δ 180.10, 139.10, 136.90, 134.45, 130.82–125.85, 46.55, 43.70, 40,67, 26.22, 21.00; MS, m/e 265 (M^+), 132, 91. Anal. Calcd for $C_{19}H_{23}N$: C, 86.04; H, 8.68; N, 5.28. Found: C, 85.97; H, 8.60; N, 5.32.

Spectral data for compounds **4b** are included as supplementary material.

Treatment of 4 with 2 N Sulfuric Acid. Preparation of 2,2-Dimethyl-3-phenyl-1-*p*-tolyl-1-propanone (3i). A solution of **4a** (5 mmol) in THF (50 mL) was heated with 2 N H_2SO_4 (10 mL) at 50 °C for 1 h. The solution was slowly poured into ice-cooled water, extracted with ether, and evaporated. The residue was distilled under reduced pressure to yield **3i**: IR (film) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, 6 H), 2.35 (s, 3 H), 3.05 (s, 2 H), 7.00–8.00 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 191.20, 141.53, 139.00, 137.10, 131.43–127.03, 49.73, 47.25, 27.03, 22.23. Anal. Calcd for $C_{18}H_{20}O$: C, 85.71; H, 7.94. Found: C, 85.60; H, 8.02.

Spectral data for compounds **3j** and **3k** are included as supplementary material.

Preparation of *N*-(2,2-Dimethyl-1,3-diphenylpropyl)methylamine (6c). Method A. Reduction of 4b with $NaBH_4$/MeOH. To a solution of imine **4b** (5 mmol) in anhydrous THF (20 mL) and anhydrous methanol (10 mL) was slowly added $NaBH_4$ (1.85 g, 50 mmol) with stirring in an ice bath. After being stirred for 4 h at room temperature, the solution was poured into 3 N KOH and extracted with ether. The extract was dried over sodium sulfate and evaporated. The resulting crude product was distilled under reduced pressure. Amine **6c** was obtained and characterized as its hydrochloride.

Method B. Reduction of 4b with Na/*i*-PrOH. A solution of **4b** (5 mmol) in anhydrous THF (20 mL) and anhydrous *i*-PrOH (10 mL) was added dropwise to a mixture of Na (2.0 g, 86 mmol) and anhydrous THF (10 mL) at room temperature. The subsequent operations were the same as those for method A. Amine **6c** was obtained and characterized as its hydrochloride. Yields and melting points are given in Table II.

6c·HCl: IR (Nujol) 3200–2500, 1590, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (s, 3 H), 1.20 (s, 3 H), 2.60 (br t, 3 H) (+D_2O, s, 3 H), 2.75 (d, 1 H, J = 12.5 Hz), 3.05 (d, 1 H, J = 12.5 Hz), 3.85 (br, 1 H) (+D_2O, s, 1 H), 7.00–7.70 (m, 10 H), 9.70 (br, s, N H); ^{13}C NMR ($CDCl_3$) δ 136.95, 132.41–126.26, 74.13, 44.96, 38.52, 33.30, 24.60, 23.80. Anal. Calcd for $C_{18}H_{24}NCl$: C, 74.61; H, 8.29; N, 4.84. Found: C, 74.57; H, 8.40; N, 4.73.

Preparation of (3-Phenyl-1-*p*-tolylpropyl)amine (6b). To a solution of **9** (R^2 = H, R^3 = *p*-tolyl) (see general preparative procedure for ketones **3a–h**) were slowly added anhydrous methanol (10 mL) and $NaBH_4$ (3.73 g, 100 mmol) with stirring in an ice bath. The subsequent operations were the same as those for method A (see above). Aniline (R^1NH_2) was distilled and the amine **6b** (80%) purified by recrystallization from *n*-hexane: mp 109–11 °C; ^1H NMR ($CDCl_3$) δ 0.60 (br s, NH), 0.75 (q, 2 H), 1.09 (s, 3 H), 1.33 (m, 2 H), 2.60 (t, 1 H), 5.85–6.18 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 145.01, 143.80, 137.10, 130.5–126.7, 56.10, 41.91, 33.30, 21.52; MS, m/e 225 (M^+), 208, 120, 91, 77. Anal. Calcd for $C_{16}H_{19}N$: C, 85.33; H, 8.44; N, 6.22. Found: C, 85.12; H, 8.51; N, 6.29.

Spectral data for compound **6a** are included as supplementary material.

Supplementary Material Available: Spectral and analytical data for compounds **3a,c,e,j,k**, **4b**, and **6a** (2 pages). Ordering information is given on any current masthead page.

Selective Formation of Five-Membered Heterocyclic Products by Anodic Oxidation of Alkyl Isothiocyanates (RNCS) in Dichloromethane and Their Thermal Isomerization and Decomposition[1]

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Received August 10, 1987

Anodic oxidation of primary and secondary alkyl isothiocyanates (RNCS) in dichloromethane yielded two isomers of five-membered heterocyclic products, 4-alkyl-5-(alkylimino)-1,2,4-dithiazolidine-3-one **2** and 2,4-dialkyl-5-oxo-1,2,4-thiadiazolidine-3-thione **3**. Their relative ratio was found to be dependent on the length or bulkiness of the alkyl group in RNCS. Isomer **2** was favorable for R = Me and Et and exclusive for R = *n*-Pr, *n*-Bu, and cyclohexyl. Upon GLC injection (at 150–200 °C), compounds of type **2** isomerized completely to **3** (when R = Me, Et), mostly to **3** and partially decomposed to RN=C=NR (**11**) (when R = *n*-Pr, *n*-Bu), and exclusively decomposed to **11** for R = cyclohexyl. Tertiary RNCS did not yield cyclic products but instead underwent chlorination to substitute a hydrogen (or "NCS" group) by chlorine. Plausible mechanistic schemes are suggested and discussed.

Introduction

The anodic oxidation of the cumulene functionality either in allenic hydrocarbons or in some selective heteroallenes was described before.[2,3] Recently we reported on the anodic oxidation of alkyl isocyanates and alkyl isothiocyanates in acetonitrile.[4] It was found that the former were oxidized at relatively high anodic potentials (3–3.2V vs Ag/Ag^+) while the latter at significantly lower ones (2–2.2 V). As to the outcome of their preparative controlled potential electrolysis, each family of compounds afforded an entirely different spectrum of products. RNCO derivatives gave low yield mixtures of products which stemmed mainly from C–NCO bond cleavage accompanied (or followed by) with nucleophilic attack by either water or acetonitrile to form carbonyl derivatives or amides, respectively. Under dry conditions, the major products involved mono-, di-, and tricyanomethylation and a loss of the cumulene functionality. RNCS derivatives were found to undergo three types of processes which their relative ratio was highly dependent on the nature of the alkyl group: (a) exclusive formation of five-membered

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* Author to whom correspondence should be addressed.

[1] Published in part in the 1st International Symposium on Electroorganic Synthesis, Kurashiki, Japan, Oct 31–Nov 3, 1986. See proceeding of the: "Recent Advances in Electroorganic Synthesis" (ed. S. Torii) In *Studies in Organic Chemistry*; Torii, S., Ed.; Elsevier: New York, 1987; Vol. 30, pp 17–23.

[2] Becker, J. Y. *Isr. J. Chem.* **1985**, *26*, 196 and references therein.

[3] Becker, J. Y.; Zinger, B. *J. Am. Chem. Soc.* **1982**, *104*, 2327.

[4] Becker, J. Y.; Zinger, B.; Yatziv, S. *J. Org. Chem.* **1987**, *52*, 2783.

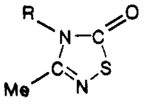
0022-3263/88/1953-1744$01.50/0

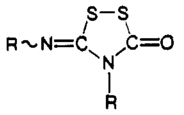
Table I. Cyclic Voltammetry Data of Alkyl Isothiocyanates[a]

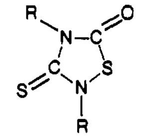
substrate	RNCS, R	Ep_{ox}/V[b]
4	Me	1.60
5	Et	1.65
6	*n*-Pr	1.70
7	*n*-Bu	1.70
8	cyclohexyl	1.85[c]
9	1-Adamantyl	*d*
10	*t*-Bu	*d*

[a] In CH_2Cl_2–0.1 M TBAP on Pt anode. [RNCS] ~ 10 mM. [b] Potentials are quoted vs Ag wire (+0.39V vs NHE) quasi-reference electrode and at 200mV/s sweep rate, for both forward and reverse scans, starting from 0 V and ending at this potential. All waves are electrochemically irreversible, and no reduction waves were found on reverse scans. [c] Could be measured only when [8] = 50 mM. [d] Could not be seen up to +2 V.

heterocyclic products, **1–3**, from primary alkyl isothiocyanates. (b) Formation of α-cleavage products (RNHCOCH$_3$) from secondary and tertiary RNCS. (c) Formation of isocyanates, RNCO (due to a substitution of sulfur for oxygen at the cumulene functionality), from secondary and tertiary RNCS.


1


2


3

In the present work we describe the electrochemical investigation of alkyl isothiocyanates in dichloromethane, an aprotic but nonpolar solvent. Unlike acetonitrile, this solvent could much less stabilize carbocations intermediates and could not react directly as a nucleophile. Therefore, it would be interesting to investigate the type of products obtainable in this medium, especially from secondary and tertiary RNCS.

Results

Seven alkyl isothiocyanates, **4–10**, were electrochemically investigated in CH_2Cl_2. Their corresponding anodic peak potentials are listed in Table I. Primary RNCS **4–7** showed anodic waves at 1.6–1.7V; the secondary derivative **8** was oxidizable at 1.85 V; for the tertiary substrates **9** and **10**, no oxidation waves were detected up to 2 V. Each of the anodic wave observed was found to be electrochemically irreversible, and no reduction waves were observed in any voltammogram on reverse scans.

The type of products formed by controlled potential electrolysis of **4–10**, their yields and electrochemical experimental conditions are described in Table II. It is obvious that only primary and secondary RNCS gave heterocyclic products of types **2** and **3**, whereas tertiary RNCS afforded chlorinated products.

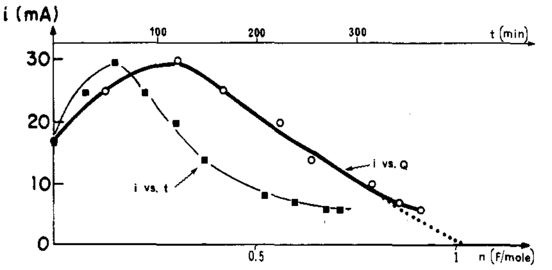


Figure 1. Current–charge and current–time curves of electrolysis of **4** (for n = 1 F/mol, the electricity consumption is 280 C).

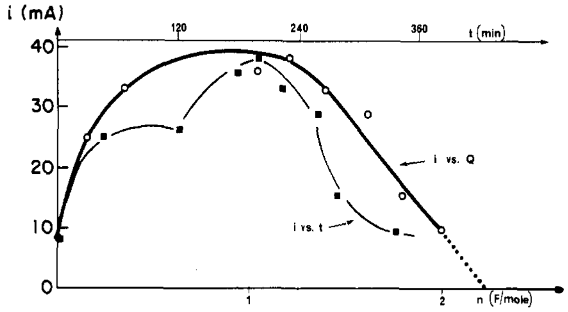


Figure 2. Current–charge and current–time curves of electrolysis of **6** (for n = 1 F/mol, the electricity consumption is 321 C).

Some of the heterocyclic derivatives underwent thermal decomposition to yield mainly carbodiimides (**11a–c**, see Table III). Kinetic data for the rate of isomerization of **2b** to **3b** were obtained by FT-IR measurements, at elevated temperatures.

"Current–charge" (which represent coulometric experiments from which one could extract "n" values) and "current–time" curves, are shown for two representative derivatives, **4** and **6**, in Figures 1 and 2, respectively. These curves demonstrate the comparative electrochemical behavior between compounds which their electrolysis terminated after consuming ~1 F/mol and those which consumed ~2 F/mol. However, in all cases electroactive intermediates were formed throughout electrolysis, as indicated by the "humps" present in each of the curves.

Discussion

As was also observed in acetonitrile,[4] **4** and **5** consumed ~1 F/mol by the end of electrolysis, with no starting material left (Table II, entries 1 and 2). However, **6** and

Table II. Product Yields and Controlled Potential Electrolysis Data

					products (%)[c]		
entry	RNCS (mM)	E_{ox}, V[a]	n, F/mol	yield, %[b]	**2**	**3**	recovd s.m.[d]
1	**4** (140)	1.85	0.7–0.9	30–60	**2a** (60)	**3a** (40)	
2	**5** (115)	1.80	0.8–1.0	34–79	**2b** (86)	**3b** (14)	
3	**6** (60)	1.85	1.7–2.0	73	**2c** (70)		(19)
4	**7** (74)	1.85	1.9	52	**2d** (61)		(39)
5	**7** (53)	1.80	0.8	47	**2d** (25)		(75)
6	**8** (52)	1.85	1.0	33–43	**2e** (43)		(32)
7	**9** (50)	2.20	1.3	20	**13a** (11)	**13b** (28)	(61)
8	**9** (52)	2.20	2.1	52	**13a** (10)	**13c** (90)	
9	**10** (70)	1.85	1.0–1.1	34–40			(80–90)
10	**10** (75)	2.20	0.9	41			(70)[e]

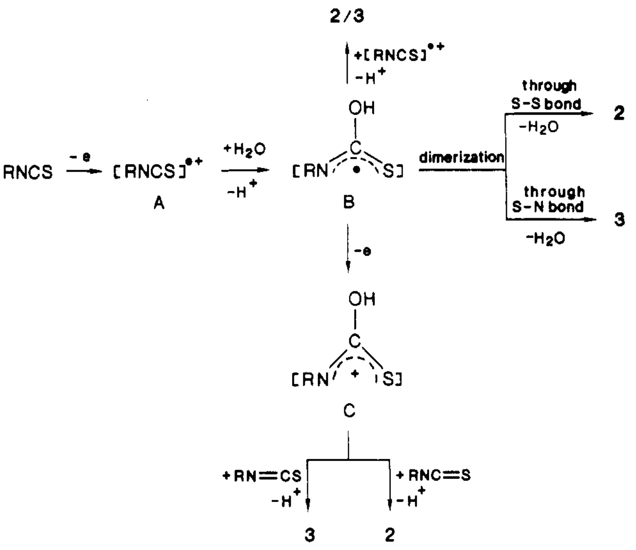
[a] Oxidation potential vs Ag wire reference electrode (+0.15 V vs SCE). [b] Yield based on ratio between weight of product mixture to weight of starting material. An average yield (or range) of three runs is given. [c] Relative ratio based on ^1H NMR integration of products mixture after workup and before GLC injection, except for entries 8–10, in which relative ratio based on GLC integration on products. [d] s.m. = starting material. Wherever the sum is not 100% means that additional unidentified products were formed (usually one). [e] ^1H NMR of the product mixture indicates the formation of $Me_2C(NCS)(CH_2Cl)$ (**14**).

Table III. Relative Product Ratios before and after GLC Separation

	relative % of products				
	before GLC separation[a]		after GLC separation		
substrate	% type 2	% type 3	% type 2	% type 3	% type 11
4	72	28	0	100	0
5	81	19	0	100	0
6	100	0	28	56	16[b]
7	100	0	20	48	32[c]
8	100	0	0	0	100

[a] For one particular run only. Note that the yields quoted in Table III are average of three runs. [b] % of **11a** + **12a**, assuming that **12a** was formed by hydrolysis of **11a**. [c] As in footnote *b* for **11b** + **12b** (see eq 4).

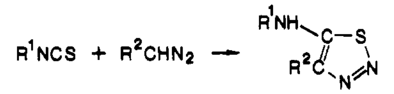
Scheme I



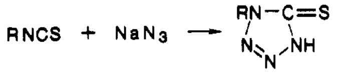
7 required ~2 F/mol, after which considerable amounts of unreacted material was left (entries 3 and 4). When arbitrarily only ~1 F/mol was allowed to be consumed in the electrolysis of **7** (entry 6), mostly starting material was recovered. These observations may indicate a change in mechanism within the primary alkyl isothiocyanates, e.g., an EC vs ECEC, as is described in Scheme I. In an EC mechanism, intermediate A could undergo a follow-up chemical reaction to form intermediate B, which then could dimerize or react with A to yield **2** and **3** as the final products. In an ECEC mechanism intermediate B is further oxidized to C, which then attacks either the C=S or N=C bond in the substrate to generate products **2** or **3**, respectively. It should be noted that Scheme I is an oversimplified one since it does not take into account all possible routes, e.g., the reaction of A or B with a neutral molecule of a substrate or the dimerization of A. Regarding the latter point, although the recombination of A to form a doubly charged dimeric species cannot be excluded we tend to disfavor such a mechanism because of the coulombic repulsion which could have been exerted by the two positive charges localyzed in the dimeric segment.

Figures 1 and 2 represent coulometric examples of current–charge curves for substrates which consumed either ~1 or ~2 F/mol of electricity, respectively. The shape of each curve is somewhat unusual since it deviates from the typical expected exponential ones (similar "humps" are also observed in the corresponding current vs time curves). The shape of this curve is known to be dependent upon a number of factors such as polarization and coverage of the electrode surface, physi- or chemisorption of substrate in competition with intermediates, catalytic processes, etc. However, it may also indicate that electroactive species are generated and compete favorably with the oxidation of the parent substrate. As an example, radical B in Scheme I may easily oxidized to the cation C, prior to the oxidation of RNCS.

It is noteworthy that addition–cyclization reactions are not unusual for alkyl isothiocyanates.[5] For instance, in the presence of diazo derivatives, a [2 + 3] cycloaddition to the C=S bond takes place[5a] (eq 1). However, in the presence of sodium azide the cycloaddition involving the N=C bond is predominant[5b] (eq 2). In general it was



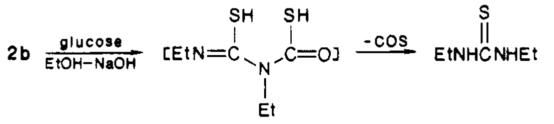
(1)



(2)

found that the [2 + 3] cycloaddition is preferred with the C=S bond because it is more polar than the C=N bond.[6] This difference in polarity is due to the observation that the nucleophilicity of the S atom is higher than that of the N atom and also because the 2π-3π interaction in C=S is weaker than the 2π-2π interaction in C=N. However, in spite of these arguments, inductive effects may cause the cycloaddition reaction to be favorable with the N=C bond of RNCS. Our results (Table II) are in agreement with the general trend of preferred addition to the C=S bond, since products of type **2** were predominant (entries 1–7, Table II). In fact, in the latter cases, steric hindrance or nonpolar bond interactions seem to lead to an exclusive addition to the C=S bond despite the increase in inductive effects. However, when the alkyl group is small (entry 1, Table II) the addition to the N=C bond competes almost equally with that of the C=S bond.

We would like to outline some of the chemical properties of the heterocyclic products. A selective reduction of the S–S bond in **2** takes place when a mixture of e.g., **2b** and **3b**, is subjected to reduction according to a known procedure,[7] as shown in eq 3. Under these conditions, isomer **3b** remains unchanged.



$$\mathbf{2b} \xrightarrow[\text{EtOH-NaOH}]{\text{glucose}} [\text{EtN}{=}\overset{\text{SH}}{\text{C}}{-}\underset{\text{Et}}{\text{N}}{-}\overset{\text{SH}}{\text{C}}{=}\text{O}] \xrightarrow{-\text{COS}} \text{EtNH}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{NHEt} \qquad (3)$$

Surprisingly, when we tried to separate products of type **2** and **3** by injecting the product mixture into a GLC column, they came out either as one peak or as two peaks whose ratio was different from what initially was observed by ^{1}H NMR, before the GLC injection. In some cases a third peak appeared (**11**, RN=C=NR) at the expense of **2** or **3**. Table III summarizes the results on the relative yield of each product in the mixture, before and after GLC separation. Careful examination of the results lead to the following conclusions: (a) A thermal decomposition of **2** followed by its isomerization to **3** took place. The isomerization process is complete in the case of substrates **4** and **5** and only partial in the case of **6** and **7**. For substrate **8** (last entry in Table III) only the decomposition product of type **11** was detected. (b) While products of type **2** were favored before GLC injection, products type **3** became

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[5] (a) Phechman, H. V.; Nold, A. *Chem. Ber.* **1986**, *29*, 2588. Sheehan, J. E.; Izzo, J. *J. Am. Chem. Soc.* **1949**, *71*, 4059. (b) Benson, F. R. *Chem. Rev.* **1947**, *41*, 1.

[6] Zabrodin, V. B. *Zh. Phys. Khim.* 1971, *45*, 682; *Chem. Abstr.* 1971, *75*, 53118Z.

[7] Bordwell, F. G.; Andersen, H. M. *J. Am. Chem. Soc.* **1953**, *75*, 6019.

predominant afterwards. (c) **6**–**8** yielded additional type of product, carbodiimide **11**, which could stem from a partial decomposition of their corresponding **2** or **3**, due to thermal instability.

First-order rate constants for the isomerization of **2b** to **3b** were extracted by FT-IR measurements at various temperatures. The rate of disappearance of the C=N absorption in **2b** at 1620 cm^{-1} was followed. Typical rate constants were calculated for this reaction at 117 °C; $k = 8.3 \times 10^{-4}$ s^{-1}, and at 100 °C, 1×10^{-4} s^{-1}. Other kinetic parameters of activation were deduced as follows: the activation energy, E_a = 36 kcal/mol; the enthalpy of activation, $\Delta H^{\ddagger}$ = 36 kcal/mol; the free energy of activation, $\Delta G^{\ddagger}$ = 28 kcal/mol; the entropy of activation, $\Delta S^{\ddagger}$ = 20 cal/mol·deg.

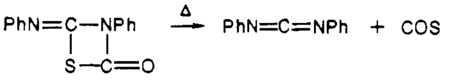
The heated sample of **2b** in the FT-IR cell was allowed to cool down slowly till it reached the room temperature. After about 2 h at 117 °C its ^{1}H NMR was recorded and was found that the ratio of **2b**/**3b** was 1/4.5, almost reverse to that of the preheated sample (ca. 3.6/1). This observation lead to the conclusion that the isomerization of **2b** to **3b** is an irreversible process, or much faster than the reverse reaction.

The question now is, how does **2** isomerize to **3**? We have not found a precedent in the literature of isomerization of particularly this type of compounds. Presumably, the isomerization **2** → **3** undergoes via thermal cleavage of the S–S bond in **2**.

As indicated earlier, the thermal decomposition of **2** (or **3**) was sometimes accompanied (Table III) by the formation of a carbodiimide **11** and dialkylurea **12** (the latter could be formed by hydrolysis of **11**; eq 4). It seems more

$$2 \text{ (or 3)} \xrightarrow{\Delta} \underset{\mathbf{11}}{\mathrm{RN{=}C{=}NR}} \xrightarrow{\mathrm{H_2O}} \underset{\mathbf{12}}{\mathrm{RNHCONHR}} \qquad (4)$$

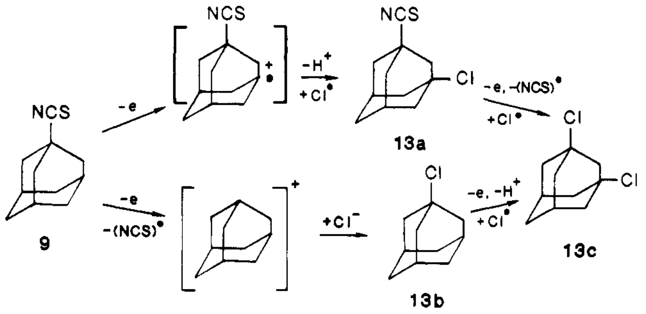
straightforward that **11** is formed directly from **2** rather than **3**, although its formation from **3** cannot be entirely ruled out for the higher homologues. Accordingly, **3** would have to isomerize to **2** before yielding **11**, and such a process may take place at higher temperatures than those we applied (no reverse isomerization **3** → **2** was detected when ^{1}H NMR samples were recorded at 145 °C, in $\mathrm{CDCl_2CDCl_2}$, and then again at ambient temperature). It is noteworthy that a similar thermal decomposition takes place in a four-membered ring derivative was reported by Ulrich and co-workers[8] (eq 5).



$$\mathrm{PhN{=}C{-}NPh\ (S{-}C{=}O\ ring)} \xrightarrow{\Delta} \mathrm{PhN{=}C{=}NPh} + \mathrm{COS} \qquad (5)$$

Tertiary RNCS. Unlike primary and secondary RNCS, the tertiary ones, **9** and **10**, did not show any oxidation wave up to 2 V, in $\mathrm{CH_2Cl_2}$. However, when **9** was arbitrarily oxidized at 2.2 V three chlorinated products, **13a–c** (Scheme II) were formed. Apparently either "NCS" group or a bridgehead hydrogen or both were replaced by chlorine. These products could be obtained either indirectly, through initially oxidized $\mathrm{CH_2Cl_2}$ or directly through the initial oxidation of **9**. With regard to these two mechanisms it is already known that $\mathrm{CH_2Cl_2}$ decomposes at relatively high anodic potentials to form chlorination products[9] or with electrogenerated reactive intermediates.[10] As to the observation that chlorination took place only at the bridgehead position, it is with agreement with the results of chemical chlorination of adamantane either by a radical mechanism[11] or ionic one.[12] Table III shows that monochlorination products were formed when ~1 F/mol was consumed (entry 8), whereas 1,3-dichloroadamantane was the major product when ~2 F/mol was passed (entry 9). Scheme II demonstrates some of the possibilities of formation of products **13a–c**, by a direct mechanism, in which the cation–radical of **9** is initially formed. *t*-BuNCS (**10**) was oxidized at the same anodic potential (Table III, entries 10 and 11), and surprisingly, mostly the starting material was observed in the product mixture (by ^{1}H NMR and GLC) after passing ~1 F/mol. It seems that polymerization took place which also affected the anode surface, resulting in difficulties to pass more electricity due to very low currents. It is noteworthy that although not isolated, there is an indication (by ^{1}H NMR) that one product, $\mathrm{Me_2C(NCS)CH_2Cl}$ (**14**), was formed (1.57 ppm, 6 H; 3.1 ppm, 2 H) in which one of the methyl hydrogen was substituted by chlorine, with retention of the NCS group. The marked difference between the electrochemical behavior of **9** and **10** may be due to the chemically[13] and spectroscopically[14] supported suggestion that the HOMO in **9** involves mainly the adamantyl skeleton, which causes **9** to be oxidized at a significantly lower potential than that of **10** and hence compete favorably with the oxidation of $\mathrm{CH_2Cl_2}$.

Scheme II



In conclusion, it would be interesting to compare briefly our recent results on the anodic oxidation of alkyl isothiocyanates in $\mathrm{CH_3CN}$ with the present ones in $\mathrm{CH_2Cl_2}$. It is evident that the reaction in acetonitrile was not as selective as in dichloromethane in terms of the number and type of products obtained. The fact that the former solvent is more polar (and thus could stabilize both secondary and tertiary carbocations more efficiently than dichloromethane), and also a better nucleophile, favored the formation of products in addition to the two types (**2** and **3**) found in $\mathrm{CH_2Cl_2}$. Moreover, acetonitrile has an unsaturatd triple bond which could participate in the [2 + 3] cycloaddition-type process to form five-membered heterocyclic products of type **1** with RNCS derivatives.

In both solvents, there is a similar trend favoring the formation of products of type **2** over **3** with increasing chain length of R in RNCS. Also, generally, the production yield of the sum of products **2** + **3** decreases upon increasing chain length in both solvents.

Experimental Section

Materials. Alkyl isothiocyanates **4**–**10** (Aldrich), dichloromethane (Merck, analytical grade), tetrabutylammonium per-

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chlorate, and tetraethylammonium tetrafluoroborate (Fluka AG) were all used without further purification.

Cyclic Voltammetry and Controlled Potential Electrolysis. For comprehensive details, see ref 3. All voltammograms were recorded vs Ag wire quasi-reference electrode (+0.39 V vs NHE). Pulses were employed in preparative electrolysis whenever it was necessary to maintain a reasonable level of current. Pulses were given every 10 s for 1 s at 0.5 V (it should be noted that they did not affect the products or their distribution but only shortened the electrolyses duration). By the end of the electrolysis the anolyte was worked up separately from the catholyte solution. The electrolyte was washed several times with water, and the remainder, dichloromethane solution, was dried over $MgSO_4$, filtered, and evaporated. The residue was weighed and sampled for ^{1}H NMR, IR, GC/MS, and GLC. Separation of products was conducted either by silica gel column (40 cm × 1 cm o.d.) using a 4:1 mixture of petroleum ether (60–80) and ether (or acetone), respectively, or by GLC column (10% SE-30 on Chromosrb W, 7 ft × $^1/_4$ in.) at 150 °C for product mixtures from oxidation of **4** and **5**, at 190 °C for **6** and **7**, and at 200 °C for **8**–**10**.

Products. Spectral data (^{1}H NMR, MS, IR, and elemental analysis for **2a**–**e** and **3a**–**d** were given elsewhere.[3] Carbodiimides **11a**–**c** showed a typical stretching frequency at $\sim$2120 cm^{-1} in the IR and each afforded M + 1 mass unit by MS. As to the ^{1}H NMR, the protons adjacent to nitrogens have chemical shifts in the range of 3.1–3.2 ppm. Spectral data for the dialkylurea derivatives **12a**,**b** were in agreement with the literature.[15] Oxidation products from **9**: **13a**, ^{1}H NMR δ 1.58 (s, 2 H), 1.94 (d, 4 H), 2.05 (d, 4 H), 2.32 (br s, 4 H); MS *m/e* (relative intensity) 227 (M$^+$, 8), 171 (28), 169 (100), 133 (31), 91 (29); **13b**, ^{1}H NMR δ 1.67 (s, 6 H), 2.14 (br s, 9 H) [in good agreement with 1-bromoadamantane];[16] **13c**, ^{1}H NMR δ 1.63 (br s, 2 H), 2.06 (d, 8 H), 2.30 (br s, 2 H), 2.46 (s, 2 H) [in good agreement with the corresponding spectrum of 1,3-difluoroadamantane];[16] **14**, ^{1}H NMR δ 1.74 (s, 6 H), 3.38 (s, 2 H).

Kinetic Measurements by FT-IR. Infrared spectra were taken with a DX-20 Nicolet FT-IR spectrometer operating with a nominal resolution of 2 cm^{-1}. Samples were studied as 0.045 M solutions in $CHBr_3$ by using a cell equipped with KBr windows and having an optical path of 0.1 mm. For kinetic studies the cell was heated to the desired temperature (100 or 117 °C), at which it could be maintained to within better than ±0.5 °C, and the solution introduced into the hot cell. Although the temperature of the solution could not be measured directly it could be judged from the time dependence of the spectral absorption. The heating time of the solution, which takes several minutes, introduces an uncertainty in the origin of the time axis (which in our runs extended over several hours). Clearly, for a first-order reaction, as is the case here, this small uncertainity in time hardly affects the determination of the rate constants.

Acknowledgment. We are grateful to Prof. S. Weiss for his kind assistance and helpful suggestions in carrying out the kinetic experiments by FT-IR and to Elias Shakur for carrying out the chemical reduction of **2**.

Registry No. **2a**, 6320-65-6; **2b**, 108168-82-7; **2c**, 108168-83-8; **2d**, 108168-84-9; **2e**, 113162-00-8; **3a**, 103031-01-2; **3b**, 98484-44-7; **3c**, 98492-89-8; **3d**, 108168-85-0; **4**, 556-61-6; **5**, 542-85-8; **6**, 628-30-8; **7**, 592-82-5; **8**, 1122-82-3; **9**, 4411-26-1; **10**, 590-42-1; **11a**, 821-79-4; **11b**, 693-64-1; **11c**, 538-75-0; **12a**, 623-95-0; **12b**, 1792-17-2; **13a**, 113162-01-9; **13b**, 935-56-8; **13c**, 16104-50-0; **14**, 63206-58-6; EtNHC(S)NHEt, 105-55-5.

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Synthesis of (Trimethylsilyl)thiazoles and Reactions with Carbonyl Compounds. Selectivity Aspects and Synthetic Utility[1]

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Received July 14, 1987

Synthetic routes to all possible regioisomeric mono- and bis(trimethylsilyl)thiazoles as well as to the tris(trimethylsilyl) derivative via lithiation–silylation sequences of the thiazole ring followed by selective protodesilylation in some cases are described. (Trimethylsilyl)thiazoles serve as thiazolyl donor synthons upon reaction with carbonyl compounds (ketenes, acyl chlorides, aldehydes) for the preparation of mono- and bis-substituted thiazoles in very good yields. Carbodesilylation occurs more readily at the 2- than the 5-position, whereas no reaction takes place at the 4-position. A mechanism via a thiazolium 2-ylide as an intermediate is suggested for the carbodesilylation at the 2-position.

The synthetic utility of silicon substitution on carbon–carbon bond-forming processes to heteroarenes[2] is inherent not only in the ready cleavage of the heteroaryl–silicon bond (ipso attack) by a variety of carbon electrophiles (e.g. carbonyl compounds) in the presence of nucleophilic catalysts but also in the high regio- and chemoselectivity of these operations. Thus heteroaryl silanes can be viewed as stable yet reactive heteroaryl carbanion equivalents[3] which allow the synthesis of otherwise poorly accessible functionalized heterocycles. For instance, we have recently described[4] the preparation of 4- and 5-substituted 2-(tri-

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[1] Presented in part by A.D. at the Tenth International Congress of Heterocyclic Chemistry, Waterloo (Canada), April 11–16, 1985. See also: Dondoni, A. *Lect. Heterocycl. Chem.* **1985**, *8*, 13.

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