

A NEW GENERAL ROUTE TO OLEFINS FROM SELENIDES

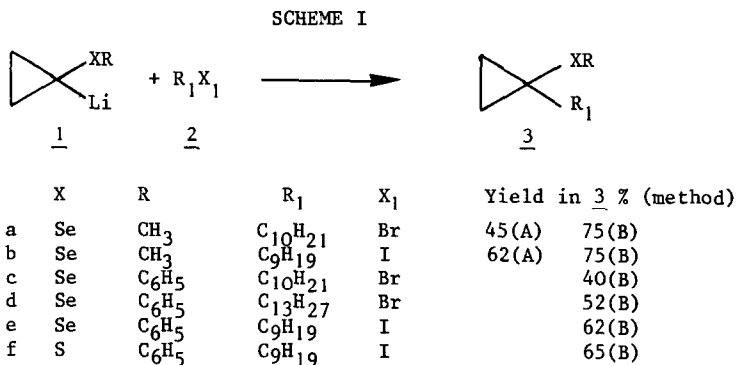
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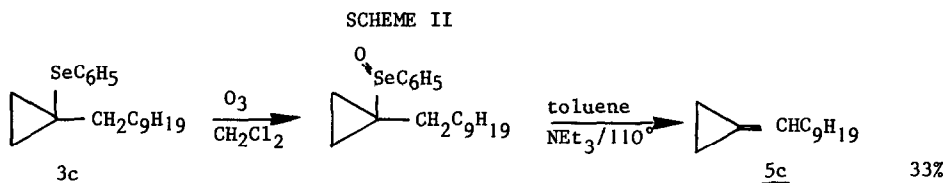
Olefins including alkylidenecyclopropanes are readily prepared from the corresponding selenides by reaction of base on the corresponding selenonium salt. The reaction also applies to cyclopropylsulfides.

The synthesis of olefins from selenides is a valuable transformation which takes advantage of easy selenoxide formation/elimination reaction^{1,2} which usually occurs at low temperature (20° or 50°C²).

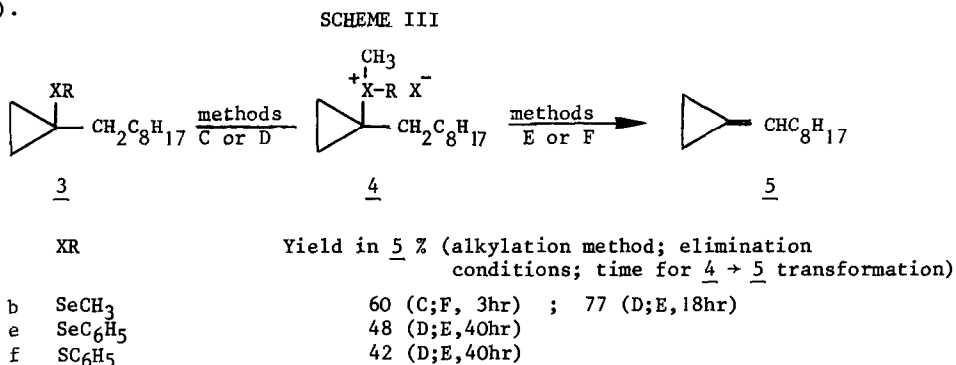
Applying these reactions to cyclopropylphenyl- or methylselenides readily available from α -lithiocyclopropylselenides³ and primary alkylhalides in THF (method A, Scheme I) or better in THF-HMPT (method B, Scheme I) leads however to disappointing results.



For example, the phenylselenocyclopropane 3c yields 1-decylidenecyclopropane in only 33% yield⁴, on reaction with ozone in CH₂Cl₂ and reflux of the corresponding selenoxide for 30 hr in toluene/triethylamine solution (Scheme II). Under similar conditions the corresponding methylselenoxide gives the starting selenide 3a and the valuable t. butyl hydroperoxide/alumina method² is not applicable due to the sensitivity of alkylidene cyclopropanes and cyclopropenes to oxidants⁵.



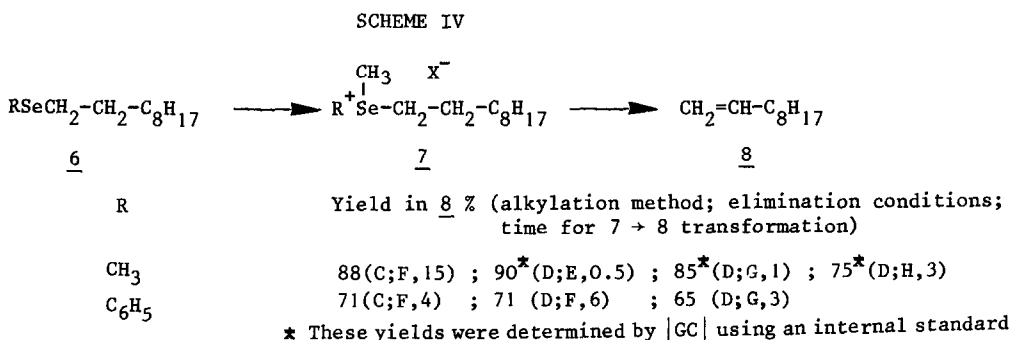
The desired transformation 3 → 5 was successfully achieved by reacting the methyl selenonium salts corresponding to 3a and 3b, prepared from 3 and magic methyl in ether (method C) or $\text{CH}_3\text{I}/\text{AgBF}_4$ (method D), with excess potassium t.butoxide in THF (method E) or in DMSO (method F) at 20° (Scheme III).



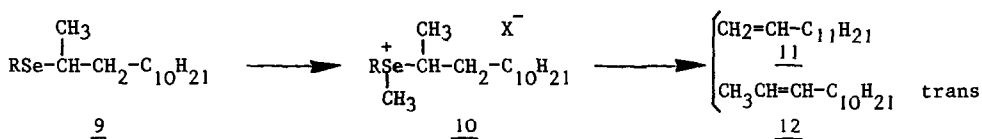
Methylseleno derivatives are more readily transformed and in higher yield than their phenylseleno analogues and phenylthiocyclopropanes prepared from α -lithiocyclopropylsulfides⁶ and alkylhalides (Scheme I, entry f) behave similarly (Scheme II, entry c).

Careful monitoring of the reaction $|\text{GC}|^2$ shows that the cyclopropene is preponderantly formed at the early stage of the synthesis but equilibrates to the more stable isomer⁷ during the reaction. All attempts to recover substantial amounts of the cyclopropene failed until now but in some cases small amounts remain at the end of the reaction along with the cyclopropylidene 5. In such cases complete isomerisation⁷ can be achieved by addition of tBuOK (1 eq) at the end of the reaction and stirring for a further hour at 20° the THF solution.

The elimination reaction just described seems to be general and produces olefins in high yield from primary and secondary alkylselenides (Schemes IV and V).



SCHEME V



R Yield in 11-12 % from 9 (conditions, time for 10 to 11 conversion)

CH₃ 82 (C;F, 3)
 C₆H₅ 88 (C;F, 3) ; 87 (D;H, 3)

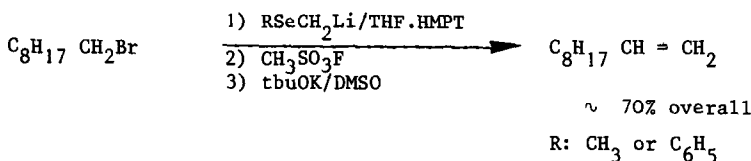
As expected, the reaction is easier than with cyclopropyl derivatives and can be achieved even with potassium hydroxide in THF (method G) or in DMSO (method H).

Both olefinic regioisomers 11/12 are formed from secondary alkylselenides in an about 65/35 ratio and olefin 12 is quite exclusively the trans isomer as observed by |GC|². Furthermore, we do not detect by |GC|² and MS analysis rearranged olefins, cyclopropanes or olefins resulting from an eventual carbene insertion.

Finally the reactions involving methylselenides are particularly interesting since the olefins are usually obtained free from any by-product at the end of the reaction due to the volatility of dimethylselenide.

The intimate mechanism of the reaction has not been yet determined⁸ but we suspect the formation of a methylene selenurane⁹ which produces the olefin via a mechanism close to the selenoxide elimination reaction. The absence of 1-decene when diphenyl decyl selenonium fluoroborate is reacted with potassium t-butoxide in DMSO seems to support but not confirm this hypothesis, since in the case of the simple E₂ mechanism, diphenylselenide which is a better leaving group than dimethylselenide is expected to be expelled at least with the same rate.

The reaction presented in the following scheme which takes advantage of the result just disclosed allows the high yield synthesis of terminal olefins from alkylhalides.¹⁰



The reactions disclosed in these letters should be in some instances a good substitute to selenoxide elimination reactions which produce selenenic, seleninic, selenonic acid which can in turn react on other functionalities present^{11,12}.

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Typical experiments

Method B: *n*BuLi (2.3 mmole, 2M in hexane) is added to a solution of bis(methylseleno)cyclopropane (540 mg, 2.3 mmole) in THF (4 ml) maintained, under nitrogen, at -78°C. After stirring 0.6 hr at this temperature, 1-iodononane (640 mg, 2.5 mmole) and HMPT (448 mg, 2.5 mmole) in THF (3 ml) is added at -78°C. The resulting solution is stirred at -78°C (1.5 hr) and allowed to reach 20° (1 hr) prior hydrolysis and usual work up. BuSeMe is pumped off (0.1 mm, 30°) and 1-methylseleno-1-cyclopropylnonane (456 mg, 75% yield) is isolated after PLC purification (SiO₂, pentane, R_f:0.5).

Methods D/E: silver tetrafluoroborate (349 mg, 1.8 mmole) is added at 20°C at once to a solution of the selenide just prepared (397 mg, 1.5 mmole) and methyl iodide (426 mg, 3 mmole) in ether (4 ml) a yellow precipitate immediately appears. It is extracted after 2 hr by CH₂Cl₂ (10 ml). Removal of CH₂Cl₂ under vacuum leads to an oil which crystallizes on washing with pentane (3 times). The crude salt is further dissolved in THF (3 ml) and added at 20°C on a suspension of *t*BuOK (513 mg, 4.5 mmole) in THF (4 ml). The suspension is stirred for 18 hr at this temperature. *t*BuOK (171 mg, 1.5 mmole) is added to isomerize completely the olefin and the mixture stirred for a further hour at 20°C prior hydrolysis and usual work up. The crude mixture is purified by PLC (SiO₂, pentane) leading to nonylidene cyclopropane (195 mg, 77% yield, R_f:0.95) and the starting β-hydroxy selenide (60 mg, 15% yield, R_f:0.57).

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