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Title: "Synthesis of 4-iodo-3-(2-iodoaryl) and 4-bromo-3-(2-bromoaryl)sydnones and their Reactions with Sodium Sulfite, Sodium Borohydride, and Iodine Monochloride"

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Abstract

One goal of the Turnbull research group has been the synthesis of dihalogenated arylsydnones; *i.e.* sydnones with halogen substitution on the sydnone ring itself, as well as at the position on the aryl ring *ortho* to the sydnone. Further, it has been of interest to explore the reactivity of these compounds, once obtained. The present study examined the synthesis of 4-iodo-3-(2-iodoaryl)-, or "diiodo", and 4-bromo-3-(2-bromoaryl)-, or "dibromo", sydnones and the reactions of these compounds with Na₂SO₃ (sodium sulfite) and NaBH₄ (sodium borohydride) to create a better understanding of the reactivity of diiodo and dibromo arylsydnones in general. Additionally, the reactivity of these compounds toward ICl (iodine monochloride) was examined, with the expectation that a sydnone ring iodine atom would be replaced with a chlorine atom. The expected products could be useful in carbon-carbon bond forming reactions where substitution of the more labile iodine atom and retention of the less reactive chlorine atom would result.

The results of the present study showed the effectiveness of Na₂SO₃ in removing an iodine or bromine from the C-4 position of the sydnone ring, with this process leading to high product purity and respectable yields. Second, the use of NaBH₄ to remove iodine from both the sydnone C4 position and the *ortho* position of the aryl ring attached to the sydnone ring was exhibited for several diiodo sydnones. Extension to similar dibromo sydnones resulted in removal of only the sydnone-attached bromine atom, with both sodium sulfite and sodium borohydride. Lastly, the use of a newly developed process for chlorination of sydnones with ICl was extended to diiodo sydnones, resulting in differentiated halogen substitution (replacement of the sydnone-attached iodine with a chlorine atom) in high yield and purity.