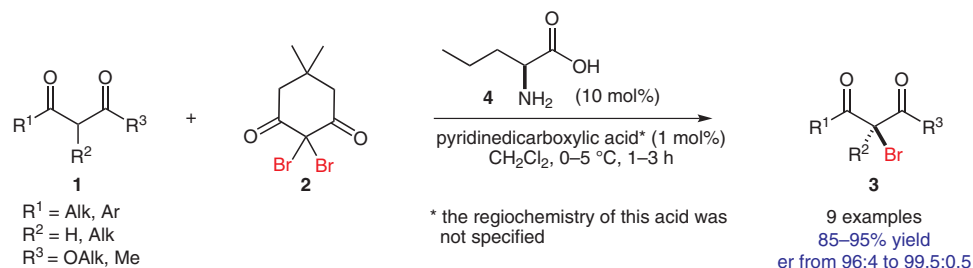


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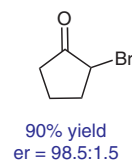
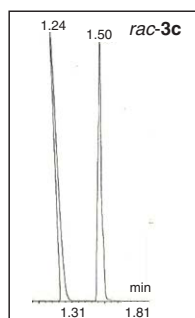
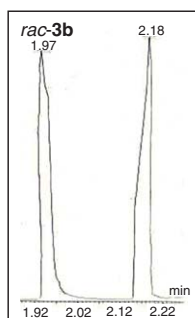
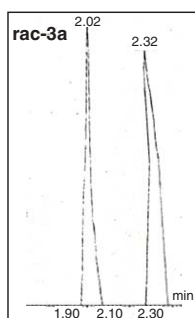
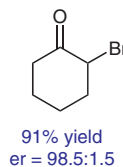
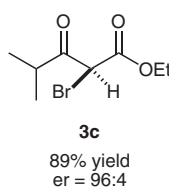
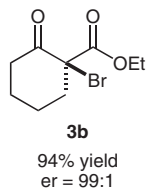
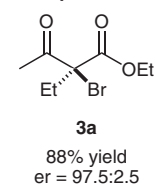
Design and Application of 2,2-Dibromodimedone as Organic Brominating Reagent for Asymmetric Bromination of 1,3-Dicarbonyl Compounds and Ketones Catalysed by Chiral Amino Acids

Adv. Synth. Catal. **2009**, *351*, 1483-1487.

A Highly Enantioselective α -Bromination?



Selected examples:



(*S*)-**3b** (reported): $[\alpha]_D^{25} = -8.0^\circ$ ($c = 1.0$, CHCl_3)
Lit: $[\alpha]_D^{25} = -50.2^\circ$ ($c = 0.87$, CHCl_3 , er = 91.5:8.5)
Angew. Chem. Int. Ed. **2005**, *44*, 6219

Significance: Goswami, Baruah and Das report a highly efficient α -bromination of 1,3-dicarbonyl compounds and cyclic ketones. Using 2,2-dibromodimedone **2** as a brominating agent and a simple primary amino acid catalyst **4**, products **3** are reported to form in high yields and enantioselectivities. It is noteworthy that an enantioselective synthesis of the highly stereolabile products **3** where $R^2 = \text{H}$ is unprecedented.

Comment: While an intriguing transformation is presented, the supporting documentation raises significant concerns. Considering the high stereolability of some of the compounds **3**, their purification by silica gel chromatography followed by direct chiral GC analysis seems incompatible with the reported er values. Given the unusual appearance of the GC traces and inconsistent optical rotations (see, for example **3b**), even the results for configurationally stable products appear questionable. Careful consideration of the results is therefore needed.

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