Reactions of α-Diazo Ketones with Selenium-based Reagents. A General Synthesis of α-Chloro-, α-Bromo, α-Phenylseleno-, α-Acetoxy-, and α-Methoxy-αβ-unsaturated Ketones

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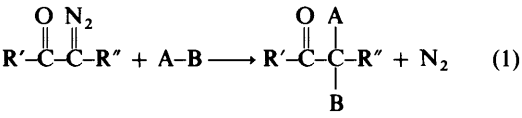
Benzeneselenenyl derivatives, PhSe–X (X = Cl, Br, $OCOCH_3$, and SCN) react readily with α-diazo ketones, $RCOC(N_2)R^1$ (R^1 = H or alkyl), with loss of nitrogen, furnishing αα-adducts of the type $RCOCR^1(X)SePh$. The α-chloro and α-bromo adducts can be converted into α-methoxy adducts in methanol–sodium hydrogen carbonate. The utility of these adducts in synthesis is illustrated by their conversion (where structural considerations permit) *via* selenoxide fragmentation into α-heterosubstituted αβ-unsaturated ketones. Treatment of the series $RCOCR^1(X)SePh$ (R^1 = alkyl; X = Cl, Br, $OCOCH_3$, and OCH_3) with hydrogen peroxide–pyridine produces α-chloro-, α-bromo-, α-acetoxy-, and α-methoxy-αβ-unsaturated ketones, whereas treatment of the series $RCOCR^1(X)SePh$ (R^1 = alkyl; X = Cl and Br) with lithium carbonate in dimethylformamide produces α-phenylseleno-αβ-unsaturated ketones. Several α-substituted cyclopentenones, cyclohexenones, and cycloheptenones have been synthesised in this way and acyclic examples are illustrated by the synthesis of 3-chloro-, 3-bromo-, 3-acetoxy-, 3-methoxy-, and 3-phenylselenobut-3-en-2-one from 3-diazobutan-2-one.

α-Diazo ketones are versatile reaction intermediates.[1] They are easily prepared by well established procedures and can be induced to undergo chemical change under very mild conditions. Of the various pathways open to α-diazo ketones, that in which the diazo function is replaced by two new substituents without rearrangement is potentially very useful in synthesis. This process, summarised in equation (1) and referred

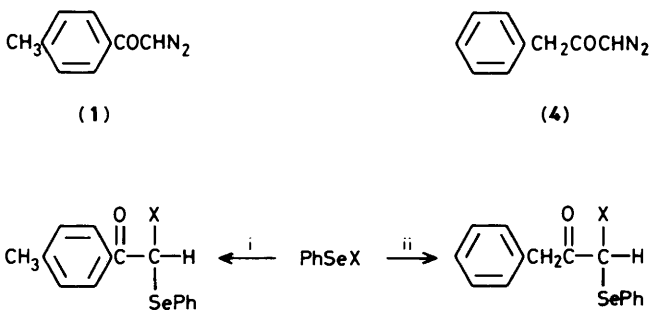


(1)

A–B: (a) halogens,[1,2] (b) hydrogen halides (excluding HI),[1] (c) HO–H,[1] (d) RO–H,[1] (e) RCO_2–H,[1] (f) RSO_3–H,[3] (g) RNH–H and R_2N–H,[1,4,5] (h) RS–H,[1,4,6] (i) RS–SR,[1,7] (j) RS–Cl,[8] (k) R–H (from R_3B),[9] (l) CH_2=$CHCH_2$–X (X = Cl,[10] Br,[10] I,[10] OR,[11] SMe,[10,11,12] NMe_2 [10]), (m) selenium-based reagents (see text)

to here as αα-addition, represents a quite general approach to the regiospecific mono- or di-functionalisation of a ketone without resort to conventional enol or enolate chemistry; and since many acyclic α-diazo ketones can be synthesised from acyl halides, αα-addition represents an approach to regiospecific functionalisation which does not depend on the availability of the parent ketone. Scope for variation in the reagent A–B is considerable, with substantial information already available on the combinations summarised in equation (1). In an effort to extend the range of αα-addition reactions that might prove useful in synthesis we have explored systems in which A–B is a sulphur-[6b,8c] or selenium-containing reagent. In this paper we present new examples of the use of selenium-based reagents and illustrate how the adducts formed may be used as intermediates in the synthesis of a variety of α-heterosubstituted αβ-unsaturated ketones.[13]

Preliminary experiments in which equimolar quantities of diazomethyl *p*-tolyl ketone (**1**) and benzeneselenenyl chloride (**2**) were mixed in dichloromethane at 20 °C revealed that nitrogen evolution commenced immediately (copper catalysis not required) and the product formed in essentially quantitative yield was the α-chloro-α-phenylseleno adduct (**3**). Benzyl diazomethyl ketone (**4**) produced adduct (**5**) when similarly

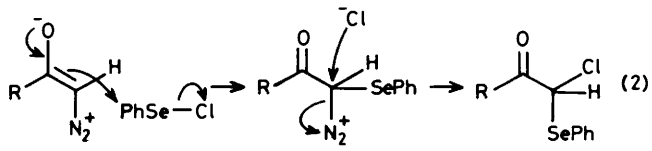


(1) (4)

(3) X = Cl (2) X = Cl (5) X = Cl
(7) X = Br (6) X = Br (8) X = Br
(9) X = OAc (10) X = OAc (11) X = OAc
(12) X = SCN (13) X = SCN

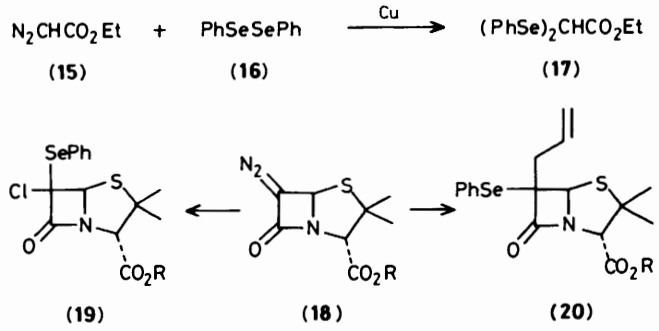
Reagents: i, (1); ii, (4)

treated. We envisage these αα-additions as proceeding *via* the displacement processes shown in equation (2). Diazo ketones (**1**) and (**4**) also reacted with benzeneselenenyl bromide (**6**) in

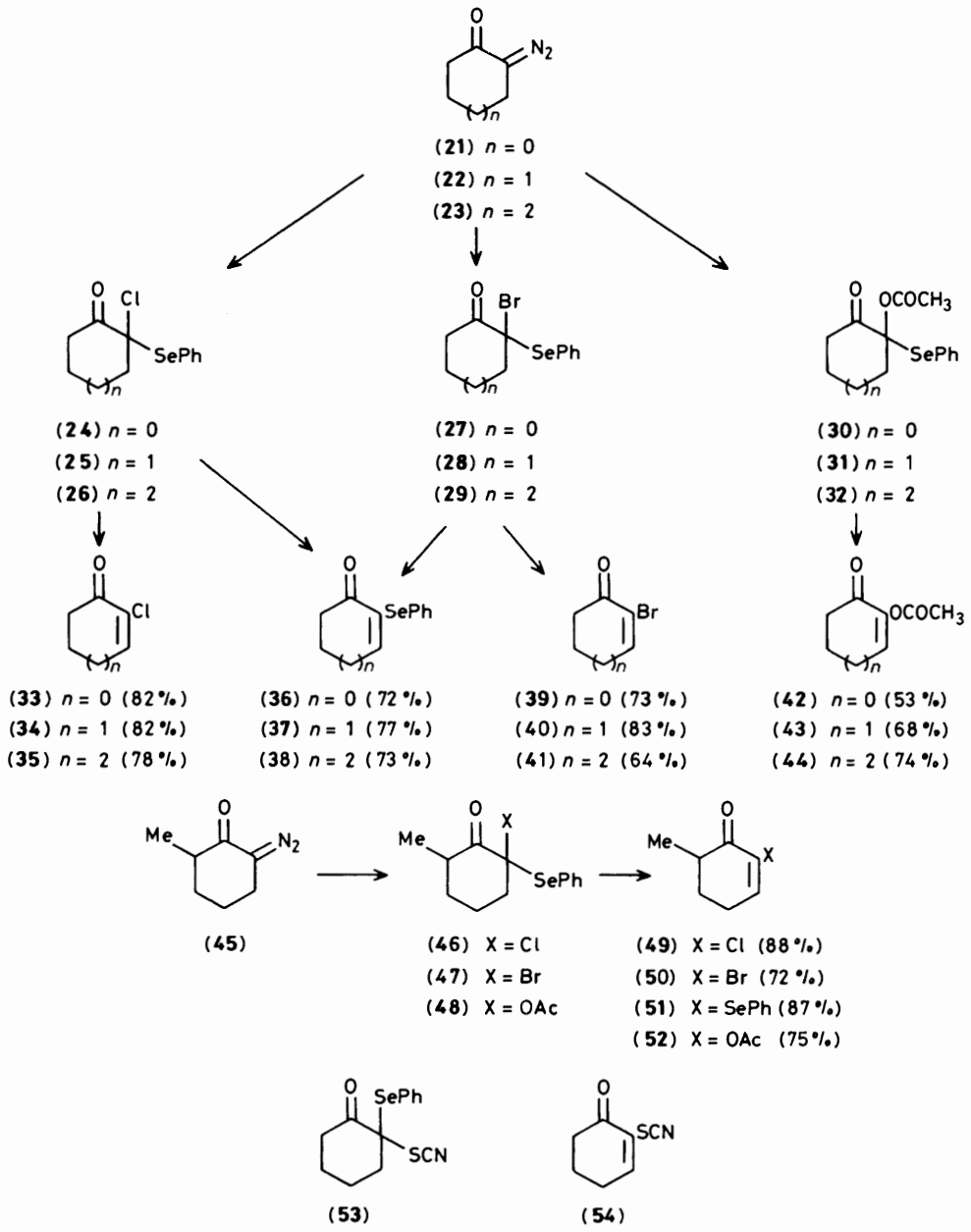


(2)

dichloromethane, yielding the corresponding bromo adducts (**7**) and (**8**). Product structures in all cases were easily confirmed by n.m.r. and i.r. spectroscopy. During this phase of our work two reports of related chemistry appeared. Pellicciari and his co-workers[14] found that ethyl diazoacetate (**15**) and diphenyl diselenide (**16**) produced the αα-bisphenylseleno adduct (**17**). This reaction required copper catalysis and the yield was poor. Thomas and his co-workers[12] reported the formation of αα-adducts (**19**) and (**20**) from the reaction of 6-diazopenicillanate (**18**) with benzeneselenenyl chloride (**2**) and allyl phenyl selenide, respectively.



αα-Addition of benzeneselenenyl chloride (**2**) or bromide (**6**) also proceeded efficiently with a range of α-diazocycloalkanones and we have used these reactions as a basis of a new route to α-heterosubstituted αβ-unsaturated ketones, the α-substituent being chloro, bromo, or phenylseleno depending on the nature of the elimination process used to introduce the carbon–carbon double bond. Thus, treatment of α-diazocyclopentanone (**21**) (1 mol equiv.) in dichloromethane at room temperature with benzeneselenenyl chloride (**2**) (1 mol equiv.) led to rapid nitrogen evolution and the quantitative production of α-chloro-α-phenylselenocyclopentanone (**24**). The phenylseleno group in compound (**24**) should be susceptible to elimination under very mild conditions *via* selenoxide fragmentation[15] and this was found to occur very efficiently at room temperature when the compound was exposed to 30% hydrogen peroxide (9 mol equiv.) in dichloromethane containing pyridine (2.5 mol equiv.), whereupon 2-chlorocyclopent-2-enone[16] (**33**) was obtained in 85% yield after purification. In practice, isolation of the αα-adduct was unnecessary *en route* to the chloro enone. Thus addition of α-diazocyclopentanone (**21**) to a dichloromethane solution of benzeneselenenyl chloride (**2**) at room temperature,

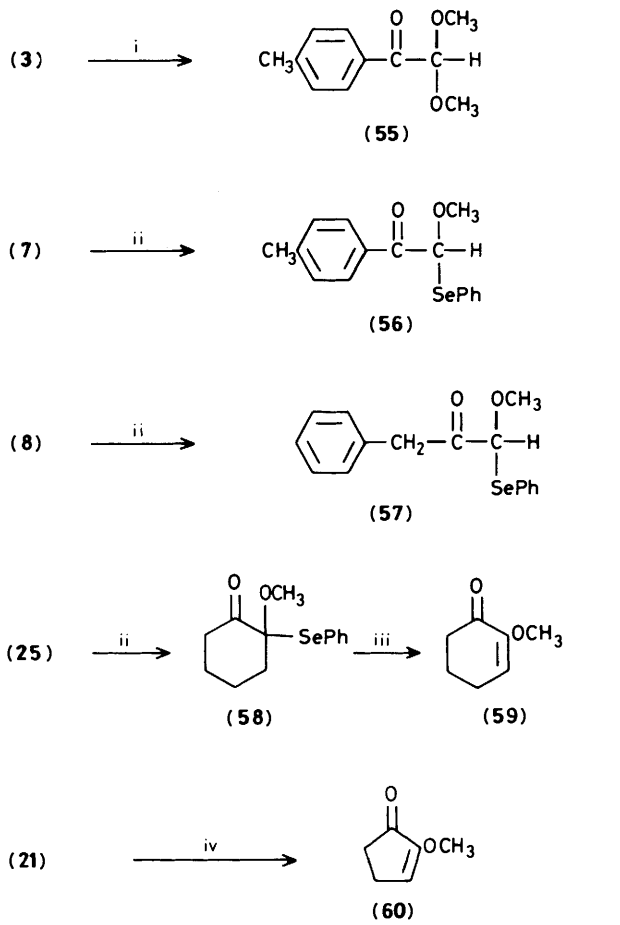


Scheme 1.

followed, after 30 min, by 30% hydrogen peroxide and pyridine (total reaction time 40 min) produced the enone (**33**) in 82% yield. The alternative mode of elimination in the selenide (**24**), that of the chloro substituent, was also possible, initially through the action of sodium carbonate in hot xylene, but significantly better yields (up to 72%) of 2-phenylselenocyclopent-2-enone[17] (**36**) were later realised using lithium carbonate as the base in hot dimethylformamide (DMF).* In like manner, α-diazocyclohexanone (**22**), its 6-methyl derivative (**45**), and α-diazocycloheptanone (**23**) were individually converted into the corresponding α-chloro-α-phenylseleno adducts (**25**), (**46**), and (**26**), and thence to the 2-chloro cycloalk-2-enones (**34**),[16] (**49**), and (**35**),[18] and the 2-phenylselenocycloalk-2-enones (**37**),[17] (**51**), and (**38**). The yields for all the products quoted in Scheme 1 refer to analytically pure materials obtained by the two-step addition–elimination sequence. The phenylselenocycloalkenones had spectral data in complete accord with expectations. Scheme 1 also summarises the yields of 2-bromocycloalk-2-enones (**39**),[19] (**40**),[20] (**41**),[21] and (**50**) produced when benzeneselenenyl bromide (**6**) was used instead of the chloride in the addition step of the sequence; as with the chlorides, the α-bromo-α-phenylseleno adducts (**27**), (**28**), (**29**), and (**47**) were used directly without purification.

This 2-heterosubstituted enone synthesis is capable of further extension through simple reagent variations. Addition of diazomethyl *p*-tolyl ketone (**1**) to an equimolar mixture of benzeneselenenyl chloride (**2**) and silver acetate in acetic acid was also accompanied by nitrogen evolution and the product isolated in 74% yield was the α-acetoxy-α-phenylseleno ketone (**9**). The reaction of benzeneselenenyl chloride (**2**) and silver acetate is known to produce benzeneselenenyl acetate (**10**);[22] addition of this reagent to the diazo ketone produces the observed result. Benzyl diazomethyl ketone (**4**) and the cyclic diazoketones (**21**), (**22**), (**23**), and (**45**) all produced α-acetoxy-α-phenylseleno adducts when similarly treated. Those adducts in which β-elimination is possible were readily converted, *via* oxidation to the selenoxide, into α-acetoxy enones. Thus, α-diazocyclopentanone (**21**) and benzeneselenenyl acetate (**10**) produced adduct (**30**) which, without purification, furnished 2-acetoxycyclopent-2-enone (**42**)[23] (53%) on treatment with 30% hydrogen peroxide in the presence of pyridine. Application of this sequence to α-diazocyclohexanone (**22**) and its 6-methyl derivative (**45**) furnished 2-acetoxycyclohex-2-enone (**43**)[24] (68%) and 2-acetoxy-6-methylcyclohex-2-enone (**52**) (75%) *via* intermediates (**31**) and (**48**), respectively. The first part of the two-step procedure behaved somewhat differently with α-diazocycloheptanone (**23**) in that 2-phenylselenocycloheptan-2-enone (**38**) (20%) was isolated in addition to the αα-adduct (**32**). Exposure of the latter to hydrogen peroxide–pyridine produced 2-acetoxycycloheptan-2-enone (**44**) in 74% yield. This regiospecific route to monoenol acetates of α-diketones is reminiscent of that developed by Trost[25] using sulphur as the activating atom. In the Trost approach the sulphur atom, usually in the form of a methylthio or phenylthio group, and the acetoxy group are introduced consecutively by sulphenylation of a preformed enolate followed by acetoxylation with lead tetra-acetate, whereas with the diazo ketone the difunctionalisation is achieved in a single step. Furthermore, selenoxide fragmentation usually occurs at temperatures substantially lower than those needed for the equivalent sulphoxide fragmentation, a difference which should be advantageous in the synthesis of very reactive monoenol acetates of α-diketones.

Other selenium-based reagents that displace nitrogen from α-diazo ketones include benzeneselenenyl thiocyanate (**13**).[26]

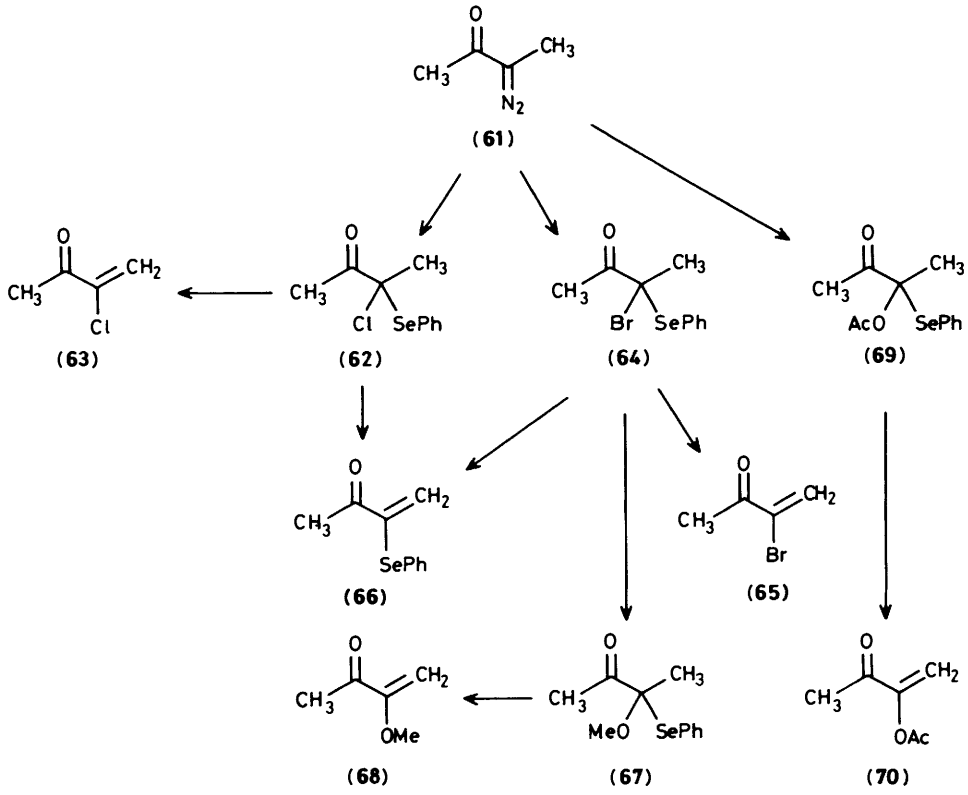


Reagents: i, $AgClO_4$–CH_3OH; ii, $NaHCO_3$–CH_3OH; iii, H_2O_2; iv, PhSeCl–CH_3OH

Diazomethyl *p*-tolyl ketone (**1**) reacted with PhSeSCN (**13**) much more slowly than with benzeneselenenyl chloride (**2**) or bromide (**6**), though addition of a trace amount of rhodium(II) acetate did increase the rate of reaction considerably, to produce the α-phenylseleno-α-thiocyanato adduct (**12**). α-Diazocyclohexanone (**22**) also gave an adduct, (**53**), with PhSeSCN, but attempts to convert the latter into 2-thiocyanatocyclohex-2-enone (**54**) by hydrogen peroxide oxidation at selenium were not successful. We were able, however, to extend these addition–elimination reactions to include the synthesis of 2-methoxy enones, though in a somewhat less direct fashion. The introduction of the methoxy group posed some problems initially. Methyl benzeneselenenate $PhSeOCH_3$ appears to be unknown, and attempts to generate it *in situ* from benzeneselenenyl bromide (**6**) and silver acetate in methanol † in the presence of a diazo ketone were unsuccessful. Accordingly, methods of replacing the halogen in α-chloro- and α-bromo-α-phenylseleno ketones by a methoxy group were then investigated. Treatment of α-chloro-α-phenylselenomethyl *p*-tolyl ketone (**3**) with 1 mol equiv. of silver perchlorate in dry methanol at 20 °C for 4 h caused replacement of both α-substituents to give the α-keto acetal (**55**) in 26% yield; with 2 mol equiv. of silver perchlorate the yield of compound (**55**) increased to 49%. Even dry methanol alone under reflux was sufficient to convert the selenide (**3**) into the α-keto acetal (60%

* Dehydrohalogenation conditions previously employed by R. Joly, J. Warnant, G. Nomine, and D. Bertin, *Bull. Soc. Chim. Fr.*, 1958, 366, and P. L. Stotter and K. A. Hill, *J. Org. Chem.*, 1973, **38**, 2576.

† However, methyl 2,4-dinitrobenzeneselenenate has been prepared by this route (W. S. Cook and R. A. Donia, *J. Am. Chem. Soc.*, 1951, **73**, 2275).



Scheme 2.

yield after 24 h). However, it was also found that treatment of α-bromo-α-phenylselenomethyl *p*-tolyl ketone (**7**) with dry methanol containing 2 mol equiv. of sodium hydrogen carbonate under gentle reflux for 4 h produced the desired result and α-methoxy-α-phenylselenomethyl *p*-tolyl ketone (**56**) was isolated in 61% yield. A similar reaction with bromide (**8**) produced benzyl α-methoxy-α-phenylselenomethyl ketone (**57**) in 58% yield. Both these methoxy compounds were unstable at room temperature and although we were unable to obtain satisfactory analytical data from combustion, the spectroscopic data were in full accord with the assigned structures (see Experimental section). In the cyclic series we found that exposure of α-chloro-α-phenylselenocyclohexanone (**25**) to dry methanol containing sodium hydrogen carbonate for 17 h at room temperature gave α-methoxy-α-phenylselenocyclohexanone (**58**) in 77% yield. Application of the hydrogen peroxide–pyridine oxidation procedure to compound (**58**) produced 2-methoxycyclohex-2-enone (**59**)[27] in 67% yield; this enone decomposed rapidly when left at room temperature. Interestingly, when α-diazocyclohexanone (**22**) was stirred in methanol containing benzeneselenenyl chloride (**2**) for 2 h at room temperature the enone (**59**) was obtained in 29% yield. Application of the latter procedure to α-diazocyclopentanone (**21**) produced 2-methoxycyclopent-2-enone (**60**)[28] in 30% yield.

Several α-heterosubstituted methyl vinyl ketones are also readily accessible from acyclic α-diazo ketones using these addition–elimination reactions (Scheme 2). For example, 3-diazobutan-2-one (**61**),[29] prepared from acetyl chloride and diazoethane in dry ether, and benzene selenenyl chloride (**2**) produced the α-chloro-α-phenylseleno adduct (**62**) (>95%), which on treatment with hydrogen peroxide–pyridine at room temperature furnished 3-chlorobut-3-en-2-one (**63**)[30] in 79% yield. In the bromo series, 3-diazobutan-2-one (**61**) was converted, *via* adduct (**64**), into 3-bromobut-3-en-2-one (**65**)[31] in 68% yield. Dehydrohalogenation of adducts (**62**) and (**64**) was effected by lithium carbonate in DMF, giving 3-phenylselenobut-3-en-2-one (**66**)[32] in 50—60% yield. The synthesis of 3-methoxybut-3-en-2-one (**68**)[33] was brought about by treatment of the crude bromo adduct (**64**) with methanol containing sodium hydrogen carbonate at room temperature, thus forming the methoxy adduct (**67**) (70%); conversion of the latter compound into the enone depended closely on the amounts of hydrogen peroxide and pyridine used in the selenium oxidation stage, the optimum yield (54%) being realised with 3 mol equiv. of hydrogen peroxide and 2 mol equiv. of pyridine. Our final illustration of the method is the conversion of 3-diazobutan-2-one (**61**) into 3-acetoxybut-3-en-2-one (**70**)[34] *via* 3-acetoxy-3-phenylselenobutan-2-one (**69**) in an overall yield of 75%.

In summary, we have explored new αα-addition reactions of acyclic and cyclic α-diazo ketones with selenium-based reagents and by taking advantage of room-temperature selenoxide fragmentation we have developed a mild, one-pot procedure for the synthesis of a variety of α-heterosubstituted αβ-unsaturated ketones which are useful intermediates in organic synthesis.[35,36] Although several of these compounds have been synthesised previously, most routes are inefficient, or multistep, or require the parent unsubstituted α, β-unsaturated ketone as the precursor.* For example, 2-chlorocyclopent-2-enone (**33**)[16] can be obtained from cyclopentanone by chlorination–dehydrochlorination, but yields are of the order of 10—25% and the product is difficult to purify. 2-Chlorocyclohept-2-enone (**35**)[18] has been obtained from a cyclohexanone enamine *via* a cyclopropanation–ring-expansion method, but the yield is only 17%. The ease with which the phenylseleno group can be introduced and subsequently manipulated makes the 2-phenylselenocycloalk-2-enone series particularly useful as synthetic intermediates. The route to these compounds described here

* For a recent synthesis of α-chloro and α-bromo enones from enones and benzeneselenenyl halides see ref. 16*b*.

has advantages over the only other general route to these compounds which requires the availability of the parent cycloalkenone as starting material.[17] Recent work by several groups has demonstrated the efficacy of α-phenylseleno αβ-enones in synthesis,[37] an attractive example being the conversion of 2-phenylselenocyclopent-2-enone (**36**) into jasmone in 76% overall yield. In the acyclic series, a few α-phenylseleno αβ-enones have been prepared,[38,39,40] mostly by multistep routes. McMurry's[32] synthesis of 3-phenylselenobut-3-en-2-one (**66**), however, is superior to ours in overall yield, but his method is not applicable to cyclic systems. The ^{13}C n.m.r. spectra of the new α-heterosubstituted cycloalkenones reported here are summarised in the Experimental section.

Experimental

M.p.s were determined on a Thomas Hoover apparatus and are uncorrected. ^1H N.m.r. spectra were recorded on an Hitachi Perkin-Elmer R-20A spectrometer and ^{13}C spectra on a Jeol FX60 spectrometer. Elemental analysis were performed by the Microanalysis Laboratory, University College, Cork. Merck HF_{254} silica gel was used for both t.l.c. and preparative t.l.c. (p.l.c.) with chloroform as the developer. Column chromatography was performed on BDH silica gel (60—120 mesh) using chloroform as the eluant. Magnesium sulphate was employed as the drying agent.

Diazomethyl *p*-tolyl ketone (**1**) and benzyl diazomethyl ketone (**4**) were prepared from the appropriate acyl chloride and diazomethane. Cyclic diazo ketones (**21**), (**22**), (**23**), and (**45**) were prepared from the parent ketone following the general procedure by Regitz, Ruter, and Liedhegener,[41] and were purified by column chromatography rather than by distillation. The improved procedure of Curphey was used to prepare toluene-*p*-sulphonyl azide.[42] 3-Diazobutanone (**61**) was prepared by a literature procedure.[29] Diphenyl diselenide (**16**), benzeneselenenyl chloride (**2**), and benzeneselenenyl bromide (**6**) were prepared by literature procedures.[43]

General Procedure for α-Chloro-α-phenylselenoalkyl Ketones.—To a dichloromethane or benzene solution of benzeneselenenyl chloride (1 mol equiv.) (normally a 5% solution) was added dropwise at room temperature a 5% solution of the diazoketone (1 mol equiv.) in the same solvent. Evolution of nitrogen was observed during the addition period. T.l.c. analysis after 30 min indicated the complete disappearance of starting materials. Removal of the solvent at reduced pressure yielded the α-chloro-α-phenylselenoalkyl ketone in essentially quantitative yield. In some runs small quantities of diphenyl diselenide (**16**) were removed from the crude product by passage through a short column of silica gel with chloroform as solvent. The following compounds were thus prepared.

α-Chloro-α-phenylselenomethyl p-tolyl ketone (**3**). The compound was obtained as a yellow oil (100%) (Found: C, 55.8; H, 4.1; Cl, 11.1. $C_{15}H_{13}ClOSe$ requires C, 55.7; H, 4.1; Cl, 11.0%); $\nu_{max.}$(film) 1 676 cm^{-1}; δ_H 2.40 (3 H, s, CH_3), 6.41 (1 H, s, CHCO), and 7.07—7.93 (9 H, m, ArH); δ_C 188.43 (CO), 144.95, 135.86, 130.86, 129.49, 129.17, 127.17, and 127.02 (aryl), 59.32 (*C*HCO), and 21.70 p.p.m. (CH_3).

Benzyl α-chloro-α-phenylselenomethyl ketone (**5**). The compound was obtained as a yellow oil (100%) (Found: C, 55.9; H, 4.1; Cl, 10.7%); $\nu_{max.}$(film) 1 723 cm^{-1}; δ_H 3.85 (2 H, s, CH_2Ar), 5.62 (1 H, s, CHCO), and 7.12—7.73 (10 H, m, Ph); δ_C 196.22 (CO), 135.86, 133.20, 129.45, 128.65, and 127.28 (Ph), 60.17 (*C*HCO), and 44.57 p.p.m. (CH_2Ar).

Preparation of 2-Chloro Cycloalk-2-enones. General Procedure Used on 5—10 mmol Scale.—A dichloromethane solution of the α-chloro-α-phenylselenocycloalkanone, prepared from the α-diazocycloalkanone and benzeneselenenyl chloride (**2**) as described above for compounds (**3**) and (**5**), was subjected to the following oxidation–fragmentation procedure. Pyridine (2.5 mol equiv.) was added in one portion to the dichloromethane solution followed by the dropwise addition of 30% hydrogen peroxide (9 mol equiv.) to the stirred mixture, with periodic cooling of the reaction flask in an ice-bath to maintain the temperature below 30 °C. The two-phase system was then stirred vigorously at room temperature for a further 1—2 h after which the mixture was poured into a mixture of dichloromethane and 7% aqueous sodium hydrogen carbonate. The dichloromethane layer and dichloromethane extracts (2 ×) of the aqueous layer were combined, washed successively with 10% aqueous hydrochloric acid and saturated aqueous sodium chloride, and dried. After removal of the solvent, the pure chloro enones were isolated by distillation at reduced pressure. The yields quoted below are based on α-diazo cycloalkanone:

2-Chlorocyclopent-2-enone (**33**)[16] (82% yield), b.p. 34—38 °C at 0.3 mmHg (lit.,[16a] 80—88 °C at 10 mmHg); $\nu_{max.}$(film) 1 712 cm^{-1}; δ_H 2.45—2.95 (4 H, m, CH_2CH_2) and 7.68 (1 H, t, *J* 3 Hz, =CH); δ_C 201.22 (CO), 158.21 (C-3), 135.60 (C-2), 38.07 (C-5), and 25.99 p.p.m. (C-4).

2-Chlorocyclohex-2-enone (**34**) (82% yield), b.p. 53—56 °C at 0.3 mmHg; m.p. 70—72 °C (lit.,[16b] 71—72 °C); $\nu_{max.}$(film) 1 685 cm^{-1}; δ_H 1.90—2.30 (2 H, m, CH_2), 2.35—2.80 (4 H, m, CH_2CO and CH_2CH=), and 7.23 (1 H, t, *J* 4.5 Hz, =CH); δ_C 191.54 (CO), 146.84 (C-3), 132.09 (C-2), 38.53 (C-6), 27.09 (C-4), and 22.61 p.p.m. (C-5).

2-Chloro-6-methylcyclohex-2-enone (**49**) (88% yield), b.p. 63—66 °C at 0.35 mmHg (Found: C, 58.0; H, 6.2; Cl, 24.8. C_7H_9ClO requires C, 58.1; H, 6.3; Cl, 24.5%); $\nu_{max.}$(film) 1 683 cm^{-1}; δ_H 1.21 (3 H, d, *J* 7.5 Hz, CH_3), 1.50—2.20 (2 H, m, CH_2), 2.30—2.70 (3 H, m, CHCO and CH_2C=), and 7.13 (1 H, t, *J* 4.5 Hz, =CH); δ_C 194.27 (CO), 145.93 (C-3), 131.77 (C-2), 42.56 (C-6), 30.54 (C-4), 26.25 (C-5), and 15.33 p.p.m. (CH_3).

2-Chlorocyclohept-2-enone (**35**)[18] (78% yield), b.p. 49—53 °C at 0.05 mmHg; $\nu_{max.}$(film) 1 673 cm^{-1}; δ_H 1.60—2.10 (4 H, m, CH_2CH_2), 2.30—2.90 (4 H, m, CH_2CO and CH_2C=), and 7.11 (1 H, t, *J* 6 Hz, =CH); δ_C 195.70 (CO), 144.24 (C-3), 41.65 (C-7), 27.74 (C-4), 24.76 (C-6), and 20.99 p.p.m. (C-5). This compound decomposes rapidly at room temperature.

3-Chlorobut-3-en-2-one (**63**)[30] (79% yield); $\nu_{max.}$ 1 680 cm^{-1}; δ_H 2.44 (3 H, s, CH_3) and 6.08 and 6.37 (2 H, 2 d, *J* 2.5 Hz, $=CH_2$).

Preparation of 2-Phenylselenocycloalk-2-enones. General Procedure Used on 3—6 mmol Scale.—A dichloromethane solution of the α-diazo ketone (1 mol equiv.) was added dropwise to a dichloromethane solution of benzeneselenenyl chloride (**2**) (1 mol equiv.) at room temperature to form the α-chloro-α-phenylselenoalkylketone adduct in the usual way. The solvent was then removed at reduced pressure and the residue was taken up in dry DMF. Dehydrochlorination was then accomplished by dropwise addition of the DMF solution of the adduct (1 mol equiv.) during *ca.* 15 min to a stirred suspension of anhydrous lithium carbonate (3 mol equiv.) and anhydrous lithium chloride (2.5 mol equiv.) in dry DMF maintained at 110—120 °C under nitrogen. The mixture was then stirred at this temperature for 1.5—2.0 h (prolonged heating caused lower yields). After filtration, the filtrate was concentrated at reduced pressure, the residue was taken up in chloroform, and the solution was washed with water and dried. Pure products were then obtained by p.l.c.

2-Phenylselenocyclopent-2-enone (**36**)[17] (72% yield), m.p. 35—37 °C (Found: C, 55.45; H, 4.25. $C_{11}H_{10}OSe$ requires C, 55.71; H, 4.25%); $\nu_{max.}$(film) 1 698 cm^{-1}; 2.40—2.85 (4 H, m, CH_2CH_2), 7.12 (1 H, t, *J* 3 Hz, =CH), and 7.24—7.80 (5 H, m,

Ph); δ_C 205.90 (CO), 159.45 (C-3), 139.11, 135.21, 129.56, 128.52, and 126.37 (Ph and C-2), 34.05 (C-5), and 28.98 p.p.m. (C-4).

2-Phenylselenocyclohex-2-enone (**37**)[17] (77% yield), m.p. 49.5—51.0 °C (Found: C, 57.4; H, 4.9. $C_{12}H_{12}OSe$ requires C, 57.38; H, 4.82%); $\nu_{max.}$(KBr) 1 661 cm^{-1}; δ_H 1.90—2.80 (6 H, m, $[CH_2]_3$), 6.56 (1 H, t, *J* 4 Hz, =CH), and 7.35—7.80 (5 H, m, Ph); δ_C 195.83 (CO), 146.12 (C-3), 136.51, 134.82, 129.56, 128.65, and 126.76 (Ph and C-2), 38.33 (C-6), 27.81 (C-4), and 22.81 p.p.m. (C-5).

6-Methyl-2-phenylselenocyclohex-2-enone (**51**) (87% yield), an oil (Found: C, 58.6; H, 5.6. $C_{13}H_{14}OSe$ requires C, 58.87; H, 5.32%); $\nu_{max.}$(film) 1 672 cm^{-1}; δ_H 1.16 (3 H, d, *J* 7 Hz, CH_3), 1.50—2.10 (2 H, m, CH_2), 2.10—2.70 (3 H, m, CHCO and CH_2CH=), 6.41 (1 H, t, *J* 5 Hz, =CH), and 7.28—7.75 (5 H, m, Ph); δ_C 198.56 (CO), 145.08 (C-3), 136.58, 134.56, 129.56, 128.58, and 127.09 (Ph and C-2), 42.17 (C-6), 30.80 (C-4), 27.42 (C-5), and 15.27 p.p.m. (CH_3).

2-Phenylselenocyclohept-2-enone (**38**) (73% yield), an oil (Found: C, 58.9; H, 5.5. $C_{13}H_{14}OSe$ requires C, 58.87; H, 5.32%); $\nu_{max.}$(film) 1 655 cm^{-1}; δ_H 1.43—2.12 (4 H, m, CH_2CH_2), 2.12—2.90 (4 H, m, $COCH_2$ and CH_2CH=), 6.44 (1 H, t, *J* 6 Hz, =CH), and 7.14—7.72 (5 H, m, Ph); δ_C 200.96 (CO), 144.05 (C-3), 138.07, 135.93, 129.49, 128.90, and 128.39 (Ph and C-2), 41.97 (C-7), 29.63 (C-4), 25.08 (C-6), and 21.38 p.p.m. (C-5).

3-Phenylselenobut-3-en-2-one (**66**)[32] (50—60% yield), an oil; $\nu_{max.}$(film) 1 670 cm^{-1}; δ_H 2.4 (3 H, s, CH_3CO), 5.56 and 6.52 (2 H, 2 d, *J* 2 Hz, $=CH_2$), and 7.20—7.78 (5 H, m, Ph).

General Procedure for α-Bromo-α-phenylselenoalkyl Ketones.—Benzeneselenenyl bromide (**6**) was generated *in situ* by the slow addition of a solution of bromine (1 mol equiv.) in dry dichloromethane to a stirred solution of diphenyl diselenide (**16**) (1 mol equiv.) in dichloromethane at room temperature. After the addition was complete the mixture was stirred for an additional 30 min and then a solution of the α-diazo ketone (2 mol equiv.) in dichloromethane was added dropwise at room temperature. Nitrogen evolution occurred during the addition period and for a short time thereafter. Removal of the solvent at reduced pressure yielded the crude α-bromo-α-phenylseleno ketone; where necessary purification was accomplished by p.l.c. The following compounds were thus prepared.

α-Bromo-α-phenylselenomethyl p-tolyl ketone (**7**) (88% yield), an oil (Found: C, 49.1; H, 3.5; Br, 21.5. $C_{15}H_{13}BrOSe$ requires C, 48.94; H, 3.56; Br, 21.71%); $\nu_{max.}$(film) 1 664 cm^{-1}; δ_H 2.40 (3 H, s, $ArCH_3$), 6.44 (1 H, s, CHCO), and 7.10—8.00 (9 H, m, ArH); δ_C 189.01 (CO), 145.08, 135.47, 129.95, 129.43, and 127.80 (aryl), 48.15 (CH), and 21.77 p.p.m. ($ArCH_3$).

Benzyl α-bromo-α-phenylselenomethyl ketone (**8**) (84% yield), an oil (Found: C, 49.2; H, 3.75; Br, 21.4%); $\nu_{max.}$(film) 1 718 cm^{-1}; δ_H 4.07 (2H, s, $ArCH_2$), 5.60 (1 H, s, CHCO), and 7.12—7.73 (10 H, m, ArH); δ_C 196.35 (CO), 135.41, 131.50, 129.56, 128.71, and 127.35 (aryl), 48.47 (CH), and 44.25 p.p.m. (CH_2Ar).

Preparation of 2-Bromocycloalk-2-enones. General Procedure Used on 3.5 mmol Scale.—Dichloromethane solutions of the α-bromo-α-phenylseleno adducts were prepared as described above and were used directly without purification. They were subjected to the same oxidation–fragmentation conditions (pyridine–30% hydrogen peroxide; 30 °C) used for the preparation of the 2-chlorocycloalk-2-enones. The yields quoted below are based on the starting α-diazo ketone.

2-Bromocyclopent-2-enone (**39**)[19] (73% yield), b.p. 38—43 °C at 0.06 mmHg; m.p. 38—39 °C (lit., 39.0—39.5 °C); $\nu_{max.}$(film) 1 697 cm^{-1}; δ_H 2.45—2.91 (4 H, m, $[CH_2]_2$) and 7.88 (1 H, t, *J* 3 Hz, =CH).

2-Bromocyclohex-2-enone (**40**)[20] (83% yield), m.p. 69—71 °C (lit.,[20] 75—76 °C); $\nu_{max.}$(KBr) 1 688 cm^{-1}; δ_H 1.95—2.46 (2 H, m, CH_2), 2.46—2.98 (4 H, m, CH_2CO and CH_2CH=), and 7.37 (1 H, t, *J* 4.5 Hz, =CH).

2-Bromo-6-methylcyclohex-2-enone (**50**) (72% yield), b.p. 63—67 °C at 0.1 mmHg); $\nu_{max.}$(film) 1 687 cm^{-1}; δ_H 1.21 (3 H, d, *J* 6.5 Hz, CH_3), 1.60—2.25 (2 H, m, CH_2), 2.30—2.75 (3 H, m, CHCO and CH_2C=), and 7.28 (1 H, t, *J* 4.5 Hz, =CH).

2-Bromocyclohept-2-enone (**41**)[21] (64% yield), b.p. 67—70 °C at 0.1 mmHg (lit.,[21] 70—77 °C at 0.35 mmHg); $\nu_{max.}$(film) 1 680 cm^{-1}; δ_H 1.60—2.10 (4 H, m, $[CH_2]_2$), 2.10—2.80 (4 H, m, CH_2CO and CH_2C=), and 7.26 (1 H, t, *J* 6 Hz, CH=).

3-Bromobut-3-en-2-one (**65**)[31] (68% yield); $\nu_{max.}$(film) 1 690 cm^{-1}; δ_H 2.43 (3 H, s, CH_3) and 6.45 and 6.83 (2 H, 2 d, *J* 3 Hz, $=CH_2$).

General Procedure for α-Acetoxy-α-phenylselenoalkyl Ketones.—Benzeneselenenyl acetate (**10**) was generated *in situ* by the addition of silver acetate (1 mol equiv.) to a stirred solution of benzeneselenenyl chloride (**2**) (1 mol equiv.) in acetic acid at room temperature. After 1.5 h a solution of the diazo ketone (1 mol equiv.) in dichloromethane was added dropwise and the resulting mixture was stirred at room temperature until nitrogen evolution had ceased. The silver salts were removed by filtration and the solvents were removed at reduced pressure. The residue was taken up in chloroform, washed successively with 10% aqueous sodium carbonate and water, then dried and concentrated at reduced pressure. Where necessary, purification was accomplished by p.l.c. The following compounds were prepared.

α-Acetoxy-α-phenylselenomethyl p-tolyl ketone (**9**) (74% yield), an oil (Found: C, 59.1; H, 4.5. $C_{17}H_{16}O_3Se$ requires C, 58.80; H, 4.64%); $\nu_{max.}$(film) 1 677 and 1 742 cm^{-1}; δ_H 2.19 (3 H, s, CH_3CO_2), 2.41 (3 H, s, $ArCH_3$), and 7.13—7.88 (10 H, m, COCH and ArH); δ_C 188.81 (CO), 169.84 (CO_2), 144.43, 136.12, 131.38, 129.23, 128.65, and 126.11 (aryl), 73.60 (CH), 21.70 and 20.90 p.p.m. ($ArCH_3$ and $OCOCH_3$).

α-Acetoxy-α-phenylselenomethyl benzyl ketone (**11**) (69% yield), an oil (Found: C, 59.05, H, 4.8%); $\nu_{max.}$(film) 1 720 and 1 739 cm^{-1}; δ_H 2.12 (3 H, s, CH_3CO_2), 3.80 (2 H, s, $ArCH_2$), 6.52 (1 H, s, CH), and 7.13—7.76 (10 H, m, Ph); δ_C 197.13 (CO), 169.51 (CO_2), 135.67, 133.13, 129.62, 129.36, 128.58, 127.15, and 125.79 (aryl), 76.08 (CH), 45.29 ($ArCH_2$) and 20.79 p.p.m. ($OCOCH_3$).

Preparation of 2-Acetoxycycloalk-2-enones. General Procedure Used on 4—5 mmol Scale.—The crude α-acetoxy-α-phenylselenoalkyl ketones were prepared as described above and used directly without purification. They were redissolved in dichloromethane and subjected to exactly the same oxidation–fragmentation conditions used in the synthesis of the 2-chloro and 2-bromo enones. The following compounds were thus prepared.

2-Acetoxycyclopent-2-enone (**42**)[23] (53% yield), an oil, b.p. 46—52 °C at 0.2 mmHg (lit.,[23] 115—117 °C at 15 mmHg); (Found: C, 60.1; H, 6.0. $C_7H_8O_3$ requires C, 59.99; H, 5.75%); $\nu_{max.}$(film) 1 707 and 1 766 cm^{-1}; δ_H 2.21 (3 H, s, CH_3CO_2), 2.25—2.75 (4 H, m, CH_2CH_2), and 7.24 (1 H, t, *J* 3 Hz, =CH); δ_C 201.02 (CO), 167.70 (CO_2), 149.83 (C-2), 146.32 (C-3), 32.55 (C-5), 23.13 (C-4), and 20.73 p.p.m. (CH_3).

2-Acetoxycyclohex-2-enone (**43**)[24] (68% yield), an oil b.p. 63—65 °C at 0.2 mmHg (lit.,[24] 99—102 °C at 3 mmHg); (Found: C, 62.3; H, 6.6. $C_8H_{10}O_3$ requires C, 62.33; H, 6.45%); $\nu_{max.}$(film) 1 683 and 1 754 cm^{-1}; δ_H 1.85—2.20 (2 H, m, CH_2), 2.17 (3 H, s, CH_3CO_2), 2.34—2.64 (4 H, m, CH_2CO and CH_2CH=), and 6.67 (1 H, t, *J* 4 Hz, =CH); δ_C 191.87 (CO), 168.80 (CO_2), 145.34 (C-2), 142.29 (C-3), 38.01 (C-6), 24.82 (C-4), 22.61 (C-5), and 20.34 p.p.m. (CH_3).

2-Acetoxy-6-methylcyclohex-2-enone (**52**) (75% yield), an oil, b.p. 63—67 °C at 0.1 mmHg (Found: C, 64.0; H, 7.3. $C_9H_{12}O_3$

requires C, 64.27; H, 7.19%); $\nu_{max.}$(film) 1 685 and 1 755 cm^{-1}; δ_H 1.17 (3 H, d, *J* 6 Hz, CH_3), 1.80—2.20 (2 H, m, CH_2), 2.19 (3 H, s, CH_3CO_2), 2.25—2.72 (3 H, m, CHCO and CH_2CH=), and 6.62 (1 H, t, *J* 4 Hz, =CH); δ_C 194.59 (CO), 168.80 (CO_2), 144.95 (C-2), 135.15 (C-3), 41.84 (C-6), 30.60 (C-4), 23.72 (C-5), 20.27 (CH_3CO), and 14.75 p.p.m. (CH_3).

2-Acetoxy-2-phenylselenocycloheptanone (**32**). Treatment of α-diazocycloheptanone (**23**) with benzeneselenenyl acetate (**10**) generated *in situ* as described above, gave a mixture of 2-acetoxy-2-phenylselenocycloheptanone (**32**) (48%) and 2-phenylselenocyclohept-2-enone (**38**) (20%). P.l.c. separation gave the acetate (**32**) as an oil, $\nu_{max.}$(film) 1 700 and 1 738 cm^{-1}; δ_H 1.50—2.30 (6 H, m, $[CH_2]_3$), 2.10 (3 H, s, CH_3CO_2), 2.30—2.78 (4 H, m, CH_2CO and CH_2C), and 7.25—7.70 (5 H, m, Ph).

2-Acetoxycyclohept-2-enone (**44**). 2-Acetoxy-2-phenylselenocycloheptanone (**32**), isolated as described above, was subjected to the usual oxidation–fragmentation conditions to give the *acetoxy enone* (**44**) as an oil, b.p. 65—69 °C at 0.05 mmHg (74% yield) (Found: C, 64.2; H, 7.4. $C_9H_{12}O_3$ requires C, 64.27; H, 7.19%); $\nu_{max.}$(film) 1 669 and 1 751 cm^{-1}; δ_H 1.62—2.10 (4 H, m, CH_2CH_2), 2.17 (3 H, s, CH_3CO_2), 2.31—2.82 (4 H, m, CH_2CO and CH_2CH=), and 6.47 (1 H, t, *J* 6 Hz, =CH); δ_C 195.96 (CO), 169.38 (CO_2), 147.62 (C-2), 132.55 (C-3), 41.52 (C-7), 25.60 (C-4), 25.27 (C-6), 21.05 (C-5), and 20.34 p.p.m. (CH_3).

3-Acetoxy-3-phenylselenobutan-2-one (**69**). Treatment of 3-diazobutan-2-one (**61**) with benzeneselenenyl acetate (**10**), generated *in situ* as described above, gave the *acetoxy compound* (**69**) (75% yield) as an oil, b.p. 130—140 °C (bath temperature) at 0.005 mmHg (Found: C, 50.8; H, 4.9. $C_{12}H_{14}O_3Se$ requires C, 50.53; H, 4.95); $\nu_{max.}$(film) 1 710 and 1 742 cm^{-1}; δ_H 1.80 (3 H, s, CH_3), 2.05 (3 H, s, CH_3CO_2), 2.12 (3 H, s, CH_3CO), and 7.20—7.59 (5 H, m, Ph); δ_C 199.60 (CO), 169.52 (CO_2), 87.97 (C-3), 137.68, 129.04, and 126.24 (aryl), and 23.78, 22.94, and 21.05 (CH_3CO, CH_3C, and CH_3CO_2).

3-Acetoxybut-3-en-2-one (**70**).[34] 3-Acetoxy-3-phenylselenobutan-2-one (**69**) was subjected to the usual oxidation procedure (H_2O_2–pyridine) to give the enone (**70**) (95% yield) as an oil, $\nu_{max.}$(film) 1 697 and 1 760 cm^{-1}; δ_H 2.20 (3 H, s, CH_3CO_2), 2.31 (3 H, s, CH_3CO), and 5.63 and 5.95 (2 H, 2 d, *J* 2.5 Hz, $=CH_2$).

α-Methoxy-α-phenylselenomethyl p-Tolyl Ketone (**56**).—The α-bromo-α-phenylseleno adduct (**7**) (0.47 g) was prepared from the diazo ketone and benzeneselenenyl bromide (**6**) in dichloromethane as described earlier. The solvent was removed at reduced pressure and was replaced by dry methanol (10 ml). Sodium hydrogen carbonate (0.22 g) was added and the mixture was stirred and heated under reflux for 4 h. The cooled solution was evaporated to drynesss and chloroform (20 ml) was added to the residue. The chloroform solution was washed with water, dried, and concentrated. Purification by p.l.c. gave the methoxy compound (**56**) as an oil (0.25 g, 61%), $\nu_{max.}$(film) 1 685 cm^{-1}; δ_H 2.35 (3 H, s, $ArCH_3$), 3.57 (3 H, s, OCH_3), 6.12 (1 H, s, COCH), and 7.08—7.90 (9 H, m, ArH). Satisfactory analytical data could not be obtained; the compound decomposed slowly at room temperature.

Benzyl α-Methoxy-α-phenylselenomethyl Ketone (**57**).—The α-bromo-α-phenylseleno adduct (**8**) was treated with methanol and sodium hydrogen carbonate exactly as described above for the *p*-tolyl series. T.l.c. analysis in this case showed that solvolysis was complete within 1 h. P.l.c. purification of the product gave the methoxy compound (**57**) as an oil (58%), $\nu_{max.}$ (film) 1 720 cm^{-1}; δ_H 3.39 (3 H, s, OCH_3), 3.63 (2 H, s, $ArCH_2$), 5.32 (1 H, s, CHCO) and 7.02—7.60 (10 H, m, Ph). Satisfactory analytical data could not be obtained; the compound decomposed slowly at room temperature.

2-Methoxy-2-phenylselenocyclohexanone (**58**).—A dichloromethane solution of benzeneselenenyl chloride (**2**) (0.3 g) was added dropwise to a stirred dichloromethane solution of α-diazocyclohexanone (**22**) (0.19 g) at room temperature. When addition was complete the mixture was stirred for an additional 30 min and the solvent was then removed at reduced pressure. Dry methanol (10 ml) and sodium hydrogen carbonate (0.27 g) were added to the residue and the mixture was stirred under nitrogen at room temperature for 17 h. The methanol was removed at reduced pressure and was replaced by chloroform. After being washed with the water, the solution was dried and concentrated. Purification of the crude product by p.l.c. gave the *methoxy compound* (**58**) as an oil (0.34 g, 77%) (Found: C, 54.8; H, 5.5. $C_{13}H_{16}O_2Se$ requires C, 55.13; H, 5.69%); $\nu_{max.}$(film) 1 700 cm^{-1}; δ_H 1.50—1.94 (4 H, m, CH_2CH_2), 1.94—2.62 (4 H, m, CH_2CO and CH_2C), 3.42 (3 H, s, OCH_3), and 7.14—7.72 (5 H, m, Ph); δ_C 203.43 (CO), 136.32, 128.91, 128.52, and 126.70 (aryl), 96.42 (C-2), 52.24 (OCH_3), 39.31 (C-6), 38.40 (C-3), 26.70 (C-5), and 22.74 p.p.m. (C-4).

2-Methoxycyclohex-2-enone (**59**).[27]—2-Methoxy-2-phenylselenocyclohexanone (**58**) (0.3 g) was subjected to the standard oxidation–fragmentation conditions to yield the enone (**59**) (0.09 g, 67%), b.p. 80—87 °C at 0.15 mmHg (lit.,[28] 116—119 °C at 18 mmHg); $\nu_{max.}$ (film) 1 685 cm^{-1}; δ_H 1.60—2.20 (2 H, m, CH_2), 2.20—2.64 (4 H, m, CH_2CO and CH_2CH=), 3.54 (3 H, s, OCH_3), and 5.90 (1 H, t, *J* 5 Hz, =CH); δ_C 194.47 (CO), 151.52 (C-2), 116.43 (C-3), 54.71 (OCH_3), 38.79 (C-6), 24.37 (C-5), and 23.00 p.p.m. (C-4). This compound decomposed rapidly at room temperature.

2-Methoxycyclopent-2-enone (**60**).[28]—Benzeneselenenyl chloride (**2**) (0.68 g) was stirred in dry methanol (10 ml) for 5 min. A solution of α-diazocyclopentanone (**21**) (0.39 g) in dry methanol (10 ml) was added dropwise during 15 min and the mixture was then stirred at room temperature for a further 2 h. The solvent was removed at reduced pressure and the residue was chromatographed on silica gel with chloroform as the eluant, to yield 2-phenylselenocyclopent-2-enone (**36**) in 14% yield. Further elution of the column yielded the methoxy enone (0.12 g, 80%) as a liquid, b.p. 70—75 °C at 0.15 mmHg (lit.,[28] 112–114 °C at 16 mmHg); $\nu_{max.}$ film 1 700 cm^{-1}; δ_H 2.23—2.68 (4 H, br s, CH_2CH_2), 3.74 (3 H, s, OCH_3), and 6.42 (1 H, t, *J* 3.5 Hz, =CH); δ_C 202.52 (CO), 157.63 (C-2), 127.15 (C-3), 57.11 (OCH_3), 33.20 (C-5), and 21.83 p.p.m. (C-4).

3-Methoxy-3-phenylselenobutan-2-one (**67**).—3-Bromo-3-phenylselenobutan-2-one (**64**) (1.3 g), prepared from 3-diazobutan-2-one (**61**) and benzeneselenenyl bromide (**6**) as described earlier, was dissolved in dry methanol (25 ml) containing sodium hydrogen carbonate (0.74 g) and the mixture was stirred under nitrogen at room temperature for 2 h. The methanol was then removed at reduced pressure and was replaced by chloroform. The chloroform solution was washed once with water, then dried, and concentrated. Purification of the product by p.l.c. gave the *methoxy compound* (**67**) (0.76 g, 70%) as an oil (Found: C, 51.7; H, 5.4. $C_{11}H_{14}O_2Se$ requires C, 51.37; H, 5.49%); $\nu_{max.}$ 1 707 cm^{-1}; δ_H 1.64 (3 H, s, CH_3), 2.02 (3 H, s, CH_3CO), 3.54 (3 H, s, OCH_3), and 7.15—7.69 (5 H, m, Ph); δ_C 203.75 (CO), 137.10, 129.04, and 127.61 (aryl), 95.18 (C-3), 52.50 (OCH_3), 24.88 (CH_3CO), and 20.92 p.p.m. (CH_3).

3-Methoxybut-3-en-2-one (**68**).[33]—Attempts to convert 3-methoxy-3-phenylselenobutan-2-one (**67**) to 3-methoxybut-3-en-2-one (**68**) by the usual procedure employed for the other enones above, *i.e.* 8—9 mol equiv. H_2O_2 and 2.5 mol equiv. pyridine, yielded a mixture of products. However, utilisation of 3 mol equiv. H_2O_2 in the presence of 2 mol equiv. pyridine

yielded the enone (**68**) in 54% yield, $\nu_{max.}$(film) 1 712 cm^{-1}; δ_H 2.29 (3 H, s, CH_3CO), 3.60 (3 H, s, OCH_3), and 4.45 and 5.19 (2 H, 2 d, *J* 3 Hz, $=CH_2$). Oxidation–fragmentation of the selenide (**67**) with ozone, *m*-chloroperbenzoic acid, or sodium metaperiodate as oxidising agent failed to improve the yield of the enone product. 3-Methoxybut-3-en-2-one (**68**) is reasonably stable as a dilute solution in inert solvents, but highly purified samples when neat undergo noticeable polymerisation when stored overnight at −20 °C.

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