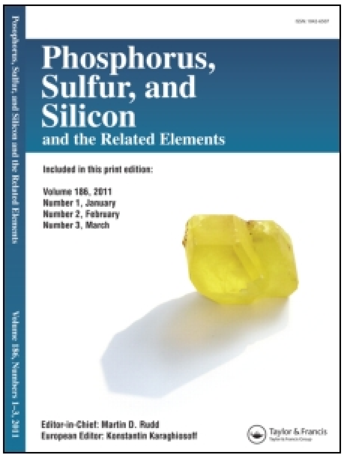

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SYNTHESIS OF α-AND β-OLEFINIC DITHIOESTERS - REACTIONS WITH GRIGNARD REAGENTS - SYNTHESIS OF ARTEMISIA KETONE

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SYNTHESIS OF α-and β-OLEFINIC DITHIOESTERS - REACTIONS WITH GRIGNARD REAGENTS - SYNTHESIS OF ARTEMISIA KETONE.

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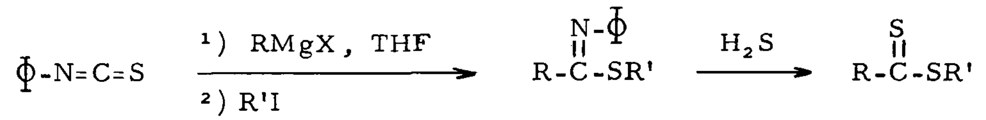
A new synthesis of dithioesters, starting from phenylisothiocyanate is described (scheme I) and this method is convenient for the preparation of β-olefinic dithioesters (e.g. 1, scheme II).

Scheme I

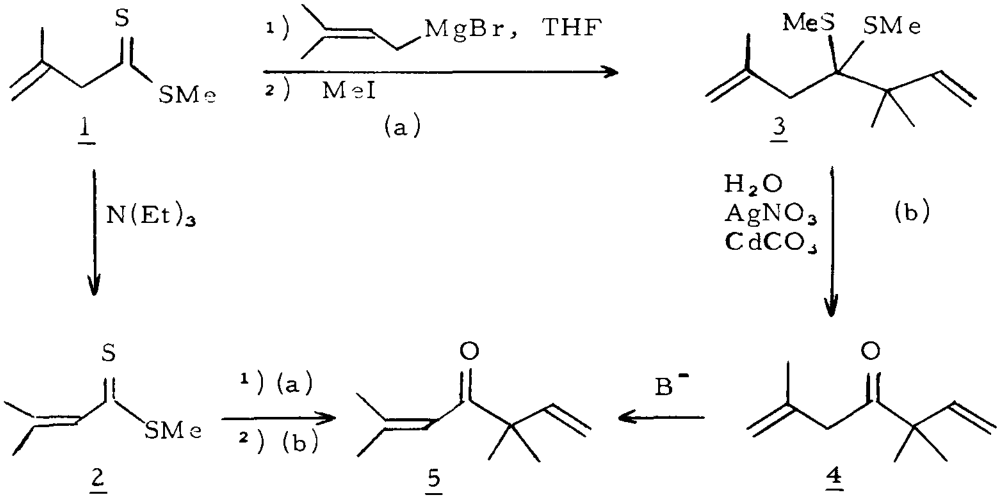


$$\Phi\text{-N=C=S} \xrightarrow[2)\ R'I]{1)\ RMgX,\ THF} R\text{-}\overset{\overset{N\text{-}\Phi}{\|}}{C}\text{-}SR' \xrightarrow{H_2S} R\text{-}\overset{\overset{S}{\|}}{C}\text{-}SR'$$

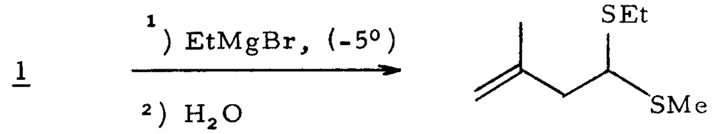
The β-olefinic dithioesters can be converted by catalytic amounts of base into α-olefinic dithioesters (e.g. 2) which are isolated either as monomers or dimers*.

Reactions of organomagnesium compounds with these olefinic dithioesters are examined. Carbophilic additions are observed with allylic Grignard reagents and these reactions are used to prepare iso-Artemisia (4) and Artemisia (5) ketones with good yields.

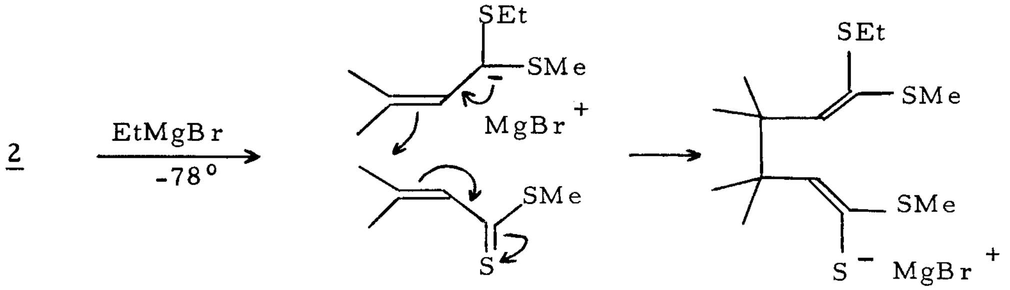
Scheme II



Alkylmagnesium bromides give thiophilic additions and from dithioester 1 , a dithioacetal of β-unsaturated aldehyde is obtained :



With α-olefinic dithioesters the carbanion initially formed by thiophilic addition undergoes Michael type addition with a second mole of dithioester :



*The dimerisation at room temperature of the less substituted α-olefinic dithioesters results from a regioselective Diels-Alder cycloaddition and cycloreversion is observed thermally.