

THE DOUBLE CYCLOPROPANATION OF ENONE SILYL ENOL ETHERS.
A GOOD ROUTE TO 1-CYCLOPROPYL-CYCLOPROPANOLS
AND TO CYCLOPROPYLKETONES.

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(Received in UK 16 July 1974; accepted for publication 25 July 1974)

It has been reported that trimethylsiloxy-cyclopropanes, easily prepared by cyclopropanation of trimethylsilyl enol ethers of carbonyl compounds by the Simmons-Smith reaction with Zn/Ag couple and pyridine work-up (1), are useful intermediates in organic synthesis. For instance, they allow the preparation of various cyclopropanols (2, 3), the α -monomethylation of saturated aldehydes and ketones (2), the α - or α' -monomethylation of cycloalkenones as required (3) and the facile synthesis of numerous cyclobutanones and cyclopentanones (4).

From silyl enol ethers of α -ethylenic ketones, the selectivity of cyclopropanation is remarkable, the double bond bearing the OSiMe₃ group being virtually the only one which is attacked when not more than 1.1 equivalent of the Simmons-Smith reagent is used.

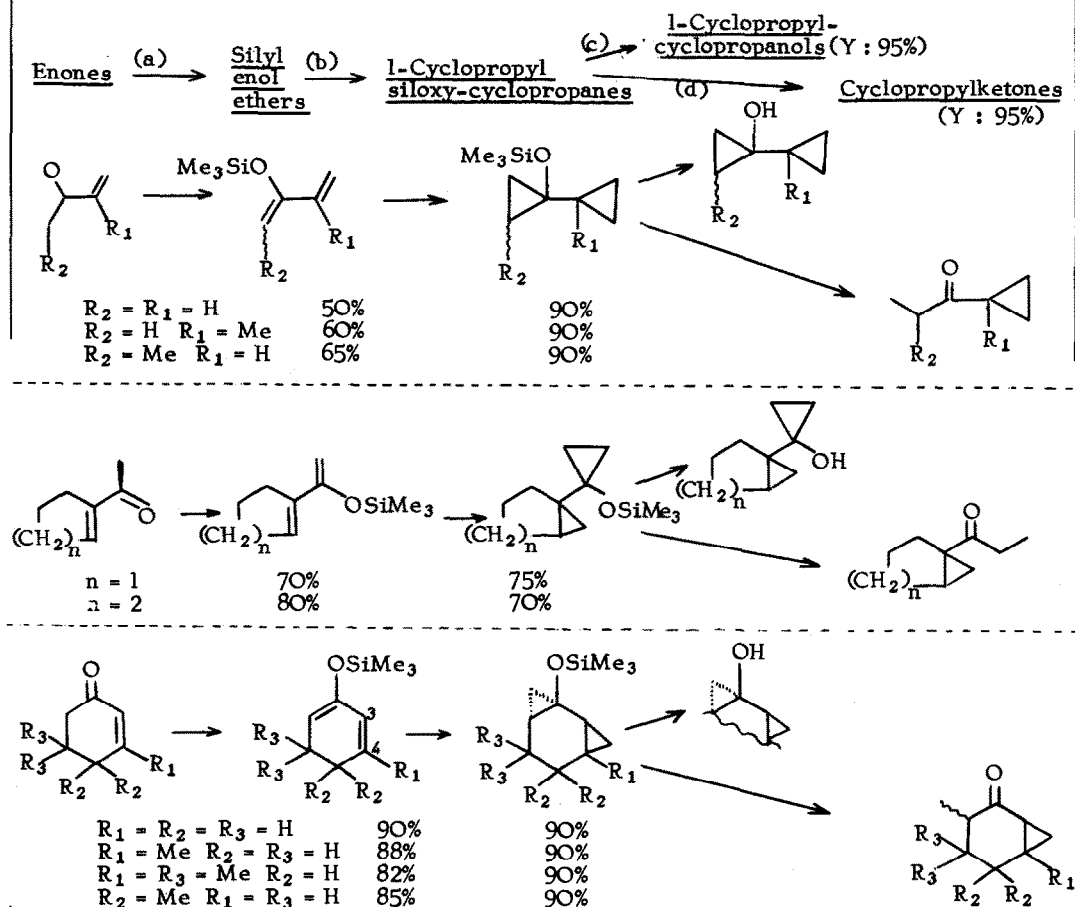
The purpose of the present communication is to show that with an excess of the latter (3 equiv.) with respect to the silyl enol ethers, the products of double cyclopropanation are obtained in good yield (Y : 80 - 90%) (see Table). Their subsequent treatment with methanol leads to 1-cyclopropyl-cyclopropanols, and with 1 M methanolic NaOH to ring opening of the silyl-cyclopropyl-ether moiety, giving the corresponding cyclopropyl-ketone, in both cases in excellent yields (Y \geq 95%).

Each of the four cycloalkenones (see Table) leads to a single bis-cyclopropanated product and thence to a single cyclopropylcyclopropanol (g.l.c. and n.m.r.) ; the product configuration is very probably anti since the second cyclopropanation, that of the 3,4-double bond, should be directed so as to occur on the same side as the siloxy group is situated. In addition, the n.m.r. spectra of the products do not show any particularly shielded protons whilst, from models, there should be two protons in the syn-isomers which are within the shielding zone of a cyclopropane ring.

By hydrolysis, the siloxy compounds give both of the epimeric 3-methylbicyclo[4.1.0]heptan-2 ones as equilibrium mixtures (g.l.c. and n.m.r. ; cis-trans ratios, in same order as Table, are 57 : 43 ; 50 : 50 ; 70 : 30 ; 84 : 16). For details concerning such pairs of isomers, see (6).

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Table - The conversion of enones to 1-cyclopropyl-cyclopropanols and cyclopropylketones



(a) Silyl enol ethers were prepared by reaction with $ClSiMe_3 + NEt_3$ in DMF, except those of cyclohexenones which were obtained by $LiN(i-C_3H_7)_2$ at 0° and $ClSiMe_3$ in THF, Et_2O (see 5).

(b) As in the preceding communication (4), but with 3 equivalents of $CH_2I_2 + Zn/Ag$ couple and then 6 equiv. of pyridine.

(c) The cyclopropyl-siloxy-cyclopropanes were heated in boiling MeOH for 10 hours. The IR spectrum reveals the formation of only 3-4% of the corresponding ring opening ketone.

(d) Boiling N/10 methanolic NaOH, 12 hrs; mixture of epimers obtained.

All yields refer to pure, distilled products, except for some of the cyclopropylcyclopropanols.

REFERENCES

- 1) J.M. Denis, C. Girard and J.M. Conia, *Synthesis*, 549 (1972).
- 2) J.M. Conia and C. Girard, *Tetrahedron Letters*, 2767 (1973).
- 3) C. Girard and J.M. Conia, this journal, communication before the preceding one and references therein.
- 4) C. Girard, P. Amice, J.P. Barnier and J.M. Conia, this journal, preceding communication and references therein.
- 5) H.O. House, L.J. Czuba, M. Gall and H.D. Olmstead, *J. org. Chem.*, 2324 (1969).
- 6) W.G. Dauben, C.W. Shaffer and E.J. Deviny, *J. amer. chem. Soc.*, 92, 6273 (1970).