As the bismuth oxide cluster ions we used have no terminal oxygen atoms, the reactions we carried out show quite clearly that bridging oxygen atoms can indeed participate in oxidation reactions. This is all the more astonishing when one considers that the bismuth oxide clusters detected should be particularly stable compounds due to their "magic" character.[5] In addition, an analysis of the mass spectra indicated—in contrast to what was expected—that no clear size-dependent reactivity could be established for the metal oxides. Even the smallest cluster ions studied behaved similarly to solid bismuth oxide and were reduced by propene. In order to be sure that the reactions did not occur simply due to the higher energy associated with the accelerated and charged particles, the same reactions were performed with neutral bismuth oxide clusters. These experiments also resulted exclusively in a reduction of the oxides. The reduction admittedly first set in at partial propene pressures about one order of magnitude higher in the case of the nonaccelerated uncharged bismuth oxide clusters.[10] The higher energy of the cations thus leads to an increase in the reaction cross-section, but the special selectivity of bismuth oxide clusters is independent of charge and not due to the increased kinetic energy of the cations. As further proof of the special reactivity of the bismuth oxide cluster ions in the oxidation of propene, the reaction introduced here was also carried out with antimony oxide cluster ions. These form stable polyoxides with the general formula $SbO^+(Sb_2O_3)_n$ similar to the bismuth oxide clusters.[11] Here too, experiments were carried out both with propene and argon. In both cases, however, an increase in the partial pressure of the collision gas merely led to a decrease in the intensities of all observed peaks. These results are also a clear indication that the reactivity of the bismuth oxide cluster cations is not due to the fact that they are higher in energy than the solid because of ionization and sublimation.

The work presented here proves for the first time that mass-selected bismuth oxide cluster ions can be reduced by propene in just the same way as solid bismuth oxide. Moreover, it has been shown for the first time that supposedly unreactive bridging oxygen atoms can actively participate in oxidation reactions. Bismuth oxide clusters may possibly provide suitable model systems for bismuth oxide catalyst systems.

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Self-Organization and Formation of Liquid Crystal Phases by Molecular Templates Related to Membrane Components of Archaebacteria**

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Daniel Plusquellec,* Grahame Mackenzie,
Julie A. Haley, and John W. Goodby*

Molecular self-assembly and self-organization are becoming increasingly significant for the elucidation of life processes and the generation of new supramolecular structures or ensembles and molecular materials.[1–9] Concomitantly, the most important inspirations for the conceptual development of such structures and materials are those provided by biological cells, which exemplify the assembly of a variety of microstructures of different sizes and functions. Archaebacteria, with their resistance to extreme conditions, are one class of organisms that serve as a rich source of inspiration. This

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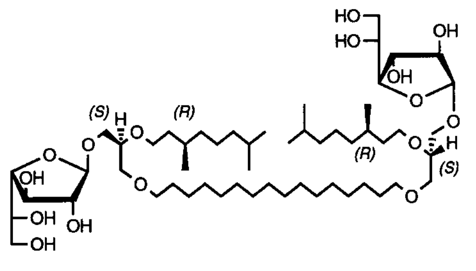
view becomes all the more poignant in the realization that mankind's increasing ability to investigate volcanoes, for example the volcano on Monseratt, has lead to the discoveries of many new strains of archaebacteria.

The Archaea domain is composed of a variety of extremophilic microorganisms and represents a third evolutive kingdom which is distinct from the well-known Eubacteria (the classical prokaryotes) and Eukarya domains.[10–12] At a molecular level, the lipid components of Archaea membranes are strikingly different from their bacterial and eukaryotic counterparts.[13–15] Of particular interest is the molecular topology of the lipids derived from thermophilic Archaea. These molecules are characterized by a bipolar architecture with two polar heads linked together by two C40 polyisoprenoid chains, which are thought to span the membrane and therefore determine the thickness of the lipid layer. Unique features of tetraether-based lipids are the high proportion of glycosylated lipids in the membranes of both methanogenous and sulfur-dependent thermophiles as well as the occurrence of unusual carbohydrate moieties, that is, β-D-galactofuranosyl units.[13–15] These structural units may further stabilize the membrane structure through cooperative inter-glycosyl hydrogen bonding.[16, 17] Nevertheless, the presence of furanosyl units in such environments remains a striking feature, as the glycofuranosides are much more rapidly hydrolyzed than their pyranosyl counterparts.[18]

In spite of the growing attention to archaeal glycolipid structure and function, very few studies have been performed so far to elucidate relationships between the molecular structure of monomeric glycolipids and the architecture of their supramolecular aggregates. This is in part due to the difficulty of obtaining sufficient amounts of chemically pure compounds from natural sources or by synthetic methods. Here we report the total synthesis of glycosylated pseudotetraethers **1**–**3**, which were designed to mimic natural archael glycolipids; the investigation of their thermotropic and lyotropic liquid crystal properties; and the characterization of their supramolecular aggregates in aqueous media observed by electron microscopy.

The most characteristic structural feature of our target molecules **1**–**3** are 1) the presence of a hexadecamethylene bridging chain attached to two glycerols at the sn3 and sn3′ positions; 2) two dihydrocitronellyl chains having a combined length equal to that of the spacer, which are linked to glycerol at the sn2 and sn2′ positions; and 3) two glycosyl polar head groups derived from D-galactose in its furanose form. These lipids are therefore closely related to the natural tetraether **4**, a quasi-symmetrical polar lipid obtained from the methanogen *Methanospirillum hungatei*.[19]

The strategic plan for the synthesis of glycolipids **1**–**3** was based upon a suitable synthesis of pseudo-macrocyclic diols **7**–**9** and subsequent diglycosylation with the appropriate galactofuranosyl donor. Bisalkylation of 1,16-hexadecandiol with (*R*)-epichlorhydrin afforded the diepoxide **6** with complete inversion at the sn-2 carbon atom (Scheme 1). Treatment of **6** with allyl alcohol resulted in the regiospecific opening of the epoxide rings and allowed introduction of allyl ether protecting groups at the primary positions. Alkylation at the sn2 and sn2′ positions with (*R*)-citronellyl bromide



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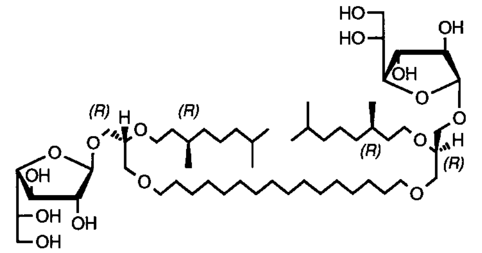

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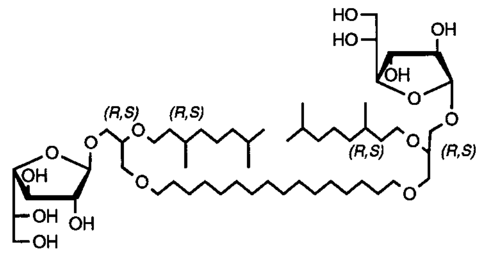

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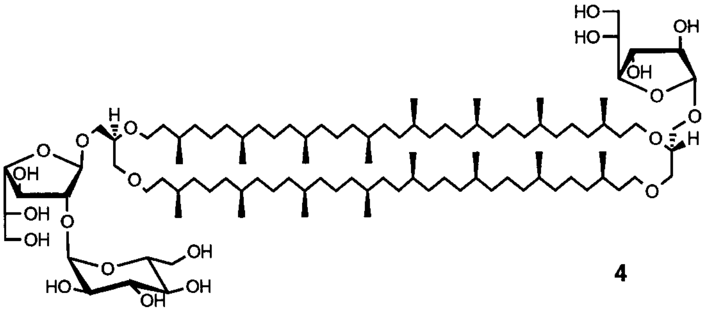

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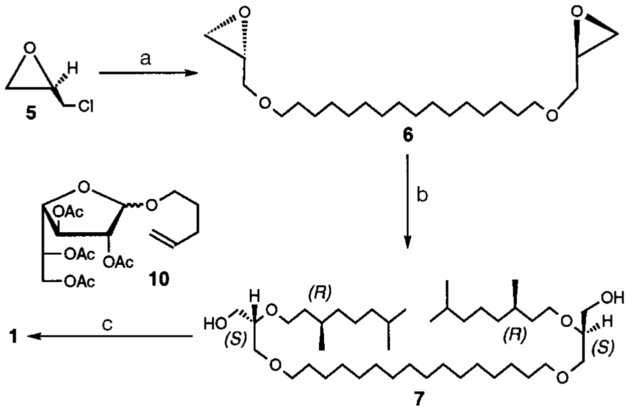
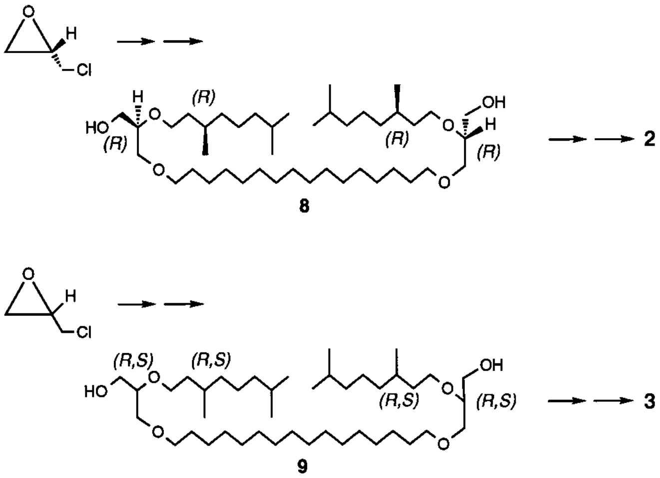


Scheme 1. Synthesis of **1**. a) 1,16-Hexadecanediol/*n*-hexane: 50% aqueous sodium hydroxide (2:1), Bu_4NBr, 55%; b) 1. allyl alcohol, NaOMe (cat.), 90%, 2. (*R*)-citronellyl bromide, NaH, 80%, 3. $[RhCl(Ph_3P)_3]$, ethanol: toluene:water (7:3:1), 80%, 4. Raney nickel, H_2, ethanol, 95%; c) 1. **10**, CH_2Cl_2, NIS, TESOTf, 67%, 2. MeOH, MeONa (cat.), 79%. NIS = *N*-iodosuccinimide, TESOTf = triethylsilyl trifluoromethanesulfonate, Ac = acetyl.

followed by removal of the *O*-allyl groups and reduction of the citronellyl to dihydrocitronellyl chains afforded the diol **7**. The best yield achieved for the overall sequence was 35%, with an average of 30% for repeated runs. A procedure similar to that described for the synthesis of **7** was used to synthesize the isomeric diol **8** and the racemic diol **9** starting, respectively, from (*S*)- or racemic epychlorhydrins (Scheme 2).



Scheme 2. Syntheses of **2** and **3** (for reagents and reaction conditions, see Scheme 1).

The last crucial step involved the introduction of galactofuranose units as the polar head groups. It proved possible to introduce both β-D-galactofuranosyl residues in one step by using donor **10**, which was available in a one-pot procedure from D-galactose,[20] thereby affording the diglycosylated lipids stereospecifically in 65–70% yield. The successful glycosylation was followed by deacetylation of the glycosyl hydroxyl groups under standard conditions. The structures of **1**–**3** were fully substantiated by NMR spectroscopy, mass spectrometry, and elemental analysis.

The self-assembling and self-organizing properties of **1**–**3** were investigated in a variety of ways. Initially, their melting and recrystallization behaviors were examined in detail by thermal polarized transmitted-light microscopy using a Zeiss Universal Polarizing Microscope in conjunction with a Mettler FP52 hot-stage and FP5 controller, and by differential scanning calorimetry using a Perkin Elmer DSC 7 PC system operating on UNIX software (scan rates 1, 5, and 10° min^{-1}). The results obtained were standardized relative to indium (onset 156.7 °C, $\Delta H = 28.5\,\mathrm{J\,g^{-1}}$, literature value 156.6 °C, $\Delta H = 28.45\,\mathrm{J\,g^{-1}}$).[21]

All three materials exhibited similar melting behaviors; that is, upon heating they melted to give thermotropic liquid crystal phases. Identification of the resulting mesophases proved to be impossible because of the formation of paramorphotic defect textures associated with the solid state. However, on cooling from the isotropic liquid each material provided classical defect textures associated with the disordered columnar hexagonal phase (Col_{hd}).[22–24] Fanlike textures were formed, but no hyperbolic or elliptical lines, associated with the lamellar smectic state, were observed.[25, 26] Conversely, rectilinear defect lines, diagnostic of a hexagonal columnar phase, were present. The fanlike domains exhibited no banding and were completely smooth, indicating that the positions of the molecules in the phase are disordered. Polarized-light microscopy shows that the molecules in the mesophase are organized into columns, that the columns are hexagonally close-packed, and that within the columns the molecules themselves have a disordered arrangement. Figure 1 shows the defect texture of compound **3** formed on cooling from the isotropic liquid; the grey coloration of the observed specimens indicates the weak birefringence of the material. It is interesting to note that no homeotropic textures were observed, which would almost certainly have been expected if the phase was lamellar.

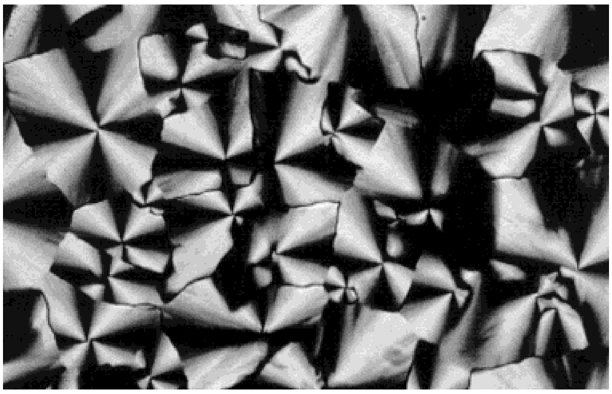


Figure 1. The fan texture of the columnar mesophase of **3** (× 100).

The clearing point temperature for each compound is shown in Table 1. The values found do not vary much as a function of change in stereochemistry. In fact, given the small variations in purity and the experimental error in the measurements of the clearing temperatures, the isotropization points are effectively the same for all three compounds.

Table 1. Transition temperatures [°C] and enthalpies of transition [J g^{-1}] (in parentheses) for **1**–**3**.

Compound	Glass → columnar	Columnar → isotropic liquid	Columnar → glass
1	64.8	115.2 (1.53)	− 37.7
2	56.7	117.6 (2.93)	− 43.89
3	51.7	118.4 (1.38)	− 37.8

The liquid crystal phase of each compound supercooled quite substantially to temperatures well below 0 °C. Recrystallization was often not observed, and instead a glassy state was formed. For this situation, the defect texture of the liquid crystal phase became frozen into the glassy specimen. Upon heating the glassy state converted smoothly back into the liquid crystal with virtually no changes occurring in the defect texture; therefore, well-defined glass transitions could not be observed by microscopy. Glass transitions, however, were determined by differential scanning calorimetry (see Table 1).

These results show that the mesophase has a columnar structure. As a consequence we can postulate two structures for the phase, one where the aliphatic chains are on the exterior and the sugar moieties are in the inside of the columns, and one where the aliphatic chains are in the interior and the sugar moieties are on the outside. However, the controlled addition of water to the neat phase shows that the thermotropic columnar phase is not continuously miscible with water. This indicates that the aliphatic chains must be located towards the exterior of the columnar structure. Thus, the columnar structure shown in Figure 2 is preferred where the molecules are bent and have hairpinlike conformations. This molecular folding allows the chains to be located towards the exterior of the columnar structure and the sugar units to be in the interior. This conclusion is supported to some degree by the results recently reported by Taguchi et al.[27] on dotriacontan-1,32-diylphosphate (C32P) and the nearly isomeric double-chain phosphate 2C16P. The alkyl chain in C32P has mostly a *trans* structure with some *gauche* conformers present; the molecule therefore has a hairpin structure with a bend at the center of the chain. In the resulting columnar structure, in which the molecules are disordered along the column axis and are in a relatively fluid state, the liquidlike columns are packed into a hexagonal array to give a disordered hexagonal columnar thermotropic liquid crystal.

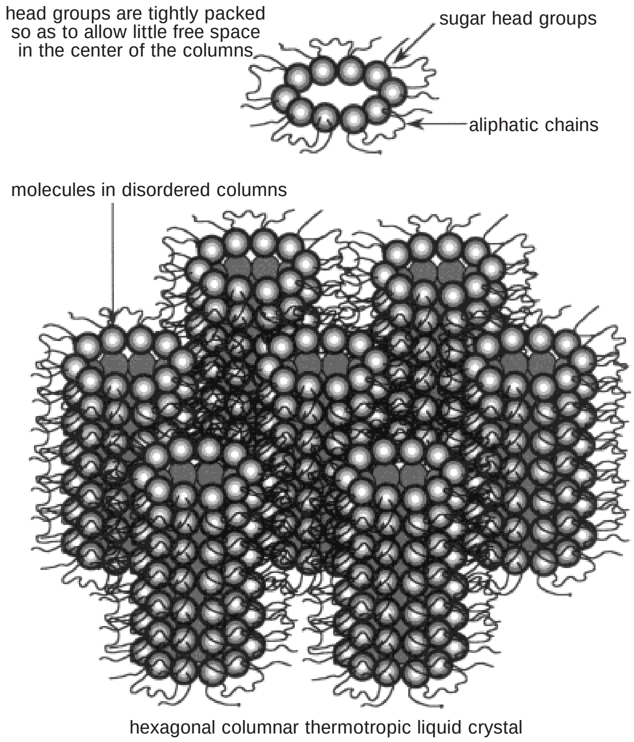


Figure 2. The disordered columnar structure of the thermotropic phase exhibited by **1**–**3**.

Lyotropic studies show that the three compounds exhibit hexagonal phases. However, as the thermotropic columnar phases are not continuously miscible with water, the hexagonal lyotropic phases are more likely to have structures based on ensembles where the polar head groups are on the outside of the columns. The fact that some of the materials are capable of forming tubules in aqueous media suggests that a double-layer structure, as in a membrane, is the more likely self-assembled configuration as the basis of the structure of the hexagonal lyotropic phase.

The supramolecular aggregates formed by the materials in aqueous media were observed under electron microscopy. Compounds **1** and **3** provided tubules, whereas **2** did not (Figure 3). Thus, unlike the self-assembling properties which lead to the formation of liquid crystal phases, this self-organization to tubules is sensitive to the stereochemistry of the material in question. Interestingly, the tubules resulting from **1** and **3** appear to have almost equidistantly separated

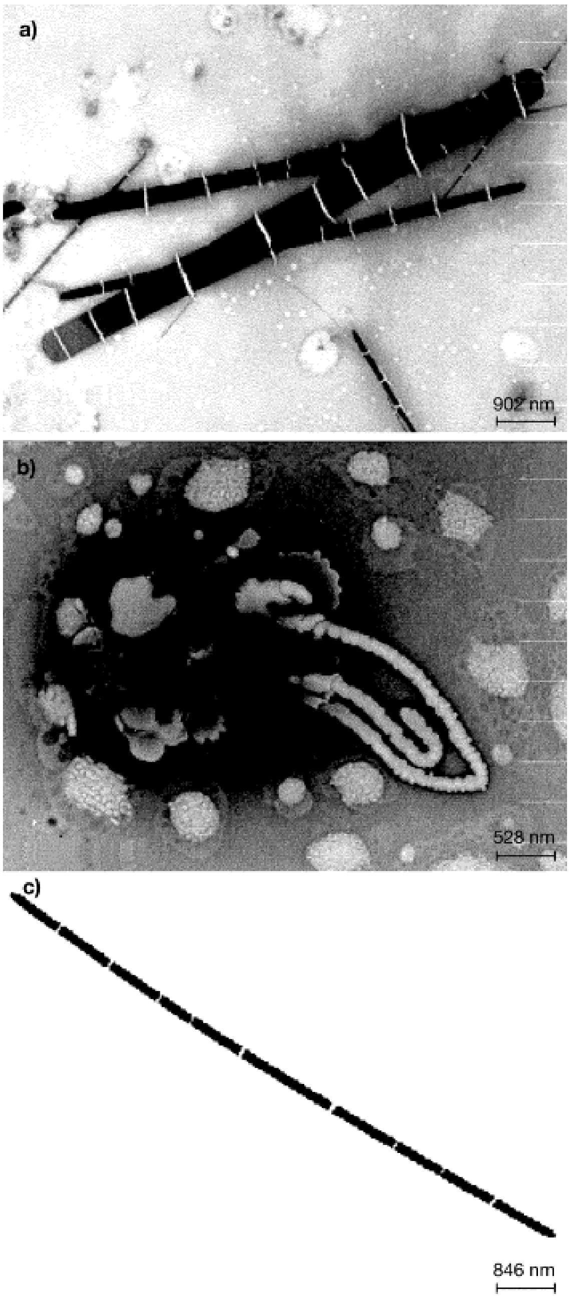


Figure 3. Electron microscopy micrographs of typical supramolecular aggregates formed by glycolipids **1**–**3** (a–c) in aqueous media (negative staining with uranyl acetate).

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parallel defect lines running across the long axes of the tubules (Figure 3a and c). Lines of this nature are usually associated with chirality, and in particular helicity which results from the way the chiral molecules pack together. These results suggest that the tubules either have a helical multilayer structure composed of several hundred molecular layers, or else they have a periodic defect structure that is based on some form of helicity. Periodic defect structures are well known for thermotropic liquid crystals, and are often manifested when the need for the molecules to form a twisted macrostructure is confronted with some structural or spatial limitation (e.g., Blue Phases, TGB Phases). This competition results in a frustration which is relieved by the creation of defects.

In the case of **1** and **3**, the lines running across the tubules could be related to defects produced by a localization of the twist, in a similar way to how twist is localized in the structure of the twist grain boundary phase.[28] Conversely, **2** does not exhibit tubules. This may be because it has a different stereochemical structure to **1** and **3**, and as a result may not experience the same competition in the packing of the asymmetric moieties of its molecules. Detailed studies and explanations of these self-assembled structures are, however, complex, and a more comprehensive explanation of their properties will be given elsewhere.

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A Facile Generation of a Cyclopropylzinc Compound from an Alkenylzinc Derivative and Its Reaction with Electrophiles[**]

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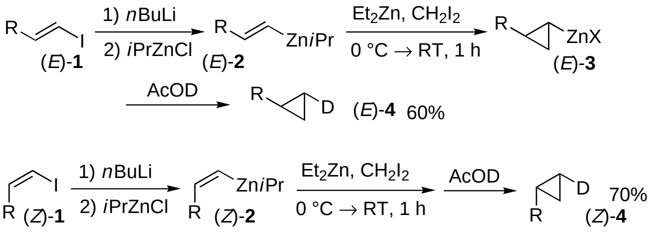
Koichiro Oshima[*]

Cyclopropylmetal compounds are useful reagents for the construction of cyclopropane derivatives. The most common method for the preparation of these reagents is metalation of halocyclopropane derivatives with metals or organometallic compounds such as lithium, magnesium, or butyllithium.[1, 2] However, present synthetic approaches to the halocyclopropanes[3] are very lengthy and rather inefficient. Thus, development of a more convenient and direct access to cyclopropylmetal derivatives should expand their synthetic utility. Although the direct cyclopropanation of some 1-alkenylmetal compounds[4] (B, Al, Si, Sn) by the Simmons–Smith reaction[5] has been reported, the resulting cyclopropylmetal compounds have low reactivities with respect to electrophiles; there are no examples of their direct reaction with carbon electrophiles. Here we report the first example of the preparation of a cyclopropylzinc derivative from a 1-alkenylzinc compound and its synthetic use for further reaction with electrophiles in a one-pot procedure.

The 1-alkenylzinc compound was prepared from isopropylzinc chloride[6] and a 1-alkenyllithium reagent, which was generated from a 1-iodo-1-alkene upon treatment with butyllithium in hexane (Scheme 1).[7] Diethylzinc and CH_2I_2 were



Scheme 1. Stereospecific cyclopropanation of alkenylzinc compounds. R = n-$C_{10}H_{21}$; X = I, iPr.

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