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

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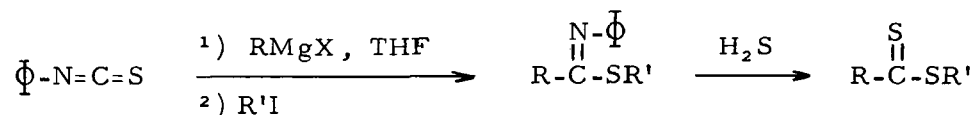
SYNTHESIS OF α - and β -OLEFINIC DITHIOESTERS - REACTIONS WITH GRIGNARD REAGENTS - SYNTHESIS OF ARTEMISIA KETONE.

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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).

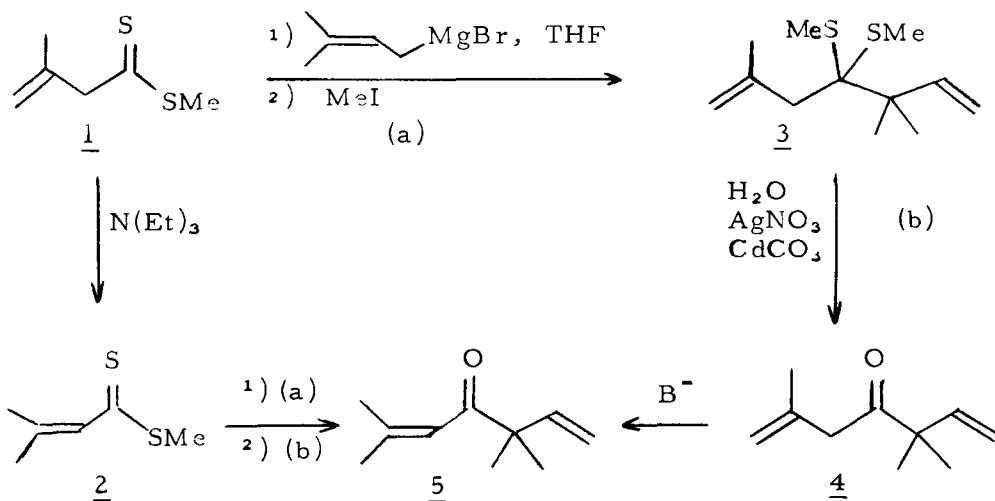
Scheme I



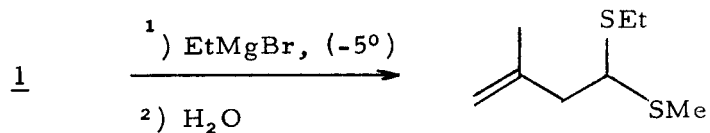
The β -olefinic dithioesters can be converted by catalytic amounts of base into α -olefinic dithioesters (e.g. 2) which are isolated either as monomers or dimers*.

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.

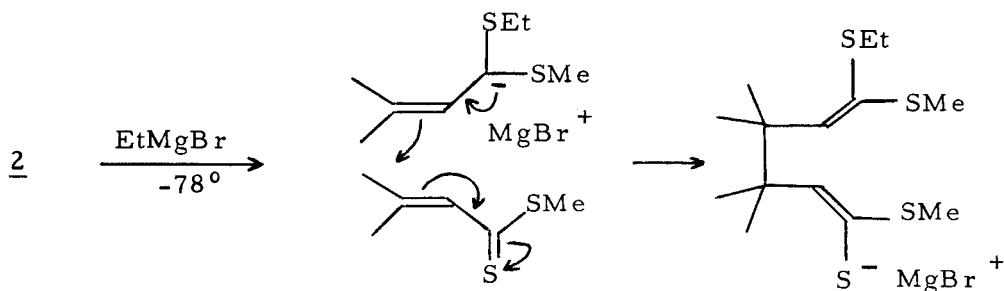
Scheme II



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.

