When compound **2b** was electrolyzed in methanol, the electrolyzed solution became dark brown. The solution showed several spots on TLC. The main products were isolated by silica gel chromatography using chloroform–ethyl acetate (9:1) as eluate. These were compounds **3b** (41%) and **6** (4.5%). The physical constants of compound **3b** obtained here were in complete agreement with those described above. Compound **6** (syrup) was a mixture of cis and trans isomers: NMR ($CDCl_3$) δ 2.14 and 2.24 (s and s, 3 H), 3.55 and 3.52 (s and s, 3 H), 3.8–4.0 and 4.0–4.2 (m and m, 1 H), 5.1–5.5 (m, 2 H), 6.6–7.6 (m, 6 H). The ratio of these isomers is 7:6 (cis/trans).

Compound 3c. Electrolysis of compound **2c** gave the titled compound: bp 99–100 °C (1 mm); IR (film) 3150, 1740–1710 (broad) cm^{-1}; NMR ($CDCl_3$) δ 1.34 (t, 3 H), 2.22 (s, 3 H), 2.48 (s, 3 H), 4.33 (q, 2 H), 6.05 (d, 1 H), 7, 12 (d, 1 H); MS (intensity) 185 (M^+, 41), 143 (base peak), 115 (36), 43 (23). Anal. Calcd for $C_{10}H_{13}O_3N$: C, 61.52; H, 6.71; N, 7.18. Found: C, 61.33; H, 6.43; N, 7.01.

Compound 3d. Anodic oxidation of compound **2d** afforded the titled compound: bp 41–42 °C (2 mm); IR (film) 3050, 1715 cm^{-1}; NMR ($CDCl_3$) δ 2.07 (s, 3 H), 2.45 (s, 3 H), 6.0–6.2 (m, 1 H), 6.9–7.1 (m, 1 H), 7.1–7.3 (m, 1 H); MS (intensity) 123 (M^+, 26), 97 (10), 81 (43), 80 (base peak), 53 (18), 43 (48). Anal. Calcd for C_7H_9ON: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.31; H, 7.32; N, 11.31.

Preparation of *cis*-4. *N*-Acetyl-2,2-diethoxycarbonyl-3-phenylpyrrolidine[12] was saponified with potassium hydroxide under the same conditions as described above to afford the title compound in 49% yield; this was recrystallized from ethyl acetate–*n*-hexane: mp 97–99 °C; IR (Nujol) 1740, 1720, 1620, 1560 cm^{-1}; NMR ($CDCl_3$) δ 1.01 (t, 3 H), 2.22 (s, 3 H), 2.0–2.9 (m, 2 H), 3.5–4.5 (m, 3 H), 3.88 (q, 2 H), 7.35 (s, 5 H). Anal. Calcd for $C_{16}H_{19}O_5N$: C, 62.94; H, 6.27; N, 4.59. Found: C, 62.94; H, 6.23; N, 4.56.

Electrolysis of *cis*-4. After compound 4 (910 mg) was electrolyzed under the conditions as shown in Table I, the electrolyzed solution was neutralized by the addition of acetic acid, and the solvent was evaporated to dryness in vacuo. The resulting residue was extracted with ethyl acetate, and the solution was washed with water, dried over magnesium sulfate, and then evaporated to dryness in vacuo. The residue was treated with silica gel chromatography using chloroform–ethyl acetate (5:4) as eluate to afford 460 mg of *cis*-**5a** and 420 mg of *trans*-**5b**.

Compound 5a: mp 130–131 °C; NMR ($CDCl_3$) δ 1.25 (t, 3 H), 2.10 (s, 3 H), 2.0–3.0 (m, 2 H), 3.35 (s, 3 H), 3.5–3.8 (m, 3 H), 4.22 and 4.24 (q, 2 H), 7.25 (s, 5 H). Anal. Calcd for $C_{16}H_{21}O_4N$: C, 65.95; H, 7.27; N, 4.81. Found: C, 65.74; H, 7.14; N, 4.76.

Compound **5b** (syrup): NMR ($CDCl_3$) δ 0.81 and 0.89 (t and t, 3 H), 1.98 and 2.15 (s and s, 3 H), 2.0–3.0 (m, 2 H), 3.46 (s, 3 H), 3.72 and 3.79 (q and q, 2 H), 3.4–4.5 (m, 3 H), 7.1–7.4 (m, 5 H). Anal. Calcd for $C_{16}H_{21}O_4N$: C, 65.95; H, 7.27; N, 4.81. Found: C, 65.89; H, 7.31; N, 4.93.

The separation of the NMR signals of each group observed above is attributed to the rotational barrier about the C–N bond.[20]

Acknowledgment. We thank Drs. I. Chibata and M. Matsuoka for their encouragement.

Registry No.—**2a,** 64163-63-9; **2b,** 51212-32-9; **2c,** 64163-64-0; **2d,** 64163-65-1; **4,** 64163-66-2; **3a,** 64163-67-3; **3b,** 64163-68-4; **3c,** 64163-69-5; **3d,** 823-75-6; **1a,** 51212-30-7; **1b,** 64163-70-8; **1c,** 5846-04-8; **1d,** 64163-71-9; **5a,** 64175-43-5; **5b,** 64163-72-0; *cis*-**6,** 64163-73-1; *trans*-**6,** 64163-74-2; 2-ethoxycarbonyl-5-phenylpyrrole, 13355-43-6; *N*-acetyl-2,2-diethoxycarbonyl-3-phenylpyrrolidine, 51212-36-3.

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Thiocarbonyl Transfer Reagents[1]

Charles Larsen,[2] Kosta Steliou, and David N. Harpp*

Department of Chemistry, McGill University, Montreal, Quebec, Canada

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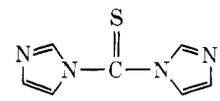
Heterocyclic thiocarbonyl transfer reagents, first prepared by Staab and co-workers,[3] have in the recent years found several important applications in the synthesis of new compounds.[4,5] Among these reagents mainly 1,1′-thiocarbonyldiimidazole (**1**) has been used, though reactions involving the



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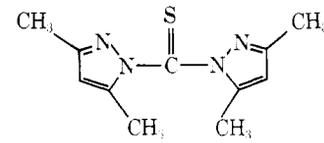

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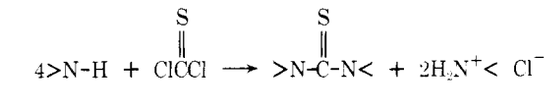
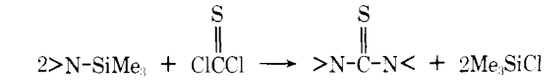
use of 1,1′-thiocarbonylbis(3,5-dimethylpyrazole) (**2**) also have been reported.[6]

Very little attention has been paid to the other members of this series, including 1,1′-thiocarbonyldibenzimidazole (**3**), 1,1′-thiocarbonyldibenzotriazole (**4**), and thiocarbonyldiindazole (**5**). Compounds **1** and **2** have been prepared in excellent yield[3,6] according to the following reaction. Compounds



3 and **5** have been synthesized by this reaction, but yields were uncertain.[7] For **4** the use of the free base is reported to be precluded, as this method results in the formation of 1-(2-benzothiazolyl)benzotriazole.[8] However, using the sodium salt of the heterocycle, compound **4** is formed, though no yield is reported.[7,8]

A more general approach to the preparation of these compounds requiring only 2 mol of the heterocycle involves the reaction between its silylated derivative and thiophosgene. In this way we have synthesized not only **1, 3,** and **4** but also



1,1′-thiocarbonyldipyrazole (**6**), for which the known methods have been reported to fail.[7] In addition, a new reagent, 1,1′-thiocarbonyldi-1,2,4-triazole (**7**), was also made (Table I). In all cases, the yields are excellent (90–100%) and the purity of the crude product very high.[9] The silylated precursors were prepared from the heterocycle and hexamethyldisilazane (HMDS) according to the method of Birkofer.[10]

Although **3, 4,** and **6** are generally less reactive (compared to **1**) with compounds having labile hydrogen atoms (amines, alcohols, and thiols), the properties of the reagents (stability toward moisture) and the low solubility of the heterocycle formed by the reaction may in certain situations give these reagents advantages superior to **1**. In the case of **7,** we found

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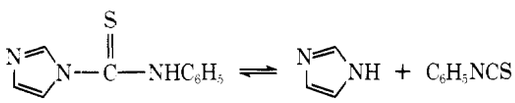
Table I. Thiocarbonyl Transfer Reagents

Compd	S = CR_2, R =	Registry no.	Mp, °C	Lit. Mp, °C	Yield, %	(C, H, N: calcd/found)
1	Imidazolyl	6160-65-2	105–106	105–106[3]	99	47.17, 3.39, 31.44/46.90, 3.87, 31.44
3	Benzimidazolyl	4314-17-4	137–138	149–150[7]	100	64.73, 3.62, 20.13/64.40, 3.52, 20.25
4	Benzotriazolyl	4314-19-6	170–171	176–178[7]	90	55.70, 2.88, 29.99/55.95, 2.80, 29.97
6	Pyrazolyl	21578-37-0	50–51		92	47.17, 3.39, 31.44/47.17, 3.22, 31.66
7	1,2,4-Triazolyl	63976-76-1	99–100		93	33.32, 2.24, 46.65/32.89, 2.80, 46.27

that it was more reactive than 1 in some reactions. For instance, 7 reacts with 2 mol of phenol to give diphenylthionocarbonate; the reaction is very fast at room temperature, while 1 requires heating to 90 °C for 6 h.

While 1 normally reacts well with 2 mol of aliphatic or aromatic primary amines, forming 1,3-disubstituted thioureas, the corresponding reaction with 1 mol of amine results in the formation of an isothiocyanate, due to dissociation of the unstable 1-(alkylthiocarbamoyl)imidazole.[3,11] However, 7 reacts instantaneously with 1 mol of amine to produce 1-(alkylthiocarbamoyl)-1,2,4-triazole. The reaction has been carried out with both aliphatic and aromatic amines, and the reaction products show no tendency to dissociate in chloroform solution, neither on prolonged standing nor on heating to 60 °C. If, however, more amine is added to the solution, 1,3-disubstituted thioureas are formed. This provides an advantage over 1 as it is possible to produce unsymmetrically



substituted thioureas directly. The orange color of reagent 7 is discharged after treatment with 1 mol of base, thus providing an added convenience for its use.

When 7 is reacted with diethylamine at room temperature, 1-(diethylcarbamoyl)-1,2,4-triazole was obtained, and even when an excess of the amine was used no tetraethylthiourea was obtained. This is in accord with the finding by Staab[3b] using 1 and diethylamine.

Reactions of 3 and 4 with aniline both gave 1,3-diphenylthiourea in good yields, but the use of these latter reagents has no advantages (compared to the use of 1 and 7) except in cases where the desired product has different properties of solubility than that of the displaced azole.

Experimental Section[12]

1,1′-Thiocarbonyldiimidazole (1). To a stirred solution of 1-trimethylsilylimidazole (0.169 mol, 23.6 g) in CCl_4 (150 mL) a solution of thiophosgene (0.085 mol, 9.73 g) in CCl_4 (25 mL) was added dropwise over a 90-min period. When ca. two-thirds of the thiophosgene solution had been added, yellow crystals of 1 began to precipitate. To ensure complete reaction, stirring was continued for 8 h. After cooling the reaction mixture in an ice–water bath, the crystals were collected, giving 13.10 g of analytically pure 1, mp 105–106 °C (lit.[3] 105–106 °C). Upon flash evaporation of the filtrate, an additional 1.95 g of slightly impure 1 was obtained; total yield 15.05 g (99%).

1,1′-Thiocarbonyldibenzimidazole (3), 1,1′-Thiocarbonyldibenzotriazole (4), and **1,1′-Thiocarbonyldi-1,2,4-triazole (7)** were all prepared according to the method described for 1. In all cases, the crude products were analytically pure. The reaction product 6 from thiophosgene and silylated pyrazole remained in solution. Flash evaporation of the solvent and chlorotrimethylsilane left a brown oil which crystallized after seeding with crystals obtained by cooling a few drops of the oil in liquid nitrogen and subsequent addition of hexane. The crystals were recrystallized from an ether/hexane mixture to give analytically pure **1,1′-thiocarbonyldipyrazole (6).**

Diphenyl Thiocarbonate. Phenol (5.0 mmol, 470 mg) was added to a solution of 7 (2.5 mmol, 450 mg) in acetone (25 mL). Upon addition of one drop of triethylamine, the colored solution immediately turned colorless, and the subsequent addition of water afforded crystals which after recrystallization from ethanol/water gave a melting point of 106–107 °C (lit.[3b] 106 °C); yield 480 mg (83%).

1-(Phenylthiocarbamoyl)-1,2,4-triazole. To a solution of 7 (1.25 mmol, 225 mg) in acetone (25 mL) aniline (1.25 mmol, 116 mg) was added. The orange color of the solution disappeared immediately. Addition of water and subsequent cooling afforded a slightly yellow precipitate which was filtered off. The crystals (230 mg, 90%) had a melting point of 80–81 °C. Recrystallization from a benzene/hexane mixture did not increase the melting point.

Anal. Calcd for $C_9H_8N_4S$: C, 52.92; H, 3.95; N, 27.44. Found: C, 52.64; H, 3.72; N, 27.73.

1-Benzyl-3-phenylthiourea. To a solution of 1-(phenylthiocarbamoyl)-1,2,4-triazole (0.93 mmol, 190 mg) in 10 mL of CH_2Cl_2 was added benzylamine (0.93 mmol, 100 mg). The solution was left overnight and then cooled to −20 °C whereupon colorless crystals were formed. Filtration gave 190 mg (84%) of the target compound (mp 153–154 °C lit.[13] 153–154 °C).

1-(Cyclohexylthiocarbamoyl)-1,2,4-triazole. This compound was prepared as above. The crude product (92% yield of colorless crystals with a melting point of 78–79 °C) was submitted for analysis without any purification.

Anal. Calcd for $C_9H_{14}N_4S$: C, 51.40; H, 6.71; N, 26.65. Found: C, 51.45; H, 6.77; N, 26.85.

1-(Benzylthiocarbamoyl)-1,2,4-traizole. Using the same method as above, a 81% yield of colorless crystals was obtained. After recrystallization from a benzene/hexane mixture, the crystals had a melting point of 130–131 °C.

Anal. Calcd for $C_{10}H_{10}N_4S$: C, 55.02; H, 4.62; N, 25.67. Found: C, 55.05; H, 4.60; N, 25.84.

1-(Diethylthiocarbamoyl)-1,2,4-triazole. In the same way as above, a 91% yield of colorless crystals (mp 53–53.5 °C) was obtained. The crystals were submitted for analysis without any purification.

Anal. Calcd for $C_7H_{12}N_4S$: C, 45.62; H, 6.56; N, 30.41. Found: C, 45.50; H, 6.30; N, 30.40.

1,3-Diphenylthiourea. To a solution of 7 (2.5 mmol, 450 mg) in CH_2Cl_2 (10 mL) aniline (5 mmol, 465 mg) was added. The orange color of the solution disappeared, and at the same time a precipitate was formed. Filtration and evaporation of the solvent and recrystallization from ethanol/water gave 540 mg (95%) of 1,3-diphenylthiourea (mp 154–155 °C, lit.[14] 155 °C).

Acknowledgment. We thank the National Research Council of Canada, Imperial Oil of Canada, and the Danish Natural Science Research Council for financial support of this work.

Registry No.—1-Trimethylsilylimidazole, 18156-74-6; thiophosgene, 463-71-8; 1-(trimethylsilyl)benzimidazole, 13435-08-0; 1-(trimethylsilyl)benzotriazole, 43183-36-4; 1-(trimethylsilyl)-1,2,4-triazole, 18293-54-4; 1-(trimethylsilyl)pyrazole, 18156-75-7; 1-(phenylthiocarbanoyl)-1,2,4-triazole, 63976-77-2; anilene, 62-53-3; 1-benzyl-3-phenylthiourea, 726-25-0; benzylamine, 100-46-9; 1-(cyclohexylthiocarbanoyl)-1,2,4-triazole, 63976-78-3; cyclohexylamine, 108-91-8; 1-(benzylthiocarbanoyl)-1,2,4-triazole, 13101-79-2; 1-(diethylthiocarbanoyl)-1,2,4-triazole, 63976-79-4; diethylanine, 109-89-7; 1,3-diphenylurea, 102-08-9.

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(9) Except for the preparation of **6**, all the crude products were analytically pure. This is usually not found when the free base is used, and as the

thiocarbonyldiazoles in general are difficult to recrystallize (e.g., analytically pure 1 is obtained by sublimation in high vacuum[3b]), the synthesis via silylated precursors is to be preferred when pure products are needed. It is also our experience that the pure products are more "nonperishable" compared to compounds having a lesser purity.

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A New Tetrahydropyran Synthesis. Acid-Catalyzed Cyclization of δ-Substituted Aldehydes

Johann G. D. Schulz* and Anatoli Onopchenko

Gulf Research & Development Company, Pittsburgh, Pennsylvania 15230

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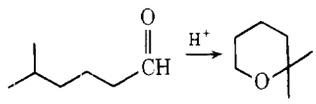
In preparing 1,1-diarylalkanes via acid-catalyzed condensation of aldehydes with alkylbenzenes, a novel rearrangement was discovered involving hydrogen exchange. While the scope of this rearrangement has not been defined, this reaction appears useful for a one-step synthesis of certain tetrahydropyran derivatives.[1] To function in this cyclization, the al-



(1)

dehydes must have at least seven carbon atoms and an alkyl substituent in the δ position.

Experiments were carried out using a C_8 aldehyde fraction, bp 148–150 °C, containing over 90% of 3,5-dimethylhexanal. This aldehyde was obtained from hydroformylation of mixed heptenes, bp 76–100 °C, synthesized in our laboratory by phosphoric acid dimerization of propylene with butenes. The novel cyclization product was isolated by distillation and characterized (Table I). Data were consistent for either 2,2,4-trimethyltetrahydropyran or 2-isopropyl-3-methyltetrahydrofuran, both unreported in the literature. For further elucidation, we prepared a simpler aldehyde, 5-methylhexanal, which on treatment with sulfuric acid gave 2,2-dimethyltetrahydropyran, a known compound.[2] Its structure was additionally verified by NMR.

Table I. Cyclization of 3,5-Dimethylhexanal[a]

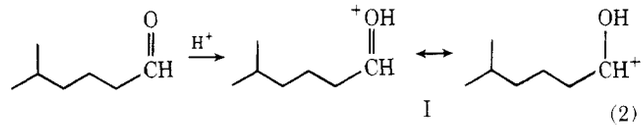
Run no.	Acid concn, wt %	Molar ratio, acid/RCHO	%yield of 2,2,4-trimethyl tetrahydropyran	Remarks
1	96% H_2SO_4	6:1	60	
2	96% H_2SO_4	9:1	74	
3	80% H_2SO_4	6:1	3	
4	100% H_2SO_4	6:1	65	
5	BF_3·H_2O	3:1	90	BF_3/H_2O ratio, 1:1
6	BF_3·H_2O	3:1	75	BF_3/H_2O ratio, 1:1.5
7	85% H_3PO_4	6:1	~0	Two-phase system.
8	100% H_3PO_4	6:1	25	
9	BF_3·H_2O·H_3PO_4	6:1	80	$BF_3/H_2O/H_3PO_4$, 1:0.23:1.27

[a] Reaction temperature 0 °C. [b] By distillation; bp 134–136 °C. Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58; O, 12.48 (diff); $[M_R]_D$ 38.6 mL/mol. Found: C, 74.5; H, 12.4; O, 13.1 (diff). mol wt (*m/e*) 128; IR 1100 cm^{-1} (s, cyclic ether); sp gr (15°) 0.8493; n^{20}_D 1.4250; $[M_R]_D$ 38.6 mL/mol.

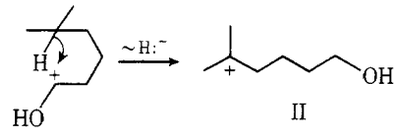
Cyclization competes with condensation and oxidation, but was favored by adding aldehyde slowly to acid. In cases where the addition sequence was reversed, cyclic ethers were not detected, and only resinous product was obtained.

The driving force for cyclization of δ-substituted aldehydes appears to be the generation of a relatively stable tertiary carbonium ion at the δ position when the hydride ion transfers. With *n*-hexanal and *n*-heptanal consequently, only condensation, but no cyclization, is observed as there is no incentive to form the less stable secondary carbonium ion. An attempt to prepare 2-phenyltetrahydropyran from 5-phenylpentanal failed, as intermolecular alkylation of the benzene ring was considerably faster than the expected benzylic carbonium ion formation.

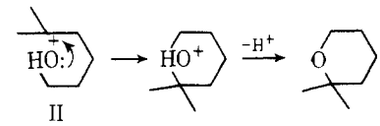
Products are rationalized by an ionic mechanism. In the first step, aldehyde is protonated to give carbonium ion I, which then undergoes intramolecular exchange to form carbonium ion II, followed by cyclization.



I (2)

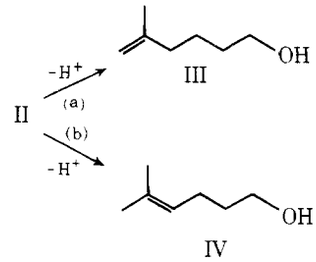


I II (3)



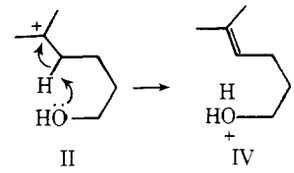
II (4)

In view of the similarity of products and also the reaction conditions between the present work and that of the Prins reaction,[3-5] it is also possible for the tetrahydropyran ring to form by a mechanism involving olefinic intermediates. Ion II can undergo deprotonation in two directions to give alcohols which are derivatives of vinylidene III or internal olefin IV, respectively.



III IV (5)

Since typical El elimination reactions afford the more highly substituted olefins as major products (Saytzeff rule),[6] the dominant pathway in our work would involve route b. Formation of IV can be assisted by a quasi-six-membered transition state. To form III, this process would require an eight-membered ring transition state which is energetically not fa-



II IV (6)

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