Preliminary calculations for the chloroethylenes indicate that the anions of these species also adopt nonplanar structures but that after the anion distorts, dissociation to R· + Cl^- occurs.[13] Recent electron scattering work confirms this instability of $C_2H_3Cl^-$.[14,15] For symmetry reasons, a nonplanar distortion must necessarily accompany chloride loss.[15]

The distortion of alkenes upon electron attachment is the same as that which occurs in the transition states of nucleophilic additions to alkenes.[10,16] Indeed, we believe that the origin of these distortions[10] is the same in both cases. The relevance of these results to the mechanisms and stereochemistries of reactions of nucleophiles with alkenes and aromatics will be reported in due course.[16-18]

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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.

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(13) Paddon-Row, M. N.; Houk, K. N.; Jordan, K. D., unpublished results.

(14) Johnson, J. P.; Christophorou, L. G.; Barter, J. G. *J. Chem. Phys.* **1977**, *67*, 2196.

(15) Burrow, P. D.; Modelli, A.; Chiu, N. S.; Jordan, K. D. *Chem. Phys. Lett.* **1981**, *82*, 270.

(16) Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N., unpublished results.

(17) After completion of this work, we learned of an independent study of the geometries of ethylene and fluorinated ethylene radical anions: Merry, S.; Thomson, C. *Chem. Phys. Lett.* **1981**, *82*, 373. The geometries and energies of the minima reported by these authors are essentially identical with ours, except for those of the ethylene and fluoroethylene radical anions, which are apparently given for the syn species in the Merry–Thomson work. These authors did not present energies for geometries other than the purported global minima.

(18) **Note Added in Proof**: We wish to note that Professor Symons [Symons, M. C. R. *J. Chem. Res.* **1981**, 286] has also concluded that the tetrafluoroethylene anion is pyramidal with either a syn or anti structure consistent with our conclusions and those of ref 17.

Chirality due to ^{18}O Substitution. Synthesis and Chiroptical Properties of (1*S*)-2,4-Adamantanedione-*4*-^{18}*O*

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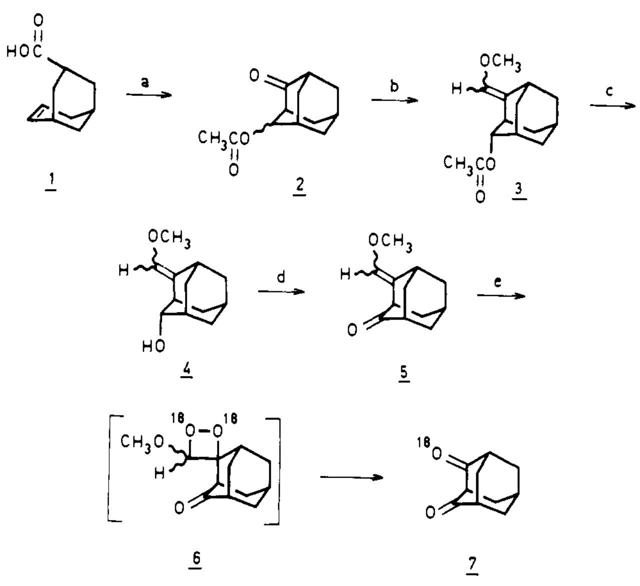
The rigid adamantane skeleton has proved of special value in the interpretation of subtle effects in the circular dichroism spectra of chiral carbonyl compounds.[1] In addition, the adamantane framework has shown its usefulness in the construction of chiral ketones whose chirality is due to isotopic substitution.[2,3] Only one example is known of an optically active cycloalkanone, the 1,2-diketone α-(^{16}O,^{18}O)fenchocamphorone quinone, whose chirality is solely due to oxygen-18 substitution.[4,5]

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 (^{18}O) water. Secondly, ketones rapidly exchange oxygen in aqueous media.[6] 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 (1*S*)-2,4-adamantanedione-*4*-^{18}*O* (**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-(^{18}O)dioxetane.

Scheme I[a]



[a] (a) Boron trifluoride etherate, $(CH_3CO)_2O$, C_6H_6, room temperature, 1 h, 85%; (b) $PH_3P^+{-}CH_2OCH_3Cl^-$, *n*-BuLi, THF, room temperature, 24 h, ~25%; (c) LiOH, C_2H_5OH, H_2O, room temperature, 12 h, ~80%; (d) PDC, CH_2Cl_2, room temperature, 4 h, 40% (anti) and 60% (syn); (e) $^{18}O_2$ (99%), methylene blue, CH_2Cl_2, *hν*, room temperature, 3 h, 70%.

The starting material in our synthesis was (+)-*endo*-bicyclo-[3.3.1]non-6-en-3-carboxylic acid (**1**).[7] The optically active 3*R*-acid **1**[8] was cyclized to an epimeric mixture of the 4-acetoxyadamantan-2-one (**2**) in a 2:1 equatorial axial[9] ratio. The equatorial **2** could be transformed into the two isomeric (syn and anti)[10] enol ethers **3** in ~25% yield. Basic hydrolysis afforded the two 4(e)-hydroxy-2-(methoxymethylene)adamantanes (**4**). The isomers could be separated and oxidized under neutral conditions to yield the corresponding (1*S*)-4-(methoxymethylene)-adamantan-2-one isomer (**5**). The optically active diketone (1*S*)-2,4-adamantanedione-*4*-^{18}*O* (**7**) was prepared by a photooxygenation of **5** with $^{18}O_2$ gas (99%) and methylene blue in CH_2Cl_2.[11] Although the 1,2-dioxetane **6** could not be isolated, it is reasonable to assume that **6** is the intermediate in the photooxygenation.[12] Purification of **7** 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.[13]

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(1) (a) Snatzke, G.; Eckhardt, G. *Chem. Ber.* **1969**, *101*, 2010–2027. (b) Snatzke, G.; Eckhardt, G. *Tetrahedron* **1970**, *26*, 1143–1155.

(2) (a) Lightner, D. A.; Chang, T. C.; Horwitz, J. *Tetrahedron Lett.* **1977**, 3019–3020. (b) Numan, H.; Wynberg. H. *J. Org. Chem.* **1978**, *43*, 2232–2236.

(3) Sing, Y. L.; Numan, H.; Wynberg, H.; Djerassi, C. *J. Am. Chem. Soc.* **1979**, *101*, 5155–5158.

(4) Kokke, W. C. M. C.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 7583–7584.

(5) Kokke, W. C. M. C. *J. Org. Chem.* **1973**, *38*, 2989–2994.

(6) (a) Samuel, D.; Silver, B. L. *Adv. Phys. Org. Chem.* **1965**, *3*, 123–186. (b) Bell, R. P. *Adv. Phys. Org. Chem.* **1966**, *4*, 1–29.

(7) (a) Numan, H.; Troostwijk, C. B.; Wieringa, J. H.; Wynberg, H. *Tetrahedron Lett.* **1977**, 1761–1764. (b) The optical purity of **1** was established as 76 ± 3%, $[\alpha]_{578}$ +114 (c 1.0, ethanol).

(8) (a) Udding, A. C.; Wynberg. H.; Strating, J. *Tetrahedron Lett.* **1968**, 5719–5722. (b) Faulkner, D.; McKervey, M. A. *J. Chem. Soc. C.* **1971**, 3906–3910.

(9) Axial and equatorial with respect to the cyclohexanone ring.

(10) Syn and anti with respect to the methoxy group and the substituent at the 4-position.

(11) The excess of $^{18}O_2$ gas could easily be isolated and reused if necessary.

(12) Meijer, E. W.; Wynberg, H. *Tetrahedron Lett.* **1979**, *3997*–4000.

0002-7863/82/1504-1145$01.25/0 © 1982 American Chemical Society

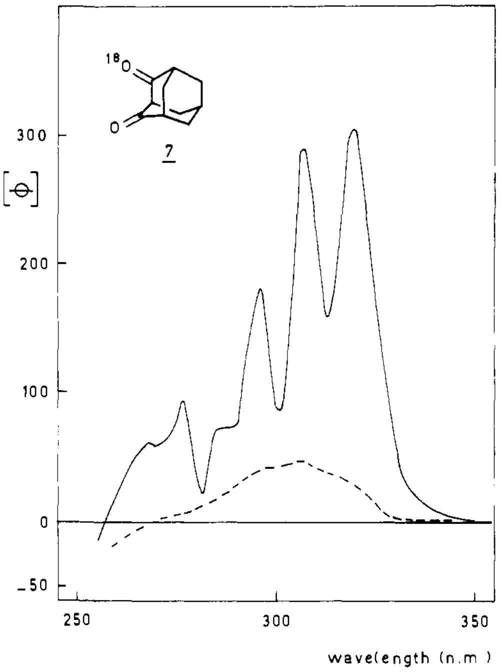

Figure 1. Circular dichroism spectrum (solid line) of (1*S*)-2,4-adamantanedione-*4*-^{18}*O* (**7**) (concentration 2.1 g/L) in cyclohexane at room temperature.[19] The spectrum is recorded with a sample which has an enantiomeric excess of 69% and an isotopic purity of 65%. This spectrum is **not** corrected to 100% optical and isotopic purity. The dotted line represents the spectrum recorded after oxygen exchange and should be regarded as the zero base line.

Thus the spectroscopic data were obtained with a sample of **7** which had a 41 ± 3% isotopic purity. On the assumption that no change in optical purity had occurred during the entire synthesis,[14] the optical purity of **7** is identical to that of the 3*R*-acid **1**, i.e., 76 ± 3%.

The circular dichorism spectrum (Figure 1) of the optically active (1*S*)-2,4-adamantanedione-*4*-^{18}*O* (**7**) is characterized by three bands at 320, 307, and 297 nm and small bands at lower wavelength. No immediate conclusion should be drawn about the considerable differences between the CD spectrum of **7** and that of the only other two optically active rigid 1,3-diketones,[3,15] since temperature and solvent effects can influence these spectra strongly as has been clearly demonstrated by Lightner[15] and was found for **7**.[19] It is reasonable to assume that the bands belong to different electronic transitions.[3,16,20]

In the light of the fast reaction of enol ethers with oxygen[12,17] and the high yield of 1,2-dioxetane, even when the "ene-reaction" is possible,[18] possible,[18] this synthetic route is unique and could be generally useful in the preparation of oxygen-18 ketones. The route is especially suitable for diketones in which one carbonyl is to be labeled with oxygen 18.

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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(13) The mass spectrum of **7** showed a percentage ^{18}O of 41 ± 3 one night after the preparation of **7**; storage of cyrstalline **7** at room temperature in a closed ($^{16}O_2$ containing air) vessel for 72 h provided material with a mass spectrum identical with the ^{16}O analogue !

(14) During the entire synthesis no crystallizations were performed.

(15) Lightner, D. A.; Christiansen, G. D.; Melquist, J. L. *Tetrahedron Lett.* **1972**, 2045–2048.

(16) Spafford, R.; Baiardo, J.; Wrobel, J.; Vala, M. *J. Am. Chem. Soc.* **1976**, *98*, 5217–5225.

(17) Meijer, E. W.; Wynberg, H. *Tetrahedron Lett.* **1981**, 785–788.

(18) Asveld, E. W. H.; Kellogg, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 3644–3646.

(19) When the CD spectrum of **7** was recorded in EPA (ether, isopentane, ethanol, 5:5:2) at room temperature and at 92 K, the amplitudes of several bands had changed dramatically and bands with negative signs appeared.

(20) For an excellent recent review on isotopically engendered chirality see: Barth, G.; Djerassi, C. *Tetrahedron* **1981**, *37*, 4123–4142.

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[1] and the microporous silica polymorphs.[2] 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 ($AlPO_4$-*n*)[3] 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 ($AlPO_4$-17), the sodalite type ($AlPO_4$-20), and the analcime type ($AlPO_4$-24).[1] One of the novel three-dimensional structures, that of $AlPO_4$-5, has been determined by single-crystal X-ray methods.[4] $AlPO_4$-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 AlO_4 and PO_4 tetrahedra. It has the framework topology of the hypothetical 4-connected three-dimensional net no. 81 (4.6.12) proposed by Smith.[5]

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: $x\mathrm{R}\cdot\mathrm{Al_2O_3}\cdot(1.0 \pm 0.2)\mathrm{P_2O_5}\cdot y\mathrm{H_2O}$. The quantities x and y represent the amounts needed to fill the microporous voids within the neutral $AlPO_4$ 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 $AlPO_4$ structures or known hydrates, $AlPO_4 \cdot n H_2O$, form.

The direct relationship between a templating agent and the resulting structure is illustrated in the synthesis of $AlPO_4$-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 $AlPO_4$-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 into the sodalite cage.

Some structures are much less template specific. $AlPO_4$-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 $AlPO_4$ 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.

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(1) Breck, D. W. "Zeolite Molecular Sieves"; Wiley: New York, 1974.

(2) For example, silicalite: U.S. Patent 4 061 724, 1977. Flanigen, E. M.; Bennett, J. M.; Grose, R. W.; Cohen, J. P.; Patton, R. L.; Kirchner, R. M.; Smith, J. V. *Nature* **1978**, *271*, 512–516.

(3) The suffix *n* denotes a specific structure type.

(4) Cohen, J. P.; Bennett, J. M., to be submitted for publication.

(5) Smith, J. V. *Am. Mineral.* **1978**, *63*, 960–969.

0002-7863/82/1504-1146$01.25/0