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HOMOLYTIC CYCLIZATION OF O-ALKENYL-Se-PHENYLSELENOCARBONATES. SYNTHESIS OF LACTONES

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Dedicated to Sir Derek Barton on the occasion of his 70th birthday.

Abstract - O-Alk-3-enyl- and O-alk-4-enyl-Se-phenylselenocarbonates undergo regiospecific exo cyclization to the corresponding γ- and δ-lactones on treatment with tri-n-butylstannane and AIBN.

In a recent communication we described the synthesis of α-alkylidene-γ-lactones by intramolecular addition of alkoxycarbonyl free-radicals to acetylenes.[1] Alkoxycarbonyl radicals are readily generated by trialkylstannane-AIBN (azobisisobutyronitrile) induced homolysis of the carbon-selenium bond of selenocarbonates.[1,2] The transient radicals produced by this method

Scheme I

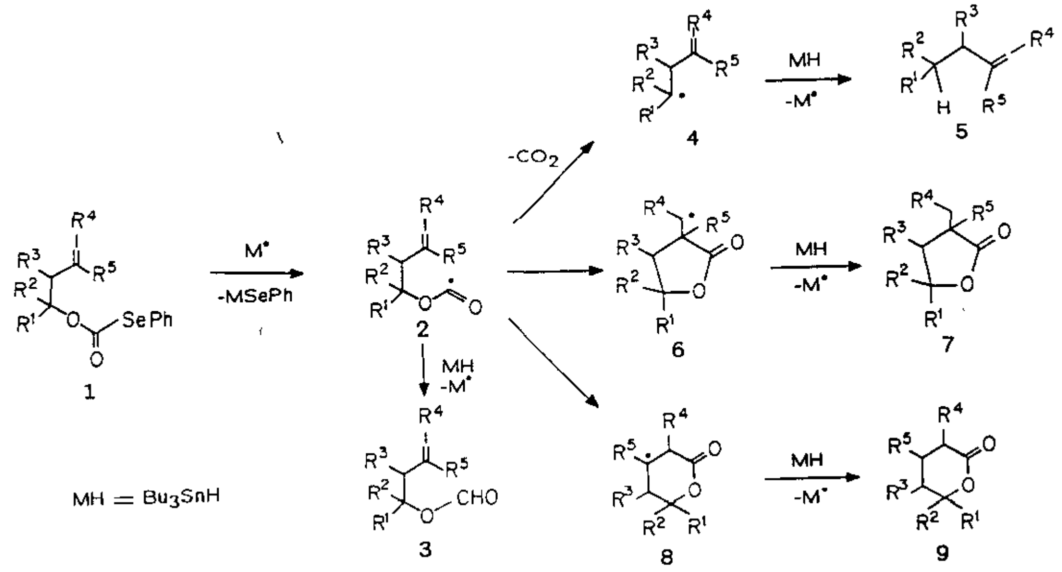
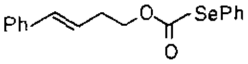
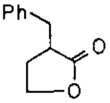
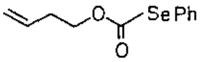
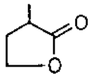
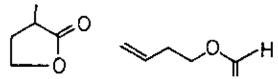
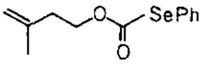
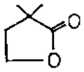
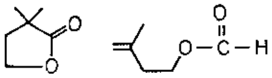
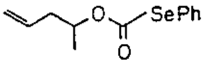
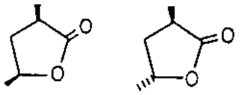
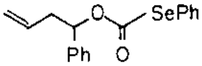
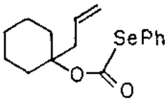
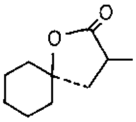


Table: Reaction of O-alk-3-enyl-Se-phenylselenocarbonates 1 with tri-n-butylstannane and AIBN

	Selenocarbonates 1	Method	Products	Isolated yields (%)
a		A		80 88 (g.c.)
b		A		91
c		B	 5.4 : 4.6	>90
d		A		99
e		C	 1 : 3	>90
f		A	 2.5 : 1	92
g		A		74
h		A		95

Methods: A. Standard conditions: A solution of the selenocarbonate (1 mmol), tri-n-butylstannane (1.15 equiv., 0.02M) and AIBN (0.1 equiv.) in benzene (57 ml) was heated at 80°C for 30 min. Products isolated by distillation (b, d, f, g, h) or flash chromatography (a).[5]

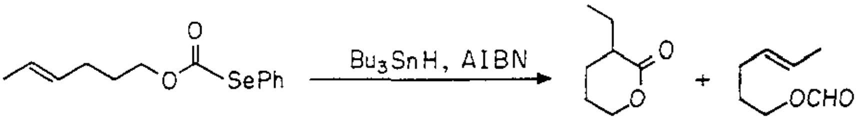
B. As for A without solvent.

C. As for A with tri-n-butylstannane concentration = 1 M.

are subject to several competing processes, principally reduction and decarboxylation;[2] consequently their use in organic synthesis has been limited. We now describe a general synthesis of lactones involving the ring closure of O-alkenyloxycarbonyl radicals which have various substitution patterns.

O-Alk-3-enyl-Se-phenylselenocarbonates 1,[3,4] were treated with tri-n-butylstannane as specified in the Table. The alkenyloxycarbonyl radicals 2 generated in this way undergo the transformations illustrated in Scheme I. The experimental results summarized in the Table indicate that the ring closure of alk-3-enyloxycarbonyl radicals proceeds exclusively in the *exo* mode, *cf*. 2 → 6. No products of *endo* addition, *cf*., 2 → 8 → 9, were detected.[5] Under standard conditions (Table, Method A) the resulting γ-lactones 7 were isolated in excellent yield (entries *a*, *b*, *d*, *f*, *h*). The sole exception (entry *g*) involves the derivative of a secondary benzylic alcohol for which decarboxylation is favoured as a highly stabilized benzylic radical 4, R^1=Ph, R^2=R^3=R^4=R^5=H) is formed.[6] Decarboxylation, *cf*. 2 → 4 → 5, does not interfere with the cyclization of other secondary (entry *f*) or tertiary selenocarbonates (entry *h*). It is noteworthy that the regiochemistry of cyclization is not altered by introduction of a second substituent on the double bond at the site to which the free-radical adds. Direct hydrogen transfer to intermediate radicals 2 to give the corresponding formyl ester 3 was only observed in experiments performed under especially high concentrations of tri-n-butylstannane (entries *c* and *e*). The homologous O-alk-4-enyl-Se-phenylselenocarbonate 10 regiospecifically cyclized to the corresponding δ-lactone 11 (91%) when reacted at low concentration of tri-n-butylstannane,[7] the formyl ester 12 (3%) being a minor by-product (Scheme II). When the reaction was performed under standard conditions (*cf*. Table, Method A) the combined yield of 11 and 12 remained high[5] but the product ratio 11:12 decreased to 4:1. This indicates that, as expected, the rate of 6-*exo* cyclization of alkoxycarbonyl radicals is considerably slower than that of the 5- *exo* cyclizations described in the Table. The reported[8] failure to cyclize a similar selenocarbonate is probably due to different (unspecified) reaction conditions. In the following paper we report the related synthesis of 6-membered ring ketones.[9]

Scheme II



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REFERENCES

1. M.D. Bachi and E. Bosch, Tetrahedron Lett., 1986, 27, 641.

2. J. Pfenninger, C. Heuberger, and W. Graf, Helv. Chim. Acta, 1980, 63, 2328.

3. Phenylselenocarbonates of primary and secondary alcohols were prepared by reacting the corresponding chloroformates with phenylselenol and pyridine in benzene (room temperature).[2] The selenocarbonate of the tertiary alcohol was prepared by treatment of the alcohol with sodium hydride (0.1 equiv.) and carbonyldiimidazole (1.1 equiv.) in THF for 24 h (room temperature) followed by phyenylselenol in benzene and mixing for an additional 3 h.

4. All compounds gave analytical and spectral data consistent with the assigned structures.

5. Nmr (270 MHz) analysis of the crude reaction mixture indicated quantitative conversion to the products indicated.

6. For a similar decarboxylation see: P. Beak and S.W. Moje, J. Org. Chem., 1974, 39, 1320.

7. Individual solutions of tri-n-butylstannane (1.1 equiv.) and AIBN (0.1 equiv.) were added during 90 min. to a solution (0.02 M) of 10 in benzene (80°)

8. D. Crich and S.M. Fortt, Tetrahedron Lett., 1988, 29, 2585.

9. M.D. Bachi and D. Denenmark, Heterocycles, the following paper.

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