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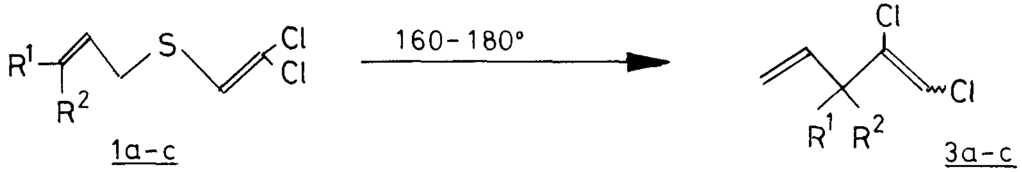
THERMAL REARRANGEMENTS OF ALLYL 2,2-DICHLOROVINYL AND 1,2,2-TRICHLOROVINYL SULFIDES

Enkou Nagashima, Kunio Suzuki, and Minoru Sekiya*

Shizuoka College of Pharmacy, 2-2-1 Oshika, Shizuoka 422, Japan

Summary: Unique rearrangements of allyl 2,2-dichlorovinyl and 1,2,2-trichlorovinyl sulfides have been found. On heating the former gave 1,2-dichloro-1,4-pentadienes and the latter 2,3-dichloro-5-chloromethyl-4,5-dihydrothiophenes and 3,5,6-trichloro-3,4-dihydro-2H-thiopyranes.

The thio-Claisen rearrangement$^{1)}$ has been a reaction of considerable synthetic significance. In the course of the work aimed at the chemistry of perchlorovinyl sulfides, allyl 2,2-dichlorovinyl (1a-c) and 1,2,2-trichlorovinyl sulfides (2a-c) have been shown to undergo previously unreported and unique rearrangements. The thermal rearrangements of 1a-c and 2a-c give the different types of products, heating the former at 160-180° affording 1,2-dichloro-1,4-pentadienes (3a-c) and heating the latter at 100-120° 2,3-dichloro-5-chloromethyl-4,5-dihydrothiophenes (4a-c) and 3,5,6-trichloro-3,4-dihydro-2H-thiopyranes (5a,b). It is striking that the reactions involve not only rearrangement of the carbon sekeletons but also migration of the chlorines.



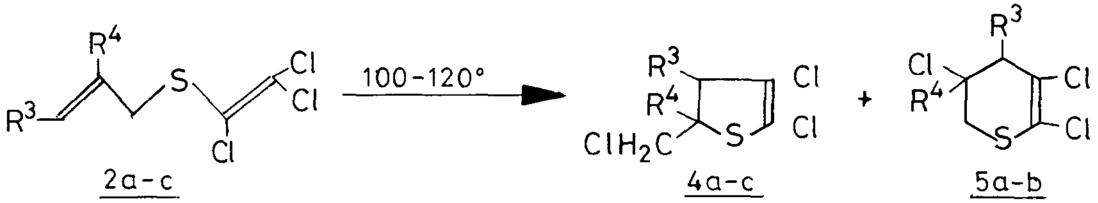


Table 1

Substrate No.	R^1	R^2	R^3	R^4	Reaction Temp(°C)[a)]	Yield of Product[b)] 3a-c[c)]	4a-c	5a-b
1a	H	H			160	53.5(3a)		
1b	Me	Me			180	38.8(3b)		
1c	Ph	H			180	35.2(3c)		
2a			H	H	120		33.2(4a)	22.1(5a)
2b			Me	H	120		27.2(4b)	16.3(4b)
2c			H	Me	100		26.1(4c)	trace

a) Substrate was heated for 0.5 hr without solvent. In the case of 1a, 3a was distilled during heating.
b) Yield of the products, 3a-c, were based on the products isolated.
Yield of the products, 4a-c and 5a-b, were determined by GLC.
c) The products 3a and 3c were determined as mixture of Z- and E-isomer, whereas 3b as a single isomer.

The starting compounds, 1a-c and 2a-c, were prepared from the corresponding 1,2,2,2-tetrachloroethyl sulfides (6a-e) by dehydrochlorination with triethylamine and dechlorination[2)] with zinc dust, respectively. The compounds, 6a-e, were prepared by the previously reported method[2)] starting from the corresponding mercaptanes and chloral.

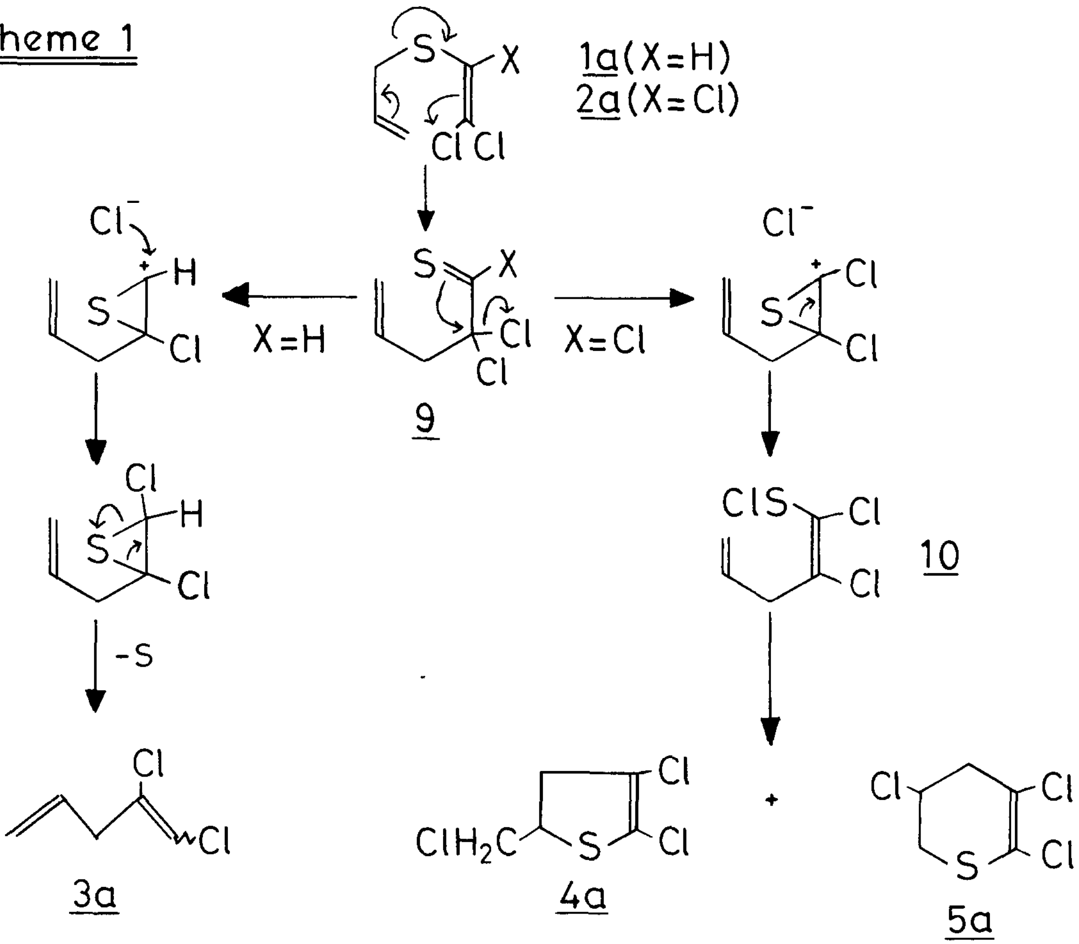
From 1a, the product 3a was obtained as a liquid of bp 92-105°/760mmHg, of which structure was supported by the following physical evidences, IR: 1645, 1620cm^{-1}(>C=C<); PMR(δ, ppm): 6.08, 6.11(1H, s, =CHCl of Z- and E-form), 5.42-5.98 (1H, m, =CH-), 4.90-5.35(2H, m, =CH$_2$), 2.95-3.35(2H, m, -CH$_2$-); MS(m/z): 136(M$^+$).

From 2a was obtained a mixture of 4a and 5a, which were separated by GLC, 4a: IR; 1610cm^{-1}(>C=C<). PMR(δ, ppm): 3.70-4.25(3H, m, H-5 and -CH$_2$Cl), 2.95-3.25 (2H, m, H-4); CMR(δ, ppm): 121.90(C-2), 115.53(C-3), 46.54, 46.22(C-4 and -CH$_2$Cl), 42.52(C-5); MS(m/z): 202(M$^+$). 5a: IR; 1610cm^{-1}(>C=C<). PMR(δ, ppm): 4.42(1H, nonet, J=7&6, H-3), 2.80-3.35(4H, m, H-2 and H-4); CMR(δ, ppm): 120.37(C-6), 118.13(C-5), 52.27(C-4), 42.57(C-3), 36.77(C-2); MS(m/z): 202(M$^+$). The product 4a was converted into 2,3-dichloro-5-methylthiophene (7) by treatment with tert-BuOK in THF. 7: yield; 39.8%, bp 95-97°/24mmHg. IR: 1575, 1565cm^{-1}(>C=C<); PMR(δ, ppm): 6.42(1H, quartet, J=1.1, H-4), 2.32(3H, d, J=1.1, -CH$_3$); CMR(δ, ppm): 136.95(C-5), 124.86(C-4), 122.71(C-3), 120.72(C-2), 15.70(-CH$_3$); MS(m/z): 166(M$^+$). The product 5a was converted into 3-phenylthio-5,6-dichloro-3,4-dihydro-2H-thiopyrane (8) by treatment with phenylthiolate in EtOH. 8: yield; 50.5%, bp 105-107°/ 0.1mmHg. IR: 1605, 1585cm^{-1}(>C=C<); PMR(δ, ppm): 7.05-7.60(5H, m, aromatic protons), 4.36(1H, nonet, J=7&6, H-3), 2.77-3.35(4H, m, H-2 and H-4); MS(m/z): 276(M$^+$).

Similarly, the products, 3b, 3c, 4b, 4c, and 5b gave spectral data consistent with their structures. Preparation of these is significant since these compounds would be difficult to synthesize otherwise.

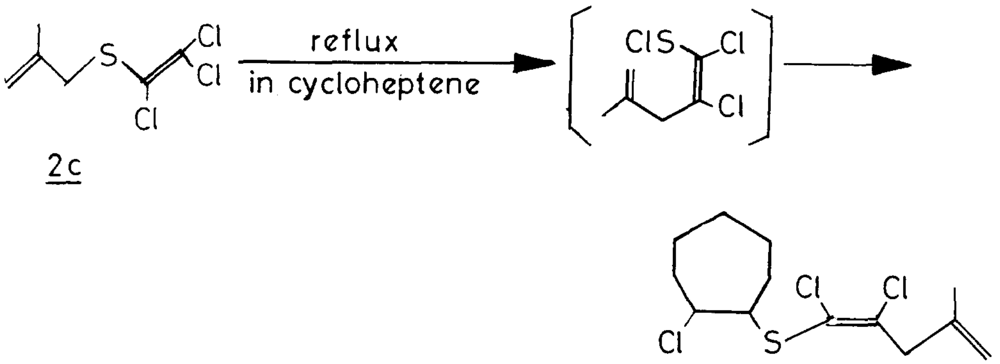
The most likely mechanism for the reaction of 1 and 2 can be depicted as illustrated in Scheme 1. Both the reactions are initiated by [3,3]sigmatropic rearrangement to form a chlorinated thiocarbonyl compound (9), which is unstable and susceptible to release of β-chlorine as anion. Between the reactions of 1 and 2 the recombination process of the chlorine anion is different each other, as illustrated in Scheme 1.

Scheme 1



In the case of 1 (X=H), desulfurization through chlorine migration and thiiran formation occurs succesively to give 3. Susceptibility of thiirans to desulfurization has been known in several papers.[3] On the other hand in the case of 2 (X=Cl), a succeeding formation of sulfenyl chloride (10) proceeds and then its intramolecular addition leads to the formation of 4 and 5. Intermediacy of the sulfenyl chloride 10 was comfirmed by trapping this as an adduct of cycloheptene.

In cycloheptene 2c was heated under reflux. By this reaction 2-chlorocycloheptanyl 1,2-dichloro-4-methyl-1,4-pentadienyl sulfide (11) was obtained as a liquid, yield, 42.6%, bp 133-135°/0.3mmHg. IR: 1645, 1565cm^{-1} ($>C=C<$); PMR(δ, ppm): 4.65-5.05(2H, m, $=CH_2$), 4.10-4.45(1H, m, cycloheptanyl H-2), 3.60-3.95(1H, m, cycloheptanyl H-1), 3.32(2H, s, $-CH_2-$), 1.40-2.40(13H, m, $(-CH_2-)_5$ and $-CH_3$); MS(m/z): 312(M^+). This would be a strong evidence supporting the above mechanism.



2c

11

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