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GENERATION OF 1-SELENO-ALLYL CATIONS AND THEIR REACTIONS WITH FURAN AND PYRROLE

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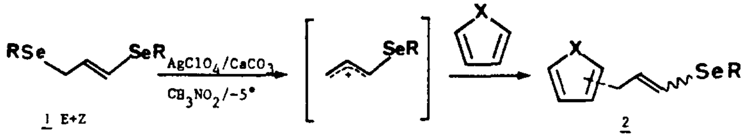
1,3-bis(seleno)-propenes are valuable precursors of selenium stabilized allyl cations which react with furan and N-methyl pyrrole in a highly stereoselective fashion to give electrophilic substitution products

It has been shown in recent years that alkylselenyl and phenylselenyl moieties bring about substantial stabilization of an α-carbocationic center [1,2], but no effort has been made to use such species for preparative purposes We now wish to report our first results which demonstrate that selenium-substituted allyl cations can be easily generated *in situ* and that they react smoothly with carbon nucleophiles such as furan or N-methyl pyrrole (Scheme)

Scheme



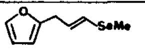
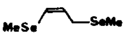
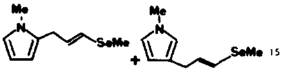
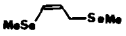
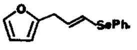
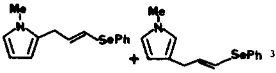
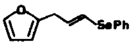
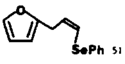
1 E+Z 2

a, R = CH_3 b, R = C_6H_5 X = O, N-CH_3

In a typical experiment a mixture of 1 equivalent of 1 (E/Z ≈ 1) and 1 equivalent of furan or N-methylpyrrole dissolved in dry nitromethane has been added by a syringe to a cooled (-5°) suspension of 1 5 equivalents of silver perchlorate and 2 equivalents of calcium carbonate in the same solvent Monitoring by TLC showed that after 4-6 hrs the reaction stopped while a substantial amount of reagent 1 was still present Adding more aromatic and/or silver perchlorate did not make the reaction progress further Quenching of the reaction mixture with sodium bicarbonate, extraction with methylene chloride and purification by PLC (SiO_2, pentane eluent) allowed to isolate product 2 as well as unreacted 1

Representative results are gathered in the Table

Table Reactions of 1-seleno-allyl cations with aromatic heterocycles [a]

Entry	Starting 1	Reaction time (hrs)	X	Product 2 yield[b] (%)	Recovered 1 (%)[b]
1	1a (E+Z)	6	O	 24	 44
2	1a (E+Z)	6	NCH_3	 15	 40
3	1b (E+Z)	6	O	 25	 43
4	1b (E+Z)	6	NCH_3	 33	 42
5	1b pure E	4	O	 50	——
6	1b pure Z	65	O	 51	——

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a) Elemental analyses and spectral data are in agreement with proposed structures
b) Yields are given relative to the total amount of starting 1

First of all we note that only electrophilic substitution reactions have taken place without any trace of 4 + 3 → 7 cycloaddition, This latter reaction occurs with allyl cations substituted at position 2, especially with 2-oxyallyl systems ^{3} As usually observed for electrophilic substitution in the five-membered heterocycles, furan exclusively gives substitution products at position 2 (Table, entries 1,3,5,6), while with N-methylpyrrole both positions 2 and 3 undergo substitution

Decoupling experiments in ^{1}H NMR have shown ^{4} that all the products 2 corresponding to entries 1-5 in the Table exhibit *trans* stereochemistry about the side chain double bond Taking into account that the Z component of the starting reagent 1 (Table, entries 1-4) has been recovered almost quantitatively, the above observation strongly suggests that the reactions have taken place with conservation of stereochemistry This is even more striking in the case of the reaction of furan with 1b of pure Z configuration Within the precision of NMR only the corresponding *cis* product 2 could be detected

Finally an important difference in the rate of reaction has been observed for the E and Z isomers of 1a and 1b, the former reacting with furan ∿ 15 times faster than the latter This rate difference might be attributed to the lack of reactivity of the intermediate cationic species derived from the Z isomer Indeed, assuming participation of the vinylic selenium atom in the heterolysis of the allylic selenium-carbon bond, the Z isomer could lead to a four-membered cyclic selenonium ion or to a six-membered cyclic bidentate silver complex, both less reactive than the species derived from the E isomer in which no such participation is possible

It follows then that using a simple practical procedure the two stereoisomers of a given product 2 can be prepared with high stereoselectivity

References and notes

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(4) Olefinic coupling constants are the following
1a J_{cis} = 9 Hz , J_{trans} = 14 9 Hz
1b J_{cis} = 8 9 Hz , J_{trans} = 15 Hz
2 (X=O, R=C_6H_5) , J_{trans} = 15 4 Hz
2 (X=O, R=C_6H_5) , J_{cis} = 8 9 Hz

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