HOST-GUEST COMPLEX FORMATION BY AN OPTICALLY ACTIVE PARACYCLOPHANE IN WATER

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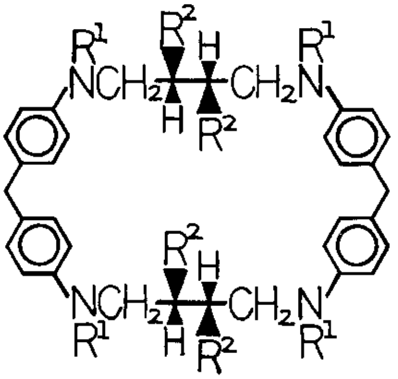
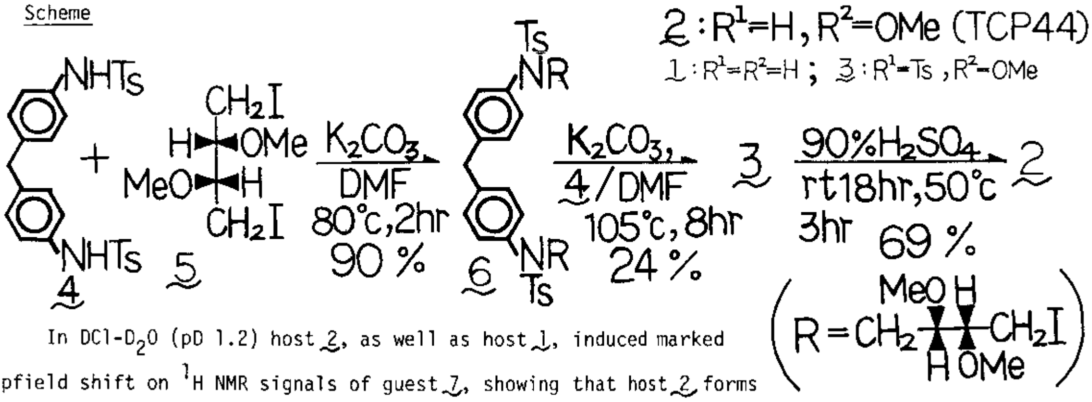
Previously we have reported the crystallographic[1] and NMR spectral[2] studies showing that CP44 (1), soluble in acidic water (pH<2), forms inclusion host-guest complexes with hydrophobic "aromatic" guests in a particular geometry. For application of this system to asymmetric reactions, we carried out the synthesis of TCP44 (2), containing the units derived from L-(+)-tartaric acid (Scheme): This is the first synthesis of a chiral, water-soluble paracyclophane.



2: R^1=H, R^2=OMe (TCP44)
1: R^1=R^2=H; 3: R^1=Ts, R^2=OMe

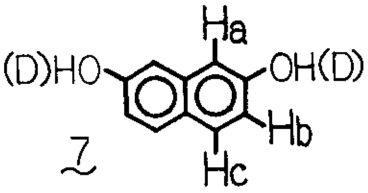
Scheme



In DCl-D_2O (pD 1.2) host 2, as well as host 1, induced marked upfield shift on ^{1}H NMR signals of guest 7, showing that host 2 forms a strong complex, comparable to that by host 1 (Table). Under similar conditions, formation of diastereomeric complexes between 2 and D-/L-mandelic acid is evidently observed. Further studies aiming asymmetric synthetic reactions are now in progress.

Table Changes of ^{1}H NMR chemical shifts of 7

Host	Δδ(Ha)	Δδ(Hb)	Δδ(Hc)
2 (pD 1.2)	−1.75	−0.61	−1.62
1 (pD 1.2)	−1.90	−0.59	−1.75



$\Delta\delta_{ppm}$= δ(Host+Guest)-δ(Guest), [2]=[1]=5.0×10^{-2}M, [7]=2.5×10^{-2}M, in DCl-D_2O (pD 1.2).

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[1] K. Odashima, A. Itai, Y. Iitaka, and K. Koga, J. Am. Chem. Soc., 102, 2504 (1980).

[2] K. Odashima, A. Itai, Y. Iitaka, Y. Arata, and K. Koga, Tetrahedron Lett., 21, 4347 (1980).