Chirality due to oxygen-18 substitution. Synthesis and chiroptical properties of (1S)-2,4-adamantanedione-4-18O
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Preliminary calculations for the chloroethylene indicate that the anions of these species also adopt nonplanar structures but that after the anion distorts, dissociation to R–Cl occurs. Recent electron scattering work confirms this instability of C2H2Cl–. For symmetry reasons, a nonplanar distortion must necessarily accompany chloride loss. The distortion of alkynes upon electron attachment is the same as that which occurs in the transition states of nucleophilic additions to alkenes. Indeed, we believe that the origin of these distortions is the same in both cases. The relevance of these results to the mechanisms and stereochemicals of reactions of nucleophiles with alkynes and aromatics will be reported in due course.

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Registry No. Ethylene radical anion, 34527-91-8; fluoroethylene radical anion, 80009-98-9; 1,1-difluoroethylene radical anion, 77845-44-4; tetrafluoroethylene radical anion, 65338-13-8.

Chirality due to 180 Substitution. Synthesis and Chiroptical Properties of (1S)-2,4-Adamantanediene-4-180

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The rigid adamantane skeleton has proved of special value in the interpretation of subtle effects in the circular dichroism spectra of chiral carbonyl compounds. In addition, the adamantane framework has shown its usefulness in the construction of chiral ketones whose chirality is due to isotopic substitution. Only one example is known of an optically active cycloalkanone, the 1,2-diketone α-(180)enochromaphorone quinone, whose chirality is solely due to oxygen-18 substitution.

Two features interfere with studies of oxygen-18 labeled carbonyl compounds. First the available oxygen-18 starting materials are limited and expensive; the incorporation is usually obtained by an exchange or hydrolysis reaction with 180O water. Secondly, ketones rapidly exchange oxygen in aqueous media. Thus a nonaqueous final step in the preparation of an oxygen-18 compound has obvious advantages. This paper reports the synthesis and circular dichroism data of (1S)-2,4-adamantanediene-4-180 (7), a rigid 1,3-diketone, in which the chirality is solely due to the oxygen isotope. The synthetic route to this ketone is new, general, and applicable to a variety of chiral and achiral oxygen-18 labeled ketones. In addition to its novelty and generality this route appears to be more effective than the present methods of introduction of oxygen 18. The critical difference in the route we followed is the nonaqueous introduction of oxygen 18, through the intermediacy of an 1,2-(180)dioxydiketone.

The starting material in our synthesis was (+)-endo-bicyclo[3.3.1]non-6-en-3-carboxylic acid (1). The optically active 3R-acid 1 was cyclized to an epimeric mixture of the 4-acetoxyadamantan-2-one (2) in a 2:1 equatorial ratio. The equatorial 2 could be transformed into the two isomeric (syn and anti) enamines 3, 4 in 85% yield. Basic hydrolysis afforded the two 4(3H)-hydroxy-2-(methoxymethylene)adamantanes (4). The isomers could be separated and oxidized under neutral conditions to yield the corresponding (1S)-4-(methoxymethylene)adamant-2-one isomer (5). The optically active diketone (1S)-2,4-adamantanediene-4-180 (7) was prepared by a photooxygenation of 5 with 180O gas (99%) and methylene blue in CH2Cl2. Although the 1,2-dioxydiketone 6 could not be isolated, it is reasonable to assume that 6 is the intermediate in the photooxygenation. Purification of 6 was achieved by sublimation. The diketone 7 was found to be very sensitive to water; even when stored as crystals a fast exchange with water in the air occurred.

Scheme F

(a) Boron trifluoride etherate, (CH3CO)3O, C6H6, room temperature, 1 h, 85%; (b) P2O5–CH2=OCH2, C6H6, n-BuLi, THF, room temperature, 24 h, ~25%; (c) LiOH, C6H5OH, H2O, room temperature, 12 h, ~80%; (d) PDC, CH2Cl2, room temperature, 4 h, 40% (anti) and 60% (syn); (e) 180O, 99%; methylene blue, CH2Cl2, hv, room temperature, 3 h, 70%.

Synthesis. 2,4-Adamantanediene-4-180


[References and footnotes are included at the end of the text.]
Aluminophosphate Molecular Sieves: A New Class of Microporous Crystalline Inorganic Solids

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A novel class of crystalline, microporous, aluminophosphate phases has been discovered that represents the first family of framework oxide molecular sieves synthesized without silica. The most widely known molecular sieves are the aluminosilicate zeolites and the microporous silica polymorphs. The novel aluminophosphate molecular sieves are similar to zeolites in some properties and may find many uses as adsorbents for separations of molecular species and as catalysts or catalyst supports.

The new family of aluminophosphate materials (AlPO₄₃) currently includes about 20, three-dimensional framework structures, of which at least 14 are microporous and 6 are two-dimensional layer-type materials. Most of the three-dimensional structures are novel; however, three appear to be structurally related to the zeolite family, with framework topologies of the erionite/offretite type (AlPO₄-17), the sodalite type (AlPO₄-20), and the analcime type (AlPO₄-24). One of the novel three-dimensional structures, that of AlPO₄-5, has been determined by single crystal X-ray methods. AlPO₄-5 has hexagonal symmetry with a = 1.372 nm and c = 0.847 nm and contains one-dimensional channels oriented parallel to the c axis and bounded by 12-membered rings composed of alternating AlO₆ and PO₄ tetrahedra. It has the framework topology of the hypothetical 4-connected three-dimensional net no. 81 (4.6.12) proposed by Smith.

The novel materials are synthesized hydrothermally at 100–250 °C from reaction mixtures containing an organic amine or quaternary ammonium salt (R) which becomes entrapped or clathrated within the crystalline products of composition: xR·Al₂O₃·(10 ± 0.2)P₂O₅·yH₂O. The quantities x and y represent the amounts needed to fill the microporous voids within the neutral AlPO₄ framework. The species R appears to fulfill an essential templating or structure-directing role in the synthesis of these novel microporous phases since without R dense AlPO₄ structures or known hydrates, AlPO₄·nH₂O, form.

The direct relationship between a templating agent and the resulting structure is illustrated in the synthesis of AlPO₄-17, with a proposed erionite framework topology, by using quinuclidine, neopentylamine, or cyclohexylamine. In each case chemical analysis corresponds to two template molecules per large cavity. Model building experiments indicate that (1) the three templating agents are similar in size, (2) two template molecules essentially fill the large cavity, and (3) there are no further voids in the erionite-type structure of sufficient volume to contain these templates. Similarly, tetramethylammonium hydroxide (TMAOH) templates the AlPO₄-20 sodalite framework topology with a template stoichiometry near 1 per sodalite cage. The spherical TMAOH molecule, with a 0.62-nm diameter, fits neatly within the sodalite cage.

Some structures are much less template specific. AlPO₄-5 can be synthesized with 23 different amine and quaternary ammonium compounds. The large one-dimensional cylindrical pore system perhaps imposes fewer constraints on the template fit. Because of the neutrality of the AlPO₄ network, the template is not needed as a charge-balancing agent; therefore, its incorporation into the structure is more a function of its size and shape relative to the channel volume to be filled.

Supplementary Material Available: Physical properties and experimental details of the synthesis of 1–5 and 7 (5 pages). Ordering information is given on any current masthead page.

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(3) The suffix n denotes a specific structure type.
(4) Cohen, J. P.; Bennett, J. M., to be submitted for publication.