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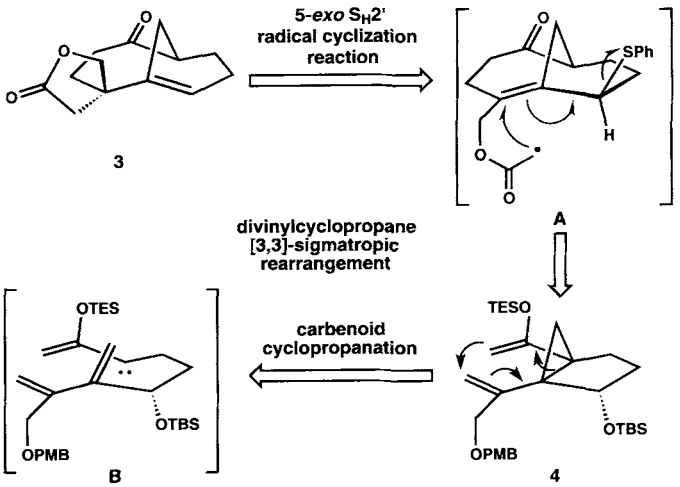
central core of these molecules relying on an intramolecular Diels–Alder reaction.[3]

In preliminary studies designed to explore the feasibility of a strategy towards the total synthesis of the CP molecules involving a rhodium-catalyzed carbenoid generation and intramolecular trapping, followed by a divinylcyclopropane rearrangement[4] and a radical cyclization (Scheme 1) the core



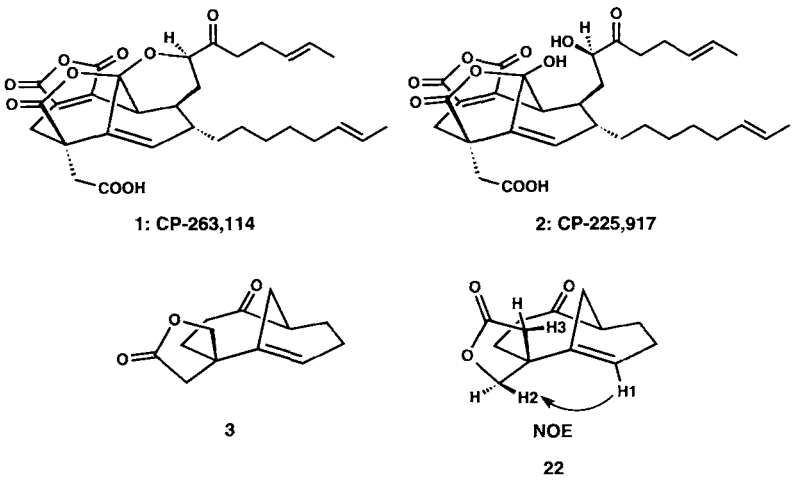
Scheme 1. Retrosynthetic analysis of the CP core model system **3**.

model system **3** was defined as a target. We wish to report here the execution of this strategy, which culminated in the construction of racemic **22** which has the opposite stereochemistry at the quaternary center.

A Novel Approach to the CP-225,917 and CP-263,114 Core**

K. C. Nicolaou,* Maarten H. D. Postema, Neil D. Miller, and Guang Yang

The naturally occurring substances CP-263,114 (**1**) and CP-225,917(**2**) possess intriguing molecular architecture,[1] important biological properties, and an interesting mechanism of action.[2] As inhibitors of squalene synthase and farnesyl transferase, these substances are attractive from the pharmaceutical point of view, particularly with regards to lowering cholesterol levels and to treating cancer. Isolated from an unidentified species of fungi, these compounds include within their structures a novel bicyclo[4.3.1]dec-1(9),4-dien-10-one framework onto which a variety of substituents are attached. We have previously reported on an approach to the



The synthesis of the requisite ketocyclopropane **15** proceeded as summarized in Scheme 2. Thus, methyl vinyl ketone (**5**) was treated with formaldehyde under Baylis–Hillman[5] conditions to afford, after *p*-methyoxybenzylation,[6] compound **6** in 25% overall yield. Formation of the enol triflate from **6** (60% yield), followed by palladium-catalyzed coupling with $Me_3SnSnMe_3$ resulted in the formation of vinyltin compound **7** (73% yield). Metal exchange followed by reaction with $TBSO(CH_2)_4CHO$ and silylation furnished bis(silyl)ether **8** in 80% overall yield. Sequential deprotection, Swern and $NaClO_2/NaH_2PO_4$/2-methyl-2-butene oxidations, followed by exposure of the resulting carboxylic acid to

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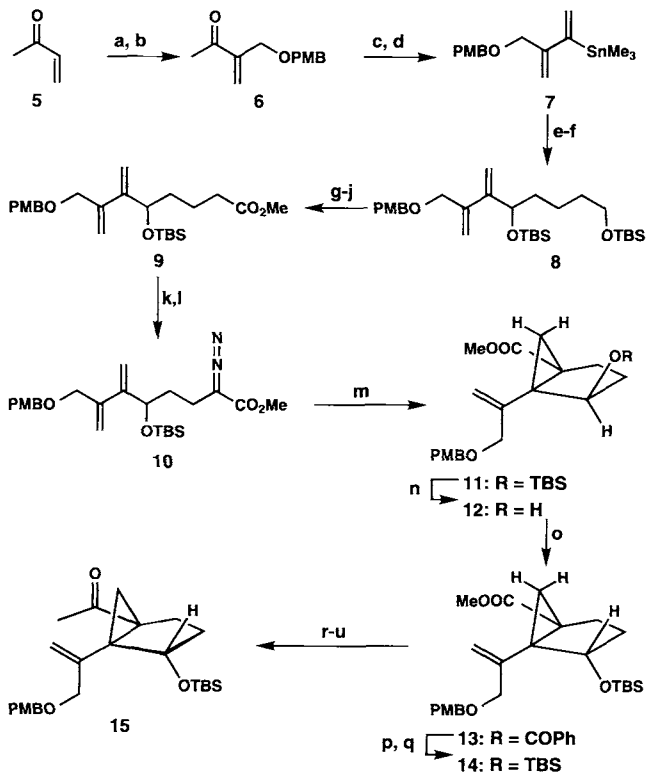
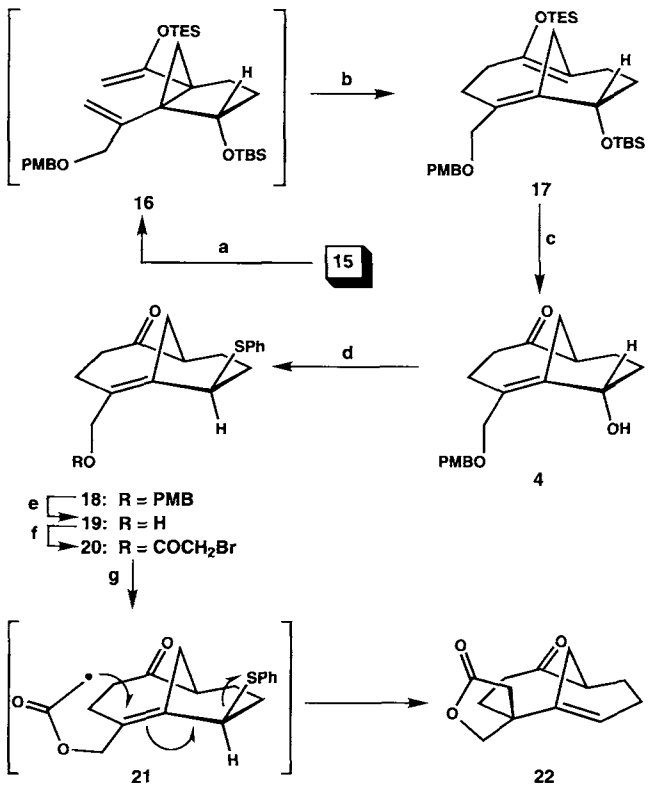


Scheme 2. Synthesis of ketocyclopropane **15**. a) DABCO (0.3 equiv), CH_2O (1.1 equiv), THF, 0→23°C, 48 h, 30%; b) $PMBOC(NH)CCl_3$ (2.0 equiv), CSA (0.1 equiv), CH_2Cl_2, 23°C, 3 h, 78%; c) NaHMDS (2.0 equiv), $PhNTf_2$ (2.0 equiv), THF, −40°C, 1 h, 60%; d) $Me_3SnSnMe_3$ (1.1 equiv), LiCl (10.0 equiv), $[(Ph_3P)_4Pd]$ (3 mol%), THF, 60°C, 8 h, 73%; e) *n*BuLi (1.1 equiv), THF, −78°C, 20 min; then $TBSO(CH_2)_4CHO$ (1.5 equiv), THF, −78→0°C, 1 h, 86% over two steps; f) TBSCl (2.0 equiv), imidazole (3.0 equiv), DMF, 50°C, 4 h, 94%; g) CSA (0.3 equiv), $MeOH/CH_2Cl_2$, 0°C, 20 min, 91%; h) DMSO (2.0 equiv), $(COCl)_2$ (1.8 equiv), Et_3N (4.0 equiv), CH_2Cl_2, −78°C, 30 min; i) $NaClO_2$ (2.0 equiv), NaH_2PO_4 (3.0 equiv), 2-methyl-2-butene (2.5 equiv), THF, H_2O, *t*BuOH, 0°C, 1 h; j) CH_2N_2, Et_2O, 23°C, 5 min, 87% over three steps; k) KHMDS (2.5 equiv), $PhCO_2Me$ (3.0 equiv), THF, −78→23°C, 4 h, 93%; l) 4-nitrobenzenesulfonyl azide (2.0 equiv), DBU (2.0 equiv), CH_2Cl_2, 0→23°C, 1 h, 95%; m) $Rh_2(OAc)_4$ (3 mol%), CH_2Cl_2, 0°C, 3 min, 87% (**11**:**14** ≈ 6.7:1, ^1H NMR); n) TBAF (1.5 equiv), THF, 0→23°C, 2 h, 95%; o) DEAD (1.5 equiv), Ph_3P (1.5 equiv), $PhCO_2H$ (1.5 equiv), THF, −20→23°C, 95%; p) NaOMe (10.0 equiv), MeOH, 23°C, 18 h, 93%; q) TBSOTf (1.5 equiv), 2,6-lutidine (2.0 equiv), CH_2Cl_2, −78→0°C, 2 h, 98%; r) DIBAL (2.2 equiv), CH_2Cl_2, −78→0°C, 2 h, 86%; s) TPAP (0.2 equiv), NMO (1.2 equiv), 4 Å molecular sieves, CH_2Cl_2, 23°C, 1 h; t) MeMgCl (3.0 equiv), THF, 0°C, 20 min; u) TPAP (0.2 equiv), NMO (1.2 equiv), 4 Å molecular sieves, CH_2Cl_2, 23°C, 1 h, 93% over three steps. CSA = (+)-camphorsulfonic acid; DABCO = 1,4-diazabicyclo[2.2.2]octane; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; DEAD = diethyl azodicarboxylate; DIBAL = diisobutylaluminum hydride; DMSO = dimethyl sulfoxide; HMDS = hexamethyldisilazanide; NMO = *N*-methylmorpholine *N*-oxide; TBAF = tetrabutylammonium fluoride; Tf = trifluoromethanesulfonyl; TPAP = tetra-*n*-propylammonium perruthenate.

diazomethane led to methyl ester **9** in 87% overall yield. The diazo ester **10** (Table 1) was synthesized from **9** by a modified Taber procedure.[7] The crucial carbenoid generation and intramolecular trapping[8] was achieved by treatment of diazo compound **10** with catalytic amounts of $Rh_2(OAc)_4$ in CH_2Cl_2 at 0°C, and led predominantly to vinylcyclopropane **11** together with its C-2 diastereoisomer **14** (ca. 6.7:1 by ^1H NMR).[9] The configuration of **11** was inverted by: 1. desilylation (95% yield for **12** and its C-2 diastereoisomer) and 2 chromatographic separation, followed by Mitsunobu inversion[10] of **12** (DEAD-Ph_3P-PhCOOH, 95% yield), leading to benzoate **13**. The inversion was deemed necessary for the pending 5-*exo*-S_H2' radical cyclization, although the stereochemical requirement for this process has not been fully established. Removal of the benzoate group from **13** generated the corresponding alcohol, which was silylated by treatment with TBSOTf/2,6-lutidine to afford compound **14** (98% yield; the minor C-2 diastereoisomer corresponding to **12** was directly converted to **14** by silylation). Finally, the desired ketocyclopropane **15** (Table 1) was reached from **14** by the following sequence: 1. DIBAL reduction (86% yield), 2. NMO/TPAP oxidation,[11] 3. MeMgCl addition, and 4. a second NMO/TPAP oxidation (93% for three steps).

Treatment of **15** with an excess of KHMDS and Et_3N/TESCl at −78°C as prescribed by Ireland[12] gave the intermediate silyl enol ether **16**, which underwent divinylcyclopropane rearrangement[13] at 45°C to give, after removal of both silyl groups, alcohol **4** in 95% overall yield (Scheme 3,



Scheme 3. Synthesis of **22**. a) KHMDS (3.1 equiv), TESCl:Et_3N:THF (3:1:1) (5.1 equiv), THF −78°C, 1 h; b) THF, −78→45°C, 4 h; c) TBAF (3.5 equiv), THF, 0→23°C, 2 h, 95% over two steps; d) PhSSPh (2.0 equiv), nBu_3P (2.0 equiv), C_6H_6, 23°C, 30 min, then **4**, 23°C, 12 h, 65% based on 50% conversion; e) DDQ (1.3 equiv), CH_2Cl_2:H_2O (10:1), 23°C, 6 h, 85%; f) $BrCH_2CO_2H$ (1.5 equiv), DCC (1.6 equiv), 4-DMAP, (0.1 equiv), CH_2Cl_2, 23°C, 1 h, 81%; g) $Me_3SnSnMe_3$ (5.0 equiv), C_6H_6, *hν*, 35°C, 8 h, 61%. DCC = dicyclohexylcarbodiimide; DDQ = 2,3-dichloro-5,6-dicyano-1,4-dibenzoquinone; 4-DMAP = 4-dimethylaminopyridine.

Table 1). The structure of **4** was rigorously assigned by a combination of 2D NMR experiments. Alcohol **4** was then converted to phenyl sulfide **18** (65% based on 50% conversion) by a modified Mitsunobu-type reaction,[14] and the PMB group was exchanged for an α-bromoacetate moiety, furnishing compound **20** via **19** (69% yield over two steps). Exposure of bromosulfide **20** to $Me_3SnSnMe_3$ and irradiation (hv) in degassed benzene led to lactone **22** (61%) by means of radical intermediates (e.g. **21**) and ring closure with concomitant expulsion of sulfenyl radical (see Scheme 3).[15] This last operation served admirably to simultaneously generate the required quaternary center (albeit

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Table 1. Selected physical properties of compounds **4**, **10**, **15**, and **22**.

10: yellow oil; $R_f = 0.69$ (ethyl acetate/benzene 9/1); FT-IR (CH_2Cl_2 cast): $\tilde{\nu}$= 2953, 2359, 2081, 1696, 1612, 1514, 1438, 1249, 1188, 1085, 836, 777 cm^{-1}; ^1H NMR (600 MHz, C_6D_6): $\delta = 7.23$ (m, 2H, Ar*H*), 6.80 (m, 2H, Ar*H*), 5.36 (s, 1H, C=CH*H*), 5.28 (s, 1H, C=CH*H*), 5.24 (s, 1H, C=CH*H*), 5.23 (s, 1H, C=CH*H*), 4.54 (dd, $J = 5.2, 5.2$ Hz, 1H, TBSO-C*H*), 4.34 (d, $J = 11.5$ Hz, 1H, ArCH*H*), 4.31 (d, $J = 11.5$ Hz, 1H, ArCH*H*), 4.06 (d, $J = 12.5$ Hz, 1H, C=CCH*H*), 4.02 (d, $J = 12.5$ Hz, 1H, C=CCH*H*), 3.36 (s, 3H, C(O)OCH_3), 3.30 (s, 3H, ArOCH_3), 2.23–2.38 (m, 2H, CH_2), 1.74–1.84 (m, 2H, CH_2), 0.97 (s, 9H, $(CH_3)_3$CSi), 0.06 (s, 3H, CH_3Si), 0.04 (s, 3H, CH_3Si); ^{13}C NMR (150.9 MHz, C_6D_6): δ = 159.7, 148.7, 143.2, 130.8, 129.5, 114.1, 114.0, 112.9, 72.5, 71.9, 71.8, 54.7, 51.3, 35.1, 26.0, 19.4, 18.4, −4.5, −5.1 (the carbonyl and diazo carbons do not appear in this spectrum); HR-MS: calcd. for $C_{25}H_{38}O_5N_2Si$ [M+H$^+$]: 475.2628, found: 475.2644

15: clear oil; $R_f = 0.20$ (hexanes/diethyl ether 6/4); FT-IR (CH_2Cl_2 cast): $\tilde{\nu}$= 2954, 2856, 1688, 1613, 1513, 1464, 1362, 1302, 1250, 1174, 1093, 1038, 890, 836, 776 cm^{-1}; ^1H NMR (600 MHz, C_6D_6): $\delta = 7.25–7.22$ (m, 2H, Ar*H*), 6.86–6.83 (m, 2H, Ar*H*), 5.38 (br. s, 1H, C=CHH), 4.99 (br. s, 1H, C=CHH), 4.41 (d, J = 11.5 Hz, 1H, ArCHH), 4.38 (d, $J = 11.5$ Hz, 1H, ArCHH), 4.14 (d, $J = 5.0$, Hz, 1H, TBSO-CH), 4.06 (d, $J = 13.0$ Hz, 1H, C=CCH*H*), 3.78 (s, 3H, ArOCH_3), 3.70 (d, $J = 13$ Hz, 1H, C=CCHH), 2.61 (ddd, $J = 12.0, 12.0, 8.2$ Hz, 1H, CH*H*), 2.10 (s, 3H, O=CCH_3), 1.78 (dd, $J = 12.5, 7.5$ Hz, CHH), 1.61–1.55 (m, 3H, CHH, includes d ($\delta = 1.58$), $J = 5.0$ Hz, cyclopropyl-H), 1.44–1.40 (m, 2H, CHH), 0.90 (d, $J = 5.0$ Hz, 1H, cyclopropyl-H), 0.83 (s, 9H, $(CH_3)_3$CSi), −0.01 (s, 3H, CH_3Si), −0.05 (s, 3H, CH_3Si); ^{13}C NMR (150.9 MHz, C_6D_6): δ = 206.9, 159.1, 140.5, 130.7, 129.2, 118.4, 113.7, 76.9, 72.8, 72.0, 55.3, 50.0, 44.5, 31.4, 28.5, 26.8, 25.9, 20.0, 18.1, −4.6, −4.8; HR-MS: calcd. for $C_{25}H_{38}O_4Si$ [M+Na$^+$]: 453.2437, found: 453.2446

4: clear oil; $R_f = 0.26$ (diethyl ether/hexanes 8/2); FT-IR (CH_2Cl_2 cast): $\tilde{\nu}$= 3418 (OH), 2924, 2820, 2360, 1696, 1612, 1513, 1453, 1248, 1174, 1034, 820 cm^{-1}; ^1H NMR (600 MHz, C_6D_6): $\delta = 7.28–7.24$ (m, 2H, Ar*H*), 6.79–6.75 (m, 2H, Ar*H*), 4.37 (d, $J = 11.3$ Hz, 1H, C=CC*H*H), 4.31 (d, $J = 11.3$ Hz, 1H, ArC*H*H), 4.26 (d, $J = 11.3$ Hz, 1H, ArCH*H*), 4.10 (d, $J = 11.3$ Hz, C=CCH*H*), 4.04 (ddd, $J = 10.6, 6.0, 6.3$ Hz, 1H, HO-C*H*), 3.26 (s, 3H, ArOCH_3), 2.98 (d, $J = 6.0$ Hz, 1H, CHO*H*), 2.53 (ddd, $J = 16.0, 11.1, 6.4$ Hz, 1H, CH*H*), 2.42 (ddd, $J = 15.5, 2.9, 2.9$ Hz, 1H, CH*H*), 2.41–2.35 (m, 2H, CH*H*), 2.13 (ddd, $J = 13.7, 11.1, 2.2$ Hz, 1H, CH*H*), 2.08–2.07 (m, 1H, CHH), 2.00 (ddd, $J = 15.2, 10.7, 2.0$ Hz, 1H, CH*H*), 1.94–1.87 (m, 1H, CH*H*), 1.58–1.51 (m, 1H, CH*H*), 1.30 (dd, $J = 12.7, 2.6$ Hz, CH*H*), 1.17–1.10 (m, 1H, CH*H*); ^{13}C NMR (150.9 MHz, C_6D_6): δ = 209.1, 159.7, 145.4, 130.8, 129.6, 127.3, 114.1, 76.4, 71.8, 70.0, 54.7, 51.2, 39.6, 39.2, 33.9, 28.2, 27.0; HR-MS: calcd. for $C_{19}H_{24}O_4$ [M+Na$^+$]: 339.1572, found: 339.1565

22: beige oil; $R_f = 0.20$ (diethyl ether); FT-IR (CH_2Cl_2 cast): $\tilde{\nu}$= 2925, 2855, 1778, 1699, 1461, 1399, 1184, 1020 cm^{-1}; ^1H NMR (600 MHz, C_6D_6): $\delta = 4.66$ (m, 1H, C=C*H*), 3.73 (d, $J = 9.0$ Hz, 1H, O=COCH*H*), 3.38 (d, $J = 9.0$ Hz, 1H, O=COCH*H*), 2.04–1.95 (m, 3H, CH*H*), 1.93 (dd, $J = 18.2, 1.3$ Hz, CC(O)CH*H*), 1.86 (dd, $J = 18.2, 1.3$ Hz, CC(O)CH*H*), 1.77 (ddd, $J = 12.0, 6.0, 2.5$ Hz, 1H, CH*H*), 1.72–1.64 (m, 1H, CH*H*), 1.62–1.58 (m, 1H, CH*H*), 1.45–1.26 (m, 3H, CH*H*), 1.16 (d, $J = 13.6$ Hz, 1H, CH*H*), 0.95 (ddd, $J = 13.4, 3.9, 1.2$ Hz, 1H, CH*H*); ^{13}C NMR (150.9 MHz, C_6D_6): δ = 212.5, 174.3, 144.9, 122.8, 75.4, 47.7, 46.4, 42.7, 38.6, 37.4, 30.2, 28.6, 23.6, 21.0; HR-MS: calcd. for $C_{13}H_{16}O_3$ [M+H$^+$]: 221.1178, found: 221.1169

with the opposite stereochemistry to that of **3**) and the bridgehead olefin, two of the most challenging structural elements in **1** and **2**. The structure of this cyclization product was assigned by spectroscopic means (see also Table 1). Thus, ^1H NMR spectroscopy (1D-GOESY) showed NOE of the H2 signal upon irradiation of H1, whereas molecular dynamics and minimization calculations (CV Force Field)[16] revealed interatomic distances of 2.5 and 4.3 Å for H1–H2 and H1–H3, respectively, supporting structure **22** rather than **3**.

The described chemistry demonstrates an efficient entry into the unusual carbon skeleton found in the CP core by combining three powerful synthetic operations (intramolecular cyclopropanation, divinylcyclopropane rearrangement, and radical cyclization). Although modifications are required, this strategy should facilitate the chemical synthesis of both natural products and relatives thereof for chemical biology investigations.

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Five-Coordinate Silicon in Zeolites: Probing $SiO_{4/2}F^-$ Sites in Nonasil and ZSM-5 with ^{29}Si Solid-State NMR Spectroscopy**

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The primary building blocks in a wide variety of tectosilicates are corner-sharing $SiO_{4/2}$ tetrahedra.[1] Silicon typically has a coordination number of four in inorganic silicates, and only a few structures are known with other coordination numbers. Six-coordinate silicon has been found in a variety of minerals and silicon phosphates.[2] Recently, van de Goor et al. found a five-coordinate silicon site ($SiO_{4/2}F^-$) by single-crystal X-ray structure analysis of the clathrasil nonasil, which was hydrothermally crystallized from a silica gel in the presence of cobaltocenium cations and fluoride anions.[3] This nonasil will be designated as [Cp_2Co]-F-[Si-NON].[4]

Fluoride ions can be used as a substitute for OH^- in the syntheses of zeolites and clathrasils. Both F^- and OH^- are

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