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(16) In view of the studies of Clarke and Johnson,[17] it might be anticipated that the endo isomer of **15** would be extremely labile due to the thermally promoted loss of carbon monoxide. This would be expected to be accompanied by concerted opening of the aziridine moiety.
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Electrosynthesis of Hetero–Hetero Atom Bonds. 2. An Efficient Preparation of (2-Benzothiazolyl)- and Thiocarbamoylsulfenamides by Electrolytic Cross-Coupling Reaction of 2-Mercaptobenzothiazole, Bis(2-benzothiazolyl) Disulfide, and/or Bis(dialkylthiocarbamoyl) Disulfides with Various Amines

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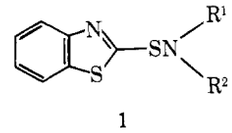
Two series of sulfenamides bearing 2-benzothiazolyl and thiocarbamoyl moieties were synthesized smoothly by electrolytic cross-coupling of either 2-mercaptobenzothiazole (**3**), bis(2-benzothiazolyl) disulfide (**4**) or bis(dialkylthiocarbamoyl) disulfides (**5**) with various amines in *N*,*N*-dimethylformamide. Electrolysis was carried out under constant voltages of 2–3 V (0.95–1.20 V vs. SCE) in an undivided cell, fitted with two platinum and/or two stainless steel Sus 27 electrodes. Direct electrosynthesis of thiocarbamoylsulfenamides (**2**) from dialkylamines and carbon disulfide was also accomplished in 81–96% yields.

During the last couple of decades, a number of synthetic methods for preparing (2-benzothiazolyl)- and thiocarbamoylsulfenamides (**1** and **2**) as important industrial chemicals[1] have been developed. The S–N bond-making reactions comprise the reaction of sulfenyl chlorides with amines,[2] coupling



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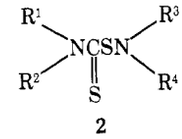

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Table I. Electrolytic Cross-Coupling of 3 and/or 4 with Cyclohexylamine[a]

entry	substrate (mmol)	cyclohexylamine,[2] mmol	electrodes (6 cm²)	current, mA/cm²	time,[b] h	sulfenamide 1 yield, %[c]
1	3[g] (0.90)	0.96	Pt	2.7–0	24	96[g]
2	3 (1.00)	1.00	Pt	1.7[e]	2.7	97[f]
3	4[g] (1.00)	2.00	Pt	3.0–0	16	95
4	4 (0.45)[d]	2.70	Pt	3.3–0	24	97
5	4 (0.45)	2.70	Sus	3.0–0	20	90
6	4 (0.45)	2.70	C	3.2–0	19	42

[a] Carried out in DMF (20 mL)–Et_4NClO_4 (100 mg) under a constant applied voltage of 2.0 V at 25–28 °C. [b] Being passed 2.0–2.5 faradays/mol of electricity based on substrates 3 or 4 except for entry 2 (1.0 faraday/mol). [c] Isolated yields. [d] Used wet DMF containing 0.5 mL of water. [e] Electrolyzed with a constant current (applied voltage 1.8–2.1). [f] Produced the disulfide 4. [g] Registry no.: 3, 149-30-4; 4, 120-78-5; 1, 95-33-0; cyclohexylamine, 108-91-8.

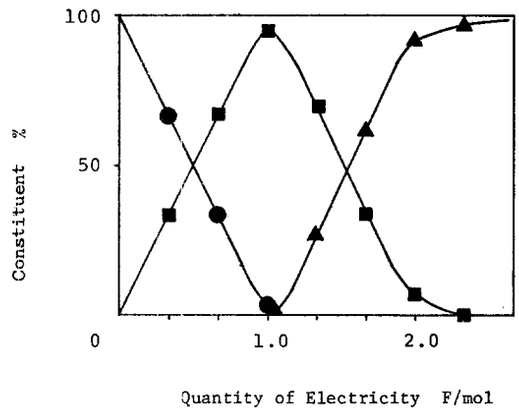


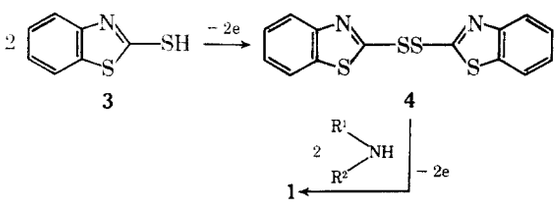
Figure 1. Experimental points (Table I, entry 1) are given every 0.33 faraday/mol for 1 (▲), 3 (●), and 4 (■).

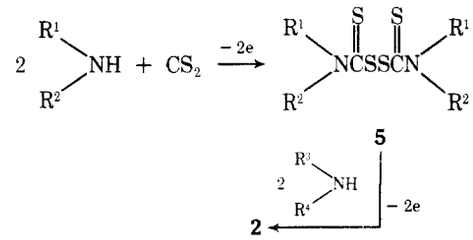
of metal mercaptides with *N*-chloroamines,[3] the amine-exchange reaction of sulfenamides,[4] the metal-assisted reaction of disulfides with amines,[5] and hydrogenation of thiooximes.[6] For large-scale preparations of 1 and 2, the oxidative cross-coupling reaction of 2-mercaptobenzothiazole (3),[7] dithiocarbamates,[8] and the related disulfides 4[9] and 5[10] with amines has been most frequently employed. However, use of stoichiometric amounts of oxidizing agents, e.g., sodium hypochlorite solution,[4a,7,8,9,10] hydrogen peroxide solution,[10b] chlorine,[7e] bromine,[7b] iodine,[7d] etc., brings about serious environmental problems.

As a simple and nonpolluting procedure for obtaining 1 and 2, we examined the electrochemical oxidation of 3, 4, and 5 under a controlled applied voltage in the presence of suitable amines and found a novel synthetic method for obtaining the sulfenamides 1 and 2.

Results and Discussion

(2-Benzothiazolyl)sulfenamides (1). According to the following general procedure, the sulfenamides 1 were electrosynthesized in an undivided cell equipped with two platinum electrodes. Electrolysis of the thiol 3 and cyclohexylamine in *N*,*N*-dimethylformamide (DMF) in the presence of tetraethylammonium perchlorate was conducted under a constant voltage of 2 V (0.95–1.2 V vs. SCE) at 26–28 °C. During the electrolysis the current varied from 2.7 mA/cm²





to almost zero. After ~2 faradays/mol of electricity had been passed for 24 h, workup of the reaction mixture gave *N*-cyclohexyl(2-benzothiazolyl)sulfenamide (1, R^1 = cyclohexyl; R^2 = H) in 96% yield (Table I, entry 1).

To follow the change of constituents in the electrolysis solution under the above electrolysis conditions, samples were taken by a microinjector at intervals of 0.33 faraday/mol. Figure 1 shows the relationship between constituents and current for entry 1. It reveals that most of the thiol 3 was converted into bis(2-benzothiazolyl) disulfide (4) when 1 faraday/mol of electricity was passed (Table I, entry 2). The most interesting fact is that further transformation of the disulfide 4 into the sulfenamide 1 is the major process in the continuing electrolysis. Thus, conversion of 3 into 1 was performed in quantitative yield after 2.1 faradays/mol of electricity were passed. It will be noted that no change of the constituent was observed when the mixture of 4 and cyclohexylamine in the same medium was stirred at room temperature for 24 h without passing electric current. The presence of excess cyclohexylamine in the electrolysis of 4 (entries 3 and 4) did not affect the yield of 1. In the latter case, stainless steel electrodes Sus 27 can be used instead of platinum electrodes without decreasing the yield of 1 (entry 5), whereas use of carbon electrodes decreases the yield to 42% due to absorption of some of the products on the electrode surface (entry 6). In a practical sense, the electrolysis reaction affording 1 from 4 is considered to be valuable as a general method for preparing 1. The results from the electrolysis of the disulfide 4 with various amines are shown in Table II.

Thiocarbamoylsulfenamides (2). The electrochemical S–N bond-making reaction can be extended with success to the synthesis of *N*-alkylthiocarbamoylsulfenamides (2), since electrolysis of a solution of bis(dialkylthiocarbamoyl) disulfides (5) and *N*-alkylamines in DMF was conducted under a constant applied voltage of 3 V (0.95–1.3 V vs. SCE) using either two platinum or stainless electrodes. After 2.1–2.5 faradays/mol, there were obtained the corresponding sulfenamides 2 in 74–98% yield (Table III).

A direct synthesis of 2 (R^1 = R^2 = R^3 = R^4) from carbon disulfide and dialkylamines was explored. Recently, the disulfides 5 have been electrosynthesized by the anodic oxidative coupling of dialkylammonium dithiocarbamates prepared in situ from carbon disulfide and dialkylamines in DMF.[11] The

Table II. (2-Benzothiazolyl)sulfenamides 1 from 4 by Electrolysis with Amines[a]

entry	amine	registry no.	electrodes (6 cm²)	applied voltage, V	current, mA/cm²	time,[b] h	sulfenamide 1 yield,[c] %	sulfenamide 1 mp (bp), °C (°C/Torr)	sulfenamide 1 registry no.
7	*n*-propylamine	107-10-8	Sus	3.0	1.8–0	6	98	(96–99/2)[d]	66552-53-2
8	isopropylamine	75-31-0	Sus	3.0	3.3–0	5	93	93.5–94.5[d]	10220-34-5
9	*tert*-butylamine	75-64-9	Sus	3.0	2.5–0	8	90	107.5–109[e]	95-31-8
10	morpholine	110-91-8	Pt	2.0	2.0–0	16	97	84.5–85.5[d]	102-77-2
11	piperidine	110-89-4	Sus	3.0	2.5–0	16	96	77–79[d]	26773-65-9
12	pyrrolidine	123-75-1	Sus	3.0	2.0–0	20	92	53–54[f]	17689-13-3
13	diethylamine	109-89-7	Sus	3.0	2.5–0	15	80	(89–92/2)[d]	2720-65-2
14	di-*n*-butylamine	111-92-2	Sus	3.0	2.5–0	19	89	(107–109/2)[d]	63451-39-8
15	diisopropylamine	108-18-9	Pt	2.0	1.0–0	15	25	58.5–59.5[g]	95-29-4
16	dicyclohexylamine	101-83-7	Pt	2.0	1.3–0	24	26	101–102[h]	4979-32-2

[a] Carried out in DMF (20 mL)–Et_4NClO_4 (100 mg) at 15–22 °C. [b] Being passed 2.1–2.5 faradays/mol of electricity based on **4**. [c] Isolated yields based on added **4**. [d] Reference 7e. [e] Reference 9. [f] Reference 4a. [g] Reference 3b. [h] Reference 14.

Table III. Sulfenamides 2 from 5 by Electrolysis with Amines[a]

entry	disulfides 5 R¹	disulfides 5 R²	disulfides 5 registry no.	amine	electrodes (6 cm²)	current, mA/cm²	time,[b] h	sulfenamide 2 yield,[c] %	sulfenamide 2 mp (bp), °C (°C/Torr)	sulfenamide 2 registry no.
17	Me	Me	137-26-8	cyclohexylamine	Pt	3.7–0.3	23	98	(100–102/2)[d]	52243-24-0
18	Me	Me		cyclohexylamine	Sus	4.7–0.7	20	98		
19	Me	Me		dimethylamine[g]	Sus	8.7–2.3	24	70	49.5–50[e]	2801-22-1
20	Et	Et	97-77-8	cyclohexylamine	Pt	3.3–0.4	29	95	63.5–64.5[d]	52185-80-5
21	Et	Et		piperidine	Sus	2.5–0.4	53	85	(84–87/2)[d]	66552-54-3
22	Et	Et		pyrrolidine	Sus	2.3–0.4	48	74	(83–86/2)	66552-55-4
23	*n*-Pr	*n*-Pr	2556-42-5	cyclohexylamine	Pt	3.0–0.5	43	92	(92–94/2)[f]	55947-00-7
24	*n*-Bu	*n*-Bu	1634-02-2	cyclohexylamime	Pt	3.3–0.3	41	84	(92–95/2)[d]	55947-01-8
25	$-(CH_2)_5-$		94-37-1	cyclohexylamine	Pt	6.3–0.5	24	89	74.5–75.5[d]	66552-56-5
26	$-(CH_2)_4-$		496-08-2	cyclohexylamine	Pt	7.2–0.8	42	82	(120–123/2)	66552-57-6

[a] Carried out under a constant applied voltage of 3 V in DMF (20 mL)–Et_4NClO_4 (100 mg) at 10–20 °C. [b] Being passed 2.1–2.5 faradays/mol of electricity based on **5**. [c] Isolated yields based on added **5**. [d] Reference 8d. [e] Reference 8c. [f] Reference 8b. [g] Registry no.: 124-40-3.

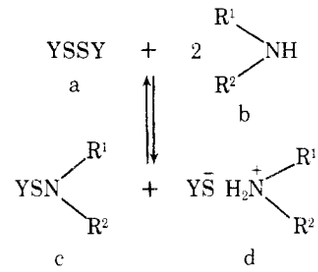
Table IV. Direct Electrosyntheses of Sulfenamides 2 from Amines and Carbon Disulfide[a]

entry	amine (mmol)	CS_2, mmol	solvent (20 mL)	current, mA/cm²	time,[b] h	sulfenamide 2 yield, %[c]	sulfenamide 2 mp, °C	sulfenamide 2 registry no.
27	piperidine (30)	6	DMF	8.0–0.4	24	92	100.5–101.5[d]	6250-27-7
28	piperidine (10)	2	MeCN	14.2–1.0	20	96	100.5–101.5[d]	
29	pyrrolidine (30)	6	DMF	8.0–0.2	25	93	86–87[e]	52345-73-0
30	morpholine (30)	6	DMF	6.2–0.2	37	81	136–137[e]	13752-51-7

[a] Carried out under a constant applied voltage of 3 V of 24–27 °C using two Pt electrodes (6 cm²) in the presence of Et_4NClO_4 (100 mg). [b] Being passed 2.5–3 faradays/mol of electricity based on CS_2. [c] Isolated yields based on added CS_2. [d] Reference 8d. [e] Reference 3a.

electrolysis solution thus obtained was submitted to the further electrochemical oxidation in the presence of excess dialkylamines (sixfold) to give the desired sulfenamides **2** smoothly (Table IV). The total conversion of carbon disulfide and dialkylamine into **2** required 2.1–2.5 faradays/mol of electricity referring to added carbon disulfide.

Mechanistic Consideration of S–N Bond Formation. To our knowledge, the electrosynthesis of the sulfenamides **1** and **2**, as mentioned above, is the first example of the electrochemical S–N bond-making reaction, involving oxidative cross-coupling of the disulfides **4** or **5** with amines. In the preparation of the sulfenamides **1** and **2** by chemical oxidation,[7c,8c] Carr et al. suggest that the reaction of disulfides (a) and amines (b) proceeds to give sulfenamides (c) and mercaptide ion (d). The latter anion (d) can be chemically oxidizing in situ to regenerate a. Recently, the metal-assisted synthesis of **1** without using oxidizing agents has been reported, where the generating mercaptide ion is removed by



filtration as insoluble metal complexes.[5] Independently, we confirmed the presence of sulfenamides (c) on a TLC plate in a stirring mixture of a and excess cyclohexylamine in DMF, although concentration of the mixed solution under diminished pressure afforded only the disulfide (a). In addition, removal of most of volatile materials from a mixture of equimolar amounts of c and d in DMF provided also a as a sole product. These experiments clearly demonstrate that the

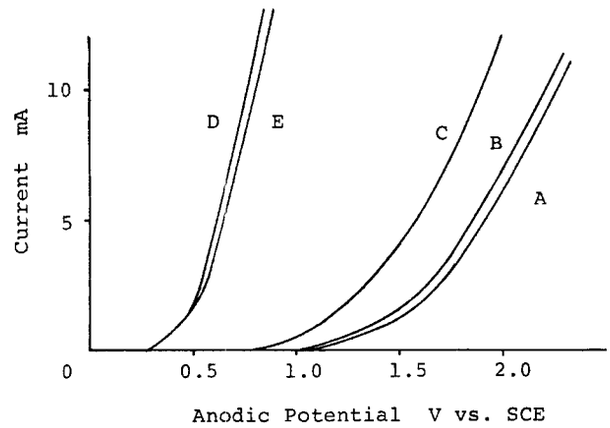
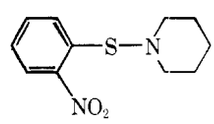


Figure 2. Current–potential curves: system A, Et_4NClO_4 (100 mg)–DMF (20 mL); system B, 4 (0.45 mmol)–Et_4NClO_4–DMF; system C, cyclohexylamine (1.03 mmol)–Et_4NClO_4–DMF; system D, 4–cyclohexylamine–Et_4NClO_4–DMF; system E, 3 (0.45 mmol)–cyclohexylamine–Et_4NClO_4–DMF.

sulfenamide formation reaction is reversible in the medium.

The present electrolysis reaction can also be rationalized by assuming that the reaction pathway involves anodic oxidation of the mercaptide ion, giving disulfide through the coupling of thio radical intermediates.[12] This assumption is consistent with the following results. The current–potential curves of various systems of the disulfide **4**, cyclohexylamine, and Et_4NClO_4 in DMF are shown in Figure 2, indicating that discharge potentials of A, B, and C systems occur over 0.8 V vs. SCE. However, in the D system the current begins to pass strikingly at lower potential, ~0.3–0.5 V vs. SCE, as similar to the corresponding thiol–cyclohexylamine system (curve E). This result in similarity on oxidation potentials implies that in the D system, stirring a mixture of **4** with cyclohexylamine in DMF would provide more or less the corresponding sulfenamide (c) as well as mercaptide ion (d) as the result of reversible reaction and the latter ion would be immediately oxidized on the anode, given a.

The above results are in sharp contrast to the unfruitful ones obtained under the same electrolysis conditions with di-*tert*-butyl disulfide, diphenyl disulfide, and dibenzyl disulfide, which have no electron-withdrawing group attached to the sulfur atom of the disulfide function. However, electrolysis of bis(*o*-nitrophenyl) disulfide (**6**) with piperidine in the same conditions afforded the corresponding sulfenamide



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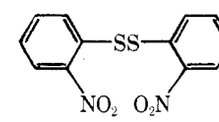

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7 in 40% yield. It will be noted as supporting evidence for the formation of mercaptide ion (d) that increase of electrophilic character of the sulfur atom ascribable to the nitro group of **6** would be allowed to undergo attack by amines.

Experimental Section

All melting points and boiling points are uncorrected. IR spectra were determined with a JASCO IRA-I infrared spectrophotometer fitted with a grating. NMR spectra were taken at 60 MHz with a Hitachi R-24 spectrometer.

Materials. Commercially available 2-mercaptobenzothiazole (**3**) and bis(2-benzothiazolyl) disulfide (**4**) were used. Bis(dialkylthiocarbamoyl) disulfides (**5**) were prepared by electrolysis of the corresponding dialkylamines and carbon disulfide according to the procedure described in the preceding paper.[11]

General Procedure of the Electrolysis. The electrolysis was carried out in a water-jacketed beaker (3.5-cm in diameter and 10-cm high) fitted with a thermometer, a stirring bar, a gas lead pipe, and two platinum foil electrodes (6 cm^2) or two stainless steel electrodes (Sus 27, 6 cm^2), being placed parallel 5 mm apart. The regulated dc power was supplied by a Metronix Model-543B instrument. The reaction conditions and the results are summarized in Tables I, II, III, and IV. The typical experimental procedures are shown below.

***N*-Cyclohexyl(2-benzothiazolyl)sulfenamide (1, R^1 = H; R^2 = cyclohexyl) from 2-Mercaptobenzothioazole (3) and Cyclohexylamine (entry 1).** A mixture of **3** (150 mg, 0.90 mmol) and cyclohexylamine (85 mg, 0.96 mmol) in DMF (20 mL) containing Et_4NClO_4 (100 mg) was electrolyzed at 2 V (0.95–1.20 V vs. SCE) at 26–28 °C using two Pt electrodes (6 cm^2). During the course of the reaction the current density varied from 2.7 mA/cm^2 to almost zero. After 2.0 faradays/mol of electricity were passed (24 h), the reaction mixture was concentrated in vacuo and the residue was chromatographed (SiO_2, benzene) to give **1** (227 mg, 96%) as white crystals: mp 98–100 °C from hexane (lit.[4c] mp 99–101 °C); IR (Nujol) 3220 (NH), 3055 (HC=C), 1430 cm^{-1}; NMR ($CDCl_3$) δ 0.80–2.50 (m, 10 H), 2.88 (br, 1 H), 3.28 (m, 1 H), 6.90–8.10 (m, 4 H).

***N*-Cyclohexyl(2-benzothiazolyl)sulfenamide (1, R^1 = H; R^2 = cyclohexyl) from Bis(2-benzothiazolyl) Disulfide (4) and Cyclohexylamine (entry 3).** A mixture of **4** (333 mg, 1.00 mmol) and cyclohexylamine (198 mg, 2.00 mmol) in DMF (20 mL) containing Et_4NClO_4 (100 mg) was electrolyzed using two Pt electrodes (6 cm^2) at 2 V (1.0–1.3 V vs. SCE) at 26 °C. The initial current of 3.0 mA/cm^2 dropped to almost zero after ~2.2×10^{-3} faradays of electricity were passed (16 h). The reaction mixture was concentrated in vacuo and the residue was chromatographed (SiO_2, benzene) to give **1** (504 mg, 95%): mp 98–100 °C from ether–hexane (lit.[4c] mp 99–101 °C).

***N*-Cyclohexyl(*N'*,*N'*-diethylthiocarbamoyl)sulfenamide (2, R^1 = R^2 = Et; R^3 = H, R^4 = cyclohexyl) from Bis(diethylthiocarbamoyl) Disulfide (5, R^1 = R^2 = Et) and Cyclohexylamine (entry 20).** A mixture of **5** (0.88 g, 3.0 mmol) and cyclohexylamine (1.81 g, 18.3 mmol) in DMF (20 mL) containing Et_4NClO_4 (100 mg) was electrolyzed at 3 V (0.95–1.30 V vs. SCE) at 11–13 °C using two Pt electrodes (6 cm^2). The initial current of 3.3 mA/cm^2 dropped to 0.4 mA/cm^2 after 7×10^{-3} faradays of electricity was passed (29 h). After evaporation of the solvent the residue was taken up with ether, washed with brine, and dried (Na_2SO_4). Removal of the solvent followed by recrystallization from hexane gave **2** (1.40 g, 95%): mp 63.5–64.5 °C (lit.[8d] mp 64–65 °C); IR (Nujol) 3230 (NH), 1498, 1423, 1270 cm^{-1}; NMR ($CDCl_3$) δ 1.00–2.30 (m, 10 H), 1.27 (t, J = 7 Hz, 6 H), 2.77 (br, 1 H), 3.30–4.30 (m, 5 H).

Similarly, electrolysis of a mixture of **5** (R^1 = R^2 = Et, 0.89 g, 3.0 mmol) and pyrrolidine (1.28 g, 18.0 mmol) in DMF (entry 22) gave **2** (R^1 = R^2 = Et; R^3, R^4 = $-(CH_2)_4-$, 0.97 mg, 74%): bp 83–86 °C (2 mm); IR (neat) 1490, 1418, 1268 cm^{-1}; NMR ($CDCl_3$) δ 1.26 (t, J = 7 Hz, 6 H), 1.65–2.30 (m, 4 H), 2.70–4.20 (m, 8 H).

Anal. Calcd for $C_9H_{18}N_2S_2$: C, 49.50; H, 8.31. Found: C, 49,64; H, 8.42.

In a similar fashion, **5** (R^1, R^2 = $-(CH_2)_4-$, 0.89 g, 3.0 mmol) and cyclohexylamine (1.81 g, 18.3 mmol) afforded **2** (R^1, R^2 = $-(CH_2)_3-$, 1.22 g, 82%) (entry 26): bp 120–123 °C (2 mm); IR (neat) 3250 (NH), 1458, 1436, 1181, 1157, 1003, 955 cm^{-1}; NMR ($CDCl_3$) δ 0.60–2.40 (m, 14 H), 2.50–3.10 (m, 1 H), 3.20–4.10 (m, 5 H).

Anal. Calcd for $C_{11}H_{20}N_2S_2$: C, 54.06; H, 8.25. Found: C, 53.89; H, 8.08.

***N*,*N*-Pentamethylene(*N'*,*N'*-pentamethylenethiocarbamoyl)sulfenamide [2, R^1, R^2 = $-(CH_2)_5-$; R^3, R^4 = $-(CH_2)_5-$] from Piperidine and Carbon Disulfide (entry 27).** A mixture of piperidine (2.55 g, 30.0 mmol) and CS_2 (0.36 mL, 6.0 mmol) in DMF (20 ml) containing Et_4NClO_4 (100 mg) was electrolyzed at 3 V (0.85–1.20 V vs. SCE, 8.0–0.4 mA/cm^2) at 27 °C for 24 h. Workup in a similar way as that above gave **2** (1.49 g, 92%): mp 100.5–101.5 °C from hexane (lit.[8d] mp 100–102 °C); IR (Nujol) 1482, 1431, 1241 cm^{-1}; NMR ($CDCl_3$) δ 1.40–1.90 (m, 12 H), 3.20–4.20 (m, 8 H).

***N*,*N*-Pentamethylene-*o*-nitrophenylsulfenamide (7) from Bis(*o*-nitrophenyl) Disulfide (6) and Piperidine.** A mixture of **6** (308 mg, 1.00 mmol) and piperidine (517 mg, 6.07 mmol) in DMF (20 mL) containing Et_4NClO_4 (100 mg) was electrolyzed at 3.0 V (2–0.9 mA/cm^2) at 25 °C using two Pt electrodes (6 cm^2). After being passed 4.8×10^{-3} faradays of electricity (26 h), the mixture was concentrated in vacuo and the residue was chromatographed (SiO_2, benzene) to give **7** (192 mg, 40%): bp 77–80 °C (2 mm); IR (neat) 3080, 3055 (CH=C), 1592, 1564, 1506, 1333 cm^{-1}; NMR ($CDCl_3$) δ 1.00–2.30 (m, 6 H), 2.60–3.60 (m, 4 H), 7.00–8.50 (m, 4 H).

Anal. Calcd for $C_{11}H_{14}N_2O_2S$: C, 55.44; H, 5.92. Found: C, 55.51; H, 6.03.

Similar electrolysis of di-*tert*-butyl, diphenyl, and dibenzyl disul-

fides in DMF in the presence of piperidine (sixfold) gave no detectable amounts of sulfenamides, resulting in recovery of the starting materials.

Registry No.—**6**, 1155-00-6; **7**, 66552-58-7; carbon disulfide, 75-15-0.

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Identification of 2,5-Dihydropyridine Intermediates in the Reactions of 2-Alkyl(phenyl)-1-lithio-1,2-dihydropyridines with Alkyl Halides

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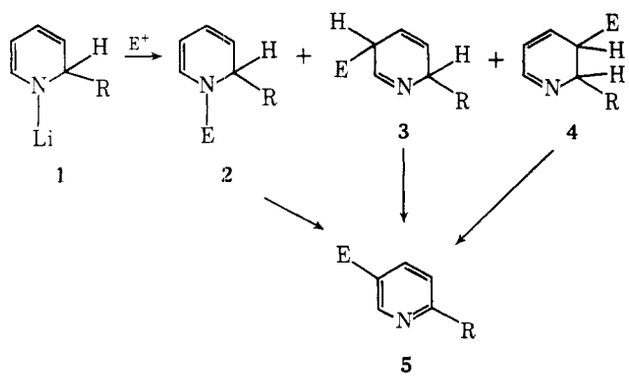
A series of 2,5-disubstituted 2,5-dihydropyridines (**10**) have been prepared from 2-alkyl(phenyl)-1-lithio-1,2-dihydropyridines (**1**) and alkyl halides and have been characterized by their IR and NMR spectra. Each 2,5-dialkyl-2,5-dihydropyridine (**10a–d**) decomposes on exposure to air or when heated to a mixture containing the corresponding 2,5-dialkylpyridine (**11a–d**) and the 2,5-dialkyl-1,2,5,6-tetrahydropyridine (**12a–d**). However, decomposition of a 5-alkyl-2-phenyl-2,5-dihydropyridine (**10d,f**) gives only the 5-alkyl-2-phenylpyridine (**11e,f**). The 2,5-dihydropyridines (**10**) are converted to the corresponding tetrahydropyridines (**12**) by lithium aluminum hydride reduction.

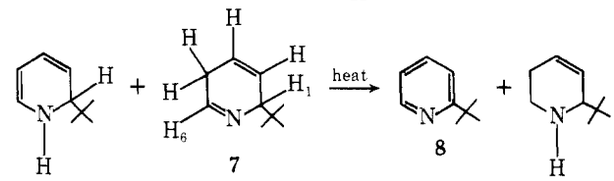
There has been little direct evidence for the existence of unstable 2,5-dihydropyridines.[1] However, they have been proposed as intermediates in reactions which include the sodium borohydride reduction of pyridinium salts,[2,3] the synthesis of 8-azasteroids,[4] the dehydrogenation of a 1,4-dihydropyridine,[5] and the reactions of lithium tetrakis(*N*-dihydropyridyl)aluminate with alkyl halides and bromine.[6]

The reactions of 1-alkyl(aryl)-1,2-dihydropyridines (**1**) with electrophiles can, in theory, lead to 1,2-, 2,5-, and 2,3-dihydropyridines as shown in Scheme I. The stable acylation products[7,8] of complex **1** (R = phenyl) are 1,2-dihydropyridines (**2**) which result from *N*-acylation and 2,5-disubstituted pyridines (**5**) which involve *C*-acylation. The latter are assumed to form from decomposition of 2,5-dihydropyridine intermediates (**3**). Alkylation[8,9,10] of complex **1** (R = phenyl) by the use of alkyl halides leads to 5-alkyl-2-phenylpyridines (**5**) which also presumably are formed on the decomposition of 2,5-dihydropyridines (**3**). Products obtained from the reaction of **1** with bromine,[9] cyanogen bromide,[11] benzophenone,[12] and phenyl disulfide[13] also are assumed to involve 2,5-dihydropyridine precursors.

Scheme I



Scheme II



The first direct evidence for a 2,5-dihydropyridine, formed in the reaction of 2-*tert*-butyl-1-lithio-1,2-dihydropyridine (**1a**) with methanol, was reported[14] from this laboratory. This reaction gave dihydropyridines **6** and **7** which were decomposed by heat to 2-*tert*-butylpyridine (**8**) and 2-*tert*-butyl-1,2,5,6-tetrahydropyridine (**9**).

Results and Discussion

We have now identified the 2,5-dihydropyridines (**10**) obtained from the reactions of pyridine–alkyllithium complexes (**1**) with methyl and ethyl halides (Table I). Structural as-

0022-3263/78/1943-3227$01.00/0