

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

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

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

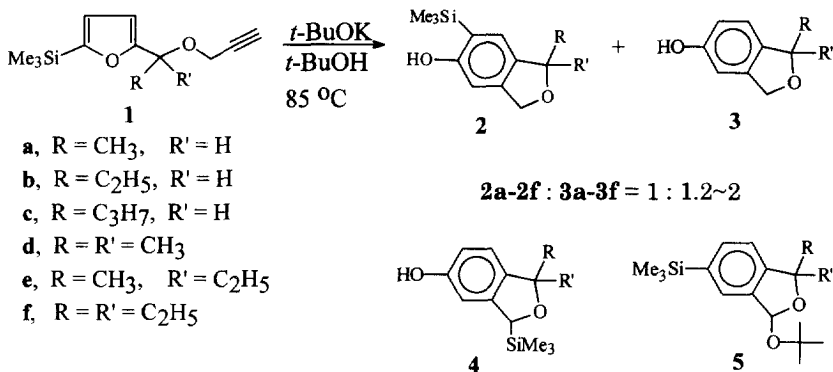
Abstract : The base-catalyzed intramolecular Diels-Alder reactions of 5-trimethylsilyl-2-furfuryl propargyl ethers **1a-1f** gave compounds **2a-2f** and **3a-3f** in 70-90% yields respectively, a novel reaction involving an intramolecular Diels-Alder reaction followed by a trimethylsilyl group 1,2-rearrangement and Brook rearrangement. Copyright © 1996 Elsevier Science Ltd

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.

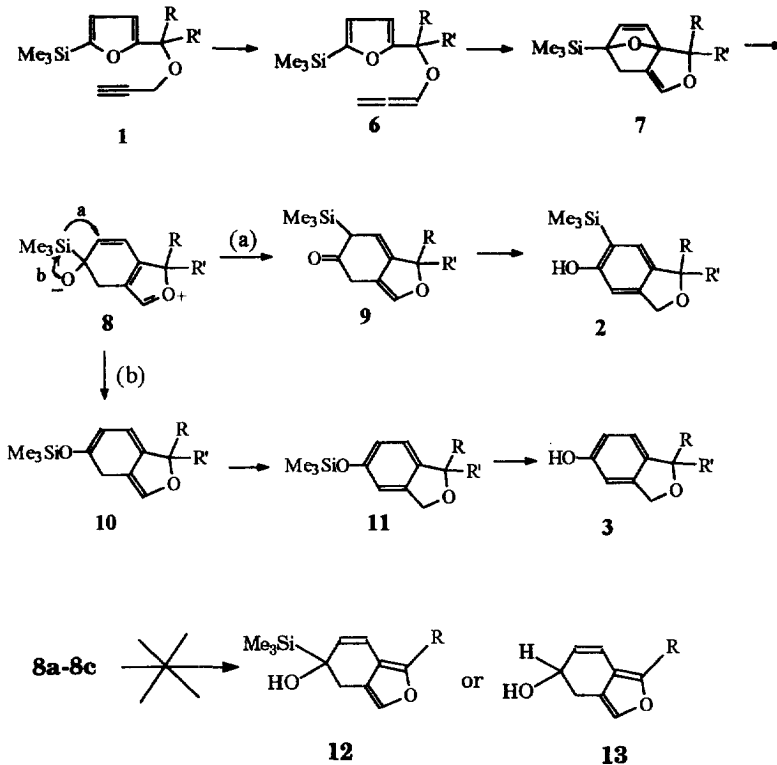
Scheme 1



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 reaction⁴ 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



Acknowledgment: We thank the National Science Council of the Republic of China for financial support (Grant No. NSC 83-0208-M009-012) .

References and Notes

- (1) For reviews see: (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 19. (b) Briger, 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 I* **1975**, 1315. (b) Himbert, G.; Diehl, K.; Mass, G. *J. Chem. Commun.* **1984**, 900. (c) Harrison, R. M.; Hobson, J. D.; Midgley, A. W. *J. Chem. Soc., Perkin I* **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) (a) Wu, H. J.; Lin, S. H.; Lin, C. C. *Heterocycles* **1994**, 38, 1507. (b) Wu, H. J.; Shao, W. D.; Ying, F. H. *Tetrahedron Lett.* **1994**, 35, 729. (c) Wu, H. J.; Ying, F. H.; Shao, W. D. *J. Org. Chem.* **1995**, 60, 6168. (d) Lin, C. C.; Chen, L. H.; Wu, H. J. *J. Chin. Chem. Soc.* **1991**, 38, 613.

(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 $\text{C}_{13}\text{H}_{20}\text{O}_2\text{Si}$ 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 $\text{C}_{10}\text{H}_{12}\text{O}_2$ 164.0837, found 164.0852.

(Received in Japan 19 July 1996; revised 21 August 1996; accepted 26 August 1996)