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THE CYCLOPROPANATION OF SILYL ENOL ETHERS OF CISOID OR LABILE α-ETHYLENIC KETONES. A GENERAL AND RAPID ROUTE TO CYCLOBUTANONES AND CYCLOPENTANONES.

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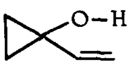
Cyclopropanols substituted in the 1-position by an electron-deficient carbon atom are now known to undergo facile ring-expansion to cyclobutanones (1). 1-Vinylcyclopropanols and oxaspiropentanes in particular constitute especially useful intermediates for the preparation of many of these ketones (1 - 7).

Notable developments in this field have been : a) the preparation, from cyclopropanone hemiketal, of vinylcyclopropanol 1 and its ring-expansion by electrophilic reagents into 2-substituted cyclobutanones (Wasserman and Coll. (2)) ; b) our own work which has led both to an easier preparation of vinylcyclopropanols from αα'-dichloroacetone and vinyl Grignard reagents and their stereospecific thermal rearrangement into cyclobutanones (1, 3), and also to a simple synthesis of oxaspiropentane 2 and its quantitative conversion, with lithium iodide (1,4) or via its chlorotrimethylsilane adduct 3 (1), into cyclobutanone itself (see also (5)) ; c) the general conversion of carbonyl compounds by sulphonium cyclopropylide 4 into cyclobutanones via oxaspiropentanes (Trost and coworkers (6)) and the preparation from the latter, by the use of lithium diethylamide and chlorotrimethylsilane, of siloxyvinylcyclopropanes of type 5, which can be thermally rearranged into cyclopentanone silyl enol ethers and thence converted by acid treatment into cyclopentanones (7) (see also (8)).



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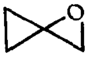

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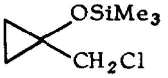

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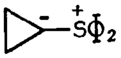

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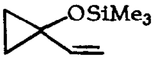

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The cyclopropanation of silyl enol ethers of saturated ketones and aldehydes using a recent improvement of the Simmons-Smith reaction (11) has been shown to be a good method for the preparation of cyclopropanols and for the α-methylation of carbonyl compounds (9) (see also 8c, 13, 14). In the preceding communication it was shown that the reaction can be applied to cycloalkenones and permits their specific methylation in the α'-position.

The purpose of this communication is to show that the same cyclopropanation of silyl enol ethers derived from cisoid or labile α-ethylenic ketones constitutes a very simple preparation of 1-siloxy-1-vinyl-cyclopropanes of type 5, thus providing a new and

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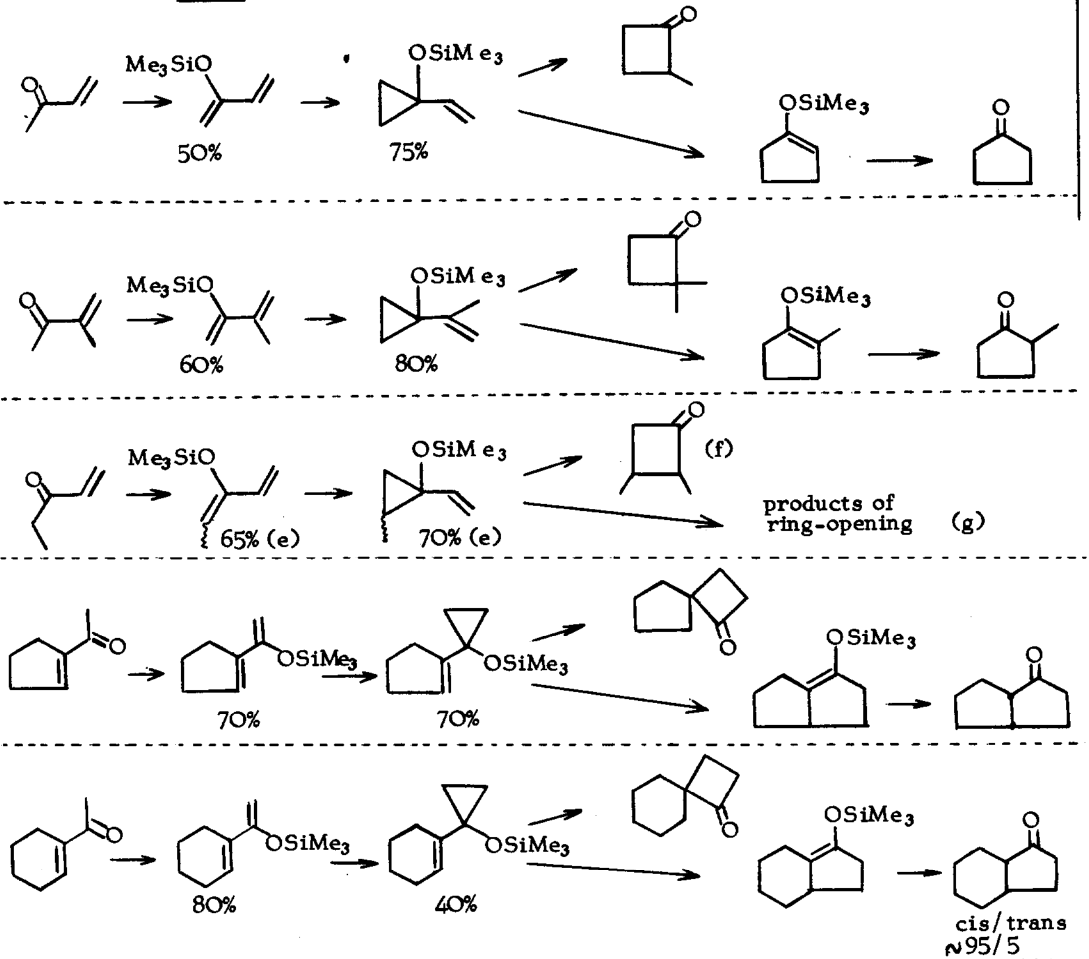
Table - The conversion of enones to cyclobutanones and cyclopentanones

Enones $\xrightarrow{(a)}$ Silyl enol ethers $\xrightarrow{(b)}$ Siloxy-vinyl-cyclopropanes $\xrightarrow{(c)}$ Cyclobutanones (Y : 95%) $\xrightarrow{(d)}$ Cyclopentanones (Y : 95%



(a) For the general procedure, by reaction with $ClSiMe_3 + NEt_3$ in DMF, see (10).

(b) Silyl enol ether is treated by 1.1 equivalents of the reagent CH_2I_2 + Zn/Ag couple in boiling ether for 18 hrs ; after cooling, 2.2 equivalents of pyridine are added, the complex $2C_5H_5N,ZnI_2$ is filtered off and the filtrate is concentrated under vacuum, – refiltered if necessary – and distilled. The product contains not more than 10% of silyl enol ether + double cyclopropanation product.

(c) By refluxing, for 1 hr, in THF with a few drops of conc. HCl.

(d) On heating in a sealed tube at 350° for 1h or, better, in the vapour phase 330° 1/2 hr.

(e) Cis/trans ratio : 83/17.

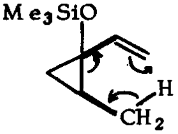
(f) A mixture of cis (30%) + trans (70%) 2,3-dimethyl-cyclobutanone is obtained plus approximately 5% of 2,4-dimethylcyclobutanone.

(g) In the vapour phase at 270°, the main compound cis-methyl-vinyl-siloxycyclopropane is opened, leading to 4-siloxy-penta-1,4-diene. (See text).

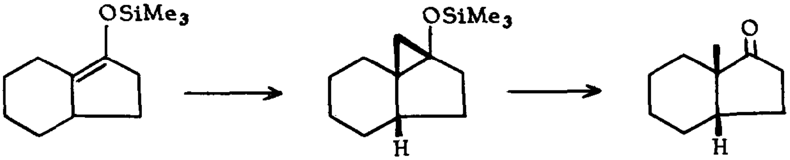
All yields refer to pure, distilled products.

faster route to cyclobutanones and cyclopentanones, via acid-catalysed (e.g.) and thermal ring-expansion respectively. The high yields which are normally obtained would seem to add to the preparative interest of these reactions which can be applied even to particularly unstable enones. (For the preparation and reactions of the double cyclopropanation products see the following communication).

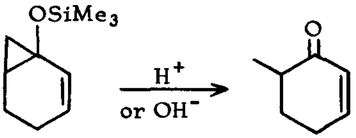
The third example in the Table shows, however, that there are certain limitations to the preparation of cyclopentanones by such a route. Thus, for instance, cis-1-trimethylsiloxy-1-vinyl-2-methylcyclopropane undergoes on heating, not the vinylcyclopropane-cyclopentene rearrangement, but ring-opening via a 1,5-hydrogen shift.

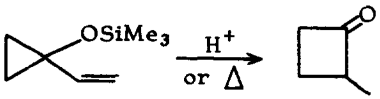


As a further possibility the 1-siloxycyclopentenes can be very easily subjected to a second Simmons-Smith reaction before hydrolysis. For example the enol ether obtained from the last reaction in the Table affords almost quantitatively the corresponding siloxycyclopropane, which can be converted by alkaline hydrolysis (see (3)) to 7a-methylhydrindanone (at least 95% cis isomer by g.l.c. and mass spectrum, showing that the original siloxy-cyclopropane is also almost totally cis).



It is essential to note the difference between the hydrolyses of the cyclopropanation products of cycloalkenone silyl enol ethers (the α'-monomethylcycloalkenone only is formed – see preceding communication) and of cisoid or labil enones (only the cyclobutanone is formed).





This dramatic difference seems to confirm our previous hypothesis (1) that the ring-expansion of type 1 vinylcyclopropanols proceeds, whether thermally or by acid catalysis, via the specific intramolecular addition of hydroxyl-hydrogen on the side of the double bond to which migration also takes place.

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