A Novel Exchange Reaction between Diselenides and Bis(*N,N*-dialkylselenocarbamoyl)selenides. Application in the Synthesis of Tetraselenafulvalene (TSF)

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A high yield synthesis of tetraselenafulvalene (TSF) involving a novel acid catalysed exchange reaction between diselenides and bis(*N,N*-dialkylselenocarbamoyl)selenides is reported.

The recent discovery of superconductivity in cation radical salts of tetramethyltetraselenafulvalene[1] has increased the interest in the synthesis of tetraselenafulvalenes (TSF's). Key intermediates in the synthesis of substituted TSF's are 2-oxoalkyl *N,N*-dialkyldiselenocarbamoyl esters (in the 'carbamate route').[2,3]

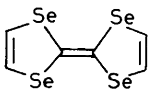
Unsubstituted TSF (**1**) has so far been prepared by two routes[4,5] (yield 5—20%) from CSe_2, which is difficult to obtain. We have been interested in preparing (**1**) by the 'carbamate' route especially since *N,N*-dimethyldiselenocarbamate salts are now more readily available from *N,N*-dimethylphosgeneiminium chloride and NaHSe or H_2Se.[3] However, α-halogenoacetaldehydes (or their acetal derivatives) do not react with diselenocarbamate salts. Instead we obtained the esters (**4**) in high yields by a novel acid catalysed exchange reaction between the diselenide (**2**) and bis(*N,N*-dialkyldiselenocarbamoyl)selenides (**3a**) or (**3b**) (Scheme 1).

The carbamoylselenides (**3**) are readily obtained from the corresponding diselenocarbamate[3,6] salts by oxidation and treatment with trimethyl phosphite.[6] Bis(2-oxoethyl)diselenide (**7**) was prepared as shown in Scheme 2. Na_2Se_2[7] reacted with 2-bromoacetaldehyde diethyl acetal in an ethanol–water (1:1) solution. The reaction mixture was extracted with ether, and distilled to give (**6**) as a yellow oil, b.p. 120 °C (0.05 mmHg) (80%). The acetal was then hydrolysed with dilute formic acid and the aldehyde (**7**) was obtained by extraction with ether and by removal of the solvent.

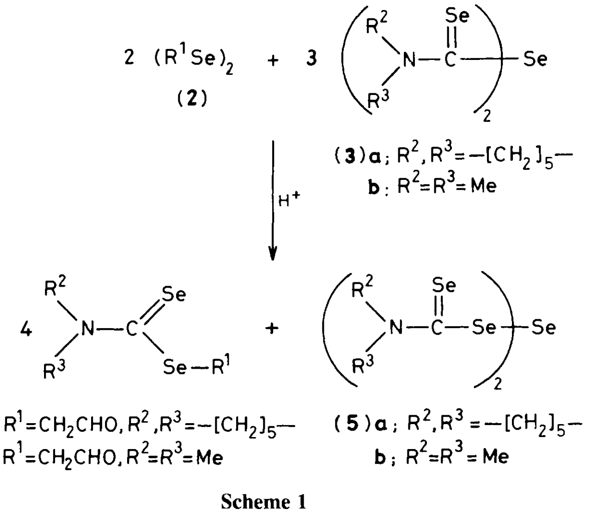
Stoicheiometric amounts of (**7**) (prepared as in Scheme 2) and (**3a**) were stirred in a $CHCl_3$ solution containing a catalytic amount of toluene-*p*-sulphonic acid. The precipitate of the triselenide (**5a**) was removed by filtration and the solvent was evaporated to give the carbamate ester (**4a**) as a partially crystalline orange oil.

The conversion of (**4a**) into TSF is shown in Scheme 3. (**4a**) was cyclized by slow dissolution into ice cold conc. H_2SO_4. The iminium compound (**8a**) was isolated as the PF_6^- salt after treatment with HPF_6 in ice–water. After dissolution in CH_2Cl_2 and precipitation with ether (**8a**) was obtained as white needles, m.p. 160 °C (decomp.), 65% yield based on (**3a**). In a similar manner (**8b**) was obtained in 60% yield.

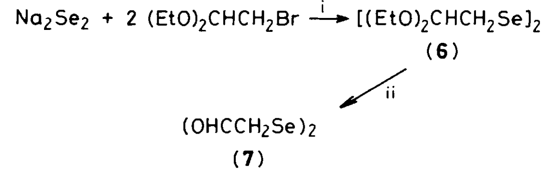
Treatment of compounds (**8**) with an excess of H_2Se in $MeOH–H_2O$ solution followed by recrystallization of the precipitate from hexane gave the selenone (**9**).[3] (**9**) was converted into TSF by treatment with $P(OMe)_3$.



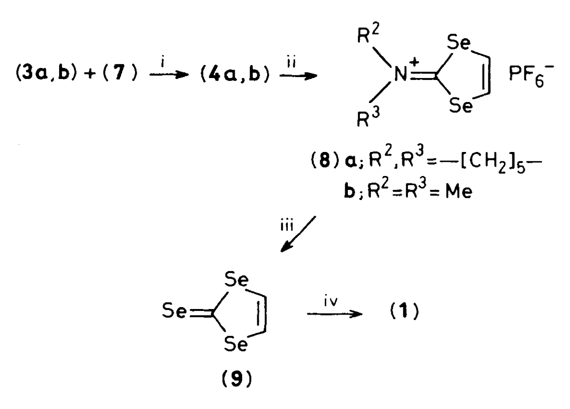
(**1**)



Scheme 1



Scheme 2. i, $EtOH–H_2O$, reflux, 16 h; ii, 1 M HCO_2H, 50 °C, 1 h.



Scheme 3. i, 3 mM toluene-*p*-sulphonic acid in $CHCl_3$, room temp., 2 h; ii, conc. H_2SO_4, 0 °C, 2 h; 2 M HPF_6, 0 °C, ½h; iii, H_2Se, $MeOH–H_2O$, 0 °C, 5 h; iv, $P(OMe)_3$, benzene, reflux, 2 h.

Thus, TSF can be prepared in 42—48% overall yield or from phosgeneiminium chloride and H_2Se or NaHSe[3] with comparable yields.

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