Reactions of α-Diazoketones with Phenylselenenyl Chloride. A New Synthesis of α-Chloro- and α-Phenylselenenyl-αβ-unsaturated Ketones

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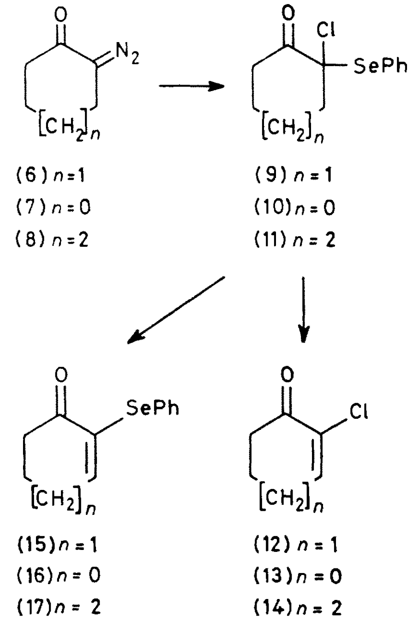
Summary α-Diazoketones react with phenylselenenyl chloride at room temperature giving α-chloro-α-phenylselenenyl ketones; where structural considerations permit these adducts can be transformed *via* elimination reactions into α-chloro- or α-phenylselenenyl-α,β-unsaturated ketones.

DURING work on new or improved procedures[1] 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*-Tolydiazomethyl 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.

$$\mathrm{RCOCHN_2 + PhSeCl \longrightarrow RCOCH(Cl)SePh}$$

(**1**) $\mathrm{R} = p\text{-}\mathrm{MeC_6H_4}$ (**3**) (**4**) $\mathrm{R} = p\text{-}\mathrm{MeC_6H_4}$
(**2**) $\mathrm{R} = \mathrm{PhCH_2}$ (**5**) $\mathrm{R} = \mathrm{PhCH_2}$

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-αβ-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 fragmentation[5] when (**9**) was exposed at room temperature to 30%



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† *Added in proof*: The reaction of 6-diazopenicillanates with phenylselenyl 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-αβ-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 route[7] to these compounds which requires the availability of the parent αβ-unsaturated ketone as starting material.

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[1] S. Kulkowit and M. A. McKervey, *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.