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Synthesis of Fused Bromofurans via Mg-Mediated Dibromocyclopropanation of Cycloalkanone-Derived Chalcones and Cloke–Wilson Rearrangement
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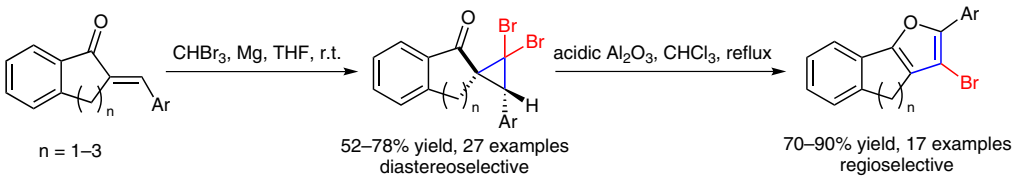
A Cloke–Wilson Rearrangement Approach to Fused Bromofurans



Significance: Reported is the synthesis of 2-aryl-3-bromofurans fused to benzocycloalkanes. The cycloalkanone-derived chalcones, when treated with magnesium and $CHBr_3$, are easily converted into spirodibromocyclopropanated intermediates. Under reflux in the presence of acidic Al_2O_3, these undergo a Cloke–Wilson rearrangement, leading to regioselective ring expansion in moderate to good yield. The substrate scope was reasonably well studied and the methodology worked well for tetralones, indanones and benzosuberones. The reaction also appears to work in open-chain α,β-disubstituted enones and acenaphthoquinones, but only one of each example was tested and this requires further study. Interestingly, almost all intermediate cyclopropanes were isolated and characterized, which can extend the scope of the methodology to other applications.

Comment: There are a lot of methodologies applied to the synthesis of furans, for example, the classical Paal–Knorr synthesis, or reactions catalyzed by transition metals such as expensive palladium and gold or toxic mercury (see Review below). The presented paper shows an elegant combination between cyclopropanation and rearrangement techniques useful for a good amount of substrates. The large excesses of magnesium (8 equiv) and $CHBr_3$ (22 equiv) used in the cyclopropanation step do not favor large-scale applications of this methodology. The overall yield (moderate to good) and the regioselectivity also encourage the use of this protocol.

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Category
Synthesis of Heterocycles

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Cloke–Wilson rearrangement
ring expansion