(d, J = 6 Hz, 3 H), 1.96 (s, 3 H), 2.30–2.52 (m, 3 H), 2.52–2.66 (m, 2 H), 6.82 (s, 1 H), 7.82 (s, 1 H).

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.11; H, 6.81; N, 7.33. Found: C, 68.90; H, 6.51; N, 7.49.

Evodone (23). To a suspension of 5 mg (0.05 mmol) of hydroquinone in 20 mL of freshly distilled ethylbenzene in a 25-mL, round-bottomed flask was added 60 mg (0.30 mmol) of acetylenic ketone **22**. The resulting solution was refluxed in the absence of light and under an atmosphere of dry N_2 for a period of 96 h. The ethylbenzene was then removed under reduced pressure to afford ~70 mg of a dark brown oil. Thick-layer chromatography (40% acetone/petroleum ether, R_f 0.65) of this material afforded 39 mg (76%) of **23** as a colorless crystalline solid. Recrystallization from MeOH/H_2O gave colorless needles, which after sublimation (0.015 mmHg, 25 °C) had a melting point of 70–71 °C (lit.[7] mp 73 °C): IR ($CHCl_3$) 3000, 2960, 1662, 1560, 1440, 1430, 1410, 1388, 1362, 1080, 1045 cm^{-1}; UV (MeOH) λ_{max} 265 nm (lit.[7] 265 nm); NMR ($CDCl_3$) δ 1.09 (d, J = 6 Hz, 3 H), 1.58 (m, 1 H), 2.14 (d, J = 1.3 Hz, 3 H), 2.30–2.58 (m, 3 H), 2.88 (dd, J = 4, 13 Hz, 1 H), 7.08 (br s, collapsing to a sharp singlet upon irradiation at 2.14, 1 H); mass spectrum, m/e 164 (M^+); mp (2,4-DNPH) 260–262 °C (lit.[20] mp 258–260 °C).

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Registry No. 7b, 76879-68-0; **7c**, 76879-69-1; **10a**, 24112-69-4; **10b**, 18335-58-5; **11a**, 76900-27-1; **13a**, 76879-70-4; **13b**, 76879-71-5; **14a**, 76879-72-6; **14b**, 76879-73-7; **15a** (isomer 1), 76879-74-8; **15a** (isomer 2), 76945-53-4; **15b** (isomer 1), 76945-54-5; **15b** (isomer 2), 76945-55-6; **16a**, 76879-75-9; **16b**, 76879-76-0; **18**, 1121-84-2; **19**, 76879-77-1; **20**, 76879-78-2; **21**, 76879-79-3; **22**, 76879-80-6; **23**, 529-63-5; **23** DNP, 76879-81-7; lithiomethyl isocyanide, 33742-77-7; propynyl bromide, 2003-82-9.

(20) Stetter, H.; Lauterbach, R. *Chem. Ber.* **1960**, *93*, 603.

Synthesis of *N*-(Tosylmethyl)carbodiimides and Their Application in the Synthesis of 2-Amino-1,3-oxazoles from Aldehydes

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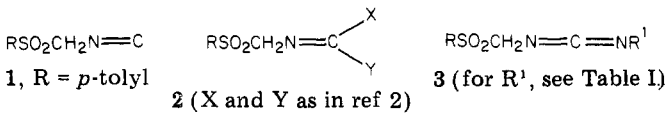
A series of *N*-(tosylmethyl)carbodiimides ($TosCH_2N{=}C{=}NR^1$, **3**) have been prepared from the corresponding thioureas. Carbodiimides **3** with R^1 = triphenylmethyl or *tert*-butyl are useful synthons in a new one-step synthesis of 2-(alkylamino)-1,3-oxazoles **10** from aromatic aldehydes. Acid-induced removal of the triphenylmethyl group from **10** gives 2-amino-1,3-oxazoles (**11**).

The successful use of tosylmethyl isocyanide (TosMIC, **1**) in organic synthesis[1] has stimulated us to investigate



1, R = *p*-tolyl

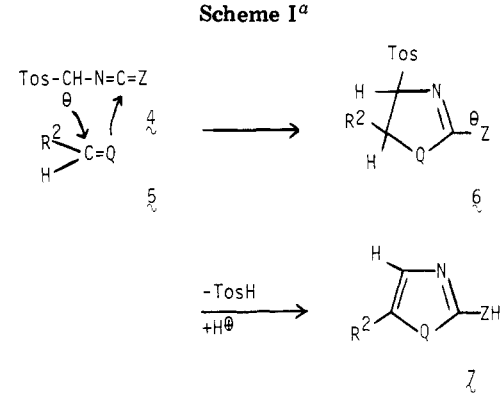
2 (X and Y as in ref 2)

3 (for R^1, see Table I)

other potential synthons operating on a comparable basis. In previous papers from this laboratory the preparation of a series of (sulfonylmethyl)imino derivatives **2** and their application to the synthesis of azoles have been discussed.[2] We now report the synthesis of a number of *N*-(tosylmethyl)carbodiimides **3** and their use in the preparation of 2-amino-1,3-oxazoles.

When applied to the synthesis of azoles, the essentials of TosMIC chemistry[1] are given in Scheme I: attack of TosMIC anion (**4**, Z = void) at the electrophilic end of certain carbon–carbon or carbon–heteroatom multiple bonds (**5**) and ring closure through the isocyano carbon (to **6**), followed by in situ elimination of *p*-toluenesulfinic acid (TosH) to give **7**.

Scheme I[a]



[a] For TosMIC: Z = void, Q = O, NR, S, CHCOOR, etc.; Tos = *p*-tolylsulfonyl.[1] Present paper: Z = NR^1 (R^1, Table I) and Q = O (R^2, Table II).

It is the purpose of this paper to show that the central carbodiimido carbon of *N*-(tosylmethyl)carbodiimides **3** can fulfil a role similar to the isocyano carbon of TosMIC. To that end it was necessary to develop a synthesis for the previously unknown (tosylmethyl)carbodiimides **3**.[3,4]

(1) A brief review: van Leusen, A. M. *Lect. Heterocycl. Chem.* **1980**, *5*, S111 (a supplementary issue of volume 17 of *J. Heterocycl. Chem.*).

(2) (a) Houwing, H. A., Wildeman, J.; van Leusen, A. M. *Tetrahedron Lett.* **1976**, 143. (b) Houwing, H. A., Ph.D. Thesis, Groningen University, 1978.

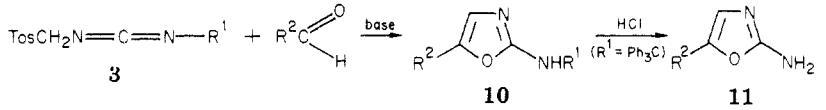
0022-3263/81/1946-2069$01.25/0

Table I. *N*-(Tosylmethyl)thiourea (9) and *N*-(Tosylmethyl)carbodiimides (3)

$$\underset{8}{\text{TosH} + \text{CH}_2\text{O} + \text{H}_2\text{NC(S)NHR}^1} \xrightarrow[-\text{H}_2\text{O}]{\text{HCOOH}} \underset{9}{\text{TosCH}_2\text{NHC(S)NHR}^1} \xrightarrow[-\text{H}_2\text{S}]{\text{HgO}} \underset{3}{\text{TosCH}_2\text{N=C=NR}^1} \quad (1)$$

	9			3			
R^1	compd	yield, %	mp, °C	compd	yield, %	mp or bp, °C	$\nu_{N=C=N}$, cm^{-1}
$C(C_6H_5)_3$	**9a**	70	183-184	**3a**	90	mp 138-139	2135
$C(CH_3)_3$	**9b**	91	148-149	**3b**	75	ca. 90% pure oil, bp 115 (0.01 mmHg)	2130
C_6H_5	**9c**	55	146-147	**3c**	94	ca. 90% pure oil	2140
c-C_6H_{11}	**9d**	66	114-115	**3d**	(90)	impure oil	2140
CH_3	**9e**	36	115-116	**3e**	(95)	impure oil	

Table II. Synthesis of 2-*tert*-Butylamino-1,3-oxazoles (10, R^1 = *t*-Bu), 2-[(Triphenylmethyl)amino]-1,3-oxazoles (10, $R^1 = Ph_3C$) and 2-Amino-1,3-oxazoles (11)



(2)

3 10 11

compd	R^1	R^2	yield, %	mp, °C	reaction conditions
10a	$(C_6H_5)_3C$	C_6H_5	78	214-215	PTC[a]
10a	$(C_6H_5)_3C$	C_6H_5	73	213-215	NaH-DME
10b	$(CH_3)_3C$	C_6H_5	80	124-125	PTC[b]
10c	$(C_6H_5)_3C$	*p*-$O_2NC_6H_4$	71	242-243	PTC[a]
10d	$(CH_3)_3C$	*p*-$O_2NC_6H_4$	73	232-233	PTC[a]
10e	$(C_6H_5)_3C$	*p*-$CH_3OC_6H_4$	60	226-227	PTC[a]
10f	$(CH_3)_3C$	*p*-$CH_3OC_6H_4$	63	130-131	PTC[b]
10g	$(C_6H_5)_3C$	*p*-ClC_6H_4	76	224-225	PTC[a]
10g	$(C_6H_5)_3C$	*p*-ClC_6H_4	70	224-225	NaH-DME
10h	$(CH_3)_3C$	*p*-ClC_6H_4	64	153-154	PTC[b]
11a		C_6H_5	84	215-216[c]	HCl-MeOH
11b		*p*-$O_2NC_6H_4$	79	235-237[d]	HCl-MeOH
11c		*p*-$CH_3OC_6H_4$	66	218-220[e]	HCl-MeOH
11d		*p*-ClC_6H_4	66	220-222	HCl-MeOH

[a] Phase-transfer-catalyzed reactions carried out in 30% NaOH-CH_2Cl_2 with Bu_4NBr at 20 °C for 1 h. [b] Phase-transfer-catalyzed carried out in 50% NaOH-CH_2Cl_2 with Bu_4NBr at 20 °C for 1 h. [c] Lit.[13] mp 216 °C. [d] Melting point not reported in ref 14. [e] Lit.[15] mp 220-222 °C.

***N*-(Tosylmethyl)carbodiimides (3).** The carbodiimides **3**, listed in Table I, were prepared by elimination of H_2S from the corresponding *N*-(tosylmethyl)thioureas (**9**, eq 1 in Table I).[7] The thioureas **9b–e** were obtained by a Mannich-type condensation of *p*-toluenesulfinic acid, formaldehyde, and a monosubstituted thiourea according to the method of Engberts.[8] For the trityl- (triphenylmethyl) substituted thiourea **9a**, however, it was essential to use a slightly modified procedure (see Experimental Section).[9]

According to our expectations, the carbodiimides **3** differ enormously in stability and hence in ease of handling.[11] The trityl-substituted carbodiimide **3a** is a perfectly stable solid, which can be stored indefinitely, the *tert*-butyl substituted one (**3b**) could be subjected in small quantities to bulb-to-bulb distillation (with some decomposition), but the other carbodiimides **3c-e** decomposed on attempted purification. Compound **3a** is hydrated to the corresponding urea only after prolonged reaction with water and acetic acid whereas **3b** gives a urea in 0.5 h in a refluxing mixture of EtOH-H_2O (see Experimental Section), but compounds **3c–e** react rapidly with moisture. Conversion of aromatic aldehydes to 2-amino-1,3-oxazoles was achieved with **3a** and **3b** only (next section).

Attempts to form (tosylmethyl)thioureas by addition of *tert*-butylamine or benzylamine to tosylmethyl isothiocyanate were unsuccessful.[10] Furthermore, reaction of *N*-(tosylmethyl)thiourea with triphenylmethyl chloride in pyridine did not give the desired compound **3a** but led to formation of *p*-tolyl triphenylmethyl sulfone instead.[10]

2-Amino-1,3-oxazoles 10 and 11. Despite the relatively slow reaction of **3a** with water (see above), the carbodiimido carbon apparently is sufficiently electrophilic to

(3) Based on previous experience with TosMIC, we have restricted ourselves in compounds **3** to R = *p*-tolyl for three reasons: (1) TosNa is a convenient, commercially available source of the sulfonyl moiety; (2) the *p*-methyl group is a useful internal NMR label; the *p*-methyl group is a useful internal NMR label; (3) the tosyl group may help to arrive at crystalline compounds, thus increasing the stability of the synthons under investigation.

(4) Of course, synthons other than **3**, for example, $TosCH_2N{=}C{=}O$ and $TosCH_2N{=}C{=}S$, can be visualized to follow the reaction pattern of Scheme I, leading to azoles with 2-OH or 2-SH substituents, respectively. We have chosen to investigate **3** first because of the following: (1) the chemical behavior of **3** can be manipulated by variation of R^1; (2) azoles with 2-OH(R) and 2-SH(R) substituents have been reported previously, for instance with the (tosylmethyl)imino derivatives **2**.[5] In this context it should be noted that Hoppe[6] has recently employed carbanions derived from $RCH_2N{=}C{=}S$ (i.e., R = COOEt) to form 2-thiono-1,3-oxazolidines from a reaction with aldehydes (cf. first step in Scheme I).

(5) The principle of this reaction can again be shown by Scheme I, replacing **4** by the corresponding carbanion of **2**, i.e., substituting Z by X and Y. When, for example, X = Y = OMe, one OMe is expelled in the ring closure reaction, the other is retained in the final product **7** (ZH = SMe).[2]

(6) Hoppe, D.; Follmann, R. *Chem. Ber.* **1976**, *109*, 3047. Hoppe, I.; Hoppe, D.; Schöllkopf, U. *Tetrahedron Lett.* **1976**, 609.

(7) See, e.g.: (a) Sandler, S. P.; Karo, W. "Organic Functional Group Preparations"; Academic Press: New York, 1971; Vol. 2, p 205. (b) Kurzer, F.; Douraghi-Zadeh, K. *Chem Rev.* **1967**, *67*, 107.

(8) Meijer, H.; Tel, R. M.; Strating, J.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 72.

(9) Before the right experimental conditions were found for the direct Mannich-type synthesis of **9a**, this compound was prepared from *N*-(hydroxymethyl)-*N'*-(triphenylmethyl)thiourea or its *N*-methoxymethyl analogue instead of *N*-(triphenylmethyl)thiourea.[10]

(10) van Nispen, S. P. J. M. Ph.D. Thesis, Groningen University, 1980.

(11) Cf.: Bredereck, H.; Reif, E. *Chem Ber.* **1948**, *81*, 426.

undergo the ring closure reaction depicted in Scheme I (Z = NR^1). We have worked out two different sets of reaction conditions for the synthesis of 2-amino-1,3-oxazoles **10** (Table II, eq 2). The reaction of tritylcarbodiimide **3a** and aromatic aldehydes can be carried out equally well under phase-transfer conditions (30% NaOH–CH_2Cl_2, *n*-Bu_4NBr) or with NaH in 1,2-dimethoxyethane (DME), although in the latter case reaction times are longer. The reactions of *tert*-butylcarbodiimide **3b** gave higher yields when carried out under phase-transfer conditions (50% NaOH–CH_2Cl_2, except for **10d** where 30% NaOH gave better results), although the same products were obtained with KOH in DME. Under similar conditions, no 2-amino-oxazoles were obtained from **3a** or **3b** with aliphatic aldehydes.

The trityl substituent can be removed readily from **10** (R^1 = Ph_3C) by heating with HCl in MeOH to give the primary 2-amino-1,3-oxazoles **11** (Table II). In a similar attempt to remove the *tert*-butyl group from **10d** with trifluoroacetic acid (4 h, 20 °C), starting material was recovered quantitatively.[10] The latter conditions have been used recently for the removal of *tert*-butyl groups from *tert*-butylsulfamides.[12]

The present method of synthesizing 2-amino-1,3-oxazoles by formation of the O–C(2) and C(4)–C(5) bonds is a useful extension of existing methodology, which is based mainly on the formation of O–C(5) and N–C(4) or the O–C(2) and N–C(4) bonds. Examples are (1) reaction of α-halocarbonyl compounds with ureas in DMF for about 50 h at 105 °C[16] and (2) reaction of α-hydroxy ketones with (substituted) cyanamides.[17] Especially the use of the tritylcarbodiimide **3a** is of interest; it is readily available, is stable, and allows variation of substituents at the 2-amino group by removal of the trityl group (**10** → **11**).

Work on other applications of **3a** and **3b** is in progress.

Experimental Section

General Methods. ^1H NMR spectra were recorded on a 60-MHz Varian A60-D or a 60-MHz Hitachi Perkin-Elmer R-24B apparatus in δ units downfield from internal Me_4Si. IR spectra were taken on a Unicam SP-200 or on a Perkin-Elmer 177 apparatus. Elemental microanalyses were carried out in the Analytical Department of our laboratories.

***N*-(Triphenylmethyl)thiourea (8a).** The literature procedure[11] was improved.

Method A. To a solution of thiourea (250 g, 3.3 mol) and triphenylmethyl chloride (200 g, 0.72 mol) in dry dimethylformamide (600 mL) heated at 80 °C was added pyridine (96 mL, 1.2 mol), and the mixture was kept at 80 °C for 1 h without stirring (to postpone the unwanted crystallization of a complex of pyridine hydrochloride with thiourea). After the mixture cooled, water (100 mL) was added, and the mixture was poured into more water (4 L) under vigorous stirring. The precipitate was collected and washed with water, ethanol, and ether to give 158 g (71%) of **8a**, mp 212–213 °C (lit.[11] yield 35%, mp 212 °C).

Method B. Triphenylmethanol (2.60 g, 10 mmol) and thiourea (7.6 g, 100 mmol) were heated in acetic acid (40 mL) for 1.5 h at 100 °C. After cooling, the mixture was carefully poured into a solution of Na_2CO_3 (76 g) in water (100 mL). The product was collected as above to give 2.70 g (85%) of **8a**, mp 212–213 °C.

***N*-*tert*-Butylthiourea[18a] (8b) and *N*-cyclohexylthiourea[18b] (8d)** were prepared according to the method of Frank and Smith described for *N*-phenylthiourea.[19] However, the *N*-alkylthioureas precipitate during the alkaline hydrolysis of the *N*-alkyl-*N'*-benzoylthioureas and are collected by filtration.

***N*-(Tosylmethyl)-*N'*-(triphenylmethyl)thiourea (9a).** A solution of *N*-(triphenylmethyl)thiourea (**8a**, 159 g, 0.5 mol), formaldehyde [36% solution in H_2O, 64 g, 0.75 mol; paraformaldehyde (22.5 g, 0.74 mol) has been used alternatively with the same results], sodium *p*-toluenesulfinate (Fluka; 177 g, 1.0 mol), and formic acid (34.5 g, 0.75 mol) in 1,2-dimethoxyethane (DME, 750 mL) was refluxed for 1.5 h. After the mixture was cooled with ice (0.5 h), a solid was removed by filtration, and the filtrate was concentrated under vacuum to a thick suspension, to which was added, with stirring, MeOH (50 mL) followed slowly by ether (200 mL). The precipitate was collected (143 g). A second crop of 27 g was obtained by concentration of the filtrate and treatment with MeOH (10 mL) and Et_2O (40 mL) as above. The total yield of **9a** was 170 g (70%), mp 180–183 °C; the material was sufficiently pure to be used as such in the next step. Analytically pure **9a** (mp 183–184 °C) was obtained by crystallization from CH_2Cl_2–pentane: IR (KBr) 1140 and 1350 (SO_2), 3400 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ 2.40 (s, 3), 4.85 (d, 2, J = 6 Hz), 5.70 (t, 1, J = 6 Hz), 7.25 (m, 20). Anal. Calcd for $C_{28}H_{26}N_2O_2S_2$: C, 69.14; H, 5.35; N, 5.76; S, 13.17. Found: C, 68.91; H, 5.44; N, 5.76; S, 12.91.

***N*-(Tosylmethyl)-*N'*-*tert*-butylthiourea (9b).** *N*-*tert*-Butylthiourea (**8b**, 30 g, 22.7 mmol) was added to a solution of sodium *p*-toluenesulfinate (40.9 g, 22.9 mmol) and formaldehyde (36% solution in water, 19.6 g, 22.8 mol) in water (275 mL). After the pH was adjusted to 2–3 with formic acid, the stirred suspension was heated at 50 °C for 4 h. After the mixture was cooled, the precipitate was collected, washed thoroughly with water, and dried at 50 °C under vacuum to give 62.5 g (91%) of **9b**, mp 148–149 °C. This material was used as such in the next step; the quality deteriorates on crystallization from EtOH: IR (Nujol) 1120 and 1310 (SO_2), 3380 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ 1.40 (s, 9), 2.47 (s, 3), 5.25 (d, 2, J = 6.5 Hz), 6.8 (br, s, 1), 7.40 and 7.87 (AB q, 4, J = 8 Hz). Anal. Calcd for $C_{13}H_{20}N_2O_2S_2$: C, 52.05; H, 6.72; N, 9.34; S, 21.38. Found: C, 51.94; H, 6.79; N, 9.36; S, 21.41.

***N*-(Tosylmethyl)-*N'*-(triphenylmethyl)carbodiimide (3a).** A stirred mixture of thiourea **9a** (170 g, 0.35 mol) and yellow HgO (220 g, 1.05 mol) in acetone (1 L) was refluxed for 0.5 h, and then a second portion of HgO (220 g, 1.05 mol) was added. After continued reflux (0.5 h) the cooled (20 °C) mixture was filtered with suction over Celite. The filter cake was extracted once with acetone (200 mL), and the filtrate plus extract were concentrated under vacuum. The residual oil was stirred with MeOH (200 mL) for 0.3 h to give a colorless solid [**3a**; 142 g (90%), mp 138–139 °C]. One crystallization from CH_2Cl_2–pentane gave an analytically pure sample with the same melting point: IR (Nujol) 1145 and 1320 (SO_2), 2135 cm^{-1} (N=C=N); ^1H NMR ($CDCl_3$) δ 2.35 (s, 3), 4.20 (s, 2), 7.20 (br, s, 19), 7.75 (lower half AB q, 2, J = 8 Hz). Anal. Calcd for $C_{28}H_{24}N_2O_2S$: C, 74.34, H, 5.31; N, 6.19; S, 7.08. Found: C, 74.52; H, 5.34; N, 6.15; S, 6.84.

***N*-(Tosylmethyl)-*N'*-(triphenylmethyl)urea.** A solution of **3a** (1.0 g, 2.2 mmol) in a mixture of THF (7 mL), AcOH (7 mL), and H_2O (1 mL) contained after 3 days at 20 °C predominantly unchanged **3a** (according to IR). After 14 days the precipitate was collected to give 0.80 g (78%) of *N*-(tosylmethyl)-*N'*-(triphenylmethyl)urea, mp 199–200 °C. Crystallization from acetone gave analytically pure material with the same melting point: IR (KBr) 1140 and 1320 (SO_2), 1700 (C=O), 3400 cm^{-1} (NH). Anal. Calcd for $C_{28}N_{26}N_2O_3S$: C, 71.49; H, 5.53; N, 5.96; S, 6.81. Found: C, 71.44; H, 5.67; N, 5.92; S, 6.78.

***N*-(Tosylmethyl)-*N'*-*tert*-butylcarbodiimide (3b).** To a refluxing solution of thiourea **9b** (2.00 g, 6.6 mmol) in CH_2Cl_2 (40 mL) was added yellow HgO (4.00 g, 18.6 mmol) in five portions (0.8 g) at intervals of ca. 4 min. After refluxing for another 40 min, the mixture was cooled and filtered over Celite. The filter cake was extracted with CH_2Cl_2 (25 mL), and the combined filtrate and extract were concentrated under vacuum to give **3b** as a clear oil (1.70 g, 85%), which was used without further purification. It can be stored for several days at −20 °C: IR (neat) 1145 and 1325 (SO_2), 2130 cm^{-1} (N=C=N); ^1H NMR ($CDCl_3$) δ 1.30 (s, 9), 2.40 (s, 3), 4.30 (s, 2), 7.27 and 7.73 (AB q, 4). Anal. Calcd for $C_{13}H_{18}N_2O_2S$: C, 58.70; H, 6.82; N, 10.23; S, 12.05. Found:

(12) Catt, J. D.; Matier, W. L. *J. Org. Chem.* **1974**, *39*, 566.
(13) Fromm, E.; Kapeller-Aldler, R. *Justus Liebigs Ann. Chem.* **1928**, *467*, 240.
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(17) Cockerill, A. F.; Deacon, A.; Harrison, R. G.; Osborne, D. J.; Prime, D. M.; Ross, W. J.; Todd, A.; Verge, J. P. *Synthesis* **1976**, 591.
(18) (a) *Beilstein 4th ed.* **1922**, *4*, 175; (b) *Ibid.* **1950**, *12*, II, 11.
(19) Frank, R. L.; Smith, P. V. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 735.

C, 58.83; H, 6.87; N, 10.17; S, 12.25. Bulb-to-bulb distillation [ca. 115 °C (0.01 mmHg)] was possible only with small quantities, even then some decomposition was observed.

***N*-Tosylmethyl-*N'*-*tert*-butylurea.** A solution of **3b** (1.00 g, 3.3 mmol) in a mixture of EtOH (10 mL) and H_2O (10 mL) was refluxed for 0.5 h. Upon addition of more H_2O a precipitate of *N*-(tosylmethyl)-*N'*-*tert*-butylurea was formed: 90% yield; mp 139–140 °C (from EtOH–H_2O). Anal. Calcd for $C_{13}H_{20}N_2O_3S$: C, 54.98; H, 7.10; N, 9.86; S, 11.59. Found: C, 55.23; H, 7.99; N, 9.48; S, 11.63.

***N*-(Tosylmethyl)carbodiimides 3c–e** were prepared similarly to **3b** from the corresponding thioureas[20] **9c–e** (10 mmol) and yellow HgO (2–3 equiv) in acetone or CH_2Cl_2. The resulting crude oils (Table I) could not be purified by column chromatography or distillation without decomposition.

5-Phenyl-2-[(triphenylmethyl)amino]oxazole (10a). By Phase-Transfer Catalysis. To a solution of carbodiimide **3a** (2.00 g, 4.4 mmol), benzaldehyde (0.47 g, 4.4 mmol), and *n*-Bu_4NBr (1.5 g, 4.4 mmol) in CH_2Cl_2 (30 mL) was added 30% (w/w) aqueous NaOH (5 mL). After the mixture was stirred for 1 h at room temperature, H_2O (100 mL) and CH_2Cl_2 (50 mL) were added. The organic layer was washed with water (3 × 50 mL), dried (Na_2SO_4), and concentrated under vacuum. The resulting oil was stirred with MeOH (10 mL) to give solid **10a**: 1.40 g (78%); mp 214–215 °C. Crystallization from CH_2Cl_2–MeOH gave an analytically pure sample with the same melting point: IR (KBr) 1610 (C=N), 3300 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ 6.30 (s, 1), 6.7–7.5 (m, 20), 7.9 (br s, 1). Anal. Calcd for $C_{28}H_{22}N_2O$: C, 83.58; H, 5.57. Found: C, 82.81; H, 5.55.

By Using NaH in DME. A solution of carbodiimide **3a** (2.00 g, 4.4 mmol) and benzaldehyde (0.50 g, 4.5 mmol) in dry DME (25 mL) was cooled with ice. NaH (0.3 g, 50% dispersion in mineral oil, ca. 6 mmol) was added, and the mixture was stirred for 20 h, while the ice bath was allowed to reach room temperature. The suspension was poured in water (100 mL). Extraction (CH_2Cl_2), washing with water (50 mL), drying (Na_2SO_4), and concentration as above gave **10a**: 1.30 g (73%); mp 213–215 °C; IR and ^1H NMR spectra identical with those of the product from the PTC reaction.

5-Phenyl-2-(*tert*-butylamino)oxazole (10b) was prepared by phase-transfer catalysis by stirring a mixture of carbodiimide **3b** (0.266 g, 1.0 mmol), benzaldehyde (0.106 g, 1.0 mmol), and *n*-Bu_4NBr (0.322 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) and 50% aqueous NaOH (5 mL) for 1 h at room temperature. After addition of water (25 mL) and CH_2Cl_2 (10 mL) and separation, the water layer was extracted with CH_2Cl_2 (10 mL). The combined organic layers were concentrated. For removal of *n*-Bu_4NBr, ether (15 mL) and water (10 mL) were added to the residue. After separation, the water layer was extracted with ether (10 mL), and the combined ether layers were washed with saturated NaCl solution (5 mL) and dried ($MgSO_4$). The solvent was removed, and the residue was crystallized once from CH_2Cl_2–pentane to give 0.172 g (80%) of **10b**: mp 124–125 °C; IR (Nujol) 1635 (C=N), 3420 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ 1.45 (s, 9), 5.3 (br s, 1), 6.95 (s, 1), 7.3 (m, 5). Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.96. Found: C, 72.20; H, 7.46; N, 12.92.

Oxazoles 10c–e,g were prepared by the PTC method analogously to **10a**, and **10f,h** were prepared analogously to **10b**.[20]

Typical Procedure for Detritylation: 2-Amino-5-phenyloxazole (11a). To a suspension of oxazole **10a** (1.50 g, 3.7 mmol) in MeOH (20 mL) was added concentrated, aqueous HCl (0.7 mL, 8.4 mmol). The mixture was refluxed for 0.5 h. After cooling, the mixture was added to 1 N aqueous NaOH (30 mL), and the precipitate was collected, washed with EtOH and with Et_2O, and crystallized from acetone to give 0.5 g (84%) of **11a**, mp 215–216 °C (lit.[13] mp 216 °C).

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Registry No. 3a, 76757-96-5; **3b**, 76757-97-6; **3c**, 76757-98-7; **3d**, 76757-99-8; **3e**, 76758-00-4; **8a**, 76758-01-5; **8b**, 7204-48-0; **8c**, 103-85-5; **8d**, 5055-72-1; **8e**, 598-52-7; **9a**, 76758-02-6; **9b**, 76758-03-7; **9c**, 76758-04-8; **9d**, 76758-05-9; **9e**, 76758-06-0; **10a**, 76758-07-1; **10b**, 76758-08-2; **10c**, 76758-09-3; **10d**, 76758-10-6; **10e**, 76758-11-7; **10f**, 76758-12-8; **10g**, 76758-13-9; **10h**, 76758-14-0; **11a**, 6826-24-0; **11b**, 13576-56-2; **11c**, 6825-91-8; **11d**, 13576-51-7; triphenylmethyl chloride, 76-83-5; thiourea, 62-56-6; triphenylmethanol, 76-84-6; *N*-(tosylmethyl)-*N'*-(triphenylmethyl)urea, 76758-15-1; *N*-tosylmethyl-*N'*-*tert*-butylurea, 76758-16-2; benzaldehyde, 100-52-7; *p*-nitrobenzaldehyde, 555-16-8; *p*-methoxybenzaldehyde, 123-11-5; *p*-chlorobenzaldehyde, 104-88-1.

Supplementary Material Available: Spectral (^1H NMR and IR) and analytical data are available of compounds **9c–e**, **10c–h**, and **11n–d** (3 pages). Ordering information is given on any current masthead page.

(20) Supplementary material available.

Studies toward Cyclic Trisulfides. Trisulfide Polymers and Sulfur Extrusion[1]

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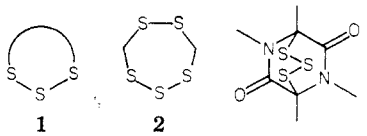
Attempts were directed toward the synthesis of a variety of cyclic trisulfides, particularly by the reaction of *N,N'*-dibenzimidazolyl sulfide with dithiols. Only one monomeric cyclic trisulfide was prepared by this method; other cases yielded either mixtures of oligomers characterized as low molecular weight (<5000) polymers or as products which spontaneously extruded sulfur to give the cyclic disulfides. We conclude that only where osmometric molecular weights or X-ray structures have been determined are monomeric cyclic trisulfides unambiguously defined.

Cyclic trisulfides (**1**) are a class of compounds of which only a few examples have been found in nature. The antibiotic compound lenthionine (**2**) has been isolated from both the edible mushroom Shiitake (*Lentinus edodes*)[2] and the red alga *Chondria californica*.[3] The bicyclic epitrithiodioxopiperazine unit **3** is a structural feature of a



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