Aminotellurinylation of Olefins and Its Utilization for Synthesis of 2-Oxazolidinones[1]

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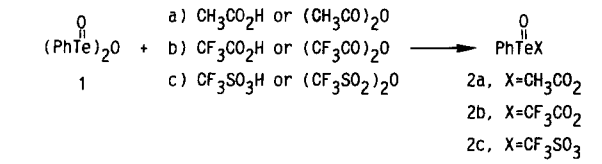
Benzenetellurinyl acetate or trifluoroacetate in combination with ethyl carbamate effected regio- and stereoselective aminotellurinylation of olefins in the presence of boron trifluoride etherate in chloroform under reflux to give ethyl [(2-phenyltellurinyl)alkyl]carbamates in high yields. Benzenetellurinyl trifluoromethanesulfonate similarly did it even at the lower temperature of refluxing dichloromethane without Lewis acid. This reaction was successfully extended to cyclofunctionalization of olefinic carbamates into nitrogen heterocycles. Furthermore, when the aminotellurinylation was carried out in refluxing 1,2-dichloroethane, 2-oxazolidinone was obtained in a high yield. A mechanism of addition followed by intramolecular substitution is proposed on the basis of the stereochemistry of 2-oxazolidinone derivatives.

Organic syntheses on tellurium-based methodology have become increasingly important.[2] The first stratagem is to develop a convenient method for introducing a tellurium functional group into organic substrates. Electrophilic additions of tellurium species to unsaturated compounds would be an effective method for this purpose, but have been little studied. Although divalent organosulfur and selenium reagents undergo versatile addition reactions toward unsaturated compounds, the tellurium counterparts are too labile to undergo such additions. Tellurium(IV) species have been developed as alternatives. Tellurium tetrachloride was first used for halotelluration of olefins and acetylenes.[3,4] Tellurium dioxide in combination with acetic acid containing lithium chloride effected intramolecular oxytelluration of hydroxyolefins.[5] As a limited example with organotellurium species, aryltellurium halides or trihalides were also recognized to effect halotelluration[3] and oxytelluration[6] of olefins. In addition, we have recently found that benzenetellurinyl acetate (**2a**) effects acetoxytelluration of olefins and cyclofunctionalization of hydroxyolefins.[7] The fertile transformations of the introduced tellurinyl function as the second stratagem may follow these reactions. Since nitrogen functional groups often play an important role in naturally occurring materials, the simultaneous introduction of both amino and telluro groups to olefins (aminotelluration) might provide a new method for the synthetic strategies. In particular, the intramolecular version of this reaction is very valuable because such a reaction has synthetic potential toward nitrogen heterocycles such as alkaloids. With these prospects we have studied aminotellurinylation of olefins induced by benzenetellurinyl reagents **2** in combination with carbamate as a nucleophile and extended this reaction to cyclofunctionalization of olefinic carbamates into nitrogen heterocycles.[8] When the aminotellurinylation was carried out at an elevated temperature, an unexpected formation of 2-oxazolidinones occurred via intramolecular cyclization of the resulting β-(phenyltellurinyl)carbamate.[9] In this paper we report the details of these new reactions.

Scheme I



Scheme II

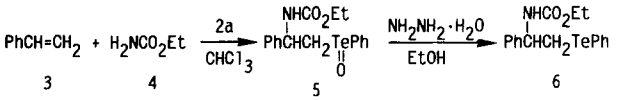


Table I. Effect of Lewis Acids on Aminotellurinylation of Styrene[a]

run	H_2NCO_2R, R =	catalyst	product	yield, %
1	Et	$BF_3{\cdot}OEt_2$	**6**	97
2	CH_2Ph	$BF_3{\cdot}OEt_2$	**7**	95
3	Et	$SnCl_4$	**6**	51
4	Et	$AlCl_3$	**6**	trace
5	Et	ZnI_2	**6**	0
6	Et	none	**6**	0

[a] The reaction was carried out in refluxing chloroform for 12 h.

Results and Discussion

Aminotellurinylation. We have recently reported that benzenetellurinic anhydride (**1**) readily reacts with acetic acid or anhydride to give benzenetellurinyl acetate (**2a**) (Scheme I), which can undergo acetoxytellurinylation of an olefin.[7] When **2a** was allowed to react with styrene (**3**)

(1) Organotelluriums. Part 20. For part 19, see: Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. *J. Org. Chem.*, previous paper in this issue.

(2) For recent reviews on the chemistry of organotelluriums, see: (a) Engman, L. *Acc. Chem. Res.* **1985**, *18*, 274-279. (b) Petragnani, N.; Comasseto, J. V. *Synthesis* **1986**, 1-30. (c) Engman, L. *Phosphorus Sulfur* **1988**, *38*, 105-119.

(3) (a) Campos, M. M.; Petragnani, N. *Tetrahedron Lett.* **1959**, No. 6, 11-13. (b) Campos, M. M.; Petragnani, N. *Tetrahedron* **1962**, *18*, 521-526.

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(5) Bergman, J.; Engman, L. *J. Am. Chem. Soc.* **1981**, *103*, 5196-5200.

(6) (a) Campos, M. M.; Petragnani, N. *Chem. Ber.* **1960**, *93*, 317-320. (b) Comasseto, J. V.; Petragnani, N. *Synth. Commun.* **1983**, *13*, 889-899. (c) Uemura, S.; Fukuzawa, S.; Toshimitsu, A.; Okano, M. *Tetrahedron Lett.* **1982**, *23*, 1177-1180. (d) Uemura, S.; Fukuzawa, S.; Toshimitsu, A. *J. Organomet. Chem.* **1983**, *250*, 203-215. (e) Comasseto, J. V.; Ferraz, H. M. C.; Petragnani, N., Brandt, C. A. *Tetrahedron Lett.* **1987**, *28*, 5611-5614.

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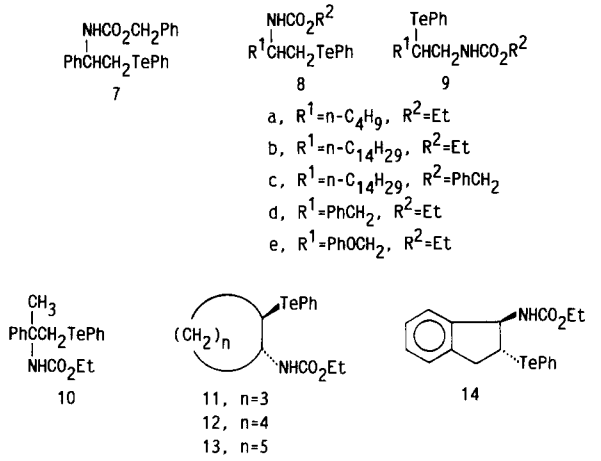
(8) A preliminary result has been published in the following paper: Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. *Chem. Lett.* **1987**, 1327-1330.

(9) A preliminary result has been published in the following paper: Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. *J. Chem. Soc., Chem. Commun.* **1987**, 1447-1448.

0022-3263/89/1954-4398$01.50/0

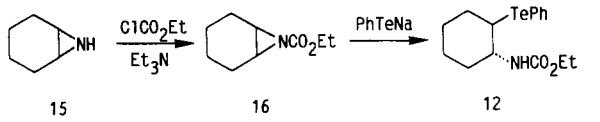
Chart I



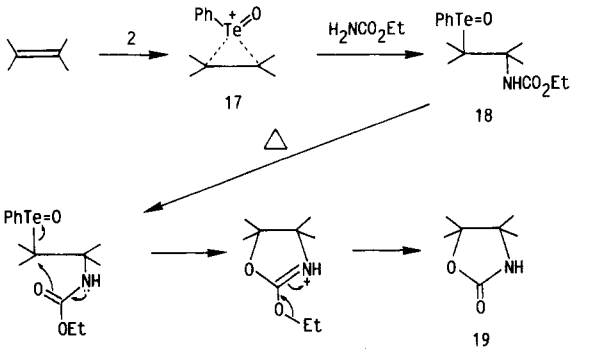
in the presence of excess ethyl carbamate (4) and 1.1 equiv of a Lewis acid in refluxing chloroform, aminotellurinylation proceeded in preference to acetoxytellurinylation, giving ethyl [1-phenyl-2-(phenyltellurinyl)ethyl]carbamate (5) (Scheme II). Because of difficulty in purification of telluroxide 5, the corresponding telluride 6 was isolated after reduction with hydrazine hydrate in ethanol. The reactivity largely depended on the added Lewis acid as in the case of oxytellurinylation[7b] (Table I). When the additive was omitted, no reaction occurred. Among several Lewis acids examined, boron trifluoride etherate was found to be most effective, forming 6 in 97% yield (run 1). The other Lewis acids such as zinc iodide and aluminum chloride were ineffective, although tin(IV) chloride somewhat prompted the reaction. This reaction proceeded equally well with benzyl carbamate to give 7 in 95% yield (run 2) (Chart I). A variety of olefins underwent this aminotellurinylation (Table II). However, the yields of the adducts from 1-hexene and allylbenzene were unsatisfactory, 46% and 45%, respectively. This prompted us to explore more effective tellurinylating agents. Benzenetellurinyl trifluoroacetate (**2b**) and trifluoromethanesulfonate (**2c**) might be appropriate candidates due to the higher leaving abilities of their counter groups. These compounds like **2a** were generated by treatment of 1 with the corresponding acids or anhydrides. The reactivities of three tellurinylating reagents are also demonstrated in Table II. The use of benzenetellurinyl trifluoroacetate (**2b**) highly improved the yields for aminotellurinylation of 1-hexene and allylbenzene in a shorter reaction time. Furthermore, the reaction using benzenetellurinyl trifluoromethanesulfonate (**2c**) occurred even in refluxing dichloromethane without the aid of Lewis acid.

As seen in Table II, the aminotellurinylation reaction of terminal olefins mainly proceeds with Markovnikov-type regioselectivity to favor the formation of 8 over 9, but the isomeric ratio is appreciably dependent on the steric and electronic effects of the substituent. The increasing bulkiness of the substituent tends to promote the formation of anti Markovnikov adduct 9. In the reaction of allyl phenyl ether, the electronic effect of phenoxy group led to inversion of the isomeric ratio. The conjugated olefins such as styrene and α-methylstyrene gave exclusively the Markovnikov isomers. The reactivity of central olefins is more affected by both electronic and steric factors of the substituents. Thus, two alkyl substituents electronically prompt aminotellurinylation, so that normal cyclic olefins, such as cyclopentene, cyclohexene, cycloheptene, and indene, reacted with **2b** at a temperature of refluxing dichloromethane. On the other hand, *trans*-β-methylstyrene

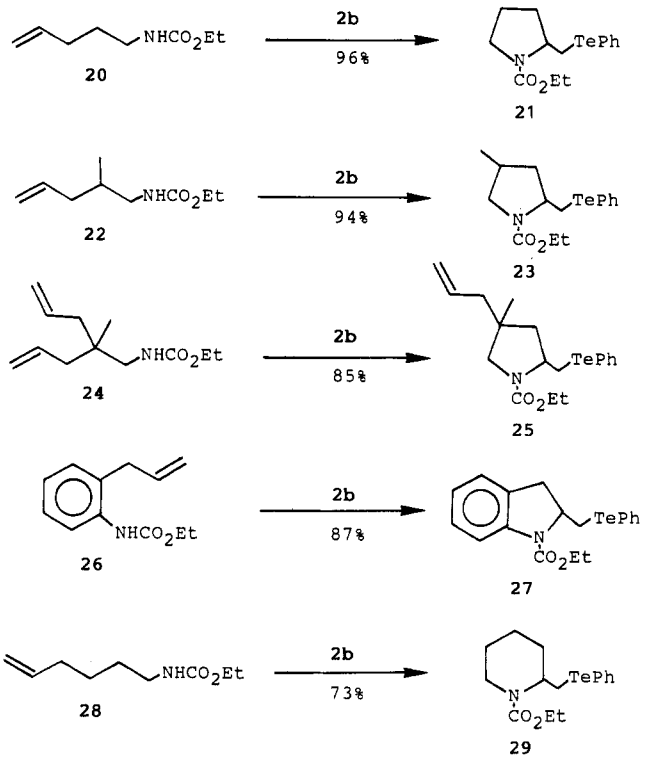
Scheme III



Scheme IV



Scheme V



and norbornene gave no adduct, even in refluxing chloroform owing to steric hindrance. The trans stereochemistry of adduct 12 from cyclohexene was confirmed by direct comparison with an authentic sample, which was separately prepared by N-ethoxycarbonylation of known 1,2-iminocyclohexane (15),[10] followed by *trans* ring opening of 16 by sodium benzenetellurolate (Scheme III). This result indicates that the aminotellurinylation reaction like oxytellurinylation proceeds with anti stereospecificity via nucleophilic attack of carbamate on epioxytelluronium intermediate 17 as shown in Scheme IV.

Cyclofunctionalization. When the aminotellurinylation reaction was extended to olefinic carbamates, an intramolecular cyclization occurred to give a nitrogen heterocycle bearing a (phenyltelluro)methyl group. As

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Table II. Aminotellurinylation of Olefins with 2 (1.1 Equiv) and Carbamate (5 Equiv) under Reflux[a]

run	olefin	reagent	solvent	time, h	product[b]	yield, %
1	styrene	**2a**	$CHCl_3$	12	**6**	97
		2b	$CHCl_3$	12		95
		2c	CH_2Cl_2	8		86
2	styrene	**2a**	$CHCl_3$	12	**7**	95
		2b	$CHCl_3$	12		95
3	1-hexene	**2a**	$CHCl_3$	20	**8a + 9a** (90:10)	46
		2b	$CHCl_3$	12		72
		2c	CH_2Cl_2	12		77
4	1-hexadecene	**2a**	$CHCl_3$	20	**8b + 9b** (85:15)	75
		2b	$CHCl_3$	12		86
		2c	CH_2Cl_2	12		72
5	1-hexadecene	**2b**	$CHCl_3$	12	**8c + 9c** (71:29)	82
6	allylbenzene	**2a**	$CHCl_3$	20	**8d + 9d** (52:48)	45
		2b	$CHCl_3$	12		82
		2c	CH_2Cl_2	12		77
7	allyl phenyl ether	**2b**	$CHCl_3$	12	**8e + 9e** (32:68)	75
8	α-methylstyrene	**2b**	$CHCl_3$	12	**10**	78
		2c	CH_2Cl_2	8		78
9	cyclopentene	**2b**	CH_2Cl_2	12	**11**	85
		2c	CH_2Cl_2	12		95
10	cyclohexene	**2b**	CH_2Cl_2	12	**12**	90
		2c	CH_2Cl_2	12		95
11	cycloheptene	**2b**	CH_2Cl_2	12	**13**	86
		2c	CH_2Cl_2	12		94
12	indene	**2b**	CH_2Cl_2	12	**14**	84
		2c	CH_2Cl_2	12		42

[a] Ethyl carbamate was mostly used as reactant. For runs 2 and 5, benzyl carbamate was used instead. [b] Values in parentheses indicate the isomeric ratios which were determined by HPLC and NMR analyses.

summarized in Scheme V, pyrrolidine and piperidine derivatives were obtained in high yields by treatment of the corresponding olefinic carbamates with **2b** in the presence of boron trifluoride etherate in refluxing chloroform, followed by reduction with hydrazine hydrate. This intramolecular cyclization is complete within 30 min and much faster than the above intermolecular reaction (8–20 h). The ring size of the cyclization product can be rationalized in terms of Markovnikov-type regioselectivity for the addition.

Synthesis of 2-Oxazolidinones. One of the current interests of organotellurium chemistry is based on versatile manipulations of tellurium functional groups, that is, reductive detelluration,[11] halogenolysis,[12] methanolysis,[13] and oxidative elimination.[14,15] Syn elimination reaction of telluroxide is one of the valuable transformations.[14] We attempted the in situ telluroxide elimination of the aminotellurinylation product. Thus, an olefin was treated with **2b** and ethyl carbamate in the presence of boron trifluoride etherate at an elevated temperature of refluxing 1,2-dichloroethane, but there was, contrary to expectation, detected no allylic carbamate formed by syn elimination of the intermediate telluroxide **18**. 2-Oxazolidinone **19** was instead obtained in a high yield. Use of ethyl alkylcarbamates led to the formation of the *N*-alkyl-2-oxazolidinone. The tellurinylating reagent **2c** similarly effects the reaction without the aid of Lewis acid at refluxing temperature of chloroform. A variety of examples are summarized in Table III. *trans*-β-Methylstyrene, which failed in the aminotellurinylation under refluxing chloro-

Table III. Syntheses of 2-Oxazolidinones from Olefins with 2b[a] or 2c[b]

run	olefin	reagent	time, h	product	yield, %
1	1-hexene	**2b**	20	**30 + 31** (75:25)[c]	91
		2c	20		77
2	styrene	**2b**	24	**32**	92
		2c	20		85
3	α-methylstyrene	**2b**	12	**33**	61
		2c	12		59
4	*trans*-β-methylstyrene	**2b**	20	**34**	79
5	*trans*-4-octene	**2b**	20	**35**	53
6	*cis*-4-octene	**2b**	20	**36**	84
7	cyclopentene	**2b**	20	**37**	92
		2c	20		85
8	cyclohexene	**2b**	20	**38**	86
		2c	20		85
9	cyclohexene	**2b**	8	**39**[d]	77
10	cyclohexene	**2b**	8	**40**[e]	76
11	cycloheptene	**2b**	20	**41**	81
		2c	8		83
12	indene	**2b**	12	**42**	79
		2c	12		40
13	1,2-dihydronaphthalene	**2b**	20	**43**	81

[a] Reaction conditions: olefin (1 mmol), **2b** (1.1 mmol), ethyl carbamate (5 mmol), BF_3·OEt_2 (1.1 mmol), and 1,2-dichloroethane (6 mL) at reflux. [b] Reaction conditions: olefin (1 mmol), **2c** (1.1 mmol), ethyl carbamate (5 mmol), and chloroform (6 mL) at reflux. [c] Isomeric ratio was determined by ^1H and ^{13}C NMR analyses. [d] Use of ethyl methylcarbamate. [e] Use of ethyl ethylcarbamate.

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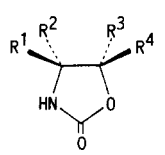
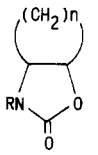
(14) (a) Lee, H.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1981**, 277–278. (b) Uemura, S.; Fukuzawa, S. *J. Am. Chem. Soc.* **1983**, *105*, 2748–2752. (c) Uemura, S.; Ohe, K.; Fukuzawa, S. *Tetrahedron Lett.* **1985**, *26*, 895–898. (d) Uemura, S.; Hirai, Y.; Ohe, K.; Sugita, N. *J. Chem. Soc., Chem. Commun.* **1985**, 1037–1038.

(15) (a) Otsubo, T.; Ogura, F.; Yamaguchi, H.; Higuchi, H.; Sakata, Y.; Misumi, S. *Chem. Lett.* **1981**, 447–448. (b) Ogura, F.; Otsubo, T.; Ohira, N.; Yamaguchi, H. *Synthesis* **1983**, 1006–1008.

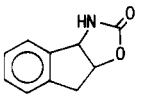
Chart II



30, R^1=n-Bu, R^2=R^3=R^4=H
31, R^1=R^2=R^4=H, R^3=n-Bu
32, R^1=Ph, R^2=R^3=R^4=H
33, R^1=Ph, R^2=Me, R^3=R^4=H
34, R^1=Ph, R^2=R^4=H, R^3=Me
35, R^1=R^3=n-Pr, R^2=R^4=H
36, R^1=R^4=n-Pr, R^2=R^3=H



37, n=3, R=H
38, n=4, R=H
39, n=4, R=Me
40, n=4, R=Et
41, n=5, R=H



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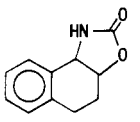

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form, gave the corresponding 2-oxazolidinone, while norbornene was still inert. This heterocyclization reaction also proceeds with regio- and stereoselectivity. Terminal olefins such as 1-hexene, styrene, and α-methylstyrene gave mainly 4-substituted 2-oxazolidinones **30**, **32**, and **33**, respectively (Chart II). The stereochemistries of 4,5-dipropyl-2-oxazolidinones from *trans*- and *cis*-4-octenes were assigned on comparison of their ^{1}H NMR spectra to those of *trans*- and *cis*-4,5-diethyl-2-oxazolidinones[16] to be trans form **35** and cis form **36**, respectively. In addition, *trans*-β-methylstyrene gave rise to known *trans*-5-methyl-4-phenyl-2-oxazolidinone (**34**) and cyclohexene to known *cis*-4,5-tetramethylene-2-oxazolidinone (**38**). From these results, a plausible mechanism for the formation of 2-oxazolidinone (**19**) was suggested to involve the initial aminotellurinylation and subsequent thermolysis of intermediate **18**, as shown in Scheme IV. As already mentioned, the aminotellurinylation is anti addition with Markovnikov-type regioselectivity. The conversion of **18** into **19** probably proceeds via backside attack by the carbonyl oxygen of the carbamate function on the carbon bearing the phenyltellurinyl group, followed by carbonylation of the ethoxy group. The net addition to the olefin is, therefore, syn-stereoselective. The latter cyclization step is reminiscent of thermolysis of β-halogenocarbamates to produce oxazolidinones.[16-18] The thermolytic temperature (83 °C) for **18** is much lower than that for the β-halogenocarbamates (120–200 °C), indicating the good leaving ability of phenyltellurinyl group.

2-Oxazolidinones are an important class of heterocyclic compounds with wide application.[19] The most common syntheses start with the corresponding *cis*-β-amino alcohols, which are often difficult to obtain. On the other hand, the previous approach from olefins requires a multistep procedure.[18] The present procedure constitutes a novel one-pot formation of 2-oxazolidinones from olefins under mild conditions in good to excellent yields. In addition, it may be useful as providing stereoselective access to *cis*-β-amino alcohols from olefins, 2-oxazolidinones being readily converted into *cis*-β-amino alcohols by hydrolysis with alcoholic base.[18,20]

Conclusions. The present aminotellurinylation reaction gives a wide range of alkylcarbamates and nitrogen heterocycles bearing a phenyltelluro group. Easy carbamate deprotection and versatile chemical modifications of phenyltelluro group might promise this reaction to be a useful new approach to β-functionalized amines from olefins and nitrogen heterocycles from olefinic carbamates. In addition, this reaction in combination with the subsequent pyrolysis constitutes a simple, direct method for the synthesis of 2-oxazolidinones from olefins.

Experimental Section

General Methods and Materials. All reactions were carried out under a nitrogen atmosphere. Melting points are uncorrected. Analytical liquid chromatography was carried out with a GILSON HPLC system equipped with a UV detector and a Microsorb C-18 HPLC column using methanol–water (95:5) as eluant. Details of other instrumentation were described in the accompanying paper.[1] IR data are reported in cm^{-1}, and ^{1}H NMR data (deuteriochloroform) in δ (ppm). MS data involving tellurium are reported on the basis of its isotope mass number 130. Olefinic carbamates used in cyclofunctionalizations were prepared by the standard Schotten–Baumann method[21] from the corresponding amines.[22] Benzenetellurinic anhydride (**1**) was prepared according to the method of Barton et al.[23] The synthetic details of benzenetellurinyl acetate (**2a**) were given in the preceding paper.[7b]

Benzenetellurinyl Trifluoroacetate (2b) and Trifluoromethanesulfonate (2c). When benzenetellurinic anhydride (**1**) (0.457 g, 1 mmol) was treated with trifluoroacetic acid (0.251 g, 2.2 mmol) or anhydride (0.231 g, 1.1 mmol) in dichloromethane (10 mL) as solvent at room temperature, it dissolved within 30 min. Evaporation gave a quantitative yield of benzenetellurinyl trifluoroacetate (**2b**), which was recrystallized from benzene to afford colorless crystals: mp 181–182 °C (sealed); IR (KBr disk) 1680 (C=O); ^{1}H NMR (60 MHz) 7.3–7.6 (m, 3 H, Ar H), 7.7–8.0 (m, 2 H, Ar H). Anal. Calcd for $C_8H_5F_3O_3Te$: C, 28.79; H, 1.51. Found: C, 28.66; H, 1.74.

In a similar manner, **2c** was smoothly obtained by treatment of **1** with 1.1 equiv of trifluoromethanesulfonic acid or anhydride: pale yellow crystals from chloroform, mp 184–185 °C; IR (KBr disk) 1260 (S=O); ^{1}H NMR (60 MHz) 7.5–7.8 (m, 3 H, Ar H), 7.8–8.1 (m, 2 H, Ar H). Anal. Calcd for $C_7H_5F_3O_4STe$: C, 22.74; H, 1.37. Found: C, 22.86; H, 1.86.

These reagents as well as **2a** were in situ used for the following experiments because of their hygroscopic natures.

General Procedure for Aminotellurinylation. Details are given in the following formation of **12** from cyclohexene. The other olefins were allowed to react in a similar fashion using conditions specified in Table II.

Ethyl [2-(Phenyltelluro)cyclohexyl]carbamate (12). Benzenetellurinyl trifluoroacetate (**2b**) (1.1 mmol) was generated in situ by treatment of benzenetellurinic anhydride (**1**) (0.252 g, 0.55 mmol) with trifluoroacetic anhydride (0.116 g, 0.55 mmol) in 6 mL of dichloromethane at room temperature for 10 min. Into the solution were successively added cyclohexene (0.082 g, 1 mmol), ethyl carbamate (0.446 g, 5 mmol), and boron trifluoride etherate (0.156 g, 1.1 mmol), and the resulting mixture was stirred at reflux temperature for 12 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure, and the residual products were reduced with hydrazine hydrate (0.1 g, 2 mmol) in 6 mL of ethanol at 60 °C for 10 min. After evaporation of the solvent under reduced pressure, the reaction mixture was dissolved in 6 mL of dichloromethane, treated with an aqueous saturated $NaHCO_3$ solution (25 mL), and extracted with dichloromethane (20 mL × 2). The extract was washed with brine (20 mL) and dried over $MgSO_4$. Evaporation of the solvent in vacuo left a yellow residue, which was subjected to column chromatography on silica gel using hexane–ethyl acetate (5:1) as eluant to give first a small amount of diphenyl ditelluride and

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then ethyl [2-(phenyltelluro)cyclohexyl]carbamate (**12**). Recrystallization from hexane–chloroform afforded white needles, 0.36 g, 96%: mp 72–73 °C; IR (KBr disk) 3350 (N—H), 1700 (C=O); ^{1}H NMR (60 MHz) 0.9–1.9 (m, 6 H, CH_2), 1.23 (t, J = 6.5 Hz, CH_3), 1.9–2.5 (m, 2 H, CH_2), 3.0–3.8 (m, 2 H, NCH and TeCH), 4.08 (q, J = 6.5 Hz, 2 H, OCH_2), 4.5–5.0 (br d, J = 8 Hz, 1 H, NH), 7.0–7.3 (m, 3 H, Ar H), 7.6–7.9 (m, 2 H, Ar H); MS, m/z 377 (M^+). Anal. Calcd for $C_{15}H_{21}NO_2Te$: C, 48.04; H, 5.60; N, 3.74. Found: C, 47.76; H, 5.60; N, 3.74.

Ethyl [1-phenyl-2-(phenyltelluro)ethyl]carbamate (6): colorless needles from hexane–ethanol, mp 65.5–66 °C; IR (KBr disk) 3325 (N—H), 1700 (C=O); ^{1}H NMR (90 MHz) 1.17 (t, J = 7 Hz, 3 H, CH_3), 3.37 (d, J = 6.5 Hz, 2 H, $TeCH_2$), 4.02 (q, J = 7 Hz, 2 H, OCH_2), 4.92 (q, J = 7 Hz, 1 H, NCH), 5.40 (br d, J = 7 Hz, 1 H, NH), 7.0–7.3 (m, 3 H, Ar H), 7.24 (s, 5 H, Ar H), 7.4–7.7 (m, 2 H, Ar H). Anal. Calcd for $C_{17}H_{19}NO_2Te$: C, 51.43; H, 4.83; N, 3.53. Found: C, 51.49; H, 4.79; N, 3.36.

Benzyl [1-phenyl-2-(phenyltelluro)ethyl]carbamate (7): pale yellow oil; IR (liquid film) 3320 (N—H), 1705 (C=O); ^{1}H NMR (60 MHz) 3.30 (d, J = 6 Hz, 2 H, $TeCH_2$), 4.8–5.3 (m, 2 H, CH, NH), 5.03 (s, 2 H, OCH_2), 7.0–7.3 (m, 13 H, Ar H), 7.5–7.8 (m, 2 H, Ar H); exact mass calcd for $C_{22}H_{21}NO_2Te$ 461.0640, found (high-resolution mass spectrum) 461.0610.

Ethyl [1-[(Phenyltelluro)methyl]pentyl]carbamate (8a) and Ethyl [2-(Phenyltelluro)hexyl]carbamate (9a). An isomeric mixture of **8a** and **9a** (90:10 based on HPLC) was obtained as a pale yellow oil by aminotellurinylation of 1-hexene: IR (liquid film) 3325 (N—H), 1700 (C=O); ^{1}H NMR (60 MHz) 0.83 (br t, 3 H, CH_3), 1.0–1.6 (m, 6 H, CH_2), 1.16 (t, J = 7 Hz, 3 H, CH_3), 3.08 (d, J = 5.5 Hz, 2 H, CH_2), 3.5–4.0 (m, 1 H, CH), 4.02 (q, J = 7 Hz, 2 H, OCH_2), 4.75 (br d, J = 8 Hz, 1 H, NH), 7.0–7.3 (m, 3 H), 7.6–7.9 (m, 2 H). Anal. Calcd for $C_{15}H_{23}NO_2Te$: C, 47.79; H, 6.16; N, 3.72. Found for an isomeric mixture: C, 47.60; H, 5.86; N, 3.50.

Ethyl [1-[(Phenyltelluro)methyl]pentadecyl]carbamate (8b) and Ethyl [2-(Phenyltelluro)hexadecyl]carbamate (9b). An isomeric mixture of **8b** and **9b** (85:15 based on HPLC) was obtained as a white semisolid by aminotellurinylation of 1-hexadecene. Column chromatography on silica gel with hexane–ethyl acetate (9:1) as eluant gave first the isomer **9b** as a pale yellow oil: IR (liquid film) 3330 (N—H), 1705 (C=O); ^{1}H NMR (60 MHz) 0.83 (br t, 3 H, CH_3), 1.0–1.8 (m, 26 H, CH_2), 1.05 (t, J = 7 Hz, 3 H, CH_3), 3.2–3.6 (m, 3 H, NCH_2 and TeCH), 4.03 (q, J = 7 Hz, 2 H, OCH_2), 4.93 (br, 1 H, NH), 7.1–7.4 (m, 3 H, Ar H), 7.6–7.9 (m, 2 H, Ar H). Further elution gave another isomer (**8b**) as white crystals: mp 45–46 °C; IR (KBr disk) 3325 (N—H), 1700 (C=O); ^{1}H NMR (60 MHz) 0.86 (br t, 3 H, CH_3), 1.0–1.8 (m, 26 H, CH_2), 1.06 (t, J = 7 Hz, 3 H, CH_3), 3.10 (d, J = 5 Hz, 2 H, $TeCH_2$), 3.6–4.0 (m, 1 H, NCH), 4.03 (q, J = 7 Hz, 2 H, OCH_2), 4.79 (br d, J = 8 Hz, 1 H, NH), 7.0–7.3 (m, 3 H, Ar H), 7.6–7.9 (m, 2 H, Ar H). Anal. Calcd for $C_{25}H_{43}NO_2Te$: C, 58.04; H, 8.40; N, 2.71. Found for an isomeric mixture: C, 58.01; H, 8.40; N, 2.70.

Benzyl [1-[(Phenyltelluro)methyl]pentadecyl]carbamate (8c) and Benzyl [2-(Phenyltelluro)hexadecyl]carbamate (9c). An isomeric mixture of **8c** and **9c** (71:29 based on HPLC) was obtained as a white semisolid by aminotellurinylation of 1-hexadecene and benzyl carbamate. Column chromatography on silica gel with hexane–ethyl acetate (8:1) as eluant gave first the isomer **9c** as a pale yellow oil: IR (liquid film) 3340 (N—H), 1690 (C=O); ^{1}H NMR (60 MHz) 0.87 (br t, 3 H, CH_3), 1.1–1.7 (m, 26 H, CH_2), 3.3–3.6 (m, 3 H, NCH_2 and TeCH), 4.80 (br, 1 H, NH), 5.03 (s, 2 H, $PhCH_2$), 7.0–7.3 (m, 3 H, Ar H), 7.23 (s, 5 H, Ar H), 7.5–7.8 (m, 2 H, Ar H). Further elution gave another isomer (**8c**): white crystals from hexane–chloroform, mp 63–64 °C; IR (KBr disk) 3330 (N—H), 1690 (C=O); ^{1}H NMR (60 MHz) 0.87 (br t, 3 H, CH_3), 1.1–1.7 (m, 26 H, CH_2), 3.07 (d, J = 5 Hz, 2 H, $TeCH_2$), 3.6–4.0 (m, 1 H, NCH), 4.80 (br d, J = 8 Hz, 1 H, NH), 4.98 (s, 2 H, $PhCH_2$), 7.0–7.3 (m, 3 H, Ar H), 7.23 (s, 5 H, Ar H), 7.5–7.8 (m, 2 H, Ar H). Anal. Calcd for $C_{30}H_{45}NO_2Te$: C, 62.19; H, 7.84; N, 2.42. Found for an isomeric mixture: C, 62.11; H, 7.81; N, 2.37.

Ethyl [2-Phenyl-1-[(phenyltelluro)methyl]ethyl]carbamate (8d) and Ethyl [3-Phenyl-2-(phenyltelluro)propyl]carbamate (9d). Gel-permeation liquid chromatography of the isomeric mixture of **8d** and **9d** (52:48 based on HPLC) from allylbenzene with methanol as eluant gave first isomer **9d**, pale yellow oil: IR (liquid film) 3340 (N—H), 1700 (C=O); ^{1}H NMR (60 MHz) 1.17 (t, J = 7 Hz, 3 H, CH_3), 3.03 (d, J = 6 Hz, 2 H, $PhCH_2$), 3.2–3.7 (m, 3 H, NCH_2 and TeCH), 4.05 (q, J = 7 Hz, 2 H, OCH_2), 4.8–5.1 (br, 1 H, NH), 7.05–7.4 (m, 3 H, Ar H), 7.20 (s, 5 H, Ar H), 7.6–7.9 (m, 2 H, Ar H). Further elution gave another isomer (**8d**): white crystals from hexane–ethanol, mp 30–32 °C; IR (KBr disk) 3350 (N—H), 1705 (C=O); ^{1}H NMR (60 MHz) 1.13 (t, J = 7 Hz, 3 H, CH_3), 2.83 (d, J = 6 Hz, 2 H, $PhCH_2$), 3.05 (d, J = 6 Hz, 2 H, $TeCH_2$), 3.8–4.3 (m, 1 H, NCH), 4.00 (q, J = 7 Hz, OCH_2), 4.77 (br d, J = 9 Hz, 1 H, NH), 7.0–7.3 (m, 3 H, Ar H), 7.12 (s, 5 H, Ar H), 7.6–7.9 (m, 2 H, Ar H). Anal. Calcd for $C_{18}H_{21}NO_2Te$: C, 52.60; H, 5.16; N, 3.41. Found for an isomeric mixture: C, 52.50; H, 5.10; N, 3.35.

Ethyl [2-Phenoxy-1-[(phenyltelluro)methyl]ethyl]carbamate (8e) and Ethyl [3-Phenoxy-2-(phenyltelluro)propyl]carbamate (9e). Column chromatography of the products (**8e**:**9e** = 32:68 based on HPLC) from allyl phenyl ether on silica gel with chloroform–hexane (5:1) as eluant gave successively two isomers.

First isomer, **8e**: pale yellow oil; IR (liquid film) 3400 (N—H), 1700 (C=O); ^{1}H NMR (90 MHz) 1.21 (t, J = 7 Hz, 3 H, CH_3), 3.0–3.4 (m, 2 H, $TeCH_2$), 3.7–4.4 (m, 3 H, NCH and $PhOCH_2$), 4.08 (q, J = 7 Hz, 2 H, OCH_2), 5.20 (br d, J = 7 Hz, 1 H, NH), 6.7–7.0 (m, 5 H, Ar H), 7.1–7.4 (m, 3 H, Ar H), 7.6–7.9 (m, 2 H, Ar H). Anal. Calcd for $C_{18}H_{21}NO_3Te$: C, 50.63; H, 4.97; N, 3.28. Found: C, 50.42; H, 4.97; N, 3.05.

Second isomer, **9e**: pale yellow oil; IR (liquid film) 3325 (N—H), 1710 (C=O); ^{1}H NMR (90 MHz) 1.20 (t, J = 7 Hz, 3 H, CH_3), 3.6–3.8 (m, 3 H, NCH_2 and TeCH), 3.9–4.5 (m, 2 H, $PhOCH_2$), 4.05 (q, J = 7 Hz, 2 H, OCH_2), 5.15 (br, 1 H, NH), 6.8–7.0 (m, 3 H, Ar H), 7.1–7.4 (m, 5 H, Ar H), 7.6–7.9 (m, 2 H, Ar H). Anal. Calcd for $C_{18}H_{21}NO_3Te$: C, 50.63; H, 4.97; N, 3.28. Found: C, 50.63; H, 4.93; N, 3.29.

Ethyl [1-methyl-1-phenyl-2-(phenyltelluro)ethyl]carbamate (10): pale yellow oil; IR (liquid film) 3340 (N—H), 1720 (C=O); ^{1}H NMR (60 MHz) 1.13 (t, J = 7 Hz, 3 H, CH_3), 1.77 (s, 3 H, CH_3), 3.63 (AB q, J = 12 Hz, 2 H, CH_2), 3.94 (q, J = 7 Hz, 2 H, OCH_2), 5.33 (br, 1 H, NH), 7.0–7.3 (m, 3 H, Ar H), 7.25 (s, 5 H, Ar H), 7.5–7.8 (m, 2 H, Ar H). Anal. Calcd for $C_{18}H_{21}NO_2Te$: C, 52.60; H, 5.16; N, 3.41. Found: C, 52.62; H, 4.80; N, 3.21.

Ethyl [2-(phenyltelluro)cyclopentyl]carbamate (11): pale yellow oil; IR (liquid film) 3325 (N—H), 1700 (C=O); ^{1}H NMR (60 MHz) 1.20 (t, J = 7 Hz, 3 H, CH_3), 1.3–2.5 (m, 6 H, CH_2), 3.1–3.6 (m, 1 H, TeCH), 3.8–4.3 (m, 1 H, NCH), 4.10 (q, J = 7 Hz, 2 H, OCH_2), 4.83 (br d, J = 8 Hz, 1 H, NH), 7.1–7.4 (m, 3 H, Ar H), 7.6–7.9 (m, 2 H, Ar H). Anal. Calcd for $C_{14}H_{19}NO_2Te$: C, 46.58; H, 5.32; N, 3.88. Found: C, 46.55; H, 5.23; N, 3.83.

Ethyl [2-(phenyltelluro)cycloheptyl]carbamate (13): colorless needles from hexane–ethanol, mp 51–52 °C; IR (KBr disk) 3330 (N—H), 1700 (C=O); ^{1}H NMR (60 MHz) 1.0–2.5 (m, 10 H, CH_2), 1.25 (t, J = 7 Hz, 3 H, CH_3), 3.3–3.7 (m, 1 H, TeCH), 3.8–4.2 (m, 1 H, NCH), 4.10 (q, J = 7 Hz, OCH_2), 4.90 (br d, J = 8 Hz, 1 H, NH), 7.1–7.4 (m, 3 H, Ar H), 7.6–7.9 (m, 2 H, Ar H). Anal. Calcd for $C_{16}H_{23}NO_2Te$: C, 49.40; H, 5.97; N, 3.60. Found: C, 49.47; H, 5.94; N, 3.60.

Ethyl [2-(Phenyltelluro)indanyl]carbamate (14): colorless needles from hexane–ethanol, mp 112–113.5 °C; IR (KBr disk) 3320 (N—H), 1695 (C=O); ^{1}H NMR (60 MHz) 1.20 (t, J = 7 Hz, 3 H, CH_3), 2.7–3.3 (m, 3 H, TeCH and CH_2), 3.3–3.75 (m, 1 H, NCH), 4.07 (q, J = 7 Hz, 2 H, OCH_2), 5.10 (br d, J = 5 Hz, 1 H, NH), 7.0–7.3 (m, 3 H, Ar H), 7.00 (s, 4 H, Ar H), 7.6–7.9 (m, 2 H, Ar H). Anal. Calcd for $C_{18}H_{19}NO_2Te$: C, 54.73; H, 4.86; N, 3.55. Found: C, 54.58; H, 4.63; N, 3.46.

Preparation of an Authentic Sample of Ethyl [*trans*-2-(Phenyltelluro)cyclohexyl]carbamate (12). To an ethereal solution (50 mL) of 1,2-iminocyclohexane (**15**) (1.4 g, 15 mmol), prepared from *trans*-azido-2-iodocyclohexane by the reported method,[10] were added triethylamine (1.8 g, 18 mmol) and then ethyl chloroformate (1.94 g, 18 mmol) under ice-bath cooling. After the resulting white suspension was stirred at 0 °C for 2 h, the white solid was filtered and thoroughly washed with ether. The ethereal filtrate was washed with an aqueous saturated $NaHCO_3$ solution and dried over $MgSO_4$. After evaporation of the solvent in vacuo, the residue was purified by distillation using a Kugelrohr apparatus (110 °C/1.6 mmHg) to give *cis*-7-(ethoxycarbonyl)-7-azabicyclo[4.1.0]heptane (**16**) as a colorless oil (1.14 g, 45%): IR

(liquid film) 1720 (C=O); ^{1}H NMR (60 MHz) 1.28 (t, J = 7 Hz, 3 H, CH_3), 1.7–2.1 (m, 8 H, CH_2), 2.62 (m, 2 H, CH), 4.10 (q, J = 7 Hz, 2 H, CH_2). Anal. Calcd for $C_9H_{15}NO_2$: C, 63.86; H, 8.95; N, 8.28. Found: C, 63.73; H, 8.93; N, 8.26.

Sodium borohydride (0.12 g, 3.2 mmol) was added in one portion to a suspension of diphenyl ditelluride (0.55 g, 1.34 mmol) in ethanol (15 mL) at room temperature. Into the colorless solution of the resulting sodium benzenetellurolate was then added a solution of **16** (0.377 g, 2.23 mmol) in ethanol (5 mL), and the mixture was stirred at room temperature for 3 h. It was then poured into aqueous HCl (0.2 N, 50 mL) and extracted with dichloromethane (30 mL × 2). The extract was washed with an aqueous saturated $NaHCO_3$ solution and dried over $MgSO_4$. After evaporation of the solvent, the residue was subjected to column chromatography (silica gel) with hexane–ethyl acetate (5:1) as eluant to give **12** as white needles (0.40 g, 48%). This product was identical in all respects with that obtained from aminotellurinylation of cyclohexene.

General Procedure for Intramolecular Aminotellurinylation of Olefinic Carbamates. 1-(Ethoxycarbonyl)-2-[(phenyltelluro)methyl]pyrrolidine (21). To a chloroform solution (6 mL) of benzenetellurinyl trifluoroacetate (**2b**) (1.1 mmol), in situ generated from benzenetellurinic anhydride (**1**) (0.252 g, 0.55 mmol) and trifluoroacetic acid (0.125 g, 1.1 mmol), were successively added a solution of ethyl (4-pentenyl)carbamate (**20**) (0.157 g, 1 mmol) in the same solvent (2 mL) and boron trifluoride etherate (0.156 g, 1.1 mmol). The resulting solution was stirred at reflux temperature for 0.5 h. The solution was cooled to room temperature. Evaporation of the solvent left a yellow product mixture, which was dissolved in ethanol (6 mL) and reduced with hydrazine hydrate (0.1 g, 2 mmol) at room temperature for 10 min. After removal of ethanol in vacuo, the residue was treated with an aqueous saturated $NaHCO_3$ solution (20 mL) and extracted with dichloromethane (20 mL × 2). The extract was washed with brine (25 mL), dried over $MgSO_4$, and evaporated in vacuo. Column chromatography of the residue on silica gel with chloroform–hexane (3:2) as eluant afforded **21** (0.346 g, 96%) as a pale yellow oil: IR (liquid film) 1695 (C=O); ^{1}H NMR (60 MHz) 1.17 (t, J = 7 Hz, 3 H, CH_3), 1.6–2.3 (m, 4 H, CH_2), 2.7–3.8 (m, 4 H, NCH_2 and $TeCH_2$), 3.9–4.3 (m, 1 H, NCH), 4.02 (q, J = 7 Hz, 2 H, OCH_2), 7.0–7.5 (m, 3 H, Ar H), 7.6–7.9 (m, 2 H, Ar H); MS, m/z 363 (M^+). Anal. Calcd for $C_{14}H_{19}NO_2Te$: C, 46.58; H, 5.32; N, 3.88. Found: C, 46.53; H, 5.32; N, 3.85.

1-(Ethoxycarbonyl)-4-methyl-2-[(phenyltelluro)methyl]pyrrolidine (23): pale yellow oil; IR (liquid film) 1700 (C=O); ^{1}H NMR (60 MHz) 0.97 (d, J = 5 Hz, 3 H, CH_3), 1.17 (t, J = 7 Hz, 3 H, CH_3), 1.4–2.5 (m, 3 H, CH and CH_2), 2.6–3.7 (m, 4 H, NCH_2 and $TeCH_2$), 3.7–4.3 (m, 1 H, NCH), 3.93 and 3.98 (each q, J = 7 Hz, 2 H, OCH_2), 7.0–7.3 (m, 3 H, Ar H), 7.5–7.8 (m, 2 H, Ar H). The appearance of two different signals for OCH_2 indicates a mixture of cis and trans stereoisomers. Anal. Calcd for $C_{15}H_{21}NO_2Te$: C, 48.04; H, 5.66; N, 3.74. Found: C, 48.05; H, 5.56; N, 3.74.

4-Allyl-1-(ethoxycarbonyl)-4-methyl-2-[(phenyltelluro)methyl]pyrrolidine (25): pale yellow oil; IR (liquid film) 1700 (C=O); ^{1}H NMR (60 MHz) 0.93 and 1.02 (each s, 3 H, CH_3), 1.17 (t, J = 8 Hz, 3 H, CH_3), 1.2–2.2 (m, 4 H, CH_2), 2.9–3.6 (m, 4 H, NCH_2 and $TeCH_2$), 3.8–4.3 (m, 1 H, NCH), 3.98 (q, J = 8 Hz, OCH_2), 4.7–5.2 (m, 2 H, $=CH_2$), 5.4–5.9 (m, 1 H, =CH), 7.0–7.3 (m, 3 H, Ar H), 7.5–7.8 (m, 2 H, Ar H). The appearance of two different signals for the methyl groups attached to the ring indicates a mixture of cis and trans stereoisomers. Anal. Calcd for $C_{18}H_{25}NO_2Te$: C, 52.09; H, 6.08; N, 3.38. Found: C, 52.10; H, 6.06; N, 3.38.

1-(Ethoxycarbonyl)-2,3-dihydro-2-[(phenyltelluro)methyl]indole (27): pale yellow oil; IR (liquid film) 1710 (C=O); ^{1}H NMR (60 MHz) 1.23 (t, J = 7 Hz, 3 H, CH_3), 2.6–3.6 (m, 4 H, CH_2), 4.16 (q, J = 7 Hz, 2 H, OCH_2), 4.3–4.9 (m, 1 H, NCH), 6.8–7.3 (m, 7 H, Ar H), 7.5–7.8 (m, 2 H, Ar H); MS, m/z 411 (M^+). Anal. Calcd for $C_{18}H_{19}NO_2Te$: C, 52.86; H, 4.69; N, 3.43. Found: C, 53.15; H, 4.57; N, 3.40.

1-(Ethoxycarbonyl)-2-[(phenyltelluro)methyl]piperidine (29): pale yellow oil; IR (liquid film) 1695 (C=O); ^{1}H NMR (60 MHz) 1.1–2.1 (m, 6 H, CH_2), 1.20 (t, J = 8 Hz, 3 H, CH_3), 2.5–3.3 (m, 4 H, NCH_2 and $TeCH_2$), 3.8–4.2 (m, 1 H, NCH), 4.10 (q, J = 8 Hz, 2 H, OCH_2), 7.0–7.3 (m, 3 H, Ar H), 7.5–7.8 (m, 2 H, Ar H); MS, m/z 377 (M^+). Anal. Calcd for $C_{15}H_{21}NO_2Te$: C, 48.04; H, 5.66; N, 3.74. Found: C, 48.03; H, 5.66; N, 4.13.

General Procedure for Synthesis of 2-Oxazolidinone. *cis*-4,5-Tetramethylene-2-oxazolidinone (38). To a 1,2-dichloroethane solution (6 mL) of benzenetellurinyl trifluoroacetate (**2b**) (1.1 mmol), generated in situ from benzenetellurinic anhydride (**1**) (0.252 g, 0.55 mmol) and trifluoroacetic acid (0.126 g, 1.1 mmol), were successively added cyclohexene (0.082 g, 1 mmol), ethyl carbamate (0.446 g, 5 mmol) and boron trifluoride etherate (0.156 g, 1.1 mmol). The resulting solution was stirred at reflux temperature for 20 h. The solution was cooled to room temperature, treated with an aqueous saturated $NaHCO_3$ solution (30 mL), and extracted with chloroform (20 mL × 2). The extract was dried over $MgSO_4$ and evaporated in vacuo. The remaining ethyl carbamate was removed by sublimation (50 °C/1 mmHg), and the residue was chromatographed on silica gel with ethyl acetate–hexane (1:1) as eluant to give diphenyl ditelluride (0.14 g, 62%) as red needles and then **38** (0.122 g, 86%) as a white solid. Recrystallization of **38** from hexane–acetone gave colorless crystals: mp 54–55 °C (lit.[24] mp 55–56 °C for cis isomer and mp 100–102 °C for trans isomer); IR (KBr disk) 3260 (N—H), 1730 (C=O); ^{1}H NMR (60 MHz) 1.1–2.2 (m, 8 H, CH_2), 3.5–4.0 (m, 1 H, NCH), 4.3–4.7 (m, 1 H, OCH), 6.08 (br, 1 H, NH).

4-Butyl- and 5-Butyl-2-oxazolidinones (30 and 31). The isomeric mixture of **30** and **31** (75:25) was obtained as a colorless oil from 1-hexene. It was subjected to column chromatography on silica gel with 1:1 hexane–ethyl acetate as eluant to give first **30** as a colorless oil: IR (liquid film) 3290 (N—H), 1760 (C=O); ^{1}H NMR (60 MHz) 0.90 (br t, 3 H, CH_3), 1.1–1.9 (m, 6 H, CH_2), 3.7–4.6 (m, 3 H, NCH and OCH_2), 6.93 (br, 1 H, NH). Anal. Calcd for $C_7H_{12}NO_2$: C, 58.70; H, 9.17; N, 9.78. Found: C, 58.64; H, 9.13; N, 9.65. Further elution gave another isomer (**31**): colorless crystals from hexane–acetone, mp 87–87.5 °C (lit.[17b] mp 88–89 °C); IR (KBr) 3295 (N—H), 1730 (C=O); ^{1}H NMR (60 MHz) 0.92 (br t, 3 H, CH_3), 1.1–1.9 (m, 6 H, CH_2), 3.20 (dd, J_1 = 8 Hz, J_2 = 16 Hz, 1 H, NCH), 3.64 (dd, J_1 = 8 Hz, J_2 = 16 Hz, 1 H, NCH), 4.59 (quin, J = 8 Hz, 1 H, OCH), 6.56 (br, 1 H, NH).

4-Phenyl-2-oxazolidinone (32): colorless needles from hexane–acetone, mp 138.5–139 °C (lit.[18] mp 138–139.5 °C); IR (KBr disk) 3280 (N—H), 1758 and 1730 (C=O); ^{1}H NMR (60 MHz) 4.12 (dd, J_1 = 7 Hz, J_2 = 5 Hz, 1 H, NCH), 4.5–5.0 (m, 2 H, OCH_2), 6.33 (br, 1 H, NH), 7.30 (s, 5 H, Ar H).

4-Methyl-4-phenyl-2-oxazolidinone (33): colorless crystals from pentane–ether, mp 78–79 °C (lit.[25] mp 78–79 °C); IR (KBr disk) 3250 (N—H), 1750 (C=O); ^{1}H NMR (60 MHz) 1.70 (s, 3 H, CH_3), 4.30 (s, 2 H, CH_2), 6.91 (br, 1 H, NH), 7.30 (s, 5 H, Ar H).

***trans*-5-Methyl-4-phenyl-2-oxazolidinone (34)**: colorless prisms from hexane–acetone, mp 124–124.5 °C (lit.[26] mp 125 °C for trans isomer and mp 111 °C for cis isomer); IR (KBr disk) 3225 (N—H), 1740 (C=O); ^{1}H NMR (60 MHz) 1.49 (dd, J_1 = 5 Hz, J_2 = 1 Hz, 3 H, CH_3), 4.43 (m, 2 H, NCH and OCH), 6.25 (br, 1 H, NH), 7.30 (s, 5 H, Ar H).

***trans*-4,5-Dipropyl-2-oxazolidinone (35)**: colorless oil; IR (liquid film) 3275 (N—H), 1760 (C=O); ^{1}H NMR (60 MHz) 0.8–1.2 (m, 6 H, CH_3), 1.2–1.9 (m, 8 H, CH_2), 3.40 (q, $J_1 = J_2$ = 5.8 Hz, 1 H, NCH), 4.13 (q, $J_1 = J_2$ = 5.8 Hz, 1 H, OCH), 6.80 (br, 1 H, NH). Anal. Calcd for $C_9H_{17}NO_2$: C, 63.11; H, 10.03; N, 8.18. Found: C, 63.35; H, 10.20; N, 8.10. The configuration was assigned on the basis of ^{1}H NMR to be trans because the chemical shifts and coupling constants of the two methine protons were of the same magnitude as those reported for *trans*-4,5-diethyl-2-oxazolidinone:[16] 3.40 (q, $J_1 = J_2$ = 5.5 Hz, NCH), 4.12 (q, $J_1 = J_2$ = 5.5 Hz, OCH).

***cis*-4,5-Dipropyl-2-oxazolidinone (36)**: colorless crystals from hexane, mp 59.5–61 °C; IR (KBr disk) 3220 (N—H), 1740 (C=O); ^{1}H NMR (60 MHz) 0.8–1.2 (m, 6 H, CH_3), 1.2–1.8 (m, 8 H, CH_2), 3.73 (dt, J_1 = 5.0 Hz, J_2 = 7.5 Hz, 1 H, NCH), 4.53 (dt, J_1 = 5.0 Hz, J_2 = 7.5 Hz, 1 H, OCH), 6.55 (br, 1 H, NH); ^{13}C NMR ($CDCl_3$, 22.5 MHz) 13.83 (CH_3), 13.92 (CH_3), 19.24 (CH_2), 19.33 (CH_2),

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31.33 (CH_2), 32.11 (CH_2), 55.61 (NCH), 80.13 (OCH), 160.14 (C=O). Anal. Calcd for $C_9H_{17}NO_2$: C, 63.11; H, 10.03; N, 8.18. Found: C, 63.45; H, 10.20; N, 8.10. The configuration was assigned on the basis of ^1H NMR to be cis because the chemical shifts and coupling constants of the two methine protons were of the same magnitude as those reported for *cis*-4,5-diethyl-2-oxazolidinone:[16] 3.70 (dt, J_1 = 5.5 Hz, J_2 = 7.5 Hz, NCH), 4.52 (dt, J_1 = 5.5 Hz, J_2 = 7.5 Hz, OCH).

***cis*-4,5-Trimethylene-2-oxazolidone (37)**: colorless needles from hexane–acetone, mp 87–88 °C; IR (KBr disk) 3025 (N—H), 1740 and 1700 (C=O); ^1H NMR (60 MHz) 1.1–2.3 (m, 6 H, CH_2), 4.1–4.4 (m, 1 H, NCH), 4.6–5.3 (m, 1 H, OCH), 6.51 (br, 1 H, NH). Anal. Calcd for $C_6H_9NO_2$: C, 56.67; H,7.15; N, 11.02. Found: C, 56.63; H, 6.97; N, 10.77.

3-Methyl-*cis*-4,5-tetramethylene-2-oxazolidinone (39):[24] colorless oil; IR (liquid film) 1745 (C=O); ^1H NMR (60 MHz) 1.0–2.3 (m, 8 H, CH_2), 2.80 (s, 3 H, CH_3), 3.4–3.8 (m, 1 H, NCH), 4.2–4.6 (m, 1 H, OCH).

3-Ethyl-*cis*-4,5-tetramethylene-2-oxazolidinone (40): colorless oil; IR (liquid film) 1740 (C=O); ^1H NMR (60 MHz) 1.17 (t, J = 8 Hz, 3 H, CH_3), 1.1–2.0 (m, 8 H, CH_2), 3.27 (m or AB q with J = 14 Hz on irradiation at δ 1.17, 2 H, CH_2), 3.5–3.9 (m, 1 H, NCH), 4.2–4.8 (m, 1 H, OCH); exact mass calcd for $C_9H_{15}NO_2$ 169.1104, found (high-resolution mass spectrum) 169.1086.

***cis*-4,5-Pentamethylene-2-oxazolidinone (41)**: colorless leaflets from hexane–acetone, mp 105–106 °C; IR (KBr disk) 3240 (N—H), 1730 (C=O); ^1H NMR (60 MHz) 0.9–2.3 (m, 10 H, CH_2), 3.7–4.3 (m, 1 H, NCH), 4.5–5.0 (m, 1 H, OCH), 6.68 (br, 1 H, NH). Anal. Calcd for $C_8H_{13}NO_2$: C, 61.90; H, 8.46; N, 9.03. Found: C, 61.82; H, 8.42; N, 8.97.

***cis*-Indano[1,2-*d*]-2-oxazolidinone (42)**: brown crystals from hexane–acetone, mp 159–160 °C (lit.[18] mp 159.5–160 °C); IR (KBr disk) 3260 (N—H), 1760 and 1715 (C=O); ^1H NMR (60 MHz) 3.35 (d, J = 4 Hz, 2 H, CH_2), 5.10 (d, J = 7 Hz, 1 H, NCH), 5.30 (dt, J_1 = 7 Hz, J_2 = 4 Hz, 1 H, OCH), 6.73 (br, 1 H, NH), 7.23 (s, 4 H, Ar H).

***cis*-Tetralino[1,2-*d*]-2-oxazolidinone (43)**: brown needles from hexane–acetone, mp 141–142.5 °C (lit.[18] mp 140.5–142 °C); IR (KBr disk) 3250 (N—H), 1730 (C=O); ^1H NMR (60 MHz) 1.7–3.1 (m, 4 H, CH_2), 4.83 (d, J = 8 Hz, 1 H, NCH), 5.06 (dt, J_1 = 8 Hz, J_2 = 3 Hz, 1 H, OCH), 6.73 (br, 1 H, NH), 7.13 (s, 4 H, Ar H).

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Reactions of Lithium Bicyclo[1.1.0]butan-2-olates Formed by Carbenoid Type Decomposition of Lithiothioacetal Enolates. A Novel Concept for One-Pot Cyclopropanation of Enones

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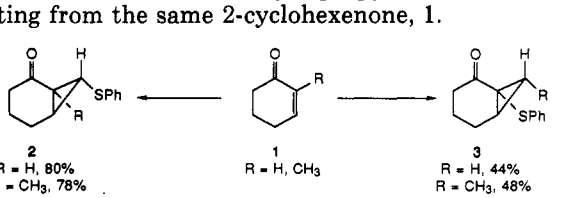
A new cyclopropanation procedure for α,β-unsaturated ketones is based upon the low-temperature decomposition of enolate carbenoids generated by conjugate addition of tris(phenylthio)methyllithium to α,β-unsaturated ketones followed by lithium/phenylthio exchange. Evidence suggests that the reactions employing 2-cyclohexenones as starting materials proceed through lithium bicyclo[1.1.0]butan-2-olate intermediates. The latter ordinarily lead to 7-(phenylthio)-substituted norcaranones via intermediate lithiocyclopropyl ketones which can be captured by various electrophiles or they can be modified in situ leading to other norcaranones or bridged cyclobutanes. The cyclopropyl ketones derived from 2-cyclopentenone and methyl vinyl ketone can only be obtained efficiently by the low-temperature deprotonation of the corresponding lithiocyclopropyl ketone to its enolate ion. Two of the cyclopropyl ketones derived from 2-cyclohexenone have been converted to potentially useful dianions by a deprotonation/reductive lithiation sequence.

Recent reports from this laboratory have enunciated and expanded the concept that, when positioned in a molecule with a second anionic site nearby, normally stable anions of bis(phenylthio) acetals behave as carbenoids which exhibit novel and selective behavior.[1] The wide availability of such carbenoids renders this mechanistically interesting concept of considerable potential synthetic utility. In this paper, we demonstrate that the application of this concept to enolate carbenoids results in a novel and apparently general cyclopropanation procedure for α,β-unsaturated ketones. In some cases, the reactions proceed through lithium bicyclo[1.1.0]butan-2-olate derivatives, which heretofore have not been generally accessible. In a preliminary report of this work,[1g] the intermediates in the cyclopropanation procedure for various 2-cyclohexenones were shown to be such strained species. The recognition of this fact allowed the stereospecific, one-flask production of two different cyclopropyl ketones, **2** and **3**, starting from the same 2-cyclohexenone, **1**.



2
R = H, 80%
R = CH_3, 78%

1
R = H, CH_3

3
R = H, 44%
R = CH_3, 48%

New data presented here have shed light on the mechanistic subtleties of the new process. The resulting insight has suggested an artifice by which the procedure can be made general for a variety of α,β-unsaturated ketones. For example, the efficient cyclopropanation of 2-cyclopentenone, a process which was reported in an earlier

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