

ELECTROPHILIC ADDITIONS TO ALLENES—II

THE REACTION OF BENZENESELENYL CHLORIDE WITH SOME 1,3-DISUBSTITUTED ALLENES

DENNIS G. GARRATT*, PIERRE L. BEAULIEU and M. DOMINIC RYAN

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada, K1N 9B4

(Received in U.S.A. 10 May 1978; received in revised form in U.S.A. 3 July 1978)

Abstract—Benzeneselenenyl chloride reacts with 1,3-dialkyl-substituted allenes in methylene chloride solution to give 1:1-adducts. Attack by selenium is found to occur exclusively at the central allenic carbon. In contrast to the analogous reaction of arenosulphenyl chlorides, the preferential formation of the *Z*-alkene is observed. A mechanism involving the preequilibrium formation of alkylideneseleniranium ions and/or alkylideneepiselenuranes which, in the product-determining step, collapse to products via an anti attack of chloride at the methine carbon of the ring is proposed to account for the preferential formation of the *Z*-isomers.

In a previous study we observed that 2,4-dinitrobenzenesulphenyl chloride reacts with 1,3-disubstituted allenes; preferentially forming the *E*-alkene with exclusive attack by the arylthio moiety on the central allenic carbon.¹ The ratio of *E*- to *Z*-alkene was found to increase as the bulk of the substituent group *cis* to the arylthio group increased. These results were interpreted in terms of steric approach control² leading to the formation of a series of alkylidenethiiranium ions³ or alkylideneepisulphuranes,⁴ in accord with the stereoselectivity previously reported by Jacobs *et al.*⁵

These observations are in contrast to those of others for the related halogenation⁶ and methoxymercuration⁷ reactions with 2,3-pentadiene which showed a preference for the formation of the *Z*-alkene. Bromination studies carried out by Caserio *et al.*⁸ with optically active 2,3-pentadiene, and by Bach *et al.*⁹ with optically active 1,2-cyclononadiene, have led to the proposal of a mechanism involving, asymmetric alkylidenebromiranium ions. Approach of the nucleophile *trans* to the bromine bridge is expected to be less sterically hindered by the substituents at the vinyl terminus of the *Z*-alkylidenebromiranium ion than in the case of the analogous *E*-isomer. If one assumes that the reaction involves a preequilibrium formation of the alkylidenebromiranium ions, preferential formation of the *Z*-alkene is readily accounted for by the Curtin-Hammett principle.

Use of the leitmotif of organic chemistry that "like substances react similarly and that similar changes in structure produce similar changes in reactivity" has often been invoked in discussion of electrophilic additions involving sulphenyl and selenenyl halides, despite the lack of definitive data.¹⁰ It was of interest, therefore, to investigate the factors affecting the nature of the products from the addition of areneseelenenyl chlorides to allenes under conditions similar to those utilized during the previous investigation.

RESULTS

We have carried out the reaction of benzeneselenenyl chloride with nine 1,3-disubstituted allenes, 1–9, at ambient temperature using methylene chloride as solvent. The kinetically controlled product distributions

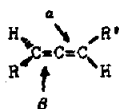
| | RCH=C=CHR ¹ | |
|---|--|---|
| | R | R ¹ |
| 1 | CH ₃ | CH ₃ |
| 2 | CH ₃ | C ₂ H ₅ |
| 3 | CH ₃ | <i>i</i> -C ₃ H ₇ |
| 4 | CH ₃ | <i>t</i> -C ₄ H ₉ |
| 5 | C ₂ H ₅ | C ₂ H ₅ |
| 6 | <i>i</i> -C ₃ H ₇ | <i>i</i> -C ₃ H ₇ |
| 7 | <i>t</i> -C ₄ H ₉ | <i>t</i> -C ₄ H ₉ |
| 8 | -(CH ₂) ₆ ⁻ | |
| 9 | -(CH ₂) ₁₀ ⁻ | |

(Table 1) were determined by immediate ¹H NMR analysis of the reaction mixture. Analysis of the respective ¹H, ¹³C NMR spectra and the mass spectral fragmentation patterns using criteria previously established for the analogous sulphur compounds indicates that the 1:1-adducts were formed via regiospecific attack of the phenylseleno moiety on the central allenic carbon.¹ With the exception of 2,2,6,6-tetramethyl-3,4-heptadiene, 7, and 1,2-cyclononadiene, 8; mixtures of *E*- and *Z*-alkenes were observed. Spectral parameters are summarized in Tables 2–4. In every case it was possible to find at least one non-overlapping signal from which the isomer distributions could be calculated.

For example, the addition of benzeneselenenyl chloride to 5,5-dimethyl-2,3-hexadiene, 4, is found to yield four products: 20, 21, 22 and 23 in the relative proportions of 7:70:9:14, respectively. Compounds 20 and 21 both exhibit quartets in the vinyl region of their ¹H NMR spectra: δ 5.88 and 6.47, respectively, and singlets for the methine protons geminal to chlorine: δ 4.92 and 4.51, respectively. These species must therefore arise from attack on the double bond to which the Bu

*Address correspondence to this author: Division of Chemistry, National Research Council of Canada, Ottawa, Canada, K1A 0R6.

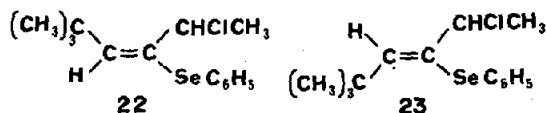
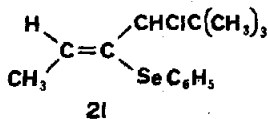
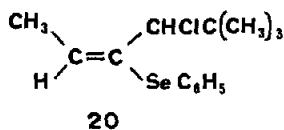
Table 1. Kinetically controlled product distributions for the reaction of benzeneselenenyl chloride with a series of 1,3-disubstituted allenes in methylene chloride



| Symmetric Allenes | | Ratio of Isomers | |
|-------------------------------------|--|------------------|-----|
| H = R' | | E : Z | |
| CH ₃ | | 26 | 74 |
| C ₂ H ₅ | | 40 | 60 |
| 1-C ₃ H ₇ | | 36 | 64 |
| t-C ₄ H ₉ | | 0 | 100 |
| -(CH ₂) ₆ - | | 100 | 0 |
| -(CH ₂) ₁₀ - | | 36 | 64 |

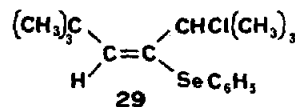
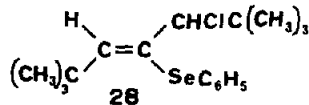
| Asymmetric Allenes | | α/β | E : Z ^a | E : Z ^{β} |
|--------------------|---------------------------------|----------------|--------------------|-------------------------------------|
| R | R' | | | |
| CH ₃ | C ₂ H ₅ | 33 : 67 | 27 : 73 | 30 : 70 |
| CH ₃ | 1-C ₃ H ₇ | 56 : 44 | 30 : 70 | 43 : 57 |
| CH ₃ | t-C ₄ H ₉ | 76 : 24 | 9 : 91 | 39 : 61 |

group is bonded. Based on the relative shieldings of the vinyl and methine protons; the relative shielding of the methine carbons bonded to chlorine;¹¹ and the magnitude of the vicinal carbon-proton coupling constants $^3J_{CC-CH} = J_{1,3}$ (Table 4)¹² we have assigned **20** and **21** as *E* and *Z*-4-chloro-5,5-dimethyl-2-hepten-3-yl phenyl selenide. Similarly one can assign **22** and **23** as *E*- and *Z*-2-chloro-5,5-dimethyl-3-hepten-2-yl phenyl selenide; the adducts from attack on the double bond to which the Me group is bound.



The reaction of benzeneselenenyl chloride with 2,2,6,6-tetramethyl-3,4-heptadiene was quite slow compared to the other allenes investigated at this time. A single product **28** was isolated as determined by ¹H NMR and i.r.¹³ The ¹H NMR spectrum of **28** consisted of two singlets at δ 1.27 and 1.07 ppm, each integrating at nine protons, and two doublets; $^4J_{HC-CCH} = 0.82$ Hz, at σ 6.67 and 4.30 ppm, each integrating at one proton, assigned to an olefinic proton and a proton geminal to chlorine. The magnitude of $^4J_{HC-CCH}$ and the difference in chemical shifts observed for the methine carbons compared to

20-23 suggests that **28** has the *Z*-configuration.¹⁴ This is supported by the observation of $^3J_{HC-CSe}$ (*trans*) = 3.4 Hz. The chemical shift of the methine carbon bonded to chlorine, δ 76.0, corresponds very well with the analogous carbon compound **21**, δ 77.3, confirming the assignment. Further support for the orientation is obtained from the mass spectrum of **28**, which in addition to a strong molecular ion cluster¹⁵ at *m/e* 344 (calcd. 343.803 C₁₇H₂₅SeCl) gave a strong ion cluster at *m/e* 239 corresponding to α -cleavage followed by loss of a C₄H₈ fragment to give an ion at *m/e* 183 (H₂C=C=SeC₆H₅⁺) which loses acetylene to give the phenylseleno cation-radical at *m/e* 157. A second fragmentation mode corresponded to the initial loss of a C₄H₈ fragment (possibly as methylpropene) to give an ion at *m/e* 288 followed by loss of a chloromethylene (CH₂Cl·) radical to give the *m/e* 239 ion. No evidence of the corresponding *E*-alkene **29** was found under our reaction conditions.¹¹

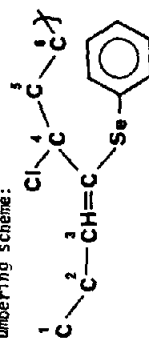


Verification of kinetic control under our reaction conditions is given by the observation of a slow isomerization of the *E*-alkenes to the corresponding *Z*-alkene over a period of a few weeks. Thus compound **24** was observed to isomerize essentially completely to **25** at room temperature in methylene chloride-d₂, probably by way of the allylic ion intermediates **33** and **34**.

Table 2. The observed proton magnetic resonance parameters for the products of addition of benzeneselenenyl chloride to some 1,3-disubstituted allenes

| R | R' | Configuration | Adduct Number | H_1 | $J_{1,2}$ | H_2 | $J_{2,3}$ | H_3 | $J_{3,4}$ | H_4 | $J_{4,5}$ | H_5 | $J_{5,6}$ | H_6 |
|---------------------------------|---------------------------------|---------------|---------------|-------|-----------|---------|-----------|---------|-----------|----------|-----------|----------|-----------|--------|
| CH ₃ | CH ₃ | E | <u>10</u> | | | 1.79 d | 7.25 | 6.01 q | ≤0.3 | 5.12 q | 6.75 | 1.61 d | | |
| | | Z | <u>11</u> | | | 1.83 d | 6.75 | 6.46 qd | 0.9 | 4.65 qdq | 6.75 | 1.63 d | | |
| C ₂ H ₅ | C ₂ H ₅ | E | <u>24</u> | | | 2.24 dq | 7.4 | 5.72 t | ≤0.2 | 4.71 t | 7.3 | 1.96 ddq | 7.2 | 0.96 t |
| | | Z | <u>25</u> | | | 2.32 dq | 6.9 | 6.29 td | 1.6 | 4.31 tm | 6.4 | 1.98 ddq | 7.2 | 0.96 t |
| t-C ₃ H ₇ | t-C ₃ H ₇ | E | <u>26</u> | | | 2.31 h' | 10.0 | 5.62 dd | 0.2 | 4.54 dd | 9.8 | 2.9 m | | |
| | | Z | <u>27</u> | | | 2.36 h' | 9.2 | 6.16 dd | 1.0 | 4.27 dd | 5.6 | 2.9 m | | |
| t-C ₄ H ₉ | t-C ₄ H ₉ | Z | <u>28</u> | | | 1.27 s | | 6.67 d | 0.82 | 4.30 d | | | | 1.06 t |
| | | E | <u>30</u> | | | 2.0 m | 8.8 | 5.90 t | ≤0.2 | 5.25 dd | 10.6 | 2.3 m | | |
| | | E | <u>31</u> | | | | | 9.5/5.5 | 5.83 dd | ≤0.2 | 4.92 dd | 9.2/5.8 | | |
| | | Z | <u>32</u> | | | | | 7.0 | 6.31 t | | 4.53 dm | 8.0/5.5 | | |
| CH ₃ | C ₂ H ₅ | E | <u>12</u> | | | 1.80 d | 7.0 | 5.99 q | ≤0.2 | 4.67 t | 7.2 | 2.2 m | 7.2 | 0.96 t |
| | | Z | <u>13</u> | | | 1.87 d | 6.7 | 6.43 qd | 1.0 | 4.43 dd | 6.8/6.7 | 2.2 m | 7.2 | 0.96 t |
| C ₂ H ₅ | CH ₃ | E | <u>14</u> | | | 2.2 m | 7.5 | 5.97 t | ≤0.2 | 5.14 q | 6.6 | 1.63 d | | |
| | | Z | <u>15</u> | | | 2.2 m | 6.8 | 6.36 t | ≈0.5 | 4.66 qm | 7.0 | 1.67 d | | |
| CH ₃ | t-C ₃ H ₇ | E | <u>16</u> | | | 1.76 d | 7.0 | 5.83 q | | 4.58 d | 8.5 | 2.3 m | | 1.23 s |
| | | Z | <u>17</u> | | | 1.88 dd | 6.7 | 6.41 q | | 4.31 dm | 6.5 | 2.3 m | | 1.06 s |
| t-C ₃ H ₇ | CH ₃ | E | <u>18</u> | | | 2.3 m | 10.0 | 5.78 d | | 5.73 q | 6.6 | 1.63 d | | |
| | | Z | <u>19</u> | | | 2.3 m | 9.0 | 6.16 d | | 4.55 qm | 7.0 | 1.65 d | | |
| CH ₃ | t-C ₄ H ₉ | E | <u>20</u> | | | 1.73 d | 6.8 | 5.88 q | | 4.92 s | | | | 1.23 s |
| | | Z | <u>21</u> | | | 1.78 d | 7.0 | 6.47 q | | 4.51 s | | | | 1.06 s |
| t-C ₄ H ₉ | CH ₃ | E | <u>22</u> | | | 1.27 s | | 6.07 s | | 5.19 q | 7.0 | 1.58 d | | |
| | | Z | <u>23</u> | | | 1.13 s | | 6.65 s | | 4.49 q | 7.0 | 1.63 d | | |

numbering scheme:



all chemical shifts are reported ppm relative to internal TMS in CDCl₃
 s = singlet; d = doublet; q = quartet; q' = quintet; h' = heptet; m = multiplet; dd = doublet of doublets;
 qd = quartet of doublets; td = triplet of doublets; qdd = quartet of doublets; t = triplet;
 dq' = doublet of quintets; qm = quartet of multiplets; dm = doublet of multiplets; tm = triplet of multiplets;
 ddm = doublet of doublets of multiplets; ddq = doublet of doublets of quartets.
 *NB: It was not possible to assign all protons, particularly the isopropyl methyl doublets for compounds 16-19, 26 & 27.

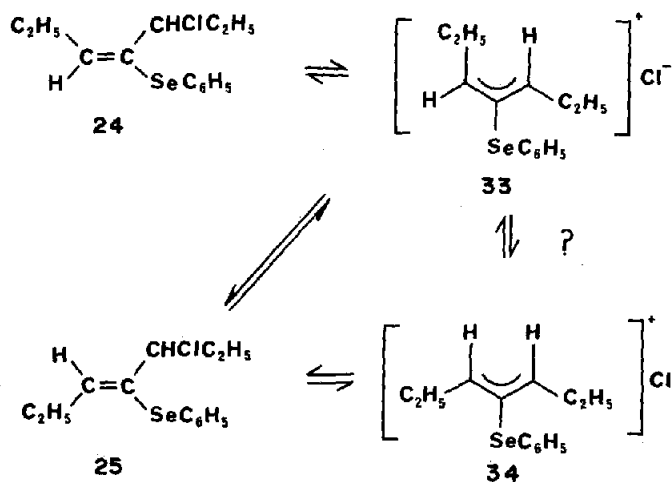


Table 3. The observed Carbon-13 magnetic resonance parameters for the products of addition of benzeneselenenyl chloride to some 1,3-disubstituted allenes

| RCH=C(SePh)CHClR' | | Configuration | Adduct Number | C ₁ | C ₃ | C ₄ | C ₅ | C ₆ | C ₇ | C ₈ | C ₉ |
|---------------------------------|------------------------------------|---------------|---------------|----------------|-----------------|-----------------|----------------|----------------|----------------|----------------|----------------|
| R | R' | | | | | | | | | | |
| CH ₃ | CH ₃ | E | <u>10</u> | | 56.0 | 24.8 | | | | | 15.2 |
| | | Z | <u>11</u> | | 63.0 | 25.2 | | | | | 17.7 |
| C ₂ H ₅ | C ₂ H ₅ | E | <u>24</u> | 143.3 | 62.6 | 31.4 | 11.5 | | | 13.7 | 23.0 |
| | | Z | <u>25</u> | 142.7 | 69.5 | 31.1 | 11.1 | | | 13.3 | 25.5 |
| i-C ₃ H ₇ | i-C ₃ H ₇ | E | <u>26</u> | 147.7 | 68.3 | 34.3 | 20.7 | | | 22.4 | 29.1 |
| | | Z | <u>27</u> | 148.2 | 73.9 | 33.1 | 20.4 | | | 22.4 | 31.7 |
| t-C ₄ H ₉ | t-C ₄ H ₉ | Z | <u>28</u> | 149.3 | 76.0 | 34.2 | 17.2 | | | 27.5 | 31.7 |
| | | E | <u>30</u> | 136.5 | 61.1 | 37.5 | 26.5 | 25.9 | 24.1 | 27.9 | 29.6 |
| | -(CH ₂) ₆ - | E | <u>31</u> | 143.4 | 59.8 | 37.7 | 28.1 | 27.2 | 26.7 | 27.7 | 31.1 |
| | | Z | <u>32</u> | 143.0 | 66.7 | 36.9 | 27.9 | 27.0 | 25.8 | 27.4 | 31.0 |
| CH ₃ | C ₂ H ₅ | E | <u>12</u> | | 62.4 | 31.4 | 11.5 | | | | 15.3 |
| | | Z | <u>13</u> | 135.9 | 69.9 | 31.2 | 11.3 | | | | 17.9 |
| C ₂ H ₅ | CH ₃ | E | <u>14</u> | 143.9 | 56.2 | 25.4 | | | | 13.7 | 23.0 |
| | | Z | <u>15</u> | 141.9 | 62.9 | 25.2 | | | | 13.3 | 25.4 |
| CH ₃ | i-C ₃ H ₇ | E | <u>16</u> | 134.7 | 66.5 | 34.8 | 20.0 | | | | 15.4 |
| | | Z | <u>17</u> | 136.1 | 74.6 | 33.3 | 19.7 | | | | 17.1 |
| i-C ₃ H ₇ | CH ₃ | E | <u>18</u> | 149.9 | 56.7 | 25.4 | 20.9 | | | 21.3 | 31.6 |
| | | Z | <u>19</u> | 147.1 | 62.6 | 25.3 | 17.9 | | | 21.1 | 31.3 |
| CH ₃ | t-C ₄ H ₉ | E | <u>20</u> | 139.9 | 70.4 | 38.1 | 27.5 | | | | 17.1 |
| | | Z | <u>21</u> | 138.6 | 77.3 | 37.7 | 27.5 | | | | 18.3 |
| t-C ₄ H ₉ | CH ₃ | E | <u>22</u> | 151.0 | 56.8 | 25.3 | | | | 28.4 | 31.2 |
| | | Z | <u>23</u> | 148.8 | 62.9 | 25.1 | | | | 27.8 | 30.7 |

all chemical shifts are reported δ ppm, with respect to internal TMS solutions were approximately 30 % w/w in CDCl₃

numbering scheme:

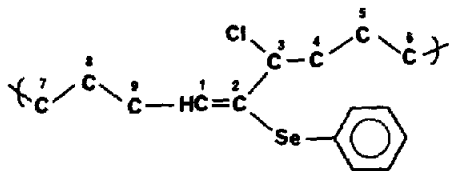


Table 4. Observed proton-Carbon-13 coupling constants (Hz)

| Adduct Number | <i>E</i> - Isomers | | Adduct Number | <i>Z</i> - Isomers | |
|---------------|--------------------|-------------|---------------|--------------------|-------------|
| | $^1J_{3,3}$ | $^3J_{3,1}$ | | $^1J_{3,3}$ | $^3J_{3,1}$ |
| <u>10</u> | 152.8 | 11.3 | <u>11</u> | 151.8 | 4.8 |
| <u>12</u> | 154.1 | 11.5 | <u>13</u> | 157.2 | 3.1 |
| <u>14</u> | 152.4 | 9.8 | <u>15</u> | 149.6 | 4.3 |
| <u>16</u> | 151.8 | 10.1 | <u>17</u> | 155.1 | 3.5 |
| <u>18</u> | 152 | 9.9 | <u>19</u> | 149.8 | 4.2 |
| <u>20</u> | | | <u>21</u> | 153.0 | 3.1 |
| <u>22</u> | | | <u>23</u> | 146.9 | 2.1 |
| <u>24</u> | 150.2 | 11.8 | <u>25</u> | 153.1 | 2.5 |
| <u>26</u> | 151.3 | 12.4 | <u>27</u> | 146.7 | 1.2 |
| | | | <u>28</u> | 153.1 | 5.2 |
| <u>30</u> | 149.4 | 8.7 | | | |
| <u>31</u> | 150.3 | 9.1 | <u>33</u> | 147.5 | 2.4 |

DISCUSSION

The addition of benzeneselenenyl chloride to allenes forms the 1:1-adducts in essentially quantitative yield. No diadducts have ever been observed. In Table 5 are compared the kinetically controlled product distributions for the additions of benzeneselenenyl chloride, benzenesulphenyl chloride and 2,4-dinitrobenzenesulphenyl chloride to our series of 1,3-disubstituted alkenes. It is quite clear that, although attack by the electrophilic portion of each reagent occurs exclusively on the central allenic carbon, the effect of alkyl groups on the product orientation and regiochemistry is quite different.

In the case of arenosulphenyl chlorides, the *E*-isomer is found to be formed, preferentially. The ratio of *E*- to *Z*-alkene increases as the bulk of the substituent group (Me < Et < *i*-Pr < *t*-Bu) *cis* to the arylthio group increases. Very little regioselectivity, with respect to which of the mutually perpendicular π bonds of the allene system is attacked, is observed, suggesting the presence of an effective mechanism for the transmission of the inductive electron donation of the alkyl groups to the remote double bond.¹⁶ Furthermore, and perhaps most surprising, one must note that the alkyl substituent on the double bond which is attacked does not affect the *E*:*Z* ratio to any degree.

In contrast to arenosulphenylation, the reaction of benzeneselenenyl chloride with the same series of 1,3-disubstituted allenes yields the *Z*-isomer preferentially or exclusively under conditions of kinetic control except for the case of 1,2-cyclononadiene, 8, which will be dealt with separately. Chemoselectivity is observed in additions to the unsymmetrically substituted allenes, in that the double bond with the most electron donating and sterically bulky substituent is preferentially attacked; the percentage of attack increasing as the electron donating ability and bulk increases (*t*-Bu > *i*-Pr > Et). In particular attack on a double bond with a Bu substituent appears to favour formation of the thermodynamically more stable *Z*-alkene. Thus attack on the double bond with a Bu substituent gives an *E*:*Z* ratio of 9:91 for 5,5-dimethyl-2,3-hexadiene, 4, and 0:100 for 2,2,6,6-tetramethyl-3,4-heptadiene, 7. The directing effect, with respect of the

E:*Z*-configuration, of a Me, Et, or Pr group appears to be essentially constant when the remote substituent is Me. Some fluctuations are apparent when the remote group is Et, Pr or Bu, but our data base is too small at this time to allow a statistically valid analysis.

The reaction of selenenyl halides with alkenes is generally considered to follow an Ad_E2 mechanism similar to that proposed for the analogous sulphenyl halides.¹⁰ It is quite clear, however, from the available data that the two reactions while superficially the same have distinctly different transition state structures in both rate and product determining steps. In general the formation of a bridged species, be it: seleniranium ion, 35, or episelenurane, 36, is believed to be rate determining; the species subsequently undergoing nucleophilic attack by the halide ion in a fast step (Scheme 1).¹⁷



The mechanistic pathway for the addition to allene and its derivatives is less clear. Second order kinetics, first order in allene and first order in selenenyl chloride have been observed for the reaction of benzeneselenenyl chloride with propadiene and its six Me substituted derivatives in methylene chloride solution.¹³ No work has, however, been reported which utilizes optically active allenes. Thus the stereospecificity of the reaction is unknown.

If one assumes a stereospecificity, at least as large as that for sulphenylation, which seems likely in view of the known propensity for *anti* stereospecific addition to simple alkenes,¹⁸ one can postulate an energy surface containing a dissymmetric intermediate such as an alkylidene-seleniranium ion, 37, or an alkylidene-episelenurane, 38. The available data, however, can not rule out the presence of alternative species, such as non-planar or resonance stabilized allylic carbonium

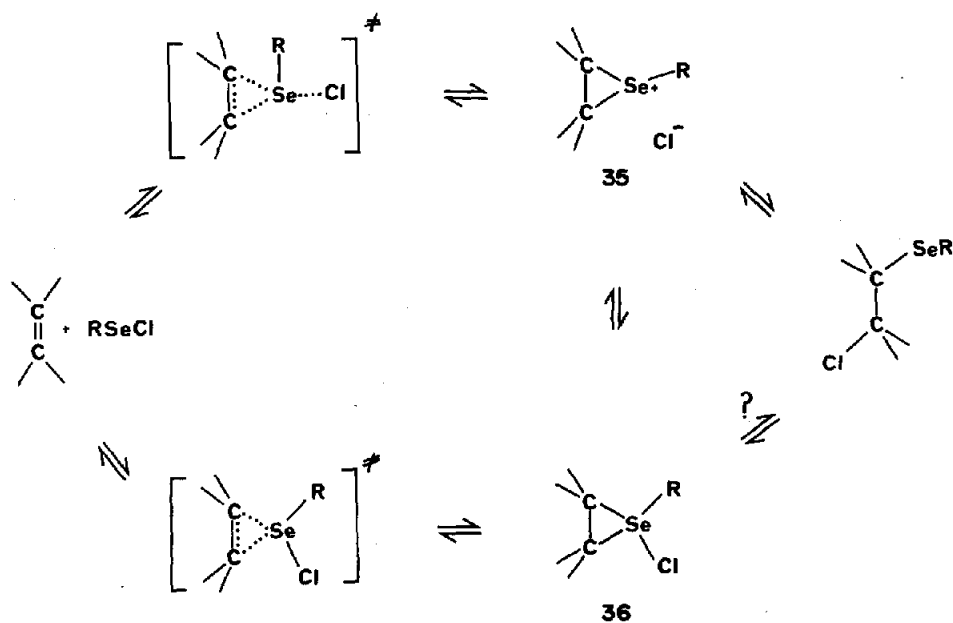
Table 5. A comparison of the kinetically controlled product distributions for the reactions of some 1,3-disubstituted allenes with benzeneselenenyl chloride, benzenesulphenyl chloride, and 2,4-dinitrobenzenesulphenyl chloride at ambient temperature (22–25°C) in methylene chloride solution

$$\begin{array}{c} \text{RCH}=\text{C}=\text{CHR}' \\ \swarrow \quad \searrow \\ \delta \quad \quad \gamma \end{array}$$

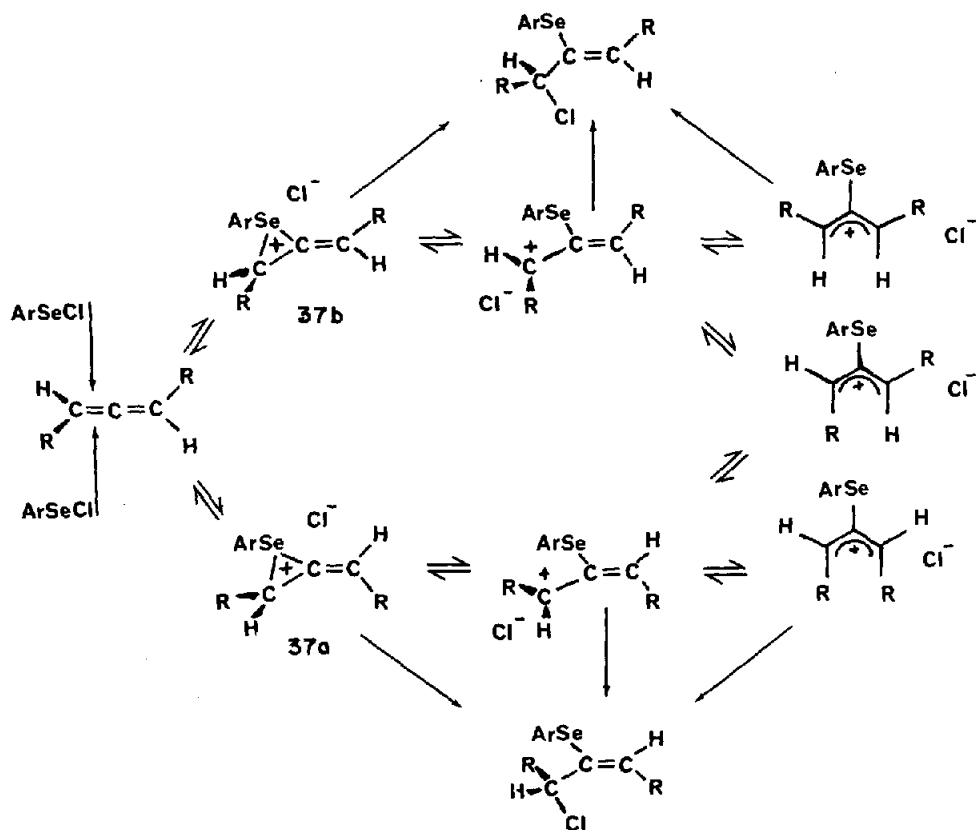
| Symmetrically Substituted Allenes | | Ratios of Isomers | | E:Z |
|-------------------------------------|--|-------------------|---------|---------|
| | | PhSeCl | ArSCl | PhSCl |
| CH ₃ | | 26 : 74 | 64 : 36 | 55 : 45 |
| C ₂ H ₅ | | 40 : 60 | 80 : 20 | 72 : 28 |
| 1-C ₃ H ₇ | | 36 : 64 | 92 : 8 | 80 : 20 |
| t-C ₄ H ₉ | | 0 : 100 | | |
| -(CH ₂) ₆ - | | 100 : 0 | 100 : 0 | 100 : 0 |
| -(CH ₂) ₁₀ - | | 36 : 64 | 86 : 13 | 81 : 19 |

| Unsymmetrically Substituted Allenes | | n/s | | |
|-------------------------------------|---------------------------------|--------------|---------|---------|
| R | R' | | | |
| CH ₃ | C ₂ H ₅ | 33 : 67 | 53 : 47 | 53 : 47 |
| CH ₃ | 1-C ₃ H ₇ | 56 : 44 | 52 : 48 | 55 : 45 |
| CH ₃ | t-C ₄ H ₉ | 76 : 24 | 42 : 58 | 59 : 41 |
| | | <u>E : Z</u> | | |
| CH ₃ | C ₂ H ₅ | 27 : 73 | 66 : 34 | 56 : 44 |
| CH ₃ | 1-C ₃ H ₇ | 30 : 70 | 65 : 35 | 57 : 43 |
| CH ₃ | t-C ₄ H ₉ | 9 : 91 | 69 : 31 | 58 : 42 |
| | | <u>E : Z</u> | | |
| CH ₃ | C ₂ H ₅ | 30 : 70 | 86 : 14 | 70 : 30 |
| CH ₃ | 1-C ₃ H ₇ | 43 : 57 | 95 : 5 | 80 : 20 |
| CH ₃ | t-C ₄ H ₉ | 39 : 61 | 100 : 0 | 83 : 12 |

Ar = 2,4-dinitrophenyl



Scheme 1.

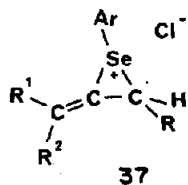


Scheme 2.

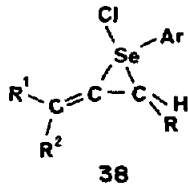
ions. In the absence of more definitive data our comments on mechanism are purely speculative.

However, assuming the presence of dissymmetric intermediates such as the isomeric *E*- and *Z*-alkylideneseleniranium ions **37a**, **b** one may rationalize the predominance of the *Z*-alkene under conditions of kinetic control in terms of a preequilibrium between the ions **37a** and **37b** with product determining attack by chloride ion on the sterically less hindered back side of the *Z*-alkylideneseleniranium ion (Scheme 2). Such a scenario has been previously hypothesized to account for the high *Z*:*E* ratios in halogenation and methoxymercuraton of 2,3-pentadiene.⁸

The presence of only one adduct from the reaction of benzeneselenenyl chloride with 1,2-cyclononadiene is rationalized in terms of steric hindrance to approach to one face of each double bond. Studies using Dreiding models clearly indicate that attack on **8** to give the *Z*-alkene would involve attack on the most hindered face of each double bond (i.e. from the inside of the ring). Similar results have been reported for halogenation,⁹ mercuration^{7,9} and areneseleenylation^{1,4} of **8**.



37



38

a $R^1 = H; R^2 = R$
b $R^1 = R; R^2 = H$

The formation of a substantial quantity of *Z*-alkene from 1,2-cyclotridecadiene, **9**, attests to the greater conformational flexibility of this larger ring system.

In summary, our data show yet another difference in the additions of areneseleenylium and areneseleenylium chlorides to C-C double bonds. It is not clear, however, if this is due to entirely different mechanism for the two reactions or small differences within the same general mechanism.

EXPERIMENTAL

General. Proton and ¹³C NMR spectra were run on Varian Associates HA-100, T-60 and FT-80 spectrometers. Chloroform-d was used as an internal lock and reference. All spectra were referenced to TMS. Determination of carbon-proton coupling constants was based on first-order analysis of the fully coupled natural abundance ¹³C spectra, and may not, thus, represent true J values. IR spectra were recorded on a Unicam SP 1100 spectrometer using neat liquid films or CCl₄ solns. Benzeneselenenyl chloride was commercially available from Aldrich. Allenes, 2,3-pentadiene was commercially available from Chemical Samples Co.

2,3-hexadiene; 3,4-heptadiene; 5-methyl-2,3-hexadiene; 5,5-dimethyl-2,3-hexadiene, 2,6-dimethyl-3,4-heptadiene, 2,2,6,6-tetramethyl-3,4-heptadiene, 1,2-cyclononadiene, and 1,2-cyclotridecadiene were synthesized by standard literature methods.¹⁹ Spectral properties previously not reported are given in Table 6.

The reaction of benzeneselenenyl chloride with allenes

General procedure. To a soln of the respective allene (6.00 mmole) in 25 ml anhyd CH₂Cl₂ was added an equivalent (6 mmole) of benzeneselenenyl chloride as a soln in 5 ml anhyd CH₂Cl₂. The addition was carried out such that the allene was always retained in excess.²⁰ The reaction occurred essentially instantaneously yielding a colorless soln. After the solvent was evaporated, the residual oil which corresponded to a quantitative yield was analyzed by ¹H and ¹³C NMR, and mass spectroscopy.

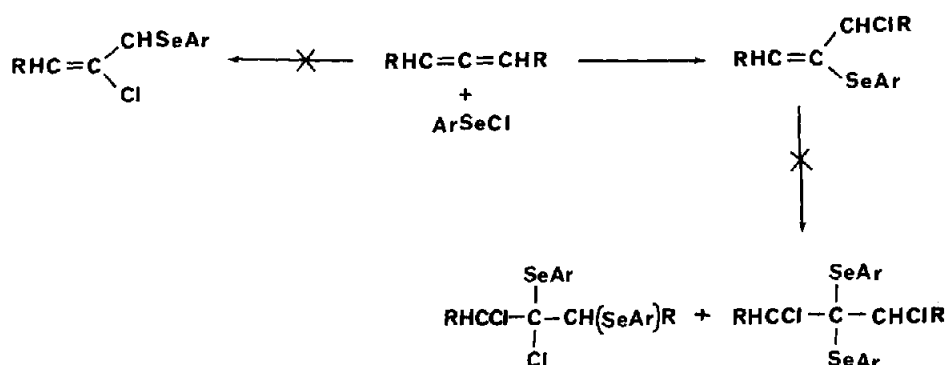


Table 6. Spectral and physical properties of some 1,3-disubstituted allenes

| Allene | bp (mm) | $\nu_{\text{C}=\text{C}}$ (cm^{-1}) | ^1H nmr (CDCl_3) |
|-----------------------------|-----------|---|---|
| 2,3-pentadiene | 48 (760) | 1980 | 5.15 q*(2H), 1.65 dd(6H) |
| 2,3-hexadiene | 75 (760) | 1980 | 4.95 m(2H), 0.97 t(3H) 1.60 d(3H), 1.9 m(2H) |
| 3,4-heptadiene | 101 (760) | 1980 | 5.10 q*(2H), 2.0 m(4H) 1.01 t(6H) |
| 5-methyl-2,3-hexadiene | | 1980 | 4.98 m(2H), 1.65 d(3H) 2.2 m(2H), 0.99 d(6H) |
| 5,5-dimethyl-2,3-hexadiene | 92 (760) | 1980 | 5.20 m(2H), 1.63 d(3H) 0.98 s(9H) |
| 2,6-dimethyl-3,4-heptadiene | | 1975 | 5.20 m(2H), 2.3 m(2H) 1.10 d(12H) |
| 1,2-cyclononadiene | 65 (20) | 1965 | 5.30 m(2H), 1.0-2.6 m(12H) |
| 1,2-cyclotridecadiene | 85 (1) | 1975 | 5.00 m(2H), 2.1 bm(4H) 1.37 m(16H) |

Control experiments run in $\text{CD}_2\text{Cl}_2/\text{TMS}$ and subjected to immediate NMR analysis showed the same product distributions (Table 1) as those above. Product isomerization was observed upon standing for a number of hrs.

Acknowledgements—Continued financial support of the National Research Council of Canada and the University of Ottawa is gratefully acknowledged. We are also indebted to Dr. J. Krauss and Mr. R. Capoor for technical assistance in the recording of some of the mass spectra and 100 MHz ^1H NMR spectra, respectively.

REFERENCES

- D. G. Garratt and P. Beaulieu, *Electrophilic Additions to Allenes-I*, *Can. J. Chem.* **57**, 119 (1979).
- D. J. Pasta and B. Lepasca, *J. Am. Chem. Soc.* **90**, 1091(1976);
- W. G. Dauben, G. J. Fouken and D. S. Noyce, *Ibid.*, **78**, 2579 (1956);
- E. C. Ashby and S. A. Noding, *J. Org. Chem.* **42**, 264 (1977).
- W. H. Mueller and P. E. Butler, *Ibid.* **33**, 1533 (1968);
- T. L. Jacobs and R. Macomber, *Ibid.* **33**, 2988 (1968).
- W. R. Moore and R. C. Bertelson, *Ibid.* **27**, 4182 (1962).
- T. L. Jacobs, R. Macomber and D. Zunker, *J. Am. Chem. Soc.* **89**, 7001 (1967).
- L. R. Byrd and M. C. Caserio, *Ibid.* **92**, 5422 (1970);
- F. Acree Jr. and F. B. Laforge, *J. Org. Chem.* **5**, 430 (1940);
- M. C. Findlay, W. L. Walters and M. C. Caserio, *Ibid.* **36**, 275 (1971).
- W. S. Linn, W. L. Waters and M. C. Caserio, *J. Am. Chem. Soc.* **92**, 4018 (1970).
- W. L. Waters, W. S. Linn and W. C. Caserio, *Ibid.* **90**, 6741 (1968).
- R. D. Bach, *Ibid.* **91**, 1771 (1969).
- See for example: G. H. Schmid and D. G. Garratt, *The Chemistry of functional groups*. Supplement A: *The Chemistry of Double-bonded Functional Groups* (Edited by S. Patai) Part 2, p. 855. Wiley, London (1977) and ref. cited; D. G. Garratt, *Can. J. Chem.* **56**, 2184 (1978).
- See for example, J. B. Stothers, *Carbon-13 NMR Spectroscopy* p. 55. Academic Press, New York (1972) and ref. cited.
- J. E. Anderson, *Tetrahedron Letters* 4079 (1975);
- G. L. Karabatsos, J. K. Graham and F. M. Vane, *J. Am. Chem. Soc.* **84**, 37 (1962).
- This reaction has been previously studied. See: (i) D. G. Garratt, Ph.D. thesis, University of Toronto; Toronto, Ontario, Canada (1975); (ii) G. H. Schmid and D. G. Garratt, *Chemical Scripta* **8A**, 110 (1975).
- M. Barfield and S. Steinbel, *J. Am. Chem. Soc.* **94**, 1905 (1972).
- The term "ion cluster" is used because of the presence of six stable natural isotopes of selenium which make the mass spectra of organoselenium compounds very rich in peaks, rendering, in some cases, the complete analysis of the spectra very difficult.
- Kinetic evidence for the transmission of substituent effects across both double bonds of allenes has been recently reported for the reaction of 4-chlorobenzenesulphenyl chloride and benzenesulphenyl chloride with the methyl substituted allenes: G. H. Schmid, D. G. Garratt and S. Yeroushahmi, *J. Org. Chem.* **43**, 3764 (1978).
- G. H. Schmid and D. G. Garratt, *Tetrahedron* **34**, 2869 (1978);
- G. H. Schmid and D. G. Garratt, *Tetrahedron Letters* 3991 (1975);
- D. G. Garratt and G. H. Schmid, *J. Org. Chem.* **42**, 1776 (1977).
- D. G. Garratt and G. H. Schmid, *Can. J. Chem.* **52**, 3599 (1974).
- W. von E. Doering and P. M. LaFlamme, *Tetrahedron* **2**, 75 (1958);
- L. Skattebol, *Acta Chem. Scand.* **17**, 1683 (1963);
- W. R. Moore and H. R. Ward, *J. Org. Chem.* **27**, 4179 (1962).
- Previous studies have indicated that the first formed species can react with excess selenenyl halide to form the corresponding dichloride or β -chloroalkyl aryl selenide dichloride see Ref. 13.