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Concerning the Preparation of Geminal DiGrignard Reagents. The Mechanism of Reaction of Geminal Dihalides with Magnesium and Sodium.

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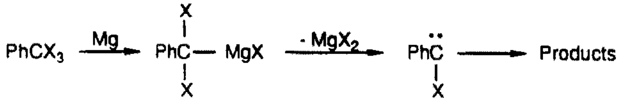
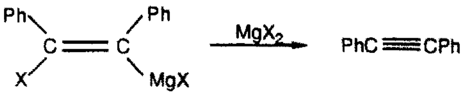
Abstract: **Mechanistic studies of the reactions of geminal dihalides with magnesium and sodium have been carried out and the possibility of preparing geminal DiGrignard Reagents for use in situ has been explored.**

It is known, from previous work, that alkyl monohalides react in the presence of magnesium via a mechanistic pathway that involves radical intermediates to form alkylmagnesium halides, which on hydrolysis, produce hydrocarbon products (monomers and dimers).[1] It is also known that the reaction of alkyl monohalides with sodium involves the formation of radicals followed by their subsequent conversion to anions as a result of a second electron transfer from the metal to the radical.[2] In contrast, the reaction of alkyl di- and trihalides with magnesium to form the corresponding Grignard compounds, especially those halides containing two or more halogen atoms on the same carbon atom, has presented serious problems in the past in terms of forming the corresponding di- and tri- Grignard reagents.[3] On the other hand, the reactions of benzotrihalides with magnesium were studied by this group and it was found that the intermediate Grignard compounds lose MgX_2 rapidly to form carbene intermediates when the MgX moiety and the halogen atom are attached to the same carbon atom (eq. 1), or carbon-carbon triple bonds when the MgX moiety and the halogen atom are on adjacent carbon atoms (eq. 2).[4]



$$PhCX_3 \xrightarrow{Mg} \underset{X}{\overset{X}{PhC}}{-}MgX \xrightarrow{-MgX_2} \underset{X}{Ph\ddot{C}} \longrightarrow Products \qquad (1)$$



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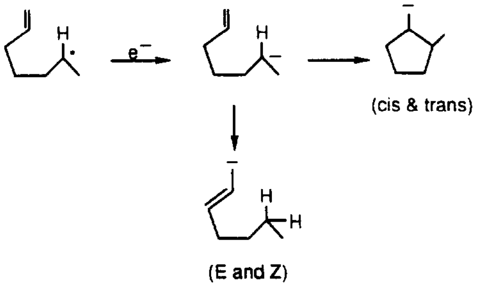
Recently we studied the reaction of alkyl monohalide radical probes with magnesium and observed the formation of straight chain hydrocarbons as well as five membered cyclized compounds that were derived from radical intermediates.[1] The effects of different activating agents, temperature, purity of magnesium, concentration of starting materials, ratio of magnesium to halide, type of halogen, type of alkyl group and solvent were also reported. The main conclusion of this work came as a result of the observation that by using radical trapping agents during the reactions, it could be determined that approximately 25% of the radicals leaving the surface of the magnesium returned to form Grignard reagent.[5]

Studies also have been carried out on the reactions of alkyl monohalide radical probes with sodium.[2] In this case the formation of cylized hydrocarbons (produced by radical as well as anionic cyclization pathways) and straight chain hydrocarbons (which suffered double bond isomerization) have been reported. Anion formation, as a result of a second electron transfer from the metal to the initially formed radical, is shown in eq. 3.



(3)

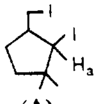
Finally, studies carried out by this group concerning the reactions of the geminal dihalide radical probes, 6,6-diido-5,5-dimethyl-1-hexene and 6,6-dichloro-5,5-dimethyl-1-hexene with LDA,[6] and 6-iodo-5,5-dimethyl-1-hexene with $LiAlH_4$[7] and LDA,[8] indicate that these halides can react to form radical intermediates (leading to the formation of five membered cyclized compounds) as well as carbene intermediates, which undergo insertion reactions characteristic of carbenes.

In an attempt to obtain evidence for the one electron donor ability of LDA, we decided to react 6,6-diiodo-5,5-dimethyl-1-hexene with known one electron donors such as magnesium and sodium in order to determine if similar products are formed thus establishing a common intermediate (radical, carbene) in both cases. Also by carrying out such a study, we wished to explore the possibility of forming DiGrignard Reagents in situ which could be utilized before subsequent collapse to the carbene intermediate. This is the first time that the mechanisms of reaction of geminal dihalides with magnesium and sodium have been explored using radical probes.

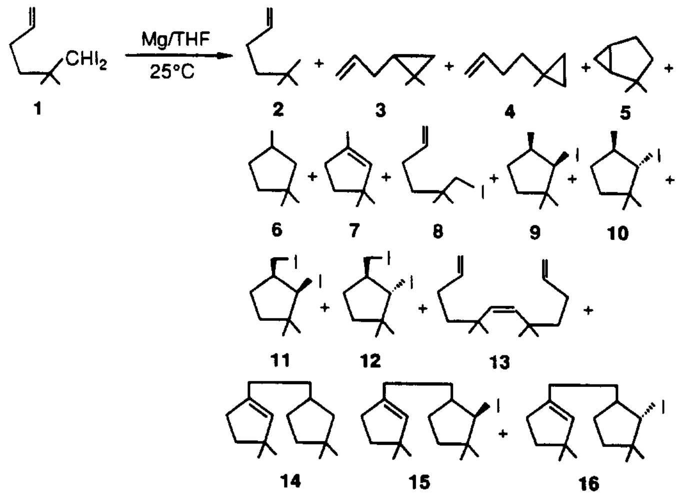
Results and Discussion

Reaction of 6,6-Diiodo-5,5-dimethyl-1-hexene with Magnesium.

The reaction of 6,6-diiodo-5,5-dimethyl-1-hexene (**1**) with excess activated magnesium in THF resulted (after hydrolysis) in the formation of 15 products (eq. 4). The major products isolated in this reaction were the cyclized diiodo compounds **11** and **12** (cis/trans = 1.7). The structural assignments for **11** and **12** were made based on ^1H NMR J values for the doublet corresponding to the proton (H_a) attached to the iodine-substituted carbon in the ring (structure A). Since both compounds (**11** and **12**) have not been



(A)



(4)

reported earlier in the literature, the experimental J values were compared with calculated values and with values reported in the literature for dimethylcyclopentanols (Table 1). The comparison between the experimental and calculated values is good, and the literature values for the pentanols are also in reasonable agreement.

TABLE 1. J Values for H_a in 11 and 12

Compound	J(exp)	J(calc)[a]	J(lit)[b]
11(cis)	4.8	4.4	4.5
12(trans)	10.5	11.5	8.0

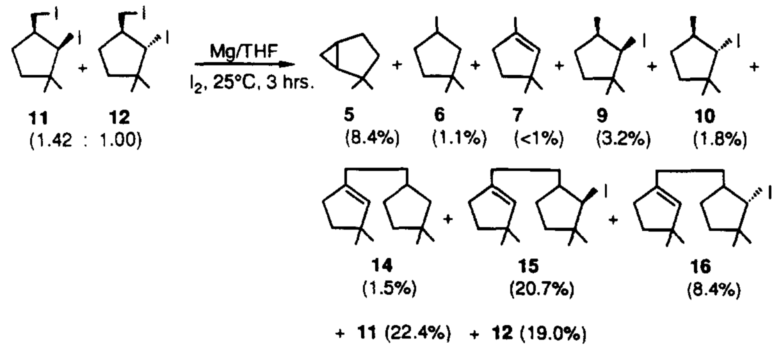
[a]Calculated by MMX. [b]Reported values for isomeric 2,5-dimethylcyclopentanols.[9]

The reaction of 1 with magnesium in THF (eq. 4) was monitored in order to determine which products are formed initially in the reaction. Table 2 shows that products 2, 3, 4, and 13 were formed in small amounts early in the reaction and their yields remained constant with time. On the other hand, the yield of 5 increased substantially with time and the yields of 11 and 12 decreased substantially with time. Products 6, 7, 9, 10, 14, 15, and 16, were not detected initially, but their yields increased gradually during the course of the reaction. The data in Table 2 show that the reaction is 84% complete after one minute and that 11 and 12 comprised 86% of the products formed. However, after 270 minutes, the reaction was 99% complete and 11 and 12 comprised only 32% of the products formed. Therefore, it is likely that products 5, 6, 7, 9, 10,

TABLE 2. Time Study of the Reaction of 6,6-Diiodo-5,5-dimethyl-1-hexene with Excess Magnesium in THF

Time (min)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
1	15.6	<1	1.8	1.4	3.6	<1	0	2.6	0	0	42.7	24.9	<1	<1	trace	trace
5	10.3	<1	1.6	1.6	5.0	<1	trace	3.4	0	0	46.0	25.9	1.1	2.0	trace	trace
13	6.3	<1	1.5	1.6	7.1	1.3	<1	2.1	0	0	35.6	20.8	1.7	3.4	1.2	trace
25	3.9	<1	1.6	1.6	9.7	2.0	<1	2.5	trace	trace	31.9	19.2	1.6	4.0	1.6	<1
50	3.4	<1	1.5	1.7	11.8	2.8	1.1	2.5	trace	trace	30.5	18.5	1.6	4.4	2.5	<1
120	1.4	<1	1.7	1.6	13.3	3.0	1.3	1.8	<1	<1	24.5	15.1	1.6	4.8	4.3	1.2
270	1.5	<1	1.7	1.9	18.5	4.4	1.7	1.8	2.0	1.2	13.0	8.9	1.7	5.4	9.1	6.9

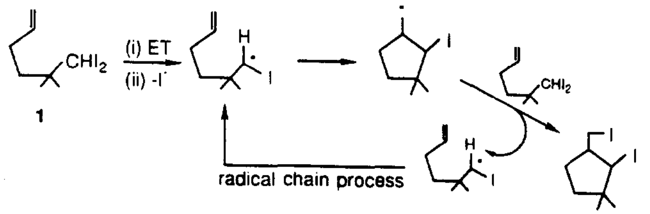
14, 15, and 16, which increase significantly in amount after one minute reaction while the amount of 11 and 12 decrease significantly, are formed from 11 and 12. In order to confirm this assumption, 11 and 12 were prepared independently by the reaction of 1 with LiAlH$_4$ and the mixture allowed to react with magnesium. The results (eq 5) are in good agreement with the conclusion that 11 and 12 are the initially formed



(5)

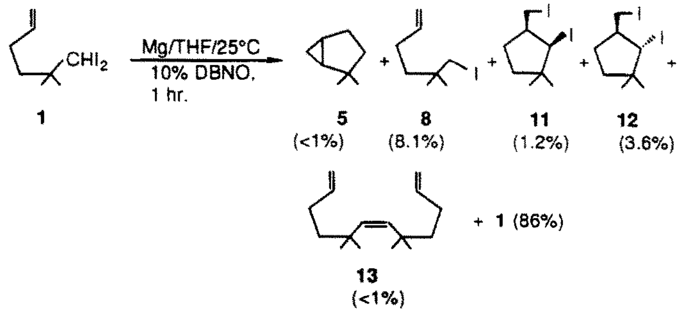
intermediates which lead to products 5, 6, 7, 9, 10, 14, 15, and 16. When 11 and 12 were allowed to react with magnesium separately, the cis compound 11 produced the cis compounds 9 and 15 in addition to 5, 6, 7 and 14 whereas the trans compound 12 produced the trans compounds 10 and 16 in addition to 5, 6, 7 and 14.

It can be seen in the reaction of 1 with magnesium, that although the formation of the cis compound 11 should be much more difficult than that of the trans compound 12 because of the steric hindrance produced by the presence of two iodine atoms adjacent to each other, the cis compound is formed predominantly. Since the 6-hepten-2-yl radical cyclizes to afford a 2.5/1 cis/trans mixture of 1,2-dimethylcyclopentane[10] (17) and since it is also known that the corresponding 6-hepten-2-yl anion cyclizes to afford a 0.8:1 cis/trans mixture of 17;[2] it is reasonable to assume that the cis/trans ratio (11/12) observe in the reaction of 1 with magnesium, is due to radical cyclization, followed by a halogen atom radical chain process (eq. 6).



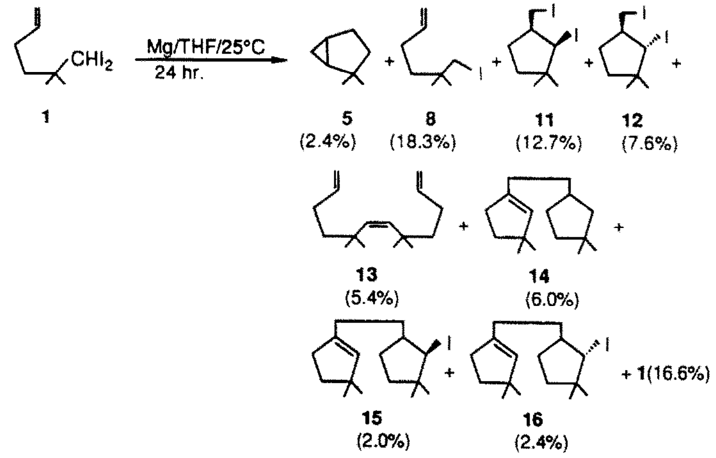
(6)

The radical chain process, shown in eq. 6, should be inhibited in the presence of a radical trap. In fact, when di-t-butylnitroxide (DBNO) was used as a radical scavenger in the reaction of 1 with magnesium, almost all of the starting diiodo compound 1 was recovered after one hour (eq. 7). Formation of the products shown in eq. 7 in very low yields indicates the intermediacy of radical precursors in the reaction of 1 with magnesium (eq. 4). On the other hand, the ratio of 11:12 = 0.3:1 (eq. 7) indicates that possibly some anionic cyclization takes place when the formation of radicals is inhibited.[2]



(7)

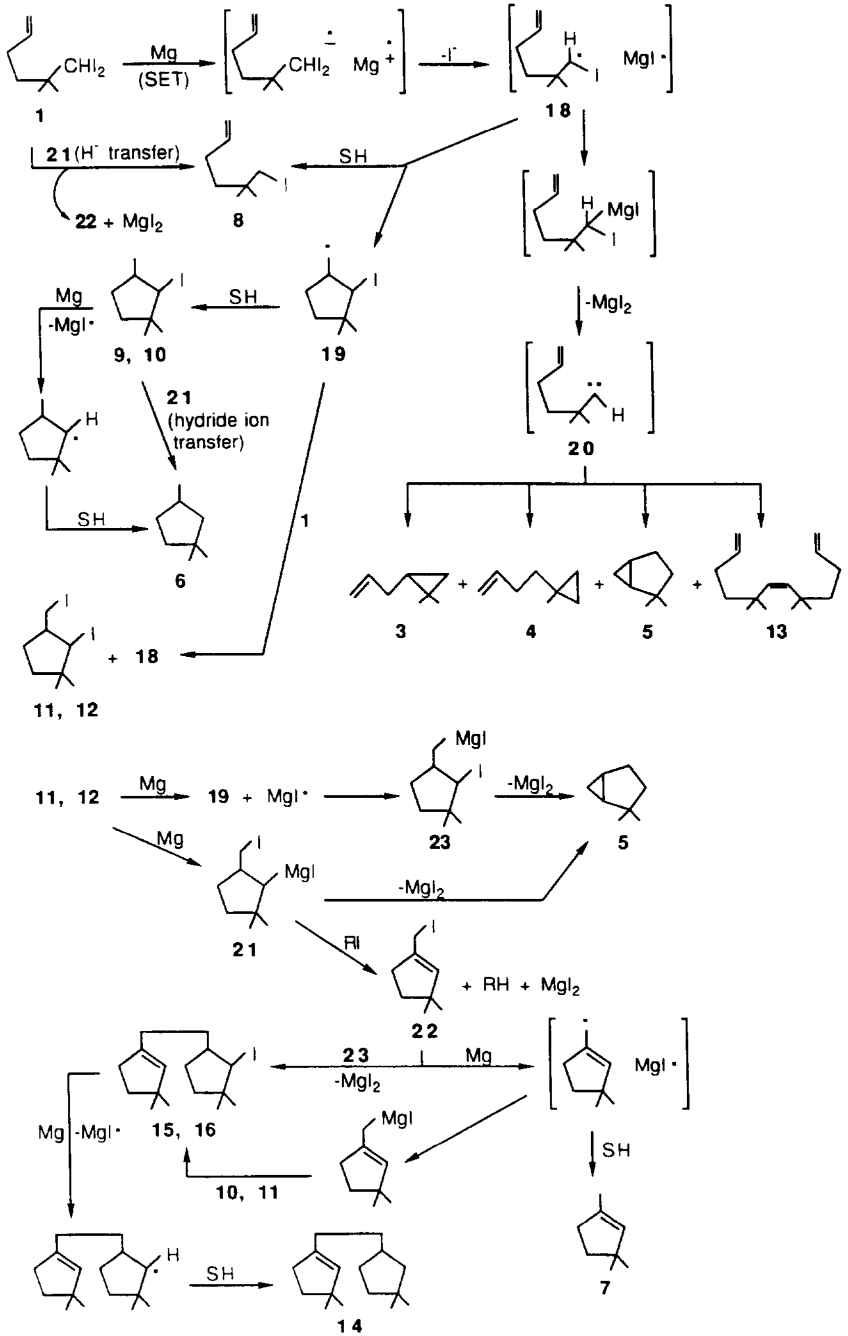
When **1** was allowed to react with 50 mole % of magnesium (eq. 8), 16.6% of the starting material was recovered after 24 hrs. indicating that a halogen atom radical chain process (eq. 6) is in operation involving **1**. The reaction is slower as expected since the amount of magnesium influences the rate of the reaction.[11]



(8)

In order to detect the formation of Grignard compounds in the above reactions, **1**, **11**, and **12** were independently allowed to react with magnesium, and the reactions were quenched with D_2O at various times. The products were then analyzed by GC-MS; none of the products showed any significant deuterium incorporation. These results indicate that the Grignard compounds formed react very rapidly to produce the carbene products **3**, **4**, **5** and **13**, and the products formed from the radical cyclized iodides (**5**, **15**, **16**, and **22**) according to Scheme 1.

The formation of unsaturated dimers **14**, **15**, and **16**, cannot be explained on the basis of dehydrohalogenation carried out by the Grignard compounds acting as bases or by the bases formed during the work up, because the reaction of **11** and **12** with n-butylmagnesium iodide did not produce any unsaturated compounds (only **5**, **9** and **10** were formed). The double bond formation can be explained by a hydride ion transfer from the Grignard compound, in a cyclic 6-membered transition state (eq. 9). A similar type of reaction had been proposed previously for the reduction of ketones, when the Grignard reagent was sterically hindered.[12]


CHI2
1
Mg
(SET)
CHI2
Mg +
-I⁻
H
I
MgI •
18
21 (H⁻ transfer)
22 + MgI2
SH
8
H
MgI
I
-MgI2
20
H
Mg
-MgI•
9, 10
SH
19
21
(hydride ion
transfer)
1
H
SH
6
3
4
5
13
11, 12
+ 18
11, 12
Mg
19 + MgI•
MgI
I
23
-MgI2
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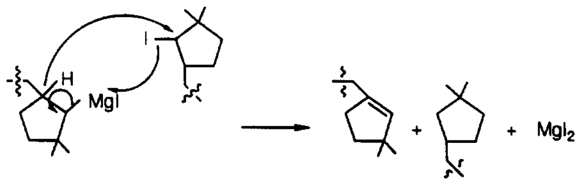
Scheme 1



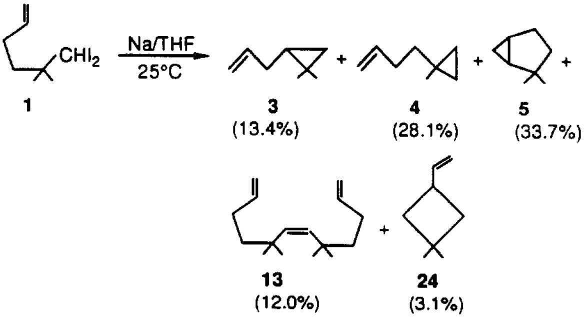
(9)

Based on all the evidence gathered, we believe that the mechanism shown in Scheme 1, for the reaction of **1** with magnesium, is the most consistent one.

According to Scheme 1, the diiodo compound **1** reacts with magnesium to form the radical **18**, which can form the Grignard (by coupling with MgI•) which then can lose MgI_2 to form the carbene **20**. Carbene **20** is a known precursor to products **3**, **4**, and **5**, and can also form **13** by dimerization. Radical **18** can also cyclize to radical **19**, which can abstract an iodine atom from the starting material **1** to produce **11**, **12**, and **18** in a halogen atom chain reaction or **19** can abstract a hydrogen atom from the solvent to form **9** and **10**. Compounds **9** and **10** can be reduced to **6** by a hydride ion transfer reaction (eq. 9) or they can react with magnesium to form a radical intermediate which then abstracts a hydrogen atom from the solvent (THF) to produce **6**. Compounds **11** and **12** can form the Grignard at either of the two carbon atoms attached to iodine, and subsequently produce the bicyclic compound **5** following elimination of MgI_2. If the Grignard compound is formed at the position of the magnesium attached to the ring (**21**), then **21** can transfer a hydride ion due to its steric hindrance, to produce the allylic iodide (**22**), which probably would not be detected due to its expected high reactivity. Compound **22** would be expected to react with magnesium to form **7** and to also react with **23** to form **15** and **16**. Reaction of **15** and **16** with magnesium and subsequent hydrogen atom abstraction from the solvent will produce hydrocarbon **14**.

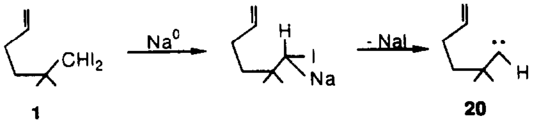
Reaction of 1 with sodium

The diiodo compound **1** was also allowed to react with sodium (eq. 10), which is a better electron donor



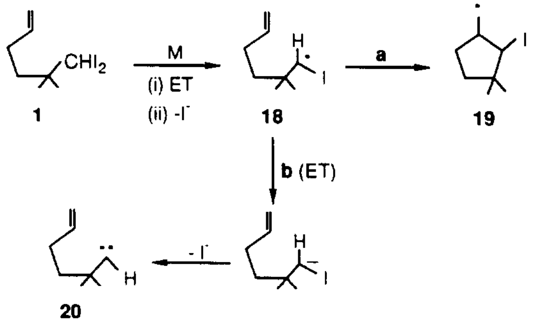
(10)

than magnesium. In this case however, no cyclized iodo compounds **11** and **12** or products derived from them were observed. The formation of all the products can be explained by a metal halogen exchange reaction which generates an intermediate which then eliminates NaI rapidly to form the carbene **20** (eq. 11). Carbene **20** can easily account for the formation of **3**, **4**, **5**, **13**, and **24**. Nevertheless, the fact that all of the products diminish in yield in the reaction of **1** with magnesium in the presence of di-t-butylnitroxide, which indicates



(11)

a common radical precursor does not exclude the possibility of a second electron transfer to the initially formed **18** to form a carbanion which leads to the formation of carbene **20** (eq. 12).



(12)

Pathways **a** (radical cyclization) and **b** (formation of a carbene) are competing pathways: **a** is faster than **b** when M = Mg; the opposite is true when M = Na, since sodium is a much better one electron donor than magnesium.

EXPERIMENTAL

General Procedures: All reactions were carried out in glassware washed with acetone, flash flamed and flushed with nitrogen. Transfers of all solvents and solutions were performed using oven-dried syringes or cannulas under a stream of dry nitrogen. Ethyl isobutyrate, diisopropylamine, and 4-bromo-1-butene, were purchased from Aldrich and purified by distillation. Methyllithium was purchased from Aldrich as a 1.4 M solution in diethyl ether and was analyzed by Watson Eastham titration[13] before use. Lithium aluminum hydride, pyridinium chlorochromate and hydrazine hydrate were purchased from Aldrich and used as received. Triply sublimed magnesium (Dow, 99.99% pure) was cut into small pieces with a diamond bit and washed with dry ether prior to use. Sodium was purchased from Aldrich and washed with dry toluene prior to use. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl just prior to use. Methylene chloride was distilled over calcium hydride prior to use.

GLC analyses were performed on a VARIAN 3700 Gas chromatograph equipped with a 30m DB-5 (0.5 mm) fused silica column and a flame ionization detector. The analyses were carried out using n-decane as the internal reference. Preparative GLC was carried out on a VARIAN Aerograph 400 Dual Column Gas Chromatograph equipped with a thermal conductivity detector. The columns used were 10′ or 4′ long with a diameter of 1/4" with 10% OV-101 packing. NMR spectra were recorded in $CDCl_3$ solutions, using the solvent peak as the internal reference (δ 7.24 ppm) on a 300 MHz Varian Gemini instrument. Mass spectra were recorded (EI) on a VG-70 SE instrument. Sonication was carried out using a BRANSON 1200 sonicator.

Preparation of 6,6-diiodo-5,5-dimethyl-1-hexene (1): This compound was synthesized from 2,2-dimethylhex-5-en-1-al, via its hydrazone, according to the general procedure described for the synthesis of geminal diiodides.[14] Accordingly, 4.0 g (0.031 mol) of the aldehyde in 30.0 mL of absolute ethanol was added slowly to 8.0 g (0.16 mol) of hydrazine hydrate with vigorous stirring. The resulting mixture was then refluxed on a steam bath for 2 hours and after cooling, it was extracted with chloroform. The organic layer was then washed with water and dried over anhydrous potassium carbonate. Removal of the solvent using a rotary evaporator gave the hydrazone (89% yield) as a colorless viscous oil. Its identification and purity was confirmed by IR and NMR.

3.0 g (0.021 mol) of the hydrazone was added, with vigorous stirring, to a solution of 11.0 g (0.045 mol) iodine in 38.0 mL of ether. Triethylamine was added dropwise at 25°C, the addition being continued until the reaction was complete, as judged by the cessation of nitrogen evolution; this required 4.2 mL (0.03 mol) of triethylamine. The resulting mixture was diluted with ether and washed with 5% sodium thiosulfate, 3N hydrochloric acid, and 5% sodium carbonate solution, in succession. Drying of the organic layer over anhydrous K_2CO_3 was followed by evaporation of the solvent. The dark oil that was obtained was then passed through silica gel (Merck grade 60, 230-400 mesh, 60Å), with hexane as the eluent. This afforded 2.1 g of **1** (as a liquid), corresponding to a 27% yield based on the hydrazone. NMR: δ 1.15 (s, 6H); 1.5-2.1 (m, 4H); 5.0 (m, 2H); 5.25 (s, 1H); 5.8 (m, 1H). M.S. 364 (M^+, 2%), 237 (3%), 195 (10%), 127 (2%), 109 (100%), 95 (25%), 81 (15%), 69 (45%), 55 (30%). H.R.M.S. : 363.9186 (calc); 363.9185 (obs.).

Reaction of 6,6-Diiodo-5,5-dimethyl-1-hexene (1) with Magnesium:

In the case of the reaction where the ratio **1**: Mg was 1 : 3, 0.020 g (0.82 mmol) of magnesium turnings were placed in a small flask under nitrogen. A solution of 0.10 g (0.27 mmol) of **1** in 0.2 ml of dry THF was then added, at 25°C, and sonication started immediately. Generally, the reaction started after 5 or 10 min. (a characteristic white turbidity was observed). At that moment 0.8 ml of THF was added. When the reaction was monitored (by GLC), 10 μL of n-decane (used as an internal standard) was added and small aliquots (approx. 50 μL each) were removed and quenched with water. The reaction was terminated by slowly adding water, and the contents extracted with ether. The organic layer was separated and the solvent evaporated.

Compound **2** was identified by comparing its GC/MS data with that reported for it in the literature.[15] Compounds **4** and **5** had identical GC/MS data as that reported earlier for the two.[8] The structure of **3** was established by comparing its GC/MS data with the literature data.[16] The GC/MS data of **6** matched with that of an authentic sample of **6** obtained from Wiley Organics. Compounds **7**[17] and **8**[18] were also identified by matching their respective GC/MS data with literature data.

Compound **11** was isolated from the reaction mixture by flash column chromatography using silica gel. ^{1}H NMR : δ 1.15 (s, 3H), 1.25 (s, 3H), 1.55 (m, 2H), 1.80 (m, 1H), 1.95 (m, 1H) 2.15 (m, 1H), 3.23 (m, 2H), 4.31 (d, J 4.8 Hz, 1H). M.S. : 364 (M^+, 85%), 254 (40%), 237 (100%), 109 (95%), 67 (90%), 55 (70%) H.R.M.S. : 363.9168 (obs.), 363.9185 (calc.)

Compound **12** was isolated from the reaction mixture by flash column chromatography, using silica gel. ^{1}H NMR: δ 0.98 (s, 3H); 1.01 (s, 3H), 1.55 (m, 2H), 1.70 (m, 1H), 1.90 (m, 1H), 2.20 (m, 1H), 3.34 (dd, J 9.9 Hz, 6.0 Hz, 1H), 3.48 (dd J 9.9 Hz, 3.0 Hz, 1H), 3.62 (d, J 10.5 Hz, 1H). M.S. : 364 (M^+, 85%), 254 (25%), 237 (100%), 127 (10%), 109 (95%), 69 (75%), 55 (50%). H.R.M.S.: 363.9196 (obs.), 363.9185 (calc.).

Reaction of 11 and 12 with Magnesium:

0.020 g (0.82 mmol) of Mg turnings was placed in a small flask under a flush of nitrogen. Then, 0.10 g (0.27 mmol) of a mixture of **11** and **12**, dissolved in 0.2 ml of dry THF, was added, at 25°C. A small quantity of iodine was added to the reaction mixture as an initiator. Sonication was begun, and the reaction started almost immediately. At that moment, 0.8 ml THF was added. The reaction was terminated by adding water, and the contents were extracted with ether. The organic layer was separated, and the solvent evaporated.

The reaction of a mixture of **15** and **16** with $LiAlH_4$ in THF produced compound **14** as the main product. Compound **14** was identified by M.S. and ^{1}H NMR. ^{1}H NMR: δ 0.92 (s, 3H), 0.99 (s, 9H), 1.20 (m, 2H), 1.35 (m, 4H), 1.62 (t, 2H), 1.80 (m, 2H), 1.95 (m, 2H), 2.23 (m, 3H), 5.10 (bs, 1H). M.S. : 220 (M^+, 10%), 205 (100%), 149 (5%), 135 (3%), 123 (5%), 109 (10%), 95 (25%), 81 (35%), 69 (8%), 55 (10%). H.R.M.S. : 220.2186 (obs.), 220.2191 (calc.).

Compounds **15** and **16** were identified by GC/MS: **15** : M.S. : 346 (M^+, 2%), 331 (10%), 219 (25%), 203 (25%), 149 (20%), 123 (20%), 109 (100%), 95 (50%), 81 (40%), 67 (30%), 55 (30%). **16** : M.S. : 346 (M^+, 3%), 331 (40%), 219 (25%), 203 (20%), 149 (15%), 123 (15%), 109 (100%), 95 (50%), 81 (40%) 67 (25%), 55 (20%).

Preparation of compounds 11 and 12.

A solution of 0.10 g (0.27 mmol) of **1** in 20 mL of dry THF was placed under nitrogen in a flask at 25°C. A solution of $LiAlH_4$ in THF (54 μL of a 1.0 M solution) was then added with stirring. The reaction was terminated after 2 hours by slowly adding water, and the contents were extracted with ether. After evaporating the solvent, **11** and **12** were isolated by flash column chromatography, using silica gel. (Spectroscopic data: see reaction of **1** with Mg). The yields, determined by GLC, were 40% for compound **11** and 25% for compound **12**.

Preparation of compounds 9 and 10.

A solution of 0.10 g (0.27 mmol) of a mixture of compounds **11** and **12** (in a ratio of 1.5 : 1) in 2.0 mL of dry THF was added (under nitrogen) to a flask at 25°C. Then, 0.27 mL of a 1.0 M solution of $LiAlH_4$ in dry THF was added with stirring. The reaction was terminated after 10 minutes by slowly adding water, and the contents were extracted with ether. Compound **10** was isolated by preparative GLC. Compound **9** could not be isolated due to its decomposition during the GLC separation, but the key ^{1}H NMR signal corresponding to the ring proton attached to the C-I unit could be clearly identified from a mixture of **9** and **10**. The yields (determined by GLC) of compounds **9** and **10** were 29% and 46%, respectively. The ^{1}H NMR of compound **9**: δ 4.27 (d, J 6.0 Hz). M.S. : 127 (5%), 111 (100%), 69 (95%), 55 (60%), 41 (35%). The ^{1}H NMR of compound **10** : δ 0.97 (s, 3H), 1.03 (s, 3H), 1.07 (d, 3H), 1.28 (m, 4H), 1.66 (m, 2H), 1.91 (m, 2H), 2.27 (m, 1H), 3.49 (d, J 11.1 Hz, 1H). M.S. : 127 (5%), 111 (80%), 69 (100%), 55 (50%), 41 (35%). H.R.M.S: Although attempts were made to get the exact molecular weight of compound **10** (and also **9**), this compound did not exhibit its molecular ion, even using the C.I. technique.

Reaction of compound 1 with Sodium:

Sodium, 0.019 g (0.82 mmol), cut into small pieces, was placed in a small flask under nitrogen. A solution of 0.10 g (0.27 mmol) of compound **1** in 1.0 mL of dry THF was added. The reaction started immediately under sonication at 25°C. The reaction was terminated by slowly adding water and the contents were extracted with ether. The products **3**, **4**, and **5** were identified by GC/MS, by comparison with authentic samples, as described earlier. Compound **24** was identified by comparing its GC/MS data with that reported in the literature.[8] Compound **13** was isolated from the mixture by preparative GLC using an OV-101 column, and identified by M.S., ^{1}H NMR, and IR. ^{1}H NMR: δ 1.00 (s, 12H), 1.35 (t, 4H), 1.95 (m, 4H), 4.93 (m, 4H), 5.21 (s, 2H), 5.80 (m, 2H). M.S. : 220 (M^+, 1%), 205 (3%), 165 (5%), 149 (5%), 123 (30%), 109 (50%), 95 (50%), 83 (100%), 69 (90%), 55 (50%). H.R.M.S.: 220.2176 (obs.); 220.2191 (calc.). IR: cm^{-1}: 990 (m, CH bend), 972 (m, CH bend), 910 (s, CH bend) 666 (s, CH bend).

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