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433. UNUSUAL SELECTIVITY OF NUCLEOPHILIC ADDITIONS OF CARBANIONS TO TETRACYCLO[5.3.0.$0^{2,5}$.$0^{4,8}$]DECANE-3,9-DIONE.

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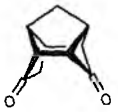

Some years ago our interest in strained cage compounds led to the synthesis of the title tetracyclic diketone which exhibits interesting properties. Mono-alkylation by organometal nucleophiles resulted in the formation of hemi-ketals as a result of close juxtaposition of the carbonyl groups. The selectivity 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 compound 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.

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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 Π-BONDS IN CLOSE PROXIMITY.

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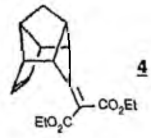
This paper deals with the synthesis of carbonyl-brendenes 1-3. These half cage systems are unique structures as they are highly strained and contain two π-systems in close proximity constrained in a rigid framework. The spectroscopic features of 1, 2 and 3 strongly suggest non-bonded interactions between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

1 n=1; 2 n=2; 3 n = 3



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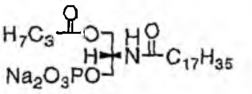
436. THE SYNTHESIS AND AGGREGATION BEHAVIOR OF OPTICALLY ACTIVE AMIDE CONTAINING SURFACTANTS.

Peter J.J.A. Buynsters, Nico A.J.M Sommerdijk, Arthur M.A. Pistorius, Mu Wang, Martinus C. Feiters, Roeland J.M. Nolte* and Binne Zwanenburg*, Department of Organic Chemistry, NSR Center, University of Nijmegen, Toernooiveld, 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 regioisomer 1 which has a lower degree of organization due to its bent conformation.



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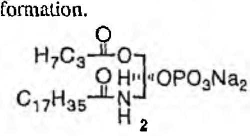

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