CHEMISTRY LETTERS, pp. 1327-1330, 1987.

Aminotellurinylation of Olefins with Benzenetellurinyl Acetate and Ethyl Carbamate[1)]

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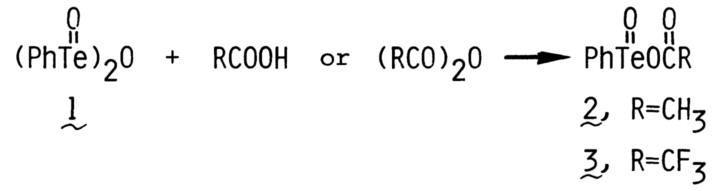
Benzenetellurinyl acetate or trifluoroacetate in combination with ethyl carbamate effected aminotellurinylation of olefins in chloroform under reflux in the presence of boron trifluoride etherate to give ethyl [(2-phenyltelluro)alkyl]carbamates in high yields after reduction with hydrazine hydrate. This reaction was extended to cyclofunctionalization of olefinic carbamates into nitrogen heterocycles.

The addition reactions of unsaturated substances with organotellurium species offer a convenient method for the introduction of a functionalized telluro group into organic structures.[2)] Such reactions have been, however, limited to halotelluration[3)] and oxytelluration[4)] in contrast to versatile addition reactions with other chalcogen reagents. We now wish to report the first aminotelluration of olefins induced by benzenetellurinyl acetate / ethyl carbamate and its extension to cyclofunctionalization of olefinic carbamates into nitrogen heterocycles.

We have recently found that benzenetellurinic anhydride **1** readily reacts with acetic acid or anhydride to generate benzenetellurinyl acetate **2**.[5)] It was treated with olefin under reflux of acetic acid to effect acetoxytellurinylation.[6)] When excess ethyl carbamate **5** and 1.2 equiv. boron trifluoride etherate were added, aminotellurinylation occurred under reflux of chloroform in preference to acetoxytellurinylation, giving ethyl [(2-phenyltellurinyl)alkyl]carbamate **6**. This reaction also worked well with benzyl carbamate. When boron trifluoride etherate was omitted, no reaction occurred. The other Lewis acids such as zinc iodide and aluminium chloride were ineffective, though tin (IV) chloride somewhat prompted



$$\underset{\mathbf{1}}{(\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{Te}}})_2\mathrm{O}} + \mathrm{RCOOH} \text{ or } (\mathrm{RCO})_2\mathrm{O} \longrightarrow \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{Te}}}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R}$$

2, R=CH_3

3, R=CF_3

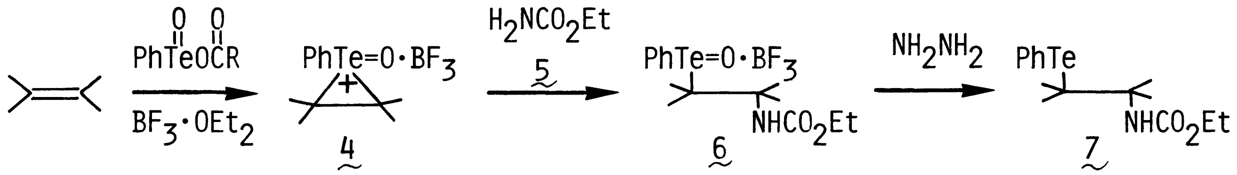
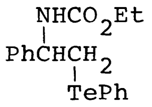
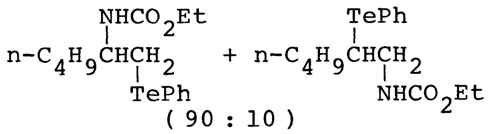
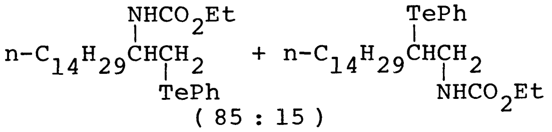
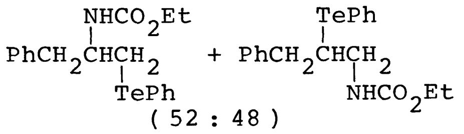
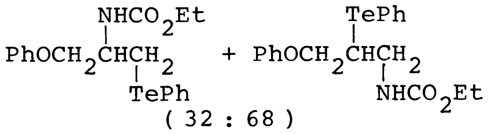
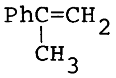
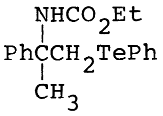
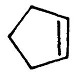
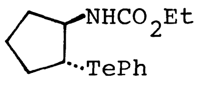
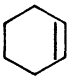
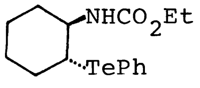
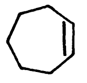
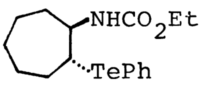
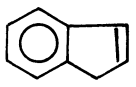
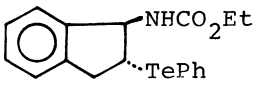


Table 1. Aminotelluration of olefins with benzenetellurinyl acetate **2** or trifluoroacetate **3** (1.1 equiv.) and ethyl carbamate (10 equiv.) in the presence of boron trifluoride etherate (1.2 equiv.)a)

Entry	Olefin	Reagent	Product (Isomeric ratio)b)	Yield %
1	$\mathrm{PhCH{=}CH_2}$	**2**	 $\mathrm{PhCH(NHCO_2Et)CH_2TePh}$	97
2	$\mathrm{n\text{-}C_4H_9CH{=}CH_2}$	**2** **3**	 $\mathrm{n\text{-}C_4H_9CH(NHCO_2Et)CH_2TePh + n\text{-}C_4H_9CH(TePh)CH_2NHCO_2Et}$ (90 : 10)	46 72
3	$\mathrm{n\text{-}C_{14}H_{29}CH{=}CH_2}$	**2** **3**	 $\mathrm{n\text{-}C_{14}H_{29}CH(NHCO_2Et)CH_2TePh + n\text{-}C_{14}H_{29}CH(TePh)CH_2NHCO_2Et}$ (85 : 15)	75 86
4	$\mathrm{PhCH_2CH{=}CH_2}$	**2** **3**	 $\mathrm{PhCH_2CH(NHCO_2Et)CH_2TePh + PhCH_2CH(TePh)CH_2NHCO_2Et}$ (52 : 48)	45 82
5	$\mathrm{PhOCH_2CH{=}CH_2}$	**3**	 $\mathrm{PhOCH_2CH(NHCO_2Et)CH_2TePh + PhOCH_2CH(TePh)CH_2NHCO_2Et}$ (32 : 68)	75
6	 $\mathrm{PhC(CH_3){=}CH_2}$	**3**	 $\mathrm{PhC(CH_3)(NHCO_2Et)CH_2TePh}$	78
7		**3**		85c)
8		**3**		96 90c)
9		**3**		86c)
10		**3**		46

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a) The reactions were carried out in refluxed chloroform for 20 h, followed by reduction with hydrazine hydrate in ethanol at 60 °C for 15 min.

b) The isomeric ratios were determined by HPLC and NMR analyses. Both isomers could be separated by elaborate column chromatography.

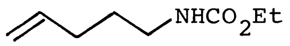
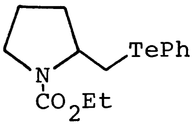
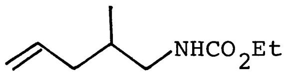
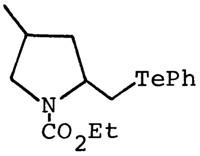
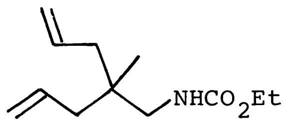
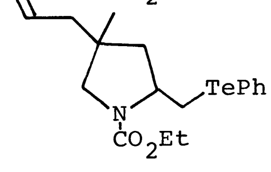
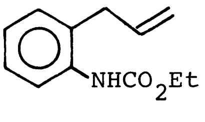
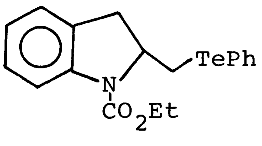
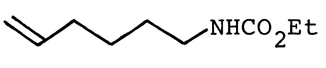
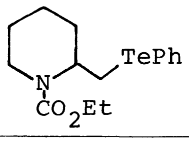
c) In refluxed dichloromethane.

the reaction. Benzenetellurinyl trifluoroacetate 3, similarly generated from 1,[5) was a more effective agent than 2, highly improving the yield of the adduct 6. Because of difficulty in purification of adduct 6, 7 was isolated after reduction with hydrazine hydrate in ethanol at 60 °C.[7)

As seen in Table 1, the addition reaction proceeds in case of terminal olefins with high Markovnikov regioselectivity where the tellurium species acts as electrophile. However, the increasing bulkiness of the substituent tends to promote the formation of anti-Markovnikov adduct. The reactivity of central olefins is considerably affected by both the electronic and steric factors of the substituents. Thus, dialkyl substitution electronically prompts the aminotellurinylation, so that cyclopentene, cyclohexene, and cycloheptene can do it in refluxed dichloromethane. On the other hand, norbornene and β-methylstyrene are inert even in refluxed chloroform owing to steric hindrance. The stereochemistry of adduct 7 from cyclohexene clearly supports trans addition with nucleophilic attack on an epitelluronium intermediate 4 by ethyl carbamate.[8)

When olefins having carbamate group at the suitable position are employed, an intramolecular cyclization might occur to give nitrogen heterocycle bearing phenyltelluromethyl group. Such cyclofunctionalization is much valuable because

Table 2. Cyclofunctionalization of olefinic carbamates with benzenetellurinic trifluoroacetate 3 (1.1 equiv.) in the presence of boron trifluoride etherate (1.2 equiv.)[a)

Entry	Olefinic carbamate	Product	Yield/%
1			96
2			94
3			85
4			87
5			73

a) All the reactions were carried out in refluxed chloroform for 30 min, followed by reduction with hydrazine hydrate in ethanol at 60 °C for 15 min.

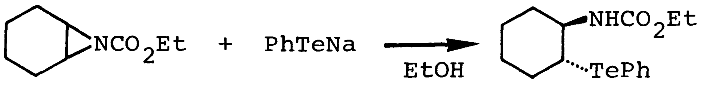
of its synthetic application to natural products and related compounds. Some examples of the transformation of olefinic carbamates into the corresponding pyrrolidine and piperidine derivatives are shown in Table 2. The cyclization reaction is complete within 30 min and much faster than the above intermolecular reaction (20 h).

Since some effective methods for carbamate deprotection and versatile chemical modifications of phenyltelluro group have been known, the present aminotelluration reaction constitutes a useful new approach to β-functionalized amines from olefins and nitrogen heterocycles from olefinic carbamates.

The authors wish to express their thanks to the Nitto Chemical Industry Co., Ltd. for the financial aid.

References

1) Organotelluriums Part IX. Part VIII; Ref. 6.
2) For recent reviews on organotellurium chemistry, see L. Engman, Acc. Chem. Res., 18, 274 (1985); N. Petragnani and J. V. Comasseto, Synthesis, 1986, 1; S. Uemura, Kagaku (Kyoto), 36, 381 (1981); Yuki Gosei Kagaku Kyokai Shi, 41, 804 (1983).
3) M. M. Campos and N. Petragnani, Tetrahedron Lett., 1959, 11; Tetrahedron, 18, 521, 527 (1962); M. Ogawa and R. Ishioka, Bull. Chem. Soc. Jpn., 43, 496 (1970); H. J. Arpe and H. Kuckertz, Angew. Chem., Int. Ed. Engl., 10, 73 (1971); S. Uemura, H. Miyoshi, and M. Okano, Chem. Lett., 1979, 1357.
4) M. M. Campos and N. Petragnani, Chem. Ber., 93, 317 (1960); J. V. Comasseto and N. Petragnani, Synth. Commun., 13, 889 (1983); J. Bergman and L. Engman, J. Am. Chem. Soc., 103, 5196 (1981); S. Uemura, S. Fukuzawa, A. Toshimitsu, and M. Okano, Tetrahedron Lett., 23, 1177 (1982); S. Uemura, S. Fukuzawa, and A. Toshimitsu, J. Organomet. Chem., 250, 203 (1983).
5) Because benzenetellurinyl acetate 2 and trifluoroacetate 3 are very hygroscopic, intractable oils, it is convenient to generate them in situ from benzenetellurinic anhydride 1. The suspension of 1 in chloroform containing equivalent amount of acetic acid or anhydride becomes clear within 15 min at reflux, indicating completion of its transformation.
6) N. X. Hu, Y. Aso, T. Otsubo, and F. Ogura, Tetrahedron Lett., 28, 1281 (1987).
7) All the new tellurium compounds were characterized by NMR, MS, IR, and elemental analyses.
8) The stereochemistry of adduct 7 from cyclohexene was confirmed by comparison with the trans form, which was separately derived from ring opening of N-ethoxycarbonyl-7-azabicyclo[4.1.0]heptane with sodium benzenetellurolate.



(Received April 15, 1987)