lation at the STO-3G level and find that neutral ascorbate has a higher electron density at O2 than at O3. An experimental indication comes from consideration of the dianion; in the dianion, it is clear that O2 is about 4 powers of 10 more basic than O3. There is synthetic evidence that in the dianion, reaction at O2 is more rapid.[6]

It is also clear that long reaction times or addition of protic solvents results in high yields of 2-ester. A reaction mixture which was predominantly 3-ester was converted to 2-ester if methanol was deliberately added. Therefore there is evidence that one reason for production of 2-esters is that a 3-ester can be initially produced but converted to a 2-ester.[29,47]

Acknowledgment. We thank Joyce Wilde for assistance with NMR spectra and Lucile Blanchard for assistance with the preparation of the manuscript. The NMR spectrometer was purchased, in part, by a grant from the Dreyfus Foundation.

Registry No. **1**, 15042-01-0; **2**, 116565-54-9; **3**, 116565-55-0; **4**, 32643-49-5; **5**, 116565-56-1; **6**, 14200-03-4; **7**, 116565-57-2; **8**, 116565-58-3; **9**, 116565-59-4; **10**, 116565-60-7; **11**, 29881-30-9; **12**, 109620-91-9; **13**, 116565-61-8; **14**, 116565-62-9; **15**, 116565-63-0; $Ph_2P(O)Cl$, 1499-21-4.

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Organic Reactions of Reduced Species of Sulfur Dioxide[1a]

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Rongalite (sodium hydroxymethanesulfinate or sodium formaldehydesulfoxylate) reacts with organic halides in a variety of ways depending on the structure of the organic compound. Benzyl and other alkyl halides give sulfones in generally good yields; but in several cases, reduction (2,4-dinitrobenzyl bromide, phenacyl halides) or coupling (*p*-nitrobenzyl bromide under basic conditions, phenacyl bromide or iodide) of the halide occurs. Addition of sodium iodide to the mixture of Rongalite and phenacyl chloride changed the reaction from one of complete reduction to acetophenone to one of mainly dimerization to 1,4-diphenyl-1,4-butanedione. The amount of acetophenone from phenacyl bromide depends on the water content of the reaction mixture, more dimer being formed when little water is present. Diphenacyl sulfone is formed from phenacyl bromide and Rongalite in the presence of excess sulfur dioxide. The intermediate β-keto sulfinate is believed to normally lose sulfur dioxide very readily to give the enolate anion, which either is protonated to give acetophenone or reacts with phenacyl halide to give the butanedione. In the presence of excess sulfur dioxide, the loss of sulfur dioxide from the sulfinate is suppressed, allowing sulfone formation to occur by reaction of the sulfinate with phenacyl halide. *o*-Xylylene dibromide gave *o*-xylylene, trapped as the Diels-Alder adduct with norbornene, along with the expected cyclic sulfone and cyclic sulfinate ester (sultine). A convenient synthesis of the sultine in 78% yield is achieved by treatment of α,α'-dichloro-*o*-xylene with Rongalite and sodium iodide. Treatment of Rongalite in DMF–H_2O with sulfur dioxide gives the blue anion radical complex $(SO_2)(SO_2^{\bullet -})$. Anion radicals are produced from *p*-dinitrobenzene and *p*-nitrobenzoate ion when they are treated with Rongalite.

Introduction

Reduced species of sulfur dioxide such as $SO_2^{\bullet -}$ and SO_2^{2-} are formed by the interaction of sulfur dioxide with the dihydropyridine coenzyme NADPH[2] and also with 1-benzyl-1,4-dihydronicotinamide,[3] a model for the important pyridine nucleotide coenzymes. The production of these anions by the interaction of sulfur dioxide with biological reducing agents may be significant with respect to the toxic effects of this common pollutant on plants and animals, particularly since $SO_2^{\bullet -}$ is said to be formed in an aqueous medium.[4,5] While the reaction of sulfur dioxide with organic compounds has been widely investigated and while much significant and fascinating chemistry has been discovered,[6] there has been relatively little attention paid to the organic chemistry of reduced species of sulfur dioxide.[7,8a] The potential biological significance of these species is one reason for the study of their reactivity with organic compounds. In addition, these anions may be useful intermediates in organic chemistry.

In a search for a more accessible laboratory source of reduced species of sulfur dioxide (other than sulfur dioxide

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(1) (a) Reported in part at the 189th National Meeting of the American Chemical Society, Miami, FL, April 1985; Abstract ORGN 51. (b) Taken in part from the Ph.D. Thesis of W. F. Jarvis, Syracuse University, 1988.

(2) Gause, E. M.; Greene, N. D.; Meltz, M. L.; Rowlands, J. R. *Biological Effects of Environmental Pollutants*; Lee, S. D., Ed.; Ann Arbor Science: Ann Arbor, 1977; p 273.

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(4) Eickenroht, E. Y.; Gause, E. M.; Rowlands, J. R. *Environ. Lett.* **1975**, *9*, 279.

(5) Aqueous solutions of sulfur dioxide consist of hydrated sulfur dioxide. There is no evidence for the hypothetical sulfurous acid: Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Saunders: Philadelphia, 1977; p 345. Steudel, R. *Chemistry of the Non-Metals*; English Ed.; Nachod, F. C.; Zuckerman, J. J., Ed.; de Gruyter: Berlin, 1977; p 222.

(6) For examples, see: (a) Burgess, E. M.; Zoller, U.; Burger, R. L., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 1128. (b) Masilamini, D.; Manahan, E. H.; Vitrone, J.; Rogic, M. M. *J. Org. Chem.* **1983**, *48*, 4918. (c) El Sheikh, S. I. A.; Smith, B. C.; Soebir, M. E. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 308.

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(8) (a) Gibson, H. W.; McKenzie, D. A. *J. Org. Chem.* **1970**, *35*, 2994. (b) The kinetics of the decomposition of Rongalite to SO_2^{2-} and reduction of an azo dye has been investigated: Polenov, U. V.; Labutin, A. N.; Tsareva, A. A.; Budanov, V. V. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1987**, *30*, 63; *Chem. Abstr.* **1988**, *108*, 130843.

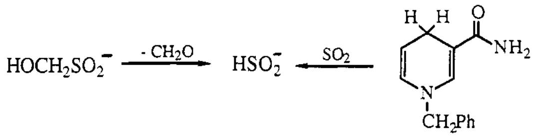
0022-3263/88/1953-5750$01.50/0

Table I. Reactions of Halides (RX) with Rongalite

R	X	products (yields)
$PhCH_2$	Br	$(PhCH_2)_2SO_2$ (86–88)[a] (44)[b] (74)[c] (63)[d]
$PhCH_2$	Cl	$(PhCH_2)_2SO_2$ (72),[e] $PhCH_2SO_2CH_2OCH_2Ph$ (2)[e]
$4\text{-}BrC_6H_4CH_2$	Br	$(4\text{-}BrC_6H_4CH_2)_2SO_2$ (70)[a] (52)[b] (56)[c]
$4\text{-}ClC_6H_4CH_2$	Br	$(4\text{-}ClC_6H_4CH_2)_2SO_2$ (70)[a]
$4\text{-}FC_6H_4CH_2$	Br	$(4\text{-}FC_6H_4CH_2)_2SO_2$ (62)[a]
$4\text{-}CH_3C_6H_4CH_2$	Br	$(4\text{-}CH_3C_6H_4CH_2)_2SO_2$ (65)[a] (54)[c]
$2\text{-}CH_3C_6H_4CH_2$	Br	$(2\text{-}CH_3C_6H_4CH_2)_2SO_2$ (77)[a]
$4\text{-}NCC_6H_4CH_2$	Br	$(4\text{-}NCC_6H_4CH_2)_2SO_2$ (45)[b]
$3\text{-}O_2NC_6H_4CH_2$	Br	$(3\text{-}O_2NC_6H_4CH_2)_2SO_2$ (60)[b]
$4\text{-}CF_3C_6H_4CH_2$	Br	$(4\text{-}CF_3C_6H_4CH_2)_2SO_2$ (47)[b]
$CH_3(CH_2)_2CH_2$	Br	$[CH_3(CH_2)_3]_2SO_2$ (46)[a]
$Br(CH_2)_5$	Br	$\overline{CH_2(CH_2)_3S}O_2$ (43)[a]
$CH_2{=}CHCH_2$	Br	$(CH_2{=}CHCH_2)_2SO_2$ (20)[c] (3),[b] $CH_2{=}CHCH_3$ (trace)[b]
$4\text{-}O_2NC_6H_4CH_2$	Br	$(4\text{-}O_2NC_6H_4CH_2)_2$ (34),[a] $(4\text{-}O_2NC_6H_4CH_2)_2SO_2$ (78)[b] (83)[c]
$2,4\text{-}(O_2N)_2C_6H_3CH_2$	Br	$2,4\text{-}(O_2N)_2C_6H_3CH_3$ (59)[f]
$PhCOCH_2$	Cl	$PhCOCH_3$ (93)[b] (30),[g] $(PhCOCH_2)_2$ (70)[g]
$PhCOCH(Ph)$	Cl	$PhCOCH_2Ph$ (58)[a] (72)[i]
$PhCOCH_2$	Br	$(PhCOCH_2)_2$ (19)[a] (52)[b] (75),[h] $PhCOCH_3$ (70)[a] (43)[b] (25)[h] (30),[j] $(PhCOCH_2)_2SO_2$ (55)[j]
$4\text{-}PhC_6H_4COCH_2$	Br	$4\text{-}PhC_6H_4COCH_3$ (66)[a] (51),[b] $(4\text{-}PhC_6H_4COCH_2)_2$ (20)[a] (40),[b] $(4\text{-}PhC_6H_4COCH_2)_2SO_2$ (55)[j]

[a] DMF (1.8)–H_2O (1), $KHCO_3$, N_2, 80 °C. [b] DMF (1.8)–H_2O (1), N_2, 80 °C. [c] DMF (1.8)–H_2O (1), N_2, 50 °C. [d] H_2O, $[CH_3(CH_2)_5]N^+(CH_3)_3$, Br^-, N_2, 50 °C. [e] EtOH (1)–H_2O (1), NaOH, 95 °C. [f] DMF (1)–H_2O (1), room temperature. [g] DMF, NaI (10%), room temperature. [h] DMF, room temperature. [i] DMF (1.8)–H_2O (1), N_2, 25 °C. [j] DMF, SO_2, room temperature.

itself either in combination with electrochemistry or a dihydropyridine), we turned to Rongalite, sodium hydroxymethanesulfinate dihydrate (also called sodium formaldehydesulfoxylate), the trade name being derived from its use as a discharge ("rongeage" in French) or decolorizing agent in cloth printing. Rongalite may be considered an adduct of sodium hydrogen sulfoxylate ($NaHSO_2$) with formaldehyde and is a possible source of HSO_2^- and SO_2^{2-},[8b] purported intermediates that we have previously trapped in the reduction of sulfur dioxide by a dihydropyridine.[3] These anions may be good nucleophiles because of the alpha effect[9] and also may be one-electron donors to appropriate substrates.



A few accounts appear in the literature concerning the reaction of Rongalite with organic compounds other than dyes. A 1908 report describes the formation of dibenzyl sulfone from Rongalite and benzyl chloride in alcoholic sodium hydroxide,[10] and the addition of Rongalite to activated double bonds and quinones to give symmetric sulfones has been described.[11-14] The latter type of reaction is a clear parallel to the trapping experiments with Michael acceptors that we reported in connection with the reaction of sulfur dioxide with 1-benzyl-1,4-dihydronicotinamide.[3] Acidified Rongalite reduces benzils to benzoins[13] and is reported to yield $SO_2^{\bullet -}$.[15] The reduction of ketones by thiourea *S*,*S*-dioxide (another potential source of sulfoxylate species) was later shown to be the result of a Meerwein–Ponndorf–Verley reduction ensuing from ambient alcohol solvent.[16a] The only aromatic halides reported to react with Rongalite to give an aryl sulfinate are 1-bromo- and 1-chlorobenzanthrone.[16b] These reactions probably proceed by an S_NAr mechanism because of the presence of the activating carbonyl group.

Results and Discussion

In order to determine if Rongalite could produce the same sulfur intermediates formed in the reduction of sulfur dioxide by 1-benzyl-1,4-dihydronicotinamide, we treated it with sulfur dioxide under similar conditions. A deep blue solution of the sulfur dioxide complex of $SO_2^{\bullet -}$ was obtained, identified by electron spin resonance and ultraviolet spectra[17,18] as being the same species observed in the dihydronicotinamide reaction.[3] This indicates that Rongalite, or one of the sulfur anions derived from it, is acting as an electron donor to SO_2. A further parallel to the SO_2–dihydropyridine reaction, the formation of sulfones from Michael acceptors and Rongalite, has already been noted.[11-14]

$$HOCH_2S\bar{O}_2 + 3SO_2 \longrightarrow 2(SO_2)(SO_2)^{\bullet -}$$

Aliphatic Halides. Treatment of benzyl chloride with Rongalite in alkaline ethanol gave dibenzyl sulfone as previously reported.[10] A byproduct, for which formula **3** was suggested by Fromm, was obtained in low yield. We have verified structure **3** by spectroscopic techniques unavailable to him. This reaction also produced the sodium salt of phenylmethanesulfinic acid, **2**. The products could be formed by either of two possible mechanisms (Scheme I). In one mechanism, the protonated sulfoxylate ion, HSO_2^-, produced by the decomposition of the Rongalite, reacts as a nucleophile to displace chloride ion, giving the sulfinate salt **2**. The sulfinate may react with formaldehyde formed in the decomposition of Rongalite to give an intermediate, **1**, which reacts with another molecule of benzyl chloride to give byproduct **3**. The sulfinate salt **2** may also react with benzyl chloride to give dibenzyl sul-

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(9) March, J. *Advanced Organic Chemistry*, 3rd ed.; McGraw-Hill: New York, 1985; p 310. In sulfoxylate ion (SO_2^{2-}), there are seven or eight lone pairs of electrons, the number depending on which Lewis structure one uses.

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(17) Martin, R. P.; Sawyer, D. T. *Inorg. Chem.* **1972**, *11*, 2644.

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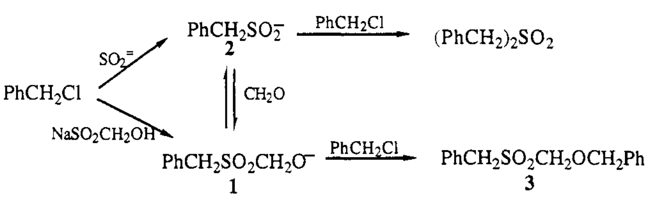
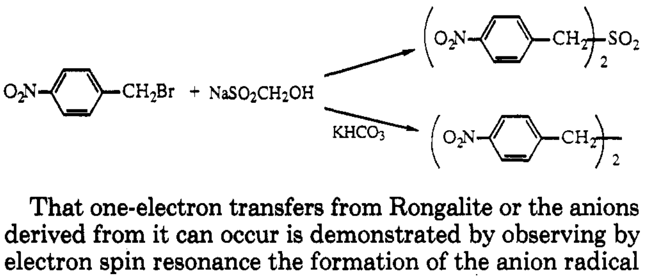
Scheme I



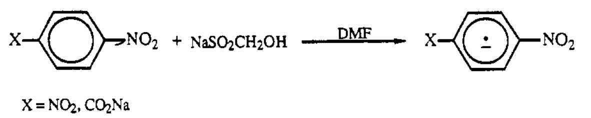
fone. The other mechanism involves displacement of chloride ion from benzyl chloride by Rongalite to give **1** followed by either loss of formaldehyde to give sulfinate **2** or reaction with benzyl chloride to give **3**. Salts of sulfinic acids are known to react with alkyl halides to give sulfones.[19] They also react with aldehydes to give α-hydroxy sulfone adducts.[20]

A number of benzyl bromides gave dibenzyl sulfones in good yields when treated with Rongalite in aqueous *N,N*-dimethylformamide (DMF). Tetramethylene sulfone, di-*n*-butyl sulfone, and diallyl sulfone were obtained from 1,4-dibromobutane, *n*-butyl bromide, and allyl bromide, respectively (Table I). With the latter, a trace of propene was formed, identified by comparison of its gas-phase infrared spectrum with that of an authentic sample. The propene formation requires further investigation but may be related to other reductions described below.

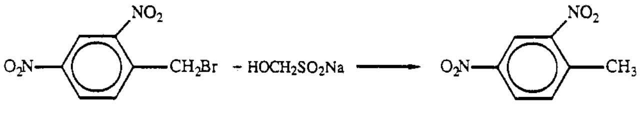
Addition of potassium bicarbonate to the reaction mixture of Rongalite and *p*-nitrobenzyl bromide gave a different result. Instead of sulfone, a 34% yield of *p,p′*-dinitrobibenzyl was obtained. This change in product with addition of a base signifies a change in mechanism, possibly to one involving a single-electron transfer from SO_2^{2-}, formed by deprotonation of HSO_2^-, the dinegative charge on the anion making it a better electron donor than HSO_2^-. The addition of bicarbonate to the reactions of less electrophilic aliphatic halides had essentially no effect. Substrates containing nitro groups are known to accept electrons readily and to undergo substitution via radical anions ($S_{RN}1$ mechanism).[21] The bibenzyl could be formed by dimerization of the benzyl radical as was observed in the treatment of *p*-nitrotoluene with potassium *tert*-butoxide.[22] Alternatively, the dimer could be formed by attack of the SO_2^{2-} nucleophile on bromine to give the *p*-nitrobenzyl anion, which could displace bromide ion from another molecule of halide either by an $S_{RN}1$ mechanism[21c,23] or an S_N2 mechanism. The *p*-nitrobenzyl anion also could be produced by loss of sulfur dioxide from the (*p*-nitrophenyl)methanesulfinate anion or by reduction of the radical by sulfoxylate.



That one-electron transfers from Rongalite or the anions derived from it can occur is demonstrated by observing by electron spin resonance the formation of the anion radical of *p*-dinitrobenzene or *p*-nitrobenzoate ion when these compounds are treated with Rongalite. Control experiments in which Rongalite was omitted indicated that no observable radicals were present. Both of these anion radicals are known species.[24,25] The *p*-nitrobenzoate anion radical also has been obtained by treating *p*-nitrobenzoate ion with alkaline sodium dithionite believed to contain $SO_2^{\bullet -}$.[26]



Treatment of 2,4-dinitrobenzyl bromide with Rongalite gave 2,4-dinitrotoluene, whereas with *p*-nitrobenzyl bromide no *p*-nitrotoluene was observed. These results may be related to different stabilities of intermediate radicals or anions and to hindrance of dimerization when an ortho substituent is present.



o-Xylylene dibromide gave a result different from that observed with other benzyl halides upon treatment with Rongalite. At 80 °C, the main isolated product is poly-*o*-xylylene. When the reaction is run at 40 °C, the sultine, 4,5-benzo-3,6-dihydro-1,2-oxathiin 2-oxide, **5**, is isolated in 43% yield along with the poly-*o*-xylylene. When the reaction is run in the presence of norbornene, the Diels-Alder adduct of *o*-xylylene, **4**, is produced along with the sultine **5** and sulfone **6** (1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide). The sultine could be converted to the sulfone upon heating to 80 °C. The sultine is known to generate *o*-xylylene (*o*-quinodimethane) at 80 °C, which can be trapped as a Diels-Alder adduct with a dienophile or react with sulfur dioxide to give the sulfone through a chelotropic process.[27a,b] Formation of the sultine, **5**, could occur by simple displacement of one of the bromine atoms to produce the sulfinate, which reacts intramolecularly. The sultine also has been reported as a product of the electrolysis of sulfur dioxide in the presence of *o*-xylylene dibromide.[7c] The sulfone **6** is stable and does not form *o*-xylylene under these reaction conditions, the reverse chelotropic process requiring temperatures of around 300 °C.[27a] The trapping of *o*-xylylene by norbornene has precedent in investigations of reactions of *o*-methylbenzyl ethers with lithium *N,N*-dialkylamides.[28a] Sultine **5** can be obtained in 78% yield by treatment of α,α'-dichloro-*o*-xylene with Rongalite and the nucleophilic catalyst sodium iodide in DMF. This new method of generation of sultine **5** appears to be more convenient than the multistep processes reported earlier.[27a,b] Generation of *o*-xylylene from the sultine has advantages over methods involving zinc and the dihalide (not useful in the presence of reducible groups) or the fluoride ion catalyzed decomposition

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(25) *p*-Dinitrobenzene anion radical: Geske, D. H.; Ragle, J. L.; Bambenek, M. A.; Balch, A. L. *J. Am. Chem. Soc.* **1964**, *86*, 987.

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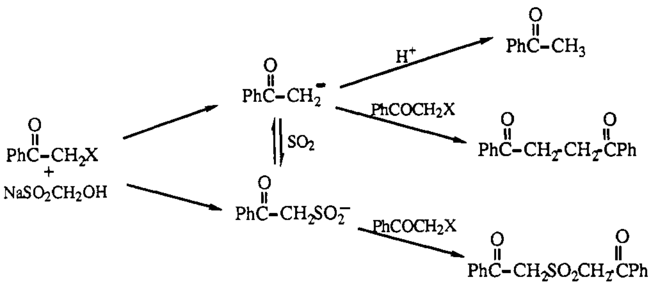
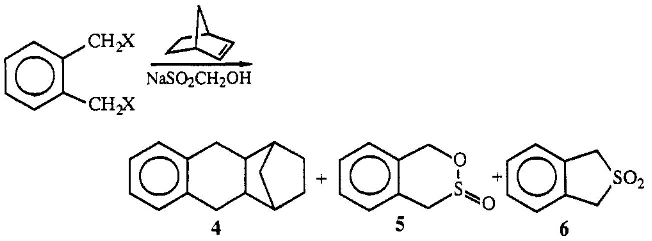
Scheme II



of [*o*-[(trimethylsilyl)methyl]benzyl]trimethylammonium bromide (unwanted enolization occurs in quinone adducts).[28b]



4 5 6

Phenacyl Halides. Phenacyl halides are good alkylating reagents, and they also have been reduced to acetophenones with a variety of reagents,[29] including sodium dithionite.[30,31] Phenacyl bromide has been reported to react with electrochemically reduced sulfur dioxide to give diphenacyl sulfone.[7c]

We observed that phenacyl chloride gave acetophenone in 85% isolated yield on treatment with Rongalite; desyl chloride was likewise reduced to deoxybenzoin. Phenacyl bromide, when treated with Rongalite in aqueous DMF with bicarbonate, gives acetophenone (70%) and a coupling product, 1,4-diphenyl-1,4-butanedione (19%). When the phenacyl bromide is reacted in DMF with no water present except that in the Rongalite dihydrate, the yield of the dione is 75% and that of the acetophenone, 25%. When phenacyl chloride is reacted under the same conditions, only acetophenone is produced and no dione is observed. When a 10% molar amount of sodium iodide is added to the reaction with phenacyl chloride, the major product is the dione (75%). Reaction of Rongalite with phenacyl bromide/chloride and 1 molar equiv of sodium iodide (making phenacyl iodide in situ) or with preformed phenacyl iodide also gave the dione as the major product (75%). This reaction promises to be a convenient way to prepare symmetrical 1,4-diones from α-halo ketones.

In the reactions where the dione was the major product, a small amount (<2%) of the diphenacyl sulfone was produced. This sulfone was removed from the organic phase with base. It has the same NMR spectrum and melting point as previously reported.[7c] The sulfone is the major product (yields >50%) when the reaction is run in the presence of excess sulfur dioxide.

The explanation most consistent with these results is that phenacyl sulfinate is produced by a nucleophilic attack upon the phenacyl halide by Rongalite (Scheme II). If this sulfinate reacted with another molecule of phenacyl halide, the sulfone would be the product. Loss of sulfur dioxide from the sulfinate salt would yield the enolate anion of acetophenone. This anion could either become protonated to give acetophenone or react with another molecule of phenacyl halide to give the dione. This would explain why the dione is the major product in the anhydrous phenacyl bromide and iodide reactions and not in the chloride reaction, since the bromide and iodide are more reactive electrophiles than the chloride and thus more likely to trap the anion. Enolate anion formation would explain why the yield of the dione is dependent upon the amount of water present in the reaction, more water diverting the anion to give an increased yield of acetophenone. The small amount of phenacyl sulfone produced indicates that the phenacylsulfinate ion, $PhCOCH_2SO_2^-$, decomposes preferentially, even at room temperature, to the enolate anion rather than undergoing a bimolecular reaction with a molecule of phenacyl halide. The relatively weak carbon–sulfur bond in the β-keto sulfinate would make the latter less stable than the salts of β-keto carboxylic acids.[32a] If sufficient sulfur dioxide is present, it can compete with the other electrophiles present to divert the enolate anion of acetophenone back to phenacylsulfinate, whose reaction with the phenacyl halide yields the diphenacyl sulfone in good yield. Inoue and co-workers reported that reaction of phenacyl bromide with the sulfinate adduct of 1-benzyl-3-carbamoylpyridinium ion gave acetophenone when performed in water and the dione when the solvent was DMF.[32b] Although they suggested the phenacylsulfinate ion as an intermediate, they did not report the formation of any sulfone. The only other cases in which dimers are obtained from phenacyl halides are those in which metallic reagents are involved.[29] The reductions reported with sodium dithionite were done in the presence of water.[30,31]

Summary. The above reactions of aliphatic and phenacyl halides taken together reveal a diverse chemistry of reduced species of sulfur dioxide in which subtle changes in substrate structure or reaction conditions open up new reaction pathways. The bioorganic chemistry of these species, as yet largely undeveloped, may prove to be equally diverse.

Experimental Section

Elemental analyses were performed at Microanalysis, Inc., Wilmington, DE. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian T60, Bruker WM-360, Mohawk 250, or General Electric GN-500 or QE-300 MHz spectrometer, and chemical shifts are reported relative to tetramethylsilane. Infrared spectra were recorded on a Beckman Model 4220 or a Perkin-Elmer Model 710097B spectrometer, ultraviolet spectra were recorded on a Cary 219 spectrometer, and mass spectra were obtained on a Finnigan 4000 GC/MS instrument. Electron spin resonance spectra were obtained on a Varian E 9 spectrometer with 100-kHz field modulation. Melting points were obtained on a Mel-Temp apparatus (uncorrected) or on a Reichert hot-stage melting point apparatus.

All starting materials were checked for purity by melting point, boiling point, and/or NMR and IR spectroscopy; solids were recrystallized and liquids were distilled where necessary. 4-Fluorobenzyl bromide and 2-methylbenzyl bromide from freshly opened bottles were used without purification. Sodium hydroxymethanesulfinate dihydrate (Rongalite) and sulfur dioxide were used without purification.

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N,N-Dimethylformamide was dried routinely over Linde molecular sieves, type 4A, and was purified further by shaking with anhydrous barium oxide under nitrogen in the dark for 3 days, followed by removal of the supernatant solvent and distillation under reduced pressure in the dark (bp <50 °C) onto fresh 4A molecular sieves. The distilled DMF was transferred under nitrogen via a syringe needle to an opaque bottle with a syringe cap and stored in the dark under nitrogen. When used for ESR solutions, this DMF and the distilled water were degassed overnight.

Reactions of Organic Halides with Rongalite. Procedure A. A mixture of organic halide, Rongalite, and potassium bicarbonate (molar ratio of 2:1.1:10, respectively) in a DMF–water mixture (1.8:1) was stirred under nitrogen at 80 °C for about 20 h. Addition of distilled water precipitated most of the solid products, which were collected by filtration, washed with water, and air-dried to yield essentially pure materials. Isolation of several of the solid products and the liquid products required extraction of the reaction mixtures with organic solvents. Further purification by recrystallization, distillation, or chromatography was performed as needed.

Procedure B. This procedure differed from A in that the potassium bicarbonate was omitted.

Procedure C. A mixture of organic halide and Rongalite (molar ratio 2:1) in DMF (purified as described above and degassed for 1 h with nitrogen) was stirred under nitrogen at ca. 50 °C. Nitrogen was passed over liquid sulfur dioxide to carry the sulfur dioxide into the reaction vessel, and the heating and stirring was continued for various lengths of time. Addition of distilled water precipitated the solid products, which were collected by filtration and washed with water. In the case of allyl bromide, the diallyl sulfone was isolated by distillation of the mixture in a Kugelrohr apparatus.

Procedure D. The effect of micellar catalysis was investigated. A mixture of benzyl bromide and Rongalite (molar ratio 2:2.1) in an aqueous solution of hexadecyltrimethylammonium bromide (1.04×10^{-2} M) was stirred under nitrogen at 50 °C. Water was added, and the insoluble dibenzyl sulfone was collected by filtration and washed with water. A control reaction also was performed on a mixture of benzyl bromide and Rongalite (molar ratio of 2:1.1) with omission of the phase-transfer catalyst.

The following benzyl sulfones were obtained.

Dibenzyl Sulfone. Procedure A: 86–88%; mp 151–152 °C ($CHCl_3$–petroleum ether) (lit.[33] mp 151.9 °C). **Procedure B**: 44%. **Procedure C**: 74%. **Procedure D**: 63% (control, 40%).

Bis(4-bromobenzyl) Sulfone. Procedure A: 70%; mp 260–262 °C (dioxane) (lit.[34] mp 261–262 °C). **Procedure B**: 52%. **Procedure C**: 56%.

Bis(4-chlorobenzyl) Sulfone. Procedure A: 70%; mp 245–246 °C (dioxane) (lit.[35] mp 246–247 °C).

Bis(4-fluorobenzyl) Sulfone. Procedure A: 62%; mp 190–191 °C ($CHCl_3$–petroleum ether); ^1H NMR (DMSO-d_6) δ 4.45 (s, 4 H, CH_2), 6.95–7.61 (m, 8 H); ^{13}C NMR (DMSO-d_6) δ 56.6, 115.3, 115.6 ($^2J_{CF}$ = 20.4 Hz), 124.3, 133.1, 133.3 ($^3J_{CF}$ = 8.5 Hz), 160.3, 164.2 ($^1J_{CF}$ = 244.1 Hz); IR (KBr) 1307 (s), 1129 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{12}F_2O_2S$: C, 59.56; H, 4.28. Found: C, 59.79; H, 4.22.

Bis(4-methylbenzyl) Sulfone. Procedure A: 65%; mp 204–205 °C ($CHCl_3$–petroleum ether) (lit.[36] mp 201–202 °C). **Procedure C**: 54%.

Bis(2-methylbenzyl) Sulfone. Procedure A: 77%; mp 174–175 °C ($CHCl_3$–petroleum ether); ^1H NMR ($CDCl_3$) δ 2.29 (s, 6 H, CH_3), 4.23 (s, 4 H, CH_2), 7.20 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 19.7, 55.9, 125.8, 126.2, 129.0, 131.7, 138.4; IR (KBr) 1314 (s), 1118 (vs) cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.04; H, 6.61. Found: C, 70.25; H, 6.75.

Bis(4-cyanobenzyl) Sulfone. Procedure B: 45%; mp 258–259 °C; ^1H NMR (acetone-d_6) δ 4.8 (s, 4 H), 7.9 (m, 8 H); IR (KBr) 2240 (m), 1290 (s), 1120 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{12}N_2O_2S$: C, 64.86; H, 4.05. Found: C, 64.72; H, 4.16.

Bis(3-nitrobenzyl) Sulfone. Procedure B: 60%; mp 184.5–186 °C (acetone–water); ^1H NMR (acetone-d_6) δ 4.70 (s, 4 H, CH_2), 7.43–8.30 (m, 8 H); ^{13}C NMR (acetone-d_6) δ 58.6, 124.2, 126.7, 130.7, 131.3, 138.3, 149.1; IR (KBr) 1525 (s), 1354 (s), 1125 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{12}N_2O_6S$: C, 50.00; H, 3.60. Found: C, 50.26; H, 3.53.

Bis[4-(trifluoromethyl)benzyl] Sulfone. Procedure B. α'-Bromo-α,α,α-trifluoro-*p*-xylene (0.48 g, 2.0 mmol) in DMF (10 mL) was added to Rongalite (0.61 g, 4.0 mmol) in water (10 mL). The reaction mixture was refluxed for 29 h. White crystals precipitated, and cold water (80 mL) was added to precipitate more product. The aqueous solution was extracted with $CHCl_3$ (4 × 25 mL). Removal of the chloroform yielded additional sulfone, which was combined with that previously collected (0.154 g, 0.472 mmol, 47%): mp 207 °C ($CHCl_3$); ^{13}C NMR ($CDCl_3$) δ 58.1, 123.7 (J = 276 Hz) 131.2, 131.7, 131.9. Anal. Calcd for $C_{16}H_{12}F_6O_2S$: C, 50.27; H, 3.16. Found: C, 50.27; H, 2.82.

Reaction of Benzyl Chloride with Rongalite in Alkaline Ethanol–Water. Benzyl chloride (99 g, 0.78 mol) in ethanol (200 mL) was added to Rongalite (60 g, 0.39 mol) and sodium hydroxide (22 g, 0.56 mol) in water (200 mL). The mixture was refluxed for 3 h, cooled, and filtered. The filtrate was added to 100 g of ice, filtered, and extracted with chloroform (100 mL). Unreacted benzyl chloride (2.02 g, 0.015 mol), dibenzyl sulfone (69.7 g, 0.283 mol, 71.8%, mp 151 °C), and a white crystalline material (2.5 g) were obtained from the extract. This latter solid was found to be a 1:1 mixture of dibenzyl sulfone and α-sulfonyl ether **3**. The ether was purified by fractional crystallization ($CHCl_3$; petroleum ether): mp 77–78 °C (lit.[10] mp 77 °C); ^1H NMR ($CDCl_3$) δ 7.4 (m, 10 H, Ph), 4.9 (s, 2 H, CH_2), 4.3 (s, 2 H, CH_2), 4.1 (s, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 56.6, 74.5, 80.1, 127.7, 128.5, 128.9, 130.8, 135.9.

The following sulfones were prepared from alkyl bromides.

Di-*n*-butyl Sulfone. Procedure A: 46%; mp 44–45 °C (chloroform–petroleum ether) (lit.[37] mp 44–45 °C). An additional 19% yield was obtained from the mother liquor by extraction with diethyl ether to give a total yield of 65%.

Pentamethylene Sulfone. Procedure A: 35%; mp 97–98 °C (ethanol) (lit.[38] mp 97 °C). An additional 8% yield was recovered from the mother liquor by extraction with methylene chloride to give a total yield of 43%.

Diallyl Sulfone. Procedure C: 20%; bp 65 °C (0.2 mm) [lit.[39] bp 92–93 °C (1.5 mm)]. **Procedure B.** Bubbles were observed coming from the DMF–water solution. A clear liquid, condensed from nitrogen flowing over the reaction mixture, was identified as propene by gas-phase IR and by its NMR spectrum ($CDCl_3$), both spectra having been previously reported.[40,41] Only a small amount of diallyl sulfone (3%) was obtained.

Treatment of 4-Nitrobenzyl Bromide with Rongalite. Procedure A. 4-Nitrobenzyl bromide (0.401 g, 1.86 mmol), Rongalite (0.315 g, 2.05 mmol), and potassium bicarbonate (1.8 g, 18 mmol) in DMF (9 mL)–water (5 mL) yielded 1,2-bis(4-nitrophenyl)ethane (0.086 g, 0.32 mmol, 34%): mp 182–184 °C (lit.[42] mp 182–183 °C); ^1H NMR (acetone-d_6) δ 7.23–8.09 (m, 8 H), 3.17 (s, 4 H); ^{13}C NMR (acetone-d_6) δ 37.4, 124.2, 130.6, 150.0. **Procedure B.** 4-Nitrobenzyl bromide (0.666 g, 3.08 mmol) and Rongalite (0.242 g, 1.57 mmol) in DMF (10 mL)–water (5 mL) in the absence of potassium bicarbonate were stirred at 80 °C for 21.5 h to give bis(4-nitrobenzyl) sulfone (0.278 g, 1.02 mmol, 78%). Recrystallization (80% acetic acid) gave pale yellow needles: mp 260–261 °C dec (lit.[43] mp 260 °C); ^{13}C NMR (DMSO-d_6) δ 57.4, 123.5, 132.5, 135.6, 147.6; IR (KBr) 1516 (s), 1299 (s), 1117 (m) cm^{-1}. **Procedure C.** Bis(4-nitrobenzyl) sulfone was obtained in 83% yield.

Treatment of 2,4-Dinitrobenzyl Bromide with Rongalite.

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2,4-Dinitrobenzyl bromide (1.8 g, 6.9 mmol), prepared by bromination of 2,4-dinitrotoluene by *N*-bromosuccinimide,[44] was treated with Rongalite (1.1 g, 7.1 mmol) in DMF–water (10 mL each). The mixture was stirred for 18 h, water (60 mL) was added, and an orange precipitate (0.73 g, 4.1 mmol, 59%) was removed by filtration and identified as 2,4-dinitrotoluene: mp 70–71 °C (lit.[45] mp 71.8–72.2 °C) (mixture mp 70–71 °C). The ^{1}H NMR and infrared spectra were identical with those of an authentic sample.

Treatment of α,α'-Dibromo-*o*-xylene with Rongalite. Solutions of α,α'-dibromo-*o*-xylene (1.01 g, 3.84 mmol) in DMF (4.0 mL) and Rongalite (0.647 g, 4.20 mmol) in distilled water (4.0 mL) were added from separate syringes by means of a syringe pump (Sage Instruments Orion Model 352) and Teflon needles over a period of 2.5 h to a solution of potassium bicarbonate (1.9 g, 19 mmol) in DMF (8 mL) and distilled water (4 mL) stirred under nitrogen at 40 °C. Additional DMF and water (5 mL each) were used to rinse the solution remaining in the syringes and Teflon needles into the reaction mixture. Heating and stirring were continued for 2 h, and the reaction flask was stoppered and placed in a freezer overnight. Distilled water (100 mL) was added, and the resulting tan precipitate, apparently polymeric, was removed by filtration. Extraction of the filtrate with ether gave essentially pure sultine, 4,5-benzo-3,6-dihydro-1,2-oxathiin 2-oxide, as a pale yellow oil (0.277 g, 1.65 mmol, 42.9%). The ^{1}H NMR and IR spectra were identical with those reported previously.[7c,46] Further washings with ether gave an additional 5% yield of sultine.

The sultine (0.085 g, 0.51 mmol) was dissolved in dry benzene (20 mL), and the solution was refluxed for 3 h under nitrogen. Removal of the benzene yielded 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide as a white solid (0.065 g, 0.51 mmol, 100%): mp 145–148 °C [lit.[47] mp 150–151 °C (with sublimation)]. The sulfone was recrystallized from methylene chloride–petroleum ether to yield prisms (0.068 g, 0.04 mmol, 78%), mp 147–148 °C. The ^{1}H NMR and IR spectra were identical with those previously reported.[48a]

When α,α'-dibromo-*o*-xylene (0.492 g, 1.86 mmol), Rongalite (0.315 g, 2.05 mmol), and potassium bicarbonate (1.8 g, 18 mmol) in DMF (9 mL)–water (5 mL) were stirred under nitrogen at 80 °C for 48 h, a mixture of poly-*o*-xylylene, 5,6,11,12-tetrahydrodibenzo[*a,e*]cyclooctane, and 5,6,11,12,17,18-hexahydrotribenzo-[*a,e,i*]cyclododecane was obtained (0.122 g, 1.17 mmol based on $(C_8H_8)_n$, 62.9%) as indicated by the lack of a definite melting point and by comparisons of NMR and IR spectra with those reported previously.[48b]

Trapping of *o*-Xylylene with Norbornene. A mixture of Rongalite (1.4 g, 9.1 mmol), potassium bicarbonate (7.6 g, 76 mmol), and norbornene (4.15 g, 48 mmol) in DMF (10 mL)–water (5 mL) was stirred under nitrogen in a round-bottomed flask equipped with a syringe cap and immersed in an oil bath (50 °C). A solution of α,α'-dibromo-*o*-xylene (2.01 g, 7.59 mmol) and norbornene (0.713 g, 7.59 mmol) in DMF (5 mL) was added via a syringe pump over about 2 h through a Teflon needle. Additional DMF (3.5 mL) was used to rinse the contents of the syringe and Teflon needle into the reaction mixture. Heating and stirring cotninued for a total of 28 h. The reaction mixture was cooled for 1 h, and distilled water (90 mL) was added, resulting in the formation of a large amount of gelatinous precipitate. The mixture was extracted with methylene chloride (100 mL), and an insoluble white solid was removed by filtration before the separation of the layers. The mixture was digested and extracted with methylene chloride (2 × 100 mL); most of the material was insoluble and was removed by filtration. Spectroscopic data suggested that this solid was poly(*o*-xylylene sulfone). The combined methylene chloride extracts were washed with distilled water (2 × 150 mL), dried over magnesium sulfate, and filtered, and the solvent was removed on a rotary evaporator, leaving a pale yellow oil (3.57 g). Diethyl ether (25 mL) and hexane (25 mL) were added to the oil to give a cloudy suspension, from which a pale yellow oil separated and partially solidified. The ether–hexane solution was removed by pipet, the remaining semisolid was washed with distilled water, dried over magnesium sulfate, and filtered, and the solvent was removed to yield a white solid with a small amount of an oil (0.471 g). This material was taken up in methylene chloride (100 mL) and concentrated to 50 mL to yield a white solid (0.233 g). Preparative-scale thin-layer chromatography (silica gel, petroleum ether eluant) yielded a major band at the origin and another at R_f 0.63. Extraction of the latter band with petroleum ether (5 × 25 mL) yielded the norbornene–*o*-xylylene adduct as a white solid (0.154 g, 0.778 mmol, 20.5%): mp 71–72 °C (lit.[28] mp 69–71 °C). The ^{1}H NMR, ^{13}C NMR, and IR spectra were essentially identical with those previously reported.[28] A sample of the adduct, prepared independently by treating α,α'-dibromo-*o*-xylene with activated zinc in the presence of norbornene, did not depress the melting point.

Extraction of the band at the origin on the preparative plate with methylene chloride (5 × 25 mL) yielded a yellow oil (0.056 g), which appears by ^{1}H NMR to be a mixture of poly-*o*-xylylene, the sultine, and the sulfone.

Treatment of α,α'-Dichloro-*o*-xylene with Rongalite and Sodium Iodide. α,α'-Dichloro-*o*-xylene (1.74 g, 10 mmol) was dissolved in DMF (30 mL) and stirred with Rongalite (7.50 g, 50 mmol) and sodium iodide (0.15 g, 1 mmol) at room temperature for 22 h. Addition of water (100 mL) and extraction with $CHCl_3$ yielded 4,5-benzo-3,6-dihydro-1,2-oxathiin 2-oxide, **5**, as a pale yellow oil (1.3 g, 7.7 mmol, 78%).

Treatment of *p*-Dinitrobenzene and *p*-Nitrobenzoic Acid with Rongalite. *p*-Dinitrobenzene (0.172 g, 1.00 mmol) was dissolved in dry, degassed DMF (10 mL). Rongalite (0.176 g, 1.14 mmol) was added. An electron spin resonance spectrum showed 17 lines, $a^H = 1$ G, $a^N = 3$ G, corresponding to the spectrum of the known anion radical of *p*-dinitrobenzene.[24,25] A similar result was obtained with *p*-nitrobenzoic acid at pH 9, the known anion radical being observed.[24] The 27-line spectrum showed hyperfine splittings, $a^N = 11.35$ G, $a^H = 2.91$, 0.97 G.

Reduction of Desyl Chloride to Deoxybenzoin. Procedure A. Desyl chloride (0.258 g, 1.12 mmol), Rongalite (0.346 g, 2.25 mmol), and potassium bicarbonate (1.1 g, 11 mmol) in DMF–water (11 mL each) at 50 °C gave deoxybenzoin (0.129 g, 0.653 mmol, 58%): mp 55–56 °C (ethanol–water) (lit.[49] mp 55–56 °C). ^{1}H NMR and IR spectra were identical with those of an authentic sample. **Procedure B.** A 72% yield was obtained at 25 °C for 24 h.

Reduction of Phenacyl Chloride to Acetophenone. Procedure B. Phenacyl chloride (2.58 g, 16.7 mmol) and Rongalite (5.15 g, 33.4 mmol) gave acetophenone (1.86 g, 15.5 mmol, 93%), identified by comparison of its NMR and IR spectra with those of authentic material.

Reaction of Phenacyl Bromide with Rongalite. Procedure A. Phenacyl bromide (1.67 g, 8.37 mmol), Rongalite (2.31 g, 15.0 mmol), and potassium bicarbonate (8.3 g, 83 mmol) in DMF–water (50 mL each) gave a precipitate of 1,4-diphenyl-1,4-butanedione (0.189 g, 0.800 mmol, 19%): mp 143–144 °C (lit.[50] mp 145–147 °C) (dioxane); ^{1}H NMR ($CDCl_3$) δ 7.17–8.13 (m, 10 H), 3.43 (s, 4 H); IR (KBr) 1685 (s) cm^{-1}. Acetophenone (0.702 g, 5.85 mmol, 70%) was obtained from the filtrate after removal of the dione. **Procedure B.** Phenacyl bromide (3.32 g, 16.7 mmol) and Rongalite (5.15 g, 33.4 mmol) in DMF–water (10 mL each) gave 1,4-diphenyl-1,4-butanedione (1.02 g, 4.29 mmol, 52%) (mp 142.5–144 °C) and acetophenone (0.85 g, 7.15 mmol, 43%).

Reaction of Phenacyl Bromide with Rongalite in Dry DMF. A solution of phenacyl bromide (19.9 g, 100 mmol) in dry DMF (150 mL) and Rongalite (15.4 g, 100 mmol) were combined, and the suspension was stirred for 24 h at room temperature. Water (400 mL) was added, and a white solid was removed by filtration. The solution was extracted with diethyl ether (4 × 200 mL). The white solid was dissolved in chloroform and extracted

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with aqueous NaOH. The chloroform layer was combined with the ether extracts and dried. Removal of the solvent gave acetophenone (2.43 g, 20 mmol, 20%) and 1,4-diphenyl-1,4-butanedione (9.06 g, 38 mmol, 76%): mp 145.5–147 °C. The aqueous NaOH solution was acidified with HCl, and a white solid precipitated (0.22 g, 0.70 mmol, 1.4%): mp 122–124 °C. It was identified as diphenacyl sulfone (lit.[7c] mp 121–122 °C).

Reaction of Phenacyl Bromide with Rongalite in the Presence of Molecular Sieves. Phenacyl bromide (1.99 g, 10 mmol) was dissolved in DMF (15 mL) that had been dried over 4A molecular sieves. The solution was stirred with Rongalite (1.54 g, 10 mmol) and 4A molecular sieves (1.0 g) for 24 h. Water (100 mL) was added, and a white solid was removed. The solution was extracted with diethyl ether (4 × 30 mL). Workup as above gave acetophenone (0.216 g, 1.8 mmol, 18%), 1,4-diphenyl-1,4-butanedione (0.89 g, 3.7 mmol, 74%), and diphenacyl sulfone (0.006 g, 0.02 mmol, 0.4%).

Reaction of Phenacyl Chloride or Bromide with Rongalite and Sodium Iodide in the Presence of Molecular Sieves. Phenacyl chloride (1.54 g, 10.0 mmol) or phenacyl bromide (1.99 g, 10 mmol) was dissolved in DMF (15 mL) that had been dried over 4A molecular sieves. This was stirred with Rongalite (1.54 g, 10 mmol), sodium iodide (0.15 g, 1.0 mmol), and 4A molecular sieves (1.0 g) for 24 h in a covered flask. Workup gave acetophenone (0.22 g, 1.8 mmol, 18%), 1,4-diphenyl-1,4-butanedione (0.90 g, 3.8 mmol, 76%), and diphenacyl sulfone (0.01 g, 0.04 mmol, 0.8%).

Reaction of Phenacyl Bromide with Rongalite and Sulfur Dioxide. Phenacyl bromide (1.99 g, 10 mmol) was added to a stirred solution of sulfur dioxide prepared by passing SO_2 into dry DMF (30 mL) for 30 min. Rongalite (3.01 g, 20 mmol) was added, and the solution was stirred for 18 h at room temperature. Workup as above gave diphenacyl sulfone (0.844 g, 2.8 mmol, 56%) and acetophenone (0.36 g, 3.0 mmol, 30%).

Reaction of 4-Phenylphenacyl Bromide with Rongalite. Procedure A. 4-Phenylphenacyl bromide (0.308 g, 1.12 mmol), Rongalite (0.345 g, 2.24 mmol), and potassium bicarbonate (1.1 g, 11 mmol) in DMF–water (11 mL each) gave 4-acetylbiphenyl (0.144 g, 0.734 mmol, 66%): mp 120.4–121.5 °C (heptane) (lit.[51] mp 120.5 °C). The ^1H NMR and IR spectra were identical with those previously reported.[52] The material that was insoluble in heptane was 1,4-bis(4-phenylphenyl)-1,4-butanedione (0.043 g, 0.11 mmol, 20%): mp 264–266 °C (benzene) (lit.[53] mp 260–263 °C); IR (KBr) 1680 (s), 1605 (s) cm^{-1}. The ^1H NMR spectrum was essentially identical with that reported previously.[29g] **Procedure B.** 4-Phenylphenacyl bromide (0.308 g, 1.12 mmol) and Rongalite (0.345 g, 2.24 mmol) gave 4-acetylbiphenyl (0.081 g, 0.41 mmol, 51%) and 1,4-bis(4-phenylphenyl)-1,4-butanedione (0.063 g, 0.16 mmol, 40%). The latter was identical with the material obtained by the Friedel–Crafts reaction of biphenyl and succinyl dichloride.

Reaction of 4-Phenylphenacyl Bromide with Rongalite and Sulfur Dioxide. 4-Phenylphenacyl bromide (1.42 g, 5 mmol) was added to a stirred solution of sulfur dioxide prepared by passing SO_2 into dry DMF (30 mL) for 30 min. Rongalite (1.54 g, 10 mmol) was added, and the solution was stirred for 18 h at room temperature. Workup as above gave 4-acetylbiphenyl (0.20 g, 20 mmol, 20%), the dione (0.244 g, 1.25 mmol, 25%), and bis(4-phenylphenacyl) sulfone (0.59 g, 1.3 mmol, 52%): mp 208–210 °C; IR (KBr) 1695 (s), 1288 (s), 1140 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.1–7.4 (m, 18 H, Ph), 5.1 (s, 4 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 59.9, 127.3, 127.6, 128.6, 129.0, 129.5, 134.3, 147.4, 148.5, 188.9. Anal. Calcd for $C_{28}H_{22}O_4S$: C, 73.99; H, 4.88. Found: C, 73.84; H, 4.81.

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(51) Gull, H. C.; Turner, E. E. *J. Chem. Soc.* **1929**, 491.

(52) Sadtler Standard Spectra, Sadtler Research Laboratories, Inc., Philadelphia, PA; NMR 6582 M, IR 22092.

(53) Private communication from Professor Howard Alper. This value is a correction of that reported in ref 29g.

PE Spectra of Disubstituted 1,2,4,5-Tetrazines†

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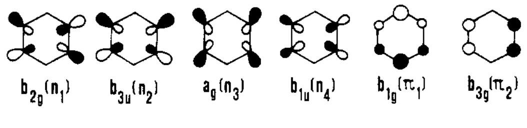
The PE spectra of 21 *s*-tetrazines, disubstituted either with electron-donating groups or with electron-withdrawing groups, have been recorded. Their interpretation is based on the comparison of the spectra using band shapes as a guide and on the results of HAM/3 calculations. The very broad band between 10 and 11 eV is ascribed to the failure of the one-electron picture. In addition electrochemical reduction potentials have been compared with calculated HAM/3 electron affinities. Our investigations reveal that the HOMO of the alkylamino derivatives (except **9**) has π character, in contrast to the *s*-tetrazines with alkyl or electron-withdrawing groups.

In 1,2,4,5-tetrazines (*s*-tetrazines) the lowest unoccupied MO (LUMO), a low-lying π^* MO, strongly determines the properties of these compounds. It is mainly responsible for the deep color ($\pi^* \leftarrow n$),[2,3] the good electron-acceptor properties[4,5] and the high reactivity as a dienophile with inverse electron demand.[6-8] The highest occupied MO's seem to play a less important role. Although the lone pairs

Scheme I



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† Dedicated to Professor Hans Bock on the occasion of his 60th birthday.

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