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ELECTROPHILIC ADDITION OF DISELENIDES TO ALKENES: NEW SYNTHESIS OF 1,2-BIS(SELENIDES).

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Abstract: While the tin tetrachloride mediated addition of dimethyldiselenide to mono- and disubstituted olefins proceeds rapidly and with good yields in most of the cases, diphenyldiselenide appears to react less efficiently.

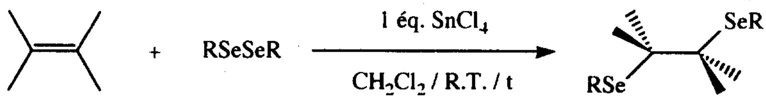
Electrophilic addition of selenenyl derivatives RSeX, where X is an electronegative atom or group of atoms, to carbon-carbon double bonds is a process of fundamental importance in organoselenium chemistry, and has been thoroughly reviewed on several occasions[1]. On the other hand, radical additions of disulphides[2-5] and diselenides[6-9] have met with success in the cases of alkynes[2,4,5,7,9] and allenes[8], but not of alkenes[2,3,6,10]. However, thioselenation of alkenes could be carried out efficiently using mixtures[10] of disulphides and diselenides, or S-benzoyl phenylselenosulphide[11] under homolytic conditions.

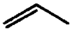
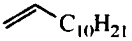
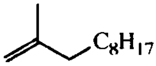
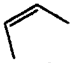
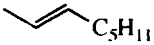
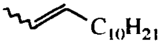
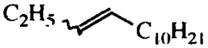
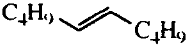
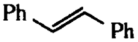
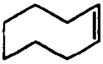
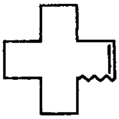
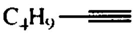
These results, as well as our continuing interest in the Lewis acid mediated reactions of organoselenium compounds prompted us to explore the title transformation, and we report here on our first results.

We have found that dimethyldiselenide activated by tin tetrachloride reacts smoothly with ethylene and common mono- and disubstituted olefins to produce the corresponding 1,2-bis(methylseleno) adducts in good to excellent yields.

In a typical experiment, 263 mg (1mM) of tin tetrachloride and 190 mg (1mM) of dimethyldiselenide were mixed in 2.5 ml of dry dichloromethane under argon at room temperature: an orange precipitate was formed instantly. To this, a solution of trans-2-octene (118 mg, 1 mM) was added by means of a syringe. An immediate bleaching and dissolution of the precipitate occurred (while bleaching was a general observation, a nearly colorless precipitate sometimes persisted). After 20 minutes of reaction 10 ml of 2N KOH and 20 ml of ether were added. The organic phase was separated, washed twice with saturated brine, dryed over magnesium sulphate, and freed from solvents under vacuum. ^1H NMR indicated that the crude product contained about 20% MeSeSeMe and 80% of the adduct. Bulb-to-bulb distillation of this mixture (0.1 torr, 90°C) led to a single stereoisomer[12] of 2,3-bis(methylseleno)octane which still contained traces of dimethyldiselenide. Redissolution in 20 ml of ether, treatment with 3 ml of methanolic $NaBH_4$, washing with aqueous KOH, drying and evaporation led to 160 mg (53% yield) of pure product[13].

Scheme



Entry	Olefin	R	t (hr)	Adduct, Yield (%)
1	$H_2C=CH_2$	Me	0.5	35 (91)
2	$H_2C=CH_2$	Ph	0.5	57 (78)
3		Me	0.3	52 (83)
4		Me	1.0	62 (75)
5		Ph	3.0	26 (40)
6		Me	0.3	75 (80)
7		Me	0.2	82
8		Me	2.0	85
9		Me	0.3	53 (80)
10		Me	2.0	57 (84)
11		Me	2.0	63 (80)
12		Me	0.5	65 (75)
13		Me	18	0
14		Me	0.5	92
15		Ph	0.5	0
16		Me	0.5	56 (75)
17		Me	2.0	50 (80)
18		Me	0.5	66 (92)

The results gathered in the Scheme show that, in the presence of $SnCl_4$, dimethyldiselenide reacts rapidly (0.2-3.0h) and efficiently with essentially all of the alkenes tried in excellent crude yields to produce the corresponding 1,2-adducts, stilbene being an exception (entry 13). The isolated yields are sometimes considerably lower because of the sensitivity of the compounds formed which often causes some decomposition during purification[13]. It is remarkable that in none of the reaction mixtures did we observe the formation of any significant amount of ß - chloroselenide resulting from the possible capture by chloride ions of the intermediate seleni ronium ions[12], whereas cyclic γ- halogenosulphides (selenides) have been reported as the Lewis acid mediated cyclisation products of unsaturated α- thio- and α-selenosulfones[14], and of unsaturated selenoacetals[15]. We think the reason for the failure of the reaction in the case of stilbene may be a thermodynamic one: the partial loss of conjugation present in stilbene disfavors formation of the adduct. Since these electrophilic additions must be reversible reactions, thermodynamics should also be at the origin of the non quantitative crude yields observed in all the cases. On the other hand, from the preparative point of view, it is not interesting to engage an excess of MeSeSeMe because of the purification problems[13]. We also note that steric bulk of the alkyl groups attached to the C,C double bond does not seem to play an important role, since mono- , 1,1- di-, and various 1,2-disubstituted olefins lead to quite similar results (compare entries 3, 4, 6, 9 - 12). The latters appear more homogeneous than those reported for the analogous reactions of dimethyldisulphide catalyzed by boron trifluoride[16]. Although all the reactions examined for MeSeSeMe have not been duplicated using PhSeSePh, the few available results suggest that, with the exception of ethylene (entry 2), the other olefins react less efficiently with diphenyldiselenide: 1-dodecene gives only a modest yield (entry 5), and no adduct could be observed at all with cyclohexene (entry 15). It would be interesting to check whether or not the nature of the Lewis acid has a profound influence on the outcome of these reactions.

Finally, the sole example of MeSeSeMe addition to a 1-alkyne we have tried (Scheme, entry 18) shows that the reaction also proceeds in this case to give the E-1,2-bis(methylseleno) alkene in high yield and with high stereoselectivity. α,β - Di(n-butylseleno)styrene has been obtained as an E/Z mixture in the photoinitiated addition of di(n-butyl)diselenide to phenylacetylene[9], and the same diselenide reacted with 1-octyne in low yield in the palladium catalyzed reaction[17]. If generalizable to other alkynes and other diselenides, the result in entry 18 appears as a useful complement to those reported earlier[9,17].

Work is being continued in order to further specify the scope and limitations of these new electrophilic addition reactions.

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12. As judged from the presence of only one signal (δ = 1.50 ppm, doublet, J = 6.8 Hz) for the methyl group in position 1 in the ^{1}H NMR spectrum ($CDCl_3$) of the pure product. Based on mechanistic considerations (electrophilic *anti* addition initiated by an "$MeSe^+$" species), the product should be *(erythro)*-2,3-bis(methylseleno)octane. This assignement is strengthened by the observation of a single ^{77}Se signalin the selenium-77 NMR spectrum (δ = 184 ppm in $CDCl_3$) of 1,2-bis(methylseleno)cyclohexane (Scheme, entry 14), which is only possible for the *trans* isomer.
13. We have experienced that SiO_2 - chromatographic purification often causes extensive decomposition of the 1,2-bisselenide adducts giving back the olefin and dimethyldiselenide. Since distillation may be affected by the same drawback, the best ways for the elimination of residual MeSeSeMe from the product are i) the $NaBH_4$ treatment, or ii) selective evaporation under good vacuum.
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