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Direct Synthesis of Methylene-1,2-dichalcogenolanes via Radical [3 + 2] Cycloaddition of Methylenecyclopropanes with Elemental Chalcogens

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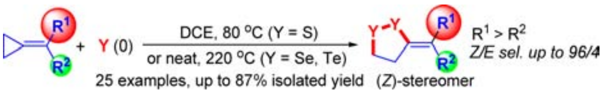
ABSTRACT



Direct [3 + 2] radical cycloaddition of methylenecyclopropanes and elemental chalcogens (S, Se, Te) can readily occur under simple thermal conditions, providing an efficient, practical method for preparation of useful but not easily accessed methylene-1,2-dichalcogenolanes.

Methylenecyclopropanes (MCPs) are readily accessible compounds of high intramolecular ring strain and high reactivity.[1,2] They have become a class of versatile building blocks in organic synthesis because they readily undergo a variety of interesting transformations under mild conditions, giving various useful organic skeletons that are otherwise difficult to achieve.[1−14] Generally, MCPs can undergo ring-breaking reactions to afford allylic and homoallylic compounds,[3,4] ring-expansion reactions to afford cyclobutane derivatives,[5,6] and cycloaddition reactions.[7−14] Cycloaddition is one of the most important transformations of MCPs, because various unsaturated compounds, such as alkenes,[8] allenes,[9] alkynes,[10] aldehydes,[11] imines,[11a,b,12] nitrones,[13] and 1,2-diazines,[14] can be employed

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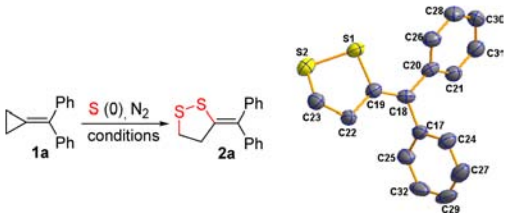
to react with MCPs to prepare a wide range of useful ring compounds.

Yet, organochalcogenides are also important chemicals recently drawing great interest due to their wide applications in many fields.[4,6,15,16] Previously, we have investigated reactions of MCPs and some organochalcogeno reagents.[6] With an ongoing interest in organochalcogenides and MCPs,[6,7,16] we envisioned a direct reaction of elemental chalcogens and MCPs that may provide certain organochalcogenide compounds in a more concise way, which may also shorten the synthetic procedures by avoiding multistep preparation of the conventional organochalcogeno reagents. Herein we report that MCPs and elemental chalcogens (S, Se, Te) can readily undergo a thermally induced direct [3 + 2] radical cycloaddition reaction to afford the useful methylene-1,2-dichalcogenolanes.[17] To our knowledge, cycloaddition of MCPs with elemental chemicals was unknown.

Initially, MCP **1a** and sulfur powder were directly heated in toluene (Table 1, run 1). The product, isolated as pale yellow crystals in low yield, was analyzed by NMR, IR, MS, and X-ray diffraction. Interestingly, it unambiguously proved to be 3-(diphenylmethylene)-1,2-dithiolane (**2a**). Obviously, it was generated via an unuaual [3 + 2] cycloaddition reaction of **1a** and S(0).

It is well-known that the 1,2-dithiolane structure is a key moiety of lipoic acid, presents in many naturally occurring chemicals, and has become a useful building block especially in materials and medicinal chemistry.[17] Since directly using S(0) as the substrate is more advantageous than the known methods for 1,2-dithiolane construction,[17a,18] the interesting results intrigued us to further investigate the reaction in more depth. First, solvents were screened. Nonpolar (xylene, 20%) and polar (CH_3CN, 28%; DMF, 27%; DMSO, 37%) solvents and neat conditions (26%) were all found not suitable for the reaction. Then, although THF (22%) and $CHCl_3$ (12%) were not effective, similar etheric and chloric solvents 1,4-dioxane and 1,2-dichloroethane (DCE) could cleanly afford good yields of **2a** at 80 °C in only 6 h (runs 2, 3). The solvent effect is possibly related to sulfur's solubility in the solvents, for DCE was found to be a comparatively better solvent for S(0) at 80 °C.[19,20] S(0) loading could be reduced to only 1.1 equiv without affecting the product yield (run 4), but the reaction of 1.0 equiv of S(0) gave a much lower yield (run 5). Temperature screening also showed its key impact on the reaction. Thus, only trace product was detected at 60 °C (run 6), and a reaction at 100 °C using dioxane as the solvent also failed to give a better result (run 7).

Table 1. Optimization of the Reaction Conditions[a]



run	S (equiv)[b]	solvent	temp (°C)	*t* (h)	**2a**%[c]
1	1.5	toluene	80	24	23
2	1.5	1,4-dioxane	80	6	60
3	1.5	DCE	80	6	69
4	*1.1*	*DCE*	*80*	*6*	*73*
5	1.0	DCE	80	10	51
6	1.1	DCE	60	24	trace
7	1.1	1,4-dioxane	100	6	61

[a] The mixture of **1a** (0.3 mmol) and sulfur powder was heated in a solvent (1 mL) under N_2 and monitored by TLC. Molecular structure of **2a** confirmed by X-ray diffraction analysis (H-atoms omitted for clarity). [b] Sulfur loading: 1.5 equiv, 0.90 mmol; 1.1 equiv, 0.66 mmol; 1.0 equiv, 0.60 mmol. [c] Isolated yields based on **1a**.

The optimized conditions (Table 1, run 4) were then applied to a series of MCPs to extend the scope of the method (Table 2). For disubstituted symmetrical MCPs ($R^1 = R^2$), such as **1a**, only one stereomer of the products was obtained in moderate to good yields (runs 1–4). Like diaryl-substituted MCPs, dialkyl-substituted **1d** also gave the target **2d** in good yield (run 4). For unsymmetrical MCPs ($R^1 \neq R^2$), both (*Z*)- and (*E*)-stereomers were obtained (runs 5–17). Most disubstituted unsymmetrical MCPs generally gave good yields of the products (runs 5–9), but the (*Z*)- and (*E*)-stereomers were not selective, which may be attributed to the steric similarities of the two aryl groups. As for **1j**, only a low yield of the product **2j** was obtained with the observation of a byproduct, 1-(4-chlorophenyl)ethanone (run 10). This is possibly because **1j** easily decomposes to give the byproduct under the reaction conditions. Besides, the selectivity of (*Z*)- and (*E*)-**2j** was determined to be 60/40 by NOESY and ^1H NMR spectroscopic analysis,[21] higher than other disubstituted MCPs. In the case of monosubstituted MCPs **1k–q** (runs 11–17), they generally gave moderate yields of the products but in much higher *Z*/*E* selectivities than disubstituted MCPs.[21]

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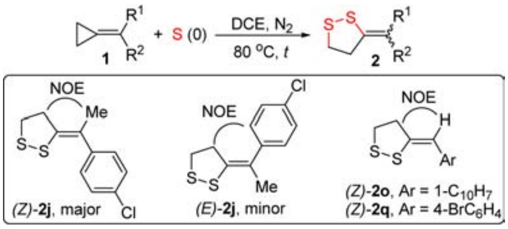
(19) We found S(0) alone (0.66 mmol) could not be totally dissolved in toluene or DMF (1 mL) at 80 °C, while total dissolution of S(0) was observed in DCE, giving a homogeneous-like emulsion.[20]

(20) We thankful the reviewers for their kind, proper suggestions.

(21) See Supporting Information for details.

For example, the highest *Z*/*E* selectivity of the products (**2o**, 96/4) was obtained from **1o** bearing the most bulky 1-naphthyl group (run 15).

Table 2. [3 + 2] Cycloaddition of MCPs with S(0)[a]



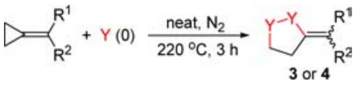
run	**1**: R^1, R^2	*t* (h)	**2**: yield% (*Z*/*E*)[b]
1	**1a**: Ph, Ph	6	**2a**: 73
2	**1b**: 4-FC_6H_4, 4-FC_6H_4	20	**2b**: 43
3	**1c**: 4-ClC_6H_4, 4-ClC_6H_4	28	**2c**: 54
4	**1d**: -$CH_2CH_2CH(Ph)CH_2CH_2$-	10	**2d**: 73
5	**1e**: 4-MeC_6H_4, Ph	7	**2e**: 87 (50/50)
6	**1f**: 4-$MeOC_6H_4$, Ph	7	**2f**: 79 (50/50)
7	**1g**: 4-FC_6H_4, Ph	20	**2g**: 52 (50/50)
8	**1h**: 4-ClC_6H_4, Ph	25	**2h**: 72 (50/50)
9	**1i**: 4-BrC_6H_4, Ph	27	**2i**: 58 (50/50)
10	**1j**: 4-ClC_6H_4, Me	23	**2j**: 28 (60/40)
11	**1k**: Ph, H	10	**2k**: 65 (70/30)
12	**1l**: 4-MeC_6H_4, H	14	**2l**: 69 (68/32)
13	**1m**: 4-$MeOC_6H_4$, H	10	**2m**: 60 (76/24)
14	**1n**: 2,4,6-$Me_3C_6H_2$, H	24	**2n**: 50 (85/15)
15	**1o**: 1-$C_{10}H_7$, H	10	**2o**: 65 (96/4)
16	**1p**: 4-$CF_3C_6H_4$, H	24	**2p**: 42 (82/18)
17	**1q**: 4-BrC_6H_4, H	36	**2q**: 57 (92/8)

[a] MCPs **1** (0.3 mmol) and sulfur powder (0.66 mmol, 1.1 equiv) in DCE (1 mL) were heated at 80 °C and then monitored by TLC. [b] Isolated yields based on **1**. Stereochemistry of the *Z*/*E* isomers was determined by NOESY spectroscopic analysis. *E*/*Z* ratios of the products were determined by ^{1}H NMR spectroscopic analysis.[21]

The above-mentioned results also showed that substituents on MCPs can affect the reaction significantly. Thus, reactions of disubstituted MCPs were usually faster and gave higher yields of products than analogous monosubstituted MCPs. Likewise, reactions of electron-rich MCPs were also faster and gave higher yields than electron-deficient ones (runs 1, 4 vs 2, 3; runs 5, 6 vs 7–9; runs 11–15 vs runs 16, 17). For unsymmetrical MCPs, the *Z*/*E* selectivity of the stereomers seemed to correlate closely with the steric and electronic properties of the substituents. Thus, monosubstituted MCPs (runs 11–17) generally gave higher *Z*/*E* selectivities of the products than disubstituted ones (runs 5–10), and MCPs (**1n**, **1o**) with higher steric asymmetry for bearing bulky groups (runs 14, 15) and those (**1j**, **1p**, **1q**) bearing electron-withdrawing groups (runs 10, 16, 17) usually afforded products in higher *Z*/*E* selectivities than analogous MCPs.

The successful reactions of S(0) encouraged us to further investigate the rections of Se(0) and Te(0) to prepare the analogous 1,2-dichalcogenolanes. However, the reactions were not effective under the standard conditions for S(0), giving only 17% (in 3 d) and 13% (in 5 d) isolated yields of the target 1,2-diselenolane (**3a**) and 1,2-ditellurolane (**4a**), respectively. The reaction of Se(0) was then investigated at high temperatures under neat conditions and was found to proceed best at 220 °C for 3 h (Table 3, run 1), giving a 63% yield of **3a**.[22]

Table 3. [3 + 2] Cycloaddition of MCPs with Se(0) and Te(0)[a]



run	**1**: R^1, R^2	Y	yield% (*Z*/*E*)[b]
1	**1a**: Ph, Ph	Se	**3a**: 63
2	**1c**: 4-ClC_6H_4, 4-ClC_6H_4	Se	**3c**: 43
3	**1d**: -$CH_2CH_2CH(Ph)CH_2CH_2$-	Se	**3d**: 56
4	**1e**: 4-MeC_6H_4, Ph	Se	**3e**: 67 (50/50)
5	**1f**: 4-$MeOC_6H_4$, Ph	Se	**3f**: 51 (50/50)
6	**1g**: 4-FC_6H_4, Ph	Se	**3g**: 51 (50/50)
7[c]	**1n**: 2,4,6-$Me_3C_6H_2$, H	Se	**3n**: 54 (68/32)
8	**1a**	Te	**4a**: 22

[a] Unless otherwise noted, MCPs **1** (0.3 mmol) and Se or Te powder (0.66 mmol, 1.1 equiv) were heated under N_2 at 220 °C for 3 h. [b] See note b in Table 2 for reference. [c] N_2, DCE (1 mL), 80 °C, 3 d.

As shown in Table 3, other disubstituted MCPs also reacted effectively with Se(0) to afford 3-methylene-1,2-diselenolanes **3** in satisfactory yields under the same conditions (runs 1–6). In contrast, only trace product was detected in the reaction of monosubstituted MCP **1n**, probably because **1n** easily decomposes under the harsh reaction conditions. Fortunately, when **1n** and Se(0) were heated in DCE at 80 °C, the original conditions for S(0), the desired **3n** could be isolated in 54% yield after 3 days (run 7). In comparison, the *Z*/*E* selectivity of **3n** was lower than that for the sulfur analogue **2n**, but higher than that of other diselenolanes **3e**–**g**. In addition, we also attempted many conditions for the reactions of MCPs and Te(0), but the results were not satisfactory, which is possibly due to the even lower reactivity of Te(0) vs Se(0). Thus, the best result was still obtained from the neat reaction at 220 °C, giving a 22% isolatd yield of **4a** (run 8).

During substrate extension, we also investigated the reactions of other reactive molecules such as cyclopropane, vinylcyclopropane, methylenecyclobutane, and allene derivatives **5**–**10** with S(0) to broaden the scope of the method (Scheme 1, eq 1). However, no cycloaddition reaction occurred under the same conditions with recovery of the reactants only. This indicated that the cycloaddition reaction is most possibly dependent on the MCP structure, further implying that the reaction should proceed via an interesting mechanism correlated with the MCP structure.

Yet, since all reactions were simply conducted under thermal conditions without using any catalysts or additives, and MCPs can readily react with chalcogeno and

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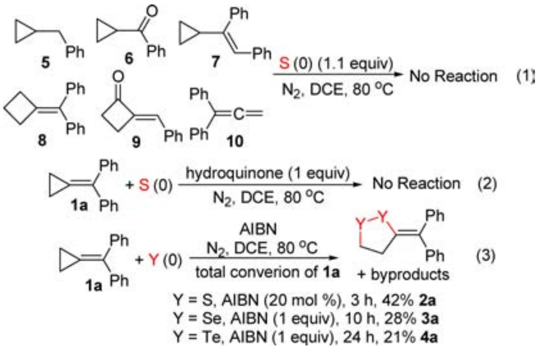
(22) For comparison, a reaction at 140 °C for 24 h gave a 26% isolated yield of **3a**, a reaction at 220 °C for 1 h gave 54% **3a**, and a reaction at 220 °C for 5 h gave 64% **3a**.

other radicals,[2,4,7] this cycloaddition reaction might also proceed via radical pathways. Thus, 1,4-hydroquinone, a well-known radical inhibitor, was first added to the reaction of **1a** and S(0), which resulted in complete inhibition of the cycloaddition reaction with revovery of **1a** (Scheme 1, eq 2). Besides, addition of a radical initiator AIBN did accelerate the reactions and can reduce the reaction temperature of Se(0) and Te(0) significantly (eq 3), but it failed to enhance the product yield. This is possibly due to the high reactivity of **1a** under radical initiator-induced conditions that may also lead to formation of unknown byproducts. These results confirmed that the reaction is indeed a radical reaction and should proceed via radical pathways.

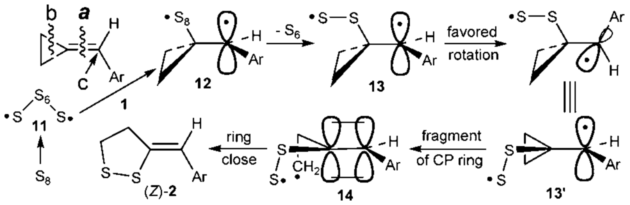
Scheme 1. Control Reactions



Based on all the above results and MCPs' radical reactions,[2,4,7] a simplified plausible mechanism was proposed (Scheme 2).[20,23] Thus, sulfur powder (S_8) may first generate a sulfur biradical **11** under thermal conditions,[23] which should then selectively attack MCPs' least hindered central carbon to give a stable radical intermediate **12** via homoscission of the C=C bond (path a).[2,4,7] Clearly, **12**'s stability depends on its substituents, which can account for the faster reactions and higher product yields of disubstituted and electron-rich MCPs than monosubstituted and electron-deficient ones. In contrast, homoscission of the proximal bonds of the cyclopropane (CP) ring (path b) and attack of **11** at the sterically more hindered exocyclic carbon of MCPs (path c) should not be preferable paths since they will give unstable radical intermediates.[2,4,7]

Then, by homoscission of the S–S bond, **12** may convert to **13** and S_6, which may be recycled to afford new sulfur biradicals such as **11**. Consequently, nearly 1 equiv of S(0) is adequate for the whole reaction. **13** can account for the high (*Z*)-selectivities of monosubstituted MCPs, since its exocyclic C–C bond may rotate to reach a favored configuration **13′**, in which the more bulky Ar group is at the *anti*-position to the more bulky CP moiety, leaving the least bulky H *cis* to CP. The subsequent radical fragment of the CP ring with coinstantaneous reformation of the exocyclic C=C bond may afford **14**, which can selectively produce (*Z*)-**2** via direct radical ring closure.[2,4,7,20]

Scheme 2. Simplified Plausible Mechanism.[20,23]



13 and **13′** may explain the nonselectivity of disubstituted MCPs, for **13** are very stable and reactive and the two Ar groups are sterically similar in these cases. Thus, exocyclic C–C rotation may not occur prior to the fast ring fragment and closure, which will directly give nonselective products. **13** and **13′** may also explain the higher (*Z*)-selectivities of electron-deficient MCPs, for radicals **13** of electron-rich MCPs are more stable, easier to be generated, and more reactive than those of electron-deficient MCPs, which can lead to faster ring fragment and closure reactions than exocyclic C–C rotation to form favored **13′**, and consequently lower stereoselectivities of the products; vice versa. For example, **1q** is the slowest in reaction rate (Table 1, run 17), but it may provide enough time for **13** to rotate to **13′** and finally give the highest *Z*/*E* (92/8) selectivity among the electron-deficient MCPs.

In conclusion, we developed an interesting thermally induced direct [3 + 2] radical cyloaddition reaction of MCPs and elemental chalcogens, providing a simple synthesis for the useful methylene-1,2-dichalcogenolanes. This method is advantageous and potentially useful in synthesis because it can directly use elemental chalcogens and avoid the conventional reagents. Further extension of the method and deeper mechanistic insights are underway.

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Supporting Information Available. Experimental procedures, product characterization, ^1H, ^{13}C NMR and NOESY spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) As suggested by a reviewer, the reactions of Se(0) and Te(0) at 220 °C may also proceed via a mechanism initiated by MCPs-derived carbon biradicals. Indeed, we found heating **1a** alone at 220 °C afforded a complex mixture of unknown byproducts with recovery of 35% **1a**, and heating **1a** and S(0) at 220 °C afforded 9% **2a** and unknown byproducts with recovery of 10% **1a**.[20] However, Se or Te biradical-initiated mechanisms cannot be excluded completely at present, since **1a** is still very stable even at 220 °C (see above) and AIBN-induced reactions could afford target **3a** and **4a** even at 80 °C in DCE (Scheme 1, eq 3), implying that Se or Te biradicals were still possibly generated at 220 °C or under AIBN-induced radical conditions.

The authors declare no competing financial interest.