(prepared as described above, but 0.1 M) and of cyclohexanone (0.4 M in THF) were mixed rapidly in a conical flask under nitrogen. The mixture was rapidly hydrolyzed by acidic water (about 2 s after mixing). The reaction product was extracted with diethyl ether, recrystallized, and identified as 2-(1-hydroxycyclohexyl)-2-phenylacetic acid: mp 139 °C (lit. mp 135 °C[3a]); yield 99%. The same result was obtained when the mixture was allowed to react for 5 min after mixing. Similar experiments were performed by using 10 mL of cyclohexanone solution (1.96 M) and 60 mL of Ivanov reagent (0.33 M). The mixture was allowed to react for 2 min at 25 °C before hydrolysis. The yield was 68%, indicating an incomplete reaction (no side reaction). From these data an equilibrium constant of 24 M was calculated, in fair agreement with that estimated from the asymptotic values of transmittance at the end of the kinetic runs.

Kinetic Measurements. Kinetic measurements were performed with an SF-3A Canterbury Stopped-Flow Spectrophotometer (Nortech Laboratories, UK)(optical path = 0.2 cm) equipped with an SFD-2S Variable Ratio Drive Unit and a memory oscilloscope (Hewlett-Packard, 5480A Memory/display), recording the voltage–time curve on a Servotrace recorder (PE Model, Sefram, France). Solutions of cyclohexanone and of the magnesium enediolate in the two reservoirs were shielded from oxygen and moisture by an argon stream. For enediolate titration, aliquots (5 mL) of Ivanov reagent solution were transferred to an argon-filled flask containing 100 μL of DCl/D_2O. Points on the voltage–time curve were converted to transmittances and to absorbances by taking into account oscilloscope-measured voltages for full (concentrated enediolate reagent solutions) and zero (THF only) absorbances. For data at 305–310 nm, least-squares Guggenheim plots were constructed to obtain pseudo-first-order rate constants. At 345 nm, apparent extinction coefficients ($\epsilon \approx 300$ M^{-1} cm^{-1}) were measured before the run from the transmittance data for the initial magnesium enediolate solution and for reagent/THF mixtures obtained by the variable ratio drive unit. Concentration–time curves were calculated with the Lambert–Beer equation, whatever the species in the solution [mono(enediolate) or bis(enediolate)].[13] Equation 4 was tested on a Vax 11 computer (Digital Equipment Corp.) with a Fortran program designed for the calculation of k_2 for a large set of K_{bis} values (typically between 40 and 100 M^{-1}) by a least-squares treatment. K_{bis} was calculated as the abcissa of the cross point between the plot of k_2 *vs.* K_{bis} and the horizontal line corresponding to the k_2 value measured at low concentration (305–310 nm). Usually, this K_{bis} corresponded to the largest value of Z (normal variate),[37] but not necessarily to the largest correlation coefficient, always larger than 0.9995.

The small excess (ca. 10%) of isopropylmagnesium chloride did not introduce errors. Kinetic measurements performed with a larger excess of Grignard reagent (ca. 20% and 50%, respectively) gave k_2 values of 18.3 and 21.3 M^{-1} s^{-1}, whereas under the same conditions, the normal value (with 10% excess) was k_2 = 18.3 M^{-1} s^{-1}. An enediolate solution containing an amount of preformed reaction product equal to that formed during the run yielded similar results (k_2 = 18.4 M^{-1} s^{-1}).

Enediolate Determination in the Ivanov Reagent. The procedure was based on the conversion of magnesium enediolate into 2-*d*-phenylacetic acid by the action of DCl/D_2O and on mass spectroscopy determination of the relative proportions of PhCHDCOOH and $PhCH_2COOH$ (the latter compound was formed by partial hydrolysis from slight moisture contamination during the kinetic procedure). To 5 mL of the Ivanov reagent was added 100 μL of a solution of DCl (20%) in D_2O (%D >99%)(Gold Label, Aldrich). THF was removed under vacuum. HCl (1 mL) was then added and the product was extracted with diethyl ether. After the organic layer had been washed with a saturated solution of NaCl, it was separated and dried with magnesium sulfate. The solvent was removed under vacuum. The resulting material was dissolved in CCl_4 (0.4 mL) and analyzed by mass spectroscopy (75 eV, JEOL JMS 200 spectrometer connected to a JEOL Gas 20K GLO and to a JEOL mass data system computer). The relative peak intensities m/e 91 and 92 (corresponding mainly to $PhCH_2^{+}\cdot$ and to $PhCHD^{+}\cdot$, respectively) were used to determine molar fractions of $PhCH_2COOH$ and PhCHDCOOH from the equation

$$\% \ PhCH_2COOH = 100[1 - 1.084h_{91}/1.084(h_{92} - 0.084h_{91})]$$

Registry No. $PhCH_2CO_2H$, 103-82-2; *i*-PrMgCl, 1068-55-9; *m*-ClC_6H_4CHO, 587-04-2; *p*-ClC_6H_4CHO, 104-88-1; PhCHO, 100-52-7; *m*-MeC_6H_4CHO, 620-23-5; *p*-MeC_6H_4CHO, 104-87-0; *p*-$MeOC_6H_4CHO$, 123-11-5; CH_3CH_2CHO, 123-38-6; $CH_3CH(CH_3)CHO$, 78-84-2; $CH_3C(CH_3)_2CHO$, 630-19-3; MeCOPh, 98-86-2; Me_2CO, 67-64-1; $CH_3CH_2COCH_2CH_3$, 96-22-0; cyclobutanone, 1191-95-3; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8; 2-(1-hydroxycyclohexyl)-2-phenylacetic acid, 5449-68-3.

(37) Draper, N. R.; Smith, H. "Applied Regression Analysis"; Wiley: New York, 1966.

Notes

Preparation of 1-(Phenylthio)cyclopentenes and 1-(Phenylthio)cyclohexenes by the Pummerer Reaction

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The synthetic potential of vinyl sulfides, relatively stable enol derivatives, is already apparent. Grignard reagents under nickel(II) catalysis lead to stereoselective substitution or reduction[1b,c,2] of the vinyl carbon–sulfur bond while palladium-catalyzed substitution of vinyl sulfides gives either 1-aryl or 2-aryl systems.[3] The Vilsmeier reaction produces β-sulfenylated α,β-unsaturated aldehydes.[4] Lead tetraacetate or *N*-bromosuccinimide oxidize the allylic position, with the resulting acetate or bromide serving as an enolonium ion equivalent or as a precursor for sulfenylated enones.[5] Finally, reductive metalation can replace the vinyl carbon–sulfur bond with a metal ion,[6] while ox-

(1) (a) Takei, H.; Sugimura, H.; Miura, M.; Okamura, H. *Chem. Lett.* **1980**, 1209. (b) Wenkert, E.; Ferreira, T. W. *J. Chem. Soc., Chem. Commun.* **1982**, 842. (c) Trost, B. M.; Ornstein, P. L. *J. Org. Chem.* **1982**, *47*, 748. The substitution reaction has recently been extended to vinyl sulfones: Fabre, J. L.; Julia, M.; Verpeaux, J.-N. *Tetrahedron Lett.* **1982**, *23*, 2469.

(2) Trost, B. M.; Ornstein, P. L. *Tetrahedron Lett.* **1981**, *22*, 3463.
(3) Trost, B. M.; Tanigawa, Y. *J. Am. Chem. Soc.* **1979**, *101*, 4743.
(4) Kano, S.; Tanaka, K.; Hibino, S.; Shibuya, S. *J. Org. Chem.* **1979**, *44*, 1580.
(5) Trost, B. M.f Tanigawa, Y. *J. Am. Chem. Soc.* **1979**, *101*, 4413. Trost, B. M.; Lavoie, A. C. *Ibid.* **1983**, *105*, 5075.
(6) Maercker, A.; Jaroschek, H.-J. *J. Organomet. Chem.* **1976**, *116*, 21. Cohen, T.; Matz, J. R. *Synth. Commun.* **1980**, *10*, 311. Cohen, T.; Matz, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6900. Kuwajima, I.; Mori, A.; Kato, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2634. Kuwajima, I.; Abe, T.; Atsumi, K. *Chem. Lett.* **1978**, 383. Duhamel, L.; Chauvin, J.; Messier, A. *J. Chem. Res., Synop.* **1982**, 48.

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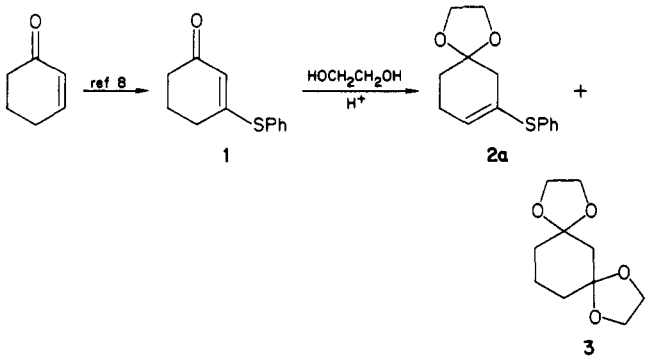
idation leads to vinyl sulfoxides and sulfones, functional groups with considerable potential in organic synthesis.[7]

Our interest in β-sulfenylated enones[8] led us to attempt the preparation of the vinyl sulfide **2** under standard ketalization conditions. The realization of this reaction, together with the chemistry associated with the parent cyclohexenone and the transformations of vinyl sulfides outlined above, would permit the selective activation of all of the carbons in the cyclohexenone ring. In the event, and unlike the bromo analogue of **1** (Br replacing the thioether group in structures **1** and **2**, prepared in a regiorandom manner[9]) the competing formation of the bisketal **3** did not permit isolation of monoketal **2** in synthetically useful yields.

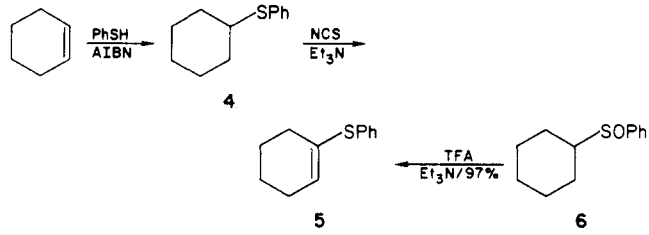


1 **2a** **3**

Because of the expected acid sensitivity of vinyl sulfide ketals **2** and their double-bond isomers **14**, a method was sought to prepare the desired vinyl sulfides under basic conditions. An additional restriction we put on the chemistry to be developed was that it should be able, in principle, to transform cycloalkenones into vinyl sulfides **2** and **14** in a regiospecific manner, the sulfide linkages of **2** and **14** appearing at the β-carbon of the precursor enones. Accordingly, we decided to examine the application of the Pummerer reaction to the above problem.

The Pummerer reaction[10] has resulted in the preparation of cyclic vinyl sulfides from tetrahydrothiapyran 1-oxides[10a,b] and sulfides or sulfoxides with carbonyl substituents on the α or β carbon.[8,10c,d] However, we are aware of only one report on the preparation of vinyl sulfides from cycloalkyl alkyl sulfoxides[11] in systems unactivated by the presence of α- or β-carbonyl groups. The method described, however, failed to give vinyl sulfides in all cases, partly because the alkyl cycloalkyl sulfoxides used had acidic hydrogens on both sides of the sulfoxide moiety.[12] The Pummerer reaction of primary[13] alkyl phenyl sulfoxides is known to give good to excellent yields of acetoxy or trifluoracetoxy sulfides under acidic or basic conditions. After completion of most of the work described below,[14] Jones[15a] and Miller[15b] reported that acyclic phenyl sulfoxides can give vinyl sulfides as major products under certain conditions, thus complementing our results on cyclic systems.

Initially, we sought to extend the *N*-chlorosuccinimide (NCS) oxidation of β-(phenylthio)cyclohexanone[8] to (phenylthio)cyclohexane (**4**) (prepared in quantitative yield by free radical addition of thiophenol to cyclohexene).



4 **5** **6**

While the desired product **5** was obtained, the yields did not exceed 50%, presumably because of the formation of side products derived from the desired vinyl sulfide.[16] Treatment of the sulfoxide **6** (prepared from **4** via peracid oxidation) with methanesulfonyl chloride in the presence or absence of Et_3N resulted in moderate yields of the reduction product, sulfide **4**.

More encouraging results were obtained upon exposure of sulfoxide **6** to classical Pummerer reaction conditions. Refluxing **6** with acetic anhydride in benzene for 36 h gave a mixture of vinyl sulfide **5** and starting material **6**. Trifluoroacetic anhydride (TFA) in CH_2Cl_2 at 0 °C gave little of the desired vinyl sulfide, the major product being the trifluoroacetoxy sulfide. In the presence of Et_3N,[17] however, the product ratio changed dramatically, the vinyl sulfide **5** being formed in a few minutes in 97% isolated yield. In a similar reaction sequence, cyclopentene was transformed into the corresponding vinyl sulfide in 73% overall yield, the lower yield being due to the preparation of an acylated byproduct similar to the major product derived from norbornyl phenyl sulfoxide (**10**) (see below).[18] The sulfoxide **7** (prepared from methylcyclohexene) gave an 11 to 8 ratio of regioisomers **8** and **9** in 91% yield.

Treatment of sulfoxide **10** (prepared from norbornene in 87% yield) with excess TFA and Et_3N resulted in the isolation of a product in 70% yield, whose spectral properties are not consistent with the expected vinyl sulfide **11**. The presence of carbonyl absorption in the IR at 1660 cm^{-1} along with the MS and ^1H NMR data (see the Experimental Section) indicate structure **12** for the product.

(7) For recent applications of vinyl sulfones see: Donaldson, R. E.; Saddler, J. C.; Byrn, S.; McKenzie, A. T.; Fuchs, P. L. *J. Org. Chem.* **1983**, *48*, 2167, and earlier papers in this series.

(8) Bakuzis, P.; Bakuzis, M. L. F. *J. Org. Chem.* **1981**, *46*, 235.

(9) Shih, C.; Swenton, J. S. *J. Org. Chem.* **1982**, *47*, 2825.

(10) (a) Oae, S.; Itoh, O.; Numata, T.; Yoshimura, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 270 and references cited therein. (b) Parham, W. E.; Christensen, L.; Groen, S. H.; Dodson, R. M. *J. Org. Chem.* **1964**, *29*, 2211. Morin, R. B.; Spry, D. O.; Mueller, R. A. *Tetrahedron Lett.* **1969**, 849. (c) Parham, W. E.; Bhavsar, M. D. *J. Org. Chem.* **1964**, *29*, 1575. Monteiro, H. J.; Gemal, A. L. *Synthesis* **1975**, 435. Iwai, K.; Kosugi, H.; Uda, H.; Kawai, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 242. Monteiro, H. J. *J. Org. Chem.* **1977**, *42*, 2324. Kim, C. U.; Misco, P. F.; McGregor, D. N. *J. Org. Chem.* **1982**, *47*, 170. (d) Chen, C. H.; Reynolds, G. A.; Val Allan, J. A. *J. Org. Chem.* **1977**, *42*, 2777. Lane, S.; Quick, S. J.; Taylor, R. J. K. *Tetrahedron Lett.* **1984**, *25*, 1039.

(11) Jones, D. M.; Helmy, E.; Whitehouse, R. D. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1329.

(12) A recent report claims that vinyl selenides were "major products" in the Pummerer reaction of several cyclic selenoxides without, however, giving any details: Marshall, J. A.; Royce, R. D. *J. Org. Chem.* **1982**, *47*, 693.

(13) Sugihara, H.; Tanikaga, R.; Kaji, A. *Synthesis* **1978**, 881. Corey, E. J.; Hoover, D. J. *Tetrahedron Lett.* **1982**, *23*, 3436. Ono, N.; Miyake, H.; Tamikaga, R.; Kaji, A. *J. Org. Chem.* **1982**, *47*, 5017. Kosuge, S.; Hayashi, M.; Hamanaka, N. *Tetrahedron Lett.* **1982**, *23*, 4027.

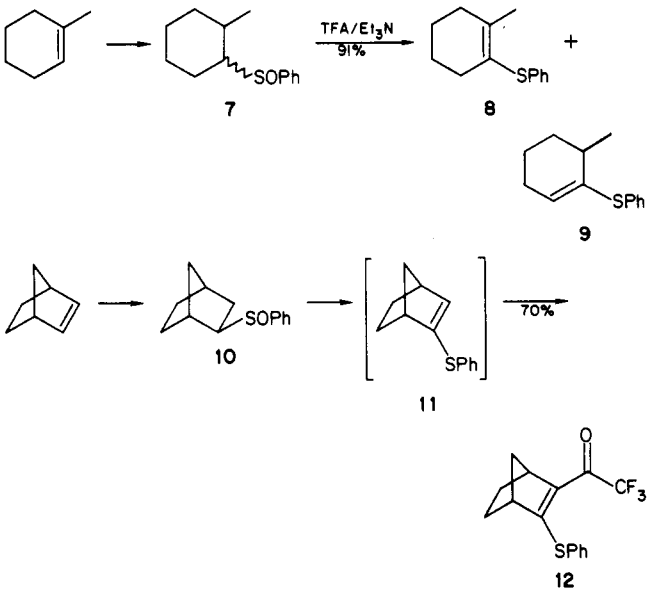
(14) Most of the results described herein were reported in preliminary form at the 33rd Annual Meeting of the Sociedade Brasileira para o Progresso da Ciênc. *Cul. (Sao Paulo), Suppl.* **1981**, *33*, 368; Abst. 02-D.2.3.

(15) (a) Brown, P. J.; Jones, D. N.; Khan, M. A.; Meanwell, N. A. *Tetrahedron Lett.* **1983**, *24*, 405. (b) Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* **1983**, *24*, 2619.

(16) (a) See ref 10d. (b) Sulfuryl chloride oxidation of **4** at −20 °C in the presence of pyridine gives the vinyl sulfide in 67% yield: Fortes, C. C.; Fortes, H. C. C.; Gonçalves, D. C. R. G. *An. Acad. Bras. Cienc.* **1983**, *55*, 235.

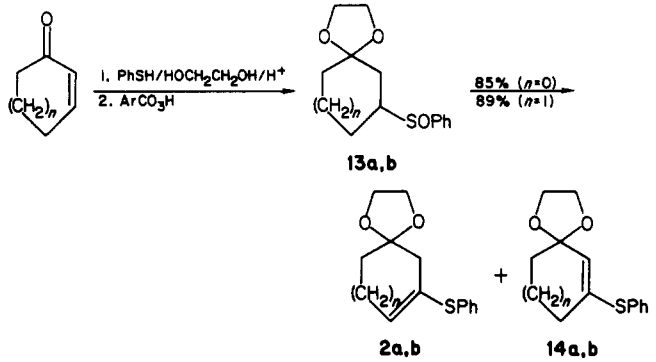
(17) The order of mixing of reagents is important (see Experimental Section) since trifluoroacetic anhydride has been shown to attack Et_3N: Schreiber, S. L. *Tetrahedron Lett.* **1980**, *21*, 1027.

(18) A second compound, not characterized by elemental analysis, was isolated by column chromatography and had the characteristic IR and NMR spectra expected (see Experimental Section) for 1-(phenylthio)-2-(trifluoroacetyl)cyclopentene.



Use of 1 equiv of TFA gave a product mixture consisting of **12**, starting sulfoxide **10**, and less than 15% of vinyl sulfide **11**, a known compound.[19] While we have not submitted compound **11** to our reaction conditions and recognize that electrophilic acylation of vinyl sulfides are rare,[20] being limited to highly reactive substrates and, with the exception of one report,[20a] apparently requiring Lewis acid catalysis, the high strain energy of the norbornene system[21] would be expected to favor such a reaction.

Synthetically more interesting results were obtained from sulfoxides prepared from 2-cyclopentenone and 2-cyclohexenone by acid-catalyzed Michael addition of thiophenol, followed by in situ ketalization[8] and peracid or periodate oxidation. Pummerer rearrangement of cyclohexyl phenyl sulfoxide **13b** gave a 1.3 to 1.0 mixture of



the sensitive vinyl sulfides **2b** and **14b** in 89% yield. The cyclopentyl analogue **13a** gave a 1 to 4.6 mixture, respectively, of the vinyl sulfides **2a** and **14a** in 85% yield. Varying the strength and steric size of bases (NEt_3, pyridine, 2.6-lutidine)[22] or reaction temperature (−40 °C to room temperature) did not significantly influence the product ratio in the cyclohexyl case. Attempted acid-catalyzed equilibration of the vinyl sulfides resulted in decomposition. Slow chromatography of the vinyl sulfide mixtures (see Experimental Section) resulted in the preferential hydrolysis of the sulfides **14** and isolation of the sulfides **2**.

Experimental Section

All reactions were performed under an atmosphere of argon. ^1H NMR spectra were taken on a Varian A-60D or EM-390 instrument with Me_4Si as an internal standard. Trifluoroacetic anhydride was freshly distilled; CH_2Cl_2 was washed with H_2SO_4 and H_2O, dried over $CaCl_2$, and distilled. Triethyl amine, pyridine, and 2,6-lutidine were dried and purified by usual procedures.

Preparation of Sulfides. The sulfides used in this study were prepared by free radical addition of thiophenol to olefins[23] or by acid-catalyzed Michael addition to enones.[8] Representative examples of experimental details are presented below.

2-*exo*-(Phenylthio)bicyclo[2.2.1]heptane. A solution of 2.26 g (24 mmol) of norbornylene, 2.6 mL (25 mmol) of thiophenol, and 0.2 g of azobis(isobutyronitrile) (AIBN) in 5.0 mL of PhH was refluxed for 5 h. After being diluted with ether, the solution was washed with 5% aqueous NaOH, H_2O, and saturated NaCl solution and dried over Na_2SO_4. Removal of solvent gave 4.96 g (101% yield) of 2-*exo*-norbornyl phenyl sulfide,[24] pure by ^1H NMR.

2-Methyl-1-(phenylthio)cyclohexane[25] was prepared as above as the cis/trans mixture in 64% yield (from 1-methyl-1-cyclohexene).

7-(Phenylthio)-1,4-dioxaspiro[4.5]decane. A mixture of 4.0 mL (41 mmol) of 2-cyclohexenone, 5.0 g (81 mmol) of ethylene glycol, 4.4 mL (43 mmol) of thiophenol, and 150 mg of *p*-TsOH in 50 mL of PhH was refluxed under Dean–Stark conditions for 2 h. After cooling, the solution was washed with dilute NaOH solution, H_2O, and saturated NaCl solution and dried over Na_2SO_4. Removal of solvent gave 10.8 g (quantitative yield) of ketal sulfide, used to prepare the sulfoxide **13b** without additional purification: IR (neat) 1600 cm^{-1}; ^1H NMR (CCl_4) δ 1.0–2.2 (m, 8 H), 3.21 (tt, J = 12 and 4 Hz, 1 H), 3.84 (s, 4 H), 7.1–7.5 (m, 5 H).

Preparation of 7-(Phenylthio)-1,4-dioxaspiro[4.4]nonane. The ketal sulfide was prepared from cyclopentenone as above and purified by chromatography on Florisil by elution with 1:1 $CHCl_3$/petroleum ether (98% yield): IR (neat) 1583 cm^{-1}; ^1H NMR (CCl_4) δ 1.4–2.4 (m, 6 H), 3.35–3.75 (m, 1 H), 3.78 (s, 4 H), 7.0–7.57 (m, 5 H); mass spectrum, m/z (relative intensity) 236 (M^+, 5), 127 (100), 109 (11), 83 (26), 65 (14), 55 (97), 41 (19), 39 (21).

Preparation of Sulfoxides. The sulfoxides were prepared in 87% to 99% yield by peracid or periodate oxidation of the above sulfides. Representative examples of experimental details are presented below.

2-*exo*-(Phenylsulfinyl)bicyclo[2.2.1]heptane (10).[25] A mixture of 3.89 g (19.1 mmol) of 2-*exo*-norbornyl phenyl sulfide, prepared as above, and 4.49 g (21.0 mmol) of sodium periodate in 80 mL of methanol was stirred for 18 h at room temperature. After filtration and evaporation of solvent, the residue was chromatographed on 150 g of silica gel. Elution with 10% $CHCl_3$/petroleum ether gave 3.65 g (87%) of sulfoxide **10**: IR (KBr) 1040 cm^{-1}; ^1H NMR (CCl_4) δ 0.65–2.9 (m, 11 H), 7.2–7.8 (m, 5 H).

(Phenylsulfinyl)cyclopentane[23] was prepared as above in 99% crude yield, pure by NMR, but, as noted earlier by Kice,[23] containing an hydroxylic impurity. The sulfoxide used below was purified by filtration through a 200-g silica gel column by elution with $CHCl_3$: IR (neat) 1060 cm^{-1}; ^1H NMR (CCl_4) δ 1.10–2.3 (m, 8 H), 2.7–3.4 (m, 1 H), 7.3–7.8 (m, 8 H).

2-Methyl-1-(phenylsulfinyl)cyclohexane (7) was prepared as above in 93% yield. An analytical sample was prepared by crystallization from petroleum ether: IR (KBr) 1020 cm^{-1}; ^1H NMR (CCl_4) δ 1.25 (d, J = 7.5 Hz, 3 H), 0.9–2.9 (m, 10 H), 7.4–7.9 (m, 5 H). Anal. Calcd for $C_{13}H_{18}OS$: C, 70.22; H, 8.16. Found: C, 70.06; H, 8.06.

(19) Bunnett, J. F.; Creary, X.; Sundberg, J. E. *J. Org. Chem.* **1976**, *41*, 1707.

(20) (a) Hojo, M.; Masuda, R.; Kamitori, Y. *Tetrahedron Lett.* **1976**, 1009. (b) Hase, T. A.; Lahtiner, L. *Ibid.* **1981**, *22*, 3285. Ager, D. J. *Ibid.* **1982**, *23*, 1945. Magnus, P.; Quagliato, D. A.; Huffman, J. C. *Organometallics* **1982**, *1*, 1240.

(21) Freeman, F. *Chem. Rev.* **1975**, *75*, 439.

(22) 2,6-Lutidine was the base that gave the cleanest reaction with **13b**.

(23) Kice, J. L.; Campbell, J. D. *J. Org. Chem.* **1967**, *32*, 1631.

(24) (a) Davies, D. I.; Parfitt, L. T.; Alden, C. K.; Claisse, J. A. *J. Chem. Soc. C* **1969**, 1585. (b) Brown, H. C.; Kawakami, J. H.; Liu, K. T. *J. Am. Chem. Soc.* **1973**, *95*, 2209.

(25) Liu, K. T.; Tong, Y. C. *J. Org. Chem.* **1978**, *43*, 2717.

(Phenylsulfinyl)cyclohexane (6).[23] To an ice-cold solution of 3.84 g (20.0 mmol) of (phenylthio)cyclohexane in 125 mL of $CHCl_3$ was added, in several portions, 3.5 g (20 mmol of *m*-chloroperbenzoic acid. After being stirred for 20 min, the mixture was filtered, and the filtrate was washed with dilute NaOH solution and saturated NaCl solution and dried over Na_2SO_4. The crude residue, 5.08 g, obtained upon evaporation of the solvent, was chromatographed on 150 g of silica gel. Elution with benzene gave 0.41 g of starting material while ether gave 3.6 g (97%) of sulfoxide **6**: IR (KBr) 1040 cm^{-1}; ^1H NMR (CCl_4) δ 0.7–2.05 (m, 10 H), 2.05–2.67 (m, 1 H), 7.35–7.8 (m, 1 H).

7-(Phenylsulfinyl)-1,4-dioxaspiro[4.4]nonane (13a). To an ice-cold mixture of 4.06 g (17.2 mmol) of 7-(phenylthio)-1,4-dioxaspiro[4.4]nonane, prepared above, 1.5 g of $NaHCO_3$, and 150 mL of $CHCl_3$ was added in several portions, 3.49 g (17.2 mmol) of 85% *m*-chloroperbenzoic acid. After being stirred for 1 h, the mixture was worked up as above to give 4.41 g of crude product. Purification by elution with $CHCl_3$ on 150 g of Florisil gave 4.09 g (94%) of the sensitive sulfoxide **13a**: IR (neat) 1030 cm^{-1}; ^1H NMR (CCl_4) δ 1.2–2.5 (m, 6 H), 2.83–3.5 (m, 1 H), 3.75–3.97 (m, 4 H), 7.3–7.8 (m, 5 H); mass spectrum, *m/z* (relative intensity) 252 (M^+, 1.6), 127 (100), 82 (22), 55 (57), 51 (17), 39 (18).

7-(Phenylsulfinyl)-1,4-dioxaspiro[4.5]decane (13b) was prepared as above in 99% yield. An analytical sample was prepared by crystallization of the crude sulfoxide from ether/petroleum ether: mp 76–85 °C; IR (KBr) 1070, 1035, 1025 cm^{-1}; ^1H NMR (CCl_4) δ 1.1–2.3 (m, 8 H), 2.4–3.2 (m, 1 H), 3.65–4.0 (m, 4 H), 7.4–7.8 (5 H); mass spectrum, *m/z* (relative intensity) 141 (M^+ – PhSO, 97), 112 (25), 99 (100), 97 (21), 77 (21), 69 (40), 55 (53), 51 (19), 41 (83). Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81. Found: C, 63.00; H, 6.73.

Preparation of Vinyl Sulfides. The vinyl sulfides were prepared by the dropwise addition of trifluoroacetic anhydride (TFA), diluted with CH_2Cl_2, to a solution of sulfoxide and excess base in CH_2Cl_2.[17] Addition of TFA neat gives mixtures of products that include considerable amounts of trifluoroacetoxy sulfides, products of the "normal" Pummerer reaction, which were shown to be stable under the conditions that lead to vinyl sulfides.

2-(Phenylthio)-3-(trifluoroacetyl)bicyclo[2.2.1]heptene (12). To a solution of 394 mg (1.77 mmol) of sulfoxide **10** and 0.6 mL of Et_3N (4.3 mmol) in 7 mL of CH_2Cl_2 at 0 °C was added a solution of 0.60 mL (4.32 mmol) of TFA in 2.0 mL of CH_2Cl_2 at a rate such that the temperature did not exceed 5 °C. After a total of 1 h at 0–5 °C, the solution was diluted with ether and extracted 3 times with dilute NaOH solution, H_2O, and saturated NaCl solution. After being dried over Na_2SO_4, the solution was evaporated and the residue was chromatographed on 15 g of silica gel. Elution with 1:6 $HCCl_3$/petroleum ether gave 369 mg (70%) of **12**: IR (neat) 1660, 1500 cm^{-1}; ^1H NMR (CCl_4) δ 0.9–2.15 (m, 6 H), 2.85 (m, 1 H), 3.53 (m, 1 H), 7.2–7.7 (m, 5 H); mass spectrum, *m/z* (relative intensity) 298 (M^+, 12), 270 (43), 201 (100), 173 (64), 129 (51), 109 (33). Anal. Calcd for $C_{15}H_{13}F_3OS$: C, 60.39; H, 4.39. Found: C, 60.26; H, 4.39.

The utilization of fewer equivalents of TFA decreased the yield of **12** but did not permit the isolation of 2-(phenylthio)bicyclo-[2.2.1]heptene (**11**) in synthetically significant amounts.

1-(Phenylthio)cyclopentene[5,26] was prepared as above and isolated upon chromatography on silica gel with petroleum ether in 89% yield (on the basis of unreacted starting material) by using 1.5 equiv of TFA in the presence of 2.5 equiv of Et_3N (70% conversion). Use of 2.0 equiv of TFA gave a 76% yield (on the basis of 100% conversion) of 1-(phenylthio)cyclopentene along with a 19% yield of a compound whose spectral characteristics are consistent with 1-(phenylthio)-2-(trifluoroacetyl)cyclopentene: IR (neat) 1670, 1515 cm^{-1}; ^1H NMR (CCl_4) δ 1.65–2.17 (m, 2 H), 2.17–2.6 (m, 2 H), 2.65–3.1 (m, 2 H), 7.15–7.7 (m, 5 H).

1-(Phenylthio)cyclohexene[5,26] was prepared as above from sulfoxide **6** by using 2 equiv of TFA and 2.1 equiv of Et_3N, the vinyl sulfide **5** being isolated in 97% yield by chromatography of the crude product mixture on silica gel with petroleum ether.

1-(Phenylthio)-2-methylcyclohexene (8)[5] **and 2-(phenylthio)-3-methylcyclohexene (9)**[5] were prepared as above from sulfoxide **7** by using 2 equiv of TFA and 2.1 equiv of Et_3N. Chromatography of the crude product mixture on silica gel with petroleum ether gave a 91% yield of vinyl sulfides **8** and **9**, shown by ^1H NMR[5] to be an 11 to 8 mixture, respectively: IR (neat) 1580 cm^{-1}; ^1H NMR (CCl_4) δ for **8** 1.93 (s, 3 H), for **9** 1.12 (d, J = 6.5 Hz, 3 H), 5.97 (m, 1 H).

7-(Phenylthio)-1,4-dioxaspiro[4.4]non-7-ene (2a) and 7-(Phenylthio)-1,4-dioxaspiro[4.4]non-6-ene (14a). To an ice-cold solution of 521 mg (2.07 mmol) of sulfoxide **13a** and 0.9 mL (6.5 mmol) of Et_3N in 5 mL of CH_2Cl_2 was added a solution of 0.44 mL (3.12 mmol of TFA in 1 mL of CH_2Cl_2 at a rate such that the temperature did not exceed 5 °C. Stirring was continued for 2.5 h (the solution coming slowly to room temperature) and the solution was poured into a separatory funnel containing a dilute NaOH solution. After diluting with ether, the organic phase was washed 3 times with dilute base and then dried over K_2CO_3. After removal of solvent, analysis of the residue (520 mg) by ^1H NMR showed that the vinyl sulfides **2a** and **14a** were present in a 1 to 4.6 ratio, respectively. (A similar reaction done in the presence of 2,6-lutidine gave the two vinyl sulfides in a 1 to 2.7 ratio.) Chromatography on 25 g of basic alumina, activity III, with benzene gave 375 mg (85%) of a mixture of vinyl sulfides **2a** and **14a**. Continued elution with 3% EtOH/benzene gave 48 mg of starting sulfoxide. Chromatography on basic alumina, activity I, with benzene gave almost pure **2a**, while the regioisomer **14a** was hydrolyzed, resulting in the isolation of 3-(phenylthio)-2-cyclopentenone.[8] For compound **2a**: IR (neat) 1590 cm^{-1}; ^1H NMR (CCl_4) δ 2.5–2.75 (m, 4 H), 3.85 (s, 4 H), 5.67 (m, 1 H), 7.2–7.6 (m, 5 H). For compound **14a**: IR (neat) 1600 cm^{-1}; ^1H NMR (CCl_4) δ 2.0–2.3 (m, 2 H), 2.3–2.7 (m, 2 H), 3.8 (s, 4 H), 5.2 (t, J = 1.5 Hz), 7.1–7.6 (m, 5 H); mass spectrum of the mixture of **2a** and **14a**, *m/z* (relative intensity) 234 (M^+, 24), 190 (7), 189 (6), 175 (32), 129 (100), 125 (57), 109 (15), 84 (19), 81 (44), 77 (15), 71 (20), 65 (27), 53 (95), 51 (38), 45 (27), 39 (29).

7-(Phenylthio)-1,4-dioxaspiro[4.5]dec-7-ene (2b) and 7-(Phenylthio)-1,4-dioxaspiro[4.5]dec-6-ene (14b). To an ice-cold solution of 353 mg (1.33 mmol) of sulfoxide **13b** in 2 mL of 2,6-lutidine was added a solution of 0.28 mL (1.98 mmol) of TFA in 2 mL of CH_2Cl_2 at a rate such that the temperature did not exceed 5 °C. After 15 min at 2 °C and 1 h at room temperature, the solution was worked up as above. The residue was filtered through a short Florisil column with benzene as eluent then purified further by a rapid chromatography on 27 g of Florisil (benzene eluent) to give 292 mg (89%) of a 1.3 to 1.0 mixture of regioisomers **2b** and **14b**, respectively. Isomer **14b** could not be obtained pure but **2b** was separated from **14b** by slow chromatography on Florisil, the more sensitive **14b** being hydrolyzed on the column. For compound **14b**: IR (neat) 1600 cm^{-1}; ^1H NMR (CCl_4) δ 5.5 (t, J = 1.5 Hz, 1 H). For compound **2b**: IR (neat) 1580 cm^{-1}; ^1H NMR (CCl_4) δ 1.7 (t, J = 6.5 Hz, 2 H), 2.2–2.5 (m, 4 H), 3.83 (s, 4 H), 6.07 (m, 1 H), 7.1–7.5 (m, 5 H); mass spectrum, *m/z* (relative intensity) 248 (M^+, 40). The vinyl sulfide **2b** was oxidized[27] under standard conditions (*m*-chloroperbenzoic acid) to the much more stable sulfone, crystallized from ether/petroleum ether: mp 97–99 °C; IR ($CHCl_3$) 1300, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73 (t, J = 6.5 Hz, 2 H), 2.4 (br s, 2 H), 2.3–2.7 (m, 2 H), 3.9 (s, 4 H), 7.05–7.2 (m, 1 H), 7.45–7.75 (m, 3 H), 7.88–8.1 (m, 2 H); mass spectrum, *m/z* (relative intensity), 280 (M^+, 6), 139 (100), 86 (49), 67 (16), 53 (13); calcd for $C_{14}H_{16}O_4S_1$ 280.0769, found 280.0776.

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Registry No. 2a, 96227-42-8; **2b**, 96227-43-9; **4**, 2206-38-4; **5**, 4922-47-8; **6**, 3324-82-1; *cis*-**7**, 96227-44-0; *trans*-**7**, 96290-74-3; **8**, 67957-91-9; **9**, 85894-85-5; **10**, 65956-70-9; **11**, 58426-16-7; **12**, 96245-25-9; **13a**, 96227-45-1; **13b**, 96227-46-2; **14a**, 96227-47-3; **14b**, 96227-48-4; PhSH, 108-98-5; cyclohexene, 110-83-8; trifluoroacetic anhydride, 407-25-0; trifluoroacetoxy sulfide, 96213-25-1; 1-methyl-1-cyclohexene, 591-49-1; 2-*exo*-(phenylthio)bicyclo-[2.2.1]heptane, 24584-22-3; norbornylene, 498-66-8; *cis*-2-methyl-1-(phenylthio)cyclohexane, 96227-49-5; *trans*-2-methyl-

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(27) We thank Dr. Demnitz for carrying out this reaction.

1-(phenylthio)cyclohexane, 96227-50-8; 7-(phenylthio)-1,4-dioxaspiro[4.5]decane, 96227-52-0; 2-cyclohexenone, 930-68-7; 7-(phenylthio)-1,4-dioxaspiro[4.4]nonane, 96227-51-9; cyclopentenone, 930-30-3; (phenylsulfinyl)cyclopentane, 10181-73-4; phenyl sulfide, 19744-72-0; 1-(phenylthio)cyclopentene, 37053-16-0; 1-(phenylthio)-2-(trifluoroacetyl)cyclopentene, 96227-53-1.

Resolution of *d,l*-2,3-Dibromobutane by Enantiomeric Dehydrohalogenation Effected by Brucine. A Refutation of a Contrary Report

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A number of years ago both Lucas[1] and Winstein[2] reported the partial resolution of *d,l*-2,3-dibromobutane which was achieved by taking advantage of the fact that the antipodal dibromobutanes showed a difference in their rates of reaction with brucine. It was suggested by Lucas that the product of the reaction was the quaternary salt of brucine, since in the resolution of propylene bromide the recovered brucine possessed different properties from the original brucine or from brucine hydrobromide and consisted of equal moles of the two reactants. It was demonstrated that this compound was not a simple complex of the two reagents. The rotation, α^{25}_D −2.04° (1 dm), reported by Lucas[1] was almost the same as that reported by Winstein[2] using the same method, α^{25}_D −2.43° (1 dm).

Subsequent to this report a publication appeared[3] which gave a conflicting report of the results of the reaction: "The partial resolution of *d,l*-2,3-dibromobutane with brucine has been described[1,2] resulting in $[\alpha]_D$ +2.5°.[4] Contrary to the earlier statements, this separation does not depend on preferential destruction of one of the enantiomers. Preferential entrapment of the (+)-dibromide in the brucine crystals is the basis of the separation." The genesis of this statement is found in the Experimental Section of the paper[3] and in the Ph.D. disertation of one of the authors.[5] "To *d,l*-2,3-dibromobutane (28.7 g, 0.14 mol) was added brucine (19 g, 41 mmol). The resulting thick paste was allowed to stand for 3 hr. Part of the 2,3-dibromobutane was pumped off under vacuum; in 16 hr, 18.7 g had distilled, α_{365} −23.6°. The brucine and 2,3-dibromobutane residue were dissolved in 10% H_2SO_4 and extracted with ether. Vacuum trap to trap distillation gave recovered dibromobutane α_{365} +48.7°, 7.4 g" (method A).

During the course of the investigation of the bromination of (−)-2-bromobutane with bromine-81 partially active 2,3-dibromobutane was obtained as the major product.[6] Since the realization of partial optical activity in the 2,3-dibromobutane precluded the intermediacy of a symmetrically bridged β-bromoalkyl radical as a mode for the formation of the largely racemic product, it was necessary to investigate the racemization of the active compound under the reaction and isolation conditions. The published results[3] for the resolution were repeated with the exception that the 2,3-dibromobutane was left in contact with the brucine for 48 h, or longer, before distillation.[6] However, only *trans*-2-bromo-2-butene and partially resolved (−)-2,3-dibromobutane were obtained from either the distillate or the brucine entrapped material. It was qualitatively observed that the amount of optical activity in the recovered 2,3-dibromobutane increased with increasing contact time between the brucine and the dibromide, with a concomitant increase in the amount of olefin formed. Since the report by Skell,[3] that the isolated material with a positive rotation (the entrapped material) was in contact with brucine for a total of <19 h, it did not seem reasonable that the same reaction was not observed (albeit, to a greater extent) at only 2 to 3 times that period of time.

Very recently a note appeared which purported to be a refutation of the observation that the resolution was a result of enantiomericly selective dehydrohalogenation.[7] The authors *republished* their original results. They explained the results of the most recent report[6] and those of Winstein[2] and Lucas[1] as resulting from the prolonged contact time between the halide and the brucine and conceded that the olefin reported[6] was a result of dehydrohalogenation.[8]

Since the method of enantiomeric entrapment is of theoretical and potential practical value, it was important to reinvestigate again and in further detail the possibility that the resolution of the halides, in fact, can be achieved by this interesting method.

The reaction was carried out *exactly* as reported[3,5,7] and as recorded verbatom in this publication. The results of this experiment are listed in Table I, method A. It can be seen from the first entry in the table that (−)-2,3-dibromobutane and *trans*-2-bromo-2-butene were obtained from the distillation of the mixture of the racemic mixture of dihalides and brucine. The isolation of the entrapped organic material from the crystal mass, likewise, yielded only (−)-2,3-dibromobutane and *trans*-2-bromo-2-butene. A mixture of all of the organic material (both the distillate and the isolated entrapped material) also showed a negative rotation. Since preferential enantiomeric entrapment was not found but only, as previously reported,[6] enantiomericly selective dehydrohalogenation was observed, an attempt was made to find a relationship between the amount of elimination and the contact time and the optical rotation obtained and the contact time. The reaction was carried out to both shorter and longer contact times and these results are also listed in Table I, methods A and B. The theory that entrapment and not dehydrohalogenation was responsible for the resolution could be disproved by allowing the materials to remain in contact for 2 or 3 h and instead of distilling the material over a 16-h period the crystal mass was triturated with pentane for 2 h (a condition under which dehydrohalogenation does not occur, see first entry method B) and the rotation of the near quantitatively (>98%) isolated dihalide was taken (method B). It was negative, and the product mixture contained the dehydrohalogenation product, *trans*-2-bromo-2-butene. If entrapment was the method of resolution, then no 2-bromo-2-butene should be present and a corequisite must also be true, that the rotation of the mixture would be zero. Since both of these criteria are simultaneously not met, the entrapment theory, although attractive, must not be

(1) Lucas, H. J.; Gould, C. W. *J. Am. Chem. Soc.* **1942**, *64*, 601.
(2) Winstein, S.; Buckles, R. E. *J. Am. Chem. Soc.* **1942**, *64*, 2780.
(3) Skell, P. S.; Pavlis, R. R.; Lewis, D. C.; Shea, K. J. *J. Am. Chem. Soc.* **1973**, *95*, 6735.
(4) The observed rotation reported in ref 2 was α_D −2.43° (1 dm). The report in ref 3 of the *absolute* rotation as positive must be in error.
(5) Pavlis, R. R. Ph.D. Thesis, Pennsylvania State University, 1969.
(6) Tanner, D. D.; Blackburn, E. V.; Kosugi, Y.; Ruo, T. C. S. *J. Am. Chem. Soc.* **1977**, *99*, 2714.
(7) Pavlis, R. R.; Skell, P. S. *J. Org. Chem.* **1983**, *48*, 1901.
(8) Contrary to the report in ref 7. Neither Lucas[1] nor Winstein[2] reported the formation of olefin from the reaction between *d,l*-2,3-dibromobutane and brucine, since it was assumed[1] that the reaction was the formation of the quaternary salt.

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