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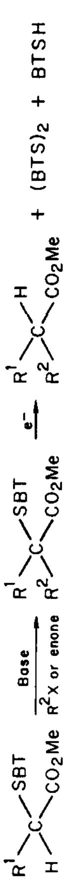
Our previous paper presented an efficient synthesis of 2-(2-benzothiazolylthio)alkanoates (**1**) by the reaction of β-keto esters with 2-benzothiazolesulfenamides.[1] 2-Sulfenylalkanoates **1** are useful precursors in the preparation of 2,2-disubstituted acetates (**3**). After alkylation of **1**,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

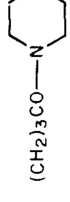
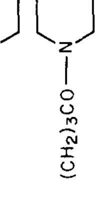
Mercury cathode reduction of ethyl 2-phenyl-2-(phenylthio)propionate,[2] ethyl 3-(*p*-tolylthio)pyruvate,[3] and 2-(thiocyanato)acetophenone[4] has been reported in an electroanalytical sense. As part of a search for the development of an electroreductive removal of alkylthio moieties which is adaptable 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**

	2				3[b]			
compd	R¹	R²	yield, %	bp, °C (torr)	yield, %	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		$EtC{\equiv}CCH_2$ [d]	98	157–163 (0.004)	53	108–114 (0.007)	78	
i		$CH_2{=}CHCH_2$ [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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(1) S. Torii, H. Tanaka, and H. Okumoto, *Bull. Chem. Soc. Jpn.*, **52**, 267 (1979).

(2) C. M. Fischer and R. E. Erickson, *J. Org. Chem.*, **38**, 4236 (1973).

(3) (a) J. Moiroux and M. B. Fleury, *Electrochim. Acta*, **18**, 691 (1973); (b) M. B. Fleury and J. Moiroux, *Bull. Soc. Chim. Fr.*, 4637 (1971).

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(5) S. Torii, H. Tanaka, Y. Kobayashi, J. Nokami, and M. Kawata, *Bull. Chem. Soc. Jpn.*, **52**, 1553 (1979).

0022-3263/80/1945-1330$01.00/0

Table II. Electroreduction of 2b ($R^1 = (CH_2)_3CO_2Me$, $R^2 = CH_2C{\equiv}CCH_2CH_3$) in Various Electrode–Electrolyte Systems[a]

			yield, %			
entry	electrodes	electrolyte	3b	BTSSBT	BTSH	2b
1	C-C	H_2SO_4	82	50	22	
2	C-C	Et_4NOTs	45		47	33
3	C-C	Et_3N	27	trace	19	64
4	Pt-Pt	H_2SO_4	21	17		61

[a] Electrolyzed at 20 mA of current, 8 F/mol of electricity, in methanol.

Table III. Results from Various Electrolytic Conditions[a] on 4

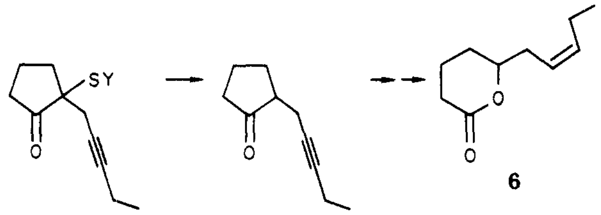
				yield, %		
entry	substrate	electrodes	electrolysis cell	5	BTSH	recovered
5	**4a**	Pt-Pt	divided	74	85	
6	**4a**	Pt-Pt	undivided	70	55	15 (**4a**)
7	**4a**	C-C	divided	26	74	15 (**4a**)
8	**4b**	Pt-Pt	divided			78 (**4b**)

[a] Carried out in MeOH with Et_4NOTs as a supporting electrolyte at a current of 25 mA (8–30 V).

F/mol of electricity, the desired **3a** was obtained in 87% yield along with BTSH (53%) and BTSSBT (31%). Results with congeners of **2a** are shown in Table I.

Table II shows some results on electroreduction of **2b** in various electrode–electrolyte systems in methanol. It should be noted that the $MeOH-H_2SO_4$-carbon system (entry 1) gave an excellent yield of **3b** compared to the other neutral and basic systems (entries 2 and 3). It is interesting to note that the platinum electrode system (entry 4) showed no advantages over carbon (entry 1) on account of a low conversion yield.

This methodology was also applied to 2-(2-benzothiazolylsulfenyl) ketones. However, electroreduction of 2-(2-pentynyl)-2-(2-benzothiazolylthio)cyclopentanone (**4a**) in $MeOH-H_2SO_4$-carbon and $MeOH-H_2SO_4$-Pt systems afforded a tarry product. The employment of the $MeOH-Et_4NOTs$-Pt system gave the desired **5** (74%), a precursor of jasmine δ-lactone (**6**),[6] as well as BTSH (85%) (Table III, entry 5). The $MeOH-Et_4NOTs$-carbon system provided unidentified various compounds (entry 7). Reduction of **4a** with the $MeOH-Et_4NOTs$-Pt system in an undivided cell led to **5** smoothly (entry 6). In contrast, reduction of **4b** in the $MeOH-Et_4NOTs$-Pt system failed (entry 8).



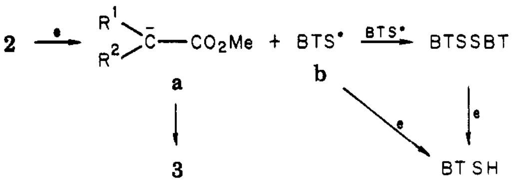
4a, Y = 2-benzothiazolyl
b, Y = phenyl

5

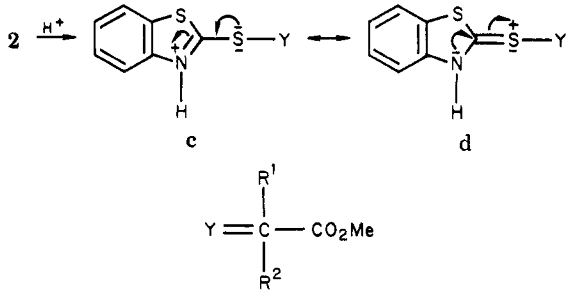
6

Mechanism. The formation of the dimer, BTSSBT, is preparatively unimportant. However, the result reveals that electroreduction of **2** leading to the formation of disulfide should proceed via one-electron transfer to give 2-benzothiazolylthio radical b along with carbanion a (see Scheme I). It must be noted that with the same experimental conditions, cathodic reduction of dimethyl 2-(2-pentynyl)-2-phenylthioadipate[7] failed. This result suggests that the 2-benzothiazolylthio moiety of **2** initially accepts an electron from the cathode. The resistance of **4a** in the acidic media is probably due to facile protonation of the carbonyl group of **4a**, which would suppress the protonation of the BTS moiety of **4a** as shown in Scheme II.

Scheme I



Scheme II



Experimental Section

All the boiling points are uncorrected. IR spectra were determined with a JASCO IRA-I grating spectrometer. ^1H NMR spectra were obtained at 60 MHz with a Hitachi R-24 spectrometer. Chemical shifts are quoted in parts per million downfield from Me_4Si used as an internal standard. Elemental analyses were performed in our laboratory.

Dimethyl 2-*n*-Pentyl-(2-benzothiazolylthio)adipate (2a, $R^1 = (CH_2)_3CO_2Me$, $R^2 = n\text{-}C_5H_{11}$) (Method A). To a cooled mixture of 1 ($R^1 = (CH_2)_3CO_2Me$, $R^2 = H$, 297 mg, 0.876 mmol) and *t*-BuOK (118 mg, 1.05 mmol) in DMF (1 mL) was added *n*-pentyl bromide (0.13 mL, 1.05 mmol). The mixture was stirred at room temperature for 1 h, quenched with aqueous 10% NH_4Cl, and taken up in ether. The extract was washed with brine, dried (Na_2SO_4), and concentrated. The crude product was chromatographed (SiO_2, 20:1 benzene/AcOEt) to give 272 mg (76%) of **2a**.

Similarly, the compounds **2c** and **f** were prepared and their yields and physical properties are given in Table I.

Dimethyl 2-(2-Pentynyl)-2-(2-benzothiazolylthio)adipate (2b, $R^1 = (CH_2)_3CO_2Me$, $R^2 = CH_2C{\equiv}CCH_2CH_3$) (Method B). To a mixture of 1 ($R^1 = (CH_2)_3CO_2Me$, $R^2 = H$, 110 mg, 0.324 mmol), K_2CO_3 (800 mg, 5.8 mmol), and KI (70 mg, 0.42 mmol) in acetone (4 mL) was added 2-pentynyl bromide (45 μL, 0.42 mmol). The mixture was heated at reflux for 24 h and centrifugated to remove the solid. The organic layer was concentrated and the residue was chromatographed (SiO_2, 16:1 benzene/AcOEt) to give 127 mg (97%) of **2b**.

Similarly, the compounds **2d**, **e**, **h**, and **i** were prepared and

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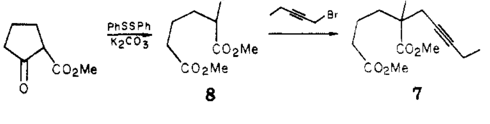
(6) The conversion of **5** into **6** was carried out as described in Japanese Patent Sho 45-26096 (1970).

(7) 2-(2-Pentynyl)-2-phenylthioadipate (**7**) was synthesized as follows: Cathodic reduction of **7** in the $MeOH-H_2SO_4$-carbon system at 20 mA (applied voltages 17–7 V) with 8 F/mol of electricity resulted in recovered starting material.



their proper data are also shown in Table I.

A General Procedure for Reductive Carbon–Sulfur Bond Cleavage of 2. A mixture of **2a** (R^1 = $(CH_2)_3CO_2Me$, R^2 = n-C_5H_{11}, 102 mg, 0.249 mmol) and 98% H_2SO_4 (120 mg) in MeOH (20 mL) was placed in a cathode cell which was divided by a fritted glass and fitted with a carbon electrode, a gas lead pipe, a thermometer, and a magnetic stirring bar. Electrolysis was carried out at a constant current of 20 mA (7–22 V), 8 F/mol of electricity, at room temperature. After removal of 13 mg (31%) of BTSSBT by filtration, the filtrate was concentrated and the residue was taken up in AcOEt. The extract was washed with aqueous 1 N NaOH and brine, dried (Na_2SO_4), and concentrated. The crude product was chromatographed (SiO_2, 20:1 benzene/AcOEt) to give 53 mg (87%) of **3a**. The alkaline solution was acidified with aqueous 10% HCl and taken up in AcOEt. The extract was washed with brine, dried (Na_2SO_4), and concentrated to give 22 mg (53%) of BTSH.

The electrolysis results and physical properties of a series of the compounds **3** are shown in Table I.

2-(2-Pentynyl)-2-(phenylthio)cyclopentanone (4b). To a cooled solution of NaH (50% in oil, 60 mg, 1.25 mmol) in DMF (1.5 mL) was added 2-(phenylthio)cyclopentanone[8] (200 mg, 1.04 mmol) and 2-pentynyl bromide (0.13 mL, 1.25 mmol). After being stirred for 30 min at 10 °C, the mixture was worked up in the usual manner to give 127 mg (47%) of **4b** after chromatography (SiO_2, 20:10:1 benzene/hexane/AcOEt): bp 93–97 °C (0.09 torr); IR (neat) 3060 (HC=), 1735 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.10 (t, J = 7 Hz, 3), 1.69–2.94 (m, 8), 2.35 (t, J = 2 Hz, 2), 6.95–7.60 (m, 5). Anal. Calcd for $C_{16}H_{18}OS$: C, 74.38; H, 7.02. Found: C, 74.39; H, 7.04.

2-(2-Pentynyl)cyclopentanone (5). A solution of **4a**[9] (224 mg, 0.711 mmol) and Et_4NOTs (200 mg) in MeOH (20 mL) as a catholyte was electrolyzed at a current of 25 mA with a Pt electrode. After passage of 7 F/mol of electricity, the usual workup gave **5** (79 mg, 74%) [bp 149–155 °C (32 torr) (lit.[10] 101 °C (9 torr))] and BTSH (101 mg, 85%).

Registry No. **1** (R^1 = $(CH_2)_3CO_2Me$), 70203-07-5; **1** (R^1 = n-C_6H_{13}), 70203-06-4; **1** (R^1 = $(CH_2)_3$CO-morpholino), 70203-09-7; **2a**, 72844-40-7; **2b**, 72844-41-8; **2c**, 72844-42-9; **2d**, 72844-43-0; **2e**, 72844-44-1; **2f**, 72844-45-2; **2g**, 70905-82-7; **2h**, 72844-46-3; **2i**, 72844-47-4; **3a**, 72844-48-5; **3b**, 72844-49-6; **3c**, 72844-50-9; **3d**, 72844-51-0; **3e**, 72844-52-1; **3f**, 72844-53-2; **3g**, 72844-54-3; **3h**, 72844-55-4; **3i**, 72844-56-5; **4a**, 68898-27-1; **4b**, 72844-57-6; **5**, 57026-62-7; *n*-pentyl bromide, 110-53-2; 1-bromo-3-methyl-2-butene, 870-63-3; 2-pentynyl bromide, 16400-32-1; 1-bromo-2-propene, 106-95-6; 2-(phenylthio)cyclopentanone, 52190-40-6; $(BTS)_2$, 120-78-5; BTSH, 149-30-4.

Supplementary Material Available: IR and ^1H NMR spectral data and elemental analyses of compounds **2** and **3** (2 pages). Ordering information is given on any current masthead page.

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[8] 2-(Phenylthio)cyclopentanone was prepared in the manner described by D. Seebach and M. Teschner, *Chem. Ber.*, **109**, 1601 (1976).

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Shielding by Methyl Groups in the ^1H NMR Spectra of Bicyclo[2.1.1]hexanes

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In the course of recent photochemical investigations[1] we have prepared a number of bicyclo[2.1.1]hexanes, most of which bear an ester or other negative group at C(5) and one or more methyl groups at C(1) and/or C(6). All of these compounds have low-field protons at one or both bridgeheads [C(1) and C(4)] and also at C(5). From examination of their ^1H nuclear magnetic resonance (NMR) spectra, along with comparisons with data already in the literature,[2] we have found effects of the methyl substituents on the chemical shifts of these low-field signals that are worthy of note.

The data are collected in Table I.[3] Because of the shielding effects discussed below, spectral assignments are based on observed integrals, spin–spin coupling, and internal consistency of the data and not on chemical shifts. In reaching these assignments, we have made use of the patterns of spin coupling previously reported by others:[2] $J_{AB} \approx 6$–9 Hz, $J_{BC} \approx 3$ Hz, $J_{AA'} \approx 7$–8 Hz, J_{AC} and $J_{BB'} \approx 0$, $J_{CC'} \approx 7$ Hz. In addition we have noted two novel long-range couplings of H_B, J_{BE} ($\equiv J_{B'D}$) $\approx$ 0–5 Hz and J_{BD} ($\equiv J_{B'E}$) $\approx$ 0–1.5 Hz. These small couplings can be seen particularly well in **13**. Spin–spin coupling constants reported for **13** were obtained by simulation[3b] and comparison with the actual 600-MHz spectrum.

We consider first shielding by bridgehead substitution. Replacement of H_C by methyl causes a small upfield shift in the remaining bridgehead hydrogen $H_{C'}$, a sizeable upfield shift in the exo proton $H_{B'}$, and apparently a much smaller change in the endo proton $H_{A'}$. The magnitude of this differential shielding of the exo proton can be great enough to cause inversion of the usual relative positions of $H_{A'}$ and $H_{B'}$ in a pair of epimers (see **5** and **6**), but this inversion does not necessarily occur (see **11** and **12**). This point is worth noting, since it has been known for some time that with hydrogen at the bridgehead in a pair of C(5)-substituted epimeric bicyclo[2.1.1]hexanes the exo proton H_B is downfield from the corresponding endo proton H_A.[2] It will be seen that in bridgehead-substituted compounds this simple rule cannot be used to assign the stereochemistry at C(5). We reported a similar finding in bicyclo[3.2.1]octanes some time ago.[4] The effects of bridgehead substitution in these two series may be contrasted with the behavior of norbornanones, where an exo proton appears reliably downfield from the corresponding endo proton, regardless of whether the adjacent bridgehead bears hydrogen or methyl.[5]

We have also noted a surprising effect of geminal methyl groups at C(6). This substitution causes the expected small shielding of the bridgehead hydrogen H_C but also leads to substantial deshielding of $H_{B'}$. Similar deshielding of a proton subject to severe steric compression by a neighboring group has been observed previously in other rigid polycyclic compounds.[6,7] In the present examples $H_{B'}$ is deshielded by 0.15–0.2 ppm by addition of two methyls at C(6), as can be seen by comparing **4** with **1** and **7** with **5**.

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[1] Wolff, S.; Barany, F.; Agosta, W. C. *J. Am. Chem. Soc.*, in press.

[2] Meinwald, J.; Lewis, A. *J. Am. Chem. Soc.* **1961**, *83*, 2769. Wiberg, K. B.; Lowry, B. R.; Nist, B. J. *Ibid.* **1962**, *84*, 1594. Gibson, T. W.; Erman, W. F. *J. Org. Chem.* **1972**, *37*, 1148. We use the proton subscripts employed by Wiberg.

[3] (a) Data for compounds 1 and **8** are at 60 MHz and are taken from ref 2. Those for **2** and **3** are at 100 MHz as reported by: Scheffer, J. R.; Wostradowski, R. A. *J. Org. Chem.* **1972**, *37*, 4317. All other data except for those for ketone **13** are from ref 1. Those for **5** and **6** were measured at 220 MHz and those for **4**, **7**, and **9–12** at 60 MHz. Data for **13** are at 600 MHz and were obtained by Dr. D. H. Live of this laboratory on a spectrometer at Carnegie-Mellon University. (b) Bothner-By, A. A.; Castellano, S. M. "Computer Programs for Chemistry"; De Tar, D. F., Ed.; W. A Benjamin: New York, 1968. "Intrcal"; Nicolet Instrument Corp.: Madison, WI, 1973.

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