Preparation of Tetramethyltetraselenafulvalene without the Use of Carbon Diselenide

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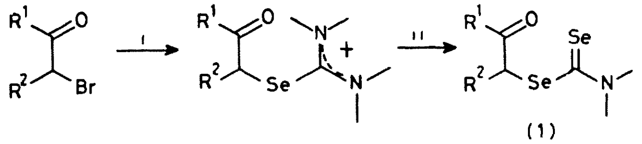
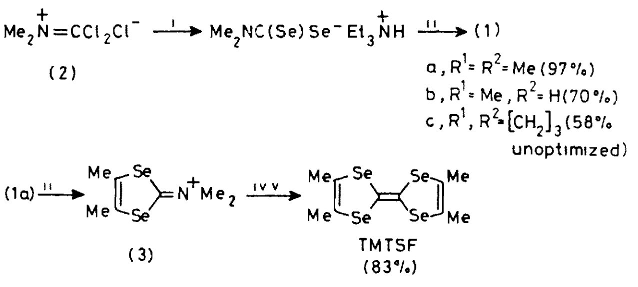
Summary Cyclization of α-diselenocarbamato ketones [prepared from dichloromethylene(dimethyl)ammonium chloride with hydrogen selenide and triethylamine] in trifluoroacetic acid with sulphuric acid, afforded the cation (**3**) efficiently and safely without the need for carbon diselenide

THE recent report on the observation of superconductivity exhibited by the 'organic metal' tetramethyltetraselenafulvalenium hexafluorophosphate [(TMTSF)$_2$PF$_6$][1] prompts us to report on an efficient and safe route for the large scale preparation of the title donor Our approach avoids the use of carbon diselenide, an extremely fetid reagent which cannot be vented completely by conventional fume cupboards and which inflicts generalized discomfort to workers in its vicinity [2] Also, this reagent is produced in only *ca* 30% yield *via* the reaction[2] of methylene chloride with selenium at 600 °C



SCHEME 1 *Reagents* i, (Me$_2$N)$_2$C=Se, ii, H$_2$Se

Another approach which avoids the use of carbon diselenide in the preparation of selenafulvalenes was reported recently by Shu [3] The disadvantage of this method (*cf* Scheme 1) is that only fair yields are obtainable in the second step (ii, Scheme 1) [4] Here we report a general procedure for the preparation of diselenocarbamates (**1a**—**c**) (and the title compound) which is superior to previous methods (*cf* Scheme 2) Dichloromethylene(dimethyl)ammonium chloride (**2**) is commercially available (phosgene imminium chloride, Aldrich) and its chemistry has been reviewed [5] This reagent reacts with hydrogen selenide in dichloromethane in the presence of triethylamine to produce a clear, orange-red solution of triethylammonium *N,N*-dimethyldiselenocarbamate which was not isolated but employed *in situ* Addition of the bromoketone to this solution at —10 to 0 °C, followed by the usual work-up[6] afforded the compounds (**1a**—**c**), the properties of these compounds were identical to those described earlier [6]



SCHEME 2 *Reagents* i, H$_2$Se–Et$_3$N, CH$_2$Cl$_2$, ii, R^{1}C(O)CH(Br)R^2, iii, TFA–H$_2$SO$_4$ iv, H$_2$Se–MeOH–H$_2$O, v, (MeO)$_3$P–C$_6$H$_6$

Modification of the cyclization of (**1a**) by use of trifluoroacetic acid (TFA) as solvent afforded a non-hygroscopic, tan-coloured salt upon ether work-up This 1,3-diselenolium salt (**3**) was used without further purification in the remaining steps of Scheme 2 The TMTSF thus obtained was identical in all respects to that prepared previously *via* carbon diselenide [7]

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