were monitored by GC as above. The reaction using filter solution A was followed by removing aliquots at 0.5-min intervals for the first 6 min and at 1-min intervals for a total time of 20 min. The cis photoproduct was not observed until 38% conversion of **4**, where 0.39% of the cis isomer was detected. This corresponds to a ca. 100:1 ratio of **8**:**9**. After 11 min, there was obtained a 76:23:1 equilibrium ratio of **8**:**9**:**4**. The reaction using filter solution B was followed by removing aliquots at 1-min intervals for the first 10 min, 2-min intervals for the next 30 min, and 4-min intervals for an additional 80 min. The earliest detected ratio (49% conversion) of **8**:**9**:**4** was 48.7:0.3:5.1, which corresponds to an **8**:**9** ratio of ca. 160:1. Extended irradiation of **4** resulted in a photostationary mixture composed of a 79:20:1 ratio of **8**:**9**:**4**. No reaction was seen using filter solution C, even after a 6-h photolysis time.

Irradiation Using a Rayonet Reactor. The photochemical reaction of **4** (80 mg, 0.25 mmol) in 260 mL of *tert*-butyl alcohol was run in a 500-mL Pyrex round-bottom flask using a Rayonet reactor (254-nm lamps). The reaction was monitored by GC as above, and aliquots were removed at 2-min intervals for the first 20 min and at 4-min intervals thereafter for a total time of 2 h. After 24 min, a 73.0:0.4:26.6 ratio of **8**:**9**:**4** was detected. This corresponds to ca. 180:1 ratio of **8**:**9**. At 95% conversion, there was observed an 88:5 ratio of **8**:**9** with 2% of an unknown product. After photolyzing 92 min there was observed a 73:24:1 ratio of **8**:**9**:**4** with 2% of an unknown product.

Irradiation Using a Shutter. A solution of 50 mg (0.15 mmol) of **4** in 160 mL of *tert*-butyl alcohol was irradiated using a Hanovia apparatus fitted with an opaque cylindrical shutter between the Pyrex filter and the immersion well cooling jacket. The shutter fit snugly into a multilayered piece of aluminum foil, which prevented light from passing out the bottom of the well. The lamp was turned on for 3 min with the shutter in place to enable the lamp to warm up. Once the source was at full power, the shutter was removed and the solution was photolyzed as before. The reaction was monitored by GC; aliquots were taken at 0.5-min intervals for the first 6 min and at 1.0-min intervals thereafter, for a total photolysis time of 20 min. The earliest detected ratio of products and reactant was seen after 1 min. There was observed a 39.6:0.4:60.0 ratio of **8**:**9**:**4**, which corresponds to ca. 100:1 ratio of **8**:**9**. Though the production of **9** appeared to be somewhat slower, the previously encountered photostationary state of 76:23:1 (**8**:**9**:**4**) was reached after 10 min.

Light Intensity Experiment. The photochemical reaction of **4** (40 mg, 0.13 mmol) in 130 mL of *tert*-butyl alcohol was run in a 250-mL Pyrex flask positioned 40 cm from the Pyrex-filtered 450-W light source. The reaction was monitored by GC; aliquots were removed at 1-min intervals for the first 40 min and at 3-min intervals for an additional 80 min. The earliest detected ratio, 36.0:0.4:63.6 of **8**:**9**:**4** occurred after 20 min. This corresponds to ca. 100:1 ratio. Upon extended irradiation (2 h), the equilibrium (**8**:**9**:**4**) ratio of 76:23:1 was observed.

Acknowledgment. Support of this work by the Research Corporation is greatly appreciated. We are grateful to the Department of Chemistry at Southwestern Oklahoma State University (Weatherford, OK) for the use of their Rayonet reactor. V.L.T. is grateful for support in the form of a Presidential Water Research Fellowship from the OSU Center for Water Research. Finally, we acknowledge partial support by NSF Grants DMB-8603864 and CHE-8718150 in the upgrade of our NMR facility and BSS-8704089 for our new mass spectrometry facility.

Supplementary Material Available: Tables 2–7 listing positional parameters, final anisotropic thermal parameters, and bond angles and distances for **8** and **9** (10 pages). Ordering information is given on any current masthead page. A listing of calculated and observed structure factors as well as the ORTEP drawing of molecule B from the unit cell of **8** is available from R.A.B.

Notes

Preparative Flash Vacuum Thermolysis.[1] Selective Elimination of 6-Chloro-1-hexene from Esters of 6-Chloro-1-hexanol with Schönberg Rearrangement of the *S*-Methyl Xanthate

Leonardus W. Jenneskens, Cornelis A. M. Hoefs, and Ulfert E. Wiersum*

Akzo Research Laboratories Arnhem, Corporate Research, P.O. Box 9300, 6800 SB, Arnhem, The Netherlands

Received February 27, 1989

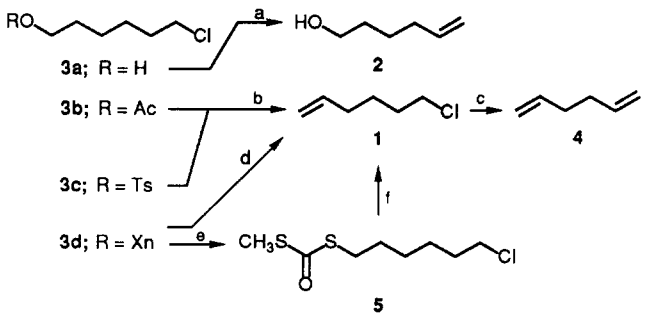
Thermal elimination from carboxylic esters, often acetates,[2] tosylates,[3] and at milder temperatures in the Chugaev reaction from *S*-methyl xanthates,[4] is a classic route for the preparation of olefins.[5] We have recommended[6] the use of flash vacuum thermolysis (FVT) as a general method for such preparations, instead of applying the traditional reaction procedures by dropping in,[7] or by vaporizing the esters with a flow of nitrogen[2-5] into a filled hot tube. FVT utilizes an unfilled quartz tube and low pressure, which prevents tar formation and generally gives quantitative mass recovery, since the pyrolysate is captured in liquid nitrogen cooled traps.[6]

As part of our polymer research program, considerable amounts of 6-chloro-1-hexene (**1**) were needed. This compound is utilized in the synthesis of natural products,[8,9] bicyclic olefins,[10] and polymers,[11] in solvomercuration reactions,[12] and as a radical probe for studying electron-transfer mechanisms.[13-15] Most workers use 5-hexen-1-ol

(1) Previous paper in this series: Batelaan, J. G.; Weber, A. J. M.; Wiersum, U. E. *J. Chem. Soc., Chem. Commun.* **1987**, 1397.
(2) DePuy, C. H.; King, R. W. *Chem. Rev.* **1960**, *60*, 431.
(3) Boyd, J.; Overton, K. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2533.
(4) Nace, H. R. In *Organic Reactions*; J. Wiley & Sons Inc.: New York, 1962; Vol. 12, p 57.
(5) Saunders, W. H.; Cockerill, A. F. In *Mechanisms of Elimination Reactions*; J. Wiley & Sons Inc.: New York, 1973.
(6) (a) Wiersum, U. E. *Recl. Trav. Chim., Pays-Bas* **1982**, *101*, 317 and 365. (b) Wiersum, U. E. *Aldrichimica Acta* **1984**, *17*, 31.
(7) Benson, R. E.; McKusick, B. C. In *Organic Synthesis*; J. Wiley & Sons Inc.: New York, 1963; Collect. Vol. IV, p 746.
(8) Black, H. K; Weedon, B. C. L. *J. Chem. Soc.* **1953**, 1785.
(9) Mihara, S.; Tateba, H.; Nishimura, O.; Machii, Y.; Kishino, K. *J. Agric. Food Chem.* **1987**, *35*, 532.
(10) Criegee, R.; Bolz, G.; Askani, R. *Chem. Ber.* **1969**, *102*, 275.
(11) Backskai, R. *J. Pol. Sci., A* **1965**, *3*, 2491.
(12) Brown, H. C.; Lynch, G. J. *J. Org. Chem.* **1981**, *46*, 930.
(13) Jenkins, C. L.; Kochi, J. K. *Ibid.* **1971**, *36*, 3103.
(14) Ashby, E. C.; Oswald, J. *Ibid.* **1988**, *53*, 6068.
(15) Cf.: (a) Giese, B.; Kretzschmar, G. *Chem. Ber.* **1984**, *117*, 3160. (b) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206. (c) Stork, G. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 149.

0022-3263/89/1954-5811$01.50/0

Scheme I[a]



[a] Ac = $CH_3(CO)$; Ts = p-$CH_3C_6H_4SO_2$; Xn = $CH_3S(CS)$. (a) 700 °C, -HCl; (b) 450–650 °C, -HAc (**3b**) and -HTs (**3c**); (c) 500–750 °C, -HCl; (d) 400–525 °C, -COS and -CH_3SH; (e) 400–575 °C; (f) 525–650 °C, -COS and -CH_3SH.

(**2**), which is fairly expensive, as starting compound for preparation of **1**.[9,11,13,14] The requirement for **1** provided a good opportunity to further examine FVT, both for convenience and selectivity, in large-scale reaction of the acetate **3b**, the tosylate **3c**, and the *S*-methyl xanthate **3d** of 6-chloro-1-hexanol (**3a**). Greater selectivity is especially important, since alkyl chlorides start to eliminate hydrogen chloride[5,16] in the temperature range needed to decompose the esters. We also report a rapid access to **2** via direct elimination of hydrogen chloride from **3a**.[17]

Results and Discussion

Eliminations from 3a–c. Conversion rates above 50 g h^{-1} have been reported in FVT eliminations.[16] Recently, in thermolysis of acetates, the much lower evaporation rates of 2–3 g h^{-1} were applied to provide favorable conditions for the elimination of acetic acid as a step in the total synthesis of the natural product peduncularine[20] and in the preparation of labeled acrylonitrile from 2-[^{13}C]-cyanoethyl acetate.[21] For preparation of **1** about 50 g of each ester **3b–d**, which is the maximum amount of material to be handled in one run in our usual apparatus,[6] was distilled at a rate of 10–15 g h^{-1}, at a pressure below 1 mmHg, into the hot quartz tube. Under these conditions 6-chloro-1-hexyl acetate (**3b**) and 6-chloro-1-hexyl tosylate (**3c**) began to decompose at 450 °C. These esters were completely converted in one pass at 650 °C (Scheme I). However, at this temperature there was already excessive elimination of hydrogen chloride, leading to formation of 1,5-hexadiene (**4**) as a consecutive product from **1**. The temperature-conversion curve, shown for **3b**, clearly indicates an optimum in the formation of **1** between 550 and 600 °C (Figure 1). In preparative runs made with **3b** at 570–575 °C **1** could be isolated from the pyrolysate in yields of ca. 50%, after neutralization of the liberated acetic acid and by fractionating it from unchanged **3b** and already formed **4**. The much less volatile tosylate **3c** gave a similar temperature profile. In experiments with **3b** and **3c** at temperatures slightly above 700 °C, all **1** had disappeared on account of almost quantitative formation of 1,5-hexadiene (**4**).[22,23]

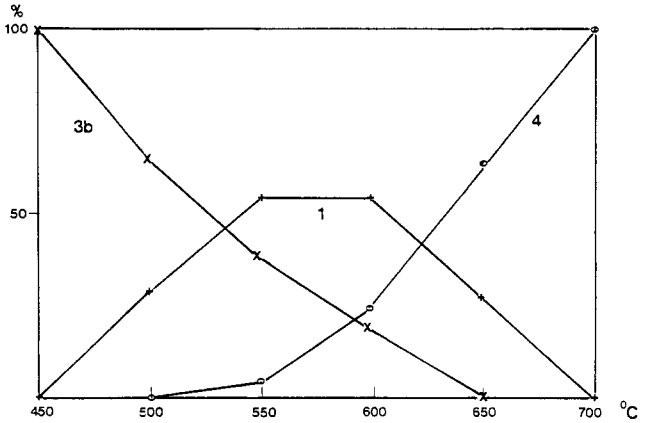


Figure 1. Temperature-conversion curves of 6-chloro-1-hexyl acetate (**3b**), 6-chloro-1-hexene (**1**), and 1,5-hexadiene (**4**).

A difference between acetates and tosylates is that acetic acid is collected in the cold trap in admixture with the olefin and that *p*-toluenesulfonic acid separates from the olefin, because it crystallizes in the bend of the quartz tube.[24] This implies that FVT of a tosylate sometimes has technical advantages over FVT of the corresponding acetate, similar to benzoates.[25] The preparation of 1,5-hexadiene (**4**) from **3c**, instead of **3b**, is a good example. Because of the smooth elimination around 700 °C of hydrogen chloride, preparative FVT was also attempted directly with 6-chloro-1-hexanol (**3a**). This turned out to be an excellent synthesis for 5-hexen-1-ol (**2**, yield 87%, vide supra).

Elimination and Rearrangement of 3d. The best preparative route for making **1** is the FVT of yellow 6-chloro-1-hexyl *S*-methyl xanthate (**3d**), at 525 °C. At this temperature, **1** was obtained in yields of 75–80% with complete conversion of **3d**, although a persistent yellow color in the pyrolysate suggested that not all of it had reacted. The yellow component, remaining in the distillation residue from the crude pyrolysate after removal of **1**, was shown to be a rearranged product of **3d**, *S*-(6-chloro-1-hexyl) *S'*-methyl dithiocarbonate (**5**, Scheme I). This rearrangement of xanthates, first observed by Freudenberg[26] with methyl xanthates of diacetonehexoses, has become known as the Schönberg reaction,[27] which is well documented for xanthates that lack a β-hydrogen atom.[28,29] In a run with **3d** at 600 °C, the rearranged dithiocarbonate **5** was still present in the pyrolysate. A separate experiment with pure **5** showed that it was completely converted at 650 °C to a mixture of **1** and **4** (Scheme I).

The present FVT reaction of **3d** is surprisingly clean in comparison with earlier reported eliminations from *S*-methyl xanthates of primary alcohols.[4] Moreover, rearrangement of a *S*-methyl xanthate, with simultaneous

(16) Schiess, P. *Chimia* **1985**, *39*, 213.
(17) It was also attempted to prepare **1** according to a liquid-phase borate ester procedure.[18] However, with alcohol **3a** severe loss of hydrogen chloride and rearrangement to secondary olefins occurred. In a recent similar procedure with esters of 8-quinolinesulfonic acid, primary alcohols also gave rearranged olefins.[19]
(18) Majerski, Z.; Skare, D.; Vulic, L. *Synth. Commun.* **1986**, *16*, 51.
(19) Corey, E. J.; Posner, G. H.; Atkinson, R. F.; Wingard, A. K.; Halloran, D. J.; Radzik, D. M.; Nash, J. J. *J. Org. Chem.* **1989**, *54*, 389.
(20) Klaver, W. J.; Hiemstra, H.; Speckamp, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 2588.
(21) Van den Berg, E. M. M.; Richardson, E. E.; Lugtenburg, J.; Jenneskens, L. W. *Synth. Commun.* **1987**, *17*, 1189.
(22) Up to 7% of benzene was found as a contaminant in **4**. Mechanistic studies of the formation of benzene from **4** will be subject of a separate paper.
(23) The dehydrochlorination curve made for **1** fits exactly with that of 1-hexene formation measured from 6-chlorohexane, indicating that there is no influence of the terminal double bond on the elimination temperature.
(24) It is also possible that the olefin deposits, free from acetic acid, in the bend of the quartz tube.[20]
(25) (a) Chou, C. H.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1986**, *108*, 4138. (b) Jenneskens, L. W.; Wiersum, U. E. *Aldrichimica Acta* **1988**, *21*, 58.
(26) Freudenberg, K.; Wolf, A. *Chem. Ber.* **1927**, *60*, 232.
(27) Schönberg, A.; Vargha, L. *Ibid.* **1930**, *63*, 178.
(28) Araki, Y.; Aritsune, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3214.
(29) Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1988**, 183.

formation of an olefin, has never been observed in traditional pyrolysis.[30] It is unlikely that **5** is a necessary intermediate in the decomposition of **3d**. The direct cleavage reaction of **3d** must involve a six-membered ring transition state with hydrogen transfer to the C=S bond, which has a lower activation energy than the corresponding elimination from **5**, requiring the hydrogen be transferred to the C=O bond.[5,29] The rearrangement of **3d** to **5** is a side reaction to a thermodynamically somewhat more stable compound, ultimately cleaving into the same fragments. Strictly taken, cleavage of **5** may also involve reversible formation of **3d**, which cannot be observed, however, since it fragments in the process.

Conclusion

In the development of FVT the most appealing results have been the isolation and characterization of highly reactive intermediates.[6] Typical examples of this kind are also reported via elimination from esters and chlorides, e.g. the synthesis of benzofulvene,[33] *o*-xylylenes,[16] dimethylenedihydrofurans,[25a] 2,3-dihydrothiophene,[34] and dimethylenedihydrothiophenes.[35] It is clear that FVT conditions, which involve simple handling, give better yields than in the case of traditional ester pyrolysis and provide a larger preparative scope, in particular with respect to synthesis of primary olefins. FVT also enables the observation of a more refined reaction pattern during pyrolysis of esters,[36] like the occurrence of Schönberg rearrangement in xanthates, even when olefin formation is expected to be the major reaction.

Experimental Section

The ^1H and ^{13}C NMR spectra were recorded on a Bruker WM 270 spectrometer, operating at 270 and 67.9 MHz, respectively, with tetramethylsilane (δ 0.00 ppm) or chloroform (δ 77.0) as internal standards. Mass spectra were recorded on a Finnigan MAT 312 spectrometer operating at 70 eV. IR spectra were obtained with a Perkin-Elmer 983 spectrophotometer. All boiling and melting points are uncorrected. All compounds were analyzed by capillary GC (purity >98%).

Preparation of the Esters 3b–d. 6-Chloro-1-hexanol (**3a**) purchased from Aldrich, was converted to the esters **3b–d**, according to literature procedures for acetates[3,20] (**3b**, yield 85%), tosylates[3,14] (**3c**, yield 75%), and *S*-methyl xanthates[37] (**3d**, yield 88%).

General Pyrolysis Procedure. Preparative Experiments. The commercial equipment described in Figure 1 of ref 6, including a Thermolyne 21100 tube furnace (equipment piece 20), was used.[38] In a single experiment ca. 50 g of each of the starting compounds **3a–d** was placed in a 100-mL flask, Model 1, connected to the quartz tube 19 via auxiliary piece 3,[38] and than vaporized by heating it with infrared radiators.[39] The pyrolysate was collected in a liquid nitrogen cooled wide trap, Model 7, equipment piece 21, with inner tube diameter of 2.5 cm.

Temperature-Conversion Curves. These were determined by evaporating ca. 300-mg quantities of starting material in 10–15 min from a 25-mL flask, at the temperatures shown in the figure, through the quartz tube. Each crude pyrolysate, was taken up into 3 mL of carbon tetrachloride, washed with sodium hydrogen carbonate solution and dried over magnesium sulfate. The carbon tetrachloride solutions were directly analyzed by ^1H NMR and capillary GC.

6-Chloro-1-hexene (1). From the Acetate 3b. Compound **3b** (50 g, 0.28 mol) was distilled in 3 h through the quartz tube kept at 575 °C. After warming up the cold trap to room temperature, the pyrolysate became a colorless liquid that was taken up in 100 mL of methylene chloride, neutralized with sodium carbonate solution, dried over magnesium sulfate, concentrated, and fractionated under reduced pressure. The fraction with bp 89–90 °C (100 mmHg) is 1; yield 48% (15.8 g, 0.13 mol). 1,5-Hexadiene (4, vide infra), bp 60 °C, disappears as a volatile contaminant on removal of the methylene chloride and in the forerun of the distillation.

From the Tosylate 3c. Runs were made at 570 °C with maximal 25-g quantities (0.086 mol) of **3c**, in order to avoid that the bend of the quartz tube becomes clogged up with *p*-toluenesulfonic acid and unconverted **3c**. Evaporation of **3c** took 2.5 h and required much stronger heating than with **3b** or **3d**. The pyrolysate was an opaque liquid, from which **1** was isolated in the same way as described for **3b**; yield 52% (5.3 g, 0.045 mol).

From the *S*-Methyl Xanthate 3d. Yellow **3d** (60 g, 0.265 mol) was in 3.5 h distilled at 525 °C into the quartz tube which was in advance coupled with two traps. On warming the yellow pyrolysate, collected in the first trap, to room temperature, temperature while maintaining the vacuum in the system, the volatile fragments carbonoxy sulfide and methylmercaptan are automatically transferred to the second trap. This trap, still at liquid nitrogen temperature, is coupled off and placed in the hood to let the content evaporate, thus avoiding the smell that is so characterisitc of *S*-methyl xanthate pyrolysis. The crude pyrolysate (45 g) in the first trap was fractionated, yielding 25.3 g (0.21 mol, 81%) of **1** and leaving a viscous yellow residue, which was identified as compound **5** (vide infra). The physical data of **1** were in agreement with those of an authentic sample.[9]

1,5-Hexadiene (4) from 3c. Compound **3c** (25 g, 0.086 mol) was pyrolyzed at 700 °C in a similar way as above, except that two traps were coupled with the quartz tube at the beginning of the experiment. The colorless pyrolysate was fractionated into the second trap to liberate it from less volatile contaminants, by warming up the first one. ^1H NMR and GC analyses showed that the so obtained colorless liquid (6.4 g, 0.077 mol, yield 90%) was identical with a commercial sample of **4** and that it contained 7% of benzene.[22]

5-Hexen-1-ol (2). **3a** (30 g, 0.22 mol) was pyrolyzed in 2 h at 700 °C. The cold trap was warmed up in the hood, causing fumes of dry hydrogen chloride until a light yellow liquid had remained. This was dissolved in 75 mL of methylene chloride, neutralized with sodium hydrogen carbonate solution, and dried over magnesium sulfate. After removing the solvent in a rotavap, distillation yielded 20 g (0.20 mole, 87%) of **2**, bp 75–77 °C (20 mmHg), identical with a commercial sample.

***S*-(6-Chloro-1-hexyl) *S'*-Methyl Dithiocarbonate (5).** Further distillation of the residue from the pyrolysis of **3d** gave 5.9 g of **5** (0.026 mol, 10%) as a yellow liquid; bp 175–176 °C (20 mmHg); ^1H NMR ($CDCl_3$) δ 3.53 (t, J = 6.8 Hz, 2 H), 3.00 (t, J = 6.8 Hz, 2 H), 2.43 (s, 3 H), 1.83–1.73 (m, 4 H), and 1.50–132 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 189.4 (s, C=O), 44.5 (t, J_{CH} = 149.4 Hz, CH_2Cl), 32.0 (t, J_{CH} = 127.2 Hz, CH_2), 30.1 (t, J_{CH} = 133.0 Hz, CH_2), 29.3 (t, J_{CH} = 126.9 Hz, CH_2), 27.5 (t, J_{CH} = 125.0 Hz, CH_2), 26.0 (t, J_{CH} = 125.1 Hz, SCH_2), and 12.7 (q, J_{CH} = 143.0 Hz, SCH_3); MS (EI) m/z 226 (0.1 $C_8H_{15}{}^{16}O^{35}Cl^{32}S_2^+$ with isotope pattern), 179 (0.4 $C_7H_{12}{}^{16}O^{35}Cl^{32}S^+$ with isotope pattern) 118 (5), 82 (38), and 55 (100); IR (KBr, neat) 2939, 2859, 1646, 1461, 1310, 873, 731, and 651 cm^{-1}.

(30) We have also found rearrangement without elimination in case of the methyl xanthates,[31] in a series of FVT experiments with derivatives of dianhydrosorbitol and dianhydromannitol.[1] As in the Freudenberg case,[26] elimination is probably suppressed by a combination of geometric and inductive effects.[32]

(31) Batelaan, J. G.; Wiersum, U. E., unpublished results.

(32) HaysBell, R.; Horton, D.; Williams, D. M.; Mihaly, E. *Carbohydr. Res.* **1977**, *58*, 109.

(33) Gross, G.; Schulz, R.; Schweig, A.; Wentrup, C. *Angew. Chem.* **1981**, *93*, 1078; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1021.

(34) Sauer, N. N.; Angelici, R. J.; Jason Huang, Y. C.; Trahanowsky, W. S. *J. Org. Chem.* **1986**, *51*, 113.

(35) Münzel, N.; Kesper, K.; Schweig, A.; Specht, H. *Tetrahedron Lett.* **1988**, *29*, 6239.

(36) An excellent account of possible reaction patterns with esters is in ref 29. We have found unprecedented examples of this kind with carboxylic esters: Wiersum, U. E.; Jenneskens, L. W., to be published.

(37) Withmore, F. C.; Simpson, C. T., modified Chugaev procedure, *J. Am. Chem. Soc.* **1933**, *55*, 3809.

(38) The dimensions of our equipment restrict the amount of starting material to be handled in one run to ca. 50 mL. We find more heavy equipment unsuited for general FVT purposes and less practicable than doing consecutive runs. For separate equipment pieces see ref 6 and the equipment section of the catalog of Aldrich Chemical Co., Milwaukee, WI.

(39) A suitable IR radiator is the "Epiradiateur", available from Quartz et Silice, Rue d.Anjou 75008, Paris, France.

Registry No. **3a**, 40200-18-8; **3c**, 71042-21-2; **3d**, 123333-21-1; **1**, 928-89-2; **4**, 592-42-7; **5**, 123333-22-2; **2**, 821-41-0; benzene, 71-43-2.

Supplementary Material Available: Physical data for compounds **3b-d** (1 page). Ordering information is given on any current masthead page.

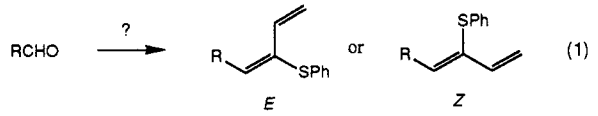
A Stereoselective Route to 2-(Phenylthio)-1,3-butadienes

William H. Pearson,* Ko-Chung Lin, and Yam-Foo Poon

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

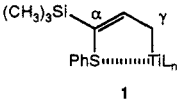
Received May 4, 1989

Sulfur-substituted 1,3-butadienes have found wide use in organic synthesis, particularly in Diels-Alder reactions, where they impart an added level of reactivity and regioselectivity to such cycloadditions.[1] These dienes also play an important role in the successful outcome of our recently developed method for the intramolecular cyclization of azides with 2-(phenylthio)-1,3-butadienes to afford 1-azabicyclo[3.3.0]oct-3-enes and 1-azabicyclo-[4.3.0]non-3-enes.[2] In our efforts to apply this cyclization methodology to alkaloid synthesis, we required an efficient method to prepare such dienes in a stereoselective fashion from aldehydes, as outlined in eq 1. We report herein a simple route to such dienes, which proceeds in high yield and with high stereoselectivity, affording either geometrical isomer.



E *Z* (1)

Several effective methods exist for the preparation of 2-(arylthio)-1,3-butadienes.[3-5] The most promising methods for dienes bearing a C-1 substituent, as required for our purposes, are those of Chou[1j-l,3b] and Yamamoto.[4] In Chou's work, extrusion of sulfur dioxide from 2-alkyl-3-(phenylthio)-3-sulfolenes in refluxing toluene affords 1-alkyl-2-(phenylthio)-1,3-butadienes with high *Z* selectivity, but does not allow access to the *E* isomers.[3b] Yamamoto has shown that condensation of the titanium reagent **1** with cyclohexanecarboxaldehyde produces 1-cyclohexyl-2-(phenylthio)-1,3-butadiene as a mixture of *E* and *Z* isomers (10:1).[4] We have used reagent **1** in our early work[2] but sought an alternative procedure for two reasons. First, ready access to either the pure *E* or pure *Z* isomer of the diene is not possible. Second, in our studies directed at natural product synthesis, we have found that more complex aldehydes which bear additional Lewis basic sites (e.g., ethers, esters, amides) give low yields of dienes with the titanium method. A major byproduct arises from addition at the γ-position of **1** (vide infra, Scheme II). Since complexation of the aldehyde oxygen to the titanium of **1** is probably an important event prior to C-C bond formation, we believe that additional Lewis basic sites interfere with the complexation and decrease the efficiency and α/γ regioselectivity of the reaction. We now report that the use of boron rather than titanium effectively addresses these limitations.



1

Table I. Stereoselective Synthesis of 2-(Phenylthio)-1,3-butadienes from Aldehydes (RCHO) with Allylborane 4

diene[a]	R	isolated yield, %	6:7[b,c]
6a	n-C_5H_{11}	80	26:1
6b	n-C_8H_{17}	78	50:1
6c	i-C_3H_7	76	30:1
6d	c-C_6H_{11}	82	20:1
6e	Ph	58	1:1
6f	CH_2Ph	68	**6f** only
6g	$(CH_2)_3CH_2Br$	73	50:1
6h	$(CH_2)_2CH_2Br$	78	20:1
6i	$(CH_2)_3CH_2N_3$	79	**6i** only
6j	$(CH_2)_2CH_2N_3$	63	99:1
6k	(*E*)-CH=CHPh	66	**6k** only
7a	n-C_5H_{11}	92	1:50
7b	n-C_8H_{17}	74	**7b** only
7c	i-C_3H_7	83	1:50
7d	c-C_6H_{11}	87	**7d** only
7e	Ph	80	**7e** only
7f	CH_2Ph	84	**7f** only
7g	$(CH_2)_3CH_2Br$	82	**7g** only
7h	$(CH_2)_2CH_2Br$	86	**7h** only
7i	$(CH_2)_3CH_2N_3$	86	**7i** only
7j	$(CH_2)_2CH_2N_3$	80	**7j** only
7k	(*E*)-CH=CHPh	83	**7k** only

[a] Workup for **6** series: H_2SO_4. Workup for **7** series: 4 N NaOH. [b] Calculated by integration of the 300-MHz ^1H NMR spectrum of the crude reaction product. The spectra for the **7** series were measured on material obtained by direct evaporation of an aliquot in order to illustrate the inherently high stereoselectivity of the reaction. The spectra for the **6** series could not be obtained by direct evaporation of an aliquot due to acid-promoted decomposition, and thus had to be measured after neutralization and aqueous workup. This extra manipulation may explain the slightly lower selectivities observed for this series. [c] Where "only" is used, none of the other isomer is detected by 300-MHz ^1H NMR. It is estimated that this corresponds to a ratio of more than 200:1.

(1) (a) Review: Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753-786. Diels-Alder reactions using 2-thiosubstituted dienes: (b) Gundermann, K. D.; Holtmann, P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 668. (c) Cohen, T.; Mura, A. J., Jr.; Shull, D. W.; Fogel, E. R.; Ruffner, R. J.; Falck, J. R. *J. Org. Chem.* **1976**, *41*, 3218-3219. (d) Hopkins, P. B.; Fuchs, P. L. *Ibid.* **1978**, *43*, 1208-1217. (e) Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 3554-3572 and earlier work cited therein. (f) Trost, B. M.; Lavoie, A. C. *Ibid.* **1983**, *105*, 5057-5090. (g) Bridges, A. J.; Fischer, J. W. *Tetrahedron Lett.* **1983**, *24*, 445, 447. (h) Liotta, C. L.; Verbicky, J. W., Jr. *Ibid.* **1985**, *26*, 1395-1398. (i) Proteau, P. J.; Hopkins, P. B. *J. Org. Chem.* **1985**, *50*, 141-143. (j) Chan, T. H.; Prasad, C. V. C. *Ibid.* **1987**, *52*, 110-119 and earlier references therein. (k) Chou, T.; Lee, S.-J.; Peng, M.-L.; Sun, D.-J.; Chou, S.-S. P. *Ibid.* **1988** *53*, 3027-3031. (l) Chou, S.-S. P.; Tsai, C.-Y. *Ibid.* **1988**, *53*, 5305-5308. (m) McDougal, P. G.; Oh, Y.-I.; VanDerveer, D. *Ibid.* **1989**, *54*, 91-97. Diels-Alder using 1-thiosubstituted dienes: ref 1c and (n) Evans, D. A.; Bryan, C. A.; Sims, C. L. *J. Am. Chem. Soc.* **1972**, *94*, 2891. (o) Cohen, T.; Kosarych, A. *J. Org. Chem.* **1982**, *47*, 4005. (p) Kozikowski, A. P.; Huie, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 2923. (q) Overman, L. E.; Petty, C. B.; Ban, T.; Huang, G. T. *Ibid.* **1983**, *105*, 6335. (r) Ihara, M.; Kawaguchi, A.; Chihiro, M.; Fukumoto, K.; Kametani, T. *J. Chem. Soc., Chem. Commun.* **1986**, 671.

(2) Pearson, W. H.; Celebuski, J. E.; Poon, Y.-F.; Dixon, B. R.; Glans, J. H. *Tetrahedron Lett.* **1986**, *52*, 6301-6304.

(3) From 3-(phenylthio)-3-sulfolenes by extrusion of sulfur dioxide: (a) References 1b,d,f,h,i,k,l. (b) Chou, S.-S. P.; Liou, S.-Y.; Tsai, C.-Y.; Wang, A.-J. *J. Org. Chem.* **1987**, *52*, 4468-4471.

(4) (a) Ikeda, Y.; Furuta, K.; Meguriya, N.; Ikeda, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1982**, *104*, 7663-7665. (b) Furuta, K.; Ikeda, Y.; Meguriya, N.; Ikeda, N.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2781-2790. This work also describes one example of a route to the *Z* isomer. Titanium-mediated addition of [1-(phenylthio)allyl]lithium to cyclohexanecarboxaldehyde affords selectively the *erythro*-β-hydroxy sulfide. Treatment of this compound with *n*-BuLi, methanesulfonyl chloride, and then *t*-BuLi afforded *Z*-**6d**. This method has not been useful in our hands for more sensitive and complex aldehydes.

(5) Other methods: (a) References 1c,e,g,j. (b) Blatcher, P.; Grayson, J. I.; Warren, S. *J. Chem. Soc., Chem. Commun.* **1978**, 657. (c) Pariza, R. J.; Fuchs, P. L. *J. Org. Chem.* **1985**, *50*, 4252-4266.

0022-3263/89/1954-5814$01.50/0