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N-(Phenylseleno)Phthalimide: A Useful Reagent For The α-Selenylation Of Ketones And Aldehydes.

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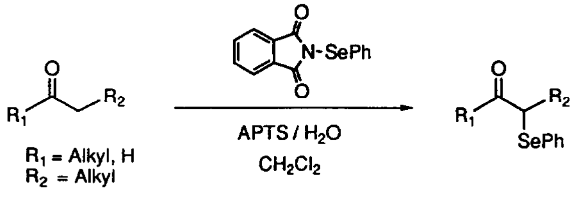
Key words: *Ketones, α-phenylselenoketones, N-(phenylseleno)phthalimide.*

Abstract: *α-phenylselenoketones and α-phenylselenoaldehydes are obtained with a good regioselectivity by treatment of the corresponding ketones or aldehydes with N-(phenylseleno)phthalimide and p-toluenesulfonic acid.*

2-Phenylselenoketones and 2-phenylselenoaldehydes are versatile intermediates which can be converted selectively into a variety of different ketones and aldehydes or to the corresponding α,β-unsaturated carbonyl compounds. Most methods for their preparation involve nucleophilic displacement such as the reaction of ketone enolates with phenylselenyl chloride [1], phenylselenyl bromide [2], benzeneselenyl trifluoroacetate [3] or with N-(phenylseleno)phtalimide [4].

Electrophilic additions have also been used to produce α-phenylselenocarbonyl compounds. N,N-Diethylbenzeneselenamide reacts selectively with aldehydes to produce the corresponding α-phenylselenoaldehydes [5]. In addition, α-phenylselenoketones have been obtained by electrophilic addition of phenylselenyl trifluoroacetate or phenylselenyl bromide in the presence of trifluoroacetate [2]. Alternatively silyl enol ether react readily with phenylselenyl bromide to give the corresponding α-phenylselenoketones [6]. A one step α-phenylselenylation of ketones with phenylselenyl chloride has also been realized but this reaction proceeds in low yield and is not general [7].

In this letter we report a very simple and general one-step method for the conversion of ketones and aldehydes into the corresponding mono α-phenylselenyl derivatives.

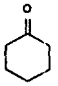
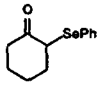
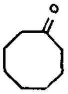
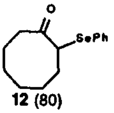
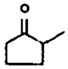
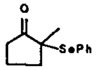
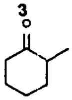
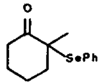
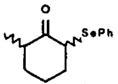
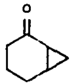
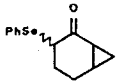
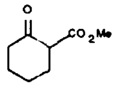
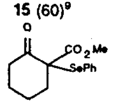
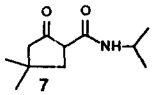
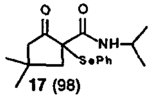
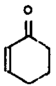
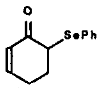
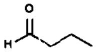
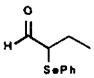


Our results are summarized in the Table

When a 1:1 mixture of a ketone or an aldehyde and N-(phenylseleno)phthalimide in CH_2Cl_2 was allowed to react with 1 equivalent of *p*-toluenesulfonic acid (TsOH) and 3 equivalents of H_2O at 20°C for 12 h, the corresponding product of α-monoselenation was formed and could be isolated in good yield after solvent evaporation and flash chromatography on silica gel. With non-symmetrical ketones, the reaction is regioselective giving preferentially the most substituted isomer probably because of the formation of the most stable enol intermediate which is quenched by N-(phenylseleno)phthalimide.

Compared with the other one-step methods of α-phenylselenation of carbonyl compounds [4], our method is extremely simple and can be applied to base-sensitive polyfunctional systems.

Table : Formation of α-phenylselenoketones and aldehydes.

Starting material	Products (yield %)	mp °C
 1	 2 (70)	63
 2	 12 (80)	–
 3	 13 (80)	–
 4	 14 (70)  14' (15)[9]	–
 5	 15 (60)[9]	–
 6	 16 (70)	–
 7	 17 (98)	–
 8	 18 (50)	–
 9	 19 (60)	–

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1- Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1973**, *95*, 5813-5815. *2*- Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434-5447. *3*- Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1973**, 695-696. *4*- ***a)*** Nicolaou, K. C.; Claremon, D. A.; Barnette, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704-3706. ***b)*** Jackson, W. P.; Ley, S. V.; Morton, J. A. *Tetrahedron Lett.* **1981**, *22*, 2601-2604. *5*- Jefson, M.; Meinwald, J. *Tetrahedron Lett.* **1981**, *22*, 3561-3564. *6*- Ryu, I.; Murai, S.; Niwa, I.; Sonoda, N. *Synthesis* **1977**, 874-876. *7*- Sharpless, K. B.; Lauer, R. F.; Teranishi, *J. Am. Chem. Soc.* **1973**, *95*, 6137-6139. *8*- N-(Phenylseleno)phthalimide was purchased from Aldrich. *9*- A mixture of cis-trans isomer is observed by 1H NMR spectra for compound 14' (ratio 17/83) anf for compound 15 (ratio 18/82).

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