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CLAISEN REARRANGEMENT IN THE SILICON SERIES.

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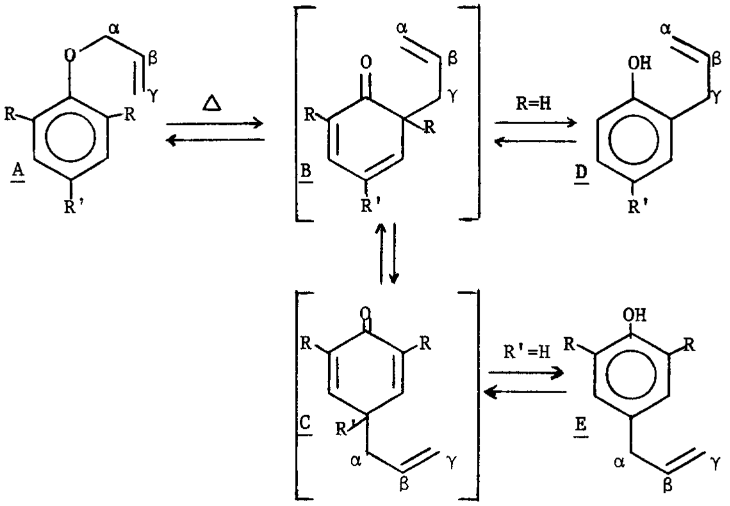
In the silicon series, a Claisen-type sigmatropic reaction is reported. The generated silicon-carbon double bond intermediate was intramoleculary trapped, leading to 1-oxa 5,6-benzo 2,2-dimethyl 2-silacyclohexane.

One of the most fascinating areas of organosilicon chemistry during the last years, has been the formation and reactions of silicon-carbon double-bonded intermediates(1). In this communication we report a new method to generate π-bonded silicon compounds, and the first example of intramolecular trapping by an oxygenated group.

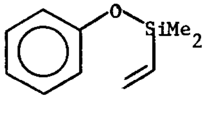
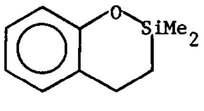
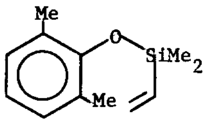
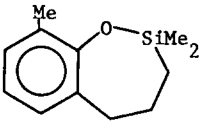
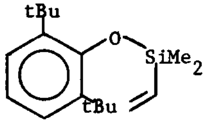
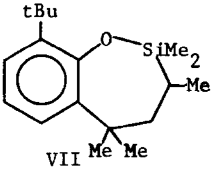
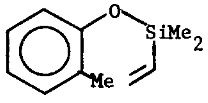
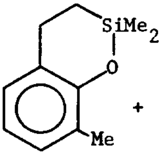
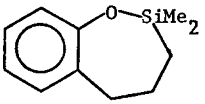
Thermolysis of allyl aryl ethers afforded two types of rearrangement product, depending on the nature of the ortho- and para-substituents R and R'(2).



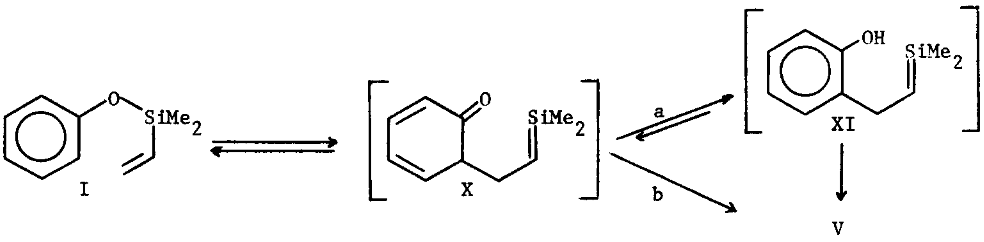
Anyway, whatever the rearrangement products obtained (ortho-Claisen product D or para-Claisen derivative E) the first cyclic rearrangement occurs with bonding of the γ carbon atom of the allylic proton to the ortho carbon atom of the ring to generate an ortho dienone B, in which the migrating allyl group has undergone a structural inversion. The tetragonal α carbon in compound A becomes trigonal in intermediate B.

Silicon analogs of these ethers, namely vinyl aryloxy dimethylsilanes were

prepared(3), and their thermolytic behaviour in sealed tubes studied.
The results are summarized in the following table:

Aryloxysilanes	T°C	Time (h)	Products (4)	yield (%)
 I	320	72	 V	37
 II	350	16	 VI	15
 III	300	72	 VII	30
 IV	320	72	 +  VIII IX	33

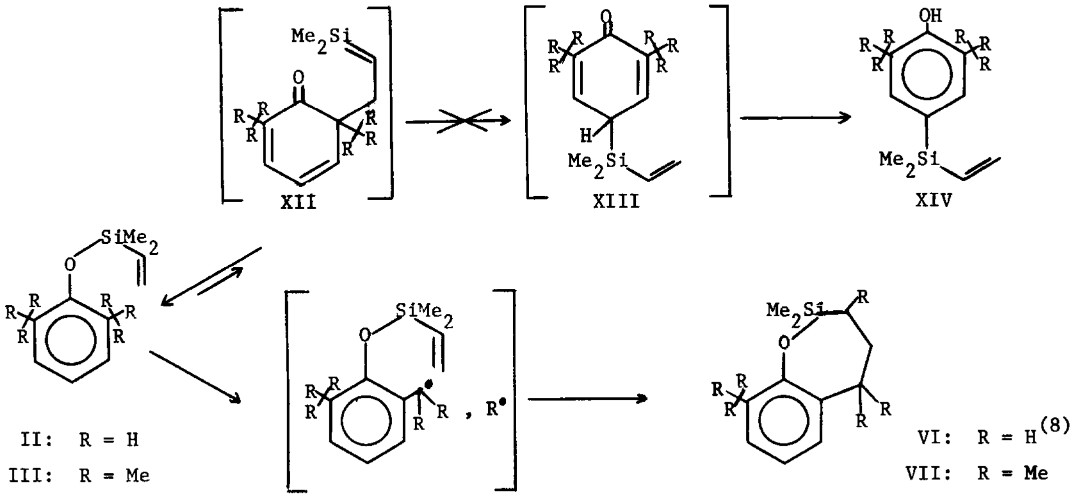
The formation of compound (V) from (I) can best be understood by the mechanism of the Claisen rearrangement leading to intermediate (X), followed by intramolecular trapping of the silaethylene.



The trapping of the silicon intermediate can be rationalized by two possible pathways (a) and (b). The first route involves rapid enolization of dienone (X) followed by the addition of the hydroxylic group on the highly polarized silaethylene(1a). However, a concerted six-center mechanism (b) cannot be excluded. SOMMER *et al.* have proposed these two pathways for addition of enolizable ketone on dimethyl silaethylene(5).

Attempts to trap silaethylene (X) or (XI) with an excess of phenol were unsuccessfull, intramolecular addition being more effective than intermolcular. However, we have noticed that the rate enhancement of the transposition of (I) to (V) is sensitive to a catalytic amount of phenol. This is in good agreement with a Claisen-type mechanism(6).

Pyrolysis of compound (II) and (III), involves a homolytic process with formation of a benzylic type radical, followed by addition on the vinyl double bond(7). The expected product (XIV), from para-Claisen transposition (Claisen+Cope rearrangement) was not observed. However, this fact does not exclude the possibility of the existence of an equilibrium between products (II) or (III) and the corresponding dienone (XII).



Trapping attempts of this dienone (XII) by acetylenic compounds were unsuccessfull(9). In fact, under the experimental conditions used, acetylenic derivatives only give rise to polymers. The carbon analog of the dienone has been characterized in the form of its adduct with maleic anhydride(10).

Next, we turned our attention to investigation of the thermolysis of cresoxy vinyl dimethylsilane (IV) because, in this compound, the two processes (Claisen and radical) are possible. It is interesting to note that the ratio of products (VIII)(Claisen) and (IX) (radical) depends on the reaction temperature.

T°C	VIII	IX
320	92%	8%
350	80%	20%
380	44%	56%

These results are consistent with a Claisen-type mechanism to explain the formation of products (V) and (VIII). Indeed, bond dissociation energy of a benzylic radical being smaller than that required for a phenyl radical(11), the obtention of product (IX) should be the major process when the lowest temperatures are used, if all the products come from a homolytic process. Besides, it appears that the Cope rearrangement requires more energy than the radical process. KWART and SLUTSKY suggested a Cope transposition to explain cis-trans isomerization in the propenyl allyl dimethylsilane at temperature above 500°C(12).

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(3). (I): Eb_{12}=78°C; ^{1}H-NMR(δ) 0.3(CH_3Si,s,6H), 5.7-6(H_{vinyl},m,3H), 6.6-7.15(H_{ar},m,5H). (II): Eb_{12}=108°C; ^{1}H-NMR(δ) 0.3(CH_3Si,s,6H), 2.1(C_{ar}-CH_3,s,6H), 5.7-6.1(H_{vinyl},m,3H), 6.4-6.9 (H_{ar},m,3H). (III): m.p.=67°C; ^{1}H-NMR(δ) 0.4(CH_3Si,s,6H), 1.4(tBu,s,9H), 5.3-7.1($H_{vinyl}$and H_{ar},m,6H). (IV): Eb_{12}=89°C; ^{1}H-NMR(δ) 0.3(CH_3Si,s,6H), 2.13(C_{ar}-CH_3,s,3H), 5.4-6.2(H_{vinyl},m, 3H), 6.8-7(H_{ar},m,4H).

(4). (V): Eb_{15}=93°C; ^{1}H-NMR(δ) 0.25(CH_3Si,s,6H), 0.85($SiCH_2$,m,2H), 2.75(C_{ar}-CH_2,m,2H), 6.4-6.7(H_{ar},m,4H). (VI): Eb_{13}=115°C; ^{1}H-NMR(δ) 0.15(CH_3Si,s,6H), 0.9($SiCH_2$,m,2H), 1.5-2($SiCH_2\underline{CH_2}$, m,2H), 2.1(C_{ar}-CH_3,s,3H), 2.6(C_{ar}-CH_2,m,2H), 6.4-6.9(H_{ar},m,3H). (VII): Eb_{15}=145°C; ^{1}H-NMR(δ) 0.33(CH_3Si,s,3H), 0.47(CH_3Si,s,3H), 0.83($CH\underline{CH_3}$,m,3H), 1.0(Me_2C,s,6H),1.3(tBu,s,9H), 1.6-2.1 (CH_2,m,2H), 6.6-7(H_{ar},m,3H). (VIII): Eb_{15}=113°C; ^{1}H-NMR(δ) 0.25(CH_3Si,s,6H), 0.85($SiCH_2$,m,2H), 2.1(C_{ar}-CH_3,s,3H), 2.7(C_{ar}-CH_2,m,2H), 6.3-6.8(H_{ar},m,3H). (IX): Eb_{15}=113°C; ^{1}H-NMR(δ) 0.15 (CH_3Si,s,6H),0.85($SiCH_2$,m,2H), 1.7-2($SiCH_2\underline{CH_2}$,m,2H), 2.7(C_{ar}-CH_2,m,2H), 6.4-6.9(H_{ar},m,4H).

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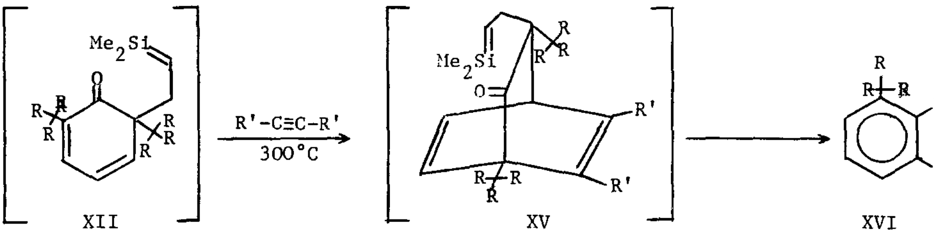
(7). This reaction was not catalyzed by the corresponding phenol.

(8). The molecular structure of product (VI) was ascertained by comparison with an authentic sample prepared by intramolecular ring closure of (2-methyl 6-allyl) phenoxy dimethyl silane in the presence of a catalytic amount of H_2PtCl_6.

(9) Ethylenic dienophile should lead, in our case, to a compound having a stable bicyclic structure, but also having a highly polymerizable silicon-carbon double bond. In contrast, using acetylenic dienophiles, the aromatic derivatives (XVI) should be obtained, resulting from thermal decomposition of adduct (XV).



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