Intramolecular Diels−Alder Reaction of Furans with Allenyl Ethers Followed by Sulfur and Silicon Atom-Containing Group Rearrangement

Hsien-Jen Wu,* Chia-Hui Yen, and Chi-Te Chuang

Department of Applied Chemistry, National Chiao Tung University, Hinchu, Taiwan, China

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The intramolecular Diels−Alder reactions of a furandiene with an allenyl ether dienophile followed by the alkylthio, alkylsulfinyl, alkylsulfonyl, and trimethylsilyl group rearrangements are reported. Refluxing the propargyl ether **3** with *t*-BuOK in *t*-BuOH at 85 °C gave the 1,4-rearrangement product **4** exclusively. The alkylthio group 1,4-rearrangement may proceed intramolecularly via the tight ion pairs. Refluxing the 5-(alkylsulfinyl)-2-furfuryl propargyl ethers **9a**−**e** and the 5-(alkylsulfonyl)-2-furfuryl propargyl ethers **19a**−**e** under the same reaction conditions gave the alkylsulfinyl group and the alkylsulfonyl group 1,2-rearrangement products **10a**−**e** and **20a**−**e**, respectively. No detectable amount of the corresponding 1,4-rearrangement products **11a**−**e** and **21a**−**e** was obtained. In the cases of **9b** and **19b**, which possess two furfurylic hydrogen atoms, no detectable amount of the furan ring-transfer reaction products was obtained. Refluxing the 5-(trimethylsilyl)-2-furfuryl propargyl ethers **25a**−**d** with *t*-BuOK in *t*-BuOH at 85 °C for 10 h gave the trimethylsilyl group 1,2-rearrangement products **26a**−**d** and Brook rearrangement products **27a**−**d**. The reaction mechanisms for these novel intramolecular Diels−Alder reactions are discussed. In the case of **37**, which possesses two furfurylic hydrogen atoms, compound **38** was obtained via an intramolecular Diels−Alder reaction followed by the furan ring-transfer reaction and Brook rearrangement.

Introduction

There is considerable current interest in the intramolecular Diels−Alder reaction, and it has been applied to a number of synthetic objectives with notable success.[1] The vast majority of the work reported in this area has dealt with reactions utilizing ethylenic and acetylenic dienophiles. On the other hand, the intramolecular Diels−Alder reaction of allene has received much less attention.[2] Over a decade ago, Kanematsu et al. demonstrated that the allene unit is a versatile synthon as a dienophile in the intramolecular cycloaddition due to the absence of unfavorable nonbonded interactions in the transition state.[3] Afterward, they developed a furan ring-transfer reaction via the intramolecular Diels−Alder reaction of a furan diene and an allenyl ether dienophile and applied this reaction to the synthesis of natural products.[4] For the purpose of the furan ring-transfer reaction, in all of their cases there was only one carbon atom and one oxygen atom connection between the furan diene and the allene dienophile for the cycloaddition. In these cases, the cycloadducts were not isolated under the reaction conditions but were further transferred to the isobenzofuran precursors via ring opening of the bridged oxygen ring of the cycloadducts.

A few years ago, we also investigated this intramolecular cycloaddition. By varying the chain length between the furan diene and the allenyl ether dienophile, we found a very high effect of the chain length on the structure and reactivity of the cycloadducts.[5] We also utilized this intramolecular cycloaddition as a new entry for the synthesis of indanones and tetralones.[6] Later on, we discovered a novel reaction involving an intramolecular Diels−Alder reaction of a furan with an allenyl ether followed by a methylthio group 1,4-rearrangement.[7] We also proposed in general that the intramolecular Diels−Alder reaction of furfuryl allenyl ethers **B**, including the furan ring transfer reaction,[4] proceeded via the corresponding zwitterions **D** as the reaction intermediates[8] (Scheme 1). When the X group of **A** is a hydrogen atom or an alkyl group, the furan ring transfer reaction takes place to give the isobenzofuran precursor **E**. On the other hand, when the X group of **A** is a methylthio group, the

(1) For reviews, see: (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* 1**977**, *16*, 10. (b) Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63. (c) Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183. (d) Ciganek, E. *Org. React.* **1984**, *32*, 1. (e) Weinreb, S. M.; Staib, R. R. *Tetrahedron* **1982**, *38*, 3087. (f) Weinreb, S. M. *Acc. Chem. Res.* **1985**, *18*, 16. (g) Craig, D. *Chem. Soc. Rev.* **1987**, *16*, 187.

(2) For some examples of the intramolecular Diels−Alder reactions of allenic dienophiles, see: (a) Bartlett, A. J.; Laird, T.; Ollis, W. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1315. (b) Himbert, G.; Diehl, K.; Maas, G. *J. Chem. Soc., Chem. Commun.* **1984**, 900. (c) Harrison, R. M.; Hobson, J. D.; Midgley, A. W. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1960. (d) Saxton, H. M.; Sutherland, J. K.; Whaley, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1449. (e) Hayakawa, K.; Yasukouchi, T.; Kanematus, K. *Tetrahedron Lett.* **1986**, *27*, 1837. (f) Hayakawa, K.; Nagatsugi, F.; Kanematsu, K. *J. Org. Chem.* **1988**, *53*, 860. (g) Hayakawa, K.; Yasukouchi, T.; Kanematsu, K. *Tertahedron Lett.* **1987**, *28*, 5895. (h) Yasukouchi, T.; Kanematsu, K. *Tetrahedron Lett.* **1989**, *30*, 6559. (i) Yoshida, M.; Hiromatsu, M.; Kanematsu, K. *Heterocycles* **1986**, *24*, 881. (j) Hayakawa, K.; Ohsuki, S.; Kanematsu, K. *Tetrahedron Lett.* **1986**, *27*, 947.

(3) Hayakawa, K.; Yodo, M.; Ohsuki, S.; Kanematsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 6735.

(4) (a) Hayakawa, K.; Yamaguchi, Y.; Kanematsu, K. *Tetrahedron Lett.* **1985**, *26*, 2689. (b) Yamaguchi, Y.; Hayakawa, K.; Kanematsu, K. *J. Chem. Soc., Chem. Commun.* **1987**, 515. (c) Yamaguchi, Y.; Yamada, H.; Hayakawa, K.; Kanematsu, K. *J. Org. Chem.* **1987**, *52*, 2040. (d) Yamaguchi, Y.; Tatsuta, N.; Hayakawa, K.; Kanematsu, K. *J. Chem. Soc., Chem. Commun.* **1989**, 470. (e) Kanematsu, K.; Soejima, S. *Heterocycles* 1**991**, *32*, 1483.

(5) Wu, H. J.; Lin, S. H.; Lin, C. C. *Heterocycles* **1994**, *38*, 1507.

(6) Lin, C. C.; Chen, L. H.; Wu, H. J. *J. Chin. Chem. Soc.* **1991**, *38*, 613.

(7) Wu, H. J.; Shao, W. D.; Ying, F. H. *Tetrahedron Lett.* **1994**, *35*, 729.

(8) Wu, H. J.; Ying, F. H.; Shao, W. D. *J. Org. Chem.* **1995**, *60*, 6168.

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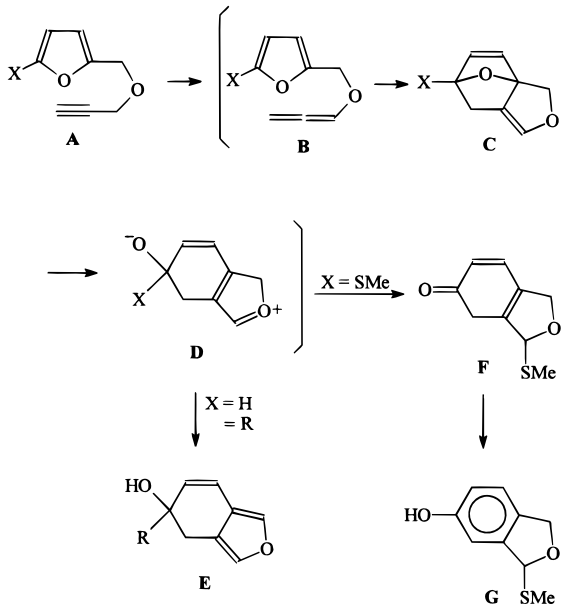
Scheme 1



methylthio group 1,4-rearrangement takes place to give the product **G** via **F**.

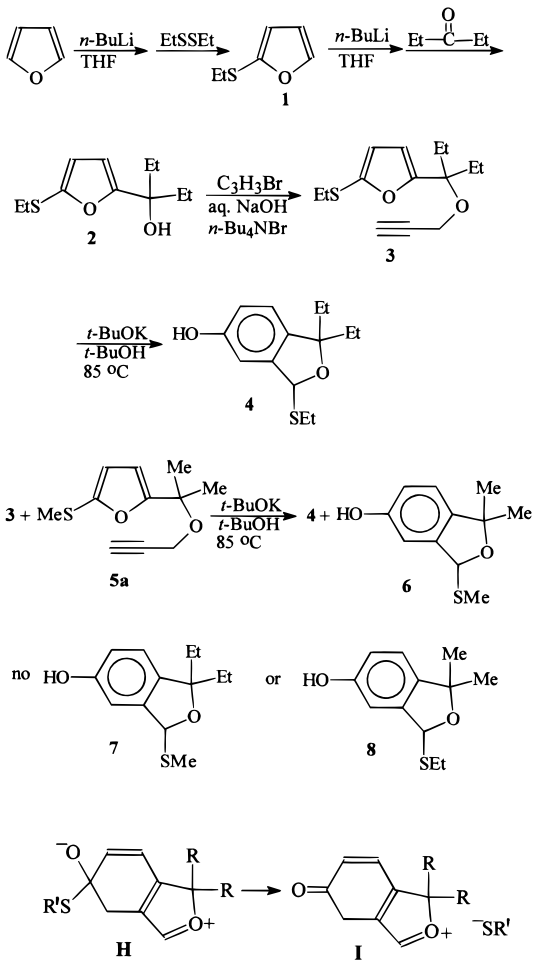
Recently, we have accomplished a series of reactions involving the intramolecular Diels−Alder reaction of a furan diene with an allenyl ether dienophile followed by the trimethylsilyl group,[9] alkylsulfinyl group, and alkylsulfonyl group rearrangements. In this paper, we wish to report the full details of our finding.

Results and Discussion

First of all, to understand in a more detail about the nature of the methylthio group 1,4-rearrangement as shown in Scheme 1, the furfuryl propargyl ether **3** was prepared. Metalation of furan with *n*-BuLi in dry tetrahydrofuran (THF) at 25 °C followed by addition of diethyl disulfide gave 2-ethylthiofuran (**1**) in 85% yield. Treatment of **1** with *n*-BuLi in dry THF followed by addition of 3-pentanone gave the alcohol **2** in 95% yield. Reaction of **2** with propargyl bromide in aqueous NaOH solution in the presence of *n*-Bu_4NBr as a phase-transfer catalyst at 25 °C gave the furfuryl propargyl ether **3** in 95% yield. Refluxing the propargyl ether **3** with *t*-BuOK in *t*-BuOH at 85 °C for 6 h gave the 1,4-rearrangement product **4** in 90% yield (Scheme 2). Refluxing the mixture of the propargyl ethers **5a**[8] and **3** with *t*-BuOK in *t*-BuOH at 85 °C for 6 h gave the rearrangement products **6** and **4**. No detectable amount of the cross-rearrangement products **7** or **8** was obtained. Thus, this reaction may involve an intramolecular Diels−Alder reaction of furan with allenyl ether followed by an intramolecular alkylthio group 1,4-rearrangement via the zwitterion **H** and the tight ion pair **I**.

To understand the effects of various substituent groups at the fifth position of the furan ring on the intramolecular Diels−Alder reaction and on the intramolecular rearrangement, the following experiments were performed. Oxidation of compounds **5a**−**d**[8] and **3** with 1 equiv of *m*-chloroperoxybenzoic acid (*m*-CPBA) in dichloromethane at 25 °C gave the sulfoxides **9a**−**d** and **9e** in

Scheme 2



75−85% yields, respectively. Refluxing **9a**−**e** with *t*-BuOK in *t*-BuOH at 85 °C for 6 h gave the sulfinyl group 1,2-rearrangement products **10a**−**e** in 80−90% yields (Scheme 3). No detectable amount of the sulfinyl group 1,4-rearrangement products **11a**−**e** was obtained. In the case of **9b**, which possesses two hydrogen atoms at the furfurylic position, no detectable amount of the furan ring transfer products **12** or **13** was obtained.

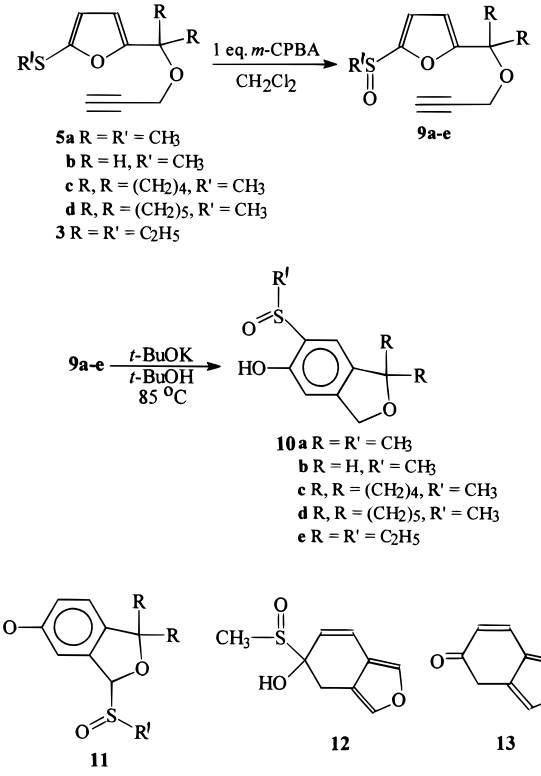
The IR spectra of **10a**−**e** showed strong absorptions at 3500−3200 cm^{-1} for the phenolic hydroxy group. The ^1H NMR spectrum of **10a** revealed two singlets at δ 6.84 and 6.76 for the two protons on the benzene ring and a singlet at δ 4.99 for the methylene protons. The ^{13}C NMR spectrum of **10a** displayed four singlets at δ 157.68, 144.39, 138.97, and 123.65 for the four quaternary benzene ring carbons, two peaks at δ 116.80 and 111.64 for the other two benzene ring carbons, and one peak at δ 70.33 for the methylene carbon. The structure of **10a** was also proved by X-ray analysis.[10]

A mechanism is proposed for this cycloaddition reation. The intramolecular Diels−Alder reactions of **9a**−**e** gave compounds **10a**−**e** as the sole product respectively, presumably via the corresponding allenyl ethers **14a**−**e** and the cycloadducts **15a**−**e**. We proposed that the cycloadducts are highly strained and under the reaction conditions they easily undergo ring opening of the bridged

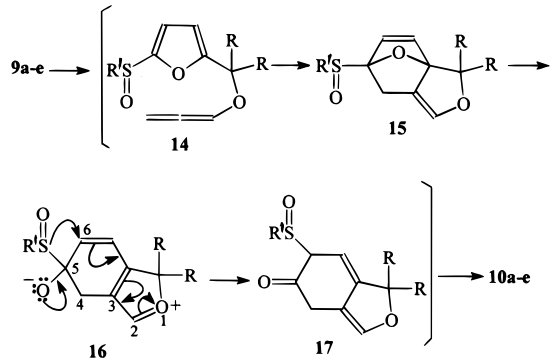
(9) Wu, H. J.; Yen, C. H.; Chuang, C. T. *Tetrahedron Lett.* **1996**, *37*, 7395.

(10) The author has deposited atomic coordinates for **10a** with the Cambridge Crystallographic Data Center. The coordinates can be obtained, on request, from the Director, Cambridge Crystallogriphic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

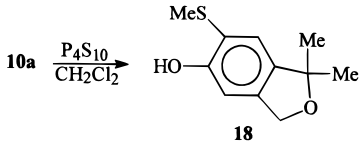
Scheme 3



Scheme 4



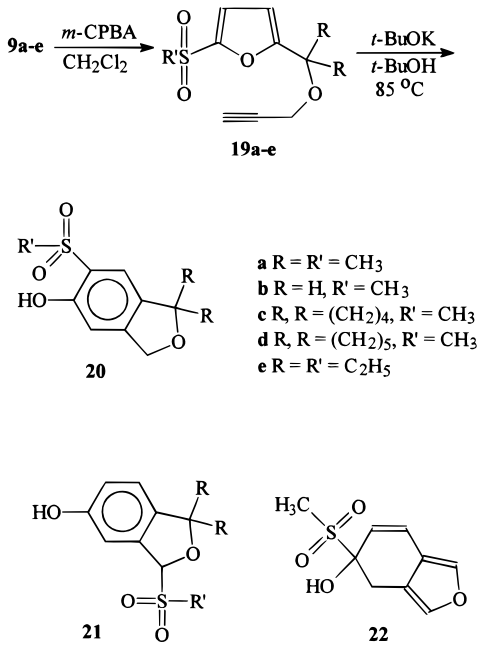
Scheme 5



oxygen atom to form the zwitterions **16a**−**e** as the reaction intermediates (Scheme 4). Elimination of the alkylsulfinyl group by the alkoxide ion of **16** followed by nucleophilic attack of the alkylsulfinyl group on the partially positively charged neighboring carbon C_6 gave the 1,2-rearrangement intermediates **17a**−**e**, which underwent aromatization to give the final products **10a**−**e**. It must be determined if the neighboring alkoxide ion of the zwitterion intermediates, such as **16**, may play a controlling role on the alkylsulfinyl group 1,2-rearrangement and the alkylthio group 1,4-rearrangement.

Treatment of the sulfoxide **10a** with P_4S_{10} in dichloromethane at 25 °C gave the reduced product **18** in a quantitative yield (Scheme 5). The overall transformation from **5** to **18** via **9** and **10** portrays the equivalence

Scheme 6



of methylthio group 1,2-rearrangement. Thus, we can perform the alkylthio group 1,4-rearrangement, such as the conversion of **3** to **4**, or the alkylthio group 1,2-migration via the sulfinyl group 1,2-rearrangement, such as the conversion of **5a** to **18** via **9a** and **10a**.

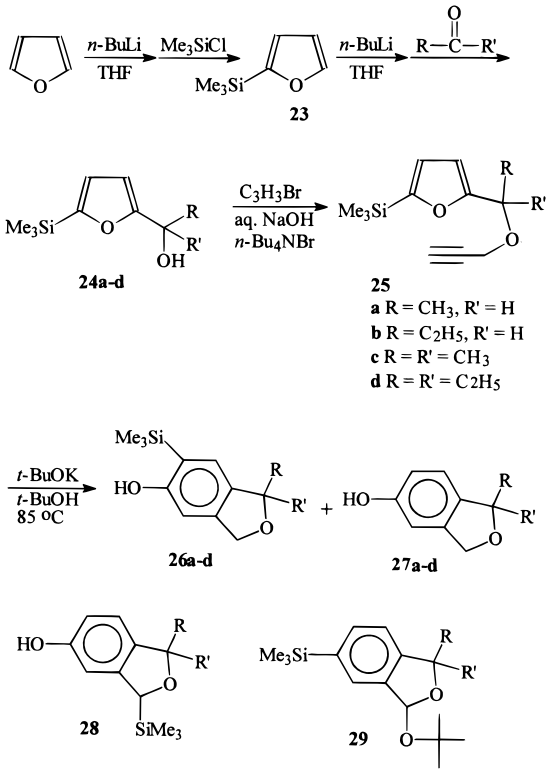
Oxidation of compounds **9a**−**e** with excess *m*-CPBA in dichloromethane at 25 °C gave the sulfones **19a**−**e**. Refluxing **19a**−**e** with *t*-BuOK in *t*-BuOH at 85 °C for 5 h gave the sulfonyl group 1,2-rearrangement products **20a**−**e** in 75−85% yields (Scheme 6). No detectable amount of the sulfonyl group 1,4-rearrangement products **21a**−**e** was obtained. Also, no detectable amount of the furan ring transfer products **22** or **13** was obtained for the case of **19b**, which possesses two hydrogen atoms at the furfurylic position. A mechanism similar to the sulfinyl group 1,2-rearrangement, such as Scheme 4, can be used to account for the sulfonyl group 1,2-rearrangement.

Metalation of furan with 1 equiv of *n*-BuLi in dry THF at 25 °C followed by addition of trimethylchlorosilane gave 2-(trimethylsilyl)furan (**23**). Metalation of **23** with *n*-BuLi in dry THF at 25 °C followed by addition of acetaldehyde, propioaldehyde, acetone, and 3-pentanone gave the alcohols **24a**−**d** in 75−85% yields, respectively. Treatment of **24a**−**d** with propargyl bromide in saturated aqueous NaOH solution in the presence of *n*-Bu_4NBr as a phase-transfer catalyst at 25 °C gave the furfuryl propargyl ethers **25a**−**d** in 75−95% yields. Refluxing the propargyl ethers **25a**−**d** with *t*-BuOK in *t*-BuOH at 85 °C for 10 h gave the trimethylsilyl group 1,2-rearrangement products **26a**−**d** (40−55%) and the trimethylsilyl group Brook rearrangement[11] products **27a**−**d** (45−35%) (Scheme 7). No detectable amount of the trimethylsilyl group 1,4-rearrangement products **28a**−**d** or compounds **29a**−**d** was obtained.

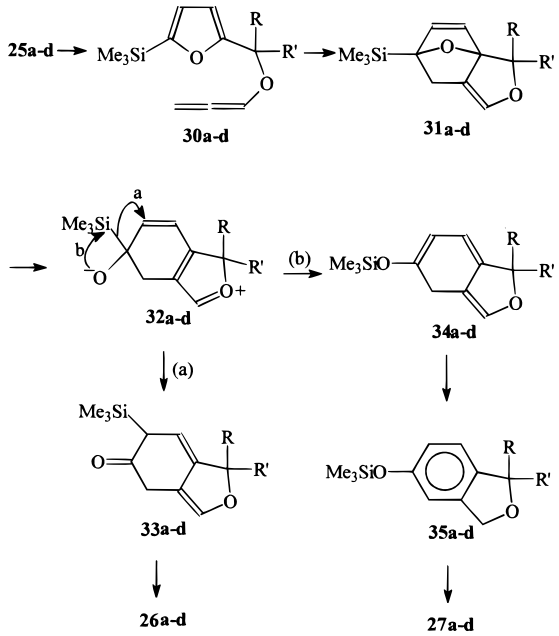
Treatment of compound **26** with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol (85 °C) for 6 h resulted in unchanged starting compound **26**. No conversion of **26** to **27** was obtained. Thus, compounds **26** and **27** were

(11) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

Scheme 7

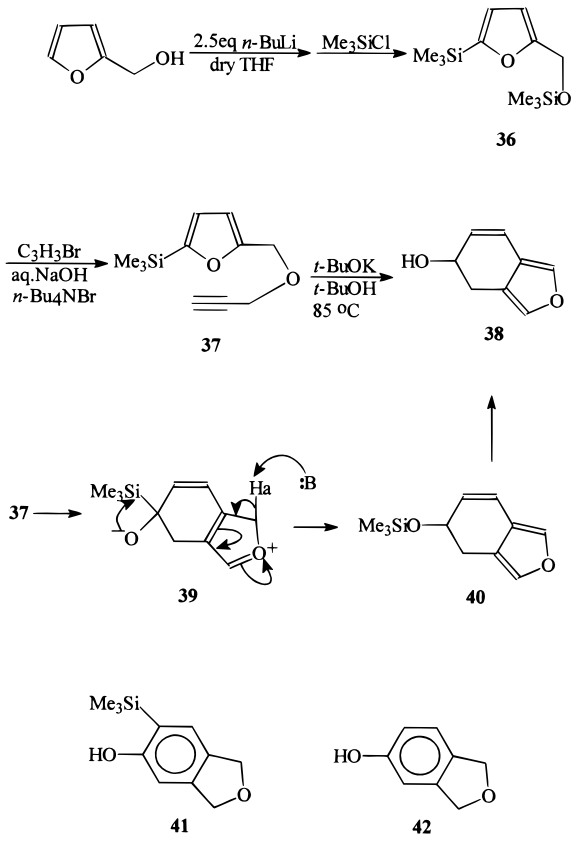


Scheme 8



obtained from **25** via different reaction pathways. A mechanism is proposed for this reaction (Scheme 8). The intramolecular Diels−Alder reactions of **25a**−**d** gave **26a**−**d** and **27a**−**d**, respectively, presumably via the corresponding allenyl ethers **30a**−**d** and the cycloadducts **31a**−**d**. Under the reaction conditions, the cycloadducts **31a**−**d** easily underwent ring opening of the bridged oxygen atom to form the zwitterions **32a**−**d** as the reaction intermediates. Elimination of the trimethylsilyl group by the alkoxide ion followed by 1,2-shift of the trimethylsilyl group (route a) gave the rearranged intermediate **33a**−**d**, which underwent aromatization to give **26a**−**d**. On the other hand, Brook rearrangement of the

Scheme 9



trimethylsilyl group of the zwitterions **32a**−**d** (route b) gave the rearranged intermediates **34a**−**d**, which underwent aromatization to give the products **35a**−**d**. Hydrolysis of the trimethylsilyl group of **35a**−**d** by the base or solvent afforded the phenols **27a**−**d**. The ratio of **26**:**27** (1:1) may imply the proximate reaction rates for the Brook rearrangement and the 1,2-rearrangement. Again, the problem of whether the neighboring alkoxide ion of the zwitterions **32** may play a controlling role on the trimethylsilyl group 1,2-rearrangement and Brook rearrangement needs to be proven by further experimental studies.

Metalation of furfuryl alcohol with 2.5 equiv of *n*-BuLi in dry THF at 25 °C followed by addition of 3 equiv of trimethylchlorosilane gave the disilylated product **36** in 90% yield. Reaction of **36** with propargyl bromide in saturated aqueous NaOH solution in the presence of *n*-Bu_4NBr as a phase transfer catalyst gave the propargyl ether **37** in 95% yield. Refluxing **37** with *t*-BuOK in *t*-BuOH at 85 °C for 8 h gave compound **38** in 90% yield (Scheme 9). Compound **38** was obtained from **37** via an intramolecular Diels−Alder reaction followed by the furan ring transfer reaction, which proceeded via proton abstraction of the proton Ha by the base and by the Brook rearrangement of the zwitterion intermediate **39**. Hydrolysis of **40** gave the final product **38**. The amount of the 1,2-rearrangement product **41** and the Brook rearrangement product **42** without furan ring-transfer reaction was too small to be isolated.

Conclusion

We have discovered novel intramolecular Diels−Alder reactions of a furandiene with an allenyl ether dienophile followed by the alkylsulfinyl group, alkylsulfonyl group,

and trimethylsilyl group rearrangements. In the cases of 5-(alkylthio)-2-furfuryl propargyl ethers, the alkylthio group 1,4-rearrangement products were obtained exclusively. Also, the alkylthio group 1,4-rearrangement may proceed intramolecularly via the tight ion pairs. In the cases of the 5-(alkylsulfinyl)-2-furfuryl propargyl ethers **9a**−**e** and the 5-(alkylsulfonyl)-2-furfuryl propargyl ethers **19a**−**e**, the alkylsulfinyl group and the alkylsulfonyl group 1,2-rearrangement products **10a**−**e** and **20a**−**e** were obtained, respectively. In the cases of the 5-(trimethylsilyl)-2-furfuryl propargyl ethers **25a**−**d**, the trimethylsilyl group 1,2-rearrangement products **26a**−**d** and Brook rearrangement products **27a**−**d** were obtained. In the case of the conversion of **37** to **38**, a mechanism via an intramolecular Diels−Alder reaction followed by the furan ring-transfer reaction and Brook rearrangement is proposed.

Experimental Section

General Methods. Melting points were determined in capillary tubes with a Laboratory Devices melting point apparatus and left uncorrected. Infrared spectra were recorded in $CHCl_3$ solutions or on neat thin films between NaCl disks. ^1H NMR spectra were determined at 300 MHz, and ^{13}C NMR spectra were determined at 75 MHz, on Fourier transform spectrometers. Chemical shifts are reported in ppm relative to TMS in the solvents specified. The multiplicities of ^{13}C signals were determined by DEPT techniques. High-resolution mass values were obtained with a high-resolution mass spectrometer at the Department of Chemistry, National Tsing Hua University. Elemental analyses were performed at the microanalysis laboratory of this department. X-ray analyses were carried out on a diffractometer at the Department of Chemistry, National Tsing Hua University. For thin-layer chromatography (TLC) analysis, precoated TLC plates (Kieselgel 60 F_{254}) were used, and column chromatography was done by using Kieselgel 60 (70−230 mesh) as the stationary phase. THF was distilled immediately prior to use from sodium benzophenone ketyl under nitrogen. CH_2Cl_2 was distilled from CaH_2 under nitrogen.

Preparation of 2-(Ethylthio)furan (1). To a solution of furan (5.0 g, 73 mmol) in dry THF (100 mL) was added *n*-BuLi (46 mL, 75 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. To this solution was added diethyl disulfide (9.8 g, 81 mmol) at 0 °C, and the reaction mixture was stirred at 25 °C for 4 h. After addition of saturated NH_4Cl (80 mL) and extraction with ether, the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by distillation to give **1** (9.2 g, 85%): bp 138−140 °C (760 mmHg); IR ($CHCl_3$) 1500, 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50−7.49 (m, 1H), 6.49−6.47 (m, 1H), 6.38−6.36 (m, 1H), 2.77 (q, J = 6.3 Hz, 2H), 1.26 (t, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 145.68 (C), 145.24 (CH), 116.77 (CH), 111.32 (CH), 29.97 (CH_2), 15.03 (CH_3); LRMS *m*/*z* (rel int) 128 (M^+, 10), 99 (100).

Preparation of α,α-Diethyl-5-(ethylthio)-2-furfuryl Alcohol (2). To a solution of 2-(ethylthio)furan (5.0 g, 39 mmol) in dry THF (100 mL) was added *n*-BuLi (17 mL, 43 mmol) at 0 °C. The reaction mixture was stirred at 25 °C for 4 h. To this solution was added 3-pentanone (3.5 g, 41 mmol) at 0 °C, and the reaction mixture was stirred at 25 °C for 1 h. After addition of saturated NH_4Cl (90 mL) and extraction with ether, the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give **2** (7.9 g, 95%): pale yellow oil; IR ($CHCl_3$) 3500−3200, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.45 (d, J = 1.8 Hz, 1H), 6.21 (d, J = 1.8 Hz, 1H), 2.74 (q, J = 6.6 Hz, 2H), 2.08 (brs, 1H), 1.90−1.80 (m, 4H), 1.23 (t, J = 6.6 Hz, 3H), 0.82 (t, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 161.61 (C), 144.10 (C), 117.82 (CH), 107.30 (CH), 75.11 (C), 31.93 ($2CH_2$), 30.24 (CH_2), 14.91 (CH_3), 7.74 ($2CH_3$); LRMS *m*/*z* (rel int) 214 (M^+, 22), 196 (95), 185 (100).

Preparation of α,α-Diethyl-5-(ethylthio)-2-furfuryl Propargyl Ether (3). To a mixture of compound **2** (1.0 g, 4.8 mmol) and saturated NaOH solution (20 mL) were added propargyl bromide (0.60 g, 5.0 mmol) and a catalytic amount (0.020 g) of *n*-Bu_4NBr at 25 °C. The reaction mixture was stirred at 25 °C for 8 h. After addition of saturated NH_4Cl (50 mL) and extraction with ether, the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give **3** (5.6 g, 95%): pale yellow oil; IR ($CHCl_3$) 3320, 2980, 2150, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.44 (d, J = 3.0 Hz, 1H), 6.30 (d, J = 3.0 Hz, 1H), 3.85 (d, J = 2.4 Hz, 2H), 2.77 (q, J = 6.6 Hz, 2H), 2.34 (t, J = 2.4 Hz, 1H), 1.90 (q, J = 6.6 Hz, 4H), 1.25 (t, J = 6.6 Hz, 3H), 0.81 (t, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 158.35 (C), 145.27 (C), 116.98 (CH), 110.48 (CH), 80.61 (CH), 79.83 (C), 72.98 (C), 50.81 (CH_2), 29.97 (CH_2), 25.63 ($2CH_2$), 14.94 (CH_3), 7.36 ($2CH_3$); LRMS *m*/*z* (rel int) 252 (M^+, 5), 149 (100); HRMS (EI) calcd for $C_{14}H_{20}O_2S$ 252.1184, found 252.1176. Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.64; H, 7.99. Found: C, 66.52; H, 7.95.

Intramolecular Diels−Alder Reaction of 3. Compound **3** (2.0 g, 7.9 mmol) was dissolved in 2-methyl-2-propanol (100 mL) in a round-bottomed flask. Potassium *tert*-butoxide (1.8 g, 17 mmol) was added to the solution, and the reaction mixture was refluxed at 85 °C for 6 h. After cooling, saturated NH_4Cl (50 mL) was added, and the reaction mixture was extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give the 1,4-rearrangement product **4** (1.7 g, 85%): pale yellow oil; IR ($CHCl_3$) 3500−3200, 1610, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.06 (brs, 1H), 6.88−6.83 (m, 3H), 6.45 (s, 1H), 2.78−2.65 (m, 2H), 1.90−1.74 (m, 4H), 1.29 (t, J = 6.9 Hz, 3H), 0.90 (t, J = 6.9 Hz, 3H), 0.69 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 155.38 (C), 140.52 (C), 134.60 (C), 121.38 (CH), 115.72 (CH), 108.70 (CH), 92.79 (C), 87.64 (CH), 32.65 (CH_2), 24.81 (CH_2), 24.64 (CH_2), 14.62 (CH_3), 8.18 (CH_3), 7.51 (CH_3); LRMS *m*/*z* (rel int) 252 (M^+, 8), 223 (20), 191 (100); HRMS (EI) calcd for $C_{14}H_{20}O_2S$ 252.1184, found 252.1189. Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.64; H, 7.99. Found: C, 66.58; H, 7.93.

Intramolecular Diels−Alder Reaction of the Mixture of Compounds 3 and 5a. Compounds **3** (1.0 g, 4.0 mmol) and **5a**[8] (0.84 g, 4.0 mmol) were dissolved in 2-methyl-2-propanol (100 mL) in a round-bottomed flask. Potassium *tert*-butoxide (2.2 g, 20 mmol) was added to the solution, and the reaction mixture was refluxed at 85 °C for 6 h. After cooling, saturated NH_4Cl (60 mL) was added, and the reaction mixture was extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give compounds **4** and **6** in 85% yields. No detectable amount of the cross-rearrangement products **7** or **8** was obtained. Compound **6** is a known compound.[8]

General Procedure for the Oxidation of Compounds 5a−d and 3 with 1 Equiv of *m*-CPBA. To a solution of **5a** (1.0 g, 4.8 mmol) in dichloromethane (50 mL) was added 1 equiv of *m*-CPBA (0.82 g, 4.8 mmol) at 0 °C. The reaction mixture was stirred at 25 °C for 1 h. The solvent was evaporated, and sodium bicarbonate solution (1 N, 15 mL) was added. The mixture was extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give compound **9a** (0.86 g, 80%).

α,α-Dimethyl-5-(methylsulfinyl)-2-furfuryl propargyl ether (9a): pale yellow oil; IR ($CHCl_3$) 2150, 1380, 1100, 1050 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.90 (d, J = 3.6 Hz, 1H), 6.40 (d, J = 3.6 Hz, 1H), 3.92 (d, J = 2.4 Hz, 2H), 2.97 (s, 3H), 2.32 (t, J = 2.4 Hz, 1H), 1.59 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 161.44 (C), 152.87 (C), 115.69 (CH), 108.70 (CH), 80.26 (CH), 73.97 (C), 73.45 (C), 51.74 (CH_2), 38.34 (CH_3), 25.40 (CH_3), 25.69 (CH_3); LRMS *m*/*z* (rel int) 226 (M^+, 10), 211 (20), 155 (100); HRMS (EI) calcd for $C_{11}H_{14}O_3S$ 226.0663, found 226.0669. Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.39; H, 6.24. Found: C, 58.25; H, 6.30.

General Procedure for the Intramolecular Diels−Alder Reaction of Compounds 9a−e. The same reaction conditions and procedure as for the intramolecular Diels−Alder reaction of **3** were applied for the intramolccular Diels−Alder reaction of **9a−e** to give the alkylsulfinyl group 1,2-rearrangement products **10a−e** in 80−90% yields.

Spectral data for 10a: viscous oil; 85% yield; IR ($CHCl_3$) 3500−3200, 1610, 1440, 1300, 1050 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.76 (s, 1H), 4.99 (s, 2H), 2.95 (s, 3H), 1.44 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 157.68 (C), 144.39 (C), 138.97 (C), 123.65 (C), 116.80 (CH), 111.64 (CH), 85.39 (C), 70.33 (CH_2), 41.60 (CH_3), 28.40 ($2CH_3$); LRMS *m/z* (rel int) 226 (M^+, 20), 211 (100), 193 (70); HRMS (EI) calcd for $C_{11}H_{14}O_3S$ 226.0663, found 226.0660. Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.39; H, 6.24. Found: C, 58.52; H, 6.34.

Reduction of Compound 10a with P_4S_{10}. To a solution of compound **10a** (0.50 g, 2.2 mmol) in dichloromethane (50 mL) was added P_4S_{10} (1.47 g, 3.32 mmol) at 25 °C. The reaction mixture was stirred at 25 °C for 6 h. The solvent was evaporated, and the crude product was purified by column chromatography to give **18** (0.46 g, 98%).

Spectral data for 18: pale yellow oil; IR ($CHCl_3$) 3500−3200, 1610, 1050 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.21 (s, 1H), 6.80 (s, 1H), 5.00 (s, 2H), 2.34 (s, 3H), 1.48 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 155.55 (C), 141.30 (C), 139.35 (C), 125.89 (CH), 120.09 (C), 107.16 (CH), 85.39 (C), 70.15 (CH_2), 28.37 ($2CH_3$), 19.48 (CH_3); LRMS *m/z* (rel int) 210 (M^+, 20), 119 (62), 85 (95), 71 (100); HRMS (EI) calcd for $C_{11}H_{14}O_2S$ 210.0715, found 210.0710.

General Procedure for the Oxidation of 9a−e with *m*-CPBA. To a solution of **9a** (1.13 g, 5.0 mmol) in dichloromethane (50 mL) was added an excess of *m*-CPBA (1.3 g, 7.4 mmol) at 0 °C. The reaction mixture was stirred at 25 °C for 2 h. The solvent was evaporated, and sodium bicarbonate solution (1 N, 20 mL) was added. The mixture was extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give the sulfone **19a** (0.98 g, 84%).

α,α-Dimethyl-5-(methylsulfonyl)-2-furfuryl propargyl ether (19a): pale yellow oil; IR ($CHCl_3$) 2150, 1325, 1140 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, J = 3.3 Hz, 1H), 6.46 (d, J = 3.3 Hz, 1H), 3.99 (d, J = 2.4 Hz, 2H), 3.17 (s, 3H), 2.36 (t, J = 2.4 Hz, 1H), 1.63 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 162.40 (C), 148.59 (C), 117.70 (CH), 108.61 (CH), 80.06 (CH), 73.82 (C), 73.59 (C), 51.74 (CH_2), 43.06 (CH_3), 25.40 ($2CH_3$); LRMS *m/z* (rel int) 242 (M^+, 62), 143 (100); HRMS (EI) calcd for $C_{11}H_{14}O_4S$ 242.0612, found 242.0616. Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.83. Found: C, 54.65; H, 5.90.

General Procedure for the Intramolecular Diels−Alder Reaction of the Sulfones 19a−e. The same reaction conditions and procedure as for the cycloaddition of **3** were applied for the intramolecular Diels−Alder reaction of compounds **19a−e** to give the alkylsulfonyl group 1,2-rearrangement products **20a−e** in 75−85% yields.

Spectral data for 20a: viscous oil; 82% yield; IR ($CHCl_3$) 3500−3200, 1440, 1305, 1120 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 (s, 1H), 6.87 (s, 1H), 4.98 (s, 2H), 3.11 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 155.61 (C), 149.23 (C), 138.13 (C), 121.29 (C), 120.33 (CH), 111.30 (CH), 85.39 (C), 70.15 (CH_2), 44.89 (CH_3), 28.40 (CH_3); LRMS *m/z* (rel int) 228 (M^+, 5), 213 (100); HRMS (EI) calcd for $C_{11}H_{14}O_4S$ 242.0612, found 242.0608. Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.83. Found: C, 54.68; H, 5.93.

Preparation of (Trimethylsilyl)furan (23). To a solution of furan (2.04 g, 30.0 mmol) in dry THF (100 mL) was added *n*-BuLi (13.2 mL, 33.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. To this solution was added trimethylchlorosilane (3.58 g, 33.0 mmol) at 0 °C, and the reaction mixture was stirred at 25 °C for 5 h. After addition of saturated NH_4Cl (60 mL) and extraction with ether, the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by distillation to give (trimethylsilyl)furan (**23**) (3.61 g, 86%): bp 108−109 °C (760 mmHg); IR ($CHCl_3$) 1280, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J = 2.4 Hz, 1H), 6.65 (d, J = 3.0 Hz, 1H), 6.39 (dd, J = 3.0, 2.4 Hz, 1H), 0.29 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 160.39 (C), 146.49 (CH), 119.42 (CH), 109.28 (CH), −1.65 ($3CH_3$); LRMS *m/z* (rel int) 140 (M^+, 12), 71 (100).

General Procedure for the Preparation of the Furfuryl Alcohols 24a−d. To a solution of 2-(trimethylsilyl)furan (2.80 g, 20.0 mmol) in dry THF (80 mL) was added *n*-BuLi (10 mL, 25 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. To this solution was added acetaldehyde (1.32 g, 30.0 mmol) at 0 °C, and the reaction mixture was stirred at 25 °C for 2 h. After addition of saturated NH_4Cl (60 mL) and extraction with ether, the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give α-methyl-5-(trimethylsilyl)-2-furfuryl alcohol **24a** (3.1 g, 85%): pale yellow oil; IR ($CHCl_3$) 3500−3200, 1260, 1100, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.53 (d, J = 3.0 Hz, 1H), 6.19 (d, J = 3.0 Hz, 1H), 4.88 (q, J = 6.9 Hz, 1H), 2.31 (brs, 1H), 1.52 (d, J = 6.9 Hz, 3H), 0.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 161.96 (C), 159.43 (C), 120.09 (CH), 104.86 (CH), 63.57 (CH), 21.26 (CH_3), −1.73 ($3CH_3$); LRMS *m/z* (rel int) 184 (M^+, 7), 169 (100).

General Procedure for the Preparation of the 5-(Trimethylsilyl)-2-furfuryl Propargyl Ethers 25a−d. The same reaction conditions and procedure as for the preparation of the propargyl ether **3** were applied for the preparation of the 5-(trimethylsilyl)-2-furfuryl propargyl ethers **25a−d**.

α-Methyl-5-(trimethylsilyl)-2-furfuryl propargyl ether 25a: pale yellow oil; 92% yield; IR ($CHCl_3$) 3300, 2100, 1100, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.55 (d, J = 3.0 Hz, 1H), 6.28 (d, J = 3.0 Hz, 1H), 4.74 (q, J = 6.6 Hz, 1H), 4.14, 4.01 (doublet of ABq, J = 15.9, 2.4 Hz, 2H), 2.41 (t, J = 2.4 Hz, 1H), 1.55 (d, J = 6.6 Hz, 3H), 0.26 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 160.39 (C), 158.89 (C), 119.92 (CH), 107.48 (CH), 79.86 (CH), 73.93 (C), 69.31 (CH), 55.41 (CH_2), 19.57 (CH_3), −1.69 ($3CH_3$); LRMS *m/z* (rel int) 222 (M^+, 4), 57 (100); HRMS (EI) calcd for $C_{12}H_{18}O_2Si$ 222.1076, found 222.1073. Anal. Calcd for $C_{12}H_{18}O_2Si$: C, 64.83; H, 8.17. Found: C, 64.94; H, 8.25.

General Procedure for the Intramolecular Diels−Alder Reaction of 5-(Trimethylsilyl)-2-furfuryl Propargyl Ethers 25a−d. Compound **25a** (2.2 g, 10 mmol) was dissolved in *tert*-butyl alcohol (100 mL) in a round-bottomed flask. Potassium *tert*-butoxide (2.2 g, 20 mmol) was added to the solution, and the reaction mixture was refluxed at 85 °C for 10 h. After cooling, saturated NH_4Cl (80 mL) was added, and the reaction mixture was extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give the trimethylsilyl group 1,2-rearrangement product **26a** (1.1 g, 50%) and the Brook rearrangement product **27a** (0.59 g, 40%).

Spectral data for 26a: viscous oil; IR ($CHCl_3$) 3500−3200, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 1H), 6.54 (s, 1H), 6.08 (brs, 1H), 5.29 (q, J = 6.6 Hz, 1H), 5.05, 4.97 (ABq, J = 12.6 Hz, 2H), 1.49 (d, J = 6.6 Hz, 3H), 0.31 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 160.71 (C), 142.06 (C), 134.78 (C), 127.14 (CH), 124.87 (C), 106.87 (CH), 79.97 (CH), 71.84 (CH_2), 21.93 (CH_3), −1.00 ($3CH_3$); LRMS *m/z* (rel int) 222 (M^+, 5), 207 (100), 191 (93); HRMS (EI) calcd for $C_{12}H_{18}O_2Si$ 222.1076, found 222.1072. Anal. Calcd for $C_{12}H_{18}O_2Si$: C, 64.83; H, 8.17. Found: C, 64.96; H, 8.27.

Spectral data for 27a: viscous oil; IR ($CHCl_3$) 3500−3200, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.99 (d, J = 8.7 Hz, 1H), 6.75 (dd, J = 8.7, 2.1 Hz, 1H), 6.68 (d, J = 2.1 Hz, 1H), 6.60 (brs, 1H), 5.30 (q, J = 6.6 Hz, 1H), 5.08, 5.00 (ABq, J = 12.6 Hz, 2H), 1.47 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 155.76 (C), 140.52 (C), 134.92 (C), 121.70 (CH), 114.62 (CH), 107.83 (CH), 79.91 (CH), 71.93 (CH_2), 21.87 (CH_3); LRMS *m/z* (rel int) 150 (M^+, 18), 135 (100); HRMS (EI) calcd for $C_9H_{10}O_2$ 150.0681, found 150.0689. Anal. Calcd for $C_9H_{10}O_2$: C, 71.97; H, 6.72. Found: C, 71.83; H, 6.60.

Preparation of 5-(Trimethylsilyl)-2-furfuryl Trimethylsilyl Ether (36). To a solution of furfuryl alcohol (0.50 g, 5.0 mmol) in dry THF (30 mL) was added *n*-BuLi (5.0 mL,

12.5 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 6 h. To this solution was added trimethylchlorosilane (1.6 g, 15 mmol) at 0 °C, and the reaction mixture was stirred at 25 °C for 4 h. After addition of saturated $NaHCO_3$ (40 mL) and extraction with ether, the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give 5-(trimethylsilyl)-2-furfuryl trimethylsilyl ether **36** (1.1 g, 90%): pale yellow oil; IR ($CHCl_3$) 1280, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.53 (d, J = 3.0 Hz, 1H), 6.22 (d, J = 3.0 Hz, 1H), 4.64 (s, 2H), 0.26 (s, 9H), 0.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 160.13 (C), 157.88 (C), 120.30 (CH), 107.80 (CH), 57.60 (CH_2), −0.45 ($3CH_3$), −1.61 ($3CH_3$); LRMS m/z (rel int) 242 (M^+, 18), 73 (100).

Preparation of 5-(Trimethylsilyl)-2-furfuryl Propargl Ether (37). The same reaction conditions and prodecure as for the preparation of the propargyl ether **3** were applied for the preparation of compound **37** in 95% yield: pale yellow oil; IR ($CHCl_3$) 3300, 2140, 1100, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.56 (d, J = 3.0 Hz, 1H), 6.35 (d, J = 3.0 Hz, 1H), 4.59 (s, 2H), 4.17 (d, J = 2.4 Hz, 2H), 2.47 (t, J = 2.4 Hz, 1H), 0.26 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 161.18 (C), 154.85 (C), 120.24 (CH), 109.95 (CH), 79.39 (CH), 74.67 (C), 63.19 (CH_2), 56.69 (CH_2), −1.67 ($3CH_3$); LRMS m/z (rel int) 208 (M^+, 26), 153 (80), 73 (100); HRMS (EI) calcd for $C_{11}H_{16}O_2Si$ 208.0920, found 208.0927. Anal. Calcd for $C_{11}H_{16}O_2Si$: C, 63.43; H, 7.75. Found: C, 63.51; H, 7.80

Intramolecular Diels−Alder Reaction of Compound 37. The same reaction conditions and procedure as for the intramolecular Diels−Alder reaction of compound **3** were applied for the reaction of **37** to give the product **38** in 90% yield: viscous oil; IR ($CHCl_3$) 3500−3200, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.20 (s, 1H), 6.51 (d, J = 9.6 Hz, 1H), 5.92 (dd, J = 9.6, 3.6 Hz, 1H), 4.52−4.48 (m, 1H), 2.88, 2.78 (doublet of ABq, J = 16.8, 6.6 Hz, 2H), 2.03 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 138.19 (CH), 137.14 (CH), 129.62 (CH), 120.33 (C), 119.74 (CH), 117.27 (C), 65.46 (CH), 27.82 (CH_2); LRMS m/z (rel int) 136 (M^+, 8), 119 (100); HRMS (EI) calcd for $C_8H_8O_2$ 136.0524, found 136.0530.

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Supporting Information Available: Spectral data for compounds **9b−e**, **10b−e**, **19b−e**, **20b−e**, **24b−d**, **25b−d**, **26b−d**, and **27b−d** and X-ray crystallographic data for compound **10a** (15 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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