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INTRAMOLECULAR DIELS-ALDER REACTION OF FURANS WITH ALLENYL ETHERS FOLLOWED BY TRIMETHYLSILYL GROUP 1,2-REARRANGEMENT AND BROOK REARRANGEMENT

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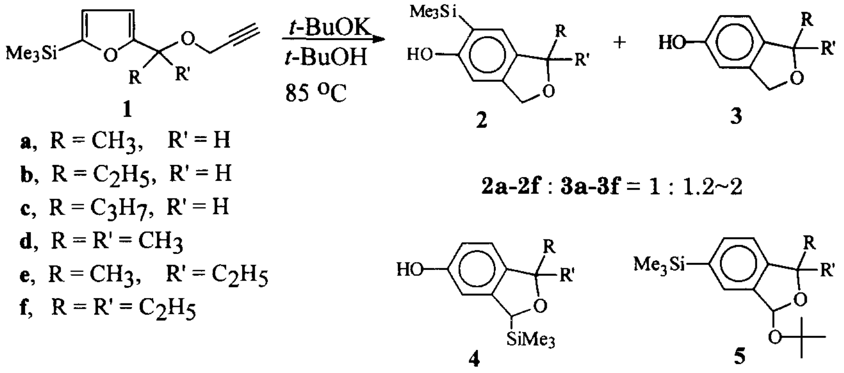
Abstract : The base-catalyzed intramolecular Diels-Alder reactions of 5-trimethylsilyl-2-furfuryl propargyl ethers **1a-1f** gave compounds **2a-2f** and **3a-3f** in 70-90% yields respectively, a novel reaction involving an intramolecular Diels-Alder reaction followed by a trimethylsilyl group 1,2-rearrangement and Brook rearrangement.

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] 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 furan diene and allenyl ether dienophile and applied this reaction to the synthesis of natural products.[4] Recently, we have also engaged the investigation of this intramolecular cycloaddition.[5] In this communication we report here a novel reaction involving an intramolecular Diels-Alder reaction of furan diene with allenyl ether followed by a trimethylsilyl group 1,2-rearrangement and Brook rearrangement.

Treatment of 5-trimethylsilyl-2-furfuryl propargyl ethers **1a-1f** with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol (85 °C) for five hours gave compounds **2a-2f** and **3a-3f** in ratios of 1 : 1.2~2 in 70-90% yields respectively, Scheme 1. These products were fully characterized by their spectral data.[6] No detectable amount of the 1,4-rearrangement[5c] products **4a-4f** or compounds **5a-5f** was obtained.

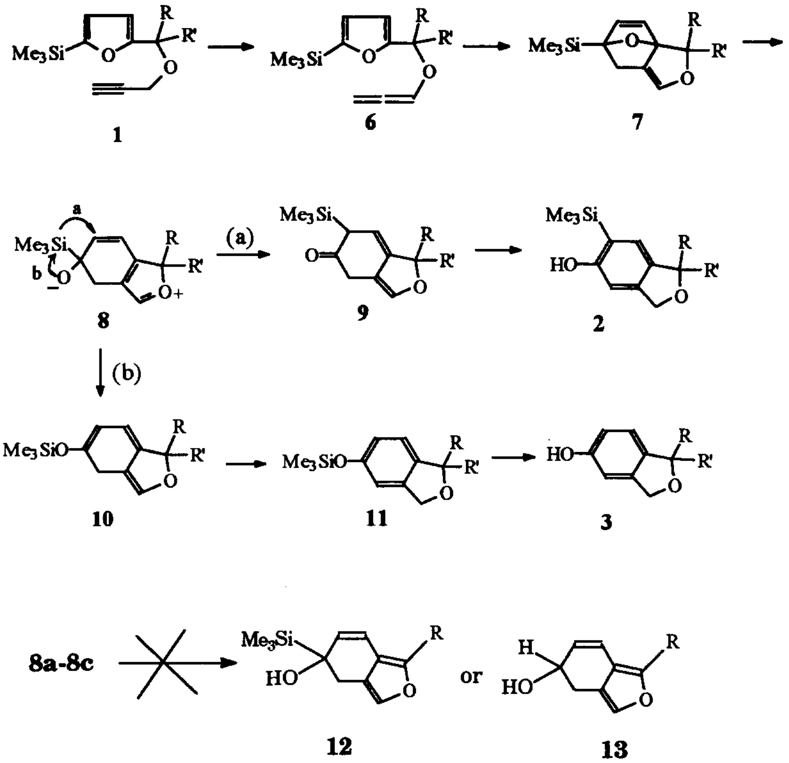
Scheme 1



Treatment of compounds **2** with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol (85 °C) for six hours remained unchanged starting compounds **2**. No conversion of **2** to **3** was obtained. Thus, compounds **2** and **3** were obtained from **1** via different reaction routes. A mechanism is proposed for the reaction. The intramolecular Diels-Alder reactions of **1a-1f** gave **2a-2f** and **3a-3f** respectively, presumably via the corresponding allenyl ethers **6a-6f** and the cycloadducts **7a-7f**. Under the reaction conditions, the cycloadducts **7a-7f** easily undergo ring opening of the bridged oxygen atom to form the zwitterions **8a-8f** as the reaction intermediates. Repelling the trimethylsilyl group by the alkoxide ion followed by 1,2-shift of the trimethylsilyl group (route a) gave the rearranged intermediates **9a-9f**, which underwent aromatization to give **2a-2f** respectively, Scheme 2. On the other hand, Brook rearrangement of the trimethylsilyl group of the zwitterions **8a-8f** gave the rearranged intermediates **10a-10f**, which underwent aromatization to give the products **11a-11f**. Hydrolysis of the trimethylsilyl group of **11a-11f** by the base or solvent afford the phenols **3a-3f**. The ratios of **2** : **3** (1 : 1.2~2) may imply the proximate reaction rates for the Brook rearrangement and 1,2 rearrangement. In the cases of **1a-1c**, which possess a proton on the furfurylic position (R' = H), no detectable amount of the furan ring transfer reaction[4] products **12a-12c** or **13a-13c** was obtained. These results may imply that the reaction rates of Brook rearrangement and 1,2-rearrangement are much faster than that of the furan ring transfer reaction from the zwitterion intermediate **8**.

Thus we found a novel reaction involving an intramolecular Diels-Alder reaction followed by a trimethylsilyl group 1,2- rearrangement and Brook rearrangement.

Scheme 2



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(6) Compound **2d**: IR (neat) cm^{-1} : 3600-3200, 2950, 2820, 1650, 1300, 850; ^1H NMR ($CDCl_3$) δ 7.05 (s, 1H), 6.50 (s, 1H), 5.63 (s, 1H), 4.98 (s, 2H), 1.48 (s, 6H), 0.29 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.39 (s, 1C), 141.48 (s, 1C), 138.48 (s, 1C), 125.74(d, 1C), 124.78 (s, 1C), 106.84 (d, 1C), 85.95 (s, 1C), 78.27 (t, 1C), 28.63 (q, 2C), -0.97 (q, 3C); LRMS *m/z* (rel inten) 236 (M^+, 12), 222 (18), 221 (98), 205 (100); HRMS (EI) calcd for $C_{13}H_{20}O_2Si$ 236.1232, found 236.1243.

Compound **3d**: IR (neat): 3600-3200, 2995, 2840, 1650, 1290 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.94 (d, J = 8.1 Hz, 1H), 6.74 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H), 6.64 (d, J = 1.5 Hz, 1H), 6.26 (s, 1H), 5.01 (s, 2H), 1.49 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.65 (s, 1C), 139.91 (s, 1C), 138.68 (s, 1C), 121.35 (d, 1C), 114.64 (d, 1C), 107.83 (d, 1C), 86.03 (s, 1C), 78.39 (t, 1C), 28.66 (q, 2C); LRMS *m/z* (rel inten): 164 (M^+, 8), 149 (100), 150 (12); HRMS (EI) calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0852.

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