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NEW REARRANGEMENTS OF THE ADDUCTS FORMED FROM ALLENES AND BENZENESELENENYL HALIDES

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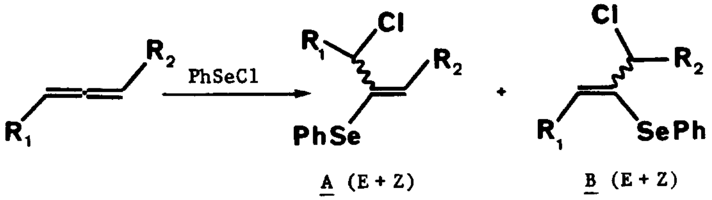
Addition products arising from the reaction of benzeneselenenyl halides and allenes undergo rearrangements and/or isomerizations which are dependent on the substitution pattern of the allenes, the nature of the halogen atom and on experimental conditions. In some cases, this makes possible the transformation of a mixture into a single product.

In the course of our work on selenium stabilized allylic carbenium ions we needed as precursors different vinyl selenides bearing chlorine or bromine in allylic position. Such compounds can be prepared by the addition of benzeneselenenyl halides to allenes. Up to date only the reaction of PhSeCl with allenes has been described [1-3] and the observed products are outlined in (Eq. 1).

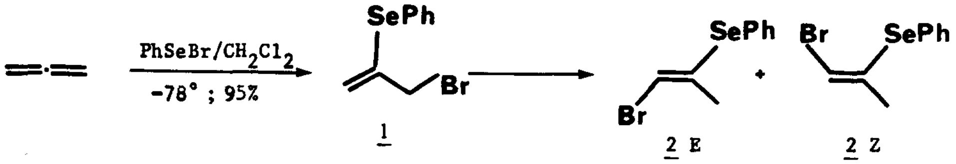


(1)

In the light of the well documented occurance of kinetic and/or thermodynamic control of the reaction of electrophilic selenium reagents with C-C double and triple bonds [4,5], it is remarkable that the sole isomerization reported [1,2] for compounds A and B is the E → Z interconversion. We found that yet unreported adducts obtained from benzeneselenenyl bromide and allenes could undergo isomerization of the type A ⇌ B. Rather surprisingly some of these adducts also produced compounds in which both bromine and the selenyl moiety are vinylic as exemplified in the Scheme. These isomerizations greatly affect the way in which the adducts can be used in subsequent synthetic work.

We report in this letter some of our observations on new rearrangements and isomerizations we discovered in this field. Some of them take place spontaneously, others require acid catalysis.

Benzeneselenenyl bromide reacts instantly (CH_2Cl_2 ; -78°) with 1,2-propadiene [6] to produce 2-phenylseleno-3-bromo-1-propene 1 in 95% yield. This compound underwent isomerization to 2-phenylseleno-1-bromo-1-propene 2 in various conditions as indicated in the Scheme.

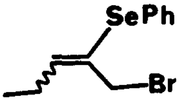


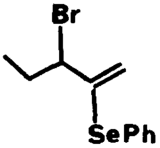
Conditions (all at room temperature)		Time (hrs)	% conversion 1 → 2	E/Z
a)	CH_3NO_2	2	17	35/65
		24	84	77/23
		48	91	80/20
b)	CH_3NO_2 dried 48 hrs over Na_2CO_3	24	85	78/22
c)	CH_3NO_2 and Na_2CO_3 in suspension	24	0	-
d)	$CDCl_3$	48	0	-
e)	$CDCl_3/10^{-3}M\ CF_3COOH$	15	17	28/72
		50	36	30/70
		100	53	40/60
		170	70	52/48
		235	85	72/28
f)	$CDCl_3/2\times10^{-3}M\ CF_3COOH$	24	47	35/65
		47	63	40/60
		80	70	47/53

Assignment of stereochemistry for 2 was made by proton NMR and by comparison with authentic [7] 2E which shows a methyl signal at 2.08 ppm in CCl_4, while the corresponding methyl signal of 2Z appears at 1.76 ppm. Since the transformation 1 → 2 is completely inhibited by the presence of sodium carbonate(Scheme, entry c) and the rate of reaction seems to increase proportionally with the acid concentration (Scheme, entries d, e, f), this isomerization appears to be an acid catalyzed prototropic rearrangement [8]. It is interesting to note that at early stages of the reaction the 2Z isomer is formed predominantly. As the reaction proceeds, the E/Z ratio is progressively inverted until the 80/20 composition is reached. The same E/Z ratio is obtained in the presence of trifluoroacetic acid when starting from the pure 2E isomer.

It is also noteworthy that the chloro analog of 1 did not rearrange when heated to 80° for 48 h in nitromethane and in carbon tetrachloride with or without acid catalyst. However, it did rearrange partially during distillation (B_{p15} : 65°).

Adducts 3 and 4 (3/4 = 60/40) [9] obtained from 1,2-pentadiene (Ether/20°/1h)


3 (E + Z)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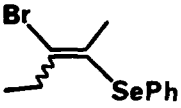
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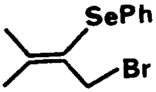
behaved differently since 4 isomerized into 3 even in CCl_4 at 0°. At room temperature 3/4 = 87/13 after 100 hrs and > 95% after 8 days. The same isomerization proceeds much faster in chloroforme it is essentially complete after 60 hrs at 20°. However, under these conditions a small amount of compound 5 can be detected (methyl signal at 1.8 ppm).

Adducts 6 and 7 formed from 3-methyl-1,2-butadiène (Ether,30°, 6/7 = 92/8)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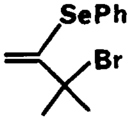
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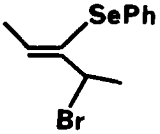
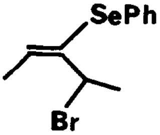
did not undergo any other rearrangement than 7 → 6 (pure, 20°, complete in 5 days).

Finally, addition of benzeneselenenyl bromide to 2,3-pentadiene (Ether, 0°) led to a mixture of 8E and 8Z (E/Z = 25/75) [10] very similar to that reported for the chloro-analogs [2].


8E


8Z

These derivatives undergo E → Z isomerization in $CDCl_3$ (nearly complete in 60 h at room temperature), but the Z isomer thus obtained is not subject to the allyl bromide → vinyl bromide rearrangement analogous to 1 → 2 in the same conditions.

These results show that the kind of rearrangement and/or isomerization which take place in the above type of compounds is greatly dependent on the alkyl substituents, the nature of the halogen atom as well as on the experimental conditions. Suitable combination of these factors should allow in favorable cases, to obtain specific regioisomers without cumbersome purification.

The structures of the above compounds have been ascertained by spectroscopic (^{1}H and ^{13}C NMR) means as well as by exact mass measurements [11].

REFERENCES AND NOTES

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5. G.H. Schmid in "The Chemistry of the Carbon-Carbon Triple Bond", p. 313 ; Ed. S. Patai, Wiley Interscience, New York (1978).

6. 1,2-propadiene was prepared according to H.N. Cripps and E.F. Kiefer, Organic Syntheses, Coll. Vol. V, p. 22, J. Wiley and Sons, New York (1973).
Alkylsubstituted allenes were prepared from the corresponding gem-dibromo cyclopropane derivatives, see L. Skattebol, Acta Chem. Scand., **17**, 1683 (1963) ; T.J. Logan, Tetrahedron Lett., 173 (1961) ; W.R. Moore and H.R. Ward, J. Org. Chem., **27**, 4179 (1962).

7. This was obtained by addition of PhSeBr to propyne ($CH_2Cl_2/Na_2CO_3/0°$)[5]. Although the sample of propyne used did not contain any 1,2-propadiene, the addition product contained various amounts (depending on the conditions) of **1** together with **2E**. At -78°, the reaction exclusively yielded **2E** very slowly. In the presence of suspended Na_2CO_3, the ratio of **2E**/**1** could be optimized to 92/8.

8. W.H. Mueller and P.E. Butler, J. Org. Chem., **33**, 1533 (1968).

9. In this case, the **3E**/**3Z** ratio could not be determined because of the limited stability of the compounds and the partial overlap of the vinylic proton signals.

10. Stereochemical assignment was made in analogy with the chloro compounds, ref. 2.

11. Spectral data are as follows :

1 ^{1}H NMR(CCl_4,δ/TMS) : 3.96(s,2H) ; 5.39(s,1H) ; 5.87(s,1H) ; 7.20 and 7.45 (m,5H)
^{13}C NMR ($CDCl_3$,δ/TMS) : 35.98(-$\underline{C}H_2$Br) ; 122.40(=$\underline{C}H_2$) ; 128.08, 129.28, 134.26(-Se$\underline{C}_6H_5$);
132.80 and 137.24 (quaternary carbons)
m/e calc. 275.90532, found 275.905 ± 0.005

2E ^{1}H NMR(CCl_4,δ/TMS) : 2.04(s,3H) ; 6.36(bs,1H) ; 7.24 and 7.44 (m,5H)
^{13}C NMR ($CDCl_3$,δ/TMS) : 22.59(-$\underline{C}H_3$) ; 106.19 (=$\underline{C}$HBr) ; 127.92,129.33,133.50(-Se$\underline{C}_6H_5$) ;
130.68 (quaternary carbon)
m/e calc. 275.90532, found 275.905 ± 0.005

2Z ^{1}H NMR(CCl_4,δ/TMS) : 1.78(s,3H) ; 6.22(bs,1H) ; 7.20 and 7.50 (m,5H)

3 E + Z ^{1}H NMR(CCl_4,δ/TMS) : 1.00 and 1.03 (t,J = 7Hz,3H) ; 2.28(quint. J = 7Hz,2H) ;
4.03(s,2H) ; 6.08 and 6.22 (t,J = 7Hz,1H) ; 7.20 and 7.40(m,5H)
m/e calc. 303.93662, found 303.936 ± 0.006

4 ^{1}H NMR (CCl_4,δ/TMS) : 1.03(t,J = 7Hz,3H) ; 2.02 (quint. J = 7Hz,2H) ; 4.45(t,J = 7Hz,1H) ;
5.17(s,1H) ; 5.83(s,1H) ; 7.20 and 7.40(m,5H)

6 ^{1}H NMR(CCl_4,δ/TMS) : 1.98(s,3H) ; 2.07(s,3H) ; 4.24(s,2H) ; 7.22 and 7.40(m,5H)
^{13}C NMR($CDCl_3$,δ/TMS) : 20.75 and 26.00($\underline{C}H_3$-) ; 35.98(-$\underline{C}H_2$Br) ; 126.68,129.00,131.60
(-Se$\underline{C}_6H_5$) ; 146.07(Me$_2\underline{C}$=) ; 121.96 and 130.36 (other quaternary carbons)
m/e calc. 303.95662, found 303.936 ± 0.006

8Z ^{1}H NMR (CCl_4,δ/TMS):1.78(d,J = 7Hz,6H) ; 4.71(q,J = 7Hz,1H) ; 6.39(q,J = 7Hz,1H) ;
7.14 and 7.28(m,5H)
m/e calc. 303.93662, found 303.936 ± 0.006.

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