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THE SYNTHESIS OF BISMETHYLENE DERIVATIVES OF TRIANGULANES

Kirill A. Lukin, Anna Yu. Masunova, Bogdan I. Ugrak, Nikolai S. Zefirov.*

Department of Chemistry Moscow State University, Moscow, 119899, USSR

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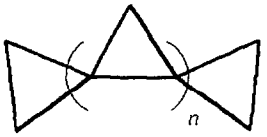
Abstract A method for the preparation of an unique type of hyrocarbons, namely, bismethylene derivatives of linear triangulanes, has been developed, and the syntheses of 1,4-bismethylenespiropentane, 1,5-bismethylenedispiro[2.0.2.1]heptanes, and 1,6-bismethylenetrispiro[2.0.0.2.1.1]nonanes were realized.

Policyclic compounds possessing small and, hence, strained rings have been an area of intensive interest by organic chemists during last two decades.[1] Special attention was paid to compounds which have double bonds attached to small rings. First, such fragments are responsible for unusual chemical behavior. Second, these compounds can be useful as building blocks for conducting a variety of unusual transformations and syntheses. Third, the problems associated with the possibility of conjugation between double bonds incorporated into polycyclic skeletons are of special interest.

Recently we defined as *triangulanes* the unique type of hydrocarbon which are constructed from spiroannulated cyclopropane fragments, and initiated a detailed study of these compounds. In particular we have examined stereochemical relationships in isomeric *linear triangulanes* (LT), **1**, and developed a general method for their synthesis.[2,3]

The present paper describes our efforts in the synthesis of bismethylene derivatives of LT, **2**. First, these compounds are prospective intermediates for the syntheses of new types of polyspirocyclopropanes. On the other hand, their study would allow one to obtain a valuable information concerning interactions between small rings and double bonds. In spite of the interest in bismethylene derivatives of polyspirocyclopropanes, and in



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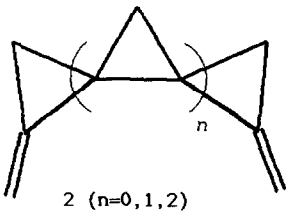
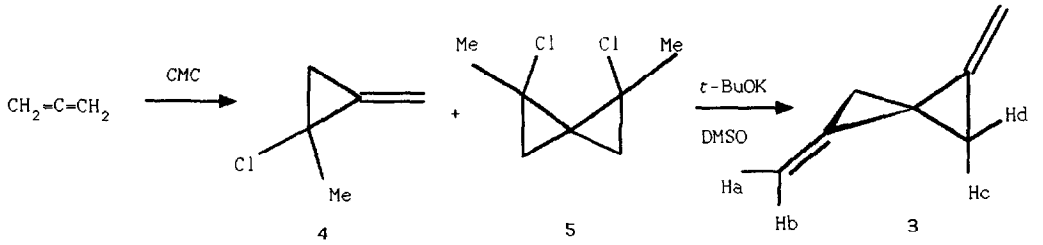


2 (n=0,1,2)

parent bismethylenespiropentane in particular,[4] to the best of our knowledge, there are no data on the synthesis of these compounds in literature.

RESULTS AND DISCUSSION.

1,4-Bismethylenespiropentane (3). At present, one of the most useful procedures for the preparation of methylenecyclopropane derivatives includes the addition of chloromethylcarbene (CMC) to an olefin and subsequent dehydrohalogenation.[5] We have also used this method in the general synthesis of LT.[2,3] Thus, we expected that the simplest route to bismethylene derivatives of LT could be based on the addition of CMC to allenes. In particular, the synthesis of 1,4-bismethylenespiropentane, **3**, could include the double addition of CMC to 1,2-propadiene and further double dehydrohalogenation.



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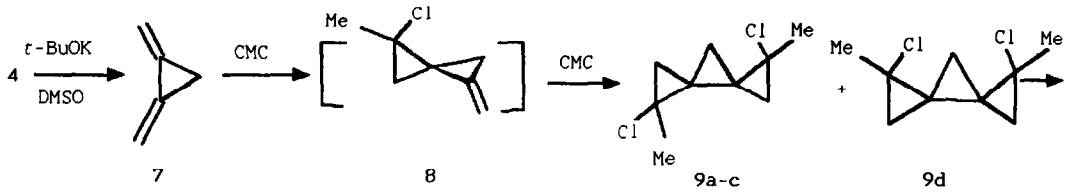
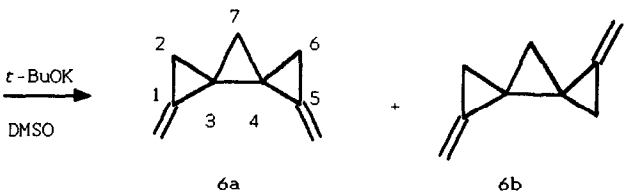
We have found recently[6] that the addition of CMC to allene or to 2-chloro-2-methyl-1-methylenecyclopropane, **4**, proceeds with low efficiency, but it was possible to isolate the corresponding bis-adducts **5**. Dehydrochlorination of compound **5** gave diene **3**, which was the only product of the reaction, according to GC-analysis. However, the yield after the preparative GC isolation was only 25% The hydrocarbon **3** was characterized by ^{1}H NMR, ^{13}C NMR and mass-spectra. An interesting feature of diene **3** is the appreciable interaction between proton H_a of methylene group and atom H_c or H_d of the neighbouring three membered ring (J = 0,8 Hz). Bismethylene-

spiropentane **3** turned out to be a ralatively stable compound: no changes in its ^{1}H NMR spectrum were found after one month at -20°C.

1,5-Bismethylenedispiro[2.0.2.1]heptane (6a,b). The low yield of diene **3** did not permit us to use it as a starting material for the preparation of bismethylenedispiroheptane **6**. Thus, we have chosen the alternative route which included dehydrohalogenation of chloride **4**, double addition of CMC to the resulting bismethylenecyclopropane **7**, and finally a double dehydrohalogenation.





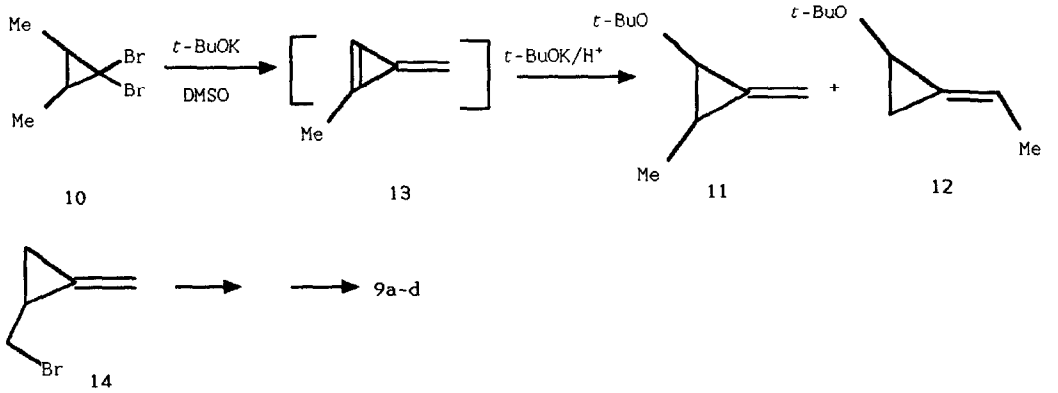
Since diene **7** was claimed to be a very unstable compound,[7] the products of dehydrohalogenation of chloride **4** were simultaneously distilled into a cold (-78°C) trap, and then treated with an excess of 1,1-dichloroethane and butyllithium. From the resulting reaction mixture we succeeded in isolating isomeric diadducts **9** in a 10% yield. Dehydrochlorination of compounds **9** afforded dienes **6** in a 50% yield. The diene **6** was obtained as a mixture of *syn*- and *anti*-isomers (**6a** and **6b**) in a 1:9 ratio, according to GC-analysis and ^{1}H NMR spectrum.

The assignment of configuration was based on the signals for the protons at the C^7 in the ^{1}H NMR spectrum. These hydrogens are not equivalent in the *syn*-isomer **6a** (molecular group of symmetry C_s), and their resonances appear as two doublets (J = 3.8 Hz). In the *anti*-isomer **6b** (molecular group of symmetry C_2) the hydrogen atoms are equivalent and their resonances appear as a singlet with δ 1.87 ppm. A characteristic feature of the ^{1}H NMR spectrum of the *syn*-isomer **6a** is an interaction of one of the protons at C^7 with a hydrogen of a neighbouring three membered ring. Additional support of structure for the dienes **6** was obtained from their ^{13}C NMR and mass-spectra.

Stereoselective formation of the *anti*-isomer of **6b** could be accounted for by the steric hindrance on one side of the double bond in the inter-

mediate olefin **8** toward addition of CMC. Actually, analysis of the ^{1}H NMR spectrum of chlorides **9** showed that only four of the six possible diastereomers were formed. Moreover, three of them (namely isomers **9a-c**) are the precursors of diene **6b** and they constituted 90% of the mixture. Formation of the *syn*-isomer **6a** can occur only from precursor **9d**.

In order to improve the procedure we tried to develop a more efficient synthesis of diene **7**. At first, the dehydrochlorination of readily available 1,1-dibromo-2,3-dimethylcyclopropane seems the most promising, because the intermediate methylcyclopropene easily isomerizes into corresponding methylenecyclopropane under the reaction conditions.[8] However, after the treatment of dibromide **10** with potassium *tert*-butoxide in DMSO we obtained only the ethers **11** and **12**. The formation of the ether **11** can be accounted for by the faster addition of *tert*-butoxy anion to the intermediate cyclopropene **13**, than its isomerization. The formation of the compound **12** results from the thermal rearrangement of the ether **11**.[9]



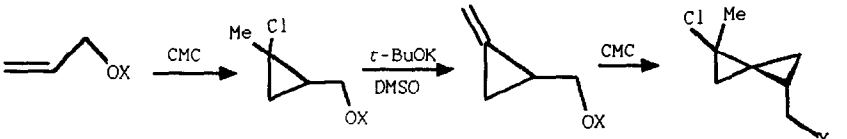
The second alternative route to diene **7** included the dehydrobromination of the known 2-(bromomethyl)-1-methylenecyclopropane **14**.[10] The formation of compounds **9** after treatment of products of this reaction with an excess of CMC indicated the intermediacy of diene **7** in the reaction; however the yield of chlorides **9** unfortunately did not exceed 10%.

Thus, we have shown that adducts of chloromethylcarbene to allene could be used as starting materials in the synthesis of bismethylene derivatives of triangulanes **3** and **6**. However the synthesis of higher homologs of these dienes requires a new approach.

General Procedure for the Preparation of Bismethylene Derivatives of Triangulanes. A general method for the preparation of compounds **2** is based on two independent procedures for the generation of methylenecyclopropane unit. Thus, the reaction sequence including addition of CMC to an olefin

with further dehydrohalogenation, was used in construction of a chain of three membered rings. The generation of a second methylenecyclopropane moiety occurred at the last step of the synthesis from an apropriate building block. Hydroxymethylcyclopropane group was chosen as such a block, and allyl alcohol was used as a starting material.

A side reaction accompaning the addition of CMC to unsaturated alcoholates[11] required the protection of the hydroxyl group. It was shown that tetrahydropyranyl protection allowed to obtain adducts of CMC to unsaturated alcohols and to perform their dehydrohalogenation.[12]



15a X=Me
15b X=THP

16a X=Me
16b X=THP

17 X=Me
18 X=THP

19 X=OTHP
20 X=OMe
21 X=OH
22 X=Br
23 X=J

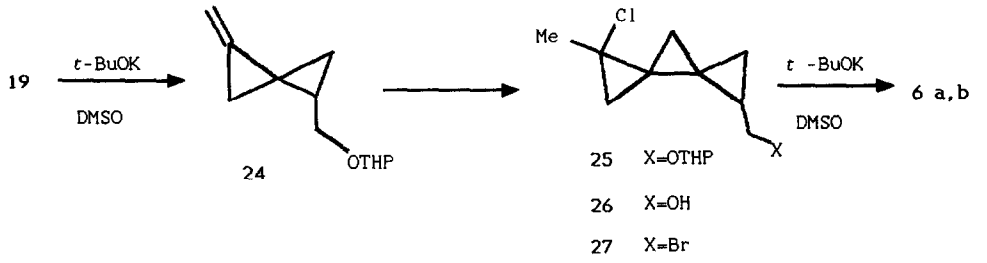
22,23 —(t-BuOK, DMSO)→ 3

We also carried out methylation of the hydroxyl group because it was shown that the methoxy group could be easily replaced by iodine.[13]

The addition of CMC to allyl methyl ether, **15a**, or allyloxytetrahydropyran, **15b**, afforded the corresponding cyclopropanes **16a** and **16b**. Their dehydrochlorination gave methylenecyclopropanes **17** and **18**. Addition of CMC to these olefins resulted in the formation of the corresponding bifunctional spiropentanes **19** and **20**. The spiropentane **19** was subsequently deprotected and brominated with PBr_3 to yield compounds **21** and **22**, respectively. On the other hand, the reaction of ether **20** with sodium iodide and chlorotrimethylsilane gave iodide **23**. The analysis of ^1H NMR spectra of compounds **20, 21** and **23** have shown that they were a mixture of only two isomers (from the four possible ones) in a 1:1 ratio. These data indicate a stereoselectivity in the addition of CMC to methylenecyclopropanes **17** and **18** which proceeded from the less hindred side of the double bond. Diastereomeric iodides **23** were separated by column chromatography. Dehydrohalogenation of compounds **22** and **23** gave diene **3** as a single product in a 25-30% yield.

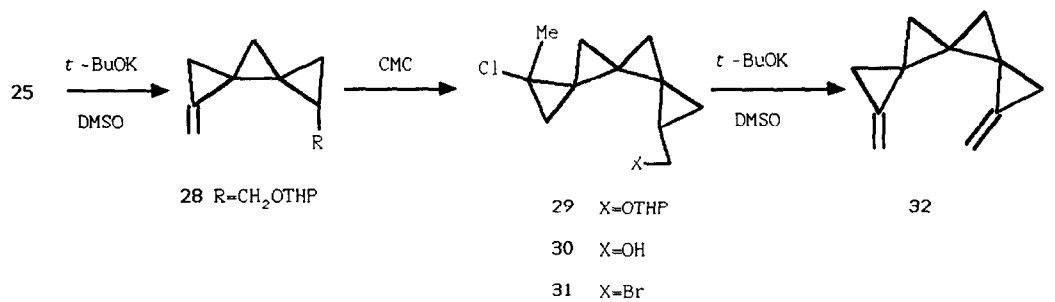
The advantage of the designed approach to bismethylene derivatives of LT was also demonstrated by the syntheses of dienes **2** (n=1,2). Only THP-protection was used in these syntheses, because such compounds appear to be easily separated and purified.

Thus, dehydrochlorination of spiropentane **19** gave alkene **24**, which reacted with CMC to yield dispiroheptane **25**. It should be pointed out that both sides of double bond in compound **24** are not significantly hindered,



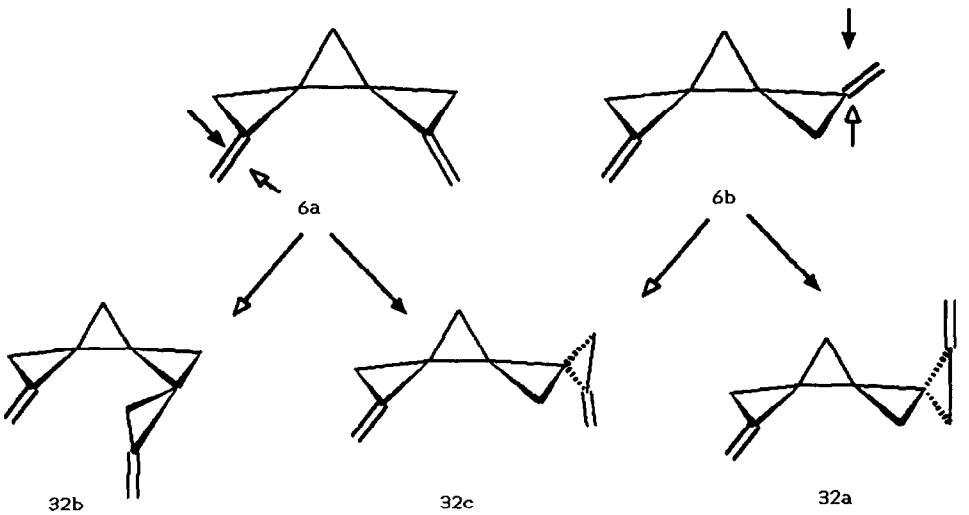
so the formation of precursors of both isomers of diene **6** in equal amounts could be expected (*cf.* the case of chloride **8**). Indeed, the diene **6**, which was obtained after sequential deprotection, bromination, and dehydrohalogenation, was a mixture of *anti*- and *syn*-isomers in a 2:3 ratio, according to the ^{1}H NMR spectrum.

The same reaction sequence was used for the synthesis of bismethylenetrispirononanes **32** (*2*; n=2). Addition of CMC to alkene **28** gave trispirononane **29**, which was subsequently transformed into alcohol **30** and bromide **31**.



It should be pointed out that three possible isomers **32a, 32b** and **32c** could exist for diene **2** (n=2). The isomer **32a** (group of symmetry C_2) could be obtained as a result of the *exo*-addition of CMC to the *anti*-iso- mer of diene **6**; *endo*-addition of CMC to the *syn*-diene **6a** could give diene **32b** (group of symmetry C_2). Isomer **32c** (group of symmetry C_1) could result from both the *exo*-addition of CMC to the *syn*-diene **6a** and *endo*-addition of CMC to the *anti*-diene **6b**. Earlier we have found that ratio of *exo*- to *endo*-addition of CMC to methylenedispiroheptane **28** (R=H) was 3.7:1.[3] Thus, we may propose that the addition of CMC to olefin **28** will afford mainly precursors of dienes **32a** and **32c**.

In fact, in accordance to ^{1}H NMR spectra, the product of dehalogenati-



on of compound **31** was the mixture of two isomers of diene **2** (n=2). The structure **32c** was assigned to the isomer, which shows the resonances of protons attached to C^7 and C^8 as four doublets in the ^1H NMR spectrum, and the structure **32a** was assigned to the isomer in which ^1H NMR spectrum the corresponding resonances appeared as two doublets (C_2-axis in the molecule).

Thus, we have developed a method for the preparation of bismethylene derivatives of LT. The possibilities of the method were demonstrated by the synthesis of bismethylenespiropentane **3**, bismethylenedispiroheptanes **6**, and bismethylenetrispirononanes **32**

Experimental Section

General. ^1H NMR spectra were recorded on Tesla BS-467 (60 MHz), Bruker WM-250 (250 MHz), and Varian XR-400 (400 MHz) spectrometers. ^{13}C NMR spectra were recorded on Bruker AM-300 (75 MHz) spectrometer in $CDCl_3$, GC-analysis was carried out with Tzvet-101 instrument equiped with FID and 3000x3 mm column packed with SE-30 on Inerton NAW phase. Preparative GC was performed on a PAHV-08 instrument with 5000x5 mm column packed with SE-30 on Inerton NAW phase. Mass spectra were obtained on a Finnigan MAT-112 spectrometer at 12 eV.

2-Chloro-2-Methyl-1-Methylenecyclopropane (**4**) and **1,4-Dichloro-1,4-Dimethylspiropentane** (**5**) were prepared according to a literature procedure.[6]

2-Allyloxytetrahydropyran (**15b**) was prepared according to a literature procedure.[14]

1,5-Dichloro-1,5-Dimethyldispiro[2.0.2.1]heptanes (9a-d). Halide **4** or **14** (7.8 mmol) was added droppwise to a solution of potassium *tert*-butoxide (1.04 g, 9.4 mmol) in dry DMSO (7 ml) at 70-80 °C. Volatile products of reaction were continuously distilled with a steam of argon through a condenser (temperature of circulating water - 50 °C) into a cooled to -78°C trap. Then the content of a trap was diluted with dry ether (12 ml), and butyllitium (20 ml of 1.28 N solution in pentane) was added dropwise over 2 h at -35 - -40 °C under argon. The reaction mixture was allowed to warm to r.t. and quenched with cold water. Organic phase was separated, washed with water, and dried with $MgSO_4$. Solvent was evaporated, and column chromatography afforded chlorides **9a-d** in 10% yield: ^{1}H NMR (250 MHz) δ 1.25 (d, J = 6 Hz, 2 H), 1.51 (s, 2 H), 1.53 (s, 6 H), 1.62 (d, J = 6 Hz, 2 H)- isomer **9a**; 1.24 (d, J = 6 Hz, 2 H), 1.37 (d, J = 4.5 Hz), 1.4 - 1.5 (m), 1.58 (d, J = 6 Hz) - total 6 H, 1.61 (s, 3 H), 1.69 (s, 3 H) - isomer **9b**; 1.29 (s, 2 H), 1.50 (d, J = 6 Hz, 2 H), 1.67 (d, J = 6 Hz, 2 H), 1.70 (s, 6 H) - isomer **9c**; 1.10 - 1.60 (m, 6 H), 1.73 (s, 3 H), 1.77 (s, 3 H) - isomer **9d**. MS *m/e* 177, 155, 139, 119 (base), 103, 91.

General Procedure for Dehydrohalogenation of Dihalides 5, 9, 10, 22, 23, 27, 31 to Dienes 3, 6, 32 and *tert*-Butylethers 11, 12. To a solution of sublimed potassium *tert*-butoxide (3.35 g, 30 Mmol) in DMSO (15 ml) dihalide (12 mmol) was added dropwise at 30 °C. The reaction mixture was quenched with chilled water. Pentane (20 ml) was added. The organic phase was separated, washed with water, and dried with $MgSO_4$. The pentane solution was consentrated and dienes **3**, **6**, **32** or *tert*-butylethers **11, 12** were isolated by preparative GC.

1,4-Bismethylenespiropentane (3) was obtained in 20% yield from chloride **5** and in 25% yield from dihalides **22, 23**: ^{1}H NMR (250 MHz) δ 1.68 (dddd, J = 8, 2.5, 1.8, 0.8 Hz, 2 H), 1.77 (ddd, J = 8, 2.5, 1.8 Hz, 2H), 5.25 (t, J = 2.5 Hz, 2 H), 5.33 (dt, J = 0.8, 1.8 Hz, 2H); ^{13}C NMR δ 13.60 (t, J = 162 Hz, 2 C), 15.9 (s, 1 C), 99 52 (t, J = 162 Hz, 2C), 136.81 (s, 2 C); MS *m/e* 92 (M^+, base),65, 64, 52, 51, 50.

1,5-Bismetnylenedispiro[2.0.2.1]heptane was obtained as a 10:90 mixture of isomers **6a** and **6b** in 50% yield from chlorides **9**, and as a 40:60 mixture of isomers **6a** and **6b** in 40% yield from halide **27**: ^{1}H NMR (250 MHz) δ 1.40 (m, 2 H), 1.50 (ddd, J = 8, 2.3, 1.8 Hz, 2 H), 1.70 (d, J = 3.8 Hz, 1 H), 1.93 (d, J = 3.8 Hz, 1 H), 5.23 (dt, J = 0.5, 2.3 Hz, 2 H), 5.31 (t, J = 1.7 Hz, 2 H) - isomer **6a**; 1 30 (ddd, J = 8, 2.4, 1.7 Hz, 2 H), 1.48 (ddd, J = 8, 2.4, 1.6 Hz, 2 H), 1.81 (s, 2 H), 5.26 (dt, J = 0.5, 2.4 Hz, 2 H), 5.33 (t, J = 1.7 Hz, 2 H) - isomer **6b**; ^{13}C NMR δ 9.91 (t, J = 162 Hz, 2 C), 19.45 (t, J = 165 Hz, 1 C), 20.27 (s, 1 C), 99.85 (t, J = 162 Hz, 2 C), 134.86 (s, 2 C) - isomer **6a**; 10.23 (t, J = 162 Hz, 2 C), 19.4 (t, J = 165 Hz, 1 C), 20 1 (s, 2 C), 100 17 (t, J = 162 Hz, 2 C), 135.10 (s, 2 C) - isomer **6b**, MS *m/e* 118 (M^+), 116, 114, 92 (base), 79, 78, 65, 63, 52, 51

1,6-Bismethylenetrispiro[2.0.0.2.1.1]nonanes were obtained as a 55:45

mixture of isomers **32a** and **32c** in 45% yield: ^{1}H NMR (400 MHz) δ 1.30-1.45 (m, 4 H), 1.48 (d, J = 4 Hz, 2 H), 1.51 (d, J = 4 Hz, 2 H), 5.28 (t, J = 2.5 Hz, 2 H), 5.0 (br s, 2 H) - isomer **32a**; 1.30 - 1.47 (m, 5 H), 1.52 (d, J = 4 Hz, 1 H), 1.55 (d, J = 4 Hz, 1 H), 1.62 (d, J = 4 Hz, 1 H), 5.12 (t, J = 2.2 Hz, 1 H), 5.25 (t, J = 2.2 Hz, 1 H), 5.33 (br s, 1H), 5.34 (br s, 1 H) - isomer **32c**; ^{13}C NMR δ 8.11 (t, 2 C), 15.75 (s, 2 C), 15.98 (t, 2 C), 26.4 (s, 1 C), 99.44 (t, 2 C), 134.78 (s, 2 C) - isomer **32a**; 8.81 (t, 1 C), 9.84 (t, 1 C), 15.31 (s, 1 C), 15.40 (t, 1 C), 15.99 (t, 1 C), 16.44 (s, 1 C), 25.9 (s, 1 C), 99.26 (t, 1 C), 100.03 (t, 1 C), 135.03 (s, 1 C), 135.46 (s, 1 C)- isomer **32c**. MS *m/e* 144 (M^+), 143, 142, 141, 129, 128 (base), 127, 115, 104, 91.

3-*tert*-Butoxy-2-Methyl-1-Methylenecyclopropane (90:10 mixture of *trans*- and *cis*-isomers **11a, 11b**) was obtained in 20% yield:for isomer **11a** ^{1}H NMR (250 MHz) δ 1.10 (d, J = 6.5 Hz, 1 H), 1.22-1.32 (m, 1 H), 1.28 (s, 9 H), 3.20 (M, 1 H), 5.52 (t, J = 2.25 Hz, 1 H), 5.63 (d, J = 3.25 Hz, 1 H); ^{13}C NMR δ 15.32 (q, J = 127 Hz), 19.99 (d, J = 157 Hz), 28.33 (q, J = 126 Hz, 3 C), 53.28 (d, J = 178 Hz), 74 92 (s), 106.50 (d, J = 162 Hz), 142.1 (s); MS *m/e* 125 (M^+-CH_3), 85, 84, 69, 57, 43.

2-*tert*-Butoxy-1-Ethylidenecyclopropane (12) was obtained in 10% yield: ^{1}H NMR δ 1.12 (m, 1 H), 1.33 (m, 1 H), 1.82 (m, 3 H), 1.28 (s, 9 H), 3.65 (m, collapses to a dd, J = 6.5, 2 8 Hz, upon irradiation at 1.82, 1 H), 6.08 (m, collapses to a qt, J = 6.5, 2.5 Hz, upon irradiation at 3.65, 1 H).

General Procedure for Cycloaddition of Chloromethylcarbene to Olefins 15a, 15b, 17, 18, 24, 28. Preparation of Chloromethylcyclopropanes 16a, 16b, 19, 20, 25, 29. To a solution of an olefin (50 mmol) and 1,1-dichloroethane (75 mmol, 6.3 ml) in dry ether (30 ml), butyllithium (60 mmol, 45 ml of 1.5 N solution in pentane) was added dropwise over 3 h at -35 - -40 °C under argon. The reaction mixture was allowed to warm to r.t. and quenched with cold water. Organic phase was separated, washed with water, and dried with $MgSO_4$ Solvent was evaporated, and distillation gave cyclopropanes **16a, 16b, 19, 20, 25, 29.**

1-Chloro-1-Methyl-2-Methoxymethylcyclopropane (16a) was obtained in 25% yield: bp 87-92 °C (150 mm), ^{1}H NMR (60 MHz) δ 0.5 -1.5 (m, 3 H), 1.7 (s, 3 H), 3.3 - 3.7 (m, 5 H); MS *m/e* 134 (M^+), 93, 91, 89, 74, 73, 63, 57, 53, 45.

1-Chloro-1-Methyl-2-(Tetrahydropyranyloxymethyl)cyclopropane (16b) was obtained in 40% yoeld (or in 90% yield based on reacted acetal **15b**): bp 68 - 73 °C (4 mm); n_D^{20} 1.4682; ^{1}H NMR (60 MHz) δ 0.9-1.8 (m, 9 H), 1.7 (s, 3 H), 3.2 - 4.0 (m, 4 H), 4.6 (m, 1 H) Anal Calcd for $C_{10}H_{17}ClO_2$: C,58.67; H, 8 37 Found: C, 58.67; H, 8.50.

1-Chloro-1-Methyl-4-(Tetrahydropyranyloxymethyl)spiropentane (19) was obtained in 60% yield: bp 92-96 °C (4 mm), n_D^{20} 1.4771; ^{1}H NMR (60 MHz) δ 0.67 - 1 7 (m, 14 H), 3.1 - 3.9 (m, 4 H), 4.4 - 4.6 (m, 1 H). Anal. Calcd for $C_{12}H_{19}ClO_2$: C, 62.46; H, 8.30. Found C, 62.63; H, 8.34

1-Chloro-1-Methyl-4-Methoxymethylspiropentane (20) was obtained in 40% yield: bp 72-75 °C (25 mm); ^{1}H NMR δ 0.7-1.5 (m, 5 H), 1.6 (s, 3 H), 3.2 - 3.7 (m, 5 H); MS *m/e* 160 (M^+), 93, 91, 77, 67, 53, 44.

1-Chloro-1-Methyl-5-(Tetrahydropyranyloxymethyl)dispiro[2.0.2.1]heptane (25) was obtained in 80% yield: bp 110-115 °C (4 mm); n_D^{20} 1.4892; ^{1}H NMR (60 MHz) δ 0.7 - 2.0 (m, 16 H), 3 5 - 4.1 (m, 4 H), 4.9 (m, 1 H). Anal. Calcd for $C_{14}H_{21}ClO_2$: C, 65.49; H, 8.24. Found: C, 65.60; H, 8.38.

1-Chloro-1-Methyl-6-(Tetrahydropyranyloxymethyl)trispiro[2.0.0.2.1.1]nonane (29) was obtained in 60% yield: bp 120-125 °C (3 mm); n_D^{20} 1.4981; ^{1}H NMR (60 MHz) δ 0.6 - 1.8 (m, 18 H), 3.0 - 3.9 (m, 4 H), 4.5 (m, 1 H). Anal. Calcd for $C_{16}H_{23}ClO_2$: C, 67.95; H, 8 20. Found: C, 68.49; H, 9.03.

General Procedure for Dehydrochlorination of Chlorides (16a, 16b, 19, 20, 25, 29) to the Olefins (17, 18, 24, 28). To a solution of sublimed potassium *tert*-butoxide (6.7 g, 60 mmol) in dry DMSO, (30 ml) chloride (50 mmol) was added dropwise at 60 °C. The reaction mixture was stirred at 60 - 70 °C for 2 h, cooled to 20° C and quenched with water. Pentane (25 ml) was added, the organic phase was separated, washed with water and dried with $MgSO_4$. Removal of the solvent and distillation gave olefins (**17, 18, 24, 28**).

1-Methylene-2-(Methoxymethyl)cyclopropane (17)[15] was obtained in 70% yield: bp 67-70 °C, ^{1}H NMR (60 MHz) δ 0.7 - 1.9 (m, 3 H), 3.1 - 3.7 (m, 5 H), 5.1 -5.4 (m, 2 H).

1-Methylene-2-(Tetrahydropyranyloxymethyl)cyclopropane (18) was obtained in 75% yield: bp 64-66 °C (4 mm), n_D^{20} 1 4713; ^{1}H NMR (60 MHz) δ 0.8 - 1.9 (m, 9 H), 3.0 - 4.0 (m, 4 H), 4.6 (m, 1 H), 5.3 -5.5 (m, 2 H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59 Found: C, 71.67; H, 9.86.

1-Methylene-4-(Tetrahydropyranyloxymethyl)spiropentane (24) was obtained in 76% yield: bp 85 -86 °C (6 mm), n_D^{20} 1.4874; ^{1}H NMR (60 MHz) δ 0.9 - 2.0 (m, 11 H), 3.3 - 4.0 (m, 4 H), 4.7 (m, 1 H), 5.1 - 5.6 (m, 2 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34 Found C, 74.24; H, 9.23.

1-Methylene-5-(Tetrahydropyranyloxymethyl)dispiro[2.0.2.1]heptane (28) was obtained in 80% yield: bp 83-85 °C (3 mm); n_D^{20} 1.4957; ^{1}H NMR (60 MHz) δ 0.4 -1.7 (m, 13 H), 3.0 - 3 7 (m, 4 H), 4.5 (m, 1 H), 5.0 - 5.3 (m, 2 H). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.70; H, 9.71.

4-Chloro-1-Iodomethyl-4-Methylspiropentane (23). To a solution of methyl ether **20** (0.8 g, 5 mmol) and sodium iodide (1.5 g, 10 mmol) in dry acetonitrile (5 ml), chlorotrimethylsilane (1.25 ml, 10 mmol) was added dropwise. The reaction mixture was stirred at 25 °C until all starting ether disappiared (TLC-control) Then water was added until the precipitate was completely dissolved. The reaction mixture was extracted with ether (20 ml); organic phase was separated, washed subsequently with $Na_2S_2O_3$ solution, brine, and dried with $MgSO_4$ Removal of the solvent gave 45% of diastereomeric iodides **23a,b** which were separated by column chromatography (eluent pentane). Isomer **23a**: ^{1}H NMR (250 MHz) δ 0.91 (t, J = 5.0

Hz, 1 H), 1.29 (d, J = 6.0 Hz, 1 H), 1.39 (dd, J = 8.3, 5 Hz, 1 H), 1.42 (d, J = 6.0 Hz, 1 H), 1.68 (s, 3 H), 1.82 - 1.94 (m, 1 H), 2.88 (t, J = 10.0 Hz, 1 H), 3.45 (dd, J = 10.0, 5.0 Hz, 1 H). Isomer **23b**: ^{1}H NMR (250 MHz) δ 0.75 (t, J = 5.0 Hz, 1 H), 1.07 (dd, J = 6.0, 1.5 Hz, 1 H), 1.38 (dd, J = 6.0, 5.0 Hz, 1 H), 1.60 (s, 3 H), 1.80 - 1.93 (m, 1 H), 3.16 (dd, J = 10.0, 8.0 Hz, 1 H), 3.23 (dd, J = 10.0, 8.0 Hz, 1 H). Anal. Calcd for $C_7H_{10}ClJ$: C, 32.78; H, 3.93; Cl, 13.82; J, 49.47. Found: J, 49.08.

General Procedure for Deprotection of Acetals 19, 25, 29 to the Alcohols 21, 26, 30. A solution of acetal (10 mmol) and hydrochloric acid (0.5 ml of 0.1 N solution) in ethanol (50 ml) was refluxed until all the acetal was reacted according to TLC (20 - 40 min). After evaporation of the solvent alcohols **21, 26, 30** were isolated by distillation or column chromatography (eluent ether:pentane 4:6)

4-Chloro-1-Hydroxymethyl-4-Methylspiropentane (21), mixture of two diastereomers (1:1) was isolated in 75% yield: bp 70-72 °C (5mm); n_D^{20} 1.4800; ^{1}H NMR (250 MHz) δ 0.79 (t, J = 5 Hz, 1 H), 0.89 (t, J = 5 Hz, 1 H), 1.09 (dd, J = 5.5, 1.5 Hz, 1 H), 1.16 - 1.25 (m, 3 H), 1.34 (d, J = 5.5 Hz, 1H), 1.41 (d, J = 5.5 Hz, 1 H), 1.61 (s, 6 H), 1.60 - 1.69 (m, 2 H), 3.49 (dd, J = 11, 7 Hz, 1 H), 3.61 (dd, J = 11.7 Hz, 1H), 3.62 (dd, J = 7, 1.5 Hz, 2 H). Anal. Calcd. for $C_7H_{11}ClO$: C, 57.34; H, 7.56. Found: C, 56.98; H, 7.25.

5-Chloro-1-Hydroxymethyl-5-Methyldispiro[2.0.2.1]heptane (26) was obtained in 80% yield: bp 75 -80 °C (3 mm); n_D^{20} 1.4950; ^{1}H NMR (60 MHz) δ 0.7 - 1.8 (m, 10 H), 2.5 (s, 1 H), 3.6 (d, J = 7 Hz, 2 H). Anal. Calcd for $C_9H_{13}ClO$: C, 62.61; H, 7.56. Found: C, 62.32; H, 7.91.

6-Chloro-1-Hydroxymethyl-6-Methyltrispiro[2.0.0.2.1]nonane (30) was obtained in 70% yield as a colorless oil: ^{1}H NMR (60 MHz) δ 0.5 - 1.9 (m, 12 H), 2.8 (s, 1 H), 3.3 - 3.7 (m, 2 H). Anal. Calcd for $C_{11}H_{15}ClO$: C, 66.49; H, 7.61. Found: C, 66.40; H, 7.83.

General Procedure for Bromination of Alcohols 21, 26, 30 to the Halides 22, 27, 31. To a cooled to -78 °C solution of alcohol (10 mmol) in dry ether (25 ml), PBr_3 (0.34 ml, 3.6 mmol) was added dropwise in argon atmosphere. The reaction mixture was stirred at -78 °C for 0.5 h and allowed to stand overnight at 0 °C. Then it was quenched with saturated $NaHCO_3$ (10 ml); organic phase was separated, washed with water and dried with $MgSO_4$. Removal of the solvent gave halides **22, 27, 31**, which were purified by column chromatography (eluent - pentane).

1-Bromomethyl-4-Chloro-4-Methylspiropentane (22) was obtained as a colorless oil in 45% yield: ^{1}H NMR (60 MHz) δ 0.7 - 2.0 (m, 8 H), 2.3- 3.8 (m, 2 H). Anal. Calcd for $C_7H_{10}BrCl$: C, 40.13; H, 4.81. Found: C, 40.30; H, 5.02.

1-Bromomethyl-5-Chloro-5-Methyldispiro[2.0.2.1]heptane (27) was obtained as a colourless oil in 65% yield: ^{1}H NMR (60 MHz) δ 0.8 -1.9 (m, 10 H), 3.5 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_9H_{12}BrCl$: C, 45.89; H, 5.14. Found: C, 45.58; H, 5.34.

1-Bromomethyl-6-Chloro-6-Methyltrispiro[2.0.0.2.1.1]nonane (31) was obtained as a colourless oil in 70% yield: ^{1}H NMR (60 MHz) δ 0.7 - 1.9 (m 12 H), 3.3 - 3.7 (m, 2 H). Anal. Calcd for $C_{11}H_{14}BrCl$: C, 50.50; H, 5.39. Found: C, 50.76; H, 6.06.

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