

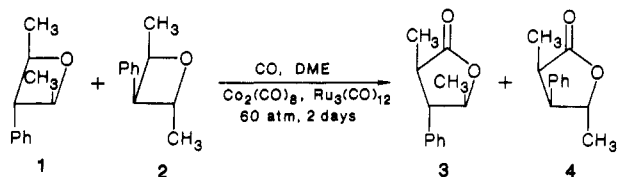
Table I. Metal-Catalyzed Carbonylation of Oxetanes and Thietanes

substrate	Co ₂ (CO) ₈ ^a	Ru ₃ (CO) ₁₂ ^a	temp, °C	product ^b	yield, %
oxetane	yes	no	190	γ-butyrolactone	50
	no	yes			20
2-hexyloxetane ^c	yes	yes	165	4-hexylbutyrolactone	70
	no	yes			40
	yes	no			80
3,3-dimethyloxetane	yes	yes	165	3,3-dimethyl-γ-butyrolactone	89
	yes	yes			39
	yes	yes			63
3-(acetoxymethyl)-3-methyloxetane	yes	yes	240	3-(acetoxymethyl)-3-methyl-γ-butyrolactone	45
	yes	no			29
thietane	yes	no	125	γ-thiobutyrolactone	61
	no	yes			100
	yes	yes			95
2-methylthietane ^d	yes	yes	120	4-methyl-γ-thiobutyrolactone	95
3-methoxythietane	yes	yes	145	3-methoxy-γ-thiobutyrolactone	87

^aThe ratio of Co₂(CO)₈/Ru₃(CO)₁₂ was 1:1 when both were used as catalysts. ^bProducts were identified by comparison of spectral data [IR, NMR (¹H, ¹³C), MS] with literature values (where described) and with authentic materials. Satisfactory C, H analyses were obtained for new compounds. ^cOkuma, K.; Tanaka, Y.; Kaji, S.; Ohta, H. *J. Org. Chem.* 1983, 48, 5133. ^dLancaster, M.; Smith, D. J. H. *Synthesis* 1982, 582.

substrate:catalyst] in 1,2-dimethoxyethane (DME), for 2 days at 190 °C and 60 atm, affords γ-butyrolactone in 50% yield. The yield is only 20% when triruthenium dodecacarbonyl is employed as the catalyst. However, use of equimolar amounts of both metal carbonyls as catalysts [i.e. 10–20:1:1 molar ratios of substrate:Co₂(CO)₈:Ru₃(CO)₁₂] results in formation of the lactone in 70% yield. Inferior results are obtained by using other ratios of Co₂(CO)₈/Ru₃(CO)₁₂ [i.e. 1:2 (20% yield), 2:1 (30%)].

When thietanes are compared with oxetanes, the contrast in catalytic activity of cobalt and ruthenium carbonyls is intriguing; ruthenium carbonyl is a superior catalyst to cobalt for thietane while the reverse is true for oxetane. However, together Ru₃(CO)₁₂ and Co₂(CO)₈ are an excellent catalytic system for thietane and substituted analogues (Table I). Thietanes are also more reactive than oxetanes with lower temperatures required for the sulfur compounds. The ring expansion process is regiospecific for both classes of heterocycles [i.e., 2-hexyloxetane, 2-methylthietane] with carbonyl insertion occurring into the least substituted of the two carbon-heteroatom bonds. Furthermore, the process proceeds with retention of substituent group stereochemistry. A 3.31/1.00 mixture (NMR analysis) of 1/2, obtained from *trans*-1-phenylpropene and acetaldehyde,⁷ affords 3/4 in a 3.28/1.00 ratio (NMR) on Co₂(CO)₈/Ru₃(CO)₁₂-catalyzed carbonylation.



The following general procedure was used: a mixture of the oxetane or thietane [2–4 mmol], Ru₃(CO)₁₂ [0.2

mmol], and Co₂(CO)₈ [0.2 mmol] in DME (10 mL) was heated for 2 days under 60 atm of carbon monoxide. The solution was cooled and filtered, and concentration of the filtrate gave the crude product. Pure lactone or thiolactone was obtained by silica gel thin layer chromatography using 2–4:1 hexane/methylene chloride as the developing solvent.

In conclusion, thiolactones and lactones can be synthesized by a regiospecific carbonylation of thietanes and oxetanes, respectively, using Co₂(CO)₈ and/or Ru₃(CO)₁₂ as the metal catalysts. In addition to being a simple route to these important classes of compounds, this process provides another illustration of the beneficial effect of using two metal complexes as homogeneous catalysts in a reaction.^{8,9}

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Registry No. 1, 73428-27-0; 2, 73466-20-3; 3, 117471-41-7; 4, 117471-42-8; Co₂(CO)₈, 15226-74-1; Ru₃(CO)₁₂, 15243-33-1; oxetane, 503-30-0; γ-butyrolactone, 96-48-0; 2-hexyloxetane, 74581-25-2; 4-hexylbutyrolactone, 706-14-9; 3,3-dimethyloxetane, 6921-35-3; 3,3-dimethyl-γ-butyrolactone, 3709-08-8; 3-(acetoxymethyl)-3-methyloxetane, 117471-37-1; 3-(acetoxymethyl)-3-methyl-γ-butyrolactone, 117471-39-3; thietane, 287-27-4; γ-thiobutyrolactone, 1003-10-7; 2-methylthietane, 17837-41-1; 4-methyl-γ-thiobutyrolactone, 117471-40-6; 3-methoxythietane, 117471-38-2; 3-methoxy-γ-thiobutyrolactone, 96862-65-6.

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Reduction of (*E,E*)-(η⁶:η⁶-1,4-Diphenyl-1,3-butadiene)bis(tricarbonylchromium), Followed by Reaction with Electrophiles. A Regioselective Method for the Preparation of Substituted 1,4-Diphenylbutenes

Summary: Reduction of (*E,E*)-(η⁶:η⁶-1,4-diphenyl-1,3-butadiene)bis(tricarbonylchromium) with lithium na-

phthalenide followed by reaction with alkyl halides and acyl chlorides yields, after oxidative cleavage of the tri-

carbonylchromium groups, dialkylated and diacylated 1,4-diphenylbutenes.

Sir: Recently we reported that the bis(tricarbonylchromium complexes) of arene compounds with two conjugated phenyl rings reduced electrochemically^{1a,d} or chemically with one electron per tricarbonylchromium group, in contrast to those complexes of naphthalene or benzene, where the reduction was two electrons per Cr(CO)₃ group.^{1b,c} Furthermore, the dianion of the biphenyl complex reacted smoothly with alkyl halides to give an alkylated complex, which after decomplexation gave good yields of alkylated biphenyls or cyclohexadienes.^{1e,f,g}

We now report that dianions generated from similarly conjugated bis(arene)tricarbonylchromium systems can be readily prepared and that they react with a variety of electrophiles to give dialkylated products. In this paper, we wish to report the products of the reduction of (*E*)-(η^6 : η^6 -1,4-diphenyl-1,3-butadiene)bis(tricarbonylchromium) (1) with lithium naphthalenide followed by reactions with alkyl and acyl halides (see Scheme I).

The preparation of 1 was carried out by standard methods to give a 64% isolated yield of pure 1.² In a typical reaction, lithium naphthalenide in THF (2.7 equiv) was transferred under argon at -78 °C to a solution of 1 in THF/HMPA (ratio 6:1). An instantaneous color change to a dark brown solution was observed. After the mixture was stirred for 30 min, the electrophile was added.³ While acyl chlorides caused an instantaneous color change from dark brown to pale brown, the color change observed upon the addition of alkyl halides took place over the course of a few minutes. The color of the reaction mixture eventually faded completely to a pale orange or yellow above 0 °C. Decomplexation of the chromium tricarbonyl moieties was then accomplished by the addition of iodine at -78 °C. Standard methods of workup, separation, and purification⁴ then resulted in moderate to good yields of the dialkyl- and diacyl-substituted diphenylbutenes (see Table I).

The two sharp IR bands observed at 1962 and 1893 cm⁻¹ for 1 disappeared upon formation of the dianion,⁵ while new bands appeared at 1904, 1814, and 1795 cm⁻¹. The observed new frequencies are totally consistent with the proposed structure 2 as well as several model systems.^{1a,d} The increase in the number of IR-active bands from two to three is also consistent with the proposed reductive rearrangement of 1 in going to 2 with the Cr(CO)₃ bonding going from η^6 to η^5 .^{6,7}

(1) (a) Milligan, S. N.; Rieke, R. D. *Organometallics* **1983**, *2*, 171. (b) Henry, W. P.; Rieke, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6314. (c) Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* **1987**, *26*, 420. (d) Rieke, R. D.; Milligan, S. N.; Schulte, L. D. *Organometallics* **1987**, *6*, 699. (e) Schulte, L. D.; Rieke, R. D. *J. Org. Chem.* **1987**, *52*, 4827. (f) Rieke, R. D.; Schulte, L. D., unpublished results. (g) Rieke, R. D.; Daruwala, K. P., unpublished results.

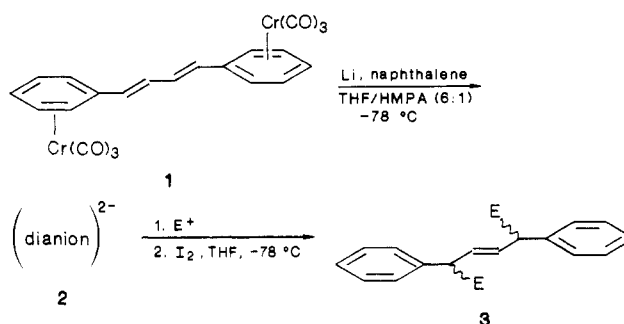
(2) (a) Feldkimmel, M.; Cais, M. *Tetrahedron Lett.* **1961**, 444. (b) Manuel, T. A.; Stafford, S. L.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3597.

(3) The addition of alkyl halides was made at room temperature while the acyl chlorides were added at -78 °C.

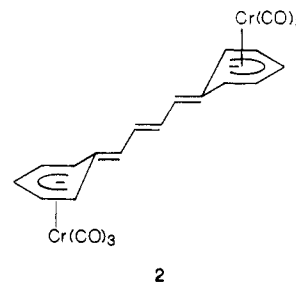
(4) The reaction mixture was taken up in diethyl ether and washed with saturated Na₂S₂O₃ solution, water, and saturated NaCl solution, respectively, and dried over MgSO₄. Filtration, followed by rotary evaporation of the solvent ether, gave the crude product. The crude product mixture obtained from the reactions with alkyl halides was purified by means of column chromatography while preparative thick-layer chromatography was used for the separation and purification of reactions with acyl chlorides.

(5) Unlike the case of the biphenyl system where the dianion 1 was stable and easily precipitated out as a fine brown solid, the dianion 2 was soluble at room temperature and did not precipitate out of solution. Even at low temperatures of -78 °C, no solid precipitate was conceived.

Scheme I



Reaction of 2 with a variety of electrophiles was found to be highly regioselective with attack occurring exclusively at the 1,4-positions. This is consistent with studies reported for systems containing a single benzylic anion that was stabilized by a Cr(CO)₃ group.⁸ As 2 can be reacted



stepwise with two different electrophiles (entries 10 and 11), it is acting, in many ways, as a bisbenzylic anion species. The initial attack of 2 at the 1,4-positions and the second attack on the complexed 1-phenylallylic anion are consistent with HOMO-LUMO considerations^{9,10} as well as the conformational preferences of the Cr(CO)₃ group.¹¹

It should also be noted that there are two prochiral centers present in the 1,4-benzylic positions of the neutral

(6) For a theoretical discussion of η^6 -cyclohexadienyl complexes, see: Hoffmann, R.; Hoffmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598.

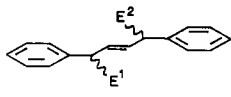
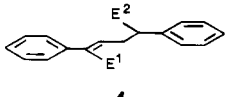
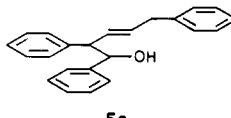
(7) For some recent (η^5 -cyclohexadienyl)metal tricarbonyl complexes and their spectra, see: (a) Jones, D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2479. (b) Fischer, E. O.; Schmidt, M. W. *Chem. Ber.* **1967**, *100*, 3782. (c) Churchill, M. F.; Scholer, F. R. *Inorg. Chem.* **1969**, *8*, 1950. (d) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1969**, 2024. (e) Walker, P. J. C.; Mawby, R. *Inorg. Chim. Acta* **1973**, *7*, 621. (f) Connelly, N. G.; Kelly, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2334. (g) Semmelhack, M. F.; Hall, H. T.; Farina, R.; Yoshifujii, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535. (h) Pauson, P. L. *J. Organomet. Chem.* **1980**, *200*, 207. (i) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1980**, *102*, 3490. (j) Sievert, A. C.; Muetterties, E. Z. *Inorg. Chem.* **1981**, *20*, 2276. (k) Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1982**, *1*, 1053. (l) Brookhart, M.; Lukacs, A. *Organometallics* **1983**, *2*, 649. (m) Werner, R.; Werner, H.; Burschka, C. *Chem. Ber.* **1984**, *117*, 142, 152, and 161.

(8) (a) Knox, G. R.; Leppard, D. G.; Pauson, P. L.; Watts, W. E. *J. Organomet. Chem.* **1972**, *34*, 347. (b) Jaouen, G.; Meyer, A. *Tetrahedron Lett.* **1976**, 3547. (c) Jaouen, G.; Top, S.; McGlinchey, M. J. *J. Organomet. Chem.* **1980**, *195*, C5. (d) Top, S.; Jaouen, G.; McGlinchey, M. J. *J. Chem. Commun.* **1980**, 643. (e) Meyer, A.; Hofer, O. *J. Am. Chem. Soc.* **1980**, *102*, 4410. (f) Semmelhack, M. F.; Seyfert, W.; Keller, L. *J. Am. Chem. Soc.* **1980**, *102*, 6586. (g) Brocard, J.; Lebibi, J.; Couturier, D. *Chem. Commun.* **1981**, 1264. (h) Lebibi, J.; Brocard, J.; Couturier, D. *Bull. Soc. Chim. Fr.* **1982**, II, 357. (i) Davies, S. G.; Holman, N. J.; Loughton, C. A.; Mobbs, B. E. *Chem. Commun.* **1983**, 1316. (j) Caro, B.; LeBihan, J. Y.; Guillot, J. P.; Top, S.; Jaouen, G. *Chem. Commun.* **1984**, 602. (k) Halet, J. F.; Saillard, J. Y.; Caro, B.; LeBihan, J. Y.; Top, S.; Jaouen, G. *J. Organomet. Chem.* **1984**, *267*, C37. (l) Jaouen, G.; Top, S.; Laconi, A.; Couturier, D.; Brocard, J. *J. Am. Chem. Soc.* **1984**, *106*, 2207.

(9) Values of coefficients are given by: Coulson, A.; Streitwieser, A. *Dictionary of π Electron Calculations*; W. H. Freeman and Co.: San Francisco, 1965; p 30.

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Table I. Reduction of (*E,E*)-(η⁶,η⁶-1,4-Diphenyl-1,3-butadiene)bis(tricarbonylchromium) with Lithium Naphthalenide, Followed by Reaction with Electrophiles and Oxidation with Iodine

entry	reagent ^a (equiv)	product	% yield ^b
		 3	
1	H ₃ CCH ₂ CH ₂ CH ₂ Br (4.0)	3a E ¹ = E ² = (CH ₂) ₃ CH ₃	74 ^c
2	H ₃ CCH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ Br (4.0)	3b E ¹ = E ² = (CH ₂) ₆ CH ₃	40 (22)
3	(H ₃ C) ₂ CHBr (5.5)	3c E ¹ = E ² = CH(CH ₃) ₂	67
4	NCCH ₂ CH ₂ Br (3.0)	3d E ¹ = E ² = (CH ₂) ₂ CN	49 (26) ^d
5	<i>c</i> -C ₃ H ₅ CH ₂ Br (4.0)	3e E ¹ = E ² = CH ₂ - <i>c</i> -C ₃ H ₅	89
6	H ₂ C=CHCH ₂ CH ₂ CH ₂ CH ₂ Br (4.0)	3f E ¹ = E ² = (CH ₂) ₄ CH=CH ₂	85
7	H ₂ C=CHCH ₂ Br (3.7)	3g E ¹ = E ² = CH ₂ CH=CH ₂	85
8	HC≡CHCH ₂ Br (4.0)	3h E ¹ = E ² = CH ₂ CH≡CH	78
9	(<i>E</i>)-H ₃ CCH=CHCH ₂ Cl (3.0)	3i E ¹ = E ² = CH ₂ CH=CHCH ₃ -(<i>E</i>)	76
10	H ₃ CCH ₂ CH ₂ CH ₂ I (1.2)/ H ₂ C=CHCH ₂ Br (1.2)	3j E ¹ = (CH ₂) ₃ CH ₃ E ² = CH ₂ CH=CH ₂	40 ^e
11	H ₃ CCH ₂ CH ₂ CH ₂ CH ₂ CH ₂ I (1.2)/ NCCH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ Br (1.2)	3k E ¹ = (CH ₂) ₆ CH ₃ E ² = (CH ₂) ₆ CN	44
12	(H ₃ C) ₃ CCOCl (2.2)	3l E ¹ = E ² = (CH ₂) ₆ CN 3m E ¹ = E ² = CO(CH ₃) ₃	10 67
		 4	
13	PhCOCl (2.2)	4n E ¹ = E ² = COC ₆ H ₅	75
14	H ₃ CCOCl (2.7)	4o E ¹ = E ² = COCH ₃	40
15	H ₃ CCH ₂ CH ₂ COCl (2.7)	4p E ¹ = E ² = CO(CH ₂) ₂ CH ₃	22
16	PhCHO (4.0) ^f		76
		 5a	

^aThe addition of alkyl halides was made at room temperature, while acyl chlorides were added at -78 °C. ^bAll yields given are isolated. The figure in parentheses indicates the percentage isolated yield of the monoalkylated product. ^cAn isolated yield of 66% was obtained when the reaction was carried out in the absence of HMPA. ^dAn isolated yield of 37% was obtained when the reaction was carried out in the absence of HMPA. ^eThe reaction also gave 24% of the dibutyl substituted product (**3a**), along with 10% of the diallyl substituted compound (**3c**). ^fThe reaction was worked up with excess trifluoroacetic acid.

bis complex. Reactions at these sites then resulted in the formation of two diastereomers, the *d,l* and meso diastereomers. Proton and ¹³C NMR spectroscopy clearly revealed the presence of two diastereomers formed in nearly equal amounts for compounds **3a–m**. In the case of acyl chlorides, however, the major product obtained was the one with the 2,3-central double bond having been isomerized to the 1,2-position (compounds **4n–p**). This could be easily attributed to the inherent high acidity of the benzylic protons also attached to carbonyl groups. NMR spectroscopy indicated the presence of a single isomer in these cases.¹²

The assignment of the *trans* orientation of the 2,3-central double bond in the alkylated and one acylated product **3m** (entry 12) is based upon the formation of *trans*-1,4-diphenyl-2-butene, which was obtained exclusively when

the dianion **2** was quenched with trifluoroacetic acid.^{13,14} The fact that no *cis*-1,4-diphenyl-2-butene was produced clearly indicates that the formation of the dianion has been stereospecific. IR data obtained for all products further supports the assigned *trans* configuration.

Reaction of **2** with (1-bromomethyl)cyclopropane (entry 5) yielded a product with no ring opening.¹⁵ Also **2** reacted with 6-bromo-1-hexene (entry 6) to give a product with no cyclopentylmethyl-substituted diphenylbutene.¹⁶ While

(12) All new compounds obtained in diastereomeric form after purification by chromatography were fully characterized by 360-MHz ¹H NMR, 50-MHz ¹³C NMR, and IR spectra and gave satisfactory high-resolution mass spectra and combustion analyses. Special spectral experiments like DEPT and COSY were carried out for some compounds where the structural assignment was ambiguous.

(13) *trans*-1,4-diphenyl-2-butene: mp 40.5–42.0 °C; ¹H NMR (CDCl₃) δ 7.1–7.3 (m, 10 H), 5.66 (m, 2 H), 3.35 (d, 4 H); ¹³C NMR (CDCl₃) δ 140.7, 130.5, 128.5, 128.4, 126.0, 39.0.

(14) 1,4-Diphenyl-2-butene; *trans* isomer: lit. mp 43–45 °C. (a) Blum, J.; Becker, Y. *J. Chem. Soc., Perkins Trans. 2* 1972, 982. (b) Crotti, P.; Ferretti, M.; Macchia, F.; Stoppioni, A. *J. Org. Chem.* 1984, 49, 4706. *Cis* isomer: lit. mp 176–178 °C (17 mm). Lambert, J. B.; Mark, H. W.; Magyar, E. S. *J. Am. Chem. Soc.* 1977, 99, 3059.

(15) For cyclopropylcarbonyl ring opening reactions, see: (a) Warner, C. R.; Struck, R. J.; Kruvillia, H. G. *J. Org. Chem.* 1966, 31, 3381. (b) Halgren, T. A.; Howden, M. E. H.; Medof, M. E.; Roberts, J. D. *J. Am. Chem. Soc.* 1967, 89, 3051. (c) Montgomery, L. K.; Mott, J. W. *Ibid.* 1967, 89, 3050. (d) Cristol, S. J.; Barbour, R. V. *Ibid.* 1966, 88, 4262; 1968, 90, 2382. (e) Chambers, V. M. A.; Jackson, W. R.; Young, G. W. *Chem. Commun.* 1970, 1275.

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these two experiments do not completely rule out the possibility of an SET mechanism for either the initial step or the second step,^{17,18} they do suggest that both steps may be best viewed as direct substitution by S_N2 processes. Entries 8 and 9 further indicate that S_N2 processes are favored over S_N2' for both the initial as well as the second attack.

In summary, this work provides a facile route for the regioselective introduction of substituents in the 1,4-positions of 1,4-diphenyl-1,3-butadiene. While the addition

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(17) The SET mechanism is favored by the presence of small amounts of transition metals. This was evident by the dimerization of ketyls to give pinacols, during the addition of Grignard reagents to ketones. Ashby, E. C.; Buhler, J. D.; Lopp, I. G.; Wieseman, T. L.; Bowers, J. S.; Laemmle, J. T. *J. Am. Chem. Soc.* **1976**, *98*, 6561.

(18) About 10% of benzil was obtained in the reaction with benzoyl chloride (Table I, entry 13).

Ortho-Metalated Aryl *tert*-Butyl Sulfones. Comparison with Other Directing Groups and New Methodology for Polysubstituted Aromatics

Summary: The general utility of ortho-lithiated aryl *tert*-butyl sulfones for the synthesis of a variety of 2- and 2,6-carbon- and -heteroatom-substituted products in good to excellent yields is described (Schemes I, VI, VII).

Sir: During the recent emergence of the aromatic directed metalation strategy in organic synthesis,¹ a number of sulfur-based directed metalation groups have been studied: SO₂NR₂,^{2a} SO₂NHR,^{2b} SO₂R,^{2c} SO₂Li,^{2d} SR,^{2e} SLi.^{2f} The *tert*-butyl sulfone group, despite its early discovery³ and adequate recognition,^{1a} has not received methodological attention.^{4,5} We have pursued the early observations of

(1) (a) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1. (b) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 305. (c) Snieckus, V. *Lectures in Heterocyclic Chemistry*; R. N. Castle, Ed., Heterocorp. *J. Heterocycl. Chem.* **1984**, *95*. (d) Snieckus, V. *Bull. Soc. Chim. Fr.* **1988**, 67.

(2) See, inter alia (a) Watanabe, H.; Schwarz, R. A.; Hauser, C. R.; Lewis, J.; Slocum, D. W. *Can. J. Chem.* **1969**, *47*, 1543. (b) Lombardino, J. G. *J. Org. Chem.* **1971**, *36*, 1843. (c) Bonfiglio, J. N. *Ibid.* **1986**, *51*, 2833. (d) Figuly, G. D.; Martin, J. C. *Ibid.* **1980**, *45*, 3728. (e) Narasimhan, N. S.; Chandrachud, P. S. *Synthesis* **1979**, 589. Babin, D.; Fourneron, J. D.; Harwood, L. M.; Julia, M. *Tetrahedron* **1981**, *37*, 325. Horner, L.; Lawson, A. J.; Simons, G. *Phosphorus Sulfur* **1983**, *12*, 779. (f) Smith, K.; Lindsay, C. M.; Pritchard, G. *J. Am. Chem. Soc.*, in press. Figuly, G. D.; Loop, C. K.; Martin, J. C. *Ibid.*, in press. Recently, the X-ray structure of *o*-lithiophenyl *tert*-butyl thioether has been determined: Bauer, W.; Klusener, P. A. A.; Harder, S.; Kanters, J. A.; Duisenberg, A. J. M.; Brandsma, L.; Schleyer, P. v. R. *Organometallics* **1988**, *7*, 552.

(3) Truce, W. E.; Amos, M. F. *J. Am. Chem. Soc.* **1951**, *73*, 3013. Gilman, H.; Esmay, D. L. *Ibid.* **1953**, *75*, 278. For recent studies, see: Krizan, T. D.; Martin, J. C. *Ibid.* **1983**, *105*, 6155. Vollhardt, J.; Gais, H. J.; Lukas, L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 610. Hartman, G. D.; Halczenko, W. *Tetrahedron Lett.* **1987**, *28*, 3241. McCombie, S. W.; Shankar, B. B.; Ganguly, A. K. *Ibid.* **1987**, *28*, 4123.

(4) *o,o*-Dilithioallyl phenyl sulfone has been generated and used in synthesis with ingenuity (Gais, H.-J.; Ball, W. A.; Bund, J. *Tetrahedron Lett.* **1988**, 781 and references therein) while *o,o*-dilithioisopropyl phenyl sulfone was extensively studied some time ago by Meyers and Parady (Parady, T. E. M.S. Thesis, Southern Illinois University, 1977). We are grateful to Professor Meyers for informing us of these results. For solid state structures of *o*-lithiated and dilithiated sulfones, see: Hollstein, W.; Harms, K.; Marsch, M.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1287. Gais, H.-J.; Vollhardt, J.; Hellmann, G.; Paulus, H.; Lindner, H. J. *Tetrahedron Lett.* **1988**, *29*, 1259.

of alkyl halides gives a mixture of two diastereomers, the reaction with acyl chlorides results predominantly in the formation of one isomer after isomerization of the double bond. Mixed alkylation, i.e. introduction of one substituent at one benzylic position followed by trapping the other anionic benzylic position with a different alkyl halide, has also been successful (entries 10 and 11). Minor amounts of disubstitution with the same electrophile, however, was also observed in both cases. The addition of a carbonyl compound (entry 16) gave only monosubstitution (compound 5g). Further work exploring the mechanistic aspects of these reactions as well as development of other synthetic applications are continuing in our laboratories.

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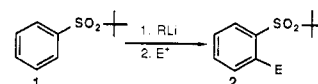
Department of Chemistry

University of Nebraska—Lincoln

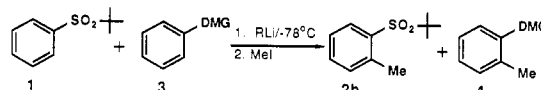
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Scheme I

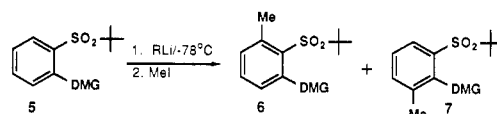


Scheme II



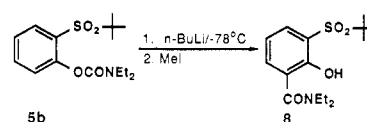
DMG (directed metalation group) = a, CON(i-Pr)₂; b, OCON(i-Pr)₂; c, OMOM; d, NHCO₂t-Bu

Scheme III



DMG = a, CONEt₂ (=2f); b, OCONEt₂; c, OMOM; d, NHCO₂t-Bu

Scheme IV



Stoyanovich and Fedorov⁶ and report that the *tert*-butyl sulfone group (a) is an excellent directed ortho metalation

(5) This state may be contrasted with the continuing high rate of synthetic activity in which the ArSO₂ is a carbanion stabilizing and disposable group, see, inter alia, e.g.: Trost, B. M.; Ghandiri, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 7260. Najera, C.; Yus, M. *Tetrahedron Lett.* **1987**, *28*, 6709. Fuchs, P. L.; Hutchinson, D. K. *J. Am. Chem. Soc.* **1987**, *109*, 4755. Denmark, S. E.; Harmata, M. A.; White, K. S. *J. Org. Chem.* **1987**, *52*, 4031. Thomsen, M. W.; Handwerker, B. M.; Katz, S. A.; Belser, R. B. *Ibid.* **1988**, *53*, 906. For ArSO use, see: Hua, D. H.; Venkataraman, S.; Ostrander, R. A.; Sinai, G.-Z.; McCann, P. J.; Coulter, M. J.; Xu, M. R. *Ibid.* **1988**, *53*, 507. Theobald, P. G.; Okamura, W. H. *Tetrahedron Lett.* **1987**, *28*, 6565. Marino, J. P.; Laborde, E.; Paley, R. S. *J. Am. Chem. Soc.* **1988**, *110*, 966. Bäckvall, J.-E.; Najera, C.; Yus, M. *Tetrahedron Lett.* **1988**, *29*, 1445.