diastereotopicity are apparent in the aryl portion. Carbon assignments were made from the ^1H-coupled (^{31}P-decoupled) spectrum, which revealed, in order of increasing ppm, multiplicities q, q, t, q, s, d, d, d, d, s, s, the latter two singlets arising from the two diastereotopic quaternary aryl carbons at 137.8 and 140.5 ppm); mass spectrum, *m/e* 100 (100%), 185 (22.5%), 256 (47.0%), 299 (3.1%) (the fragment CH_3S is lost); $[\alpha]^{21}_D$ −133.2° (*c*, 1.08, $CHCl_3$) (assuming an ee of 81% the theoretical rotation is −164.4°).

Owing to an administrative mistake, the sample submitted for analysis was lost. The material has not been resynthesized nor was there any material for an exact mass spectral determination.

(*R*)-5,5-Dimethyl-4-[(diphenylphosphino)methyl]-1,3-thiazolidine (15e, (*R*)-cyclopenphos) was obtained in 20% yield: bp (Kugelrohr) 250 °C (10^{-3} torr); ^1H NMR ($CDCl_3$) δ 7.70–7.12 (m, 10 H), 4.07 (d, *J* = 8 Hz, 1 H), 3.78 (d, *J* = 8 Hz, 1 H), 2.53 (s, 3 H), 2.60–2.08 (m, 3 H), 1.45 (s, 3 H), 1.26 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 133.2 (d, *J* = 19.9 Hz), 132.2 (d, *J* = 18.6 Hz), 128.9 (s), 128.4 (s), 128.3 (s), 73.3 (*J* = 12.4 Hz), 59.2 (s), 56.4 (d, *J* = 4.9 Hz), 39.7 (d, *J* = 6.1 Hz), 30.15 (d, *J* = 1.8 Hz), 27.9 (s), 27.4 (d, *J* = 15.8 Hz); mass spectrum, *m/e* 144 (100%), 328 (7.3%), 329 (2.5%, parent), 330 (6.1%), theoretical *m/e* 329 for $C_{19}H_{24}NSP$. The optical rotation was not measured and a satisfactory elemental analysis could not be obtained.

(*S*)-2-(Dimethylamino)-1-(diphenylphosphino)-3-methylbutane (valphos) was prepared in 25% yield using the described procedure.[17]

Cross Coupling Reactions. The synthesis of the Grignard reagent of 1-phenyl-1-chloroethane was carried out by two different procedures.

Method A: In $(C_2H_5)_2O$ (80 mL) 1-phenyl-1-chloroethane (10.5 g, 75 mmol) was dissolved. Freshly activated Mg turnings (2.02 g, 83 mmol) were added, and the reaction was started with a crystal of I_2 and held at 0–5° until cessation of reaction. The entire Grignard solution was decanted from the unreacted turnings into an addition funnel. This was added to a suspension of $NiCl_2$ (7 mg, 0.13 mmol), ligand (0.13 mmol), and vinyl bromide (2.68 g, 25 mmol) in $(C_2H_5)_2O$ (10 mL). The Grignard suspension was added at such a rate that the temperature did not rise above −40 °C. The entire solution was stirred magnetically and held under constant N_2 pressure. After addition the solution was allowed to come to room temperature over a period of 14 h. The reaction mixture was hydrolyzed at 0 °C with 10% HCl solution (30 mL). The resulting mixture was poured into a separatory funnel and the flask rinsed with $(C_2H_5)_2O$ (50 mL). The aqueous HCl layer was drawn off, and the ether layer was again washed with 10% HCl solution (30 mL). The ether layer was dried over $MgSO_4$. After removal of the solvent the crude material was distilled, bp 90–110 °C (30 torr), and the sample was then analyzed by ^1H NMR spectroscopy and polarimetry.

Method B differs in the preparation of the Grignard reagent: For both 1-phenyl-1-chloroethane and 2-chlorooctane the Grignard reagents were prepared on a 500-mmol scale as described above but in a large Schlenk vessel under N_2 dried by passage over P_2O_5/CaO and Cu turnings. The solid materials were allowed to settle, and then the supernatant *solution* was removed by syringe prior to reaction, which was carried out as described above. In the case of the Grignard reagent of 1-phenyl-1-chloroethane, prepared by method A or B, an aliquot was removed, hydrolyzed with 10% HCl solution, and then back-titrated with base. In some cases the hydrocarbon formed on hydrolysis was analyzed by ^1H NMR spectroscopy to determine the ratio of ethylbenzene to the (diastereomeric) 2,3-diphenylbutanes.

Acknowledgment. We are grateful to Prof. M. P. Doyle for his aid in arranging the stay of J. H. G. at Groningen. B. K. Vriesema aided in and supplied data needed for the determination of some enantiomeric excesses. Prof. T. Hayashi kindly provided information on some experimental procedures.

Registry No. L-**3**, 52-90-4; L-**4**, 63-68-3; (*R*)-**7a**, 97071-92-6; (*R*)-**7b**, 97071-93-7; (*S*)-**7c**, 79546-64-8; (*R*)-**9**, 97072-01-0; (*R*)-**10**, 97071-94-8; (*R*)-**12**, 97071-95-9; (*S*)-**15a**, 97071-96-0; (*S*)-**15b**, 97071-97-1; (*S*)-**15c**, 97071-98-2; (*R*)-**15d**, 97071-99-3; (*R*)-**15e**, 97072-00-9; (*S*)-**15f**, 74492-09-4; **19**, 593-60-2; (*S*)-**20a**, 58717-85-4; (*R*)-**20a**, 36617-88-6; (*R*)-**20b**, 54541-44-5; (*S*)-**20b**, 54541-45-6; HCHO, 50-00-0; CH_3SO_2Cl, 124-63-0; $(C_6H_5)_2Ph$, 829-85-6; *S*-methyl-*N*,*N*-dimethyl-L-cysteine, 70706-62-6; D-penicillamine, 52-67-5; (*S*)-2-(dimethylamino)-3-methyl-1-butanol, 64584-88-9; (*R*)-3,3,3-tris(fluoromethyl)-2-methoxy-2-phenylpropionyl chloride, 39637-99-5; (*R*)-2-(dimethylamino)-3-methyl-3-(methylthio)-1-butyl (*S*)-3,3,3-tris(fluoromethyl)-2-methoxy-2-phenylpropionate, 97072-02-1; (±)-1-phenyl-1-chloroethane, 38661-82-4; (±)-2-chlorooctane, 51261-14-4.

Formation and Uses of the Dianion Formally Produced by Conjugate Addition of Bis(phenylthio)methyl Dianion to Cyclohex-2-en-1-one. Configurations and Conformations of the Products of Conjugate Addition of Tris(phenylthio)methyllithium to Carvone

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When the enolate anion formed by the addition of tris(phenylthio)methyllithium to 2-cyclohexen-1-one is treated at −50 °C with *sec*-butyllithium, the enolate thioacetal dianion **3** is generated. The latter forms useful compounds by the attack of electrophiles (protons, aldehydes, and methyl iodide) at the thioacetal carbanionic site, but alkylating agents bulkier than methyl iodide are unreactive toward this site; the behavior toward some of these is chronicled. Methylation of the protonation product **14** of **3** apparently occurs at a sulfur atom, yielding the norcaranone **15**. A similar dianion is produced when (−)-carvone is the substrate; in this case, the conjugate addition occurs from the side opposite the isopropenyl substituent, and the structures and conformations of the original adduct have been determined by 300-MHz NMR spectroscopy.

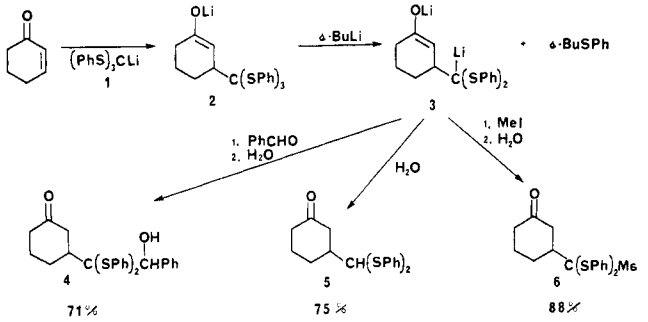
The readily prepared tris(phenylthio)methyllithium (**1**) undergoes high-yield conjugate addition to cyclohex-2-en-1-one.[1,2] We have found that the proximate product, the enolate anion **2**, undergoes clean sulfur–lithium exchange at −45 °C in the presence of *sec*-butyllithium to produce the dianion **3** (Scheme I), the formal conjugate adduct of the unknown bis(phenylthio)methyl dianion to

(1) Manas, A. R. B.; Smith, R. A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 216. Smith, R. A. J.; Lal, A. R. *Aust. J. Chem.* **1979**, *32*, 353.

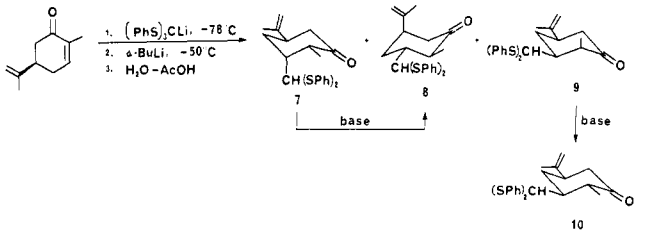
(2) Cohen, T.; Nolan, S. M. *Tetrahedron Lett.* **1978**, 3533.

0022-3263/85/1950-3266$01.50/0

Scheme I



Scheme II



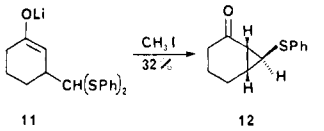
cyclohexenone.[3] This dianion (**3**) can be detected by reaction with the electrophiles water, benzaldehyde, and methyl iodide and by its decomposition at 0 °C to 3-[(phenylthio)methyl]cyclohex-2-en-1-one, apparently via a carbenoid–enolate.[4] Since the electrophiles shown in Scheme I attack the carbon atom bearing the sulfur atoms, **3** can be considered a keto carbanion with the ketone function protected as its enolate anion.[5]

Two of the products, **5** and **6**, from this sequence have been prepared by the conjugate addition of the appropriate thioacetal anions to cyclohexenone in the presence of HMPA.[6] However, the yields and regioselectivity in the current procedure are considerably superior.

Because of the great versatility of the phenylthio group in organic chemistry, the side chain that has been created at the 3-position by this one-pot sequence has considerable potential for further elaboration. One obvious reaction of this type is hydrolysis of the thioacetal group to a carbonyl function. Indeed, a previous report[2] from this laboratory has demonstrated that **5** and analogous compounds can be hydrolyzed in good yield to the corresponding keto-aldehydes; in that account, tris(phenylthio)methyllithium was shown to be a formyl anion equivalent in a sequence that includes its conjugate addition to an enone, reduction of the tris(phenylthio)methyl group of the 1,4-adduct to a bis(phenylthio)methyl group by the use of chromous chloride, and hydrolysis to the aldehyde. The present one-pot procedure is obviously simpler and more efficient, and the dianion can be trapped with electrophiles other than the proton.

An analogous dianion can be produced in a similar fashion when (−)-carvone is used as the enone. This dianion has been shown[4] to decompose upon warming to a norcaranone derivative, again via a carbenoid–enolate intermediate. As in other conjugate additions to carvone,[7] the nucleophile attacks very predominantly from the side of the molecule opposite the isopropenyl group. When the reaction mixture is quenched at −45 °C with aqueous acetic acid and worked up immediately, 52% of **7** is produced in addition to 3% of its C-2 epimer **8** (Scheme II); attack from the opposite side results in 9% of **9**. If, on the other hand, the reaction mixture is quenched at −45 °C with water and it is allowed to remain at 25 °C overnight the major product (62.6%) is **8** the base-catalyzed epimerization product of **7**, and the minor product (10.4%) is **10**, the epimerization product of **9**. Samples of **7** and **9** were also shown to epimerize quantitatively to **8** and **10**, respectively, by treatment with sodium hydroxide dissolved in THF/water at 25 °C for 30 min. The structures and conformations of the products are clear from the NMR spectra (see Experimental Section); this constitutes the first NMR analysis of the products of conjugate addition to carvone. The direction of nucleophilic attack on carvone is completely consistent with the structure of the norcaranone obtained by thermal decomposition of the derived dianion via a carbenoid mechanism[4] and with Heathcock's rational for the direction of such attacks on cyclohexenones.[8] The structure of the protonation product (**7**) of this dianion is expected if the latter, which is thought[4] to exist with the sulfur-bearing appendage in the quasi-axial conformation, is protonated as is usual from the axial direction.

Presumably because of steric hindrance, the thioacetal anionic site of **3** and of its monopotassium analogue (produced by treatment of the adduct **2** with potassium naphthalenide[9]) was completely resistant to attack by alkylating agents bulkier than methyl iodide, and this led to generally unsatisfactory results in attempts to capture these dianions with dielectrophiles or sequentially with two different electrophiles. In one such attempt, the protonation product **11** of **3** was treated with methyl iodide



whereupon the norcaranone derivative **12** was produced, indicating that the phenylthio group is more exposed to attack than the enolate carbon atom; the novel concept of cyclopropane formation via activation of a phenylthio group contained in a conjugatively added substituent has been exploited in our laboratory in a useful cyclopropane synthesis.[10]

In summary, readily generated dianions of the type **3** react at the thioacetal carbanionic site with protonating agents, aldehydes, and methyl iodide to provide useful products in a one-flask sequence, but alkylation at this sterically hindered site with bulkier alkyl halides is unsuccessful. Protonation of the dianion followed by treat-

(3) A species analogous to **3** has been briefly described. It was prepared in a medium containing HMPA by a far more cumbersome procedure involving the preparation and deprotonation (LDA in THF/HMPA at −30 °C) of bis(methylthio)(trialkylstannyl)methane, the addition of cyclohexenone, the removal of the diisopropylamine by distillation at reduced pressure and its replacement by THF, and metal–lithium exchange with methyllithium. The dianion underwent protonation and methylation (on the carbon atom bearing the sulfur atoms) in unspecified yield. Seebach, D.; Bürstinghaus, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 57.

(4) Cohen, T.; Yu, L.-C. *J. Am. Chem. Soc.* **1983**, *105*, 2811.

(5) For another example of the protection of a ketone via its enolate anion, see: Wender, P. A.; Erhardt, J. M.; Letendre, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 2114.

(6) Lucchetti, J.; Dumont, W.; Kreif, A. *Tetrahedron Lett.* **1979**, 2695.

(7) Djerassi, C.; Schneider, R. A.; Vorbrueggen, H.; Allinger, N. L. *J. Org. Chem.* **1963**, *28*, 1632. Narayanaswamy, M.; Sathe, V. M.; Rao, A. S. *Chem. Ind. (London)* **1969**, 921. Tamao, K.; Ishida, N. *Tetrahedron Lett.* **1984**, *25*, 4249.

(8) Blumenkopf, T. A.; Heathcock, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 2354.

(9) (a) Cohen, T.; Daniewski, W. M.; Weisenfeld, R. B. *Tetrahedron Lett.* **1978**, 4665. Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1978**, *43*, 1064. (b) Similar reductive potassiations have been performed by R. Ritter in this laboratory.

(10) Cohen, T.; Myers, M., manuscript in preparation.

ment with methyl iodide results in methylation on sulfur and the novel production of a three-member ring. The configurations and conformations of the conjugate addition products of tris(phenylthio)methyllithium (1) to (−)-carvone have been elucidated by 300-MHz NMR spectroscopy.

Experimental Section

All reactions were performed under argon. Flash chromatography[11] was performed with 40–63 μm silica gel 60 (E. Merck). Thin-layer chromatograms (TLC) were run on glass-supported silica gel 60 plates (0.25-mm layer, F-254, E. Merck). Reversed-phase TLC was performed on uniplate TLC plates (250 μm) precoated with RPS-F (Analtech). Preparative reversed-phase medium-pressure liquid chromatography (MPLC) was performed at 30 psi with a Merck LiChroprep RP-8 (40–63 μm) column (240 mm × 10 mm).

Formation and Capture of Dianion 3. To a solution of 1.12 g (3.30 mmol) of tris(phenylthio)methane[12] in 15 mL of dry THF was added 2.25 mL of *n*-butyllithium (1.55 M solution in hexanes, 3.50 mmol) at −78 °C. The mixture was stirred for 30 min to form tris(phenylthio)methyllithium (1).[4] Cyclohex-2-en-1-one (0.32 mL, 3.3 mmol) was added and the stirring was continued for 2.5 h before the addition of 1.05 equiv of *sec*-butyllithium (3.00 mL of 1.15 M solution in cyclohexane, 3.45 mmol). The resulting orange-red solution was maintained at −45 °C (hexyl alcohol/dry ice bath) for 5 h before being quenched with 3 mL of water. The mixture was partitioned between ether and water, and the aqueous layer was extracted with ether (3 × 25 mL). All organic layers were combined, washed with water (10 mL) and then with brine (10 mL), dried (magnesium sulfate), and concentrated in vacuo to give 1.52 g of crude product, which contained mainly *sec*-butyl phenyl sulfide and 3-bis(phenylthio)methylcyclohexanone (5). The latter could be obtained in pure form (0.81 g, 75%) by flash chromatography. Trituration with pentane, after recrystallization from hexane–ethyl acetate (20:1), afforded white crystals: mp 51.5–53.5 °C; ^{1}H NMR δ 1.51–1.61 (m, 1 H), 1.69–1.81 (m, 1 H), 2.06–2.39 (m, 5 H), 2.50–2.68 (m, 2 H), 4.34 (d, J = 3.23 Hz, 1 H, C*H*(SPh)$_2$), 7.27 (m, 6 H), 7.40 (m, 4 H); IR (CCl_4) 1710 (CO) cm^{-1}; mass spectrum (15 eV), m/e 328 (M$^+$, 15%), 219 (M$^+$ − PhS, 100%), 109 (PhSH$^+$, 14%). Anal. Calcd for $C_{19}H_{20}OS_2$: C, 69.51; H, 6.09. Found: C, 69.44; H, 6.14.

A similar reaction using 0.75 mmol of 1 and substituting benzaldehyde (0.08 mL, 0.82 mmol) for water gave, by flash chromatography, 0.23 g (71%) of spectroscopically pure 3-(1,1-bis(phenylthio)-2-hydroxy-2-phenylethyl)cyclohexanone (4), which contained two diastereomers in a ratio of 1.7 to 1. Recrystallization from heptane yielded white crystals: mp 54–55 °C; ^{1}H NMR δ 1.09–2.28 (m, 7 H), 2.49 (t, J = 13 Hz), 2.60 (t, J = 13 Hz, total 1 H for the latter two peaks), 2.88 (br d, J = 13 Hz), 2.96 (br d, J = 13 Hz, total 1 H for the latter two peaks), 3.49 (d, J = 2.83 Hz), 3.49 (d, J = 2.63 Hz, total 1 H for the latter two peaks, OH), 4.92 (d, J = 2.63 Hz), 4.97 (d, J = 2.83 Hz, total 1 H for the latter two peaks, C*H*OH), 7.24–7.63 (m, 15 H); IR ($CHCl_3$) 3600 (OH), 1703 (CO) cm^{-1}; mass spectrum (70 eV), m/e 327 (M$^+$ − PhCHOH, 24%), 324 (M$^+$ − PhSH, 24%), 110 (PhSH$^+$, 100%); exact mass calcd for $C_{19}H_{19}O_2S$ (M$^+$ − PhCHOH) 327.0877, found 327.0874; exact mass calcd for $C_{20}H_{20}O_2S$ (M$^+$ − PhSH) 324.1184, found 324.1180.

In a similar experiment starting with 0.75 mmol of 1, methyl iodide (0.050 mL, 0.76 mmol) was added to the dianion 3 at −45 °C, and the mixture was allowed to warm to 25 °C slowly and then stirred at that temperature overnight. The mixture was quenched with water and worked up as above to give a crude product from which pure 3-(1,1-bis(phenylthio)ethyl)cyclohexanone (6) was isolated in 88% yield by flash chromatography. 6: ^{1}H NMR δ 0.84–1.98 (m, overlapping a 3 proton singlet at 1.25, 12 H), 7.26–7.42 (m, 6 H), 7.51–7.65 (m, 4 H); IR (neat) 1695 (CO) cm^{-1}; mass spectrum (15 eV), m/e 327 (M$^+$ − CH_3, 4%), 233 (M$^+$ − PhS, 100%); exact mass calcd for $C_{19}H_{19}OS_2$ (M$^+$ − CH_3) 327.0877, found 327.0877.

Conjugate Addition to Carvone. (−)-Carvone (0.12 mL, 0.76 mmol) was added at −78 °C with stirring to a solution of the anion 1 produced as above by using 0.75 mmol of tris(phenylthio)-methane and 0.78 mmol of *n*-butyllithium. After the solution had been stirred for 2 h at −78 °C, *sec*-butyllithium (0.72 mL, 0.83 mmol, 1.15 M solution in cyclohexane) was added. The resulting orange-red solution was then maintained at −45 °C (hexyl alcohol/dry ice bath) for 4.5 h and quenched with a mixture of acetic acid/water. Workup as in the above experiment provided 0.40 g of crude product. Flash chromatography yielded 0.15 g (52%) of 7 and 0.034 g (12%) of a mixture of 9 and 8 in a ratio of 3 to 1. Recrystallization of 7 from pentane afforded white crystals: mp 64.5–65.0 °C; ^{1}H NMR δ 1.13 (d, J = 7.07 Hz, 3 H, CH_3C-2), 1.78 (s, 3 H, allylic CH_3), 2.07 (ddd, J = 14.15, 8.08, 4.04 Hz, 1 H, axial HC-4), 2.34 (m, 2 H, equatorial HC-4 and axial HC-6), 2.50 (m, 1 H, HC-3), 2.64 (dd, J = 15.16, 5.66 Hz, 1 H, equatorial HC-6), 2.75 (m, 1 H, HC-2), 2.92 (m, 1 H, HC-5), 4.42 (d, J = 6.67 Hz, 1 H, *H*C(SPh)$_2$), 4.72 (s, 1 H, vinyl), 4.83 (s, 1 H, vinyl), 7.28 (m, 6 H, Ph), 7.38 (m, 4 H, Ph) [irradiation at δ 1.13 caused the peaks at δ 2.75 to become a doublet, J = 5.26 Hz; irradiation at δ 2.92 caused the peaks at δ 2.07 to become a dd, J = 14.15 and 4.04 Hz, the peaks at δ 2.64 to become a doublet, J = 15.16 Hz, and the peaks at δ 2.34 to become simplified; irradiation at δ 2.50 caused the peaks at δ 4.42 to become a singlet and the peaks at δ 2.07 to become a dd, J = 14.15 and 8.08 Hz; while these NMR data are consistent with structure 7, more definitive evidence was provided by the structure of 8, the epimerization product of 7; the NMR spectrum of 8 conclusively identifies its structure (see below)]; IR (KBr) 1685 (CO), 1640 (C=C) cm^{-1}; mass spectrum (15 eV), m/e 382 (M$^+$, 12%), 273 (M$^+$ − PhS, 100%), 163 (M$^+$ − PhS − PhSH, 57%); exact mass calcd for $C_{23}H_{26}OS_2$ 382.1425, found 382.1412.

The mixture obtained in 12% yield from the above reaction contained mainly 9, which was not separated from 8. Instead, the mixture was subjected to base equilibration to give a mixture of 8 and 10 (see below). The diagnostic peaks in the ^{1}H NMR spectrum of 9 are as follows: δ 1.18 (d, J = 7.28 Hz, 3 H, CH_3C-2), 1.75 (s, 3 H, allylic CH_3), 3.36 (m, 1 H), 4.30 (d, J = 8.89 Hz, 1 H, C*H*(SPh)$_2$), 4.74 (s, 1 H vinyl), 4.80 (br s, 1 H, vinyl). The structural assignment of 9 is clearly established by the conclusive assignment of structure by NMR spectroscopy to its epimerization product 10 (see below).

In a similar run starting from 0.51 g of tris(phenylthio)methane (1.50 mmol) and 0.24 mL of (−)-carvone (1.50 mmol), the reaction mixture was quenched with water (instead of acetic acid/water mixture) at −45 °C and then maintained at ambient temperature overnight before it was worked up. The same workup as above and flash chromatography gave 0.42 g (73%) of 8 and 10 (6:1 by NMR integration). The mixture was further separated by MPLC to provide pure 8 and 10. Compound 8: ^{1}H NMR (C_6D_6) δ 1.02 (d, J = 6.47 Hz, 3 H, CH_3C-2), 1.59 (s, 3 H, allylic CH_3), 1.79 (ddd, J = 13.45, 11.72, 4.65 Hz, 1 H, axial HC-4), 2.06 (dd, J = 13.34, 6.27 Hz, 1 H, axial HC-6), 2.13 (tt, J = 11.0, 3.0 Hz, 1 H, HC-3), 2.36 (br s, 1 H, HC-5), 2.55 (m, 2 H, equatorial HC-4 and equatorial HC-6), 2.64 (m, 1 H, HC-2), 4.70 (d, J = 3.03 Hz, 1 H, *H*C(SPh)$_2$), 4.72 (d, J = 0.81 Hz, 1 H, vinyl), 4.78 (s, 1 H, vinyl), 6.88 (m, 2 H, Ph), 6.99 (m, 2 H, Ph), 7.20 (m, 4 H, Ph), 7.54 (m, 2 H, Ph) [irradiation at δ 1.02 caused the peak at δ 2.64 to become a doublet, J = 11.12 Hz; when the peak at δ 2.36 was irradiated, that at δ 1.79 became a triplet, J = ~12 Hz, and that at δ 2.55 was simplified; irradiation at δ 4.70 caused the peak at δ 2.13 become a td, J = 11.52, 3.03 Hz]; IR (neat) 1703 (CO), 1640 (C=C) cm^{-1}; mass spectrum (15 eV), m/e 382 (M$^+$, 14%) 273 (M$^+$ − PhS, 100%), 163 (M$^+$ − PhS − PhSH, 100%); exact mass calcd for $C_{23}H_{26}OS_2$ 382.1425, found 382.1430. Compound 10: ^{1}H NMR δ 0.93 (d, J = 6.47 Hz, 3 H, CH_3C-2) 1.66 (q, J = 12 Hz, 1 H, axial HC-4), 1.79 (s, 3 H, allylic CH_3), 1.90 (tt, J = 11.92, 2.83 Hz, 1 H, HC-3), 2.23 (tt, J = 10.71, 3.03 Hz, 1 H, HC-5), 2.34 (t, J = 12.53 Hz, 1 H, axial HC-6), 2.47 (ddd, J = 12.33, 3.23, 2.43 (W coupling) Hz, 1 H, equatorial HC-6), 2.57 (ddd, J = 12.94, 3.0, 2.43 (W coupling) Hz, 1 H, equatorial HC-4), 2.80 (m, 1 H, HC-2), 4.62 (d, J = 2.63 Hz, 1 H, *H*C(SPh)$_2$), 4.80 (s, 1 H, vinyl), 4.82 (s, 1 H, vinyl), 7.29 (m, 8 H, Ph), 7.47 (m, 2 H, Ph) [irradiation at δ 4.62 caused the peak at δ 1.90 to become a triplet of doublets, J = 11.92 and 2.83 Hz; irradiation at δ 0.93 caused the peak at δ 2.80 to become a doublet, J = 11.32 Hz; irradiation at δ 1.90

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(12) Seebach, D.; Geisss, K.-H.; Beck, A. K.; Graf, B.; Daum, H. *Chem. Ber.* **1972**, *105*, 3280.

caused the peak at δ 4.62 to become a singlet, that at δ 1.66 to become a broad triplet, that at δ 2.57 to become a broad doublet, and the peak at δ 2.80 to become less complex]; IR (neat) 1703 (CO), 1640 (C=C) cm^{-1}; mass spectrum (15 eV), *m/e* 382 (M^+, 12%), 273 (M^+ - PhS, 100%), 163 (M^+ - PhS - PhSH, 100%); exact mass calcd for $C_{23}H_{26}OS_2$ 382.1425, found 382.1426.

Epimerization of 7 to 8 and 9 to 10. To a solution of **7** (0.044 g, 1.14 mmol) in 3 mL of THF was added an aqueous solution of sodium hydroxide (0.023 g, 0.58 mmol) in water (2 mL). The mixture was stirred at ambient temperature for 0.5 h. Workup as above gave **8** in quantitative yield.

In a similar experiment, a mixture of **7** (R_f 0.59, reversed-phase TLC, 4:1 methanol–water) and **8** (R_f 0.51) was converted to a mixture of **7** and **10** (R_f 0.48) in quantitative yield.

***exo*-7-(Phenylthio)bicyclo[4.1.0]heptan-2-one (12).** Absolute methanol (0.030 mL, 0.75 mmol) was added to a solution of **3** prepared from 0.75 mmol of tris(phenylthio)methane in THF; the orange-red solution turned light yellow and became turbid. Stirring was continued for 20 min before the addition of hexamethylphosphoric triamide (0.26 mL, 1.50 mmol) and methyl iodide (0.047 mL, 0.75 mmol). The mixture was allowed to warm to 25 °C slowly and was maintained at that temperature for a period of 15 h. Quenching with water, the same workup as above, and flash chromatography gave 0.052 g (32%) of pure *exo*-7-(phenylthio)bicyclo[4.1.0]heptan-2-one (**15**): mp 62–63 °C; ^1H NMR δ 1.57–2.38 (m, 8 H), 2.83 (t, J = 3.84 Hz, 1 H, CHSPh),[13] 7.14–7.31 (m, overlapping two singlets at δ 7.29 and 7.31, 5 H); IR (CCl_4) 1695 (CO) cm^{-1}; mass spectrum (15 eV), *m/e* 218 (M^+, 100%); exact mass for $C_{13}H_{14}OS$ (M^+) 218.0765, found 218.0765. The chemical shift of the C-7 proton and the carbonyl frequency are almost identical with those of an analogous compound in the carvone series.[4]

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Registry No. **1**, 14572-78-2; **3**, 97336-66-8; **4** (isomer I), 97336-59-9; **4** (isomer II), 97336-60-2; **5**, 69814-21-7; **6**, 89969-02-8; **7**, 97336-61-3; **8**, 97336-62-4; **9**, 97336-63-5; **10**, 97336-64-6; **12**, 97336-65-7; *sec*-BuSPh, 14905-79-4; tris(phenylthio)methane, 4832-52-4; cyclohex-2-en-1-one, 930-68-7; benzaldehyde, 100-52-7; (−)-carvone, 6485-40-1.

(13) This coupling constant is chaaracteristic of the exo phenylthio group in this system.[4,14]

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Reaction of Perfluoroalkyl Iodides with Electron Donor Nucleophiles. Addition of Perfluoroalkyl Iodides to Olefins Initiated by Electron Transfer†

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The radical chain addition of primary and secondary perfluoroalkyl iodides to olefins is initiated by sodium arene- and alkanesulfinates. The process occurs at room temperature and is favored by the use of dipolar aprotic solvents. The reaction of perfluorooctyl iodide with sodium *p*-toluenesulfinate in the absence of olefin requires higher temperatures and gives only 1-H-perfluorooctane; no anion–perfluoroalkyl radical coupling products were detected. Reaction of perfluorooctyl iodide with the sodium salt of diethyl methylmalonate also gives no coupling product; only 1-H-perfluorooctane and a dimer of the malonate anion are produced. These results are compared with the reactions of perfluoroalkyl iodides with nitronate and thiolate anions where formation of $S_{RN}1$ substitution products was observed.

Several groups[1-7] have described the very facile reactions of perfluoroalkyl iodides with certain electron donor nucleophiles. Reactions of the iodides with enamines,[3] thiolates,[2,4] selenates,[5] sulfinates,[6] enolates,[7] and nitronates[1] result in displacement of iodide by the nucleophiles. Since perfluoroalkyl iodides are known to be very resistant to normal nucleophilic attack,[8] these reactions may proceed by an $S_{RN}1$ mechanism[9-12] (Scheme I).

Scheme I

$$R_fI + Nuc:^- \rightarrow R_fI^-\cdot + Nuc\cdot$$

$$R_fI^-\cdot \rightarrow R_f\cdot + I^-$$

$$R_f\cdot + Nuc: \rightarrow R_f\text{–}Nuc^-\cdot$$

$$R_f\text{–}Nuc^-\cdot + R_fI \rightarrow R_f\text{–}Nuc + R_fI^-\cdot$$

† Contribution No. 3349.

Recently, we presented firm evidence for the $S_{RN}1$ pathway in reactions of the iodides with nitronate[1] and

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