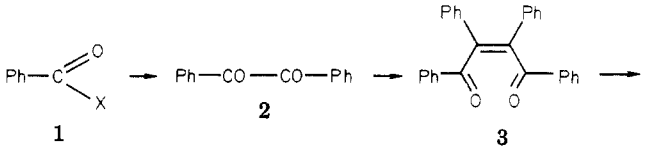
Table I. Product Balance of the Reaction of C_6H_5COX with $LiAlH_4$ + $TiCl_3$

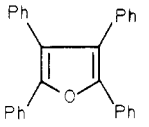
X	% 4	% 3	% 2	% unreacted starting material
OCH_3	30	2	43	20
ONa	10	8	21	45
OH	8	1	10	75
Cl	80	5	10	0
OCH_2CH_3	30	8	40	15
OC_6H_5	10	3	55	20

can reverse this process. Also they are known to produce dibenzoylstilbene from benzil.[11] Third, the titanium reagent will abstract many oxygen- and halogen-containing groups from organic molecules, suggesting that benzil could be formed from C_6H_5COX (X = OCH_3, OH, ONa, Cl, etc.).

Indeed the expected sequence of reactions 1 → 2 → 3 → 4 was observed, although with different X groups in 1



1 2 3



4

the products 2–4 are produced in different relative amounts (see Table I). The reason why benzoyl chloride produces the highest yield of 4 is not yet clear. However, it could be coupled to differences in the Ti species involved in the sequence 2 → 3 → 4. Obviously, the properties of the coupling site can be influenced when different leaving groups (e.g., Cl or OCH_3) become ligands to the low-valent Ti species.

Experimental Section

Instrumentation. The ^1H NMR spectra were recorded on a JEOL PS 100 spectrometer, the IR on a Perkin-Elmer 580 IR-spectrophotometer between 3000 and 600 cm^{-1}, the mass-spectra with a JEOL 01SG2 mass spectrometer, and the UV spectra on a Beckman Model DBGT. Melting points are uncorrected.

Reagents. $TiCl_3$ (Alpha Ventron) and $LiAlH_4$ (Merck) were stored under a nitrogen atmosphere in a glovebox. THF (Aldrich) was dried over Na and $LiAlH_4$ and was distilled under Ar prior to use. Benzoyl chloride, methyl benzoate, ethyl benzoate, phenyl benzoate, and benzoic acid (Aldrich) were used without further purification. All reactions were carried out under argon in Schlenk-type glassware.

Procedure for Reductive Coupling. Lithium aluminum hydride (0.38 g, 0.01 mol) was added in small portions to an ice-cooled slurry of $TiCl_3$ (3.12 g, 0.02 mol) in 80 mL of dry THF under an Ar atmosphere. Immediate H_2 evolution was observed. The resulting black suspension was refluxed for 1 h.

Next, 0.005 mol of carbonyl compound was added in small portions, after which the mixture was refluxed for 24 h. The reaction was stopped by adding 20 mL of 2 N hydrochloric acid and the mixture was extracted with 40 mL of $CHCl_3$ and 40 mL of diethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$. After removal of the solvent, the reaction mixture was separated by column chromatography on alumina. The eluant was petroleum ether–ethyl acetate (10:1). Three reaction products—benzil[13] (mp 95 °C), dibenzoylstilbene[12] (mp 213–214 °C), and tetraphenylfuran[7] (mp 172–174 °C)—were obtained. Melting points and UV, IR, NMR, and mass spectra correspond to those reported.

Acknowledgment. R.D. thanks the Belgian Organisation IWONL for a predoctoral grant. M.M. is grateful for receiving a post-doctoral grant within the framework of the Polish-Belgian Exchange Treaties. We gratefully acknowledge the help of Dr. E. Esmans and Dr. R. Dommisse (University of Antwerp, RUCA) for recording spectra.

Registry No. 1 (X = OCH_3), 93-58-3; 1 (X = ONa), 532-32-1; 1 (X = OH), 65-85-0; 1 (X = Cl), 98-88-4; 1 (X = OCH_2CH_3), 93-89-0; 1 (X = OC_6H_5), 93-99-2; 2, 134-81-6; 3, 6313-26-4; 4, 1056-77-5; $TiCl_3$, 7705-07-9.

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Synthetic Methods and Reactions. 101. Reduction of Sulfonic Acids and Sulfonyl Derivatives to Disulfides with Iodide in the Presence of Boron Halides[1]

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Many sulfonic acid derivatives can be reduced to compounds of lower oxidation state by using traditional reducing agents (metal/acid,[2] HI,[3] SO_3^{2-},[2-4] etc.). Two reports dealing with improved methods to reduce sulfonic acids and their derivatives have appeared in the recent literature. We reported[5] that iodotrimethylsilane or its in situ equivalents can be used to reduce sulfonyl halides and sulfinic acid derivatives to the corresponding symmetrical disulfides under mild, neutral conditions. Oae et al.[6] reported the reduction of sulfonic acids to thiols and thiol derivatives on treatment with trifluoroacetic anhydride/sodium iodide.

All of the reported reductions presumably proceed via initial complexation of a sulfonyl oxygen with a Lewis acid which facilitates stepwise reduction of the sulfur. Our previous work with iodotrimethylsilane and our continued

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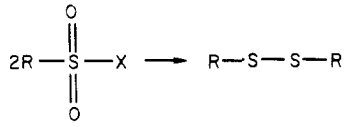
Table I. Reduction of Arylsulfonyl Derivatives to Aryl Disulfides



substrate	reagent	conditions	% yield[a]
$C_6H_5SO_2Cl$	BI_3	*b*	88
	BBr_3/KI/TBAI	*b*	93
p-$CH_3C_6H_4SO_2Cl$	BI_3	*b*	98
	BBr_3/KI/TBAI	*b*	90
p-$BrC_6H_4SO_2Cl$	BI_3	*c*	97
	BBr_3/KI/TBAI	*b*	90
p-$ClC_6H_4SO_2Cl$	BI_3	*c*	98
	BBr_3/KI/TBAI	*b*	89
	BCl_3/KI/TBAI	*d*	30
	BF_3/KI/TBAI	*e*	95
p-$CH_3C_6H_4SO_2F$	BI_3	*f*	98
	BBr_3/KI/TBAI	*f*	98
p-$CH_3C_6H_4SO_2OCH_3$	BBr_3/KI/TBAI	*b*	93
p-$CH_3C_6H_4SO_3H$	BI_3	*f*	97
	BBr_3/KI/TBAI	*f*	96
p-$CH_3C_6H_4SO_3H\cdot H_2O$	BBr_3/KI/TBAI	*f*	96
o-$CH_3C_6H_4SO_3H$	BBr_3/KI/TBAI	*f*	86
$C_6H_5SO_3H\cdot H_2O$	BBr_3/KI/TBAI	*f*	79
p-$CH_3C_6H_4SO_3Ag$	BBr_3/KI/TBAI	*f*	96
n-$C_4H_9SO_3H\cdot H_2O$	BBr_3/KI/TBAI	*f*	64
n-$C_3H_7SO_3H\cdot H_2O$	BBr_3/KI/TBAI	*f*	71

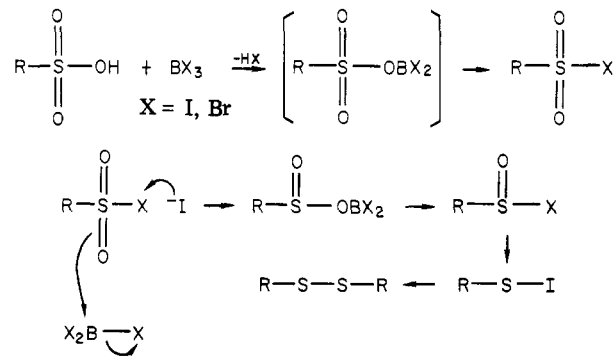
[a] All disulfides gave satisfactory analysis, physical data (melting or boiling point), and NMR and IR spectra. [b] Solvent $CHCl_3$, 16 h at 25 °C. [c] Solvent $CHCl_3$, 16 h at 61 °C (reflux). [d] Solvent CH_2Cl_2, 16 h at 25 °C. [e] Solvent CH_2ClCH_2Cl, 16 h at 80 °C, 1000 psi. [f] Solvent CH_2ClCH_2Cl, 16 h at 80 °C.

interest in Lewis acid catalyzed reactions has prompted us to study the reduction of sulfonic acids and their derivatives with iodide in the presence of boron halides.

In the absence of n-donor solvents, boron halides are particularly potent Lewis acids. In weakly or noncoordinating solvents (dichloromethane, chloroform, 1,2-dichloroethane), sulfonyl chlorides, sulfonyl bromides, sulfinic acids, and sulfinic acid salts and esters are rapidly reduced by iodide at room temperature in the presence of BBr_3 or BI_3 to yield the corresponding symmetrical disulfides (Table I). With BCl_3, the reaction proceeds at a much slower rate, the reduction of sulfonyl halides being only partially complete after 16 h at room temperature. With BF_3, sulfonyl chlorides are not reduced at room temperatures, but at 100 °C, under pressure, the reduction is clean and quantitative.

In the presence of BBr_3 or BI_3, iodide reduces sulfonyl fluorides, sulfonic acids, and sulfonic acid salts and esters as well, although higher temperatures (81 °C, refluxing 1,2-dichloroethane) are required. *These reagents provide the first general method for the reduction of sulfonic acids and sulfonyl fluorides to disulfides.* The reaction is

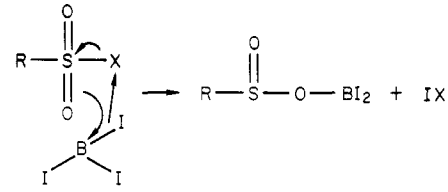
Scheme I



equally applicable to both aliphatic and aromatic sulfonic acids although α-toluenesulfonic acid yields only benzyl bromide and benzyl iodide due to the facile cleavage of the C–S bond in this system.

The reaction with sulfonic acids probably proceeds via initial formation of a sulfonyl bromide (or iodide) followed by stepwise reduction to sulfinyl and then sulfenyl halides which couple to yield symmetrical disulfides (Scheme I).

It should be mentioned that boron triiodide itself is capable of bringing about the above reduction of sulfonyl halides without added iodide. After initial coordination it can act as an internal nucleophile to yield the corresponding sulfinate derivatives.



In a typical reaction, the sulfonic acid is added to a suspension of potassium iodide in a solution of the boron halide in an inert solvent (1,2-dichloroethane). A small quantity of a phase-transfer catalyst (tetra-*n*-butylammonium iodide) is then added and the reaction mixture heated under reflux for 16 h. HX is evolved during the initial phase of the reaction and iodine crystallizes from the solution as the reaction proceeds. Sulfonic acids frequently occur as hydrates but the presence of water does not hinder the course of the reaction provided sufficient excess of the boron halide is employed.

Although all of the boron halides are effective in mediating the reduction of sulfonyl compounds, BBr_3 appears to provide the best compromise between ease of manipulation, lower cost, and high reactivity.

Experimental Section

All sulfonyl halides, sulfonic acids, and derivatives were either commercially available materials of high purity or were synthesized by standard procedures. NMR and IR spectra were recorded on Varian A56/60 and Perkin–Elmer 297 spectrometers, respectively. Melting points were obtained on a Mettler FP-I melting-point apparatus and are uncorrected.

Boron triiodide (Alfa), boron tribromide (Aldrich), and boron trichloride (dichloromethane solution, Alfa) were stored and manipulated in a drybox. A stock solution of boron tribromide (1 mmol/mL) in 1,2-dichloroethane was prepared and stored in a drybox and was manipulated under a flow of dry nitrogen in an efficient hood.

Reduction of *p*-Toluenesulfonic Acid to *p*-Tolyl Disulfide with BBr_3/I^-. Potassium iodide (16.6 g, 100 mmol) was suspended in a stirred solution of boron tribromide (50 mmol) in 1,2-dichloroethane (50 mL) containing a catalytic amount (200 mg) of tetra-*n*-butylammonium iodide. *p*-Toluenesulfonic acid hydrate (2.0 g, 10.2 mmol) was added and the reaction mixture

was heated under reflux for 16 h under a dry nitrogen atmosphere. The reaction mixture was cooled, quenched with ice–water, neutralized with aqueous sodium bicarbonate, and extracted with dichloromethane (2 × 50 mL). The combined organic extracts were washed with saturated sodium thiosulfate solution and dried over anhydrous magnesium sulfate. The solvent was evaporated and the crude product chromatographed on a silica gel column with hexane. Removal of the solvent afforded *p*-tolyl disulfide as a colorless crystalline solid (1.25 g, 96%) mp 48 °C (lit.[7] mp 48 °C).

Reduction of *p*-Chlorobenzenesulfonyl Chloride to *p*-Chlorophenyl Disulfide with BF_3/I^-. A mixture of *p*-chlorobenzenesulfonyl chloride (2.0 g, 9.5 mmol) and potassium iodide (16.7 g, 100 mmol) in 1,2-dichloroethane (30 mL) was placed in a high-pressure stainless-steel bomb (125-mL capacity). The bomb was charged with boron trifluoride gas (Matheson) to a pressure of 1000 psi and the reaction mixture shaken at 80 °C for 16 h. The bomb was cooled, boron trifluoride was vented, and the reaction mixture quenched with ice–water. Workup and purification as described above yielded *p*-chlorophenyl disulfide (1.3 g, 95%) as a colorless crystalline solid, mp 72 °C (lit.[7] mp 73 °C).

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No. Benzenesulfonyl chloride, 98-09-9; 4-methylbenzenesulfonyl chloride, 98-59-9; 4-bromobenzenesulfonyl chloride, 98-58-8; 4-chlorobenzenesulfonyl chloride, 98-60-2; 4-methylbenzenesulfonyl fluoride, 455-16-3; methyl 4-methylbenzenesulfonate, 80-48-8; 4-methylbenzenesulfonic acid, 104-15-4; 2-methylbenzenesulfonic acid, 88-20-0; benzenesulfonic acid, 98-11-3; Ag(I) 4-methylbenzenesulfonate, 16836-95-6; butanesulfonic acid, 2386-47-2; propanesulfonic acid, 5284-66-2; diphenyl disulfide, 882-33-7; bis(4-methylphenyl) disulfide, 103-19-5; bis(4-bromophenyl) disulfide, 5335-84-2; bis(4-chlorophenyl) disulfide, 1142-19-4; bis(2-methylphenyl) disulfide, 4032-80-8; dibutyl disulfide, 629-45-8; dipropyl disulfide, 629-19-6; BI_3, 13517-10-7; BCl_3, 10294-34-5; BBr_3, 10294-33-4; KI, 7681-11-0; TBAI, 311-28-4.

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Elimination Reactions in 1-Amino-2-phenylhexahydroazepine Derivatives

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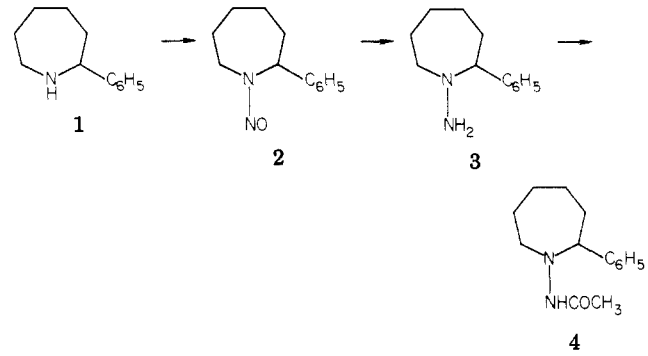
Aminimides derived from 2-phenylpyrrolidine[2] and 2-phenylpiperidine[3] upon being heated undergo ring expansion to the phenylhexahydropyridazine and phenylhexahydrodiazepine derivatives, respectively, and cleavage to the corresponding amine and isocyanate. Studies aimed at extending this reaction to the 2-phenylperhydroazepine series reveal a different behavior which is reported here.

The reaction sequence used for preparation of the key intermediate **4** paralleled that used for the homologues. The next reaction, which involved treating 1-acetamino-2-phenylperhydroazepine (**4**) with methyl iodide, did not give the desired 1-acetamino-1-methyl-2-phenylperhydroazepinium iodide (**5**) but yielded instead 1-(acetyl-



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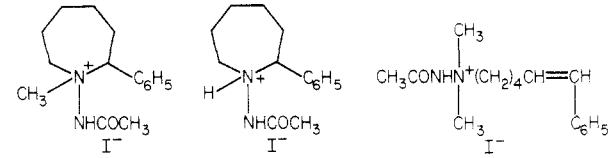
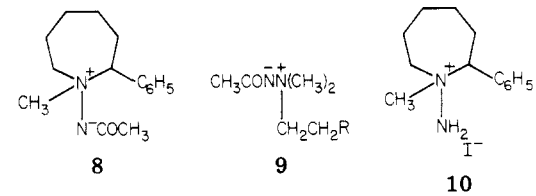
amino)-2-phenylperhydroazepine hydroiodide (**6**) and 1-



5 6 7

acetyl-2,2-dimethyl-2-(6-phenyl-5-hexenyl)hydrazinium iodide (**7**). The structure of the hydroiodide **6** was shown by its synthesis from **4**, and that of **7** was based on its IR and NMR spectra. The coupling constant of 16 Hz for the olefinic protons suggested trans stereochemistry about the double bond.

These results indicated that methylation of **4** occurred normally and that the resulting salt **5** was converted by **4** into the hydroiodide **6** and the desired aminimide (**8**).



8 9 10

This product (**8**) is not stable at the boiling point of acetonitrile but undergoes elimination and forms 1-acetyl-2-methyl-2-(6-phenyl-5-hexenyl)hydrazine which upon methylation gave the salt **7**, which was isolated. None of the rearranged product from the aminimide **8**, 1-methyl-2-acetyl-3-phenylperhydro-1,2-diazocine,[4] or fragmentation product 1-methyl-2-phenylperhydroazepine were detected among the reaction products.

Eliminations have been reported with aminimides of type **9** in the alicyclic series, usually at the melting point of the compound.[5] The facile elimination observed in the present work is unusual since the five- and six-membered homologues are isolable and show little propensity for elimination. A possible explanation for this behavior is the ability of the seven-membered ring to attain the proper stereochemical relationship for intramolecular elimination. Assuming that the perhydroazepine ring system will not differ greatly from cycloheptane, a twisted chair form[6] would be the preferred arrangement over other alternatives. An axial acetamino group in the 1-position would allow excellent overlap of a hydrogen on the 3-carbon by the carbonyl group.

An intramolecular process has likewise been proposed to explain the facile elimination observed with 1-methyl-

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