Tetrahedron Letters No. 17, pp 1493 - 1496, 1978. Pergamon Press. Printed in Great Britain.

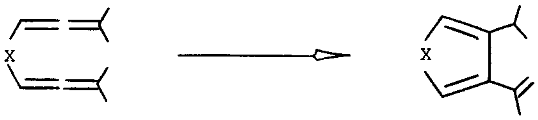
CYCLOAROMATIZATION OF BRIDGED DIALLENES: MECHANISTIC STUDY

S. Braverman* and Y. Duar
Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel

(Received in UK 17 February 1978; accepted for publication 9 March 1978)

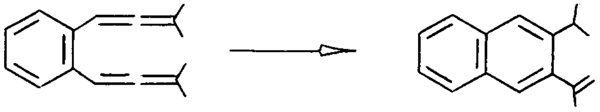
Recently, we have reported on the cycloaromatization of several bridged diallenic systems, 1, 3, 7.[1] This previous work, as well as the present one, concern bridged diallenes in which the bridge contributes an aromatic character, and consequently an extra driving force for the cyclization. The methyl substituents give rise to a possibility of an ene reaction, which does not exist in the case of the unsubstituted diallenic systems.[2]

The bis-γ,γ-dimethylallenyl sulfide 1 and ether 3 were undetectable under the reaction conditions, and were converted by spontaneous cycloaromatization to 3-isopropenyl-4-isopropylthiophene 2 and furan 4, respectively. In contrast, the o-bis(γ,γ-dimethylallenyl) benzene 7 was isolated and identified. We have now also succeeded in preparing and isolating the bis-γ,γ-dimethylallenyl selenide 5.[3]



1 X = S
3 X = O
5 X = Se

2 X = S
4 X = O
6 X = Se



7

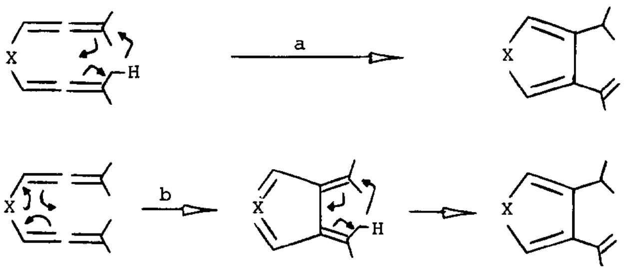
8

Furthermore, the transformation of the selenide 5 to the selenophene derivative[3] 6, as well as the transformation of 7 to the naphthalene derivative 8, proceeded at a measurable rate at room temperature in pentane or chloroform and in quantitative yield (100%).

The synthesis of 1-4, 7, 8 was reported earlier[1b,c]. The diallenyl selenide 5 was obtained by a S_N2' type reaction of Na_2Se, which was prepared by sodium in liquid ammonia with metallic selenium,[4] on α,α-dimethylpropargyl bromide in THF at room temperature under nitrogen[5] (25% yield). It is interesting to note that Na_2S under the same conditions and in various solvents, failed to give the analogous diallenyl sulfide 1 or thiophene 2.

There are three possible mechanisms which can be related to the cycloaromatization of diallenes 1, 5: an ionic mechanism, an intramolecular ene reaction (mechanism a) or a two step process involving an electrocyclic six-electron reaction in the first step followed by 1,5 hydrogen shift (mechanism b, Scheme I).

Scheme I



X = Se, S

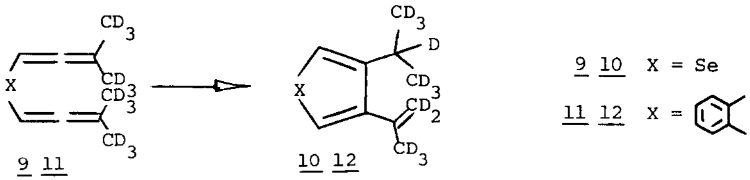
A kinetic study on the cyclization of the diallenyl selenide 5 in various solvents, indicated that the rate of the rearrangement was practically insensitive to the change in the ionizing power of the solvent (Table I). These results eliminate the possibility of an ionic mechanism and are reminiscent of the results obtained by Kiefer.[6] Thus there remain only the two other alternatives as shown in Scheme I.

In order to obtain more information on this rearrangement, the bis-γ,γ-dimethyl-d_6-allenyl selenide[3] 9 was synthesized from α,α-dimethyl-d_6-propargyl bromide[3] which was prepared by condensation of lithium monoacetylide[7] with acetone-d_6, followed by bromination with PBr_3.

Table I Rate Constants[a] for the Rearrangement of Selenide 5 to Selenophene 6 (k_H), and Selenide 9 to Selenophene 10 (k_D)

Solvent	Temp °C	$10^5 k_H$, sec^{-1} [b]	$10^5 k_D$, sec^{-1} [b]	k_H/k_D
Carbon Tetrachloride	30	1.229 ± 0.090	1.134 ± 0.013	1.08
Chloroform-d_1	30	1.446 ± 0.009	1.410 ± 0.026	1.02
Acetone-d_6	30	1.359 ± 0.030		

a. Determined by nmr b. [diallene] = 0.45 -0.9M



9 11 → 10 12

9 10 X = Se

11 12 X =

The rate constants for the thermal cyclization of selenide 9 to selenophene 10 were determined and are presented in Table I. These rate constants give isotope effects (k_H/k_D) of 1.08 in carbon tetrachloride, and 1.02 in chloroform (Table I). Bearing in mind that in an ene reaction the hydrogen shift occurs in the rate determining step, as it does in 1,5 hydrogen shifts, and since considerably higher isotope effects have been found for the latter, *e.g.* 12.2 (25°C) and 5.15 (27°C)[8], we must conclude that the cyclization mechanism is a two step process involving intramolecular formation of the quinodimethane-type intermediate in the first slow step, followed by a fast hydrogen transfer in the second (mechanism b, Scheme I).

A kinetic study of the cyclization of the diallenyl benzene (7 → 8) has also been done, and as in the case of the selenide 5, there was no effect of the solvent ionizing power on the reaction rate (Table II). Consequently, the two different mechanisms shown in Scheme II, which parallel those suggested above for the selenide system, should be considered.

Scheme II

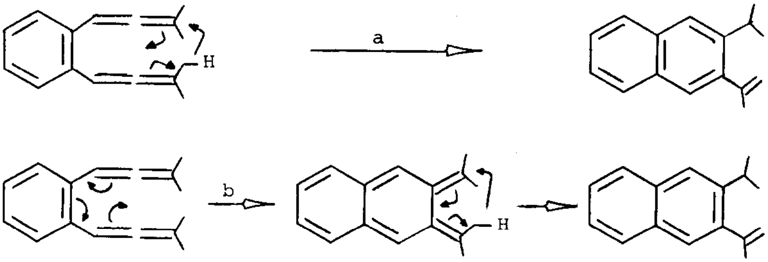


Table II Rate Constants[a] for the Rearrangement of Diallenylbenzene 7 to Naphthalene 8 (k_H), and Diallenylbenzene 11 to Naphthalene 12 (k_D)

Solvent	Temp °C	10^5k_H, sec^{-1} [b]	10^5k_D, sec^{-1} [b]	k_H/k_D
Carbon Tetrachloride	30	7.625 ± 0.188	7.753 ± 0.289	0.98
Chloroform-d_1	30	9.430 ± 0.244	9.386 ± 0.179	1.00
Acetone-d_6	30	8.707 ± 0.205		

a. Determined by nmr b. [diallene] = 0.45 -0.8M

It is possible to distinguish between route a and route b by means of an isotope effect. The o-bis-(γ,γ-dimethyl-d_6-allenyl) benzene[3] 11 was synthesized using the dibromocarbene method[1c], starting from o-bis-(β,β-dimethyl-d_6-vinyl) benzene[3] which was obtained by reduction of acetone-d_6 followed by bromination with HBr and Wittig reaction[1c]

The rate constants for the cylization of 11 to 12[3] were measured and the k_H/k_D values were found to be 0.98 in carbon tetrachloride and 1.00 in chloroform (Table II). Once again, as in the case of the selenide, there is no detectable isotope effect. This eliminates the possibility of a one-step ene reaction, but is compatible with route b in Scheme II.

References and Notes

1. a. Presented at the 43rd Annual Meeting of the Israel Chemical Society, Beer-Sheba, October 8-9th, 1975, see S. Braverman and Y. Duar, Abstract p.16, S. Braverman and D. Segev, Abstract p.29.
   b. S. Braverman and D. Segev, J. Am. Chem. Soc., 96, 1245 (1974).
   c. S. Braverman, Y. Duar and D. Segev, Tetrahedron Lett., 3181 (1976).
2. a. C.M. Bowes, D.F. Montecalvo and F. Sondheimer, Tetrahedron Lett., 3181 (1973).
   b. P.J. Garratt and S.B. Neoh, J. Am. Chem. Soc., 97, 3257 (1975).
3. All new compounds gave satisfactory elemental analysis and/or showed ir, nmr and mass spectral data in accord with the assigned structures.
4. Na_2Se was prepared by procedure similar to Na_2Te. F. Fringueli, J. Chem. Soc. Perkin Trans. I, 199 (1972).
5. G. Pourcelot and P. Cadiot, Bull. Soc. Chim. France, 3016 (1966).
6. E.F. Kiefer and M.Y. Akamura, J. Am. Chem. Soc., 90, 4187 (1968).
7. M.M. Midland, J. Org. Chem. 40, 2250 (1975).
8. C.W. Spangler, Chem. Rev. 76, 187 (1976) and references cited therein.