in a Lloyd-type extractor in turn with petroleum ether and 95% ethanol, and the air-dried ethanol extract was subjected to partitioning between chloroform and water. The water-soluble extract was lyophilized and stored at −10 °C prior to further fractionation.

A 600-g portion of the lyophilized water extract was dissolved in water (2500 mL) and repeatedly extracted in portions with *n*-butanol (3500 mL). The butanol-insoluble phase was air-dried, and the resulting syrup was dissolved in the minimum amount of methanol (800 mL) and left in the refrigerator overnight. The supernatant liquid, after filtration by decantation, was passed through a small column of silica gel 60 and eluted exhaustively with methanol. The methanol eluent on standing overnight at room temperature gave a dark brown residue which was removed by decantation. The clear methanol eluent was concentrated and subjected to silica gel 60 (2 kg) column chromatography. The column was eluted with hexane/dichloromethane/methanol (20:20:10) as the initial solvent system followed by a gradual change in the concentration of dichloromethane and methanol. Forty 1-L fractions were collected, and the solvent from each fraction was evaporated off in vacuo. The resulting residue was dissolved in the minimum amount of ethyl acetate/methanol (1:3) and left at room temperature for a few days. Liriodendrin (IV), which was separated from fractions 6–10 as a colorless residue (mp 256–257 °C), crystallized from pyridine as colorless needles: mp 265–266 °C; $[\alpha]^{25}_{D}$ −12.1° (*c* 0.596, pyridine); UV (H_2O) λ_{max} 268 (ϵ 1966). The mixture melting point with an authentic sample showed no depression. The IR, mass, and ^1H and ^{13}C NMR spectra (described under Results and Discussion) were in accord with structure IV.

Anal. Calcd for $C_{34}H_{46}O_{18}$: C, 54.98; H, 6.24. Found: C, 55.26; H, 6.15.

Liriodendrin demonstrated an activity of 147 [test/control (T/C)] at 12.5 mg/kg in the PS test system. Activity in the PS test systems is defined as an increase in the survival of treated animals over that of controls resulting in a T/C value of ≥126%.[12]

Liriodendrin Octaacetate. Acetylation of liriodendrin with acetic anhydride–pyridine at room temperature for 48 h afforded an octaacetate, mp 121–124 °C (MeOH) (lit.[1] mp 124–125 °C).

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Registry No. IIa, 21453-69-0; IV, 573-44-4; IV octaacetate, 66007-45-2.

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Formation of Dimethylmercury in the Oxidation of Methylhydrazine by Mercuric Oxide

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With the objective of finding a method for the synthesis of 1,4-dimethyl-2-tetrazene, we have recently examined the oxidation of monomethylhydrazine by mercuric oxide. Renouf[1] reported in 1880 that 1,1,4,4-tetramethyl-2-tetrazene is formed by the corresponding reaction of *unsym*-dimethylhydrazine with mercuric oxide (eq 1). It was hoped that methylhydrazine would react similarly. The reaction was carried out in anhydrous ethyl ether and, in addition to a variety of products, not including 1,4-dimethyl-2-tetrazene, a considerable amount of dimethylmercury was obtained. To our knowledge this highly hazardous substance has not previously been detected in the products of mercuric oxide oxidations of the methylhydrazines.

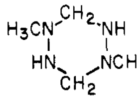
$$2(CH_3)_2NNH_2 + 2HgO \rightarrow (CH_3)_2NN{=}NN(CH_3)_2 + 2Hg + 2H_2O \quad (1)$$

Table I

meaSd mass	calcd mass for $(CH_3)_2Hg$	measd mass	calcd mass for $(CH_3)_2Hg$
234.0209	234.0204	230.0139	230.0153
232.0162	232.0176	229.0133	229.0152
231.0158	231.0172		

Results and Discussion

In addition to those resulting from the solvent and air, three peaks were observed on the gas chromatograph of the liquid reaction mixture from the methylhydrazine–mercuric oxide reaction. Two of these were at retention times 5.81 and 4.83 min and can be attributed, respectively, to water and to $CH_3NHN{=}CH_2$ or its dimer.[2]



The third major component was isolated by drying the solution over $CaSO_4$ for 14 h and evaporating it under reduced pressure. Approximately 1 mL of a colorless liquid whose peak on the gas chromatograph had a retention time identical with the third peak of the mixture, viz., 2.42 min, remained. On the basis of the gas chromatographic analysis, this liquid contains about 97.9% dimethylmercury. The proton NMR spectrum of this material gave a single resonance at τ 9.71 in agreement with that reported for dimethylmercury.[3] Anal. Calcd for $(CH_3)_2Hg$: C, 10.40; H, 2.61. Found: C, 11.41; H, 2.92. The identification of this compound was further confirmed by comparing its infrared and mass spectra with those reported[4,5] for dimethylmercury.

The infrared spectrum of the product contained the following peaks: 2970–1900 (s), 1640 (w), 1400 (br), 1240 (w), 1110–1000 (m), 750 (s), 520 (s) cm^{-1}. The 1240-cm^{-1} peak may result from an impurity.

The mass spectrum of this product is in excellent agreement with that expected for dimethylmercury. The precisely measured masses of the parent peaks agreed well with those calculated for dimethylmercury as shown in Table I. We are continuing to explore this and similar reactions. We recommend care in such processes to minimize the danger introduced by the possible formation of dimethylmercury.

On the basis of the gas chromatographic data, the yield of dimethylmercury in this reaction approximated 5–10%.

Experimental Section

Materials. Methylhydrazine obtained from the Aldrich Chemical Co. was refluxed and distilled over solid KOH no more than 1 day before use and was stored at −4 °C. The fraction boiling at 87.5 °C was collected and used in the study. The mercuric oxide (yellow) used was CP grade.

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Spectra. NMR spectra were recorded on a Varian Model A-60-A spectrometer, tetramethylsilane being used as an internal standard in solutions in carbon tetrachloride. Infrared spectra were obtained on a Beckman IR-10 spectrometer using KBr plates. A Varian 3700 gas chromatograph equipped with a CDS 111 data analyzer and a Soltic Model 252 integrator recorder and using a Carbowax column having a composition of 10% Carbowax 20M plus 5% KOH on Chrom WAW, 80/100 mesh, was used to analyze the product mixture. Mass spectral data were obtained by using an AEI MS-30 mass spectrometer equipped with a DS-30 data system.

Reaction Procedure. Methylhydrazine (0.25 mol) in 160 mL of anhydrous diethyl ether was placed in a flask under a dry nitrogen atmosphere and 0.26 mol of yellow mercuric oxide added over a 90-min period with continuous stirring. The exothermic reaction was controlled by constant cooling, keeping the temperature below 5 °C during the addition of the mercuric oxide. The reaction was stirred for a further 90 min, after which the liquid was separated from the mercury and the remaining mercuric oxide by decantation and was analyzed.

Acknowledgment. The authors gratefully acknowledge the support of the research by the Air Force Office of Scientific Research through a grant to the University of Florida.

Registry No. Dimethylmercury, 593-74-8; methylhydrazine, 60-34-4; mercuric oxide, 21908-53-2.

Cathodic Cleavage of Carbon-Sulfur Bond of 2-Substituted 2-(2-Benzothiazolylthio)alkanoates and 2-(2-Pentynyl)-2-(2-benzothiazolylthio)cyclopentanone

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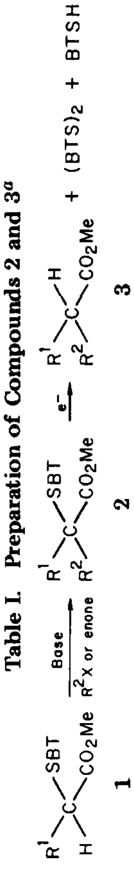
Our previous paper presented an efficient synthesis of 2-(2-benzothiazolylthio)alkanoates (**1**) by the reaction of β-keto esters with 2-benzothiazolesulfenamides.[1] 2-Sulfenylalkanoates **1** are useful precursors in the preparation of 2,2-disubstituted acetates (**3**). After alkylation of **1**, the 2-benzothiazolylthio (BTS) group must be removed. We now describe a convenient procedure for electroreductive removal of the BTS moiety of **2**.

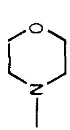
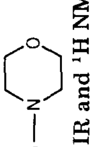
Mercury cathode reduction of ethyl 2-phenyl-2-(phenylthio)propionate,[2] ethyl 3-(*p*-tolylthio)pyruvate,[3] and 2-(thiocyanato)acetophenone[4] has been reported in an electroanalytical sense. As part of a search for the development of an electroreductive removal of alkylthio moieties which is adaptable to work on a preparative scale, we first studied the cathodic reduction of **2** in the MeOH-H_2SO_4-carbon system as a facile handling medium.

Electroreduction of **2a** was carried out in a cathode cell which was fitted with a carbon electrode and charged with methanol containing a few drops of concentrated sulfuric acid, at a constant current of 20 mA. After passage of 8

Table I. Preparation of Compounds 2 and 3[a]



1 2 3

compd	2: R¹	2: R²	2: yield, %	2: bp, °C (torr)	3[b]: yield, %	3[b]: bp, °C (torr)	$(BTS)_2$ yield, %	BTSH yield, %
a	$(CH_2)_3CO_2Me$	n-C_5H_{11}[c]	76	134-137 (0.007)	87	75-80 (2.0)	31	53
b	$(CH_2)_3CO_2Me$	$EtC{\equiv}CCH_2$[d]	97	130-134 (0.004)	82	78-84 (2.0)	50	22
c	$(CH_2)_3CO_2Me$	$Me_2C{=}CHCH_2$[c]	75	135-140 (0.008)	74	77-82 (1.0)	96	
d	$(CH_2)_3CO_2Me$	$CH_2{=}CHCH_2$[d]	99	124-127 (0.005)	66	89-93 (5.0)	53	8
e	n-C_6H_{13}	$CH_2{=}CHCH_2$[d]	87	113-117 (0.006)	72	90-94 (10.0)	36	25
f	n-C_6H_{13}	$Me_2C{=}CHCH_2$[c]	90	105-110 (0.005)	84	89-92 (3.0)	63	24
g	n-C_6H_{13}	$MeCO(CH_2)_2$[e]	80	124-128 (0.005)	80	92-100 (5.0)	33	25
h	$(CH_2)_3CO$— 	$EtC{\equiv}CCH_2$[d]	98	157-163 (0.004)	53	108-114 (0.007)	78	
i	$(CH_2)_3CO$— 	$CH_2{=}CHCH_2$[d]	91	150-157 (0.005)	55	94-98 (0.005)	73	

[a] All new compounds have IR and ^1H NMR spectra consistent with the proposed structure, and elemental analyses (C, H) are within 0.3% of theory. See supplementary material for additional IR and ^1H NMR data and elemental analyses of the compounds 2 and 3. [b] The electrolysis was carried out with a divided cell fitted with carbon electrode in methanol (20 mL) containing 98% H_2SO_4 (120 mg). During the electrolysis, 8 F/mol of electricity was passed at 20 mA, 7-20 V. [c] Carried out in the manner as described in the Experimental Section for 2a. [d] Carried out in the manner as described for 2b. [e] 2g was prepared from the reaction of 1 (R^1 = n-C_6H_{13}) with methyl vinyl ketone as described in the literature procedure.[5]

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