Diazine-Substituted *tert*-Butylureas and *tert*-Butylthioureas and a Convenient Access to the Related Carbodiimides

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Dedicated with best personal wishes to Professor Dr. F. Sauter on the occasion of his 65th anniversary.

An efficient procedure for the preparation of diazine-substituted urea and thiourea derivatives **3a-c**, **5a-c** is proposed. On attempts to prepare the related *S*-methylisothioureas **6a-c** under phase-transfer conditions smooth conversion into carbodiimides **7a-c** was found to occur.

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The *N*-arylurea and the *N*-arylthiourea moieties represent important substructures of a wide variety of bioactive compounds. Recently, much attention has been paid to pyridine congeneric molecules, due to various interesting biological activities observed in this series. Thus for instance, anticonvulsant [1], analgesic [2], 5-HT_{1c} antagonistic [3], antiviral [4], acetylcholinesterase inhibitoric [5], and antineoplastic [6] activities have been reported for *N*-alkyl or *N*-aryl substituted *N'*-pyridylureas and thioureas (**A**).

However, so far there are only a few reports on the synthesis and biological properties of isosters characterized by the replacement of the azine system by a diazine nucleus [7,8]. Our continuing interest in the exploitation of the bioisosteric potential of the pyridazine, pyrimidine and pyrazine system now prompted us to elaborate convenient synthetic pathways to compounds of general structure **B**, which may be considered versatile synthetic precursors for novel potential drug substances. The *N*-*tert*-butyl-substituted urea or thiourea substructure was chosen not only in view of the reported activity of 4-pyridazinyl derived congeners as plant growth regulators [7], but also in order to facilitate the interpretation of spectral data of our target compounds.

X = O, S
R = alkyl, aryl

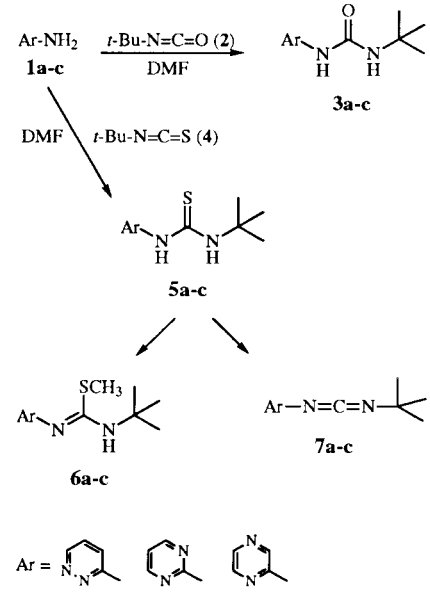
A

X = O, S
Ar = 3-pyridazinyl, 2-pyrimidinyl, 2-pyrazinyl

B

Initial attempts to prepare the thiourea **5a** from 3-aminopyridazine (**1a**) following the procedure given in ref [9] for the synthesis of *N*-alkyl-*N'*-3-pyridylthioureas (*i.e.* treatment of the heteroaromatic amine with thiophosgene and subsequent reaction with an aliphatic amine) resulted in failure, since we were not able to obtain the required isothiocyanate. On the other hand, **1a** did not react with *tert*-butylisothiocyanate (**4**) under a variety of standard conditions [10], obviously due to the poor nucleophilicity of the amino function. However, reaction of **1a-c** with **4** in dry *N*,*N*-dimethylformamide in the presence of sodium hydride in analogy to ref [11] turned out to afford the desired compounds **5a-c** smoothly (yields 76-79%). Under these conditions also the new diazinyl-substituted urea derivatives **3a-c** became conveniently available, when *tert*-butylisocyanate was reacted with the amines **1a-c**.

Scheme 1



In order to gain access to the corresponding *S*-methylisothioureas **6a-c**, which may be anticipated to represent useful synthetic building blocks, the thioureas **5a-c** were reacted with iodomethane under various conditions [12]. The best results were obtained when a solution of the heteroaromatic thiourea in a solvent system consisting of aqueous potassium hydroxide/2-propanol/tetrahydrofuran was treated for 30 minutes with 0.5 equivalents and subsequently with another 0.5 equivalents of the alkylating

agent. Under these conditions, quarternization of the diazine nuclei can largely be avoided, provided that complete deprotonation of the isothiourea moiety had occurred, which, however, can be achieved simply by stirring the solution of compounds **5** for 90 minutes prior to the addition of the alkyl halide.

Only moderate yields (35-50%) of compounds **6a-c** thus obtained prompted us to investigate reactions of the thioureas **5a-c** with iodomethane also under phase-transfer conditions. Surprisingly, when the reactions were carried out in 1,2-dichloroethane/30% aqueous sodium hydroxide employing tetrabutylammonium bromide as the phase-transfer catalyst, instead of the *S*-alkylated products the corresponding diazinyl-substituted *tert*-butylcarbodiimides **7a-c** were obtained (almost complete conversion occurred, as indicated by tlc-monitoring). Column chromatography afforded analytically pure materials in 62-76% yield. To our knowledge, this simple procedure is an unprecedented method for the preparation of carbodiimides from thioureas; investigations with regard to a generalization of this approach are envisaged.

It should be emphasized that the transformation of the thioureas **5** into the carbodiimides **7** can also be achieved in the absence of iodomethane, albeit in only lower yield owing to the formation of significant amounts of by-products [13]. The conversion of **5** into **7** in the absence of iodomethane, however, in any case requires performance of the reaction in a solvent exhibiting alkylating properties (1,2-dichloroethane, dichloromethane); employment of toluene as the organic layer does not result in the above mentioned elimination process. The smooth conversion of compound **6c** into **7c** upon treatment with dichloromethane/30% aqueous sodium hydroxide/tetrabutylammonium bromide supports our assumption that the discussed thiourea→carbodiimide transformation proceeds *via* an *S*-alkylisothiourea intermediate.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. The ir spectra (potassium bromide pellets, sodium chloride plates) were recorded on a Mattson Galaxy Series FTIR 3000 spectrophotometer. The ms analyses were carried out on a Varian MAT 44/S. The ^{1}H-nmr and ^{13}C-nmr spectra were obtained on a Varian Gemini 200 spectrometer (^{1}H: 199.98 MHz, ^{13}C: 50.29 MHz). The center of the solvent multiplet (DMSO-d_6) was used as an internal standard, which was related to TMS with δ 2.49 ppm for ^{1}H and δ 39.5 ppm for ^{13}C. Reactions were monitored by tlc using Polygram SIL

Table 1

Yields and Analytical Data of Compounds **3**, **5**, **6**, **7**

No.	Yield (%)	mp (°C)	Purification	Molecular Formula (MW)	Elemental Analyses (Calcd%/Found%) C	H	N	MS m/e (%)
3a	78	190-193	recrystallized from diisopropylether	$C_9H_{14}N_4O$ (194.24)	55.65 55.88	7.27 7.12	28.84 29.13	194 (M^+, 4), 179 (25), 95 (100), 67 (31), 58 (85), 57 (52), 43 (27), 42 (29), 41 (83)
3b	81	204-207	recrystallized from diisopropylether	$C_9H_{14}N_4O$ (194.24)	55.65 55.89	7.27 7.21	28.84 28.89	194 (M^+, 6), 179 (23), 95 (86), 68 (30), 58 (100), 57 (26), 43 (34), 42 (30), 41 (43)
3c	69	133-135	recrystallized from diisopropylether	$C_9H_{14}N_4O$ (194.24)	55.65 55.91	7.27 7.09	28.84 29.10	194 (M^+, 4), 95 (100), 68 (41), 58 (27), 57 (27), 43 (43), 42 (32), 41 (50)
5a	76	169-172	recrystallized from diisopropylether	$C_9H_{14}N_4S$ (210.30)	51.40 51.58	6.71 6.72	26.64 26.69	210 (M^+, 43), 121 (28), 95 (100), 67 (25), 57 (37), 43 (37), 41 (75)
5b	76	134-136	recrystallized from diisopropylether	$C_9H_{14}N_4S$ (210.30)	51.40 51.62	6.71 6.76	26.64 26.81	210 (M^+, 50), 154 (36), 121 (55), 96 (38), 95 (100), 68 (39), 58 (60), 43 (57), 41 (77)
5c	79	175-177	recrystallized from diisopropylether	$C_9H_{14}N_4S$ (210.30)	51.40 51.51	6.71 6.82	26.64 26.86	210 (M^+, 46), 95 (100), 68 (52), 57 (51), 43 (36), 41 (88)
6a	51	oil	column chromatography	$C_{10}H_{16}N_4S$ (224.33)	53.54 53.53	7.19 7.31	24.98 24.92	224 (M^+, 4), 209 (18), 177 (19), 121 (100)
6b	51	75-77	recrystallized from diisopropylether	$C_{10}H_{16}N_4S$ (224.33)	53.54 53.61	7.19 7.34	24.98 25.23	224 (M^+, 4), 209 (12), 177 (17), 121 (100), 95 (11), 43 (71), 42 (25), 41 (37)
6c	33	59-60	recrystallized from light petroleum	$C_{10}H_{16}N_4S$ (224.33)	53.54 53.81	7.19 6.92	24.98 24.93	224 (M^+, 27), 209 (14), 121 (100), 79 (31), 57 (21)
7a	62	oil	column chromatography	$C_9H_{12}N_4$ (176.22)	61.34 61.58	6.86 6.74	31.79 32.05	176 (M^+, 32), 121 (53), 120 (100), 57 (45), 41 (28)
7b	70	oil	column chromatography	$C_9H_{12}N_4$ (176.22)	61.34 61.41	6.86 6.74	31.79 32.05	176 (M^+, 33), 121 (100), 120 (53), 79 (21), 57 (53), 43 (24), 41 (33)
7c	67	oil	column chromatography	$C_9H_{12}N_4$ (176.22)	61.34 61.24	6.86 7.01	31.79 32.09	176 (M^+, 24), 121 (26), 120 (100), 57 (19), 41 (14)

Table 2

Spectroscopic Data of Compounds **3**, **5**, **6**, **7**

No.	^{1}H-NMR (DMSO-d_6) δ (ppm)	^{13}C-NMR (DMSO-d_6) δ (ppm)	IR (cm^{-1})
3a	9.29 (br s, 1H, NH), 8.75 (dd, 1H, H-6, J_{46} = 1.3 Hz, J_{56} = 4.7 Hz), 7.84 (dd, 1H, H-4, J_{45} = 9.1 Hz, J_{46} = 1.3 Hz), 7.55 (br s, 1H, NH), 7.51 (dd, 1H, H-5 J_{45} = 9.1 Hz, J_{56} = 4.7 Hz), 1.30 (s, 9H, $C(CH_3)_3$)	156.4 (s), 153.3 (s), 146.5 (d, C-6), 128.2 (d, C-5), 116.7 (d, C-4), 49.7 (s, $C(CH_3)_3$), 28.8 (q, $C(CH_3)_3$)	3316, 2969, 1705, 1551, 1454, 1267
3b	9.42 (br s, 1H, NH), 8.99 (br s, 1H, NH), 8.54 (d, 2H, H-4, H-6, $J_{45=56}$ = 4.9 Hz), 7.00 (t, 1H, H-5, $J_{45=56}$ = 4.9 Hz), 1.34 (s, 9H, $C(CH_3)_3$)	158.3 (s), 158.0 (d, C-4, C-6), 152.6 (s), 114.3 (d, C-5), 49.7 (s, $C(CH_3)_3$), 28.9 (q, $C(CH_3)_3$)	3259, 3148, 2982, 1688, 1554, 1302
3c	9.13 (br s, 1H, NH), 8.90 (d, 1H, H-3, J_{36} = 1.5 Hz), 8.20 (dd, 1H, H-6 J_{56} = 2.7 Hz, J_{36} = 1.5 Hz), 8.14 (d, 1H, H-5, J_{56} = 2.7 Hz), 7.33 (br s, 1H, NH), 1.33 (s, 9H, $C(CH_3)_3$)	153.1 (s), 150.0 (s), 141.3 (d), 136.8 (d), 135.0 (d), 49.8 (s, $C(CH_3)_3$), 28.9 (q, $C(CH_3)_3$)	3258, 2964, 1694, 1502, 1300
5a	11.80 (br s, 1H, NH), 10.41 (br s, 1H, NH), 8.83 (dd, 1H, H-6, J_{46} = 1.5 Hz, J_{56} = 4.5 Hz), 7.64 (dd, 1H, H-5, J_{45} = 9.1 Hz, J_{56} = 4.5 Hz), 7.47 (dd, 1H, H-4, J_{45} = 9.1 Hz, J_{46} = 1.5 Hz), 1.55 (s, 9H $C(CH_3)_3$)	177.8 (s, C=S), 156.9 (s, C-3), 147.1 (d, C-6), 129.4 (d, C-5), 118.4 (d, C-4), 53.5 (s, $C(CH_3)_3$), 28.0 (q, $C(CH_3)_3$)	3194, 3011, 2972, 1601, 1568, 1439, 1304
5b	11.34 (br s, 1H, NH), 10.08 (br s, 1H, NH), 8.65 (d, 2H, H-4, H-6, $J_{45=56}$ = 4.9 Hz), 7.13 (t, 1H, H-5, $J_{45=56}$ = 4.9 Hz), 1.53 (s, 9H, $C(CH_3)_3$)	177.5 (s, C=S), 158.0 (d, C-4, C-6), 157.3 (s, C-2), 115.3 (d, C-5), 53.4 (s, $C(CH_3)_3$), 27.8 (q, $C(CH_3)_3$)	3227, 2976, 1692, 1574, 1516, 1414, 1148
5c	11.14 (br s, 1H, NH), 10.57 (br s, 1H, NH), 8.53 (s, 1H, pyrazine-H), 8.18 (s, 2H, pyrazine-H), 1.52 (s, 9H, $C(CH_3)_3$)	178.1 (s, C=S), 149.7 (s, C-2), 139.1 (d), 137.0 (d), 136.4 (d), 53.5 (s, $C(CH_3)_3$), 28.0 (q, $C(CH_3)_3$)	3208, 3034, 2968, 1591, 1526, 1476, 1416, 1362
6a	8.74 (dd, 1H, H-6, J_{46} = 1.6 Hz, J_{56} = 4.6 Hz), 8.05 (br s, 1H, NH), 7.47 (dd, 1H, H-5, J_{45} = 8.7 Hz, J_{56} = 4.7 Hz), 7.06 (dd, 1H, H-4, J_{45} = 8.7 Hz, J_{46} = 1.6 Hz), 2.32 (s, 3H, SCH_3), 1.43 (s, 9H, $C(CH_3)_3$)	162.9* (s, C-3), 156.8* (s, C=N), 146.3 (d, C-6), 127.8 (d, C-5), 123.2 (d, C-4), 52.7 (s, $C(CH_3)_3$), 28.7 (q, $C(CH_3)_3$), 14.7 (q, SCH_3)	3206, 2969, 1584, 1574, 1427, 1370
6b	8.53 (d, 2H, H-4, H-6, $J_{45=56}$ = 4.8 Hz), 7.60 (br s, 1H, NH), 6.94 (t, 1H, H-5, $J_{45=56}$ = 4.8 Hz), 2.26 (s, 3H, SCH_3), 1.41 (s, 9H, $C(CH_3)_3$)	164.7 (s), 157.7 (d, C-4, C-6), 157.2 (s), 114.3 (d, C-5), 52.8 (s, $C(CH_3)_3$), 28.6 (q, $C(CH_3)_3$), 14.6 (q, SCH_3)	3181, 2967, 1555, 1412
6c	8.20 (dd, 1H, H-6, J_{36} = 1.5 Hz, J_{56} = 2.7 Hz), 8.13 (d, 1H, H-3, J_{36} = 1.5 Hz), 8.06 (d, 1H, H-5, J_{56} = 2.7 Hz), 7.76 (br s, 1H, NH), 2.32 (s, 3H, SCH_3), 1.42 (s, 9H, $C(CH_3)_3$)	157.4 (s), 156.8 (s), 141.3 (d), 141.1 (d), 136.4 (d), 52.9 (s, $C(CH_3)_3$), 28.6 (q, $C(CH_3)_3$), 14.6 (q, SCH_3)	3258, 2968, 1572, 1499
7a	8.97 (dd, 1H, H-6, J_{46} = 1.5 Hz, J_{56} = 4.7 Hz), 7.61 (dd, 1H, H-5, J_{45} = 8.7 Hz, J_{56} = 4.7 Hz), 7.22 (dd, 1H, H-4, J_{45} = 8.7 Hz, J_{46} = 1.5 Hz), 1.42 (s, 9H, $C(CH_3)_3$)	159.6 (s, C-3), 148.5 (d, C-6), 131.9 (s, N=C=N), 129.0 (d, C-5), 121.4 (d, C-4), 58.6 (s, $C(CH_3)_3$), 31.0 (q, $C(CH_3)_3$)	2976, 2139 (N=C=N)
7b	8.63 (d, 2H, H-4, H-6, $J_{45=56}$ = 4.8 Hz), 7.18 (t, 1H, H-5, $J_{45=56}$ = 4.8 Hz), 1.40 (s, 9H, $C(CH_3)_3$)	162.6 (s, C-2), 159.6 (d, C-4, C-6), 132.3 (s, N=C=N), 117.5 (d, C-5), 58.9 (s, $C(CH_3)_3$), 31.4 (q, $C(CH_3)_3$)	2976, 2143 (N=C=N)
7c	8.38 (dd, 1H, H-6, J_{36} = 1.4 Hz, J_{56} = 2.6 Hz), 8.35 (d, 1H, H-5, J_{56} = 2.6 Hz), 8.25 (d, 1H, H-3, J_{36} = 1.4 Hz), 1.40 (s, 9H, $C(CH_3)_3$)	152.1 (s, C-2), 143.4 (d), 140.3 (d), 139.0 (d), 132.6 (s, N=C=N), 58.6 (s, $C(CH_3)_3$), 31.0 (q, $C(CH_3)_3$)	2976, 2135 (N=C=N)

G/UV$_{254}$ (Macherey-Nagel) plastic-backed plates (0.25 mm layer thickness) and visualized using an uv lamp or iodine vapor. Column chromatography was performed on Kieselgel 60 (230-400 mesh; Merck). Elemental analyses were carried out by Mikroanalytisches Laboratorium, Institute of Physical Chemistry, University of Vienna. Light petroleum refers to the fraction of bp 40-60°. For yields, melting points, elemental analyses and spectral data of compounds **3**, **5**, **6** and **7** see Tables 1 and 2.

General Procedure for the Synthesis of *N*-(1,1-Dimethylethyl)-*N'*-3-pyridazinylurea (**3a**), *N*-(1,1-Dimethylethyl)-*N'*-2-pyrimidinylurea (**3b**) and *N*-(1,1-Dimethylethyl)-*N'*-2-pyrazinylurea (**3c**).

A solution of 1.00 g (10.5 mmoles) of **1a-c** in 20 ml of dry *N,N*-dimethylformamide was added *via* a syringe to a stirred suspension of sodium hydride (0.42 g, 10.5 mmoles, 60% dispersion in mineral oil) in 10 ml of dry *N,N*-dimethylformamide, kept at 0°. To the stirred reaction mixture a solution of 1.14 g (11.6 mmoles) of **2** in 2 ml of dry *N,N*-dimethylformamide was added slowly at 0°. The mixture was then allowed to warm up to room temperature. After stirring for additional 3 hours, the mixture was poured into water (200 ml) and kept at 4° overnight. The colorless crystals were collected by filtration, washed with cooled light petroleum and were recrystallized to give **3a-c**.

General Procedure for the Synthesis of *N*-(1,1-Dimethylethyl)-*N'*-3-pyridazinylthiourea (**5a**), *N*-(1,1-Dimethylethyl)-*N'*-2-pyrimidinylthiourea (**5b**) and *N*-(1,1-Dimethylethyl)-*N'*-2-pyrazinylthiourea (**5c**).

A solution of 3.00 g (31.5 mmoles) of **1a-c** in 40 ml of dry *N,N*-dimethylformamide was added *via* a syringe to a stirred suspension of sodium hydride (1.26 g, 31.5 mmoles, 60% dispersion in mineral oil) in 30 ml of dry *N,N*-dimethylformamide, kept at 0°. To the stirred reaction mixture a solution of 5.00 g (43.2 mmoles) of **4** in 5 ml of dry *N,N*-dimethylformamide was added slowly at 0°. The mixture was then allowed to warm up to room temperature. After stirring for additional 3 hours, the mixture was poured into water (100 ml) and kept at 4° overnight. The colorless crystals were collected by filtration, washed with

cooled light petroleum and were recrystallized to give **5a-c**.

General Procedure for the Synthesis of *N*-(1,1-Dimethylethyl)-*N'*-3-pyridazinylcarbamimidothioic Acid Methyl Ester (**6a**), *N*-(1,1-Dimethylethyl)-*N'*-2-pyrimidinylcarbamimidothioic Acid Methyl Ester (**6b**) and *N*-(1,1-Dimethylethyl)-*N'*-2-pyrazinylcarbamimidothioic Acid Methyl Ester (**6c**).

To a solution of 0.13 g (2.37 mmoles) of potassium hydroxide in a mixture of 10 ml of water, 10 ml of 2-propanol and 5 ml of tetrahydrofuran, 0.50 g (2.37 mmoles) of **1a-c** was added. The bright yellow mixture was stirred for 1.5 hours at room temperature. After addition of 0.17 g (1.19 mmoles) of iodomethane *via* a syringe stirring was continued for 30 minutes, and subsequently another 0.17 g (1.19 mmoles) of iodomethane was added. Then stirring was continued for an additional 24 hours and the solution was evaporated *in vacuo*. The residue was purified by column chromatography (silica gel, dichloromethane-ethyl acetate 5:1) to give **6a-c**.

General Procedure for the Synthesis of *N*-(1,1-Dimethylethylcarbonimidoyl)-3-pyridazinamine (**7a**), *N*-(1,1-Dimethylethylcarbonimidoyl)-2-pyrimidinamine (**7b**) and *N*-(1,1-Dimethylethylcarbonimidoyl)-2-pyrazinamine (**7c**).

To a solution of 0.25 g (1.19 mmoles) of **5a-c** and 0.03 g (0.01 mmoles) of tetrabutylammonium bromide in 30 ml of dichloroethane was added 0.17 g (1.19 mmoles) of iodomethane. After addition of 20 ml of 30% aqueous sodium hydroxide, the vigorously stirred reaction mixture was refluxed for 3 hours and was then extracted with dichloromethane. The organic layer was washed with water and with brine and was then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the remaining residue was purified by column chromatography (silica gel, dichloromethane-ethyl acetate 5:1) to give **7a-c**.

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[10] Attempted reactions of **1a** with **4** in tetrahydrofuran (reflux), also in the presence of a base (triethylamine, DBU, DABCO, sodium hydride), or in *N,N*-dimethylformamide using DABCO as a base.

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[12] Reactions of compounds **5** with one equivalent of iodomethane resulted in only low conversion to compound **6**, using two equivalents, on the other hand, was found to favor attack of the alkylating agent at the diazine nucleus as did the employment of dimethylsulfate.

[13] After purification by column chromatography (silica gel, dichloromethane-ethyl acetate 5:1) one by-product (20% yield) of the reaction of **5b** could be identified as the urea derivative **7b**. This compound obviously results from hydrolysis of the corresponding *S*-2-chloroethylisothiourea under the strongly basic conditions applied. According to the nmr data, the structure of a 3-(1,1-dimethylethyl)-*N*-(2-pyrimidinyl)-2-thiazolidinimine [^{1}H-nmr: 8.53 (d, 2H, pyr-H4, pyr-H6, $J_{45=56}$ = 4.8 Hz), 6.93 (t, 1H, pyr-H5, $J_{45=56}$ = 4.8 Hz), 3.73 (t, 2H, N-CH_2, J = 7.2 Hz), 2.96 (t, 2H, S-CH_2, J = 7.2 Hz), 1.52 (s, 9H, $C(CH_3)_3$); ^{13}C-nmr: 163.1* (s, C=N), 157.6 (d, C-4, C-6), 146.5* (s, C-2), 114.5 (d, C-5), 57.5 (s, $C(CH_3)_3$), 48.3 (t, N-CH_2), 27.7 (q, $C(CH_3)_3$), 25.7 (t, S-CH_2)] has to be assigned for the second by-product detected (20% yield). The formation of the latter can be explained by intramolecular cyclization of the above mentioned intermediate.