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THE ELECTROPHILIC ADDITION OF SELENENYL THIOCYANATES TO OLEFINS

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Abstract:- Benzeneselenenyl thiocyanate in methanol reacts with olefins to give adducts; kinetic data for attack upon styrenes are presented.

The addition of benzeneselenenyl chloride[1] to olefins in inert solvents has received considerable attention[2], and recently the use of benzeneselenenyl thiocyanate in such solvents has been reported[3,4]. At room temperature we have found methanolic PhSeCl solutions to give UV spectra which remain unchanged for several days, direct solvolysis[5] not occurring; since beginning our investigation the reaction of PhSeCl with olefins in methanol has been reported[6], but no kinetic data were given.

The reaction of PhSeCl with KSCN at 25° occasioned an increase in UV absorbance between 400 and 270 nm (ε_{340}, PhSeCl = 350; ε_{340}, PhSeSCN = 420) and was an equilibrium reaction, reaching 60% conversion after several hours with equimolar reactants ($k_f = 1.21$, $k_r = 0.56\ \mathrm{l\ mol^{-1}s^{-1}}$). Use of a ten-fold molar excess of KSCN gave complete conversion to PhSeSCN.

Reaction of methanolic PhSeSCN with 2-methylpent-1-ene gave, after immediate workup, an oil whose NMR spectrum indicated the adducts $PhSeCH_2C(OMe)(Me)Pr$, $PhSeCH_2C(NCS)(Me)Pr$ to be present in the ratio 68:32. A similar reaction with styrene gave an NMR spectrum containing signals at 4.75, 4.50, and 4.25 δ, attributable to the Ph$C\underline{H}$ protons of the adducts $PhCH(NCS)CH_2SePh$, $PhCH(SCN)CH_2SePh$, and $PhCH(OMe)CH_2SePh$, present in the ratio 27:9:64. The occurrence of Markownikoff adducts, and the preference for solvent incorporated adducts agrees with related results[3,6].

The kinetics of the reaction between methanolic PhSeSCN and some substituted styrenes have been studied by monitoring the UV absorbance at 340 nm; results are shown below. This reaction followed second-order kinetics, being first-order in each reactant (cf. ref. 6).

Olefin	k_2(l $mol^{-1}s^{-1}$) at 30° for PhSeSCN/MeOH	Relative rate	k_2(l $mol^{-1}s^{-1}$) at 25° for $PhSeCl/CH_2Cl_2$ [2]	Relative rate
Styrene	1.11	1	25	1
α-Me Styrene	2.54	2.3	47.8	1.9
trans-β-Me Styrene	0.143	0.13	7.9	0.32
p-Me Styrene	12.99	11.7		
p-Cl "	0.33	0.3		
p-Br "	0.225	0.2		

PhSeSCN also adds to olefins more slowly than PhSeCl in inert solvents[3]. Rate measurements made between 30° and 50° gave $\Delta H^{\ddagger}$ estimates of 8.29 ± 1.80, 8.76 ± 0.69 kcal/mole, and $\Delta S^{\ddagger}$ estimates of -31.13 ± 5.74, -33.90 ± 2.19 cal/K, for attack upon styrene and trans-β-methylstyrene respectively. A Hammett type plot gave a ρ^{+} value of -3.78 for the addition of PhSeSCN to ring-substituted styrenes, larger than that reported[2] for PhSeCl addition in CH_2Cl_2, perhaps implying a more open ion-like structure in the rate determining transition state.

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