through a micro column at 2 mm Hg to afford **2e** (0.23 g, 67%) as a colorless oil. b.p. 92-93 °C (2 mm Hg). ^{1}H NMR (δ, ppm): 0.77-0.78 (m, 1 H, C(5)H_A), 0.78-0.80 (m, 1 H, C(4)H_A), 0.93-0.96 (m, 1 H, C(5)H_B), 0.97-1.01 (m, 2 H, C(2)H_A, C(4)H_B), 1.46-1.50 (m, 1 H, C(2)H_B), 2.21-2.26 (m, 1 H, C(1)H), 3.82 (s, 3 H, C(12)H_3), 6.85-7.10 (m, 4 H, Ph). ^{13}C NMR (δ, ppm): 4.8 (C(5)), 7.3 (C(4)), 17.1 (C(2)), 18.1 (C(3)), 21.8 (C(1)), 55.3 (C(12)), 113.7 (2 C, C(8,10)), 127.0 (2 C, C(7,11)), 135.2 (C(6)), 157.5 (C(9)). Mass *m/z* (%): 174 (35), 159 (100), 146 (34), 134 (39), 131 (55), 119 (32), 115 (38), 103 (79), 91 (52). Anal. calcd for $C_{12}H_{14}O$, %: C, 82.7; H, 8.1. Found, %: C, 82.8; H, 8.2.

Dispiro[2.0.2^4.1^3]heptane (***2f***).[48] Using the procedure described above, 0.16 g (2 mmol) of 1,1'-bi(cyclopropylidene) gave a crude product that was distilled through a micro column at 750 mm Hg to afford **2f** (0.12 g, 62%) as a colorless oil. The spectral properties (^{1}H NMR, ^{13}C NMR) were in good agreement with those reported in the literature. b.p. 126-130 °C (750 mm Hg).

Dispiro[2.0.4.1]nonane (***2g***). Using the procedure described above, 0.22 g (2 mmol) of cyclopropylidenecyclopentane gave a crude product that was distilled through a micro column at 20 mm Hg to afford **2g** (0.19 g, 77%) as a colorless oil. b.p. 78-81 °C (20 mm Hg). ^{1}H NMR (δ, ppm): 0.69 (br.s., 4 H, C(4,5)H_2), 0.82 (br.s., 2 H, C(2)H_2), 1.40-1.75 (m, 8 H, C(6-9)H_2). ^{13}C NMR (δ, ppm): 5.4 (2 C, C(4,5)), 19.1 (C(2)), 20.6 (C(3)), 26.6 (2 C, C(7,8)), 26.7 (C(1)), 33.9 (2 C, C(6,7)). Mass *m/z* (%): 122 (2) $[M]^+$, 107 (82), 93 (57), 79 (100), 67 (33). Anal. calcd for C_9H_{14}, %: C, 88.5; H, 11.6. Found, %: C, 88.2 H, 11.4.

Dispiro[2.0.5.1]decane (***2h***). Using the procedure described above, 0.24 g (2 mmol) of cyclopropylidenecyclohexane gave a crude product that was distilled through a micro column at 10 mm Hg to afford **2h** (0.22 g, 82%) as a colorless oil. b.p. 76-78 °C (10 mm Hg). ^{1}H NMR (δ, ppm): 0.56 (br.s., 2 H, C(2)H_2), 0.60-0.65 (m, 2 H, C(4)H_A, C(5)H_A), 0.72-0.77 (m, 2 H, C(4)H_B, C(5)H_B), 1.25-0.37 (m, 4 H, C(6,7,9,10)H_A), 1.37-1.47 (m, 6 H, C(6,7,9,10)H_B, C(8)H_2). ^{13}C NMR (δ, ppm): 3.6 (2 C, C(4,5)), 19.0 (C(2)), 20.7 (C(3)), 22.4 (C(1)), 25.8 (2 C, C(6,10)), 26.3 (C(8)), 34.5 (2 C, C(7,9)). Mass *m/z* (%): 136 (2) $[M]^+$, 121 (16), 107 (84), 93 (59), 79 (100), 67 (36). Anal. calcd for $C_{10}H_{16}$, %: C, 88.2; H, 11.8. Found, %: C, 87.9; H, 11.9.

1-Adamantylidenespiro[2.2]pentane (***2i***). Using the procedure described above, 0.24 g (2 mmol) of cyclopropylidenecyclohexane gave a crude product that was distilled through a micro column at 10 mm Hg to afford **2i** (0.20 g, 76%) as a colorless oil. b.p. 75-76 °C (10 mm Hg). ^{1}H NMR (δ, ppm): 0.56 (s, 2 H, C(2)H_2), 0.61-0.64 (m, 2 H, C(4,5)H_A), 0.83-0.86 (m, 2 H, C(4,5)H_B), 1.29 (br.s., 2 H, C(6)H), 1.50-1.60 (m, 1 H, C(7)H_A), 1.68-1.80 (m, 6 H, C(8,11)H_2), 1.80-1.90 (m, 1 H, C(9)H), 1.90-2.00 (m, 2 H, C(7)H_B, C(10)H). ^{13}C NMR (δ, ppm): 2.8 (2 C, C(4,5)), 19.0 (C(2)), 20.8 (C(3)), 27.5 (C(9)), 28.3 (C(10)), 30.2 (C(1)), 36.4 (2 C, C(8,14)), 36.4 (2 C, C(6,13)), 36.4 (2 C, C(7,12)). Mass *m/z* (%): 188 (23) $[M]^+$, 173 (19), 159 (72), 145 (73), 117 (68), 91 (100), 79 (55). Anal. calcd for $C_{14}H_{20}$, %: C, 89.3; H, 10.7. Found, %: C, 89.3; H, 10.6.

Synthesis of substituted spiro[2.3]hexanes

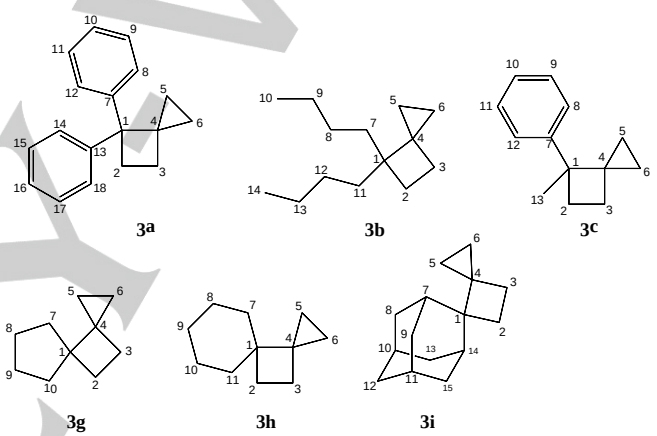


Figure 3. The numbering of atoms in the reported ^{13}C- and ^{1}H-NMR spectral data of the compounds **3a**-**3c**, **3g-3i**.

4,4-Diphenylspiro[2.3]hexane (***3a***). To a solution of 0.413 g (2 mmol) of (cyclopropylidenemethylene)dibenzene and 0.80 mL of CH_2I_2 (10 mmol) in CH_2Cl_2 (8 mL), 1 mL of Me_3Al (10 mmol) (caution: organoaluminums are pyrophoric and can ignite on contact with air, water or any oxidizer) was added at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 8 h. Then, the reaction mixture was diluted with 5 mL of CH_2Cl_2, and 3 mL of water was added dropwise while cooling the flask in an ice bath. The precipitate was collected on a filter paper. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $CaCl_2$ and concentrated in vacuo to give the crude product as a colorless oil. The residue was distilled through a micro column at 1 mm Hg to give **3a** (0.37 g, 78%) as a colorless oil. b.p. 147-148 °C (1 mm Hg).^{1}H NMR (δ, ppm): 0.53-0.57 (m, 2 H, C(5)H_A, C(6)H_A), 0.57-0.63 (m, 2 H, C(5)H_B, C(6)H_B), 2.15 (t, *J* = 7.4, 2 H, C(3)H_2), 2.67 (t, *J* = 7.4, 2 H, C(2)H_2), 7.00-7.47 (m, 10 H, Ph). ^{13}C NMR (δ, ppm): 9.8 (2 C, C(5,6)), 27.3 (C(3)), 29.0 (C(4)), 31.6 (C(2)), 55.1 (C(1)), 125.6 (2 C, C(10,16)), 127.5 (4 C, C(9,11,15,17)), 128.0 (4 C, C(8,12,14,18)), 147.5 (2 C, C(7,13)). Mass *m/z* (%): 234 (49) $[M]^+$, 219 (24), 205 (68), 180 (47), 165 (48), 128 (55), 115 (47), 91 (100), 77 (25), 51 (15), 41 (3). Anal. calcd for $C_{18}H_{18}$, %: C, 92.3; H, 7.7. Found, %: C, 92.2; H, 7.6.

5,5-Dibutylspiro[2.3]hexane (***3b***). Using the procedure described above with an increase of the reaction time to 48 hours, 0.332 g (2 mmol) of nonan-5-ylidenecyclopropane gave a crude product that was distilled

through a micro column at 4 mm Hg to give **3b** (0.27 g, 69%) as a colorless oil. b.p. 92-93 °C (4 mm Hg). ^{1}H NMR (δ, ppm, *J*/Hz): 0.15-0.25 (m, 2 H, C(6)H_A, C(5)H_A), 0.45-0.57 (m, 2 H, C(5)H_B, C(6)H_B), 0.93 (t, *J* = 7.2, 6 H, C(10,14)H_3), 1.00-1.15 (m, 4 H, C(8,12)H_2), 1.15-1.40 (m, 8 H, C(7,9,11,13)H_2), 1.75-1.85 (m, 2 H, C(2,3)H_A), 1.85-1.95 (m, 2 H, C(2,3)H_B). ^{13}C NMR (δ, ppm): 8.7 (2 C, C(5,6)), 14.2 (2 C, C(10,14)), 23.7 (2 C, C(9,13)), 26.3 (2 C, C(8,12)), 28.1 (C(4)), 26.8 and 28.4 (C(2) and C(3)), 38.8 (2 C, C(7,11)), 42.5 (C(1)). Mass *m/z* (%): 194 (<1) $[M]^+$, 165 (11), 152 (9), 151 (72), 137 (10), 123 (17), 109 (62), 95 (100), 81 (88), 67 (68). Anal. calcd for $C_{14}H_{26}$, %: C, 86.5; H, 13.5. Found, %: C, 86.5; H, 13.3.

4-Methyl-4-phenylspiro[2.3]hexane (***3c***). Using the procedure described above with an increase of the reaction time to 18 hours, 0.29 g (2 mmol) of (1-cyclopropylideneethyl)benzene gave a crude product that was distilled through a micro column at 1 mm Hg to afford **2c** (0.27 g, 79%) as a colorless oil. b.p. 77-78 °C (1 mm Hg). ^{1}H NMR (δ, ppm): 0.30-0.35 (m, 2 H, C(5)H_2), 0.35-0.41 (m, 1 H, C(6)H_A), 0.52-0.58 (m, 1 H, C(6)H_B), 1.49 (s, 3 H, C(13)H_3), 1.95-2.00 (m, 1 H, C(2)H_A), 2.30-2.40 (m, 1 H, C(3)H_A), 2.05-2.10 (m, 1 H, C(2)H_B), 2.57-2.65 (m, 1 H, C(3)H_B), 7.15-7.35 (m, 5 H, Ph). ^{13}C NMR (δ, ppm): 8.7 (C(6)), 11.6 (C(5)), 26.1 (C(13)), 26.8 and 31.6 (C(2) and C(3)), 30.1 (C(4)), 44.5 (C(1)), 125.4 (C(10)), 125.9 (2 C, C(9,11)), 128.0 (2 C, C(8,12)), 147.8 (C(7)). Mass *m/z* (%): 172 (3) $[M]^+$, 157 (34), 143 (52), 129 (100), 118 (51), 103 (21), 91 (31), 77 (27). Anal. calcd for $C_{13}H_{16}$, %: C, 90.6; H, 9.4. Found, %: C, 90.4; H, 9.3.

Dispiro[2.0.4.2]decane (***3g)***. Using the procedure described above with an increase of the reaction time to 48 hours, 0.29 g (2 mmol) of cyclopropylidenecyclopentane gave a crude product that was distilled through a micro column at 10 mm Hg to afford **3g** (0.22 g, 81%) as a colorless oil. b.p. 78-81 °C (10 mm Hg). ^{1}H NMR (δ, ppm): 0.18-0.33 (m, 2 H, C(5)H_A, C(6)H_A), 0.39-0.51 (m, 2 H, C(5)H_B, C(6)H_B), 1.21-1.66 (m, 8 H, C(7-10)H_2), 1.96-1.89 (m, 2 H, C(3)H_2), 1.96-2.02 (m, 2 H, C(2)H_2). ^{13}C NMR (δ, ppm): 8.9 (2 C, C(5,6)), 24.0 (2 C, C(8,9)), 27.1 and 32.5 (C(2) and C(3)), 27.2 (C(4)), 36.7 (2 C, C(7,10)), 48.9 (C(1)). Mass *m/z* (%): 136 (<1) $[M]^+$, 121 (12), 107 (96), 93 (57), 79 (100), 67 (55), 53 (18). Anal. calcd for $C_{10}H_{16}$, %: C, 88.2; H, 11.8. Found, %: C, 88.1; H, 11.7.

Dispiro[2.0.5.2]undecane (***3h***). Using the procedure described above with an increase of the reaction time to 48 hours, 0.24 g (2 mmol) of cyclopropylidenecyclohexane gave a crude product that was distilled through a micro column at 10 mm Hg to afford **3h** (0.20 g, 68%) as a colorless oil. b.p. 94-96 °C (10 mm Hg). ^{1}H NMR (δ, ppm, *J*/Hz): **:** 0.15-0.21 (m, 2 H, C(5)H_A, C(6)H_A), 0.45-0.51 (m, 2 H, C(5)H_B, C(6)H_B), 0.77-1.16 (m, 2 H, C(7,11)H_A), 1.21-1.40 (m, 2 H, C(8,10)H_A), 1.39-1.58 (m, 4 H, C(8,10)H_B, C(9)H_2), 1.58-1.75 (m, 2 H, C(7,11)H_B), 1.81-1.88 (m, 2 H, C(2)H_2), 1.93-2.02 (m, 2 H, C(3)H_2). ^{13}C NMR (δ, ppm): 7.3 (2 C, C(5,6)), 22.7 (2 C, C(8,10)), 26.2 (C(3)), 26.2 (C(9)), 28.3 (C(4)), 29.5 (C(2)), 35.5 (2 C, C(7,11)), 40.6 (C(1)). Mass *m/z* (%): 150 (<1) $[M]^+$, 136 (2), 121 (16), 107 (82), 93 (57), 79 (100), 67 (33). Anal. calcd for $C_{11}H_{18}$, %: C, 87.9; H, 12.1. Found, %: C, 87.9; H, 12.1.

1-Adamantylidenespiro[2.3]hexane (***3i***). Using the procedure described above with an increase of the reaction time to 48 hours, 0.35 g (2 mmol) of 2-cyclopropylideneadamantane gave a crude product that was distilled through a micro column at 1 mm Hg to afford **3h** (0.34 g, 83%) as a colorless oil. b.p. 109-110 °C (1 mm Hg). ^{1}H NMR (δ, ppm): 0.20-0.27 (m, 2 H, C(5)H_A, C(6)H_A), 0.78-0.87 (m, 2 H, C(5)H_B, C(6)H_B), 1.55 (br.s., 2 H, C(7)H), 1.64-1.68 (m, 2 H, C(12)H_2), 1.70-1.80 (m, 2 H, C(10,11)H), 1.78-1.85 (m, 1 H, C(2)H_A), 1.82-1.88 (m, 4 H, C(9)H_2), 1.85-1.90 (m, 1 H, C(2)H_B), 1.87-1.93 (m, 1 H, C(3)H_A), 1.88-1.92 (m, 4 H, C(8)H_2), 1.93-1.97 (m, 1 H, C(3)H_B). ^{13}C NMR (δ, ppm): 7.8 (2 C, C(5,6)), 27.2 and 27.6 (2 C, C(10,11)), 27.8 and 30.8 (C(2) and C(3)), 33.6 (2C, C(7,14)), 34.3 (2 C, C(9,15)), 35.9 (2 C, C(8,13)), 38.0 (C(12)). Mass *m/z* (%): $[M]^+$, 202 (26), 187 (27), 173 (57), 159 (25), 145 (44), 131 (42), 105 (50), 91 (100), 79 (70). Anal. calcd for $C_{15}H_{22}$, %: C, 89.0; H, 11.0. Found, %: C, 89.9; H, 10.9.

Synthesis of substituted spirohexanes by the reaction of alkylidenecyclobutanes with Me_3Al and CH_2I_2

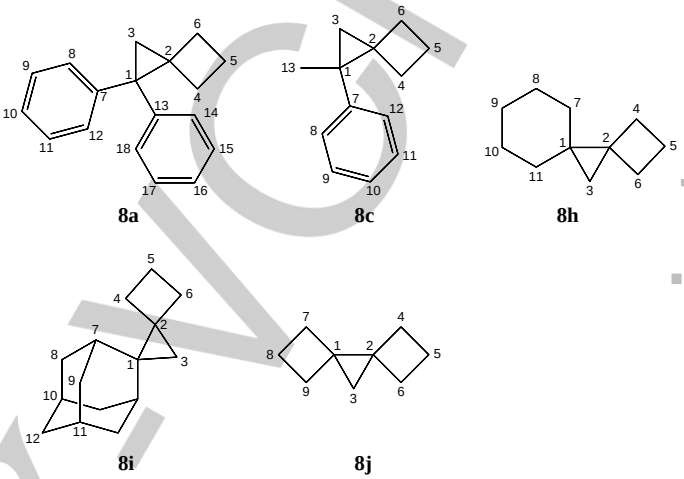


Figure 4. The numbering of atoms in the reported ^{13}C- and ^{1}H-NMR spectral data of the compounds **8a**, **8c**, **8h-8j**.

1,1-Diphenylspiro[2.3]hexane (***8a***). To a solution of 0.442 g (2 mmol) of (cyclobutylidenemethylene)dibenzene and 0.80 mL (10 mmol) of CH_2I_2 in CH_2Cl_2 (8 mL) was added 1 mL of Me_3Al (10 mmol) (caution: organoaluminums are pyrophoric and can ignite on contact with air, water or any oxidizer) at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 18 h. Then, the reaction mixture was diluted with 5 mL of CH_2Cl_2, and 3 mL of water was added dropwise while cooling the flask in an ice bath. The precipitate was collected on a filter paper. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $CaCl_2$ and concentrated in vacuo to give the crude product as a colorless oil. The residue was distilled through a micro column at 1 mm Hg to give **8a** (0.37 g, 79%) as a colorless oil. b.p. 147-148 °C (1 mm Hg). ^{1}H NMR (δ, ppm): 1.48 (s, 2 H, C(3)H_2), 1.90-2.03 (m, 3 H, C(4,6)H_A, C(5)$_A$), 2.07-2.21 (m, 1 H, C(5)H_B), 2.27-2.37 (m, 2 H, C(4,6)H_B), 7.15-7.35 (m, 10 H, Ph). ^{13}C NMR (δ, ppm): 16.1 (C(5)), 28.3 (C(3)), 29.2 (2 C, C(4,6)), 33.5 (C(2)), 37.5 (C(1)), 125.8 (2 C, C(10,16)), 128.1 (4 C (9,11,15,17), 129.2 (4 C, C(8,12,14,18)), 143.3 (2 C, C(7,13)). Mass *m/z* (%): 234 (26) $[M]^+$, 219 (6), 206 (100), 178 (18), 165 (27), 128 (47), 115 (28), 91 (77), 77 (15), 51 (8). Anal. calcd for $C_{18}H_{18}$, %: C, 92.3; H, 7.7. Found, %: C, 92.1; H, 7.7.

(1-Methylspiro[2.3]hexan-1-yl)benzene (***8c***)**.** Using the procedure described above, 0.316 g (2 mmol) of (1-cyclobutylideneethyl)benzene gave a crude product that was distilled through a micro column at 4 mm Hg to afford **8c** (0.23 g, 67%) as a colorless oil. b.p. 101-103 °C (4 mm Hg). ^{1}H NMR (δ, ppm): 0.71 (d, *J* = 4.8, 1 H, C(3)H_A), 1.13 (d, *J* = 4.7, 1 H, C(3)H_B), 1.35 (s, 3 H, C(13)H_3), 1.80-1.88 (m, 1 H, C(4)H_A), 1.88-1.99 (m, 2 H, C(4)H_B, C(5)H_A), 1.99-2.06 (m, 1 H, C(6)H_A), 2.06-2.20 (m, 1 H, C(5)H_B), 2.39-2.49 (m, 1 H, C(6)H_B), 7.15-7.40 (m, 5 H, Ph). ^{13}C NMR (δ, ppm): 15.9 (C(5)), 22.2 (C(13)), 26.2 (C(3)), 27.0 (C(2)), 27.4 and 28.0 (C(4) and C(6)), 31.7 (C(1)), 125.2 (C(10)), 127.5 (2 C, C(9,11), 128.0 (2 C, C(8,12)), 144.6 (C(7)). Mass *m/z* (%): 172 (4) $[M]^+$, 157 (8), 144 (49), 129 (100), 115 (18), 105 (11), 91 (16), 77 (14), 65 (4), 51 (7). Anal. calcd for $C_{13}H_{16}$, %: C, 90.6; H, 9.4. Found, %: C, 90.5; H, 9.4.

Dispiro[3.0.5.1]undecane (***8h***). Using the procedure described above, 0.27 g (2 mmol) of cyclobutylidenecyclohexane gave a crude product that was distilled through a micro column at 5 mm Hg to afford **8h** (0.23 g, 76%) as a colorless oil. b.p. 85-88 °C (5 mm Hg). ^{1}H NMR (δ, ppm): 0.17 (s, 2 H, C(3)H_2), 1.10-1.30 (m, 4 H, C(7,11)H_2), 1.40-1.70 (m, 6 H, C(8-10)H_2), 1.80-2.00 (m, 3 H, C(4)H_A, C(5)H_A, C(6)H_A), 2.00-2.15 (m, 1 H, C(5)H_B), 2.15-2.25 (m, 2 H, C(4)H_B, C(6)H_B). ^{13}C NMR (δ, ppm): 16.7 (C(5)), 22.6 (C(2)), 25.1 (C(3)), 25.8 (2 C, C(8,10)), 26.4 (C(9)), 27.1 (2 C, C(4,6)), 32.1 (2 C, C(7,11)), 35.7 (C(1)). Mass *m/z* (%): 150 (4) $[M]^+$, 135 (17), 122 (84), 107 (52), 93 (59), 79 (100), 67 (72), 53 (27), 41 (54). Anal. calcd for $C_{11}H_{18}$, %: C, 87.9; H, 12.1. Found, %: C, 88.7; H, 11.9.

1-Adamantylidenespiro[2.3]hexane (***8i***). Using the procedure described above, 0.38 g (2 mmol) of 2-cyclobutylideneadamantane gave a crude product that was distilled through a micro column at 1 mm Hg to afford **8i** (0.33 g, 82%) as a colorless oil. b.p. 112-113 °C (1 mm Hg). ^{1}H NMR (δ, ppm): 0.18 (s, 2 H, C(3)H_2), 1.05 (br.s, 2 H, C(7)H), 1.68-1.92 (m, 8 H, C(8,9)H_2), 1.75-1.82 (m, 2 H, C(12)H_2), 1.92-2.00 (m, 4 H, C(10,11)H, C(4)$_A$, C(6)$_A$), 1.98-2.05 (m, 1 H, C(5)H_A), 2.05-2.15 (m, 1 H, C(5)H_B), 2.18-2.25 (m, 2 H, C(4)$_B$, C(6)$_B$). ^{13}C NMR (δ, ppm): 17.4 (C(5)), 25.0 (C(3)), 26.8 (2 C, C(4,6)), 27.7 and 28.1 (C(10) and C(11)), 29.6 (C(2)), 32.0 (C(1)), 33.6 (2 C, C(7)), 36.3 (2 C, C(9)), 36.4 (2 C, C(8)), 37.4 (C(12)). Mass *m/z* (%): $[M]^+$, 202 (31), 187 (34), 174 (63), 159 (23), 145 (24), 131 (43), 117 (43), 105 (37), 91 (100), 79 (90). Anal. calcd for $C_{15}H_{22}$, %: C, 89.0; H, 11.0. Found, %: C, 88.9; H, 11.0.

Dispiro[3.0.3^5.1^4]nonane (***8j***).[49] Using the procedure described above, 0.22 g (2 mmol) of 1,1'-bi(cyclobutylidene) gave a crude product that was distilled through a micro column at 20 mm Hg to afford **8j** (0.21 g, 86%) as a colorless oil. b.p. 75-78 °C (20 mm Hg). ^{1}H NMR (δ, ppm): 0.33 (s, 2 H, C(3)H_2), 1.80-2.20 (m, 12 H, C(4-9)H_2). ^{13}C NMR (δ, ppm): 16.2 (2 C, C(5,8)), 24.0 (C(3)), 26.7 (4 C, C(4,6,7,9)), 27.7 (2 C, C(1,2)). Mass *m/z* (%): 122 (2) $[M]^+$, 107 (2), 94 (45), 79 (100).

The reaction of the monosubstituted alkylidenecyclopropanes 1d,e and 1,1'-bi(cyclopropylidene) (1f) with Et_3Al/CH_2I_2 reagent in CH_2Cl_2

(a) *1-Heptylspiro[2.2]pentane* (***2d***). To a solution of 0.304 g (2 mmol) of octylidenecyclopropane and 0.80 mL of CH_2I_2 (10 mmol) in CH_2Cl_2 (8 mL), 1 mL of Me_3Al (10 mmol) (caution: organoaluminums are pyrophoric and can ignite on contact with air, water or any oxidizer) was added at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 42 h. Then, the reaction mixture was diluted with 5 mL of CH_2Cl_2, and 3 mL of water was added dropwise while cooling the flask in an ice bath. The precipitate was collected on a filter paper. The aqueous layer was extracted with diethyl ether (3×5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $CaCl_2$ and concentrated in vacuo to give the crude product as a colorless oil. The residue was distilled through a micro column at 5 mm Hg to afford **2d** (0.21 g, 64%) as a colorless oil. b.p. 73-75 °C (5 mm Hg). The spectral properties (^{1}H NMR, ^{13}C NMR) were in good agreement with those obtained in the previous run for the synthesis of **2d**.

(b) *1-Methoxy-4-(spiro[2.2]pentan-1-yl)benzene* (***2e***). Using the procedure described above, 0.32 g (2 mmol) of 1-(cyclopropylidenemethyl)-4-methoxybenzene gave a crude product that was distilled through a micro column at 5 mm Hg to afford **2e** (0.18 g, 52%) as a colorless oil. b.p. 109-110 °C (5 mm Hg). The spectral properties (^{1}H NMR, ^{13}C NMR) were in good agreement with those obtained in the previous run for the synthesis of **2e**.

(c) *Dispiro[2.0.2^4.1^3]heptane* (***2f***). Using the procedure described above, 0.16 g (2 mmol) of 1,1'-bi(cyclopropylidene) gave a crude product that was distilled through a micro column at 750 mm Hg to afford **2f** (0.15 g, 78%) as a colorless oil. The spectral properties (^{1}H NMR, ^{13}C NMR) were in good agreement with those obtained in the previous run for the synthesis of **2f**.

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Keywords: alkylidenecyclopropanes • spiro[2.2]pentanes • spiro[2.3]hexanes • cyclopropanation • aluminum carbenoid

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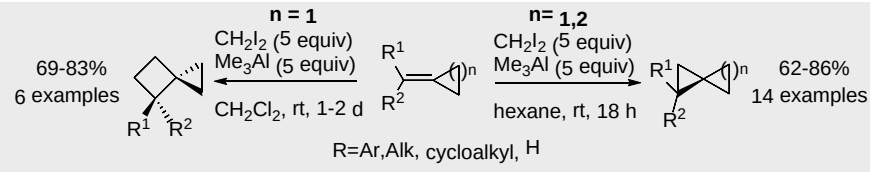

Alkylidenecyclopropanes and alkylidenecyclobutanes with Me_3Al/CH_2I_2 reagent in hexane gave substituted spiro[2.2]pentanes and spiro[2.3]hexanes in high yields. The same reaction with alkylidenecyclopropanes in CH_2Cl_2 afforded exclusively 1,1-disubstituted spiro[2.3]hexanes. The transformation of 1,1-diphenylspiro[2.2]pentane into 1,1-diphenylspiro[2.3]hexane was studied with the use of CD_2I_2 and a plausible mechanism was suggested.

Spiro[2.2]pentanes and spiro[2.3]hexanes synthesis

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Synthesis of Spiro[2.2]pentanes and Spiro[2.3]hexanes Employing the Me_3Al/CH_2I_2 Reagent