A New, Convenient Synthesis of Selenoketones

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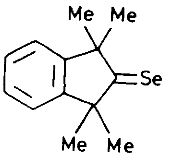
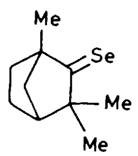
Dimagnesium salts of hydrazones react with Se_2Cl_2 in the presence of tri-n-butylamine to give selenoketones in moderate to good yields.

Although considerable attention has been paid to the chemistry of selenoketones (selones) in recent years,[1,2] the only known synthetic route to these compounds is the reaction of triphenylphosphoranylidenehydrazones with selenium metal above their melting points developed by Barton and his co-workers.[1a]


(1)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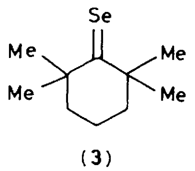
(3)

We report here a new, convenient synthesis of selenoketones from the reaction of hydrazones with diselenium dichloride (Se_2Cl_2) [equation (1) and Table 1]. A typical procedure was as follows. A tetrahydrofuran (THF) solution of 1,1,3,3-tetramethylindan-2-one hydrazone (1 mmol) was added to a solution of EtMgBr (1.90—1.95 mmol) in THF at 60 °C and stirred for 1 h at that temperature. The THF was removed by evaporation and benzene (80 ml) and tri-n-butylamine (1 mmol) were added. To this solution a benzene solution (20 ml) of Se_2Cl_2 (1.2 mmol) (prepared by reaction of selenium, selenium dioxide, and hydrogen chloride)[3] was added at 5 °C over 20 min. After being stirred for 30 min at room temperature, the solution was heated at 60 °C for 3 h. After the usual work-up, the crude products were heated at 130 °C for 0.5—1.0 h *in vacuo* and purified by column chromatography to give pure 1,1,3,3-tetramethylindan-2-selone in 82% yield.

$$R^1R^2C{=}NN(MgBr)_2 \xrightarrow[Bu_3N]{Se_2Cl_2} R^1R^2C{=}Se \qquad (1)$$

Table 1. Yields and some spectral data of selenoketones.

Entry	Selenoketone	Yield (%)[a]	Spectral data δ (^{13}C n.m.r.)[b]	δ (^{77}Se n.m.r.)[c]	$\lambda_{max}(\epsilon)$[d]
1	**(1)**	82			
2	$Bu^t_2C{=}Se$	49 (58)[e]			
3	**(2)**	24			
4	(1-Ad)$_2$C=Se[f,g,j]	53	293.9	2134	712 (23.7)
5	Bu^t(1-Ad)C=Se[f,h,j]	43	292.9	2120	708 (23.7)
6	**(3)**[i,j]	35	294.4	2026	686 (24.3)

[a] Isolated yield of purified compounds. [b] δ (C=Se) in p.p.m. from Me_4Si in $CDCl_3$. [c] δ (C=Se) p.p.m. from Me_2Se in $CDCl_3$. [d] nm in cyclohexane. [e] The value in parentheses indicates a yield obtained by the simultaneous addition method (see text). [f] 1-Ad denotes 1-adamantyl. [g] Blue crystals, m.p. 161—162 °C. [h] Blue crystals, m.p. 39—41 °C. [i] Blue liquid. [j] New compounds gave satisfactory elemental or exact mass analyses.

Yields and properties of other selenoketones are listed in Table 1. Relatively volatile selones (entries 2, 3, and 6) were distilled into a cold trap during the heating at 130 °C and the distillate was purified by chromatography.

The present method has some interesting features. (1) It provides selenoketones in a one-pot reaction unlike Barton's method which requires isolation of the phosphoranylidenehydrazones; the yields of known selenoketones (entries 1—3 in Table 1) are comparable to those (from hydrazones) of Barton's procedure.[1] (2) Since the reaction is conducted in a homogeneous solution, there are none of the problems in a small scale synthesis encountered in the heterogeneous reaction of Barton's method. (3) When benzene solutions of dimagnesium salts of hydrazones and Se_2Cl_2 are added simultaneously and dropwise to a benzene solution of tri-n-butylamine, the yield is somewhat improved (entry 2). (4) The direct reaction of Se_2Cl_2 with a hydrazone in the presence of tertiary amine instead of its dimagnesium salt gives a selenoketone in much lower yield in contrast to the analogous synthesis of thiones from S_2Cl_2 and hydrazones.[4]

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