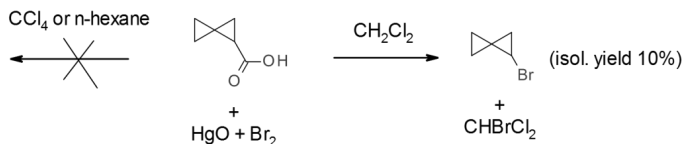


CHALLENGES IN SYNTHESIS OF BROMOSPIROPENTANE VIA CRISTOL-FIRTH-HUNSDIECKER REACTION*Medvedko S. P.*¹, Stambirskiy M. V.², Dmytriv Y. V.^{1,2}¹National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute",
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Bromospiropentane, which poses special interest due to great synthetic potential was formerly synthesized via Simmons-Smith cyclopropanation and consequent reduction of 1,1-dibromospiropentane. Another approach, namely via Hunsdiecker halodecarboxylation of corresponding acid had yet to be employed, although it's widely used for preparation of similar small-ring bromides.

In present work it was found that the most widely used Cristol-Firth modification of Hunsdiecker reaction with 1 equiv. of red mercuric oxide in tetrachloromethane fails to give the desired compound, and even more so, the total consumption of bromine was not observed. Working under assumption that the first intermediate to form was corresponding mercuric carboxylate more polar solvents, namely dichloromethane and 1,2-dichloroethane were tested to find that indeed conversion of acid to bromide does occur, albeit not fully, despite the observed full consumption of bromine.

Upon attempted isolation of compound it was found that reaction that took place in 1,2-dichloroethane exhibited higher conversion rate, but a copious amount of solid was crashing out of filtrate during concentration, which was found to contain spiropentylcarboxylate. Bromospiropentane purified by distillation was found to contain large amounts of brominated solvents, bromodichloromethane and 1-bromo-1,2-dichloroethane respectively. The main reason for that is the fact that mercuric oxide and bromine combined make a strong brominating agent, therefore a portion of bromine becomes used up for radical bromination of solvent, leaving mercury spiropentylcarboxylate unreacted in solution.

Working under assumption that it is therefore necessary to make sure that no mercuric oxide is left in mixture, mercuric salt was isolated prior to addition of bromine, but in this case no evidence of reaction was observed.

We conclude that for synthesis of bromospiropentane the Cristol-Firth-Hunsdiecker reaction clearly has limited efficacy due to physical and chemical properties of compounds and solvents. The search for alternative ways of halodecarboxylation is underway.