

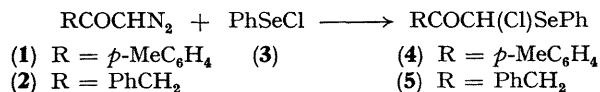
Reactions of α -Diazoketones with Phenylselenenyl Chloride. A New Synthesis of α -Chloro- and α -Phenylselenenyl- $\alpha\beta$ -unsaturated Ketones

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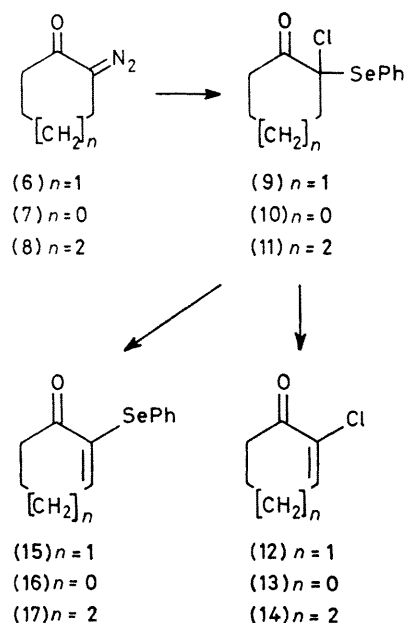
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Summary α -Diazoketones react with phenylselenenyl chloride at room temperature giving α -chloro- α -phenylselenenyl ketones; where structural considerations permit these adducts can be transformed *via* elimination reactions into α -chloro- or α -phenylselenenyl- $\alpha\beta$ -unsaturated ketones.

DURING work on new or improved procedures¹ based on α -diazocarbonyl compounds we examined the reaction of some α -diazoketones with phenylselenenyl chloride. The preparative potential implicit in such reactions appears not to have been explored, although the related reaction of ethyl diazoacetate with diphenyl diselenide is known.^{2,3}† *p*-Tolyldiazomethyl ketone (1) (1 equiv.) and phenylselenenyl chloride (3) (1 equiv.) combined rapidly and quantitatively at room temperature in dichloromethane or benzene solution with evolution of nitrogen (copper catalysis not required), giving a liquid product whose spectral properties were consistent with the α -chloro- α -phenylselenenyl ketone structure (4). Benzyl diazomethyl ketone (2) produced the adduct (5) when similarly treated.



This carbenoid-like insertion reaction was also very effective with α -diazocycloalkanones,⁴ and we have used it as the basis of a new route to α -substituted- $\alpha\beta$ -unsaturated ketones, the α -substituent being either chloro- or phenylselenenyl depending on the nature of the elimination process



used. Thus treatment of phenylselenenyl chloride (1 equiv.) in dichloromethane at room temperature with α -diazocyclohexanone (6) (1 equiv.) produced α -chloro- α -phenylselenenylcyclohexanone (9) in quantitative yield. The phenylselenenyl group was readily lost *via* selenoxide fragmentation⁵ when (9) was exposed at room temperature to 30%

† Added in proof: The reaction of 6-diazopenicillanates with phenylselenenyl chloride has been described recently by P. J. Giddings, D. I. John, and E. J. Thomas, *Tetrahedron Lett.*, 1980, 395.

hydrogen peroxide (9 equiv.) in dichloromethane containing pyridine (2.5 equiv.) whereupon α -chlorocyclohexenone (**12**)⁶ was isolated in 85% yield. In practice, isolation of (**9**) was unnecessary *en route* to the chloro-enone (**12**). Thus, addition of the α -diazocyclohexanone to a dichloromethane solution of phenylselenenyl chloride followed in 30 min by 30% hydrogen peroxide and pyridine (total reaction time 40 min) produced (**12**) in 82% yield. The chloro substituent in (**9**) should also be susceptible to elimination and this was found to be the case when (**9**) was exposed to anhydrous sodium carbonate in boiling xylene. The product, isolated in 55% yield, was found to be α -phenylselenenylcyclohexenone (**15**).⁷

Application of the geminal chlorination-phenylselenenylation procedure to α -diazocyclopentanone (**7**) and α -diazocycloheptanone (**8**) produced the adducts (**10**) and (**11**), respectively, in quantitative yield. Further treatment of

(**10**) and (**11**) with hydrogen peroxide/pyridine gave the chloro-enones (**13**)⁶ (81%) and (**14**)⁸ (78%), whereas use of the sodium carbonate in xylene treatment produced the α -phenylselenenylcycloalkenones (**16**)⁷ and (**17**) in 50–60% yield.

This new procedure makes readily available in very simple operations a range of cyclic α -substituted- $\alpha\beta$ -unsaturated ketones which are themselves versatile synthetic intermediates. Although we have yet to optimise the yields of the α -phenylselenenylcycloalkenones, (**15**), (**16**), and (**17**), it is already clear that the route described here has advantages over the only other general route⁷ to these compounds which requires the availability of the parent $\alpha\beta$ -unsaturated ketone as starting material.

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¹ S. Kulkowit and M. A. McKervery, *J. Chem. Soc., Chem. Commun.*, 1978, 1069.

² R. Pellicciari, M. Curini, P. Ceccherelli, and R. Fringuelli, *J. Chem. Soc., Chem. Commun.*, 1979, 440.

³ The reaction of diazomethane with phenylselenenyl bromide and diphenyl diselenide has been described by N. Petragnani, R. Rodrigues, and J. V. Comasseto, *J. Organomet. Chem.*, 1976, **114**, 281 and N. Petragnani and G. Schill, *Chem. Ber.*, 1970, **103**, 2271.

⁴ The α -diazoketones used in this work were prepared by the procedure of M. Regitz, J. Ruter, and A. Liedhegener, *Org. Synth.*, 1971, **51**, 86.

⁵ For a comprehensive survey of selenium-based organic reactions including details of selenoxide fragmentation see D. L. J. Clive, *Tetrahedron*, 1978, **34**, 1049.

⁶ K. Mitsuhashi and K. Namura, *Chem. Pharm. Bull.*, 1965, **13**, 951.

⁷ G. Zima and D. Liotta, *Synth. Commun.*, 1979, **9**, 697.

⁸ Previously synthesised in 15% yield from the reaction of dichlorocarbene and the morpholine enamine of cyclohexanone: M. Ohno, *Tetrahedron Lett.*, 1963, **25**, 1753.