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Reaction of 1,3-Bis(alkylseleno)allenes with Diphenyl Diazomethane

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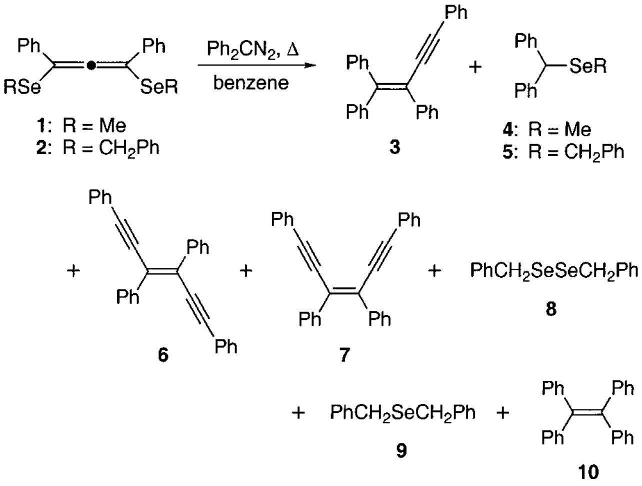
Introduction

Allenes substituted by heteroatoms have been the subject of considerable interest.[1] Sulfur-substituted allenes have also been focused upon since the 1960s.[2] We also studied the syntheses and reactivities of allenes substituted by sulfenyl groups at the 1- and 3-positions.[3,4] On the other hand, several selenium-substituted allenes are also known as isolable compounds or reactive intermediates.[5] Recently, we synthesized 1,3-bis(alkylseleno)allenes, by reacting the Ph_2C_3 dianion (1,3-dilithiated allene) with diselenide or selenocyanate, and clarified their thermal and photochemical reactivities.[6,7] We also examined the reaction of 1,3-bis(alkylseleno)allenes with diphenyl diazomethane, and it was found that the reactivities were different from those of corresponding sulfur-substituted allenes. We report here the reaction of 1,3-bis(alkylseleno)allenes with diphenyl diazomethane.

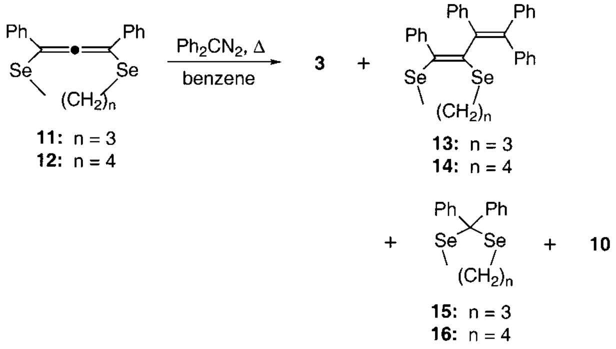
Results and Discussion

Scheme 1



allene	reaction time (h)	conversion (%)	product (%)							
			3	4	5	6	7	8	9	10
1	13.5	67	46	4						41[a]
2	7	52	11		7	35	9	38	32	72[a]

Scheme 2



allene	reaction time (h)	conversion (%)	product (%)					
			3	13	14	15	16	10
11	6	58	37	55		23		31[a]
12	6	63	32		43		12	19[a]

When a benzene solution of 1,3-bis(methylseleno)-1,3-diphenylpropadiene (**1**)[7] and 2 equiv of diphenyl diazomethane was refluxed for 13.5 h, 67% of **1** was consumed and tetraphenyl-1-butene-3-yne (**3**) was obtained in 46% yield along with a small amount of selenide **4**, as shown in Scheme 1. In this reaction, tetraphenylethylene **10** was also obtained in 41% yield (based on diphenyl diazomethane). Compound **10** may have been formed by the thermal reaction of diphenyl diazomethane, because independent thermal reaction of diphenyl diazomethane yielded compound **10** in 22% yield after 5 h. Similarly, refluxing a benzene solution of 1,3-bis(benzylseleno)-1,3-diphenylpropadiene (**2**)[7] and diphenyl diazomethane (2 equiv) also afforded eneyne **3**, although the yield was low (11%), together with selenide **5**. In this reaction, consumption of **2** was faster than in the case of **1**, and enediynes **6** and **7**, diselenide **8**, and selenide **9** were also obtained, formation of which is due to the thermal reaction of allene **2** because of the high thermal reactivity.[6,7]

Reactions of two diselenocyclic allenes **11**[7] and **12**[7] with 2 equiv of diphenyl diazomethane also afforded eneyne **3** in yields of 37 and 32%, respectively, together with butadiene derivative **13** (55%) or **14** (43%) and diselenocycloalkane **15** (23%) or **16** (12%), as shown in Scheme 2. Reactions of cyclic bisallenes *dl*- and *meso*-**17**[7] with diphenyl diazomethane also yielded eneyne **3** (Scheme 3). In this reaction, 1,3-diselenolane **18** and cyclic mono-

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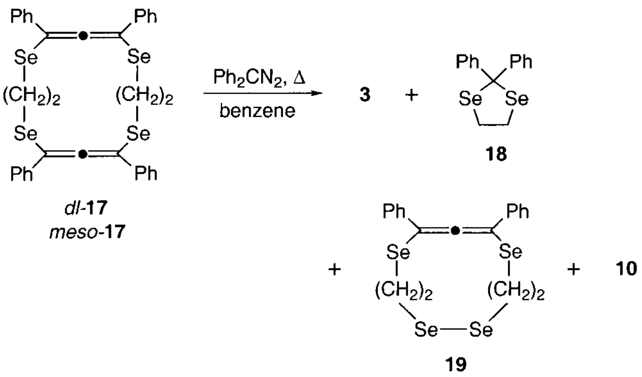
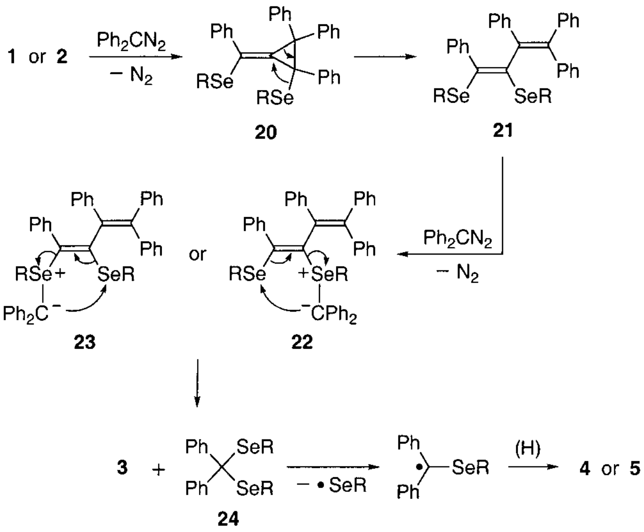
Scheme 3



allene	reaction time (h)	conversion (%)	product (%)					
			3	18	19	10	*dl*-17	*meso*-17
dl-17	6	62	26[a]	14[a]	4	28[b]		19
meso-17	6	55	36[a]	21[a]	4	26[b]	18	

Scheme 4

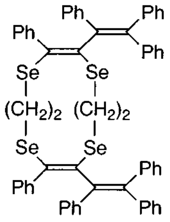


allene **19** were also obtained. Compound **19** must be a result of the thermal reaction of the starting material.[7] Furthermore, *dl*-**17** also isomerized to *meso*-**17** and *meso*-**17** isomerized to *dl*-**17** under the reaction conditions used, and the isomerization is also due to the thermal reactions of *dl*- and *meso*-**17**.[7] In the reaction of the corresponding tetrathiacyclic bisallene with diphenyl diazomethane, the thermal reaction of the allene was much faster than the reaction with diphenyl diazomethane, and no product was obtained by the direct reaction between the starting material and diphenyl diazomethane.[4]

The first step for the reactions of allenes **1** and **2** with diphenyl diazomethane may be the 1,3-dipolar addition of diphenyl diazomethane to the double bond of the allene to give benzylidene cyclopropane derivative **20** with extrusion of nitrogen (Scheme 4). Under the reaction conditions used, the ring-opening reaction of **20** proceeds with the migration of the selenenyl group on the cyclopropane ring to form a butadiene derivative **21**, which is the type of compound that has been obtained by the reaction of 1,3-bis(methylthio)-1,3-diphenylpropadiene with diphenyl diazomethane.[4] However, in this case, further addition of diphenyl diazomethane to **21** occurs to give ylide **22** or **23**. Rearrangement of the ylide affords eneyne **3** and benzophenonediselenoacetal **24**. Homolytic cleavage of the carbon–selenium bond of **24** occurs in the refluxing benzene solution followed by hydrogen abstraction to give selenide **4** or **5**. Selenides **4** and **5** may also be obtained by the reaction of diphenyl diazomethane and diselenide, since isolated dibenzyl diselenide reacts with diphenyl diazomethane under the reaction conditions used to give selenide **5** in 26% yield together with selenide **9** (23%).

In the reactions of cyclic allenes **11** and **12**, eneyne **3** is obtained through a similar mechanism. In these cases, the butadiene derivative **13** or **14** could be isolated whereas the intermediary **21** was not isolated in the cases of **1** and **2**. Furthermore, diselenocycloalkanes **15** and **16**, which correspond to **24**, were also isolated. These results support the proposed mechanism for the reactions of **1** and **2** with diphenyl diazomethane. When 1 equiv of diphenyl diazomethane was used in the reaction with **11**, yield of **13** increased (68%) and those of **3** and **15** went down (29 and 17%, respectively), and isolated **13** reacted with diphenyl diazomethane to give eneyne **3** and 1,3-diselenane **15** in 35 and 8% yields, respectively. These results also indicate that the butadiene derivative **13** is a precursor of compounds **3** and **15**. In the case of cyclic bisallenes *dl*- and *meso*-**17**, addition of diphenyl diazomethane and the subsequent rearrangement occur to give cyclic bisbutadiene derivative **25** or **26**. Addition of diphenyl diazomethane to **25** or **26** affords a cyclic ylide, e.g., **27**. Intramolecular cyclization of **27** will give a zwitterion, such as **28**, with extrusion of eneyne **3**. Finally, the intramolecular or intermolecular rearrangement of **28** yields 1,3-diselenolane **18** and another molecule of **3**. This mechanism can explain the ratio for the formation of **3** and **18**, although the diselenide released by the reaction could not be detected.

In either reaction, the benzylidene cyclopropane derivative was not obtained, whereas carbon-substituted allenes are known to react with diphenyl diazomethane to give alkylidene cyclopropanes.[8,9] This difference is perhaps due to the fast migration of the selenenyl group on the cyclopropane ring.



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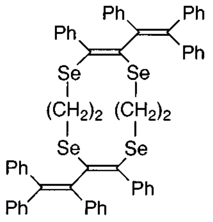

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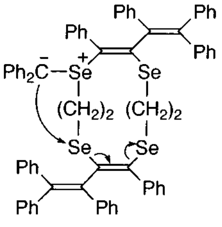

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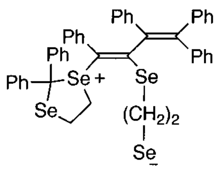

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Conclusion

1,3-Bis(alkylseleno)-1,3-diphenylpropadienes were found to react with diphenyl diazomethane to give benzylidene cyclopropane derivatives as reactive intermediates with extrusion of nitrogen. The benzylidene cyclopropanes rearranged easily to afford butadienes via migration of the selenenyl group on the cyclopropane rings. Diphenyl diazomethane also reacted with the selenium-substituted butadienes to form selenonium ylides, which provided tetraphenyl-1-butene-3-yne.

Experimental Section

Benzene was distilled from sodium metal before use. Column chromatography was performed with Merck Kieselgel 60 (70−230 mesh). All reactions were carried out under nitrogen in a hood.

General Procedure for Reaction of 1,3-Bis(alkylseleno)-allenes with Diphenyl Diazomethane. A benzene solution (10 mL) of 1,3-bis(alkylseleno)allene[6,7] (0.3 mmol) and diphenyl diazomethane[10] (2 equiv) was refluxed for the desired period under nitrogen. After removal of solvent in vacuo, the residue was subjected to silica gel column chromatography. **1**: 67% conversion (13.5 h), **3** (46%), **4** (4%), **10**[11] (41%). **2**: 52% conversion (7 h), **3** (11%), **5** (7%), **6**[6,12] (35%), **7**[6,12] (9%), **8**[13] (38%), **9**[13] (32%), **10** (72%). **11**: 58% conversion (6 h), **3** (37%), **10** (31%), **13** (55%), **15** (23%). **12**: 63% conversion (6 h), **3** (32%), **10** (19%), **14** (43%), **16** (12%). *dl*-**17**: 62% conversion (6 h), **3** (26%), **10** (28%), *meso*-**17** (19%), **18** (14%), **19**[7] (4%). *meso*-**17**: 55% conversion (6 h), **3** (36%), **10** (26%), *dl*-**17** (18%), **18** (21%), **19** (4%).

Tetraphenyl-1-butene-3-yne (3). Mp 120.8−122.0 °C (yellow solid); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.01 (dd, 2H, J = 1.8, 7.5 Hz), 7.12−7.25 (m, 10H), 7.33−7.37 (m, 6H), 7.57 (dd, 2H, J = 1.8, 6.7 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 92.4, 93.0, 121.5, 123.6, 127.0, 127.2, 127.6, 127.8, 127.87, 127.89, 127.93, 128.2, 130.0, 130.5, 131.1, 131.3, 139.6, 141.4, 142.8, 148.9; IR (KBr) ν_{max} 3078, 3020, 1594, 1489, 1441, 1027, 775, 754, 740, 697, 688, 606 cm^{-1}; MS m/z 356 (M$^+$), 279, 178. Anal. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 93.98; H, 5.78.

Diphenylmethyl Methyl Selenide (4). Yellow liquid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.79 (s, 3H), 5.26 (s, 1H), 7.14 (tt, 2H, J = 1.3, 7.6 Hz), 7.23 (t, 4H, J = 7.6 Hz), 7.36 (dd, 4H, J = 1.3, 7.6 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 6.3, 48.6, 127.0, 128.5, 128.6, 141.5; IR (neat) ν_{max} 3059, 3026, 2923, 1598, 1494, 1449, 1274, 1075, 1031, 748, 695 cm^{-1}; MS m/z 262 (M$^+$), 260, 245, 178; HRMS calcd for $C_{14}H_{14}{}^{80}Se$ 262.0215, found 262.0260.

Benzyl Diphenylmethyl Selenide (5). Yellow liquid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.62 (s, 2H), 5.25 (s, 1H), 7.14 (d, 2H, J = 7.1 Hz), 7.18−7.31 (m, 9H), 7.41 (d, 4H, J = 7.3 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 29.5, 47.9, 126.6, 127.0, 128.4, 128.5, 128.8, 128.9, 138.9, 141.3; IR (neat) ν_{max} 3060, 3027, 2923, 1598, 1494, 1449, 1076, 1030, 748, 696 cm^{-1}; MS m/z 338 (M$^+$), 336, 245, 167; HRMS calcd for $C_{20}H_{18}{}^{80}Se$ 338.0523, found 338.0573.

1-Phenyl-2-(triphenyl)vinyl-3,7-diseleno-1-cycloheptene (13). Mp 147.6−150.0 °C (yellow prisms from ethanol); ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.17−2.24 (m, 1H), 2.34−2.40 (m, 1H), 3.14−3.20 (m, 2H), 3.40−3.45 (m, 1H), 3.50−3.54 (m, 1H), 6.73 (dd, 2H, J = 1.4, 8.4 Hz), 6.92 (dd, 2H, J = 1.4, 8.0 Hz), 6.96−7.25 (m, 16H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 27.3, 27.4, 30.1, 126.5, 126.8, 127.0, 127.16, 127.18, 127.3, 127.4, 127.6, 128.6, 130.7, 131.0, 131.1, 133.8, 136.5, 139.9, 140.2, 140.5, 142.1, 143.2, 143.4; IR (KBr) ν_{max} 3051, 3018, 2929, 2894, 1597, 1541, 1488, 1442, 1285, 1077, 1030, 762, 745, 695 cm^{-1}; MS m/z 556 (M$^+$), 436, 356. Anal. Calcd for $C_{31}H_{26}Se_2$: C, 66.91; H, 4.71. Found: C, 66.84; H, 4.74.

1-Phenyl-2-(triphenyl)vinyl-3,8-diseleno-1-cyclooctene (14). Mp 155.2−157.5 °C (pale yellow needles from ethanol); ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.10−2.35 (m, 4H), 2.80−2.88 (m, 2H), 3.11−3.15 (m, 1H), 3.91−3.97 (m, 1H), 6.70 (d, 2H, J = 7.2 Hz), 6.84 (d, 2H, J = 6.7 Hz), 6.94−7.01 (m, 5H), 7.06−7.12 (m, 6H), 7.17−7.20 (m, 5H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 26.5, 30.1, 31.0, 31.1, 126.4, 126.5, 126.8, 127.1, 127.3, 127.36, 127.40, 127.44, 127.9, 130.9, 131.1, 131.2, 132.9, 139.8, 141.27, 141.29, 142.3, 143.0, 143.2, 143.3; IR (KBr) ν_{max} 3048, 3018, 2915, 2839, 1597, 1489, 1441, 1266, 1076, 1030, 913, 762, 745, 700 cm^{-1}; MS m/z 570 (M$^+$), 436, 356. Anal. Calcd for $C_{32}H_{28}Se_2$: C, 67.37; H, 4.95. Found: C, 67.27; H, 4.98.

2,2-Diphenyl-1,3-diselenane (15). Mp 91.0−93.8 °C (pale yellow solid); ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.11 (quint, 2H, J = 5.8 Hz), 2.89 (t, 4H, J = 5.8 Hz), 7.23 (t, 2H, J = 7.6 Hz), 7.31 (t, 4H, J = 7.6 Hz), 7.69 (d, 4H, J = 7.6 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.9, 25.1, 48.8, 127.2, 128.3, 130.0, 144.1; IR (KBr) ν_{max} 3058, 3027, 2916, 1491, 1443, 1408, 1243, 1035, 842, 750, 712, 699, 641 cm^{-1}; MS m/z 366 (M$^+$), 246, 165. Anal. Calcd for $C_{16}H_{16}Se_2$: C, 52.47; H, 4.40. Found: C, 52.30; H, 4.38.

2,2-Diphenyl-1,3-diselenepane (16). Mp 97.2−98.8 °C (pale yellow solid); ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.25−2.27 (m, 4H), 3.03−3.05 (m, 4H), 7.20 (t, 2H, J = 7.6 Hz), 7.28 (t, 4H, J = 7.6 Hz), 7.55 (d, 4H, J = 7.6 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 27.1, 31.4, 58.8, 127.0, 128.1, 129.1, 146.0; IR (KBr) ν_{max} 3052, 2899, 1590, 1487, 1440, 1404, 1215, 1032, 750, 712, 696, 639 cm^{-1}; MS m/z 380 (M$^+$), 246, 165. Anal. Calcd for $C_{17}H_{18}Se_2$: C, 53.70; H, 4.77. Found: C, 53.57; H, 4.66.

2,2-Diphenyl-1,3-diselenolane (18). Mp 59.0−61.0 °C (pale orange solid); ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.81 (s, 4H), 7.19 (t, 2H, J = 7.6 Hz), 7.26 (t, 4H, J = 7.6 Hz), 7.62 (d, 4H, J = 7.6 Hz); ^{13}C NMR (125 MHz, CDCl$_3$) δ 38.3, 67.0, 126.8, 127.9, 128.8, 146.4; IR (KBr) ν_{max} 3051, 3013, 2920, 1589, 1489, 1440, 1259, 1078, 1032, 750, 713, 698, 645 cm^{-1}; MS m/z 352 (M$^+$), 324, 246, 165. Anal. Calcd for $C_{15}H_{14}Se_2$: C, 51.15; H, 4.01. Found: C, 50.95; H, 3.99.

Thermal Reaction of Diphenyl Diazomethane. A benzene solution (3 mL) of diphenyl diazomethane (69 mg, 0.36 mmol) was refluxed for 5 h under nitrogen. The reaction mixture was subjected to silica gel column chromatography to give tetraphenylethylene **10** in 22% yield.

Reaction of Dibenzyl Diselenide (8) with Diphenyl Diazomethane. A benzene solution (2.5 mL) of dibenzyl diselenide **8** (48 mg, 0.14 mmol) and diphenyl diazomethane (58 mg, 0.28 mmol) was refluxed for 2.5 h under nitrogen. After removal of solvent in vacuo, the residue was subjected to gel-permeation chromatography to give selenides **5** (26%) and **9** (23%) with 19% conversion of **8**.

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