neously with the actinometer at the appropriate wavelength. The conversion of the diazo compound was monitored by IR spectroscopy. The results are summarized in Table III.

Measurement of k_{AMS}/k_{HFB} for 18DAF. The ratio of the reaction rate constants was obtained from the analysis of the yield ratio of the products. The calculation is based on the following equation:

$$\frac{k_{AMS}}{k_{HFB}} = \frac{(\text{yield of } \mathbf{2}) \times [\text{HFB}]}{S \times (\text{yield of } \mathbf{3}) \times [\text{AMS}]}$$

where S is obtained from Table I and is the fraction of the cyclopropane that comes from the singlet carbene.

Acknowledgment. This work was supported by a grant from the National Science Foundation and a fellowship to Y.-Z. Li from the Ministry of Education of the People's Republic of China.

Registry No. 1, 103621-89-2; 2, 103621-86-9; 3, 109929-84-2; 18DAF, 1807-47-2; 18FL, 103621-90-5; HFB, 392-56-3; AMS, 98-83-9; (*E*)-β-deuterio-α-methylstyrene, 69912-51-2.

Supplementary Material Available: Description of the solution of the kinetic network for Scheme I (7 pages). Ordering information is given on any current masthead page.

Formation of 4-Nitrocyclohexa-2,5-dienols by Addition of Organolithium Reagents to 4-Alkyl-4-nitrocyclohexa-2,5-dienones[1]

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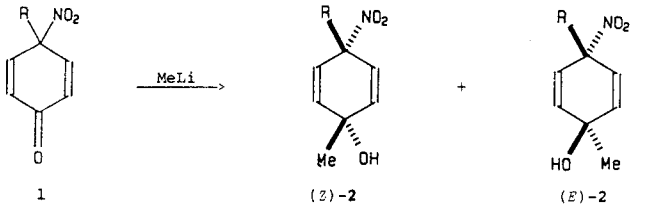
Addition of methyllithium to 4-alkyl-4-nitrocyclohexa-2,5-dienones **1a–d** (alkyl = Me, Et, *i*-Pr, *t*-Bu), to 2,6-dichloro- and 2,6-dibromo-4-methyl-4-nitrocyclohexa-2,5-dienone, and to 4a-nitro-2-oxo-2,4a,5,6,7,8-hexahydronaphthalene gives the corresponding dienols **2a–d**, **4e** and **4f**, and **7g**, generally as a pair of diastereomers. Addition of methyl lithioacetate to the same substrates gives dienols **8a–d**, **5e** and **5f**, and **7h**. Addition of substituted methyllithiums (XCH_2Li, X = CN, $CONH_2$, $CONMe_2$, COMe, SMe, SPh, SOMe, SO_2Me, $SiMe_3$, PSMePh, $PSPh_2$), 2-lithio-1,3-dithiane, or lithium phenylacetylide to **1a** gives the dienols **9i–u**.

Nitronium acetate adducts (nitrocyclohexadienyl acetates), in which the nitro group is attached to an activated substituted site, are often formed when arenes and their derivatives are nitrated in acetic anhydride.[2-4] With appropriate substrates good yields of adducts are obtained, but as a means of preparing such adducts direct nitration suffers from some inherent limitations. Thus, the ipso position to which the nitronium ion is to be added must be relatively activated; regioisomers may be formed in the ipso nitration;[5-8] and some substituents, such as those containing sulfur, phosphorus, or silicon are sensitive to the nitration conditions.[9-11]

Myhre and co-workers developed an efficient process for the synthesis of ipso nitration products in which a 4-alkyl-4-nitrocyclohexa-2,5-dienone is reduced with sodium borohydride in methanol to form the corresponding 4-alkyl-4-nitrocyclohexadienol.[12] They also showed that addition of methyllithium to 4-methyl-4-nitrocyclohexa-2,5-dienone (**1a**) gave an excellent yield of 1,4-dimethyl-4-nitrocyclohexa-2,5-dienol (**2a**). We have extended the latter reaction to the preparation of 4-alkyl-4-nitrocyclohexa-2,5-dienols from a number of different 4-alkyl-4-nitrocyclohexadienones using methyllithium and a series of substituted alkyllithium reagents. Our results demonstrate that this is a very effective method for the synthesis of such cyclohexadienols.

Scheme I



a, R = Me. b, R = Et. c, R = i-Pr. d, R = t-Bu.

Results and Discussion

Preparation of 4-Nitrocyclohexadienones. Methods for the preparation of 4-methyl-, 4-ethyl-, and 4-isopropyl-4-nitrocyclohexa-2,5-dienones and of 2,6-dichloro- and 2,6-dibromo-4-methyl-4-nitrocyclohexadienones are well established.[12,13] Higher yields of dienone are obtained on nitration of the aryl acetate rather than the phenol.[12] However, we have found that nitration of the phenol with nitric acid and trifluoroacetic anhydride in ether is a particularly simple way of making dienones. Although the yields of dienone is inferior to that obtained by nitration of the aryl acetate with nitric acid in acetic anhydride, this

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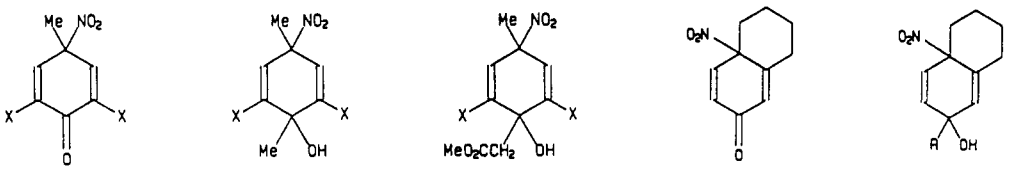
0022-3263/87/1952-4464$01.50/0

Chart I



3 4 5 6 7

e, X = Cl f, X = Br g, R = Me h, R = CH_2CO_2Me

is offset by the very easy isolation procedure, which consists of washing the reaction solution with ice-cold aqueous sodium hydroxide to remove the nitrophenol, followed by evaporation of the ether at low temperature. The nitrodienones were obtained as crystalline solids and characterized by ^1H and ^{13}C spectra. The ease of isolation is of particular value for the preparation of labile dienones.

Nitration of 5,6,7,8-tetrahydro-2-naphthyl acetate in acetic anhydride gave 4a-nitro-2-oxo-2,4a,5,6,7,8-hexahydronaphthalene (**6**) (92%) and the 1-nitro- and 3-nitrotetrahydronaphthyl acetates. Nitration of 5,6,7,8-tetrahydro-2-naphthol in ether using trifluoroacetyl nitrate yielded nitrodienone **6** (40%) and the 1-nitro- and the 3-nitrotetrahydronaphthols. Preparative-scale nitration was carried out on the acetate in acetic anhydride. 2,6-Dichloro- (**3**) and 2,6-dibromo-4-methyl-4-nitrocyclohexa-2,5-dienone (**3f**) were obtained by the nitration of the corresponding 2,6-dihalophenols in aqueous acetic acid.[13]

Addition of Methyllithium to 4-Nitrocyclohexadienones. Addition of methyllithium to 4-alkyl-4-nitrocyclohexa-2,5-dienones **1a–d** gave both diastereomers of the corresponding 4-alkyl-1-methyl-4-nitrocyclohexa-2,5-dienols **2a–d** (Scheme I). The diastereomers were separated by high-pressure liquid chromatography. The new compounds had the appropriate microanalyses and infrared and ^1H and ^{13}C NMR spectra. Note that the acetates of dienols **2c** and **2d** cannot be obtained by nitration of the corresponding 4-alkyltoluenes. Nitration ipso to the isopropyl group does occur, but it results in loss of the isopropyl group as a cation and the formation of 4-nitrotoluene.[14,15] Nitration ipso to *tert*-butyl does not occur, presumably because of steric hindrance.[16]

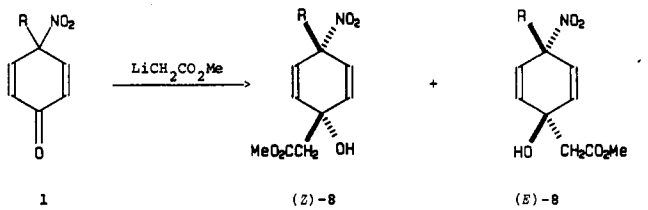
Addition of methyllithium to the 2,6-dihalo-4-methyl-4-nitrocyclohexa-2,5-dienones **3e,f** gave both diastereomers of the 2,6-dihalo-1,4-dimethyl-4-nitrocyclohexa-2,5-dienols **4e,f** (Chart I). Addition of methyllithium to nitro dienone **6** gave one of the diastereomers of nitrodienol **7g**, assigned as the *Z* isomer.

Addition of Methyl Lithioacetate to 4-Nitrocyclohexadienones. Addition of methyl lithioacetate to **1a–d** gave the corresponding nitro dienols **8a–d**, in each case as a pair of diastereomers and in close to quantitative yield (Scheme II) The diastereomers were separated by high-pressure liquid chromatography.

Addition of methyl lithioacetate to **3e,f** gave the diastereomeric dienols **5e,f**. Addition of methyl lithioacetate to **6** yielded the corresponding nitro dienol **7h** as a pair of diastereomers in a 3:2 ratio. The isomers were separated by high-pressure liquid chromatography and characterized.

Addition of Other Functionalized Organolithium Reagents to 4-Methyl-4-nitrocyclohexa-2,5-dienone. Dienone **1a** was chosen as the basic substrate for study of

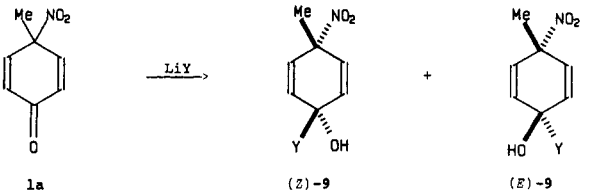
Scheme II



1 (Z)-8 (E)-8

a, R = Me. b, R = Et. c, R = i-Pr. d, R = t-Bu.

Scheme III



1a (Z)-9 (E)-9

i, Y = CH_2CN. j, Y = CH_2CONH_2. k, Y = CH_2CONMe_2.
l, Y = CH_2COMe. m, Y = CH_2SMe. n, Y = CH_2SPh.
o, Y = CH_2SOMe. p, Y = CH_2SO_2Me. q, Y = CH_2SiMe_3.
r, Y = $CH_2PSMePh$. s, Y = CH_2PSPh_3. t, Y = $\overline{CHS(CH_2)_3S}$.
u, Y = CCPh.

addition reactions in which other organolithium reagents were used. Addition of functionalized organolithium reagents yielded the nitro dienols **9i–u** in yields ranging from 65% to 100% (Scheme III). Usually a pair of diastereomers was obtained and the individual diastereomers were separated, either by high-pressure liquid chromatography or by column chromatography or, in some cases, by fractional crystallization. The diastereomers of **9o** and **9p** were not separated. Attempts were made to add $LiCH_2PPhMe$ and $LiCH_2PPh_2$ to the nitrodienone to prepare the corresponding phosphine dienes. However, the only identifiable product was the phosphine oxide. Oxidation of trivalent phosphorus by nitro compounds is well documented. Thus, the deoxygenation of the nitro group by phosphines and phosphites is one of methods of generating aromatic nitrenes:[17] 2-nitrobiphenyl gives carbazole when treated with triethyl phosphite. However, it was possible to obtain nitro dienols **9m,n,t**, bearing a divalent sulfur side chain, and the silyl dienol **9q**, compounds which cannot be prepared by direct nitration.

Stereochemistry of the Adducts. The stereochemistry of the diastereomers of **2a** and **2b** is known.[18,19] The

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Table I. Relative Gradients of ^1H Chemical Shifts of 8a and 9i

dienol	CH_2	H-2,6	H-3,5	4-CH_3	OCH_3
(*Z*)-**8a**	1.00	0.90	0.29	0.17	0.15
(*E*)-**8a**	1.00	0.85	0.28	0.21	0.20
(*Z*)-**9i**	1.00	0.78	0.28	0.16	
(*E*)-**9i**	1.00	0.77	0.41	0.26	

stereochemistry of the diastereoisomers of **8a** and **9i** was assigned on the basis of shift reagent studies.[20] Addition of the shift reagent tris(1,1,1,2,2,3,3-heptafluoro-7,7-([$^2H_6$]dimethyl)-4,6-[$^2H_3$]octanedionato)europium(III) [Eu(fod)$_3$], which complexes at the hydroxyl function moved the 4-methyl protons (and carbon) in the *E* isomer, with these protons (carbon) cis to europium, more rapidly downfield than in the case of the *Z* isomer (Tables I and II). For the dienols for which the stereochemistry is established, viz., **2a,b**, **8a**, and **9i** the lower melting isomer has the *Z* and the higher melting isomer the *E* configuration. Such regularity of physical properties with stereochemistry has previously been observed for the 1-alkyl-4-methyl- and 1-alkyl-4-ethyl-4-nitrocyclohexadienyl acetates and alcohols.[18] We therefore assigned the stereochemistry of the other 4-alkyl-1-methyl-4-nitrocyclohexadienols, **2c** and **2d**, and of the dienols **8c,d**, **5e,f**, and **9j–m,r** on the assumption that in each case the *Z* isomer is the lower melting isomer.

Significant diastereoselectivity was observed in a number of the addition reactions. Diastereoselectivity for addition of methyllithium to both **1a** and **6** is greater than that for methyl lithioacetate and likely reflects differences in the sizes of the reagents. The diastereoselectivity observed in the addition of methyllithium to **1a** has been accounted for in terms of the steric and field effects of the nitro group.[12] The reagent prefers to attack the carbonyl group from the ring face opposite to that of the nitro group leading to the formation of the *Z* isomer as the major product. Methyllithium is known to exist as a tetramer in tetrahydrofuran solution[21] and may be bulkier than the less aggregated methyl lithioacetate. Significant diastereoselectivity was also observed in the addition of lithium phenylacetylide, 2-lithio-1,3-dithiane, lithioacetone, (lithiomethyl)methylphenylphosphine sulfide, and (lithiomethyl)diphenylphosphine sulfide. These reagents behave as if they have large nucleophiles either because they are inherently large or, possibly, they are extensively aggregated in solution like methyllithium. The carbanions which do not exhibit diastereoselectivity are either smaller or stabilized by resonance such that aggregation would be expected to be less important.

In some cases in which the melting point data were not available for the diastereomers a tentative assignment of stereochemistry was made on the basis of the diastereoselectivity. Thus the single isomer of nitro dienol **7g** is assigned as the *Z* isomer on the basis that the angular nitro group should direct the addition of the methyl group from the opposite face of the cyclohexa-2,5-dienone ring (cf. ref 22).

Reduction of 4-Nitrocyclohexa-2,5-dienones by Alkyllithium Reagents. 4-Alkylphenols were obtained as a minor product in the addition of alkyllithium reagents to 4-alkyl-4-nitro-cyclohexa-2,5-dienones. For the additions to **1a** the yield of *p*-cresol varied from 0% to 35%. Very reactive carbanions and higher temperature favored the formation of *p*-cresol. More *p*-cresol was obtained when the dienone was added to the alkyllithium reagent rather than vice versa. Addition of methyllithium to nitrodienone **1a** at −78 °C gave 10% of *p*-cresol. When the reverse addition was carried out at 0 °C, *p*-cresol was obtained as the major product. Addition of *tert*-butyllithium gave only *p*-cresol and 2-methyl-2-nitropropane, identified by ^1H NMR and GC analysis. No 1,2-addition product was obtained. The formation of 2-methyl-2-nitropropane suggests that the reduction might occur through nucleophilic attack on the nitrogen of the nitro group, although an electron transfer from *tert*-butyl anion to nitro dienone followed by radical cleavage to the phenoxide and nitrogen dioxide and radical recombination of the latter and *tert*-butyl could lead to the same result. Attempts to isolate nitromethane from the methyllithium addition reactions were unsuccessful, possibly because of the difficulty of extracting the small amount of nitromethane formed from aqueous solution.

Conclusions

Addition of methyllithium, substituted methyllithiums, or related organolithiums to 4-alkyl-4-nitrocyclohexa-2,5-dienones and derivatives in THF at −78 °C gives good yields of 1-methyl- and 1-(substituted-methyl)-4-alkyl-4-nitrocyclohexa-2,5-dienols or related dienols. Elimination of the nitro group to form the corresponding phenol is the only significant side reaction, and, for the specified reagents and conditions, only in one instance does as much as 35% of the reaction occur by this pathway. Many of the nitro dienols made in this way are not accessible via direct nitration.

Experimental Section

Illustrative preparations for **1c**, **2c**, and **8c** are described. Preparative details and NMR data for all of the compounds obtianed are given in the supplementary material (see paragraph at the end of the paper). Elemental analyses were performed by Canadian Microanalytical Service Ltd, Vancouver, BC, Canada.

4-Isopropyl-4-nitrocyclohexa-2,5-dienone (1c) was obtained by nitration of 4-isopropylphenol. Fuming nitric acid (15.2 g, 0.24 mol) was added rapidly with stirring to a solution of 4-isopropylphenol (27.2 g, 0.2 mol) in ether at −78 °C. A solution of trifluoroacetic anhydride (29.8 mL, 0.21 mol) in ether (50 mL) was then added dropwise. After the addition was complete, stirring was continued for 45 min at −78 °C and for an additional 30 min at −40 °C to ensure complete reaction. ^1H NMR showed that the products were the dienone **1c** (15%) and 4-isopropyl-2-nitrophenol (85%). The reaction mixture, at −78 °C, was neutralized by the dropwise addition of 10% aqueous sodium hydroxide (250 mL) with stirring. The rate of addition was controlled to maintain the temperature of the mixture below −60 °C. After the addition was complete the mixture was warmed to 0 °C and transferred to a precooled separating funnel. The aqueous layer was removed, and the ether layer was washed with ice-cold saturated brine solution (2 × 50 mL). The ether layer was dried over anhydrous magnesium sulfate at −60 °C and filtered through a column of basic alumina (100 g, packed with ether) precooled to −78 °C. The column was further eluted with cold ether (250 mL, −60 °C). The eluate was collected at −78 °C, and the solvent was evaporated below −30 °C. Dienone **1c** was obtained as a white crystalline solid (3.34 g, 10%): ^1H NMR ($CDCl_3$) δ 7.14 (d, J = 10 Hz, 2 H, H-3 and H-5), 6.46 (d, J = 10 Hz, 2 H, H-2 and H-6), 2.71 (h, J = 7 Hz, 1, H, $CH(CH_3)_2$), 1.35 (d, J = 7 Hz, 6 H, $CH(CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ_C 183.9 (C-1), 141.1 (C-3 and C-5), 131.7 (C-2 and C-6), 91.1 (C-4), 37.5 ($CH(CH_3)_2$), 16.7 ($CH(CH_3)_2$).

Addition of Organolithium Reagents to 4-Nitrocyclohexa-2,5-dienones. Reactions involving organolithium reagents were carried out in a flame-dried, two-necked flask fitted with an argon purging line and a mercury bubbler. The reactions were conducted under an argon atmosphere at positive pressure. The

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Table II. Relative Gradients of ^{13}C Chemical Shifts of 8a and 9i

dienol	CH_2	C-1	CO/CN	C-2,6	C-3,5	C-4	4-CH_3	OCH_3
(*Z*)-**8a**	1.00	1.91	0.90	0.40	0.47	0.27	0.08	0.19
(*E*)-**8a**	1.00	1.90	1.07	0.46	0.39	0.29	0.13	0.26
(*Z*)-**9i**	1.00	2.29	−1.20	0.66	0.52	0.39	0.15	
(*E*)-**9i**	1.00	2.14	−0.92	0.76	0.59	0.47	0.26	

alkyllithium reagents and other dry reagents were transferred either with a dry hypodermic syringe or by using a double-tipped stainless steel needle as a transfer line and pressurizing the reagent container with argon. The organolithium reagents were commercial products or were generated by using either lithium diisopropylamide (LDA), methyllithium, *n*-butyllithium, or complexed *n*-butyllithium. LDA was prepared as follows. Diisopropylamine (0.12 mol, 16.8 mL) was added to dry tetrahydrofuran (or dry ether) (300 mL) in a 500-mL flask, and the solution was stirred and cooled to −78 °C. *n*-Butyllithium (0.12 mol, 1.65 M solution in hexane, 72.7 mL) or methyllithium (0.12 mol, 1.4 M solution in ether, 85.7 mL) was added, and the mixture was stirred at −78 °C for 15 min.

The addition of methyl lithioacetate is illustrative of the standard procedure. Methyl acetate (0.12 mol, 9.5 mL) was added rapidly from a syringe to a stirred solution of lithium diisopropylamide (0.12 mol) in THF at −78 °C. Stirring was continued for additional 30 min at −78 °C. The solution of methyl lithioacetate was added dropwise, through the transfer line, over 1 h, to a stirred solution of the nitro dienone (0.1 mol) in tetrahydrofuran at −78 °C.[23] After the addition was complete, the reaction mixture was stirred at −78 °C for 1 h. The reaction mixture was quenched by adding aqueous ammonium chloride (125 mL, 3 M) and allowed to warm to ambient temperature and the aqueous layer separated. The aqueous layer was extracted with ether (2 × 100 mL), the ether extracts were combined with the organic layer, and the combined solution was washed with a saturated solution of brine and dried. Crude product was obtained upon evaporated of the solvent at ambient temperature and was separated by HPLC at 0 °C. The individual diastereomers were recrystallized from ether–petroleum ether at −20 °C to give colorless crystals.

4-Isopropyl-1-methyl-4-nitrocyclohexa-2,5-dienol (2c) was obtained in quantitative yield by addition of methyllithium to **1c** (4.7 g, 0.026 mol). (*E*)-**2c** was eluted first with 3:2 ether–petroleum ether and had mp 100–101 °C: IR (KBr) 3260 (br, OH), 2980, 1535 and 1345 (NO_2), 1075, and 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.15 (d, *J* = 10 Hz, 2 H, H-2 and H-6), 6.05 (d, *J* = 10 Hz, 2 H, H-3 and H-5), 2.52 (h, *J* = 7 Hz, 1 H, C*H*(CH_3)$_2$), 1.95 (br s, 1 H, OH), 1.29 (s, 3 H, 1-CH_3), 0.86 (d, *J* = 7 Hz, 6 H, CH(C*H*$_3$)$_2$); ^{13}C NMR ($CDCl_3$) δ_C 138.1 (C-2 and C-6), 122.7 (C-3 and C-5), 90.9 (C-4), 65.3 (C-1), 36.6 (*C*H(CH_3)$_2$), 27.6 (1-CH_3), 16.8 (CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{10}H_{15}NO_3$: C, 60.91; H, 7.61; N, 7.10. Found: C, 60.78; H, 7.55; N, 7.10. (*Z*)-**2c** had mp 73–74 °C: IR (KBr) 3320 (br, OH), 2975, 1540 and 1340 (NO_2), 1070, 935, 820, and 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.18 (d, *J* = 10 Hz, 2 H, H-2 and H-6), 6.01 (d, *J* = 10 Hz, 2 H, H-3 and H-5), 2.52 (h, *J* = 7 Hz, 1 H, C*H*(CH_3)$_2$), 1.63 (br s, 1 H, OH), 1.32 (s, 3, 1-CH_3), 0.88 (d, *J* = 7 Hz, 6 H, CH(C*H*$_3$)$_2$); ^{13}C NMR ($CDCl_3$) δ_C 138.7 (C-2 and C-6), 122.9 (C-3 and C-5), 90.8 (C-4), 65.7 (C-1), 36.0 (*C*H(CH_3)$_2$), 27.6 (1-CH_3), 17.0 (CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{10}H_{15}NO_3$: C, 60.91; H, 7.61; N, 7.10. Found: C, 61.79; H, 7.94; N, 6.73.

Methyl (1-hydroxy-4-isopropyl-4-nitrocyclohexa-2,5-dienyl)acetate (8c) was obtained in quantitative yield as a 70:30 mixture of the *Z* and *E* isomers, respectively, by addition of methyl lithioacetate to **1c**. Elution with ether–petroleum ether (9:1 by volume) gave first (*E*)-**8c**, which had mp 57–58 °C: IR (KBr) 3500 (OH), 2980, 1750 (C=O), 1540 and 1350 (NO2), 1240, 1150, 1000, and 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.19 and 6.10 (q, *J* = 11 Hz, 4 H, H-2, H-6 and H-3, H-5), 3.64 (s, 3 H, $COOCH_3$), 3.44 (br s, 1 H, OH), 2.48 (s, 2 H, CH_2COO), 2.47 (h, *J* = 7 Hz, 1 H, C*H*(CH_3)$_2$), 0.81 (d, *J* = 7 Hz, 6 H, CH(C*H*$_3$)$_2$); ^{13}C NMR ($CDCl_3$) δ_C 171.0 (*C*OOCH$_3$), 135.3 (C-2 and C-6), 124.1 (C-3 and C-5), 90.5 (C-4), 65.5 (C-1), 51.9 (COO*C*H$_3$), 44.7 (*C*H$_2$COO), 36.7 (*C*H(CH$_3$)$_2$), 16.9 (CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{12}H_{17}NO_5$: C, 56.47; H, 6.66; N, 5.49. Found: C, 56.35; H, 6.64; N, 5.51. (*Z*)-**8c** had mp 45–46 °C: IR (KBr) 3480 (OH), 2980, 1740 and 1720 (C=O), 1540 and 1335 (NO_2), 1175, 1015, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.23 (d, *J* = 10 Hz, 2 H, H-2 and H-6), 6.07 (d, *J* = 10 Hz, 2 H, H-3 and H-5), 3.67 (s, 3 H, $COOCH_3$), 2.54 (s, 2 H, CH_2COO), 2.53 (h, *J* = 7 Hz, 1 H, C*H*(CH_3)$_2$), 0.88 (d, *J* = 7 Hz, 6 H, CH(C*H*$_3$)$_2$); ^{13}C NMR ($CDCl_3$) δ_C 171.7 (*C*OOCH$_3$), 136.2 (C-2 and C-6), 124.2 (C-3 and C-5), 90.6 (C-4), 65.9 (C-1), 51.9 (COO*C*H$_3$), 44.1 (*C*H$_2$COO), 36.1 (*C*H(CH$_3$)$_2$), 16.9 (CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{12}H_{17}NO_5$: C, 56.47; H, 6.66; N, 5.49. Found: C, 56.25; H, 6.69; N, 5.49.

Attempted Addition of *tert*-Butyllithium to 1a. *tert*-Butyllithium (10 mmol, 5 mL, 2 M solution in pentane) was added dropwise to a stirred solution of **1a** (10 mmol, 1.53 g) in tetrahydrofuran (15 mL) at −78 °C. During the addition a violent reaction occurred, and the color of the solution turned deep blue. After being stirred for 5 min at −78 °C, the reaction mixture was worked up. ^1H NMR of the product indicated the formation of 2-nitro-4-methylphenol (27.5%), *p*-cresol (58%), and 2-methyl-2-nitropropane (1.55 ppm) (14.5%). GC analysis and coinjection of authentic samples confirmed the identifications.

Shift reagent studies were made with dienes **8a** and **9i**. The ^1H NMR spectra were recorded on the 90-MHz instrument using tetramethylsilane as internal reference. The ^{13}C NMR spectra were recorded at 62.9 MHz with tetramethylsilane as internal reference. For ^1H NMR a solution of the diene (0.05 g) in $CDCl_3$ (0.3 mL) was used. A solution of the shift reagent (0.5 g) in $CDCl_3$ (1 mL) was prepared, and the solution was added in increments (0.04 mL) from a syringe. A solution of the diene (0.125 g) in $CDCl_3$ (1.5 mL) was used to record the ^{13}C NMR spectra, and the solid shift reagent was added in 0.05-g increments. After the addition of the reagent the solution was allowed to stand for 5 min before the spectrum was recorded. For each diene the shifts of the various hydrogens (carbons) were plotted against the shift of the methylene hydrogens (carbon). Relative gradients are listed in Tables I and II.

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Registry No. **1a**, 62622-59-7; **1b**, 71462-76-5; **1c**, 71462-77-6; **1d**, 109928-37-2; *trans*-**2a**, 54874-33-8; *cis*-**2a**, 54913-24-5; *trans*-**2b**, 79744-68-6; *cis*-**2b**, 79744-69-7; *trans*-**2c**, 109928-38-3; *cis*-**2c**, 109928-39-4; *trans*-**2d**, 109928-40-7; *cis*-**2d**, 109928-41-8; **3e**, 104678-53-7; **3f**, 878-59-1; *trans*-**4e**, 109928-77-0; *cis*-**4e**, 109928-78-1; *trans*-**4f**, 109928-79-2; *cis*-**4f**, 109928-80-5; *trans*-**5e**, 109928-83-8; *cis*-**5e**, 109928-84-9; *trans*-**5f**, 109928-85-0; *cis*-**5f**, 109928-86-1; **6**, 109928-75-8; **7g**, 109928-76-9; *trans*-**7h**, 109928-81-6; *cis*-**7h**, 109928-82-7; *trans*-**8a**, 109928-44-1; *cis*-**8a**, 109928-45-2; *trans*-**8b**, 109928-46-3; *cis*-**8b**, 109928-47-4; *trans*-**8c**, 109928-42-9; *cis*-**8c**, 109928-43-0; *trans*-**8d**, 109928-48-5; *cis*-**8d**, 109928-49-6; *trans*-**9i**, 109928-50-9; *cis*-**9i**, 109928-51-0; *trans*-**9j**, 109928-52-1; *cis*-**9j**, 109928-53-2; *trans*-**9k**, 109928-54-3; *cis*-**9k**, 109928-55-4; *trans*-**9l**, 109928-56-5; *cis*-**9l**, 109928-57-6; *trans*-**9m**, 109928-58-7; *cis*-**9m**, 109928-59-8; *trans*-**9n**, 109928-60-1; *cis*-**9n**, 109928-61-2; *trans*-**9o**, 109928-62-3; *cis*-**9o**, 109928-63-4; *trans*-**9c**, 109928-64-5; *cis*-**9p**, 109928-65-6; *trans*-**9q**, 109928-66-7; *cis*-**9q**, 109928-67-8; *trans*-**9r**, 109928-68-9; *cis*-**9r**, 109928-69-0; *trans*-**9s**, 109928-70-3; *cis*-**9s**, 109928-71-4; *trans*-**9t**, 109928-72-5; *cis*-**9t**, 109928-73-6; **9u**, 109928-74-7; PMETA, 3030-47-5; TMS, 75-76-3; 4-*i*-PrC_6H_4OH, 99-89-8; 4-MeC_6H_4OAc, 140-39-6; 4-*t*-BuC_6H_4OH, 98-54-4; 4-EtC_6H_4OAc, 3245-23-6; AcOMe, 79-20-9; *t*-BuLi, 594-19-4; MeC(Me)(NO_2)Me, 594-70-7; MeCN, 75-05-8; Me_3SiN=CMeOSiMe_3, 10416-59-8; $MeCONMe_2$, 127-19-5; Me_2S, 75-18-3; MeSOMe, 67-68-5; $MeSO_2Me$, 67-71-0; Me_2PPh, 672-66-2;

(23) Although some of the lithium derivatives were prepared at higher temperatures all of the additions of these reagents to the dienones were carried out at −78 °C.

$PhMe_2PS$, 1707-00-2; Ph_2PMe, 1486-28-8; Ph_2MePS, 13639-74-2; $PhC{\equiv}CH$, 536-74-3; 4-isopropyl-2-nitrophenol, 1576-10-9; 2-nitro-4-methylphenol, 119-33-5; *p*-cresol, 106-44-5; acetone, 67-64-1; thioanisole, 100-68-5; 2-nitro-*p*-cresol, 119-33-5; 1,3-dithiane, 505-23-7; 2,6-dichloro-4-methylphenol, 2432-12-4; 2,6-dibromo-4-methylphenol, 2432-14-6; 5,6,7,8-tetrahydro-2-naphthyl acetate, 89228-44-4; 1-nitro-5,6,7,8-tetrahydro-2-naphthyl acetate, 109928-87-2; 3-nitro-5,6,7,8-tetrahydro-2-naphthyl acetate, 100192-99-2; 3-nitro-5,6,7,8-tetrahydro-2-naphthol, 6240-79-5.

Supplementary Material Available: Additional experimental details including preparative and characterization data for all new compounds prepared (27 pages). Ordering information is given on any current masthead page.

Regio- and Stereoselective Synthesis of Substituted 2-(Phenylthio)-1,3-butadienes

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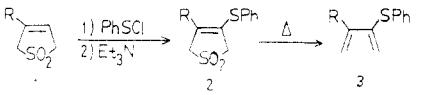
Sulfur-substituted 1,3-butadienes are useful reagents in organic synthesis. We now report two general methods for the regio- and stereoselective synthesis of substituted 2-(phenylthio)-1,3-butadienes **4** and **5**. 3-(Phenylthio)-3-sulfolenes **2** can be specifically alkylated at C5 under basic conditions. Extrusion of sulfur dioxide by lithium aluminum hydride then gives the dienes **4**. On the other hand 2-substituted 3-sulfolenes **11** can be converted to the 3-phenylthio derivatives **9**, which upon heating give the dienes **5**.

Sulfur-substituted dienes have widely been used in the Diels–Alder reaction.[1] The sulfur atom not only increases the reactivity of the diene but also adds control to the regioselectivity of this reaction. Since the sulfur is more directive than an alkyl group, after removing the sulfur group reductively, a reversed Diels–Alder regioselectivity is then achieved. With this strategy Hopkins et al. have recently synthesized 1,5-disubstituted cyclohexenes.[2]

It is now well established that 3-sulfolenes are useful precursors for substituted 1,3-butadienes.[3] Thus, the most convenient method for the synthesis of 2-(phenylthio)-1,3-butadienes **3** is by extrusion of sulfur dioxide from 3-(phenylthio)-3-sulfolenes **2**, which in turn are readily prepared from 3-sulfolenes **1** by chlorosulfenylation–dehydrochlorination.[2,4] So far, however, only two compounds of the structure **3** are known (R = H, Me).



1 2 3

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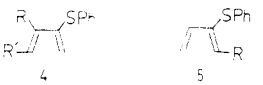
Table I. Preparation of Dienes 4

		6		4	
2, R	R′X		% yield		% yield
2a, H	MeI	**6a**	92	**4a**	99
	EtI	**6b**	75	**4b**	71
	$CH_2{=}CHCH_2Br$	**6c**	65	**4c**	92
	$PhCH_2Br$	**6d**	85	**4d**	99
2b, Me	MeI	**6e**	71	**4e**	99
	EtI	**6f**	67	**4f**	82
	$CH_2{=}CHCH_2Br$	**6g**	64	**4g**	99
	$PhCH_2Br$	**6h**	55	**4h**	99

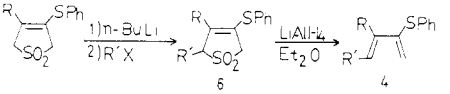
We now report two general methods for the regio- and stereoselective synthesis of substituted 2-(phenylthio)-1,3-butadienes **4** and **5**.



4 5

Results and Discussion

3-(Phenylthio)-3-sulfolenes **2** can be deprotonated[5] by *n*-butyllithium in THF/HMPA at low temperatures (−105 °C for **2a**; −78 °C for **2b**) to give immediately a dark green solution. Addition of an alkyl halide then gives the 5-alkylated product **6**. Treatment of **6** with lithium aluminum hydride then gives the desired dienes **4** in good yield (Table I).



6 4

2a, R = H
2b, R = Me

The structures of **6** are based on spectral and chemical methods. The ^1H NMR spectrum of **2a** has two sets of methylene protons at δ 3.65 and 3.8. The more downfield signals correspond to the C5 hydrogens because these are more split by the vinyl proton. After alkylation the ^1H

(5) For part of our preliminary results, see: Tao, Y.-T.; Liu, C.-L.; Lee, S.-J.; Chou, S.-S. P. *J. Org. Chem.* **1986**, *51*, 4718.

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