# New Method of Synthesis of Substituted Cyclohex-1-enyl Alkyl Sulphides

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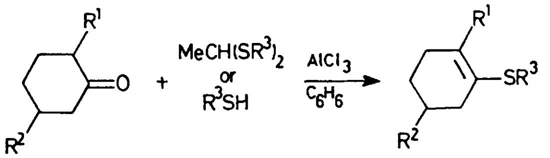
*Summary* The reaction of substituted cyclohexanones with thioacetals or thiols in the presence of aluminium chloride gives substituted cyclohex-1-enyl alkyl sulphides.

Organic sulphides which have a carbon–carbon double bond adjacent to the sulphur atom have been synthesized by the reaction of α-halogenoalkenes with sodium ethanethiolate,[1] cyclohexanethione with alkyl halides,[2] and di(chloroalkyl) sulphides with base.[3] Substituted cyclohexanones have been converted by reaction with $PCl_5$ in the presence of base into 1-chlorocyclohexene derivatives,[4] treatment of which with sodium ethanethiolate gave substituted cyclohex-1-enyl ethyl sulphides.[5] I now report a one-step synthesis of substituted cyclohex-1-enyl alkyl sulphides from substituted cyclohexanones.



When a mixture of a thioacetal (0·02 mol) and a substituted cyclohexanone (0·02 mol) in benzene (20 ml) was heated under reflux for 15 min in the presence of 1 mol. equiv. of $AlCl_3$, substituted cyclohex-1-enyl alkyl sulphides were obtained in good yield (Table).† Heating of a mixture containing a thiol instead of the thioacetal for 1 min gave the same product, but heating for 15 min caused disappearance of the sulphide. Reactions using thioacetals have the advantage that quick heating and quenching are not necessary and are suitable for large scale reactions.

Table. Yield of substituted cyclohex-1-enyl alkyl sulphides.

| Ketone[a] | $R^3SH$[b] | $MeCH(SR^3)_2$[c] | Product (%) |
|---|---|---|---|
| (A) | $R^3$ = Et | | (I) (35) |
| (A) | $R^3$ = Pr$^n$ | | (II) (29) |
| (A) | | $R^3$ = Et | (I) (25) |
| (A) | | $R^3$ = Pr$^n$ | (II) (19) |
| (B) | $R^3$ = Et | | (III) (48) |
| (B) | $R^3$ = Pr$^n$ | | (IV) (64) |
| (B) | | $R^3$ = Et | (III) (46) |
| (B) | | $R^3$ = Pr$^n$ | (IV) (57) |

[a] A = 2-Methylcyclohexanone; B = 2-isopropyl-5-methylcyclohexanone. [b] Reaction time: 1 min. [c] Reaction time: 15 min.

In the similar reaction of cyclohexanone itself with thioacetals or thiols, quick disappearance of the product was also observed. Thus, the stability of the product under the experimental conditions seems to be important factor for success in this reaction.

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† Satisfactory analytical data were obtained for all products, whose spectroscopic properties were in accord with the assigned structures.

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