New Insight into the Source of Biomolecular Homochirality: An Extraterrestrial Origin for Molecules of Life?

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Crucial organic molecules associated with life (for example, amino acids, nucleic acids, sugars) are chiral and usually occur in nature in only one of the two enantiomeric forms. The reason for this homochirality, which seems to be essential for the existance of life, is still a puzzle and several controversial theories have been presented.[1–3] Since all mechanisms discussed can justify only small amounts of enantiomeric excess, several amplification theories have been proposed.[1, 4] Extraterrestrial processes have been considered as well. Nevertheless, the parity-violating aspect of the electroweak interaction, which might be suspected to be responsible for homochirality, seems to be too weak. Amplification by factors of about 10^{17} would be required to account for homochirality.[5] Evidence is hard to obtain in this field and, understandably, proofs are less conclusive. Support for an extraterrestrial origin has come from recent findings.

Carbonaceous, chondritic meteorites, especially the Murchison meteorite (which fell in Australia in 1969), have been examined intensively. A plethora of amino (α-, β-, γ-, δ-),[6] hydroxy,[7] phosphonic, and sulfonic acids,[8] as well as other organic compounds[9] have been found in these meteorites (Figure 1).

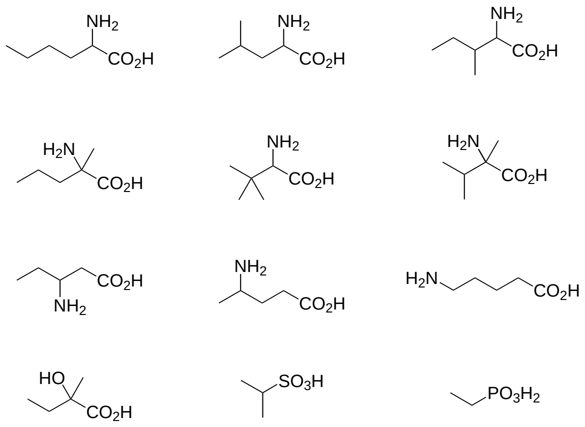
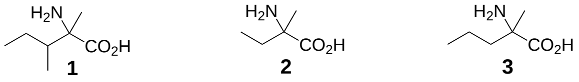


Figure 1. A selection of amino, hydroxy, sulfonic, and phosphonic acids isolated from the Murchison meteorite.

In particular the amino acids, which are essential for life, have attracted considerable interest. In this context a report by Cronin et al. on the enantiomeric excesses in several meteoritic amino acids was quite surprising.[10] To avoid enantiomeric enrichment by the analytic methods and to exclude terrestric contamination the authors focused on α-ramified amino acids, which have never been reported in the geosphere (Figure 2).[11] Additionally, the amino acid **1** bears two centres of chirality; therefore an enantiomeric enrichment as an analytical artefact (for example, by the aqueous processing) seems to be highly unlikely. The analyses were carefully carried out and gave enantiomerical excesses up to 10% for amino acids **1**–**3**. α-Aminobutyric acid and norvaline gave no significant *ee* values.



1 (2*S*,3*S*): 7.6 % *ee*
(2*S*,3*R*): 10.4 % *ee*

2 (2*S*): 8.4 % *ee*

3 (2*S*): 2.8 % *ee*

Figure 2. Nonracemic amino acids from the Murchison meteorite and their corresponding enantiomeric excesses.

With this result, the origin of these findings was still elusive! A recent contribution of Bailey and co-workers brought new insight in this topic. They reported on the observation of circularly polarized infrared light, whose source is a cloud of dust in the Orion constellation.[5] This cloud is a region of high-mass star formation that contains many organic molecules. The authors suspect that this polarization might be caused by light scattering on nonspherical grains, which are aligned by a magnetic field, but other mechanisms are possible as well. Calculations show that the presence of circularly polarized IR light implies the existence of the corresponding polarized UV radiation. Unfortunately, the dust cloud responsible for the polarization obscures UV radiation and prevents it from being observed directly. It has been known since the 1970s that amino acids and other chiral compounds can be enantiomerically enriched by circularly polarized UV light. One of the enantiomers is photodegragated predominantly depending on the sign of polarization.[12] The *ee* values obtained are about the same as have been found in the Murchison meteorite.

A simple calculation shows that during the history of the earth about 6×10^7 million tons of amino acids (present in a

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concentration of 60 ppm in the carbonaceous chondrites, which are 3% of all meteorites) have reached the earth, with 6×10^5 million tons arriving during a period when the earth was cold enough for the persistence of the amino acids.[2] Therefore, it seems possible that during development of life the earth was covered with matter (dust, meteorites, or comets) that stemmed from a region that was exposed to circularly polarized irradiation. The thus resulting enantiomeric excess of the amino acids might have tipped the scales towards the development of life. The global enantiomeric excess on earth—from racemization and dilution—was certainly less than in the meteorites. Bailey et al. guess that it might have been in the range of 5×10^{-3} to 10^{-7}% *ee*, and eventually higher in the vicinity of meteorite impacts.[5] These enantiomeric excesses are larger by orders of magnitudes than those explainable by the parity violation (10^{-17}%) or by stochastic effects.[1, 5] From this mechanism one might find molecules with opposite homochirality in other regions of the universe, depending on the polarization of the radiation.

Undoubtedly many questions on this topic are still unanswered and arguments are far from closed. Nevertheless, the herein presented perceptions possibly give new ideas as to where life might have originated.

German version: *Angew. Chem.* **1999**, *111*, 501–502

Keywords: amino acids · chirality · extraterrestrial chemistry · prebiotic chemistry

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Alkyne Metathesis as a New Synthetic Tool: Ring-Closing, Ring-Opening, and Acyclic

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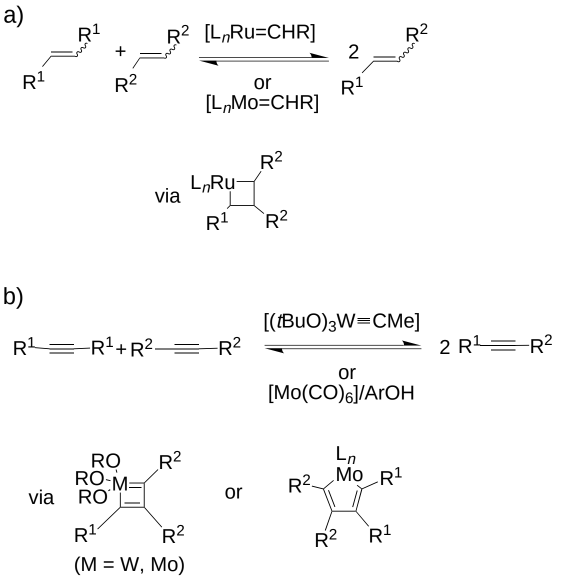
In recent years alkene metathesis (Scheme 1a) has firmly established itself in the "tool box" of the organic chemist, and it is increasingly replacing other methods of C=C bond formation such as the Wittig reaction or the McMurry coupling. Schrock[1] and Grubbs[2] have developed active and efficient catalysts for metathesis which are commercially available and thus have made a major contribution to the spectacular success of this method in the preparation of complex natural products and novel materials. Recent reviews by Blechert[3a] and Fürstner[3b] summarize current developments in this area. An additional and important commercial aspect of the continuing interest in homogeneously catalyzed alkene metathesis is its potential for the synthesis of highly cross-linked polymers.[4]



Scheme 1. a) Alkene metathesis; b) alkyne metathesis.

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