Table II. Two-Center Overlap Populations (Two-Center Population in Parentheses)

	SDPDPH	S_2TPP	thiophene
N–C_α[a]	0.5174 (0.1049)	0.5342 (0.1069)	
C_α–C_β[a]	0.5060 (0.0678)	0.4939 (0.0587)	
C_β–C_β[a]	0.6368 (0.2036)	0.6383 (0.1879)	
S–C_α[b]	0.4653 (0.0689)	0.4558 (0.0699)	0.4639 (0.0830)
C_α–C_β[b]	0.5457 (0.0951)	0.5451 (0.0999)	0.6362 (0.1912)
C_β–C_β[b]	0.6114 (0.1572)	0.6168 (0.1751)	0.5410 (0.1110)
C_α–C_m[c]	0.5558 (0.1173)	0.5642 (0.1279)	
C_m–C_α[d]	0.5813 (0.1293)	0.5691 (0.1253)	
S–S′		0.0039 (0.0039)	

[a] The pyrroline moiety. [b] The thiophene moiety. [c] C_α from thiophene. [d] C_α from pyrroline.

lengths within the thiophene portion of these macrocycles is modified so that it conforms to the pattern seen in the pyrrole positions. However, the C_α–S bond length remains practically unchanged in all of these substances. These changes suggest that the π electron density has been altered within the thiophene portion so that it is increased in the C_β–C_β bond, decreased in the C_α–C_β bonds and unchanged in the C_α–S bonds. The overlap populations shown in Table II confirm this interpretation.

Comparison of the data for 1 and 2 indicates that whatever S···S interaction is present has negligible effect on the structure of the thiophene portion. The Mulliken overlap population data in Table II shows that there is a very small S···S overlap (0.0039) when d orbitals on sulfur are not included. When d orbitals are included, that overlap population increases only to a very small extent. For comparison we conducted a calculation for diatomic S_2 with the sulfur atoms separated by 3.06 Å (the S···S distance found in 2). The corresponding two-center overlap (0.1965) is considerably larger. We conclude that the S···S interaction is very weak in 2 and that it does not play a role in determining the delocalization pathway within the dithiaporphyrin.

The chemical shifts in the ^{1}H NMR spectra of dithiaporphyrin were discussed in terms of changes in the pathway of inner and outer aromaticity produced by specific core interaction,[9] but the structural results do not support this suggestion.

Experimental Section

Preparation of Compounds. Samples of 1 (R = C_6H_5, R′ = p-$C_6H_5NO_2$)[1] and 2 (R = Ph)[6] were obtained by previously describe routes.

Crystal Structure Analysis. Dark blue prisms of 1 (R = C_6H_5, R′ = p-$C_6H_4NO_2$ were obtained as a 0.5 M n-hexane solvate by diffusion of hexane into a dichloromethane solution of the macrocycle. Crystal data at 130 K: triclinic, space group P$\bar{1}$, a = 11.361 (3) Å, b = 12.708 (3) Å, c = 14.819 (4) Å; α = 108.91 (2)°; β = 93.84 (2); γ = 114.65 (2)°, Z = 2; R = 0.072; R_w = 0.081 for 5073 reflections with $I > 2\sigma I$ and 511 parameters.

Dark brown plates of 2 (R = C_6H_5) were obtained by crystallization of the macrocycle from a mixture of acetonitrile and dichloromethane. They form in the monoclinic space group $P2_1/c$ with a = 11.972 (5) Å, b = 11.607 (5) Å, c = 11.738 (4) Å, β = 103.36 (3)°, Z = 2 at 130 K. Refinement of 1753 reflections with $I > 2\sigma(I)$ and 217 parameters yielded R = 0.059, R_w = 0.051.

Acknowledgment. We thank the the Polish Academy of Sciences (CPBP 01.12) and the National Institutes of Health (GM 26226) for financial support.

Supplementary Material Available: Tables of atomic coordinates, bond distances bond angles, hydrogen atom coordinates, and thermal parameters for 1 (R = C_6H_5, R′ – p-$C_6H_4NO_2$) and 2 (R = C_6H_5) and perspective views of the entire molecules 1 and 2 (18 pages). Ordering information is given on any current masthead page.

Unexpected Behavior of Dienol Thioethers Gives Versatile Access to a Large Set of Functionalized Dienes

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Received October 29, 1990

Thio dienol ethers are useful synthons of special interest in cycloaddition reactions and have been extensively studied throughout the literature in intra[1] and intermolecular[2] situations. Because of their substitution pattern and functionalities methoxy(phenylthio)butadienes have found several applications in the synthesis of natural products such as carvone[3] or eudesmane sesquiterpenes precursors.[4] Preparation of 1,4-disubstituted dienes is generally known to be complicated by both the nature of the substituents and control of the stereochemistry; the proposed route to these structures based upon conrotatory opening of appropriately substituted cyclobutenes[5] leads, in the case of 4-methoxy-1-(phenylthio)buta-1,3-diene, to a mixture of isomers.[6] Thus, the problem of an efficient stereocontrolled synthesis of this potent building block remains to be solved. We present in this work: (i) the first stereoselective access to 4-methoxy-1-(phenylthio)buta-1,3-diene based on 1,4-elimination of corresponding thioether acetal 4, (ii) the exceptional ability of nucleophilic additions to take place on such substrates, giving easy access to a large set of functionalized dienes.

As an extension of our previous studies on polyvinylogation reactions[7] and alkylation using thio enol ether derivatives,[8] we decided to investigate the possibilities of various vinylic thioethers as alkylating systems. The compounds studied have been conveniently prepared according to Scheme I. Crotonaldehyde (1a) or senecialdehyde (1b) are transformed into the corresponding silyl enol ethers **2a,b**[9] (62%, 74% yield, respectively), which, in turn, are brominated and then directly acetalized by methanol,[10] leading to allylic bromo acetals **3a,b** (60%, 89% respectively). Displacement of bromide by thiophenol/triethylamine[11] gives allylic thioethers 4 in 92% and 96% yields, respectively. The stereochemistry is completely controlled in crotonaldehyde derivatives at each step (E isomer only) while the corresponding intermediates from senecialdehyde are obtained as a mixture of isomers with the ratios reported in Scheme I.

When treated at low temperature (–60 °C) with strong bases such as alkyllithium or lithium amide reagents, allyl thioethers 4 undergo γ-elimination of the methoxy group,

(1) Chou, S. S. P.; Wey, S. J. *J. Org. Chem.* **1990**, *55*, 1270.
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(6) Trost, B. M.; Godleski, S. A.; Ippen, J. *J. Org. Chem.* **1978**, *43*, 4559.
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(9) Bazouin, A.; Dunogues, J.; Lefort, M.; Rhône-Poulenc Industrie, French Patent no. 1436568 (1964) and extension no. 88358 (1965).
(10) Rhône-Poulenc Industrie, French Patent no. 7700855 (1977).
(11) Valnot, J. Y. Ph.D. Thesis, Rouen University (1977).

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Scheme I

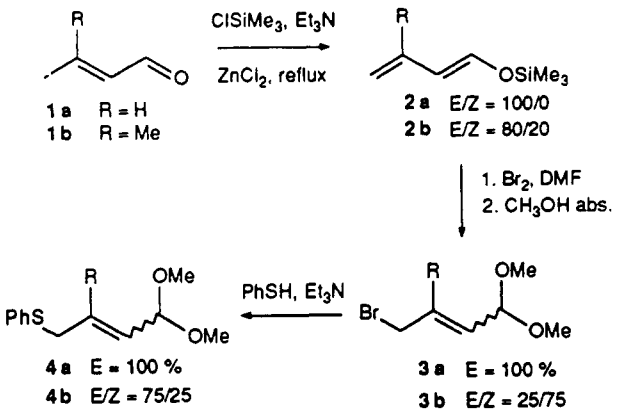
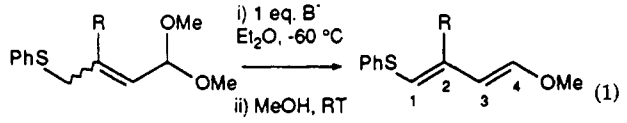


Table I. Functionalized Buta-1,3-dienes Prepared According to Equation 2

compd	substituents R	substituents R′	reactn temp, °C	isomer ratio,[a] %	yield,[b] %
6a	H	*n*-Bu	35	60:40	50
6b	Me	*n*-Bu	−60	61:25:10:4[c]	45
			35	30:40:10:20[c]	60
7a	H	*t*-Bu	−60	64:36	40
7b	Me	*t*-Bu	−60	70:30	60
			35	57:43	80
8b	Me	Me	35	50:50	90
9a	H	morpholino	35	53:47	80
9b	Me	morpholino	35	50:50	80

[a] 1*E*,3*E*:1*Z*,3*E* ratio in all cases except **6b**. [b] Yields after flash chromatography. [c] Identity of isomers has not been determined to date.

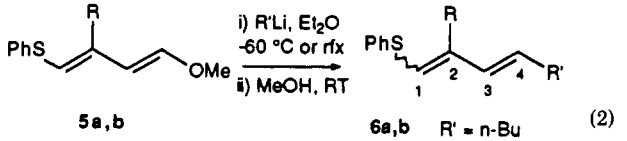
thus leading to 1,4-disubstituted thiodienol ethers **5** (eq 1) in quantitative yield.



(1)

This observation, already described for a related situation,[12] is of interest since it leads, when starting from acetal **4a**, to a total control of stereochemistry of diene **5a**, as determined by 400-MHz ^{1}H NMR spectroscopy. Furthermore, this facile elimination can take place thermally since vacuum distillation of **4a** leads to the enol ether **5a**, but in this case as a complex mixture of isomers.[13] The same elimination has been observed on the methyl acetal of benzenethioacetaldehyde.[14]

Surprisingly, when heated to reflux in ether in the presence of an excess of base, functionalized diene **5a** leads (see eq 2) to 1,4-disubstituted butadienes **6–9**, generally



(2)

as mixtures of *E* and *Z* isomers about the vinyl sulfide with complete control of the 3,4 double-dond geometry in all but one case (see Table I). We emphasize that not only nucleophilic alkyllithium reagents such as *n*-BuLi or MeLi but also compounds that tend to behave as bases rather than nucleophiles such as the lithium amide of morpholine[15] or *t*-BuLi lead to the corresponding addition adducts. This behavior of a lithium amide, not reported before to our knowledge,[16] gives, for instance, an unconventional and versatile access to functionalized dienamines never prepared previously. Compounds **9**, despite the known thermal instability of these structures,[2] could be flash chromatographed and fully characterized by all the usual spectroscopic methods (see Experimental Section). Furthermore, compounds **6** to **9** may be directly prepared from **4** by using 2 equiv of corresponding reagents in a convenient one-pot reaction.

The set of dienes presented in this work are useful synthons for cycloaddition reactions, since they may give easy access to highly functionalized precursors of natural products. Furthermore, the presence of a sulfur atom on the diene moiety should allow good control of the selectivity of the addition; oxidation of the thioether to the corresponding sulfoxide or sulfone is known to reverse the orientation and nature of dienophile[17] involved in the cycloaddition, which may be an interesting feature for future applications. Extensions of these results to the addition of other functionalized nucleophiles and the study of various reactions involving these dienes are currently under way in our laboratory.

Experimental Section

General Aspects. The silica gel used for flash chromatography was from the SDS Company (230–400 mesh). All reagents were of reagent grade and were purified prior to use.

(*E*)- and (*Z*)-3-Methyl-1-(trimethylsiloxy)buta-1,3-dienes (2b).[9] To a solution of 3-methyl-2-butenal (**1b**) (42.0 g, 0.5 mol) in ether (80 mL), triethylamine (55.6 g, 0.94 mol), and dry $ZnCl_2$ (0.6 g) was added dropwise neat chlorotrimethylsilane (59.8 g, 0.55 mol). This solution was warmed at reflux for 25 h. Then 250 mL of *n*-pentane was added at 20 °C. The precipited of triethylamine hydrochloride was filtered, and the solution was evaporated. The crude product was distilled (bp_{15} = 50 °C) to give **2b** (58.1 g, 74%) as an 80:20 mixture of *E* and *Z* isomers: IR (neat) 2950, 1635, 1090 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6) δ (ppm) *E* isomer, 0.08 (9 H, s), 1.72 (3 H, s), 4.75 (1 H, s), 4.85 (1 H, s), 6.11 (1 H, d, J = 12.2 Hz), 6.60 (1 H, d, J = 12.2 Hz); *Z* isomer, 0.00 (9 H, s), 1.56 (3 H, s), 4.90 (1 H, m), 5.08 (1 H, d, J = 6.6 Hz), 5.19 (1 H, m), 6.01 (1 H, d, J = 6.6 Hz).

(*E*)-1-(Trimethylsiloxy)buta-1,3-diene (2a). The procedure was similar to that for **2b**. Spectroscopic data are identical with a commercial sample (Aldrich).

(*E*)- and (*Z*)-4-Bromo-1,1-dimethoxy-3-methylbut-2-enes (3b).[10] To a solution of **2b** (34.2 g, 0.22 mol) in DMF (220 mL) was added dropwise at −20 °C neat Br_2 (35.5 g, 0.22 mol). After 10 min at this temperature, 220 mL of absolute methanol was added. The mixture was stirred for 1.30 h, then was poured into saturated $NaHCO_3$, and extracted three times with 250 mL of petroleum ether. The solution was dried ($NaHCO_3$), filtered, and evaporated. The crude product was purified by flash column chromatography using ether/petroleum ether (1:9) as eluent to give **3b** (40.9 g, 89%) as a 1:3 mixture of *E* and *Z* isomers; both

(12) Everhardus, R. H.; Peterse, A.; Vermeer, P.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 90.
(13) bp (**4a**) 80 °C/0.8 mmHg. Control of the stereochemistry of **5a** is lost when heating acetal **4a** to reflux of ether in presence of bases.
(14) Langlois, C.; Chauvin, J. Unpublished results.
(15) Dienamine of diisopropylamine **9a** (R′ = N(iPr)$_2$, eq 2) seems to be formed in same conditions using LDA as a base (mass spectrometry [CI, CH_4]: m/z = 262 (M + 1, 100)) but could not be isolated nor further characterized to date.
(16) Addition of *s*-BuLi or *t*-BuLi to buta-1,3-diene in hydrocarbon solution has been reported: Glaze, W. H.; Jones, P. C. *Chem. Commun.* **1969**, 1434.
(17) Evans, D. A.; Bryan, C. A.; Sims, C. L. *J. Am. Chem. Soc.* **1972**, *94*, 2891.

isomers could be isolated by flash chromatography: IR (neat) 2830, 1670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) *Z* isomer, 1.87 (3 H, d, ^4J = 1.2 Hz), 3.31 (6 H, s), 3.94 (2 H, s), 5.01 (1 H, d, *J* = 6.3 Hz), 5.63 (1 H, d, *J* = 6.3 Hz); *E* isomer, 1.91 (3 H, d, ^4J = 1.4 Hz), 3.31 (6 H, s), 4.02 (2 H, s), 5.05 (1 H, d, *J* = 5.7 Hz), 5.41 (1 H, dq, ^3J = 5.7, ^4J = 1.4 Hz); an NOE experiment showed that irradiation at δ 1.91 resulted in enhancements at δ 5.05.

(*E*)-4-Bromo-1,1-dimethoxybut-2-ene (3a). The procedure was similar to that for **3b** starting from 38.7 g of **2a**: (yield 31.6 g, 60%): ^1H NMR (400 MHz, C_6D_6) δ (ppm) 3.05 (6 H, s), 3.35 (2 H, d, *J* = 7.6 Hz), 4.57 (1 H, d, *J* = 4.2 Hz), 5.42 (1 H, ddt, ^3J = 15.3, ^3J = 4.2, ^4J = 1.0 Hz), 5.86 (1 H, ddt, ^3J = 15.3, ^3J = 7.6, ^4J = 1.2 Hz).

(*E*)- and (*Z*)-1,1-Dimethoxy-3-methyl-4-(phenylthio)but-2-enes (4b). To a solution of **3b** (39.2 g, 0.19 mol) in triethylamine (105 mL) was added dropwise, at 20 °C, a solution of thiophenol (21.7 g, 0.20 mol) in ether (21 mL). The mixture was stirred for 8 h and then the precipitate was filtered out and washed with ether. After evaporation of the filtrate, the crude product **4b** was recovered (43.5 g, 96%) as a 3:1 mixture of *E* and *Z* isomers: MS (EI) *m/z* 238 (M^+, 10), 206 (23), 175 (24), 149 (56), 128 (100); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) *E* isomer, 1.84 (3 H, d, ^4J = 1.10 Hz), 3.14 (6 H, s), 3.51 (2 H, s), 4.95 (1 H, d, *J* = 6.40 Hz), 5.30 (1 H, dq, ^3J = 6.40, ^4J = 1.10 Hz), 7.15–7.45 (5 H, m); *Z* isomer, 1.90 (3 H, d, ^4J = 1.17 Hz), 3.19 (6 H, s), 3.60 (2 H, s), 4.71 (1 H, d, *J* = 6.30 Hz), 5.34 (1 H, m, *J* = 6.30 Hz), 7.15–7.45 (5 H, m); an NOE experiment showed that irradiation at δ 1.87 resulted in enhancements at δ 4.95 and 5.34. Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61. Found: C, 65.20; H, 7.43.

(*E*)-1,1-Dimethoxy-4-(phenylthio)but-2-ene (4a). The procedure was similar to that for **4b** starting from 34 g of **3a** (yield 35.2 g, 90%): ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.07 (6 H, s), 3.22 (2 H, d, *J* = 6.9 Hz), 4.67 (1 H, d, *J* = 4.4 Hz), 5.50 (1 H, ddt, ^3J = 15.6, ^3J = 4.4, ^4J = 1.0 Hz), 5.90 (1 H, ddt, ^3J = 15.6, ^4J = 1.2, ^3J = 6.9 Hz), 6.90–7.45 (5 H, m).

(1*E*,3*E*)- and (1*Z*,3*E*)-4-Methoxy-2-methyl-1-(phenylthio)buta-1,3-diene (5b). To a solution of **4b** (0.5 g, 2.1 mmol) in THF (10 mL) was added dropwise, at –60 °C, a solution of *n*-BuLi in hexane (1.5 M, 1.4 mL, 2.1 mmol). The mixture was stirred for 30 min at –60 °C and then heated back to 20 °C before being quenched by addition of absolute methanol. After centrifugation of the precipitate, the solvents were evaporated to give the crude product **5b**, which was obtained as an 85:15 mixture of *E,E* and *Z,E* isomers (0.30 g, 90%): IR (neat) 2980, 1630, 1040 cm^{-1}; MS (CI, iBuH) *m/z* 207 (M + 1, 100); HRMS calcd for $C_{12}H_{14}OS$ *m/z* 206.0766, found 206.0775; ^1H NMR (400 MHz, C_6D_6) δ (ppm) 1*E*,3*E* isomer, 1.84 (3 H, d, ^4J = 1.0 Hz), 3.03 (3 H, s), 5.57 (1 H, d, *J* = 12.7 Hz), 5.99 (1 H, d, ^4J = 1.0 Hz), 6.47 (1 H, d, *J* = 12.7 Hz), 6.88–7.35 (5 H, m); an NOE experiment showed that irradiation at δ 1.84 resulted in enhancements at δ 6.47; 1*Z*,3*E* isomer, 1.65 (3 H, d, ^4J = 1.0 Hz), 3.02 (3 H, s), 5.78 (1 H, s), 5.41 (1 H, d, *J* = 13.2 Hz), 6.74 (1 H, d, *J* = 13.2 Hz), 7.02 (5 H, m); an NOE irradiation at δ 1.65 resulted in enhancements at δ 5.78 and 6.74.

(*E,E*)-1-Methoxy-4-(phenylthio)buta-1,3-diene (5a). The procedure was similar to that for **5b**: IR (neat) 2980, 1630, 1050 cm^{-1}; MS (CI, CH_4) *m/z* 192 (M + 1, 100); HRMS calcd for $C_{11}H_{12}OS$ *m/z* 192.0609, found 192.0609; ^1H NMR (400 MHz, C_6D_6) δ (ppm) 3.01 (3 H, s), 5.39 (1 H, dd, *J* = 12.5 Hz, *J* = 10.8 Hz), 6.00 (1 H, d, *J* = 14.7 Hz), 6.26 (1 H, d, *J* = 12.5 Hz), 6.34 (1 H, dd, *J* = 14.7, *J* = 10.8 Hz), 6.88–7.35 (5 H, m).

2-Methyl-1-(phenylthio)octa-1,3-dienes (6b). Method A. To a solution of **4b** (0.5 g, 2.1 mmol) in THF (10 mL) was added dropwise, at –60 °C, a solution of *n*-BuLi in hexane (2.5 M, 2.6 mL, 6.3 mmol). The mixture was stirred for 30 min at –60 °C and then heated back to 20 °C before being quenched by addition of absolute methanol. After centrifugation of the precipitate, the solvent was evaporated. The crude product was purified by flash column chromatography using petroleum ether as eluent to give **6b** (0.25 g, 45%). Isomer ratio (geometry undetermined to date): 61/25/10/4; IR (neat) 2920, 1580 cm^{-1}; MS (CI, CH_4) *m/z* 233 (M + 1, 100); HRMS calcd for $C_{15}H_{20}S$ *m/z* 232.1286, found 232.1288; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) isomer A (61%), 0.85–1.50 (9 H, m), 1.93 (3 H, s), 5.67 (1 H, dt, *J* = 15.0, *J* = 6.2 Hz), 6.14 (1 H, d, *J* = 15.0 Hz), 6.12 (1 H, s), 7.1–7.5 (5 H, m); isomer B (25%), 0.85–1.50 (9 H, m), 1.95 (3 H, s), 5.84 (1 H, dt, J = 15.0, *J* = 7.5 Hz), 6.70 (1 H, d, *J* = 15.0 Hz), 7.1–7.5 (5 H, m).

Method B. The same as above but addition of *n*-BuLi at reflux of ether, immediately followed by methanol quenching at room temperature. Starting from 0.3 g of **4b** the yield is 0.18 g (60%). Isomer ratio (geometry undetermined to date): 30/40/10/20.

(1*E*,3*E*)- and (1*Z*,3*E*)-1-(Phenylthio)octa-1,3-dienes (6a). The procedure was similar to method B described above for **6b** starting from 0.2 g of **4a**. The yield was 97 mg (50%) of a 60:40 mixture of *E,E* and *Z,E* isomers; IR (neat) 2920, 1580 cm^{-1}; MS (CI, CH_4) *m/z* 219 (M + 1, 100); HRMS calcd for $C_{14}H_{18}S$ *m/z* 218.1129, found 218.1106; ^1H NMR (400 MHz, C_6D_6) δ (ppm) 1*E*,3*E* isomer, 0.85–1.4 (9 H, m), 5.46 (1 H, dt, *J* = 14.6, *J* = 7.8 Hz), 5.99 (1 H, dd, *J* = 14.6, *J* = 10.7 Hz), 6.21 (1 H, d, *J* = 14.6 Hz), 6.48 (1 H, dd, *J* = 14.6, *J* = 10.7 Hz), 6.9–7.5 (5 H, m); 1*Z*,3*E* isomer, 0.85–1.4 (9 H, m), 5.71 (1 H, dt, *J* = 15.7, *J* = 7.8 Hz), 6.06 (1 H, d, *J* = 9.7 Hz), 6.27 (1 H, dd, *J* = 9.7, *J* = 9.7 Hz), 6.78 (1 H, dd, *J* = 15.7, *J* = 9.7 Hz), 6.9–7.5 (5 H, m).

(1*E*,3*E*)- and (1*Z*,3*E*)-1-(Phenylthio)-2,5,5-trimethylhexa-1,3-dienes (7b). Method A. To a solution of **4b** (0.5 g, 2.1 mmol) in THF (10 mL) was added dropwise at –60 °C a solution of *t*-BuLi in pentane (1.6 M, 3.9 mL, 6.3 mmol). The remainder of the procedure was similar to that described for **6b**. The crude product was also purified by flash chromatography using petroleum ether as eluent to give **7b** (0.29 g, 60%) as a 70:30 mixture of *E,E* and *Z,E* isomers: IR (neat) 2920, 1580 cm^{-1}; MS (EI) *m/z* 232 (M^+, 98), 175 (30), 123 (100); HRMS calcd for $C_{15}H_{20}S$ *m/z* 232.1286, found 232.1287; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 1*E*,3*E* isomer, 1.06 (9 H, s), 1.95 (3 H, d, ^4J = 1.2 Hz), 5.71 (1 H, d, *J* = 15.9 Hz), 6.08 (1 H, d, *J* = 15.9 Hz), 6.18 (1 H, s), 7.15–7.40 (5 H, m); an NOE experiment showed that irradiation at δ 1.95 resulted in enhancements at δ 5.71; 1*Z*,3*E* isomer, 1.08 (9 H, s), 1.90 (3 H, d, ^4J = 1.2 Hz), 5.87 (1 H, d, *J* = 15.9 Hz), 6.02 (1 H, s), 6.61 (1 H, d, *J* = 15.9 Hz), 7.15–7.40 (5 H, m); an NOE experiment showed that irradiation at δ 1.90 resulted in enhancements at δ 5.87 and 6.02.

Method B. The same as above but addition of *t*-BuLi at reflux of ether, immediately followed by methanol quenching at room temperature. Starting from 0.2 g of **5b** and using 0.63 mL of a solution of *t*-BuLi in pentane (1.6 M, 1.0 mmol), the yield is 0.185 g (80%); *E,E*/*Z,E* ratio 57/43.

(1*E*,3*E*)- and (1*Z*,3*E*)-1-(Phenylthio)-5,5-dimethylhexa-1,3-dienes (7a). The procedure was similar to method A described above for **7b** starting from 0.2 g of **4a**. The yield was 78 mg (40%) of a 64:36 mixture of *E,E* and *Z,E* isomers: IR (neat) 2920, 1580 cm^{-1}; MS (CI, CH_4) *m/z* 219 (M + 1, 52), 111 (86), 73 (100); HRMS calcd for $C_{14}H_{18}S$ *m/z* 218.1129, found 218.1149; ^1H NMR (400 MHz, C_6D_6) δ (ppm) 1*E*,3*E* isomer, 0.93 (9 H, s), 5.46 (1 H, d, *J* = 15.4 Hz), 5.94 (1 H, dd, *J* = 15.4, *J* = 10.3 Hz), 6.15 (1 H, d, *J* = 14.8 Hz), 6.41 (1 H, dd, *J* = 14.8, *J* = 10.3 Hz), 6.80–7.40 (5 H, m); 1*Z*,3*E* isomer, 0.94 (9 H, s), 5.72 (1 H, d, *J* = 15.3 Hz), 6.03 (1 H, d, *J* = 9.3 Hz), 6.23 (1 H, dd, *J* = 9.3, *J* = 10.0 Hz), 6.71 (1 H, dd, *J* = 15.3, *J* = 10.0 Hz), 6.80–7.40 (5 H, m).

(1*E*,3*E*)- and (1*Z*,3*E*)-2-Methyl-1-(phenylthio)penta-1,3-dienes (8b). The procedure was similar to method B described above for **6b** starting from 0.3 g of **4b**. The yield was 0.2 g (90%) of a 50:50 mixture of *E,E* and *Z,E* isomers: MS (CI, iBuH) *m/z* 191 (M + 1, 85), 190 (100); ^1H NMR (200 MHz, C_6D_6) δ (ppm) 1*E*,3*E* isomer, 1.83 (3 H, d, *J* = 0.8 Hz), 3.12 (3 H, s), 5.57 (1 H, d, *J* = 12.7 Hz), 5.98 (1 H, s), 6.48 (1 H, d, *J* = 12.7 Hz), 6.85–7.35 (5 H, m); NOE experiments showed that irradiation at δ 1.83 resulted in enhancements at δ 6.48, irradiation at δ 3.12 resulted in enhancements at δ 5.57, and irradiation at δ 5.98 resulted in enhancements at both δ 5.57 and δ 7.30; 1*Z*,3*E* isomer, 1.66 (3 H, d, *J* = 1.2 Hz), 3.12 (3 H, s), 5.78 (1 H, s), 6.40 (1 H, d, *J* = 12.9 Hz), 6.68 (1 H, d, *J* = 12.9 Hz), 6.85–7.35 (5 H, m); NOE experiments showed that irradiation at δ 1.66 resulted in enhancements at both δ 5.78 and 6.68 and irradiation at δ 3.12 resulted in enhancements at both δ 6.40 and 6.68.

(1*E*,3*E*)- and (1*Z*,3*E*)-2-Methyl-4-morpholino-1-(phenylthio)buta-1,3-dienes (9b). To a solution of morpholine (0.73 mL, 8.4 mmol) in ether (5 mL) was added dropwise, at 0 °C, a solution of *n*-BuLi in hexane (2.4 M, 2.4 mL, 5.9 mmol). The mixture was stirred for 15 min at 0 °C; then at –60 °C was added dropwise a solution of **4b** (0.5 g, 2.1 mmol) in ether (5 mL). When back to room temperature, the mixture was brought to reflux for

3 h and then quenched by addition of absolute methanol (2 mL) at room temperature. After centrifugation of the precipitate, the solvents were evaporated. The crude product was purified by column chromatography using ether/petroleum ether/triethylamine (1/9/0.1) as eluent to give **9b** (yield 0.44 g, 80%) as a 50:50 mixture of 1*E*,3*E* and 1*Z*,3*E* isomers: IR (neat) 1620 cm^{-1}; MS (CI, CH_4) *m/z* 262 (M + 1, 100); HRMS calcd for $C_{15}H_{19}NOS$ *m/z* 261.1187, found 261.1194; ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 1*E*,3*E* isomer, 1.99 (3 H, s), 2.93 (4 H, m), 3.69 (4 H, m), 5.66 (1 H, s), 5.83 (1 H, d, *J* = 13.9 Hz), 6.31 (1 H, d, *J* = 13.9 Hz), 7.1–7.3 (5 H, m); 1*Z*,3*E* isomer, 1.99 (3 H, s), 2.93 (4 H, m), 3.69 (4 H, m), 5.40 (1 H, d, *J* = 13.9 Hz), 5.89 (1 H, s), 6.22 (1 H, d, *J* = 13.9 Hz), 7.1–7.3 (5 H, m).

(1*E*,3*E*)- and (1*Z*,3*E*)-1-Morpholino-4-(phenylthio)buta-1,3-dienes (9a). The procedure was similar to that for **9b** starting from 0.4 g of **4a**. The yield was 0.35 g (80%) of a 53:47 crude mixture of 1*E*,3*E* and 1*Z*,3*E* isomers: IR (neat) 2950, 1625 cm^{-1}; MS (CI, CH_4) *m/z* 248 (M + 1, 100); HRMS calcd for $C_{14}H_{17}NOS$ *m/z* 247.1031, found 247.1040; ^1H NMR (200 MHz, C_6D_6) δ (ppm) 1*E*,3*E* isomer, 2.31 (4 H, m), 3.20 (4 H, m), 5.05 (1 H, dd, *J* = 13.4, *J* = 10.6 Hz), 5.64 (1 H, d, *J* = 13.4 Hz), 5.95 (1 H, d, *J* = 14.4 Hz), 6.59 (1 H, dd, *J* = 10.6, *J* = 14.4 Hz), 6.8–7.4 (5 H, m); 1*Z*,3*E* isomer, 2.31 (4 H, m), 3.20 (4 H, m), 5.71–5.85 (3 H, m), 6.35 (1 H, dd, *J* = 9.1, *J* = 9.1 Hz), 6.8–7.4 (5 H, m).

Acknowledgment. We are deeply indebted to Dr. G. Plé for full 400-MHz ^1H NMR spectra and help with their analysis. We wish to thank also Mr. A. Marcual for mass spectrometry and CNRS for financial support.

Supplementary Material Available: ^1H NMR spectra for compounds **4a**, **5b**, **6b**, **7a,b**, **8b**, and **9a,b** (12 pages). Ordering information is given on any current masthead page.

Regiospecific Synthesis of Hydroxyquinones and Related Compounds from 3-*tert*-Butoxycyclobutene-1,2-dione

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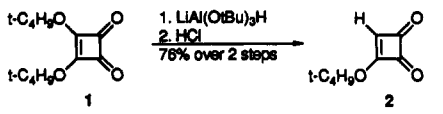
Received November 26, 1990

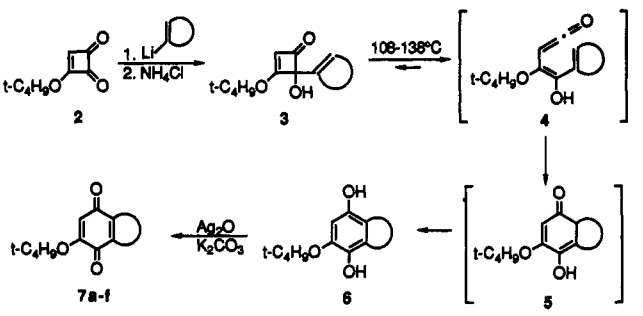
Reported here is the synthesis of 3-*tert*-butoxycyclobutene-1,2-dione, **2**, and its utility as a reagent for the regiospecific synthesis of substituted hydroxyquinones. This cyclobutenedione was readily obtained in 72% yield upon treatment of di-*tert*-butyl squarate, **1**, with lithium tri-*tert*-butoxyaluminohydride followed by hydrolysis with aqueous HCl.[1,2]

The cyclobutenedione **2** undergoes facile regiospecific addition of aryl- or alkenyllithium reagents to the more electrophilic carbonyl group at position 2 to give 4-aryl(or alkenyl)-3-*tert*-butoxy-4-hydroxycyclobutenones **3** as outlined in Scheme II. Thermolysis (refluxing *p*-xylene or toluene, 15–60 min) of these adducts followed by oxidation of the resulting hydroquinone **6** (Ag_2O, K_2CO_3) provides the quinones **7a–f** in good overall yields (Table I). These ring expansions provide further examples of the synthetic scope of the known rearrangements of 4-aryl(or alkenyl)cyclobutenones to hydroquinones. The rearrangements are envisaged to involve initial electrocyclic ring opening to the conjugated ketenes **4**, which undergo ring closure to **5** and final tautomerization to the hydroquinones **6**.[3]

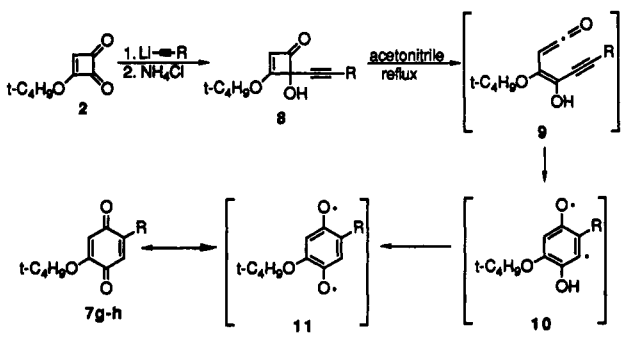
Scheme I



Scheme II



Scheme III



Scheme IV

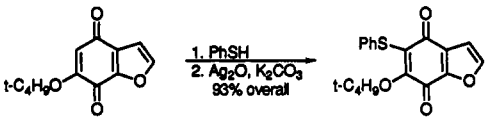
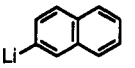
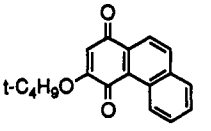
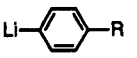
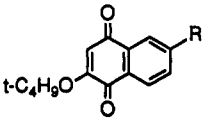
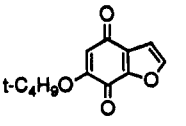
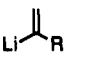
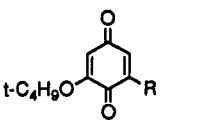
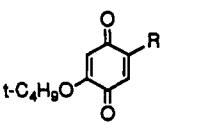


Table I *tert*-Butoxy Quinones

entry	lithium reagent	R	quinone	% yield from 2
7a				48
7b		H		63
7c		CH_3		48
7d				53
7e		CH_3		66
7f		n-Bu		58
7g		CH_3		63
7h		n-Bu		56

(1) The 3-isopropoxycyclobutene-1,2-dione has previously been prepared in an analogous fashion: Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482.

(2) Reed, M. W.; Pollart, D. J.; Perri, S. T.; Foland, L. D.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 2477.

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