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ADDITION OF S-BENZOYL PHENYLSELENOSULFIDE TO OLEFINS: SELENOTHIOCARBOXYLATION

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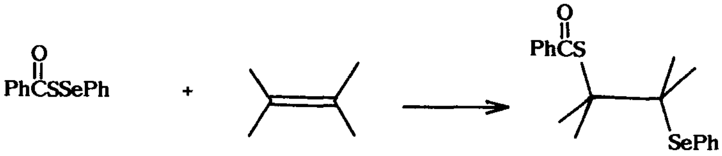
Abstract: Heating of S-benzoyl phenylselenosulfide and olefins with AIBN afforded selenothiocarboxylated products generated by a free radical process with high regiospecificity but lack of stereoselectivity.

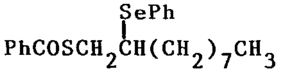
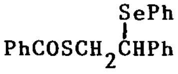
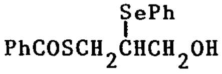
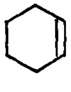
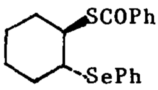
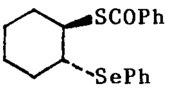
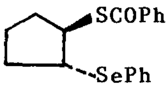
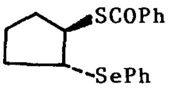
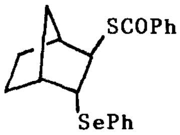
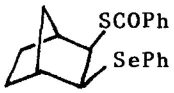
The growing importance of organoselenium chemistry in organic synthesis has recently stimulated the development of numerous useful methods for introducing the organoseleno moiety such as a phenylseleno group into a molecule[1]. Most of the methods, however, have been limited to electrophilic reactions of selenenyl halides or their analogues to unsaturated bonds[2]. Notable among these is selenosulfonation of unsaturated substrates via free radical processes induced thermally or photochemically[3]. Recently we have found an efficient and convenient synthesis of S-acyl phenylselenosulfides[4] which, we envisaged, would function as selenenylating agents.

Here we wish to report a novel addition reaction of S-benzoyl phenylselenosulfide to olefins via a free radical pathway, providing an efficient method for simultaneous introduction of phenylseleno and thiobenzoyloxy groups into an unsaturated substrate, which we have named "selenothiocarboxylation" depicted below.



The typical procedure for the present reaction is as follows: A mixture of S-benzoyl phenylselenosulfide 1, prepared from thiobenzoic acid and N-phenylselenophthalimide[4], a threefold excess of an alkene and 10 mol% of AIBN was refluxed in benzene (1 M) under an argon atmosphere. The mixture was then chromatographed on silica gel to give the product. The results are summarized in Table 1. Interestingly, selenothiocarboxylation of terminal olefins such as 1-decene 2a, styrene 2b, and allyl alcohol 2c proceeded in a regiospecific

Table 1. Addition of PhC(O)SSePh 1 to Olefins 2.

olefin	reaction time	product (isolated yield)[c]	
$CH_2{=}CH(CH_2)_7CH_3$ 2a	3 hr	 $PhCOSCH_2CH(SePh)(CH_2)_7CH_3$	3a (99%)[d]
$CH_2{=}CHPh$ 2b	0.5[a] 1	 $PhCOSCH_2CH(SePh)Ph$	3b (75%)[e] 3b (44%)[f]
$CH_2{=}CHCH_2OH$ 2c	4[b]	 $PhCOSCH_2CH(SePh)CH_2OH$	3c (81%)
 2d	17	 3dE (54%)	 3dZ (10%)
 2e	12	 3eE (76%)	 3eZ (7%)
 2f	1	 3fE (30%)	 3fZ (69%)

[a] Six portions of 0.2 equiv. of styrene were added every 5 min to the mixture of styrene (initially 0.2 equiv.) and 1 in refluxing benzene. [b] A 2 M benzene solution was refluxed. [c] Yield based on 1. [d] Unreacted 2a was recovered in 82% yield. 3a was obtained in 65% after 3 hr and 67% after 20 hr in the reaction of equimolar amounts of 2a and 1. [e] A 1:2 adduct $PhC(O)SCH_2CH(Ph)CH_2$-$CH(SePh)Ph$ (1%) was obtained as well as recovered 1 (19%). [f] The 1:2 adduct was obtained in 30% yield.

manner, giving the adducts 3a, 3b, and 3c[5], respectively. No regioisomers could be isolated in these reactions. On the other hand, addition to cycloalkenes 2d, 2e, and 2f did not proceed stereoselectively. Reactions of 2d and 2e gave respective anti-adducts 3dE and 3eE as major products accompanied with small amounts of cis adducts 3dZ and 3eZ, while the cis adduct 3fZ was a major product in the reaction of norbornene 2f. Since these reaction features appeared to involve free radical species[6] rather than bridged ion-like intermediates, we examined the reaction of 1-decene 2a with 1 in more detail. The results are illustrated in Table 2.

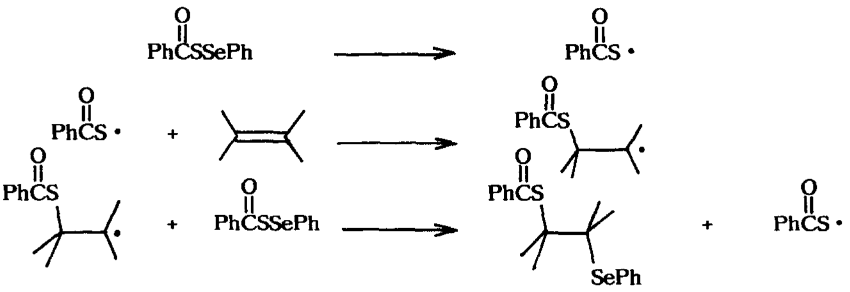
Table 2. Addition of 1 to 1-decene 2a[a].

entry No.	additive[b]	reaction time	isolated yield	
			3a	1(recovery)
1	AIBN	3 hr	99 %	-
2	none	30	30	46 %
3	AIBN + Hydroquinone	30	2	90
4	Hydroquinone	30	3	87

[a] All reactions were performed in refluxing benzene (1 M) using a threefold excess of 2a. [b] Reactions were performed in the presence of 10 mol% of AIBN and/or hydroquinone when noted.

The reaction in the presence of AIBN gave 3a in almost quantitative yield after 3 hr heating, whereas heating without AIBN afforded 3a in only 30% yield and recovered 1 in 46% yield even after 30 hr (entry 2), showing that the reaction was considerably accelerated by the radical initiator. Furthermore, the addition of hydroquinone almost supressed the formation of 3a (entry 3 and 4). These facts suggest that a free radical mechanism is involved in the selenothiocarboxylation of 1-decene and possibly other olefins in the presence of AIBN. Considering the regiochemistry of the products 3a, 3b, and 3c regiospecifically obtained, the reasonable pathway is shown in the following equations; The initially formed thiobenzoyloxyl radical adds to the olefin to generate more stable radical intermediate which would further react through a radical chain process giving the product.

This reaction offers a unique and useful method for introducing phenylseleno and thiobenzoyloxy groups at the same time into a molecule. Selenothiocarboxylated products should serve as valuable building blocks for complex compounds.



References and notes

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4. T. Toru, M. Nishigaki, T. Seko, T. Kanefusa, and E. Maekawa, Synthesis, in press.

5. All new compounds reported in this communication exhibited ^{1}H nmr, ir, mass spectra and microanalyses consistent with the assigned structures. Regio- and stereochemistry of the selenothiocarboxylated products 3 was further confirmed by the products obtained from the oxidation-elimination reaction of the phenylseleno group. Interestingly, the selenoxide elimination showed an unexpected preference for abstraction of the hydrogen attached to the carbon bearing the thiobenzoyloxy group, e.g., from 3dE vinyl thiobenzoate and allyl thiobenzoate were obtained in a ratio 9:1. These interesting reaction features will be reported elswhere.

6. The regiospecific addition in an anti-Markownikoff manner and lack of stereoselectivity appears to be characteristic of the free radical mechanism; see, F.W. Stacey and J.F. Harris,Jr., "Organic Reactions", A.C. Cope, Ed., Wiley, New York, 1963, Vol. 13; Chapter 4. In certain cases the free radical addition to 3f has been known to proceed preferentially in a syn manner, giving the exo-cis adducts; for example, see, D. Tauchard and J. Lessard, Tetrahedron Lett., 4425 (1971);S.J. Cristol and E.F. Hoegger, J. Amer. Chem. Soc., 79, 6039 (1957).

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