433. UNUSUAL SELECTIVITY OF NUCLEOPHILIC ADDITIONS OF CARBANIONS TO TETRA-
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Some years ago our interest in strained cage compounds led to the synthesis of the
title tetracyclic diketone which exhibits interesting properties. Mono-alkylation by organometal
nucleophiles resulted in the formation of hemi-ketals as a result of close juxtaposition of the
carbonyl groups. The selectivity of R-attack on cyclobutanone and cyclopentanone is governed
by steric shielding in favor of cyclopentanone attack. Competitive enolate formation resulted in
selectivity reversal and dimerization for bulky nucleophiles (s-Bu and t-Bu). The title com-
 pound could be bisfunctionalized through equilibration of the initially formed hemi-ketals to keto endo-alcohols
which were continuously taken away by excess nucleophile. The opening of the hemi-ketal to keto endo-alcohol is
resisted by steric compression of the van der Waals radii of substituent and hydrogen atoms and strongly depends
on R-size. Bisalkylation thus proved possible for R=H, Me, Ph but not n-Bu.

434. FUNCTIONALIZED FOUR-MEMBERED HETEROCYCLES. W.A.J. Starmans, L. Thijs,
B. Zwanenburg, Department of Organic Chemistry, NSR Center for Molecular Structure,
Design and Synthesis, University of Nijmegen, Toemoontveld, 6525 ED Nijmegen, The
Netherlands.

Four-membered heterocycles combine complexation ability with backbone rigidity, thus
offering promising enantioselective catalytic properties in organic synthesis. Some new functionalized
thietane-1,1-dioxides and azetidines were prepared which may serve as basis for chiral catalysts.

435. SYNTHESIS OF 2,9-CARBONYL-4-BRENDENES, STRAINED HALF-CAGE SYSTEMS
WITH ORTHOGONAL r-BONDS IN CLOSE PROXIMITY. Anton J.H. Klunder, Herbert
L.E. Dupré, Marcel P.M. van As, Asti C.L.M. van der Waals, Derek G. Wansink, and Bienne
Zwanenburg*, Department of Organic Chemistry, NSR Center for Molecular Structure, Design
and Synthesis, University of Nijmegen, Toemmoiveld, 6525 ED Nijmegen, The Netherlands

This paper deals with the synthesis of carbonyl-brendenes 1-3. These half cage systems are
unique structures as they are highly strained and contain two r-systems in close proximity contained in
a rigid framework. The spectroscopic features of 1, 2 and 3 strongly suggest non-bonded interactions
between the carbonyl and olefinic function. Charge-transfer interaction is observed for 4.

436. THE SYNTHESIS AND AGGREGATION BEHAVIOR OF OPTICALLY ACTIVE AMIDE
CONTAINING SURFACTANTS. Peter J.J.A. Buining, Nico A.J.M Sommerdijk, Arthur
M.A. Platorium, Mu Wang, Martina C. Feiters, Roeland J.M. Nolte* and Bienne Zwanenburg*,
Department of Organic Chemistry, NSR Center, University of Nijmegen, Toemoontveld, 6525
ED, Nijmegen, The Netherlands.

Two new chiral surfactant molecules, bearing an amide linked hydrocarbon chain, were
prepared with the aim to explore the use of amide functions in the construction of chiral aggregates. Only
two reaction steps were needed for the introduction of both a hydrocarbon chain and a (protected) head
group, starting from a suitable aziridine. The stretched out conformation of 2 leads to a high degree of
organization and, consequently, to the formation of chiral superstructures, in contrast to its regiosomer 1
which has a lower degree of organization due to its bent conformation.