8 Hz, H_{25}), 3.97–3.87 and 3.80–3.70 (2 H, m, CH_2OH), 3.86 (1 H, d, J = 11 Hz, H_{12a}), 3.54 (1 H, d, J = 11 Hz, H_{12b}), 3.20 (1 H, br dd, J = 10, 10 Hz, H_{20}), 3.07 (3 H, s, NCH_3), 3.08–2.95 and 2.21–2.10 (2 × 1 H, m, CH_2CH_2OH), 2.80 and 2.02 (2 × 1 H, 2 d, J = 15 Hz, H_{10}), 2.39 (1 H, dd, J = 3, 8 Hz, OH), 2.12 and 1.84 (2 × 1 H, dd, J = 10, 12 Hz, H_{19}), 1.57 (3 H, s, $C_{14}CH_3$), 1.53 and 1.51 (2 × 3 H, 2 s, H_{27} and H_{28}), 1.13 and 0.89 (2 × 3 H, 2 s, H_{22} and H_{23}). FAB-MS: m/z 616, 618 (M + H).

Single-Crystal X-ray Diffraction Analysis of 16. Crystals grown from acetonitrile–methanol–methylene chloride were obtained in the form of prisms ($C_{29}H_{32}N_3O_7Br{\cdot}CH_3CN$; M_r = 655.51; monoclinic; space group $P2_1$; a = 13.187 (1), b = 7.743 (1), c = 14.871 (3) Å; β = 97.33 (1); V = 1506 Å^3; Z = 2; D_{calcd} = 1.341 g/cm; $F(000)$ = 680; μ = 23.08 cm^{-1}; R= 0.036; R_w = 0.052; S = 2.50). The crystal was enclosed in a capillary with some saturated solvent. A CAD4 diffractometer was used for data collection. The unit cell constants and their standard deviations were determined by least-squares analysis of diffractometer setting angles of 23 reflections with $30° \leq 2\theta < 40°$. The intensities of 2203 reflections with $2° < 2\theta < 120°$ were measured with 1.5° ω scans; of these, 2121 reflections had $I > 3\sigma(I)$. The intensities of three standard reflections were monitored during the data collection, and no significant deterioration of the crystal was observed. The data were corrected for Lorentz, polarization factors and for absorption. Scattering factors for neutral atoms with f' and f'' contributions for anomalous dispersion were used. The structure was solved by determining the Br position with a vector density map; all other non-hydrogen atoms were found subsequently by a series of difference Fourier analyses. One molecule of acetonitrile was found during these calculations. The structure was refined by a full-matrix least-squares procedure[12] using F^2 magnitudes with $w = [4F_o^2/\sigma(F_o^2)^2]$. When the refinement for the scale factor, the positional coordinates, and the anisotropic temperature factor of the 43 non-hydrogen atoms had converged, the absolute stereochemistry was determined. For one enantiomer R = 0.053 57, R_w = 0.079 63, and S = 3.644 while for the other enantiomer R = 0.054 69, R_w = 0.081 61, and S = 3.891, a difference which is statistically significant.[13] Centrosymmetrically related pairs of 16 enantiomer sensitive reflections were remeasured, and all data confirmed the assignment of the absolute configuration. Figure 1 shows a stereodrawing of the correct enantiomer with the configurations at the chiral carbon atoms established as 3R,11S,13R,14R,20S. The refinement was completed with hydrogen atoms assigned calculated positional coordinates and one overall isotropic temperature factor; these parameters were not adjusted during the final calculations. There were no significant deviations in the molecular dimensions from their expected values.

Acknowledgment. We are grateful to Dr. Mike Goetz and John Ondeyka of MSDRL for a generous supply of paraherquamide. We thank Dr. L. Colwell for mass spectral measurements and Jane Wu for elemental analyses. We also thank Professor Barry Trost for many helpful discussions.

Registry No. 1, 77392-58-6; **3**, 120312-77-8; **4**, 120331-97-7; **5**, 120312-78-9; **6**, 120312-79-0; **9**, 120312-80-3; **10**, 120312-81-4; **12**, 120312-82-5; **13**, 120312-83-6; **14a**, 120312-84-7; **14b**, 120312-85-8; **14c**, 120312-86-9; **15**, 120331-98-8; **16**, 120312-88-1; $Br(CH_2)_3Cl$, 109-70-6; 12-oxoparaherquamide, 120312-87-0.

Supplementary Material Available: Tables of atomic positional parameters, anisotropic temperature factors, interatomic distances, and angles for **16**, ^1H NMR spectra (300 MHz) of all title compounds, and ^1H–^1H COSY NMR spectra of 1 and 4. (21 pages). Ordering information is given on any current masthead page.

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[12] All calculations were performed with the Enraf-Nonius Structure Determination Package, Revision 3-B, April 1980, on a DEC 11/60 computer.

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Stereoselective Reactions of Lithium and Zinc *tert*-Butyl Phenylmethyl Sulfoxide with Carbonyl Compounds and Imines[1]

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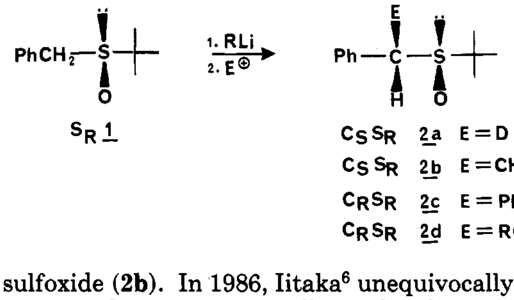
Racemic lithium *tert*-butyl phenylmethyl sulfoxide 1A when quenched with benzophenone gives $C_{R*}S_{R*}$-2-(*tert*-butylsulfinyl)-1,1,2-triphenylethanol as determined by single-crystal X-ray analysis. The diastereoselection in the reaction of 1A with various aldehydes and imines as a function of aldehyde and imine structure and metal cation (Li^+ or Zn^{2+}) is reported. Both substrates show a preference for anti diastereoselection. Transition-state structures are proposed to account for this diastereoselection.

In 1971, Durst[5] reported that the lithium carbanion of S_R-*tert*-butyl phenylmethyl sulfoxide (1) underwent highly diastereoselective reactions with deuterium oxide (D_2O), methyl iodide, and acetone. Methylation of the lithium carbanion of S_R-1 gave C_SS_R-*tert*-butyl 1-phenylethyl sulfoxide (**2b**). In 1986, Iitaka[6] unequivocally showed by neutron diffraction crystallography that quenching the

Scheme I



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[1] Chiral Sulfur Compounds. 7. Part 6: Pyne, S. G.; Griffith, R.; Edwards, M. *Tetrahedron Lett.* **1988**, *29*, 2089.

[2] University of Wollongong.

[3] Philipps-Universität.

[4] This work was performed by S.G.P. while on sabbatical leave at Marburg in 1988.

[5] Durst, T.; Viau, R.; McClory, M. R. *J. Am. Chem. Soc.* **1971**, *93*, 3077.

0022-3263/89/1954-2663$01.50/0

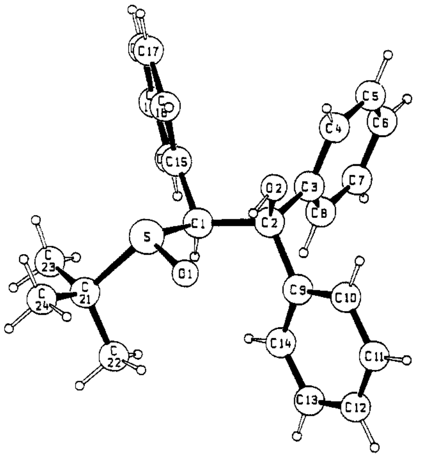
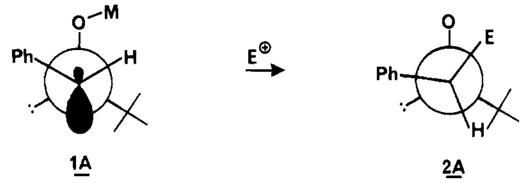


Figure 1. ORTEP drawing of the X-ray structure of compound **2c**.

Scheme II



lithium carbanion of racemic **1** with D_2O gave monodeuterated $C_{S*}S_{R*}$-*tert*-butyl phenylmethyl sulfoxide (**2a**). This result was recently confirmed by Ohno.[7] Thus both methylation and deuteration of lithio **1** occur with the same stereoselectivity (Scheme I).

Several workers have suggested the anti conformation **1A** (Scheme II) for the lithium carbanion of **1**.[7,8] Conformation **1A** would be expected on stereoelectronic grounds because of a stabilizing interaction ($n_C \rightarrow \sigma^*_{S-O}$) between the nonbonding orbital on the α-carbon and the S–O antibonding sigma orbital,[9] and furthermore, nonbonded steric interactions are minimized. An analogous conformation to **1A** has been found from single-crystal X-ray analyses of α-(phenylsulfinyl)-α-methylbenzyllithium–TMEDA.[10] Noteworthy was the finding that the α-sulfinyl carbon was not planar and that the lithium counterion was directly bonded to the sulfoxide oxygen and not the α-carbon.

The stereochemical course of deuteration of Li^+-**1A** can be readily accounted for by electrophilic assistance by lithium cation which can coordinate D_2O prior to deuteration, as first suggested by Biellmann.[11] In contrast, the stereochemical outcome of the reactions of **1A** with carbonyl compounds and imines has not been unequivocally established.

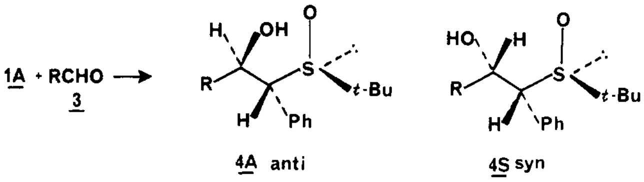
Reaction of 1A with Benzophenone. When a tetrahydrofuran (THF) solution of racemic Li^+–**1A** at −78 °C was quenched with benzophenone, essentially diastereomerically pure (diastereoselectivity >97:<3 from ^1H and ^{13}C NMR analysis) $C_{R*}S_{R*}$-2-(*tert*-butylsulfinyl)-1,1,2-triphenylethanol (**2c**) was obtained. The relative configuration of **2c** was established by single-crystal X-ray analysis (Figure 1). Hence reactions of Li^+–**1A** with D_2O, methyl iodide, and benzophenone all occur with the same stereoselectivity.

Table I. Reactions of Lithium and Zinc 1A with Aldehydes RCHO

entry	R of RCHO (3)	counterion	yield, %	diastereo-selection **4A**:**4S**
1	(*E*)-PhCH=CH (**3a**)	Li^+	100	49:51
2	(*E*)-PhCH=CH (**3a**)	Zn^{2+}	82	57:43
3	CH_3CH_2 (**3b**)	Li^+	85	65:35
4	CH_3CH_2 (**3b**)	Zn^{2+}	85	80:20
5	Ph (**3c**)	Li^+	81	63:37
6	Ph (**3c**)	Zn^{2+}	98	84:16
7	*i*-Pr (**3d**)	Li^+	90	78:22
8	*i*-Pr (**3d**)	Zn^{2+}	72	91:9
9	*t*-Bu (**3e**)	Li^+	87	57:43
10	*t*-Bu (**3e**)	Zn^{2+}	85	61:39

Reaction of 1A with Aldehydes. In general, the reactions of lithium α-sulfinyl carbanions with aldehydes are highly diastereoselective with respect to the α-sulfinyl carbon[12] but poorly diastereofacially selective with respect to attack on the carbonyl component. However, α-sulfinyl carbanions having an α or β polar substituent, which may also be involved in chelation of the metal counterion, are an exception.[12d–g]

Effect of Metal Counterion on Diastereoselection. By analogy with the advances made in enhancing the diasterofacial selectivity in the aldol reaction, we anticipated that metal counterions other than lithium may enhance the diastereoselection in the reaction of **1A** with aldehydes. A survey of various metal cations was undertaken by treating Li^+-**1A** with various metal halides ($ZnCl_2$,[14] $MgBr_2$,[14] $(Et_2N)_3TiCl$,[15] $(i\text{-}PrO)_3TiCl$,[15] Ph_3SnCl,[16] Cp_2ZrCl_2[17]) at −78 °C for 1 h followed by quenching the resulting organometallic with benzaldehyde at −78 °C for 10 min. Li^+-**1A** reacted with benzaldehyde to give a 63:37 mixture of anti **4Ac** (J_{12} = 9.4 Hz) and syn **4Sc** (J_{12} = 2.7 Hz) products, respectively (Table I).[18] A much-enhanced diastereoselection (**4Ac**:**4Sc** = 84:16) was realized from the analogous zinc reagent **1A** ($M = Zn^{2+}$).[19]



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(9) (a) Wolf, S.; Stolow, A.; LaJohn, L. A. *Tetrahedron Lett.* **1983**, *248*, 4071. (b) Wolf, S.; LaJohn, L. A.; Weaver, D. F. *Tetrahedron Lett.* **1984**, *25*, 2863.

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(13) Tsuchihashi, G.; Iriuchijima, S.; Maniwa, K. *Tetrahedron Lett.* **1973**, 3389.

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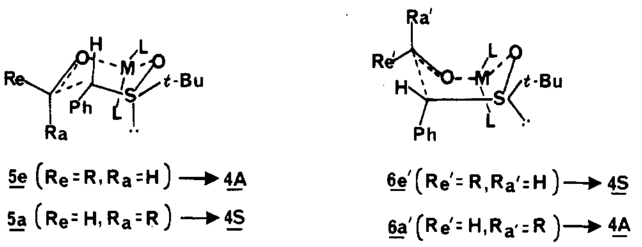
(18) We use the stereochemical descriptors syn and anti according to Masamune et al.: Masamune, S.; Ali, Sk. A.; Snitman, D. L.; Garvey, D. S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1413.

Scheme III



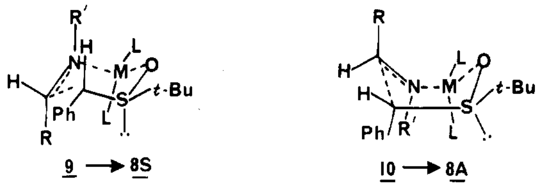
Effect of Aldehyde Structure on Diastereoselection. The effect of aldehyde structures on the diastereoselection of the reactions of Li$^+$- and Zn^{2+}-**1A** was undertaken, and these results are presented in Table I. For entries 1–8, the increasing anti diastereoselection roughly parallels the increasing steric demand of the aldehyde substituent R (conformational free energies, PhCH=CH < Et < *i*-Pr < Ph < *t*-Bu).[20] As noted above, a higher level of anti diastereoselection is observed when Zn^{2+}-**1A** is employed relative to Li$^+$-**1A**. However, only in the reaction to of Zn^{2+}-**1A** and isobutyraldehyde is a high level of anti diastereoselection observed (**4Ad**:**4Sd** = 91:9). The reaction of **1A** with the highly sterically demanding pivaldehyde was anomalous, showing little stereoselection.

We suggest that these product ratios reflect kinetic diastereoselection since (a) the anti to syn diastereoselection did not differ in these reactions if they were quenched with acetic acid (1.1 equiv) at −78 °C after 5 s, 10 min, or 1 h; (b) when Li$^+$-**1A** was quenched first with pivaldehyde (1.1 equiv) and then, after 10 min, benzaldehyde (1.1 equiv, 2 h), no crossover products (i.e., **4Ac** or **4Sc**) could be detected and, furthermore, there was no change in product (**4Ae**, **4Se**) diastereoselection.

Table II. Reactions of Lithium and Zinc 1A with Imines 7

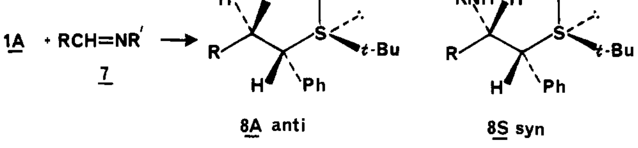
entry	imine 7 (RCH=NR′)			counterion (temp, °C; time, h)	yield, %	diastereoselection 8A:8S
		R	R′			
1	**7a**	Ph	Ph	Li$^+$ (−78; 2)	94	>97:<3
2	**7b**	(*E*)-PhCH=CH	Ph	Li$^+$ (−78; 5)	52	>97:<3
3	**7b**	(*E*)-PhCH=CH	Ph	Zn^{2+} (−78; 5)	82	>97:<3
4	**7c**	2-furyl	Ph	Li$^+$ (−78; 5)	100	97:3
5	**7d**	Ph	CH$_3$	Zn^{2+} (−78→0; 2)	28	42:58
6	**7d**	Ph (BF$_3$ complex)	CH$_3$	Zn^{2+} (−78→0; 2)	85	58:42
7	**7e**	CH$_3$CH$_2$	Ph	Zn^{2+} (−78→0; 2)	57	67:33

Scheme IV



By analogy with the aldol reaction,[21] four possible diastereomeric chelated cyclic transition states are possible for the reaction of **1A** with aldehydes. The two possible chair and boat transition states are shown in Scheme III. Clearly the preference for anti diastereoselection in these reactions suggests that the chair or boat transition states **5e** or **6a′** are favored. The anomalous results with pivaldehyde, however, are difficult to rationalize if the reaction proceeds via a chair-like transition state. A boat-like transition state would seem more likely. In the boat transition state **6e′**, the aldehyde substituent R experiences a gauche interaction with the Ph group of the sulfoxide. In the alternative boat transition **6a′**, the R substituent experiences a flagpole interaction with the sulfoxide oxygen. When R is not large, then the latter interaction would not be important and transition-state **6a′** is favored. In this case, the anti diastereoselection increases with the increasing steric bulk of the aldehyde substituent as transition-state **6e′** becomes energetically less favorable. When R is sterically demanding (R = *t*-Bu), then the flagpole interaction in **6a′** becomes significant and poor diastereoselection results.

Reaction of 1A with Imines. In contrast to the numerous reports on the reactions of sulfinyl anions with aldehydes, only one report concerning the reaction of chiral sulfinyl anions with imines has appeared.[13] Li$^+$-**1A** reacted smoothly with *N*-benzylideneaniline at −78 °C over 2 h to give essentially diastereomerically pure (diastereoselection >97:<3 from ^{1}H and ^{13}C NMR analysis) anti product **5Aa** (J_{12} = 10.9 Hz). Shorter reaction times result in poorer yields due to incomplete reaction. In contrast, the reaction of **1A** with benzaldehyde was complete after 5 s and showed poor diastereoselection. Likewise the *N*-phenyl imines **7b** and **7c** in which the imine substituent R is alkenyl and aryl, respectively, reacted in an analogous and highly diastereoselective fashion, giving the anti products **8Ab** and **8Ac**, respectively (Table II). In the reaction of Li$^+$-**1A** with **7b**, however, the yield was poor due to competing side reactions giving as yet unidentified products. A high yield of **8Ab** could be realized, without loss of diastereofacial selectivity, when the zinc reagent of **1A** was employed.



In contrast to the reaction of **1A** with *N*-benzylideneaniline (**7a**), no appreciable reaction between **1A** and *N*-benzylidenemethylamine (**7d**) occurred in the temperature range −78 to 0 °C. When the zinc reagent **1A** was employed at 0 °C, the anti and syn adducts **8Ad** and **8Sd** could be isolated in poor yield (28%) along with starting materials. A good yield of **8Ad** and **8Sd** could be realized when **7d** was precomplexed with BF$_3$·Et$_2$O prior to the addition of zinc **1A**; however, poor anti diastereoselection was observed. Both *N*-ethylideneaniline (**8e**) and *N*-iso-

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(19) Attempted transmetalation of Li$^+$-**1A** with the previously mentioned magnesium, tin, and titanium reagents at −78 °C (1 h) followed by quenching with benzaldehyde gave in high yield a mixture of **4Ac** and **4Sc** in a ratio almost identical with that obtained from Li$^+$-**1A**. These results clearly suggested little transmetalation of Li$^+$-**1A** at −78 °C. When titanation of **1A** was attempted by warming a mixture of Li$^+$-**1A** and (Et$_2$N)$_3$TiCl or (*i*-PrO)$_3$TiCl to 0 °C, extensive decomposition occurred. When titanation of the lithium carbanion of methyl phenyl sulfoxide with (Et$_2$N)$_3$TiCl was attempted, the Pummerer type rearrangement products i and ii were tentatively assigned from ^{1}H NMR analysis. Reetz has also reported problems in the titanation and subsequent reactions of the lithium carbanion of dimethylsulfoxide.[15] Attempted transmetalation of Li$^+$-**1A** with Cp$_2$ZrCl$_2$ at −78 °C (1 h) and then quenching of the resulting solution with benzaldehyde gave no recognizable products.

XCH$_2$SPh

i: X = Cl

ii: X = NEt$_2$

(20) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. In *Conformational Analysis*; American Chemical Society: Washington, DC, 1981; pp 436–442. Since the ethenyl group of PhCH=CH is sp^2 hybridized, one would expect the conformational free energy of this group to be less than that for ethyl.

(21) (a) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*, 1. (b) Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 3, Chapter 2.

propylideneaniline failed to give the desired adduct with Li^+-**1A** at 0 °C; however, highly colored reaction mixtures resulted and no starting imine **7** could be detected, suggesting that proton transfer from **1A** to **7** and subsequent polymerization reactions were occurring.

In summary, *N*-phenyl imines **7** in which the substituent R is alkenyl or aryl (**7a–c**) react at −78 °C with high anti diastereoselection (≥97%). When the substituent R or R′ of the imine **7** is aliphatic, then these substrates show poor chemical reactivity and diastereoselection. Clearly aryl and alkenyl groups that can stabilize incipient charge in the transition state are important to ensure high reactivity.

Since the imines **7a–e** must have the *E* geometry,[22] only two chelated cyclic transition states are available for the reaction of **1A** with imines **7**, the chair and boat transition states **9** and **10**, respectively (Scheme IV). Clearly the high anti diastereoselection in entries 1–4 (Table II) suggests that if a cyclic transition state is involved, then boat transition state **10** is favored over its chair counterpart **9**.

Experimental Section

Solvents were purified and chromatography was performed as previously described.[23] All reactions were conducted under a positive pressure of dry nitrogen. NMR spectra were recorded on a Brucker 300-MHz NMR spectrometer in deuterated chloroform that had been filtered through a plug of anhydrous K_2CO_3 just prior to use. Mass spectra (EI mode), single-crystal X-ray analyses, and elemental analyses were performed at the Fachbereich Chemie der Philipps-Universität. Zinc chloride in ether (1 M) was purchased from Aldrich Chemical Co. An aliquot of this solution was evaporated under vacuum, and residual solvent and HCl were removed by heating with a heat gun. The $ZnCl_2$ was cooled under an atmosphere of nitrogen and then dissolved in dry ether. *n*-BuLi was titrated against diphenylacetic acid.

Reaction of Lithium and Zinc 1A with Carbonyl Compounds: A General Procedure. To a solution of *tert*-butyl phenylmethyl sulfoxide (186 mg, 1.0 mmol) in THF (5 mL) at −78 °C was added *n*-BuLi in hexane (1.1 mmol). After 10 min, a solution of $ZnCl_2$ (1.1 mL of 1.0 M solution in ether) was added (solution turned from a pale yellow color to colorless), and stirring was continued for 10 min. The neat aldehyde (1.2 mmol) or benzophenone (1.2 mmol in THF (1 mL)) was then added dropwise. After 5 min, the solution was quenched rapidly with saturated NH_4Cl (0.5 mL), and then ether (20 mL) and water (20 mL) were added. The layers were separated, and the ether layer was dried (K_2CO_3) and concentrated. The diastereoselection of these reactions was determined from ^{1}H NMR analysis of the crude reaction product. The crude product was purified by column chromatography on silica gel employing ethyl acetate/hexane as eluent. Yields are reported in Table I. Analytical samples were secured by recrystallization from hexane containing a small quantity of ether.

(R^*_S,2R^*)-2-(*tert*-Butylsulfinyl)-1,1,2-triphenylethanol (2c): mp 149–150 °C; TLC, R_f 0.2 (20% EtOAc/hexane); ^{1}H NMR δ 7.53–7.08 (m, 15 H), 6.56 (br s, 1 H, O*H*), 4.93 (s, 1 H), 1.09 (s, 9 H); ^{13}C NMR 145.26, 143.10, 134.30, 131.39, 127.97, 127.89, 127.85, 127.71, 127.41, 127.14, 126.84, 82.43, 68.24, 56.90, 23.86.

Anal. Calcd for $C_{24}H_{26}O_2S$: C, 76.14; H, 6.94. Found: C, 75.97; H, 6.66.

4Aa (R = (*E*)-PhCH═CH): solid; ^{1}H NMR δ 7.37–7.19 (m, 10 H), 6.73 (dd, 1 H, J = 1.2, 15.9 Hz), 5.96 (br s, 1 H, O*H*), 5.74 (dd, J = 5.5, 15.9 Hz, 1 H), 5.11 (m, 1 H), 4.00 (d, J = 9.3 Hz, 1 H), 1.20 (s, 9 H).

Anal. Calcd for $C_{20}H_{24}O_2S$: C, 73.13; H, 7.38. Found: C, 73.41; H, 7.39.

4Sa (R = (*E*)-PhCH═CH): ^{1}H NMR δ 7.37–7.19 (m, 10 H), 6.52 (dd, J = 0.94, 15.9 Hz, 1 H), 6.26 (dd, J = 7.2, 15.9 Hz, 1 H), 4.97 (m, 1 H), 4.18 (d, J = 2.9 Hz, 1 H), 1.12 (s, 9 H); ^{13}C NMR (in part) 74.37, 65.84, 55.70, 23.51.

4Ab (R = CH_3CH_2): viscous liquid; ^{1}H NMR δ 7.42–7.22 (m, 5 H), 5.61 (s, 1 H, O*H*), 4.35 (m, 1 H), 3.93 (d, 1 H, J = 9.3 Hz), 1.17 (s, 9 H), 1.02–0.91 (m, 2 H), 0.89 (t, 3 H, J = 7 Hz); ^{13}C 135.15, 130.31, 129.38, 129.10, 128.65, 128.16, 128.10, 74.72, 65.67, 54.41, 27.39, 23.43, 9.26; MS 149 (88, M − S(O)-*t*-Bu), 131 (30, 149 − H_2O), 57 (100).

4Sb (R = CH_3CH_2): ^{1}H NMR (in part) δ 3.93* (d, 1 H, J = 2.7 Hz), 1.11 (s, 9 H) ((*) chemical shift dependent on ratio of anti and syn isomers in mixture); ^{13}C NMR (in part) 72.47, 65.10, 55.36, 26.79, 23.47, 10.52.

4Ac (R = Ph): mp 172–173 °C; ^{1}H NMR δ 7.15–6.96 (m, 10 H), 6.19 (d, J = 1.2 Hz, 1 H, O*H*), 5.38 (dd, J = 1.1, 9.4 Hz, 1 H, PhC*H*(OH)), *4.09* (d, J = 9.4 Hz, 1 H, C*H*S(O)), 1.22 (s, 9 H); ^{13}C NMR 140.14, 134.33, 129.56, 128.57, 127.78, 127.56, 127.04, 77.76, 66.72, 56.65, 23.34.

Anal. Calcd for $C_{18}H_{22}O_2S$: C, 71.47; H, 7.35. Found: C, 71.52; H, 7.21.

4Sc (R = Ph): mp 179–180 °C; ^{1}H NMR δ 7.25–6.97 (m, 10 H), 5.62 (m, 1 H), *4.03* (d, J = 2.7 Hz, 1 H), 3.98 (br s, 1 H), 1.16 (s, 9 H); ^{13}C NMR 140.13, 130.70, 128.11, 128.04, 127.89, 127.43, 126.61, 73.05, 67.09, 55.60, 23.53.

Anal. Calcd for $C_{18}H_{22}O_2S$: C, 71.47; H, 7.35. Found: C, 71.05; H, 7.50.

4Ad (R = *i*-Pr): solid; ^{1}H NMR δ 7.31–7.18 (m, 5 H), 5.34 (d, J = 1.6 Hz, 1 H), 4.27 (dt, J = 1.8, 9.7 Hz, 1 H), 3.97 (d, J = 9.7 Hz, 1 H), 1.11 (s, 9 H), 0.87 (d, J = 6.9 Hz, 3 H), 0.79 (d, J = 6.7 Hz, 3 H); ^{13}C NMR 134.97, 130.67, 129.39, 129.07, 128.54, 128.10, 77.13, 64.20, 56.44, 29.56, 23.45, 20.37, 13.93.

Anal. Calcd for $C_{15}H_{24}O_2S$: C, 67.11; H, 9.02. Found: C, 67.39; H, 9.12.

4Sd (R = *i*-Pr): ^{1}H NMR (in part) δ 1.13 (s, 9 H); ^{13}C NMR (in part) 75.25, 63.42, 55.18, 30.93, 23.54, 19.41, 19.15.

4Ae (R= *t*-Bu): solid; ^{1}H NMR δ 7.32–7.28 (m, 5 H), 5.89 (d, J = 2.5 Hz, 1 H), *4.18* (d, J = 9.2 Hz, 1 H), 4.14 (dd, J = 2.5, 9.2 Hz, 1 H), 1.20 (s, 9 H), 0.73 (s, 9 H); ^{13}C NMR 136.48, 130.36, 128.82, 128.15, 80.37, 64.58, 56.88, 37.20, 26.78, *23.63*.

Anal. Calcd for $C_{16}H_{26}O_2S$: C, 68.03; H, 9.30. Found: C, 68.11; H, 9.07.

4Se (R = *t*-Bu): ^{1}H NMR δ 7.33–7.28 (m, 5 H), 4.21 (dd, J = 2.1, 5.8 Hz, 1 H), 4.12 (d, J = 2.1 Hz, 1 H), 4.03 (d, J = 5.8 Hz, 1 H), 1.12 (s, 9 H), 0.80 (s, 9 H); ^{13}C NMR 135.56, 131.25, 128.78, 128.43, 127.97, 75.60, 63.28, 55.36, 36.27, 26.84, 23.70.

Reaction of Lithium and Zinc 1A with Imines: A General Procedure. A solution of lithium or zinc **1A** prepared as described above at −78 °C was treated dropwise with a solution of imine **7**[24] (1.2 mmol) in THF (1 mL). The solution was stirred at the temperature and for the period reported in Table II. The reaction mixture was quenched with 50% aqueous methanol (0.2 mL), and then ether (20 mL) and water (20 mL) were added.

After a workup and analysis procedure similar to that described above, the crude product was purified by column chromatography on silica gel employing ethyl acetate/hexane as eluent. Yields are reported in Table II. Analytical samples were secured by recrystallization from hexane containing a small quantity of ether.

(R^*_S,1S^*,2R^*)-*N*-Phenyl-2-(*tert*-butylsulfinyl)-1,2-diphenylethylamine (8Aa) (R = R′ = Ph): solid; ^{1}H NMR δ 7.31–6.98 (m, 12 H), 6.71 (d, 2 H, J = 8.3 Hz), 6.63 (t, 1 H, J = 7.3 Hz), 5.47 (dd, 1 H, J = 2.7, 10.9 Hz), 4.79 (d, 1 H, J = 10.9 Hz), 4.19 (d, 1 H, J = 2.7 Hz), 1.05 (s, 9 H); ^{13}C NMR 146.25, 139.51, 132.90, 130.00, 129.07, 128.67, 128.51, 128.22, 128.01, 127.60, 127.28, 118.20, 114.66, 67.19, 57.17, 55.63, 23.86; MS 377 (M^+, 1), 272 (M − S(O)tBu, 18), 182 (M − PhCHS(O)-*t*-Bu, 100).

8Ad (R = Ph, R′ = CH_3): viscous liquid; ^{1}H NMR δ 7.05–7.00 (m, 8 H), 6.84–6.80 (m, 2 H), 4.31 (d, 1 H, J = 7.5 Hz), 4.14 (d, 1 H, J = 7.5 Hz), 2.60 (br s, 1 H), 2.15 (s, 3 H), 1.02 (s, 9 H); ^{13}C NMR 138.81, 134.21, 130.19, 128.78, 128.06, 127.96, 127.71, 127.63, 127.13, 67.02, 66.61, 56.28, 34.13, 23.78.

8Sd (R = Ph, R′ = CH_3): ^{1}H NMR δ 7.27–7.20 (m, 6 H), 7.00 (m, 2 H), 6.85 (m, 2 H), 4.51 (d, 1 H, J = 3.1 Hz), 3.89 (d, 1 H, J = 3.1 Hz), 2.32 (s, 3 H), 1.86 (br s, 1 H), 1.04 (s, 9 H); ^{13}C NMR 139.56, 133.12, 130.43, 130.04, 128.88, 128.32, 128.17, 128.15, 127.74, 127.23, 67.87, 62.61, 55.13, 34.28, 23.89.

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8Ab (R = (*E*)-PhCH=CH, R′ = CH_3): mp 121–123 °C; ^1H NMR δ 7.38–7.13 (m, 12 H), 6.79 (d, 2 H, J = 7.8 Hz), 6.71 (t, 1 H, J = 7.3 Hz), 6.44 (d, 1 H, J = 15.9 Hz), 6.29 (dd, 1 H, J = 7.3, 15.9 Hz), 4.87 (m, 1 H), 4.67 (d, 1 H, J = 11.0 Hz), 4.26 (d, 1 H, J = 2.5 Hz), 1.05 (s, 9 H); ^{13}C NMR 146.55, 136.56, 134.32, 133.36, 129.77, 129.27, 128.99, 128.73, 128.49, 128.46, 127.70, 126.85, 126.58, 118.35, 114.85, 65.58, 58.68, 55.74, 23.81.

Anal. Calcd for $C_{26}H_{29}NOS$: C, 77.37; H, 7.26; N, 3.47. Found: C, 77.39; H, 7.18; N, 3.34.

8Ac (R = 2-furyl, R′ = Ph): mp 122–123 °C; ^1H NMR δ 7.32–7.30 (m, 4 H), 7.17–7.12 (m, 4 H), 6.83 (d, 2 H, J = 7.6 Hz), 6.72 (t, 1 H, J = 7.3 Hz), 6.20 (dd, 1 H, J = 1.8, 3.3 Hz), 6.02 (d, 1 H, J = 3.3 Hz), 5.58 (dd, 1 H, J = 2.7, 11.5 Hz), 4.42 (d, 1 H, J = 2.7 Hz), 4.23 (d, 1 H, J = 11.5 Hz), 1.08 (s, 9 H); ^{13}C NMR 153.30, 146.48, 141.66, 133.43, 129.74, 129.23, 128.76, 128.50, 118.97, 114.97, 110.47, 107.99, 64.57, 55.58, 52.94, 23.85; MS 367 (M^+, 2), 262 (M − S(O)-*t*-Bu, 24), 261 (65), 172 (100).

Anal. Calcd for $C_{22}H_{25}NO_2S$: C, 71.89; H, 6.87; N, 3.87. Found: C, 71.66; H, 6.82; N, 3.79.

8Ae (R = CH_3CH_2, R′ = Ph): viscous liquid; ^1H NMR δ 7.41–7.13 (m, 6 H), 6.86 (d, 2 H, J = 8.2 Hz), 6.71 (q, 2 H, J = 7.6 Hz), 4.29 (m, 1 H), 4.01 (d, 1 H, J = 2.3 Hz), 3.47 (d, 1 H, J = 11.3 Hz), 1.59 (m, 2 H), 1.00 (s, 9 H), 0.94 (t, 3 H, J = 7.4 Hz); ^{13}C NMR 147.92, 134.18, 129.98, 129.34, 128.87, 128.28, 117.80, 114.34, 65.08, 55.53, 55.43, 27.12, 23.86, 11.49; MS 329 (M^+, 3), 224 (M − S(O)-*t*-Bu, 34), 134 (100).

8Se (R = CH_3CH_2, R′ = Ph): ^{13}C NMR 146.71, 133.94, 130.14, 129.59, 128.55, 128.04, 117.63, 113.61, 60.76, 56.22, 53.89, 24.80, 23.56, 11.15.

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Supplementary Material Available: Tables of all atomic positional and thermal parameters and all atomic distances and angles for the crystallographic structure **2c** (18 pages). Ordering information is given on any current masthead page.

Conversion of 1-Isopropylidene-4,4-dimethyl-2,5-cyclohexadiene to Its Crisscross Dimer

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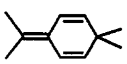
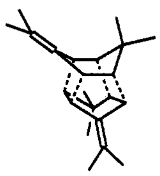
The title compound, **1**, gives only aromatization to **6** and polymerization upon treatment with acid in methylene chloride or when TFAA or TFA are added separately to the reaction mixture. When both TFAA and TFA are present at low temperatures, $HBF_4{\cdot}Et_2O$ causes remarkably efficient formation of the crisscross dimer **2**, which is isolated in up to 80% yield. Ozonolysis of **2** gives the diepoxide or rearranged compounds containing acetyl groups. One-electron oxidation of **2** produces a long-lived cation radical, which has its bis-allylic C–C bond intact, in contrast to less constrained 1,4-diene cation radicals.

Treatment of the monocyclic tetramethyl[3]dendralene[1] **1** under a rather specific set of acidic conditions causes formation of crisscross cage dimer **2**, as reported in a preliminary communication.[2] The four σ bonds shown as dotted ones on the structure of **2** are formed in one operation, which converts a monocyclic compound into a pentacyclic one having eight contiguous methyne carbons. This paper describes our work on this transformation as well as the oxygenation of **2** and spectral work on its cation radical.



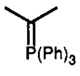
1



2

Results: Dimerization of 1

Desobry and Margaretha[3] previously prepared **1** by pyrolysis of the photoadducts of 2,3-dimethylbutene and 6-fluoro-4,4-dimethyl-2-cyclohexenone at 150 °C. We used Wittig addition of isopropylidenetriphenylphosphorane[4] (**3**) to 4,4-dimethylcyclohexa-2,5-dienone[5] (**4**). Pure **1** polymerizes rather rapidly, and we used batches as soon as possible after they were prepared; **1** may be stored at −20 °C for limited periods of time.



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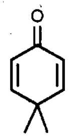

4

Our original intent was to study the cation radical chain catalyzed[6] oxygenation of **1**. Cyclic voltammetry experiments under the conditions we usually use for study of unstable hydrocarbon cation radicals[7] gave only an irreversible oxidation wave peaking at 1.35 V at −78 °C with

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[7] (a) Mixed acidic solvent consisting of a 20:1:1 v/v mixture of $CH_2Cl_2/(CF_3CO)_2O/CF_3CO_2H$ containing 0.1 M n-Bu_4NBF_4 as supporting electrolyte, at −78 °C. Potentials are reported versus a saturated calomel reference electrode. (b) For brevity, we shall refer to mixtures of volumes a, b, and c of methylene chloride, trifluoroacetic anhydride, and trifluoroacetic acid throughout this paper as a:b:c mixed acidic solvent.

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