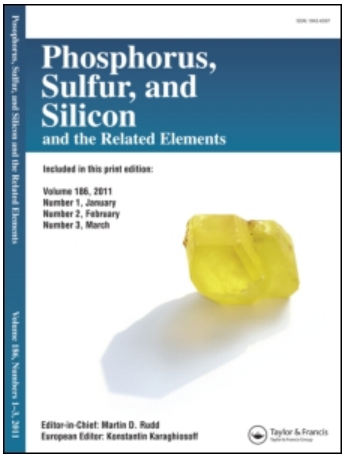

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REDUCTIVE REMOVAL OF HALOGEN BY THIOLATES FROM 1-HALOCYCLO-PROPYL SULFIDES

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REDUCTIVE REMOVAL OF HALOGEN BY THIOLATES FROM 1-HALOCYCLOPROPYL SULFIDES

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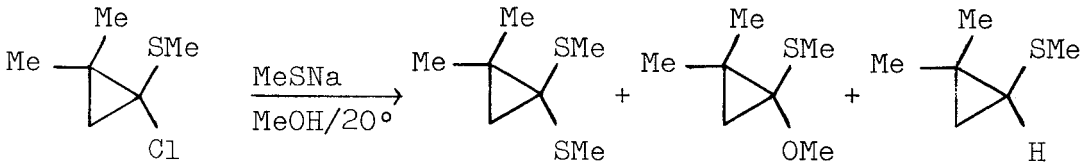
Nucleophilic substitution of cyclopropyl halides or tosylates is often accompanied by ring rupture, but this can be prevented by the presence of an electron releasing substituent in α-position (NR_2, OR, SR). Alkylthio and arylthio groups are particularly effective in stabilizing intermediate cyclopropyl cations. These give with most nucleophiles e.g. alkoxide, azide, fluoride, in relatively rapid reactions good yields of substitution products.

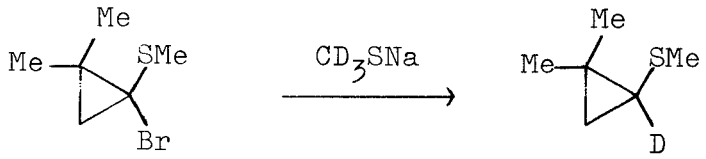
Despite their high nucleophilicity, alkanethiolates give only low yields of dithioacetals, especially when the small ring contains (two or four) methyl substituents. The major product is a reduced compound in which halogen has been displaced by hydrogen.

Thus, the chloride 1 reacts with 2M sodium methanethiolate in methanol to give no more than 35% of substitution and 65% of reduction:



1 20% 15% 65%

Experiments with CD_3SNa show that C-D rupture must be involved:



This is in accordance with the isolation of CH_3SCH_2SH, the addition product of CH_3SH to $CH_2{=}S$.
Medium effects suggest that the first step is the same for substitution and reduction i.e. dissociation to the cyclopropyl cation. Sulphur-sulphur bond formation is assumed to be one of the subsequent steps.
A complete mechanism for this new type of reduction will be presented.