Tetrahedron Letters,Vol.23,No.46,pp 4763-4764,1982 0040-4039/82/464763-02$03.00/0
Printed in Great Britain

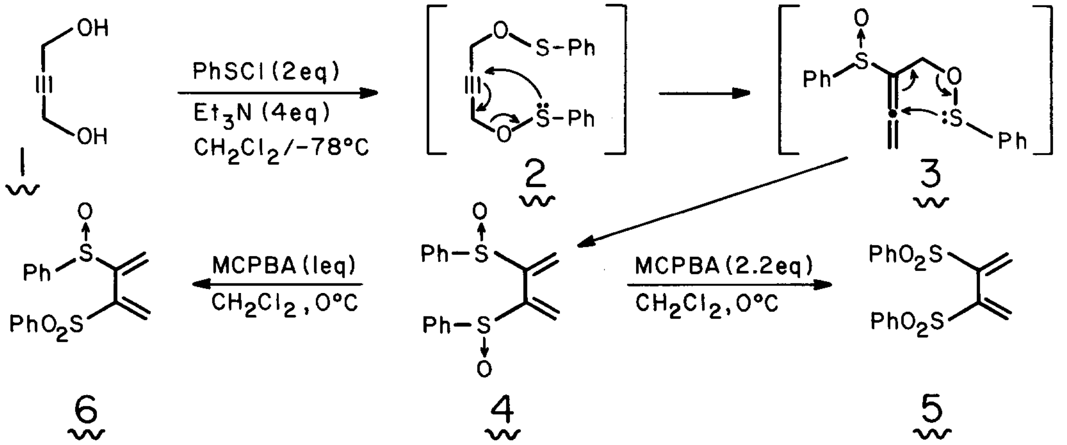
2,3-DI(PHENYLSULFINYL)-1,3-BUTADIENE VIA A DOUBLE [2,3]-SIGMATROPIC REARRANGEMENT OF THE BIS-SULFENATE ESTER OF 2-BUTYNE-1,4-DIOL.

S. Jeganathan and William H. Okamura*
Department of Chemistry, University of California, Riverside, California 92521, USA

Summary: A one-step conversion of butyne-1,4-diol (1) to 2,3-di(phenylsulfinyl)-1,3-butadiene (4) and the conversion of this bis-sulfoxide to the sulfoxide-sulfone 6 and the bis-sulfone 5 are reported.

Hetero-substituted dienes are useful for the synthesis of functionalized ring systems by way of the Diels-Alder reaction.[1] Vinylsulfoxides and sulfones are also useful dienophilic reagents in the Diels-Alder reaction in addition to serving as useful Michael acceptors.[2,3] A very recent communication[4] on the synthesis of a sulfoxide bearing 2,3-disubstituted diene from a butyne-1,4-diol derivative prompts our description of closely related studies.

Phenylsulfenyl chloride (47.8 mmol) in dichloromethane (10 mL) was added to a cooled (-78 °C) solution of butyne-1,4-diol (1, 23.9 mmol) and triethylamine (96 mmol) in dichloromethane (30 mL), and, after one hour at -78 °C, the reaction was processed in a standard manner (warmed to RT; washed with H_2O, 1N HCl, 10% $NaHCO_3$-H_2O, H_2O; dried; concentrated) to afford the title compound 4 in 76% yield (white crystalline solid from methanol; mp 127-128 °C).[5] The initially formed disulfenate ester 2 is considered to undergo a [2,3]-sigmatropic propargylic rearrangement to give allenic intermediate 3, which subsequently undergoes a second [2,3]-sigmatropic shift to afford 4.[6] The ¹H-NMR spectrum of 4 revealed it to consist of a 1.2 to 1 mixture of



diastereomers. Efforts to isolate the intermediate 3 in the form of 2-phenylsulfinylbuta-2,3-dien-1-ol[7] by reacting 1 with only one equivalent of phenylsulfenyl chloride were unsuccessful. Instead, the diene 4 was isolated in 60% yield based on PhSCl.

On oxidation of 4 (1.7 mmol) with m-chloroperbenzoic acid (3.7 mmol) in dichloromethane (10 mL; 0 °C, 10 h), the bis-sulfone 5[8] was obtained in 96% yield as a white crystalline solid, mp 183-185 °C (methanol). Similar treatment of 4 with exactly one equivalent of m-chloroperbenzoic acid afforded after chromatographic separation (silica gel, CH_2Cl_2) sulfinylsulfone 6[9] (white crystalline solid, mp 104-105 °C, methanol), bis-sulfone 5 and bis-sulfoxide 4 in 55%, 12%, and 20% yields, respectively. The recovered diene 4 was obtained as a 2:1 diastereomeric mixture (by ^{1}H-NMR).

To date, the utility of these electron deficient dienes (4-6) as four electron components in the Diels-Alder reaction has not been encouraging and other aspects of their chemistry are being explored.

Acknowledgments: This study was supported by a grant from the National Institutes of Health (AM-16595). Mass spectra were recorded at the NSF Midwest Center for Mass Spectrometry.

References and Notes:

1. Petrzilka, M.; Grayson, J. I. Synthesis 1981, 753, for a review. For specific examples, see Trost, B. M.; Bladuchick, W. C.; Bridges, A. J. J. Am. Chem. Soc. 1980, 102, 3548, 3554, and Danishefsky, S. Acc. Chem. Res. 1981, 14, 400.
2. For recent examples, see Carr, R. V. C.; Paquette, L. A. J. Am. Chem. Soc. 1980, 102, 853. Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. Ibid. 1978, 100, 1597.
3. For vinylsulfones as Michael acceptors, see Argyle, C. S.; Goadby, S. C.; Mason, K. G.; Reed, R. A.; Smith, M. A.; Stern, E. S. J. Chem. Soc. (C) 1967, 2156. For vinylsulfoxides, see Tsuchihashi, G.; Mitamura, S.; Inoue, S.; Ogura, K. Tetrahedron Lett. 1973, 323. Tsuchihashi, G.; Mitamura, S.; Ogura, K. Ibid. 1976, 855.
4. Bridges, A. J.; Fischer, J. W. J. Chem. Soc. Chem. Commun. 1982, 665.
5. Diene 4: ^{1}H-NMR ($CDCl_3$) [Isomer A, δ 5.60 and 6.18 (two s, gem-vinyl, $J\sim0$ Hz), 7.48 (sharp m, 5 ArH); Isomer B, δ 5.85 and 6.25 (two s, gem-vinyl, $J\sim0$ Hz), 7.3 (sharp m, 5 ArH)]; ^{13}C-NMR ($CDCl_3$), δ 141.3 and 140.7 (s, C-2 of each isomer), 121.0 and 118.4 (t, C-1 of each isomer); IR, 1045 cm^{-1} (s, SO); MS, m/z 302.0436 (calcd. for $C_{16}H_{14}O_2S_2$, 302.0436).
6. Horner, L.; Binder, V. Justus Liebigs Ann. Chem. 1972, 757, 33. Braverman, S.; Stabinsky, Y. Israel J. Chem. 1967, 5, 125. Smith, G.; Stirling, C. J. M. J. Chem. Soc. (C) 1971, 1530. Bickart, P.; Carson, F. W.; Jacobus, J.; Miller, E. G.; Mislow, K. J. Am. Chem. Soc. 1968, 90, 4869. Tang, R.; Mislow, K. Ibid. 1970, 92, 2100. Evans, D. A.; Andrews, G. C. Acc. Chem. Res. 1974, 7, 147. Van Rheenen, V.; Shephard, P. K. J. Org. Chem. 1979, 44, 1582.
7. This substance was reported in reference 4, but no details were given.
8. Diene 5: ^{1}H-NMR ($CDCl_3$), δ 6.65 and 6.80 (two s, gem-vinyl), 7.2-7.7 (m, 10 ArH); ^{13}C-NMR ($CDCl_3$), δ 137.1 (s, C-2), 130.8 (t, C-1); IR, 1320, 1160 cm^{-1} (s, SO_2); MS, m/z 334.0338 (calcd. for $C_{16}H_{14}O_4S_2$, 334.0334).
9. Diene 6: ^{1}H-NMR ($CDCl_3$), δ 5.82 and 6.25 (two s, vinyl next to sulfoxide) and 6.35 and 6.51 (two s, vinyl next to sulfone), 7.2-7.7 (m, 10 ArH); ^{13}C-NMR ($CDCl_3$), δ 140.9 (s, C-3), 136.8 (s, C-2), 127.7 (t, C-1), 122.4 (t, C-4); IR, 1055 cm^{-1} (s, SO) and 1160, 1325 cm^{-1} (s, SO_2); MS, m/z 318.0382 (calcd. for $C_{16}H_{14}O_3S_2$, 318.0385).

(Received in USA 30 August 1982)