EJ52-1998-789
Journal of the Chinese Chemical Society, **1998**, *45*, 789-797

Intramolecular Diels-Alder Reaction of Furans with Allenyl Ethers Followed by Phenylthio and Trialkylsilyl Groups Rearrangement

Chi-Te Chuang (莊基德), Chia-Hui Yen (嚴嘉蕙) and Hsien-Jen Wu* (吳獻仁)
Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan, R.O.C.

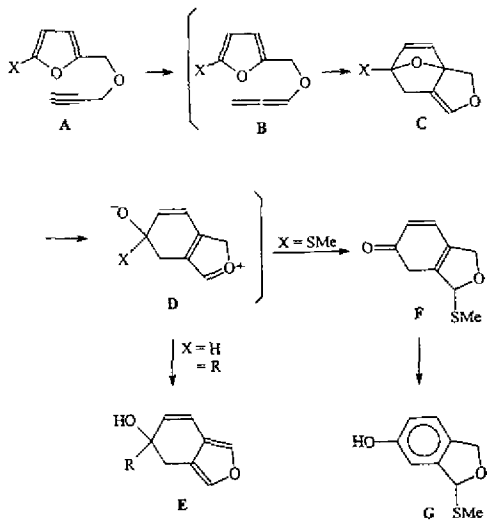
A new reaction involving an intramolecular Diels-Alder reaction of a furan diene with an allenyl ether dienophile followed by phenylthio group rearrangement was discovered. Treatment of the propargyl ethers **2a-c** with *t*-BuOK in *t*-BuOH at 85 °C gave the phenylthio group rearrangement products **5a-c** and **6a-c**. A reaction involving an intramolecular Diels-Alder reaction of a furan diene with an allenyl ether dienophile followed by trialkylsilyl group rearrangement is also demonstrated.

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, Kanematsu developed a furan ring transfer reaction via the intramolecular Diels-Alder reaction of a furan and an allenyl ether and applied this reaction to the synthesis of natural products.[4] For the purpose of the furan ring transfer reaction, in all cases there was only one carbon atom and one oxygen atom linked between the furan and the allene for the cycloaddition. In these cases the cycloadducts were not isolated under the reaction conditions but were further transferred into the isobenzofuran precursors *via* ring opening of the bridged oxygen ring of the cycloadducts.

A few years ago, we 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, we discovered a novel reaction involving an intramolecular Diels-Alder reaction of a furan with an allenyl ether followed by a methylthio group 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 I). 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 methylthio group rearrangement takes place to give the product **G** via **F**.

Scheme I



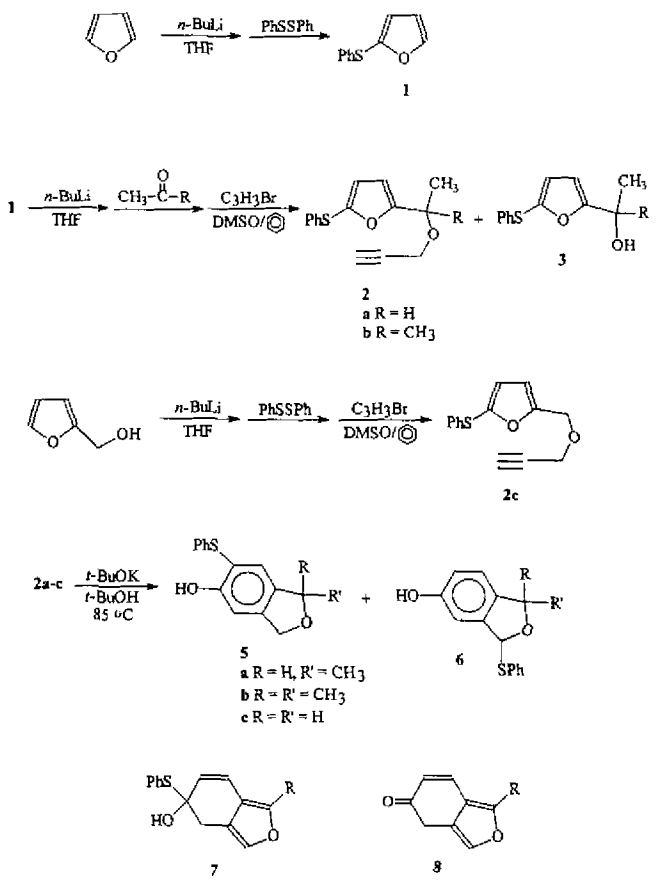
Recently, we accomplished a new reaction involving the intramolecular Diels-Alder reaction of a furan diene with an allenyl ether dienophile followed by the phenylthio group rearrangement. In this paper, we report the full details of this finding. We also report the full details of the trialkylsilyl group rearrangement.[9]

RESULTS AND DISCUSSION

Metalation of furan with one equivalent of *n*-BuLi in dry THF at 25 °C followed by addition of diphenyl disulfide

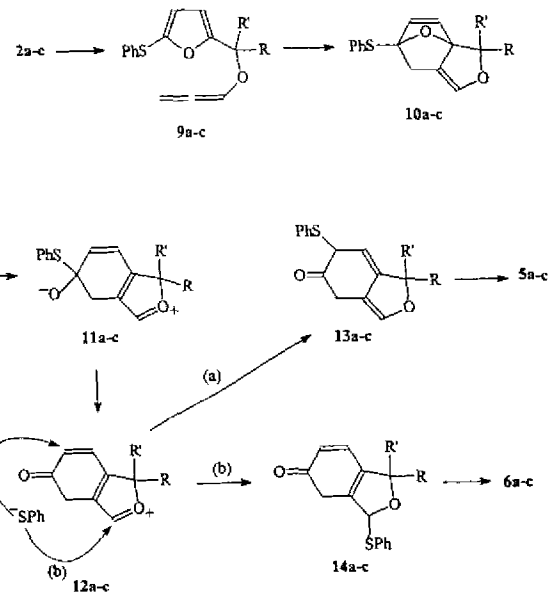
gave 2-phenylthiofuran (**1**) in 92% yield. Metalation of **1** with *n*-BuLi in dry THF at 25 °C followed by addition of acetaldehyde and acetone, then by propynylation of the reaction mixture with propargyl bromide in dry DMSO and benzene at 25 °C, gave the furfuryl propargyl ethers **2a** and **2b** as the major products (72-64%) and the alcohols **3a** and **3b** as the minor products (12-21%), respectively (Scheme II). Metalation of furfuryl alcohol (**4**) with 2.5 equivalents of *n*-BuLi in dry THF, followed by addition of diphenyl disulfide and then by propynylation of the reaction mixture with propargyl bromide in dry DMSO and benzene at 25 °C, gave the furfuryl propargyl ether **2c** in 82% yield. Treatment of the furfuryl propargyl ethers **2a-c** with *t*-BuOK in *t*-BuOH at 85 °C for 6 h gave the phenylthio group rearrangement products **5a-c** and **6a-c** in ratios of 1:1 in 80-84% yields. Compound **6a** was a mixture of two stereoisomers. In the cases of the base-promoted intramolecular Diels-Alder reaction of **2a** and **2c**, which possess one or two hydrogen atoms at the furfurylic position, we did not obtain the corresponding furan ring transfer reaction products **7** or **8**. These results might imply that the phenylthio group rearrangement proceeded faster than the furan ring transfer reaction.

Scheme II



A mechanism is proposed for this cycloaddition reaction. The intramolecular Diels-Alder reactions of **2a-c** gave the rearrangement products **5a-c** and **6a-c**, presumably *via* the corresponding allenyl ethers **9a-c** and the cycloadducts **10a-c**. We propose that the cycloadducts are highly strained and easily undergo ring opening to form the zwitterions **11a-c** as the reaction intermediates (Scheme III). β-Elimination of the phenylthio group of **11** to give the ion pairs **12a-c** followed by 1,6-addition of the phenylthio group (route a) gave the rearranged intermediates **13a-c**, which underwent aromatization to give **5a-c**. On the other hand, elimination of the phenylthio group followed by 1,2-addition of the phenylthio group (route b) *via* the ion pairs **12a-c** gave the rearranged intermediates **14a-c**, which underwent aromatization to give the products **6a-c**.

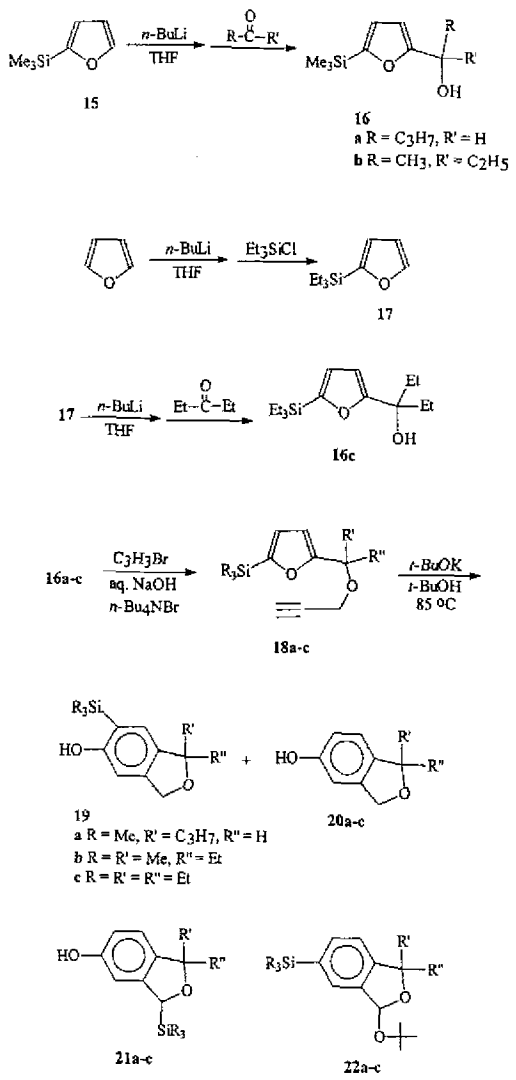
Scheme III



Metalation of 2-trimethylsilylfuran (**15**) (commercially available) with *n*-BuLi in dry THF at 25 °C followed by addition of butyraldehyde and 2-butanone gave the alcohols **16a** and **16b** in 86 and 92% yields, respectively. Treatment of furan with one equivalent of *n*-BuLi in dry THF at 25 °C followed by addition of triethylsilyl chloride gave 2-triethylsilylfuran (**17**) in 82% yield. Metalation of **17** with *n*-BuLi in dry THF followed by addition of 3-pentanone gave the alcohol **16c** in 78% yield (Scheme IV). Reaction of **16a-c** 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 **18a-c** in 86-94% yields. Refluxing the furfuryl propargyl ethers **18a-c** with *t*-BuOK in *t*-BuOH at 85 °C for 10 h gave the trialkylsilyl group rearrangement products **19a-c** (35-40%)

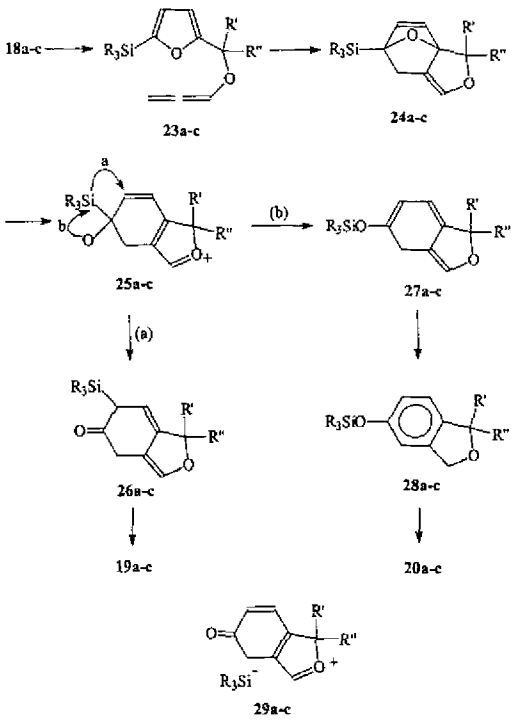
and the Brook rearrangement products **20a-c** (55-40%). No detectable amount of the trialkylsilyl group rearrangement products **21a-c** or compounds **22a-c** was obtained.

Scheme IV



Treatment of **19a** with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol (85 °C) for 6 h remained unchanged starting with compound **19a**. No conversion of **19a** to **20a** was obtained. Thus, compounds **19** and **20** were obtained from **18** *via* different reaction pathways. A mechanism is proposed for this reaction (Scheme V). The intramolecular Diels-Alder reactions of **18a-c** gave **19a-c** and **20a-c** respectively, presumably *via* the corresponding allenyl ethers **23a-c** and the cycloadducts **24a-c**. Under the reaction conditions, the cycloadducts **24a-c** easily underwent ring opening to form the zwitterions **25a-c** as the reaction intermediates. Migration of the trialkylsilyl group of **25a-c** (route a) gave the rearranged intermediates **26a-c**, which underwent aromatization to give **19a-c**. On the other hand, Brook rearrangement[19] of the trialkylsilyl group of the zwitterions **25a-c** (route b) gave the rearranged intermediates **27a-c**, which underwent aromatization to give the products **28a-c**. Hydrolysis of the trialkylsilyl group of **28a-c** by the base afforded the phenols **20a-c**. It is not clear whether this reaction proceeds *via* the ion pairs **29a-c** as the reaction intermediates.

Scheme V



CONCLUSION

We have discovered a new reaction involving an intramolecular Diels-Alder reaction of a furan with an allenyl ether followed by phenylthio group rearrangement. A mechanism *via* the zwitterions **11a-c** and the ion pairs **12a-c** as the reaction intermediates is proposed for the intramolecular cycloaddition. We have also demonstrated a reaction involving an intramolecular Diels-Alder reaction of a furan with an allenyl ether followed by trialkylsilyl group rearrangement.

EXPERIMENTAL SECTION

General

Melting points were determined in capillary tubes with a *Laboratory Devices melting point* apparatus and were un-

corrected. 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. 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-Phenylthiofuran (1)

To a solution of furan (2.04 g, 30.0 mmol) in dry THF (70 mL) was added *n*-BuLi (10.0 mL, 25.0 mmol, 2.5 M in hexane) at 0 °C. The reaction mixture was stirred at 25 °C for 4 h. To this solution was added diphenyl disulfide (5.46 g, 25.0 mmol) at 0 °C and the reaction mixture was stirred at room temperature for 4 h. After addition of saturated NH_4Cl (40 mL) and extraction with ether (3 × 50 mL), the organic layer was washed with brine, dried over $MgSO_4$ and evaporated, and the residue was purified by column chromatography to give 2-phenylthiofuran (1) (3.82 g, 86%): IR (neat) 1580, 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51-7.50 (m, 1H), 7.20-7.11 (m, 5H), 6.71-6.70 (m, 1H), 6.40-6.39 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 146.37 (CH), 142.94 (C), 136.21 (C), 128.78 (2CH), 127.38 (2CH), 126.21 (CH), 119.39 (CH), 111.76 (CH); LRMS *m/z* (rel int) 176 (M^+, 84), 115 (100); HRMS (EI) calcd for $C_{10}H_8OS$ 172.0296, found 172.0290; Anal. Calcd for $C_{10}H_8OS$: C, 68.17; H, 4.58. Found: C, 68.28; H, 4.67.

General Procedure for the Preparation of the Propargyl Ethers 2a and 2b and the Alcohols 3a and 3b

To a solution of 2-phenylthiofuran (2.00 g, 11.4 mmol) in dry THF (60 mL) was added *n*-BuLi (5.10 mL, 13.6 mmol, 2.5 M in hexane) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. To this solution was added dry acetaldehyde (0.53 g, 12.0 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 1 h. After evaporation of the solvent under reduced pressure, dry DMSO (25 mL) and dry benzene (25 mL) were added to dissolve the reaction mixture. To this solution was then added propargyl bromide (4.40 g, 37.0 mmol), and the reaction mixture was stirred at 25 °C for 5 h. After addition of saturated NH_4Cl (30 mL) and extraction with ether (5 × 30 mL), the organic layer was washed with brine, dried over $MgSO_4$ and evaporated, and the residue was purified by column chromatography to give **2a** (2.1 g, 72%) and **3a** (0.38 g, 12%).

α-Methyl-(5-phenylthio)-2-furfuryl Propargyl Ether 2a

Pale yellow oil; IR (neat) 3300, 2120, 1600, 1505, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26-7.15 (m, 5H), 6.70 (d, J = 3.0 Hz, 1H), 6.39 (d, J = 3.0 Hz, 1H), 4.71 (q, J = 6.6 Hz, 1H), 4.16, 4.02 (doublet of ABq, J = 15.6, 2.4 Hz, 2H), 2.41 (t, J = 2.4 Hz, 1H), 1.53 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 158.76 (C), 142.70 (C), 136.21 (C), 129.01 (2CH), 127.38 (2CH), 126.27 (CH), 120.15 (CH), 109.63 (CH), 79.60 (C), 74.44 (CH), 69.37 (CH), 55.67 (CH_2), 19.57 (CH_3); LRMS *m/z* (rel int) 258 (M^+, 27), 203 (100); HRMS (EI) calcd for $C_{15}H_{14}O_2S$ 258.0715, found 258.0724; Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.75; H, 5.47. Found: C, 69.87; H, 5.56.

α-Methyl-(5-phenylthio)-2-furfuryl Alcohol 3a

Pale yellow oil; IR (neat) 3600-3200, 1600, 1500, 1060 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.28-7.15 (m, 5H), 6.69 (d, J = 3.0 Hz, 1H), 6.30 (d, J = 3.0 Hz, 1H), 4.82 (q, J = 6.6 Hz, 1H), 3.61 (brs, 1H), 1.48 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 162.17 (C), 141.68 (C), 136.41 (C), 129.07 (2CH), 127.23 (2CH), 126.24 (CH), 120.59 (CH), 107.22 (CH), 63.28 (CH), 21.20 (CH_3); LRMS *m/z* (rel int) 220 (M^+, 75), 202 (100); HRMS (EI) calcd for $C_{12}H_{12}O_2S$ 220.0558, found 220.0567; Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.44; H, 5.50. Found: C, 65.54; H, 5.59.

α,α-Dimethyl-(5-phenylthio)-2-furfuryl Propargyl Ether 2b

Pale yellow oil; 64% yield; IR (neat) 3300, 2120, 1600, 1500, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.24-7.14 (m, 5H), 6.67 (d, J = 3.0 Hz, 1H), 6.36 (d, J = 3.0 Hz, 1H), 3.90 (d, J = 2.4 Hz, 2H), 2.32 (t, J = 2.4 Hz, 1H), 1.57 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 158.61 (C), 142.53 (C), 136.03 (C), 128.81 (2CH), 127.20 (2CH), 126.10 (CH), 119.90 (CH), 109.43 (CH), 79.21 (C), 74.35 (CH), 69.11 (C), 55.44 (CH_2), 19.31 ($2CH_3$); LRMS *m/z* (rel int) 272 (M^+, 4), 216 (100); HRMS (EI) calcd for $C_{16}H_{16}O_2S$ 272.0871, found 272.0860; Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.57; H, 5.93. Found: C, 70.69; H, 5.99.

α,α-Dimethyl-(5-phenylthio)-2-furfuryl Alcohol 3b

Pale yellow oil; 21% yield; IR (neat) 3600-3200, 1600, 1490, 1050 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.22-7.12

(m, 5H), 6.66 (d, J = 3.0 Hz, 1H), 6.26 (d, J = 3.0 Hz, 1H), 3.11 (brs, 1H), 1.55 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 164.73 (C), 140.93 (C), 136.50 (C), 128.81 (2CH), 126.71 (2CH), 125.89 (CH), 120.38 (CH), 105.58 (CH), 68.73 (C), 28.34 ($2CH_3$); LRMS *m/z* (rel int) 234 (M^+, 20), 216 (100); HRMS (EI) calcd for $C_{13}H_{14}O_2S$ 234.0715, found 234.0723; Anal. Calcd for $C_{13}H_{14}O_2S$: C, 66.65; H, 6.03. Found: C, 66.78; H, 6.13.

Preparation of (5-Phenylthio)-2-furfuryl Propargyl Ether 2c

To a solution of furfuryl alcohol (2.94 g, 3.00 mmol) in dry THF (80 mL) was added *n*-BuLi (30 mL, 75 mmol, 2.5 M in hexane) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. To this solution was added diphenyl disulfide (6.55 g, 30.0 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 4 h. After evaporation of the solvent under reduced pressure, dry DMSO (30 mL) and dry benzene (30 mL) were added to dissolve the reaction mixture. To this solution was then added propargyl bromide (8.70 g, 73.2 mmol), and the reaction mixture was stirred at 25 °C for 5 h. After addition of saturated NH_4Cl (50 mL) and extraction with ether (5 × 30 mL), the organic layer was washed with brine, dried over $MgSO_4$, and evaporated, and the residue was purified by column chromatography to give **2c** (6.1 g, 82%): pale yellow oil; IR ($CHCl_3$) 3300, 2140, 1590, 1480 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.16 (m, 5H), 6.69 (d, J = 3.0 Hz, 1H), 6.44 (d, J = 3.0 Hz, 1H), 4.54 (s, 2H), 4.15 (d, J = 2.4 Hz, 2H), 2.45 (t, J = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 155.70 (C), 143.58 (C), 135.94 (C), 129.01 (2CH), 127.58 (2CH), 126.36 (CH), 120.27 (CH), 111.88 (CH), 79.01 (C), 75.05 (CH), 63.19 (CH_2), 56.95 (CH_2); LRMS *m/z* (rel int) 244 (M^+, 58), 189 (100); HRMS (EI) calcd for $C_{14}H_{12}O_2S$ 244.0558, found 244.0551; Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.84; H, 4.96. Found: C, 68.95; H, 4.90.

General Procedure for the Intramolecular Diels-Alder Reaction of the (5-Phenylthio)-2-furfuryl Propargyl Ethers 2a-c

Compound **2a** (1.00 g, 3.90 mmol) was dissolved in *tert*-butanol (80 mL) in a round-bottomed flask. Potassium *tert*-butoxide (1.31 g, 11.6 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 the phenylthio group rearrangement products **5a** (0.42 g, 42%) and **6a** (0.40 g, 40%).

1-Methyl-5-hydroxy-6-phenylthio-1,3-dihydroisobenzofuran 5a

Pale yellow oil; IR ($CHCl_3$) 3500-3200, 1610, 1490, 1350 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.10 (m, 5H), 7.06 (s, 1H), 6.90 (s, 1H), 6.72 (brs, 1H), 5.25 (q, J = 6.6 Hz, 1H), 5.11, 5.02 (ABq, J = 13.2 Hz, 2H), 1.44 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 156.78 (C), 144.22 (C), 136.41 (C), 136.24 (C), 129.18 (2CH), 128.83 (CH), 126.65 (2CH), 126.10 (CH), 115.17 (C), 107.94 (CH), 79.39 (CH), 71.87 (CH_2), 21.76 (CH_3); LRMS *m/z* (rel int) 258 (M^+, 48), 243 (100); HRMS (EI) calcd for $C_{15}H_{14}O_2S$ 258.0715, found 258.0710; Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.75; H, 5.47. Found: C, 69.83; H, 5.52.

1-Methyl-3-phenylthio-5-hydroxy-1,3-dihydroisobenzofuran 6a

Pale yellow oil; IR ($CHCl_3$) 3500-3200, 1610, 1520, 1050 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.31-7.18 (m, 4H), 6.98-6.95 (m, 1H), 6.85-6.70 (m, 2H), 6.68 and 6.61 (s, 1H), 5.34-5.28 (m, 1H), 1.54 and 1.44 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 155.58 (C), 144.84 and 143.78 (C), 141.19 and 140.34 (C), 132.30 (CH), 131.95 (2CH), 128.75 (2CH), 127.38 and 127.23 (C), 121.81 and 121.67 (CH), 116.31 and 116.22 (CH), 109.34 and 109.08 (CH), 91.15 and 90.96 (CH), 80.90 and 78.91 (CH), 22.98 and 20.94 (CH_3); LRMS *m/z* (rel int) 258 (M^+, 16), 257 (100); HRMS (EI) calcd for $C_{15}H_{14}O_2S$ 258.0715, found 258.0724; Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.75; H, 5.47. Found: C, 69.87; H, 5.56.

1,1-Dimethyl-5-hydroxy-6-phenylthio-1,3-dihydroisobenzofuran 5b

Pale yellow oil; 43% yield; IR ($CHCl_3$) 3500-3200, 1610, 1490, 1350 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.05 (m, 5H), 6.89 (s, 1H), 6.64 (s, 1H), 5.04 (s, 2H), 1.48 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 156.69 (C), 143.58 (C), 140.08 (C), 135.83 (C), 129.18 (2CH), 128.46 (CH), 126.50 (2CH), 126.04 (CH), 115.02 (C), 107.97 (CH), 85.45 (C), 70.33 (CH_2), 28.46 ($2CH_3$); LRMS *m/z* (rel int) 272 (M^+, 12), 163 (100); HRMS (EI) calcd for $C_{16}H_{16}O_2S$ 272.0864, found 272.0871; Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.57; H, 5.93. Found: C, 70.66; H, 5.98.

1,1-Dimethyl-3-phenylthio-5-hydroxy-1,3-dihydroisobenzofuran 6b

Pale yellow oil; 41% yield; IR ($CHCl_3$) 3500-3200, 1610, 1520, 1050 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.30-7.24 (m, 3H), 6.92-6.80 (m, 3H), 6.63 (s, 1H), 1.47 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 155.76 (C), 139.26 (C), 139.21 (C), 132.04 (2CH),

128.80 (2CH), 127.23 (CH), 121.49 (C), 121.37 (CH), 116.45 (CH), 109.31 (CH), 90.04 (CH), 87.26 (C), 29.74 (CH_3), 29.33 (CH_3); LRMS *m/z* (rel int) 272 (M^+, 12), 163 (100); HRMS (EI) calcd for $C_{16}H_{16}O_2S$ 272.0864, found 272.0876; Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.57; H, 5.93. Found: C, 70.69; H, 5.99.

5-Hydroxy-6-phenylthio-1,3-dihydroisobenzofuran 5c

Pale yellow oil; 41% yield; IR ($CHCl_3$) 3500-3200, 1600, 1495 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.23-7.06 (m, 5H), 6.90 (s, 1H), 6.79 (brs, 1H), 5.05 (s, 2H), 5.00 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 156.63 (C), 143.81 (C), 135.77 (C), 131.60 (C), 129.10 (2CH), 128.66 (CH), 126.79 (2CH), 126.07 (CH), 115.43 (C), 107.97 (CH), 73.21 (CH_2), 72.72 (CH_2); LRMS *m/z* (rel int) 244 (M^+, 100); HRMS (EI) calcd for $C_{14}H_{12}O_2S$ 244.0558, found 244.0549; Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.84; H, 4.96. Found: C, 68.93; H, 4.90.

1-Phenylthio-6-hydroxy-1,3-dihydroisobenzofuran 6c

Pale yellow oil; 39% yield; IR ($CHCl_3$) 3500-3200, 1650, 1520, 1050 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.32-7.25 (m, 3H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.86 (s, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.72 (s, 1H), 5.10, 5.02 (ABq, *J* = 12.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 155.67 (C), 139.70 (C), 133.90 (C), 132.24 (2CH), 130.61 (C), 128.78 (2CH), 127.47 (CH), 121.75 (CH), 116.31 (CH), 109.25 (CH), 92.33 (CH), 72.34 (CH_2); LRMS *m/z* (rel int) 244 (M^+, 4), 135 (100); HRMS (EI) calcd for $C_{14}H_{12}O_2S$ 244.0558, found 244.0569; Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.84; H, 4.96. Found: C, 68.96; H, 5.03.

General Procedure for the Preparation of the Furfuryl Alcohols 16a and 16b

To a solution of 2-trimethylsilylfuran (2.80 g, 20.0 mmol) in dry THF (80 mL) was added *n*-BuLi (10.0 mL, 25.0 mmol, 2.5 M in hexane) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. To this solution was added butyraldehyde (1.58 g, 22.0 mmol) at 0 °C, and the reaction mixture was stirred at 25 °C 2 h. After addition of saturated NH_4Cl (60 mL) and extraction with ether (5 × 50 mL), the organic layer was washed with brine, dried over $MgSO_4$ and evaporated, and the residue was purified by column chromatography to give **16a** (3.65 g, 86%).

α-*n*-Propyl-(5-trimethylsilyl)-2-furfuryl Alcohol 16a

Pale yellow oil; IR ($CHCl_3$) 3500-3200, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.52 (d, *J* = 3.0 Hz, 1H), 6.17 (d, *J* = 3.0 Hz, 1H), 4.66 (t, *J* = 6.6 Hz, 1H), 2.68 (brs, 1H), 1.79 (dt, *J* = 6.6, 6.6 Hz, 2H), 1.48-1.24 (m, 2H), 0.91 (t, *J* = 6.9 Hz, 3H), 0.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 161.38 (C), 159.28 (C), 120.06 (CH), 105.35 (CH), 67.47 (CH), 37.70 (CH_2), 18.61 (CH_2), 13.72 (CH_3), -1.76 ($3CH_3$); LRMS *m/z* (rel int) 212 (M^+, 5), 57 (100); HRMS (EI) calcd for $C_{11}H_{20}O_2Si$ 212.1240, found 212.1232.

α-Ethyl-α-methyl-(5-trimethylsilyl)-2-furfuryl Alcohol 16b

Pale yellow oil; 92% yield; IR ($CHCl_3$) 3500-3200, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.53 (d, *J* = 3.0 Hz, 1H), 6.16 (d, *J* = 3.0 Hz, 1H), 2.06 (brs, 1H), 1.88 (q, *J* = 7.5 Hz, 2H), 1.52 (s, 3H), 0.85 (t, *J* = 7.5 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 163.74 (C), 159.08 (C), 120.01 (CH), 104.42 (CH), 71.99 (C), 34.49 (CH_2), 25.87 (CH_3), 8.38 (CH_3), -1.73 ($3CH_3$); LRMS *m/z* (rel int) 212 (M^+, 11), 195 (100); HRMS (EI) calcd for $C_{11}H_{20}O_2Si$ 212.1240, found 212.1226.

Preparation of 2-Triethylsilylfuran 17

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, 2.5 M in hexane) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. To this solution was added triethylchlorosilane (5.04 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 (3 × 60 mL), the organic layer was washed with brine, dried over $MgSO_4$ and evaporated, and the residue was purified by distillation to give 2-triethylsilylfuran (**17**) (5.06 g, 82%).

2-Triethylsilylfuran 17

Liquid; IR ($CHCl_3$) 1500, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.5 Hz, 1H), 6.64 (d, *J* = 3.0 Hz, 1H), 6.37 (dd, *J* = 3.0, 1.5 Hz, 1H), 0.97 (t, *J* = 6.0 Hz, 6H), 0.73 (q, *J* = 6.0 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 158.20 (C), 146.58 (CH), 120.50 (CH), 109.14 (CH), 7.28 ($3CH_2$), 3.26 ($3CH_3$); LRMS *m/z* (rel int) 182 (M^+, 2), 95 (100).

Preparation of the Furfuryl Alcohol 16c

The same reaction conditions and procedure for the preparation of the furfuryl alcohols **16a** and **16b** were used for the preparation of **16c**.

α,α-Diethyl-(5-triethylsilyl)-2-furfuryl Alcohol 16c

Pale yellow oil; 78% yield; IR ($CHCl_3$) 3500-3200, 1500, 1050 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.56 (d, *J* = 3.0 Hz, 1H), 6.18 (d, *J* = 3.0 Hz, 1H), 2.01 (brs, 1H), 1.90-1.76 (m, 4H), 1.01-0.69 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 163.01 (C), 156.86 (C), 121.06 (CH),

105.15 (CH), 75.28 (C), 32.22 ($2CH_2$), 7.83 ($2CH_3$), 7.28 ($3CH_3$), 3.26 ($3CH_2$); LRMS *m/z* (rel int) 268 (M^+, 17), 239 (100); HRMS (EI) calcd for $C_{15}H_{28}OSi$ 268.1853, found 268.1864.

General Procedure for the Preparation of the Furfuryl Propargyl Ethers 18a-c

To a mixture of compound **16a** (5.00 g, 23.5 mmol) and saturated NaOH solution (80 mL) were added propargyl bromide (4.2 g, 35 mmol) and a catalytic amount of *n*-Bu_4NBr (0.10 g) at 25 °C. The reaction mixture was stirred at 25 °C for 8 h. After addition of saturated NH_4Cl (80 mL) and extraction with ether (3 × 60 mL), the organic layer was washed with brine, dried over $MgSO_4$ and evaporated, and the residue was purified by column chromatography to give **18a** (5.6 g, 94%).

α-*n*-Propyl-(5-trimethylsilyl)-2-furfuryl Propargyl Ether 18a

Pale yellow oil; IR ($CHCl_3$) 3300, 2140, 1500, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.53 (d, *J* = 3.0 Hz, 1H), 6.26 (d, *J* = 3.0 Hz, 1H), 4.54 (t, *J* = 6.9 Hz, 1H), 4.11, 3.95 (doublet of ABq, *J* = 14.2, 2.4 Hz, 2H), 2.38 (t, *J* = 2.4 Hz, 1H), 1.96-1.72 (m, 2H), 1.48-1.24 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 160.27 (C), 158.03 (C), 119.89 (CH), 108.09 (CH), 79.97 (CH), 73.85 (C), 73.33 (CH), 55.50 (CH_2), 36.01 (CH_2), 18.76 (CH_2), 13.74 (CH_3), -1.70 ($3CH_3$); LRMS *m/z* (rel int) 250 (M^+, 8), 57 (100); HRMS (EI) calcd for $C_{14}H_{22}O_2Si$ 250.1389, found 250.1380.

α-Methyl-α-ethyl-(5-trimethylsilyl)-2-furfuryl Propargyl Ether 18b

Pale yellow oil; 86% yield; IR ($CHCl_3$) 3300, 2150, 1500, 1080 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.54 (d, *J* = 3.0 Hz, 1H), 6.25 (d, *J* = 3.0 Hz, 1H), 3.86-3.84 (m, 2H), 2.31 (t, *J* = 2.4 Hz, 1H), 2.00-1.90 (m, 2H), 1.52 (s, 3H), 0.85 (t, *J* = 7.2 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 160.16 (C), 160.01 (C), 119.89 (CH), 108.03 (CH), 81.14 (CH), 73.85 (C), 73.33 (C), 51.30 (CH_2), 31.78 (CH_2), 21.41 (CH_3), 8.21 (CH_3), -1.70 ($3CH_3$); LRMS *m/z* (rel int) 250 (M^+, 9), 73 (100); HRMS (EI) calcd for $C_{14}H_{22}O_2Si$ 250.1389, found 250.1385.

α,α-Diethyl-(5-triethylsilyl)-2-furfuryl Propargyl Ether 18c

Pale yellow oil; 92% yield; IR ($CHCl_3$) 3300, 2150, 1500, 1090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.56 (d, *J* = 3.0 Hz, 1H), 6.27 (d, *J* = 3.0 Hz, 1H), 3.80 (d, *J* = 2.4 Hz, 2H), 2.30 (t, *J* = 2.4 Hz, 1H), 1.93 (q, *J* = 7.2 Hz, 4H), 1.01-0.70 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 159.89 (C), 157.80 (C), 120.76 (CH), 108.50 (CH), 81.02 (CH), 79.97 (C), 72.69 (C), 50.86 (CH_2), 26.01 ($2CH_2$), 7.45 ($2CH_3$), 3.26 ($3CH_3$), 3.23 ($3CH_2$); LRMS *m/z* (rel int) 306 (M^+, 4), 277 (100); HRMS (EI) calcd for $C_{18}H_{30}O_2Si$ 306.2015, found 306.2018.

General Procedure for the Intramolecular Diels-Alder Reaction of the Furfuryl Propargyl Ethers 18a-c

Compound **18a** (5.02 g, 20.0 mmol) was dissolved in *tert*-butanol (100 mL) in a round-bottomed flask. Potassium *tert*-butoxide (7.4 g, 60.0 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 (5 × 50 mL). 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 **19a** (1.65 g, 35%) and the Brook rearrangement product **20a** (1.95 g, 55%).

1-*n*-Propyl-5-hydroxyl-6-trimethylsilyl-1,3-dihydroisobenzofuran 19a

Pale yellow oil; IR ($CHCl_3$) 3600-3200, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 1H), 6.52 (s, 1H), 5.86 (brs, 1H), 5.20-5.17 (m, 1H), 5.03, 4.97 (ABq, *J* = 10.5 Hz, 2H), 1.95-1.42 (m, 4H), 0.96 (t, *J* = 7.5 Hz, 3H), 0.31 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 160.59 (C), 142.30 (C), 133.73 (C), 127.32 (CH), 124.73 (C), 106.87 (CH), 83.82 (CH), 72.08 (CH_2), 38.80 (CH_2), 18.61 (CH_2), 14.15 (CH_3), -0.97 ($3CH_3$); LRMS *m/z* (rel int) 250 (M^+, 7), 191 (100); HRMS (EI) calcd for $C_{14}H_{22}O_2Si$ 250.1389, found 250.1407.

1-*n*-Propyl-5-hydroxy-1,3-dihydroisobenzofuran 20a

Pale yellow oil; IR ($CHCl_3$) 3600-3200, 1600, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.1 Hz, 1H), 6.73 (dd, *J*= 8.1, 2.1 Hz, 1H), 6.67 (d, *J* = 2.1 Hz, 1H), 6.24 (brs, 1H), 5.20-5.17 (m, 1H), 5.08, 4.98 (ABq, *J* = 15.0 Hz, 2H), 1.82-1.40 (m, 4H), 0.93 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 155.70 (C), 140.96 (C), 133.96 (C), 121.90 (CH), 114.50 (CH), 107.83 (CH), 83.64 (CH), 72.19 (CH_2), 38.63 (CH_2), 18.35 (CH_2), 14.12 (CH_3); LRMS *m/z* (rel int) 178 (M^+, 5), 135 (100); HRMS (EI) calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0985.

1-Ethyl-1-methyl-5-hydroxy-6-trimethylsilyl-1,3-dihydroisobenzofuran 19b

Pale yellow oil; 42% yield; IR ($CHCl_3$) 3600-3200, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.51

(s, 1H), 5.80 (brs, 1H), 5.00 (s, 1H), 1.78 (q, J = 7.2 Hz, 2H), 1.46 (s, 3H), 0.81 (t, J = 7.2 Hz, 3H), 0.31 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 160.51 (C), 142.09 (C), 136.76 (C), 127.09 (CH), 124.73 (C), 106.72 (CH), 88.92 (C), 71.17 (CH_2), 34.32 (CH_2), 27.06 (CH_3), 8.47 (CH_3), -0.94 ($3CH_3$); LRMS *m/z* (rel int) 250 (M^+, 11), 205 (100); HRMS (EI) calcd for $C_{14}H_{22}O_2Si$ 250.1389, found 250.1380.

1-Ethyl-1-methyl-5-hydroxy-1,3-dihydroisobenzofuran 20b

Pale yellow oil; 40% yield; IR ($CHCl_3$) 3600-3200, 1100 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (d, J = 8.1 Hz, 1H), 6.74 (d, J = 8.1 Hz, 1H), 6.65 (s, 1H), 6.42 (brs, 1H), 5.02 (s, 2H), 1.86-1.70 (m, 2H), 1.47 (s, 3H), 0.79 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 155.70 (C), 142.09 (C), 140.61 (C), 121.67 (CH), 114.59 (CH), 107.68 (CH), 88.86 (C), 71.32 (CH_2), 34.49 (CH_2), 26.01 (CH_3), 8.35 (CH_3); LRMS *m/z* (rel int) 178 (M^+, 6), 134 (100); HRMS (EI) calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0988.

1,1-Diethyl-5-hydroxyl-6-trimethylsilyl-1,3-dihydroisobenzofuran 19c

Pale yellow oil; 46% yield; IR ($CHCl_3$) 3600-3200, 1100 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93 (s, 1H), 6.54 (s, 1H), 6.20 (brs, 1H), 5.02 (s, 2H), 1.88-1.70 (m, 4H), 1.01-0.57 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 161.23 (C), 142.32 (C), 133.47 (C), 128.40 (CH), 121.58 (C), 106.40 (CH), 92.44 (C), 72.25 (CH_2), 33.27 ($2CH_2$), 8.03 ($2CH_3$), 7.45 ($3CH_3$), 3.34 ($3CH_2$); LRMS *m/z* (rel int) 306 (M^+, 2), 247 (100); HRMS (EI) calcd for $C_{18}H_{30}O_2Si$ 306.2015, found 306.2020.

1,1-Diethyl-5-hydroxy-1,3-dihydroisobenzofuran 20c

Pale yellow oil; 43% yield; IR ($CHCl_3$) 3600-3200, 1100 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (brs, 1H), 6.87 (d, J = 8.1 Hz, 1H), 6.78 (dd, J = 8.1, 2.1 Hz, 1H), 6.67 (d, J = 2.1 Hz, 1H), 5.06 (s, 2H), 1.86-1.74 (m, 4H), 0.75 (t, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, DEPT) δ 155.84 (C), 141.28 (C), 134.34 (C), 121.99 (CH), 114.73 (CH), 107.54 (CH), 92.53 (C), 72.51 (CH_2), 33.35 ($2CH_2$), 8.03 ($2CH_3$); LRMS *m/z* (rel int) 192 (M^+, 10), 138 (100); HRMS (EI) calcd for $C_{12}H_{16}O_2$ 192.1151, found 192.1163.

ACKNOWLEDGMENT

We thank the National Science Council of the Republic of China for financial support (Grant No. NSC84-2113-M009-008).

Received June 18, 1998.

Key Words

Intramolecular Diels-Alder reaction; Furans; Allenyl ethers; Phenylthio group rearrangement; Trialkylsilyl group rearrangement.

REFERENCES

1. For reviews see: (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *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.; Kanematsu, 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. *Tetrahedron 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* **1991**, *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.
9. Wu, H. J.; Yen, C. H.; Chuang, C. T. *Tetrahedron Lett.* **1996**, *37*, 7395.
10. Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.