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SOME NOVEL ROUTES TO 1-HETERO-SUBSTITUTED 1-VINYLCYCLOPROPANES

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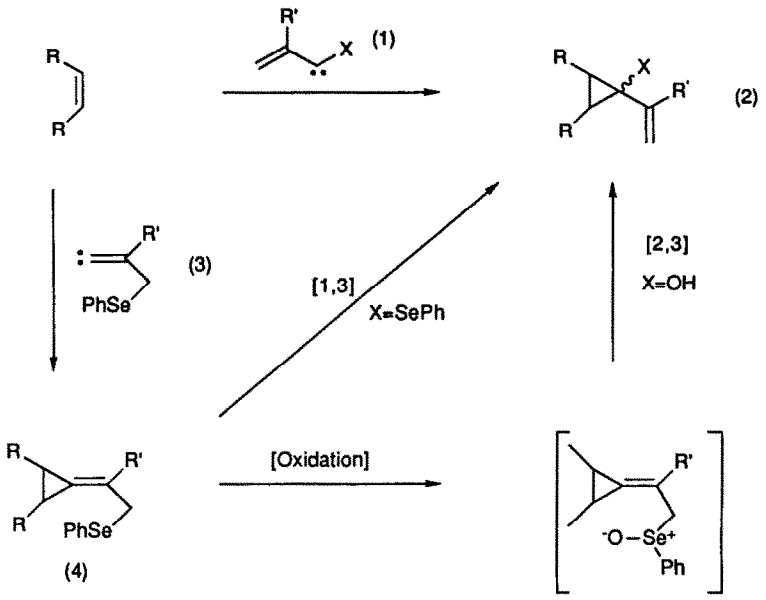
Abstract: 3-Phenylselenoalk-1-enylidene carbenes, generated in situ by base induced condensation of α-phenylseleno carbonyl compounds and diethyl diazomethylphosphonate, can be efficiently trapped by alkenes to give alkylidene-cyclopropane adducts which undergo either [1,3] allyl selenide rearrangement or oxidative selenoxide [2,3] sigmatropic rearrangement to produce 1-phenylseleno- or 1-hydroxy-1-vinylcyclopropanes respectively.

Introduction

Within the last fifteen years, the synthetic challenge posed by the isolation of polyquinane natural products has stimulated the quest for novel cyclopentanoid annulation methods. The high level of activity in this area has been appropriately reflected in a number of excellent reviews.[1] We were especially attracted, however, to the inherent potential of the vinylcyclopropane rearrangement,[2] and in particular to the case of 1-hetero-substituted-1-vinylcyclopropanes. Such precursors have often provided a strategic cornerstone for further elaboration, as in the elegant and comprehensive studies of 1-siloxy-1-vinyl-cyclopropanes by the Trost group.[3] We now report, in full detail,[4] our search for the development of a flexible and convergent route to a series of variously substituted and functionalised derivatives of this class.

Our initial considerations centred around the idea (Scheme 1) that the direct addition of the hypothetical heterosubstituted allylic carbene equivalent (1) to an olefin would constitute, in principle, a most direct and attractive route to a series of 1-hetero-substituted 1-vinylcyclopropanes (2). As in the chloroketene addition, diazoalkane ring expansion protocol developed by Greene,[5] the selection of a simple olefinic partner or electron rich alkene as one of the components was considered to be an advantage since the majority of cyclopentaannulation methods build either on the use of an electron deficient olefin as a carbanionic acceptor or on the use of enolate anion chemistry.

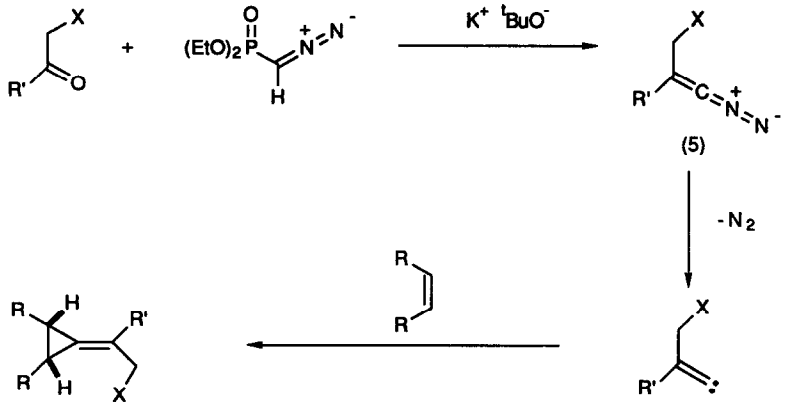
However, a major drawback to such an approach is that ample literature precedent exists in the chemistry of singlet alkoxycarbenes to show that the influence of a neighbouring heteroatom tends to increase the nucleophilic character of such carbenes and hence to favour their reaction with electron deficient alkenes.[6] These observations have been rationalised by involving oxygen lone pair overlap with the empty p-orbital of the adjacent singlet carbene. Moreover, in the case of carbenes (1), this effect would certainly be exacerbated by the presence of the adjacent π system.



Scheme 1

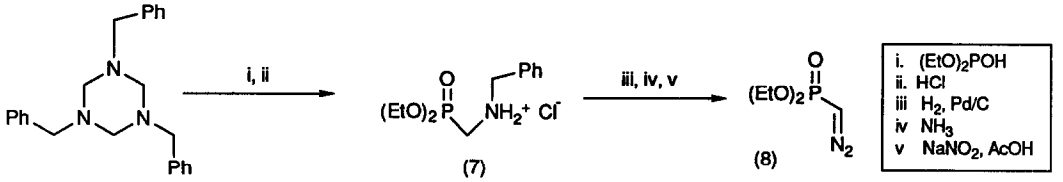
We were intrigued by the concept that a much more reactive and flexible synthetic equivalent of (1) could be developed through the generation of 3-phenylselenoalk-1-enylidene carbenes of type (3) (Scheme 1). Such species had not been previously described, presumably since they were potentially capable of "self-destruction" through the propensity of the selenide moiety itself to act as a carbene trap. Obtaining the allyl selenides (4) therefore required that external trapping of the carbene by olefins should compete effectively in the system against other possible inter- and intramolecular insertion and rearrangement reactions. The resultant adduct (4) could then undergo the [1,3] allyl selenide rearrangement to give synthetically useful 1-phenylseleno-1-vinylcyclopropanes (2, X = SePh) whose versatile chemistry has been explored by Krief and coworkers.[7] Alternatively, oxidation and selenoxide mediated [2,3] sigmatropic rearrangement would provide valuable 1-vinylcyclopropanols (2, X = OH). Both of these rearrangements were expected to benefit from the considerable thermodynamic driving force engendered by the release of some 11 Kcal mol^{-1} of strain energy[7] in the transformation of the alkylidene cyclopropane into the vinylcyclopropane. A further advantage of this approach may be discerned by examination of the regio- and stereochemical consequences which obtain in the case of an unsymmetrical olefinic substrate (R≠R). Thus, while stereospecific addition of a singlet carbene controls the geometry at carbon atoms 2 and 3, the overall sequence is "self correcting" since both resultant isomeric allyl selenides would converge again to a single regioisomer at the vinylcyclopropane stage.

Although a variety of methods are available for the generation of alkylidene carbenes, we elected in the first instance to examine the highly convergent and efficient three component one pot condensation of a carbonyl compound, an alkyl diazomethyl phosphonate and an olefin developed by Gilbert.[8] In this case, (Scheme 2, X = H, alkyl) deprotonation of the diazoalkylphosphonate by tertiary butoxide anion is followed by a Horner-Wadsworth Emmons reaction with the ketone to give a non-isolable diazoethene (5) which decomposes *in situ* at -78°C to generate the required alkylidene carbene. In terms of the generation of 3-phenylselenoalk-1-ylidene carbenes (3), this method then reduces to the selection of a readily available α-phenylselenoketone (X = SePh) as the carbonyl partner.



(4) **Scheme 2**

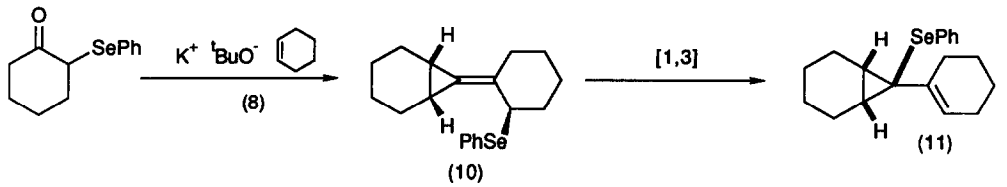
From the experimental standpoint, our first requirement was to prepare relatively large quantities of diethyl diazomethyl phosphonate. Although most workers have opted for the original Seyferth route[9] involving phosphite displacement of N-(bromomethyl)phthalimide, our own preference is for a method initially communicated by Christensen and Ratcliffe[10] involving hydrogenolytic debenzylation of the phosphonate obtained by Michaelis-Becker reaction of tri-N-benzylhexahydro-5-triazine (6) with diethyl phosphite (Scheme 3).



Scheme 3

Since we have found that careful preparation and purification of the intermediate hydrochloride salt (7) is crucial to the success of the debenzylation step, a complete description of this route has been given in the experimental section. 2-Phenylseleno-cyclohexanone[11] (9), readily prepared by reaction of the derived trimethylsilylenol ether with phenylselenyl chloride, was then selected as a suitable model for initial study. Reaction of (9) with diethyldiazomethyl phosphonate (8) in the presence of freshly sublimed potassium *tert*-butoxide, tetrahydrofuran, and cyclohexene according to the method of Gilbert[8] afforded the desired phenylseleno-alkylidene cyclopropane (10) in 55% yield, based on selenoketone (Scheme 4).

From the stereochemical standpoint, reactions involving trapping and rearrangement in the 2-phenylselenocyclohexanone series (Schemes 4,5 and 9, *vide infra*) often appear to involve the formation of a single diastereoisomer. Although unambiguous stereochemical assignment is not possible using NMR methods, the indicated structures are based on simple considerations of steric approach control which would suggest that the less hindered approach of the alkylidene carbene to the alkene involves *exo* attack from the face opposite to the phenyseleno moiety.



Scheme 4

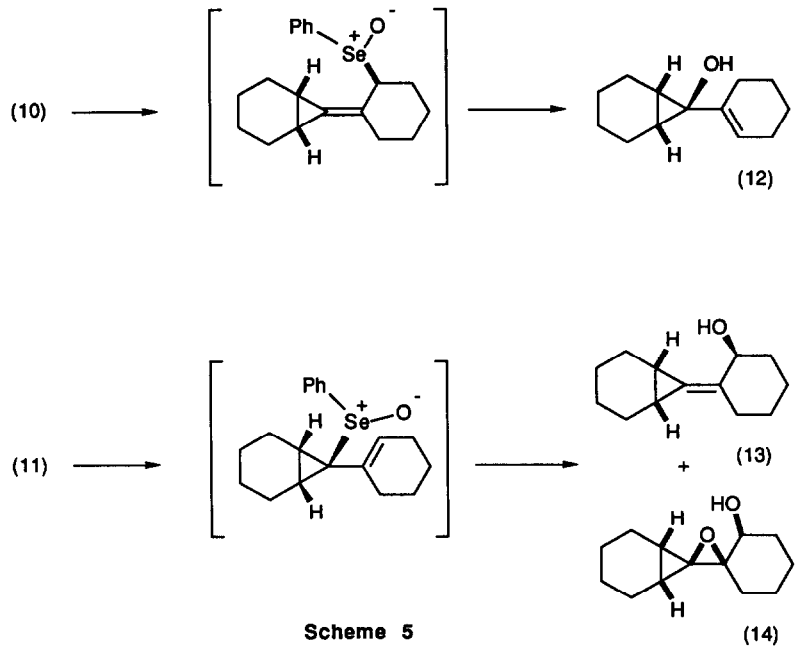
Difficulties were initially encountered in attempted isolation of pure allyl selenide (10) because of contamination with the phenylseleno- substituted vinylcyclopropane (11). Significant rearrangement was found to occur if the reaction mixtures were allowed to warm to room temperature prior to aqueous work up. However, by quenching the reaction at low temperature, regiochemically pure 7-(2-phenylselenocyclohexylidene)norcarane (10) could be isolated. A further improvement in the yield of (10) to 82% was noted at a later stage by employing 1,2-dimethoxyethane as solvent in place of tetrahydrofuran (*vide infra*). As anticipated in view of the strain energy released on rehybridisation at C-7 of the norcarane, the [1,3] allyl selenide rearrangement[12] of (10) occurs particularly readily and in quantitative yield with a half life at 4°C of around four days. The essentially irreversible nature of this process now confirms the speculation by Krief[7] that the reverse reaction is totally precluded in the parent system.

The ability to control the experimental conditions in order to achieve clean isolation of either the alkylidene cyclopropane (10) or the vinylcyclopropane (11) now set the stage for a systematic study of the [2,3] sigmatropic rearrangement of the derived selenoxide (Scheme 5).

Thus, treatment of crude selenide (10) with 30% aqueous hydrogen peroxide in tetrahydrofuran-pyridine at low temperature afforded the desired 7-cyclohexenyl-7-hydroxybicyclo[4.1.0]heptane derivative (12) in 58% overall yield from the phenylselenoketone (9), thereby establishing the feasibility of the basic tenets of Scheme 1.

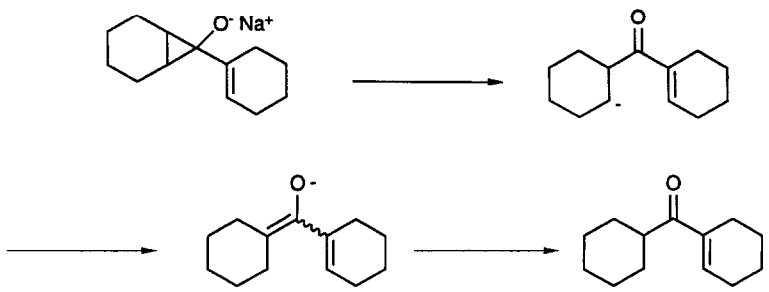
Similar oxidative treatment of (11) furnished the allylic alcohol (13) (53%). This latter reaction is a striking testimony to the power and irreversible nature of the oxidative rearrangement, requiring as it does the energetically demanding reinstatement of the strained cyclopropylidene double bond. A minor product, whose spectroscopic data are consistent with its formulation as an oxaspiropentane derivative (14), was also isolated from these and may presumably arise from phenylseleninic acid catalysed hydrogen peroxide epoxidation from the more accessible convex face of the initially formed allylic alcohol (13).

Obtaining (12) allowed us to examine the possibility of conducting an oxyanion assisted version of the vinylcyclopropane rearrangement which has been so successfully used by Danheiser[14] in the case of 2-vinylcyclopropanols. Unpublished observations by Salaun[15] state that this effect is not operative in the case of 1-vinylcyclopropanols although no product determination was reported. In the event, thermolysis of the sodium salt of (12) in toluene gave cyclohexyl cyclohex-1-enyl ketone (72%) in a process which is most easily rationalised by involving a stepwise fragmentation to a homoenolate which cannot undergo 5-endo trig ring closure, and subsequent prototropic rearrangement. (Scheme 6).



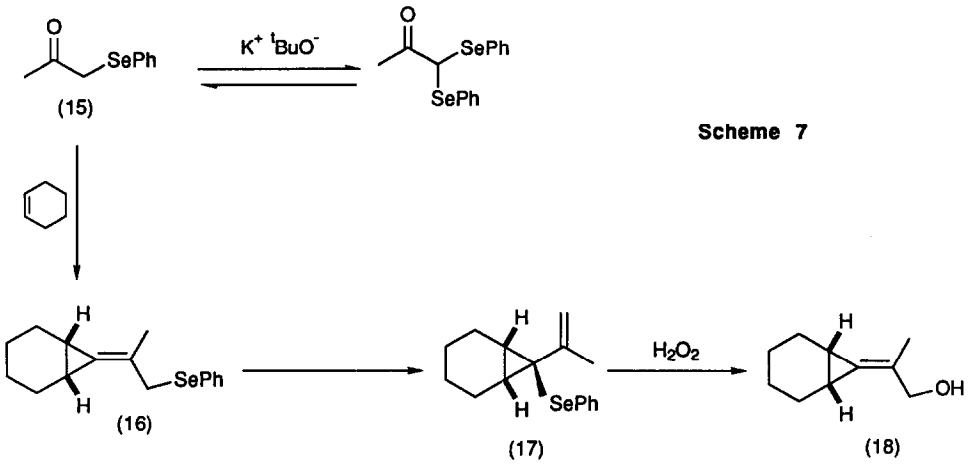
Scheme 5

At this juncture, we wished to demonstrate the general applicability of the method to other α–substituted phenylselenoketones.



Scheme 6

Accordingly, the reaction of 2-phenyl-selenoacetone[11] (15) with diethyldiazomethyl-phosphonate and cyclohexene was examined (Scheme 7). Under the experimental conditions described by Gilbert[8] using potassium *tert*-butoxide and tetrahydrofuran as solvent, a disappointing yield of 7% of the isomeric selenides (16) and (17) was obtained.



Scheme 7

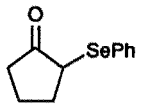
The recovery of a significant proportion of unreacted ketone (15) from this reaction was indicative of competitive enolate formation which, therefore, prevents nucleophilic attack by the alkyl diazomethyl phosphonate anion. Further evidence in support of this hypothesis came from the isolation of α,α-diphenylselenoacetone. Such a phenylseleno group migration has previously been observed under basic conditions by Liotta[16] and is postulated to arise by a series of intermolecular phenylseleno - proton exchange reactions to afford the most stable enolate.

Extensive experimentation involving a variety of metallic counterions (Li, Na, K, Zn, Cu, Ce) chosen either to enhance the nucleophilicity or to diminish the basicity of the diazomethyl phosphonate anion was unrewarding. In the event, however, a considerable improvement in the yield of (16) was found (43%) through the simple replacement of tetrahydrofuran by 1,2-dimethoxyethane as solvent. We had previously noted this solvent tendancy in other work which required condensation of an inductively stabilised phosphonate carbanion with a relatively hindered and acidic steroidal cyclopentanone.[17] A second contributory factor in the present instance may also reside in a superior ability of 1,2-dimethoxyethane to interact with the alkylidene carbene or diazoethene precursor in forming an ylide species which either behaves as a carbenoid or is in equilibrium with the free carbene, as suggested by Gilbert[8] in the case of tetrahydrofuran as solvent.

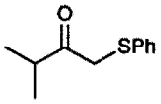
Once again, use of a low temperature work-up allowed isolation of the initial adduct (16). In this instance however, the ensuing rearrangement to give (17) takes place much more readily than in the 2-phenylselenocyclohexanone series, presumably since the allylic transposition leads to a terminal double bond which is less strained than in the cyclohexene case. In consequence, while the [2,3] sigmatropic rearrangement of the selenoxide derived from (17) affords the alkylidene cyclopropane (18) in good yield (51%), oxidation of selenide (16) to afford the corresponding vinylcyclopropanol is not sufficiently fast to be a preparatively useful reaction.

The delicate balance between the undesirable pathway of competing enolate formation from the α-phenylseleno carbonyl compound and the required deprotonation and nucleophilicity of the diazophosphonate anion was underscored by the failure of substrates (19)-(22) to yield carbene adducts. The recovery of unchanged 2-phenylselenocyclopentanone (19) and isopropyl phenylthiomethyl ketone (20) can be directly attributed to their even greater acidity[18] relative to 2-phenylselenoacetone, and clearly places a limitation in terms of pKa for the selection of the α-phenylselenocarbonyl partner in this process. Reaction of either isomer of the unsymmetrical substrates (21) or (22) led to recovery of a mixture of the diselenated ketone (23)

and both monoselenated starting materials, once again, by intermolecular rearrangement. The observed scrambling in the case of (1-methyl-1-phenylselenoethyl) methyl ketone (21), in which the phenylseleno group does not directly contribute to the acidity of the alpha protons, indicates that relief of steric congestion may also play a role in this rearrangement reaction.



(19)



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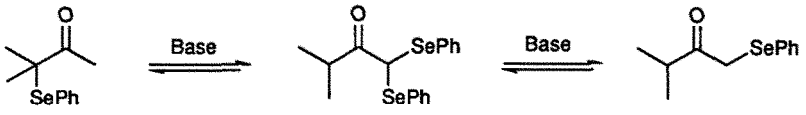
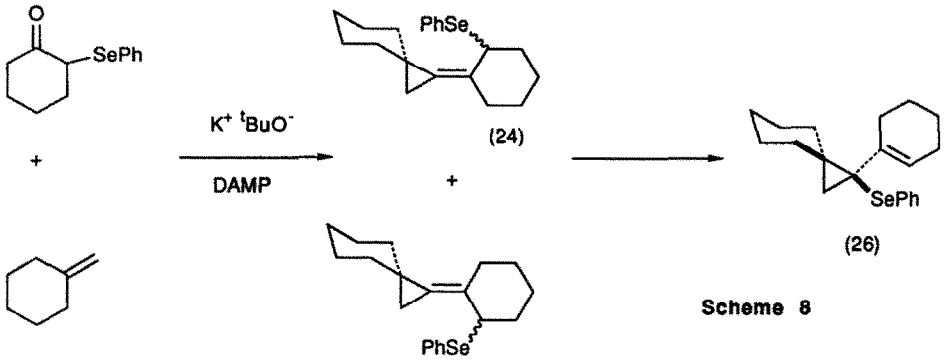


(21) (23) (22)

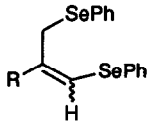
Having examined the scope of this approach with respect to the α-phenylselenocarbonyl partner, we then probed the generality with regard to the tolerance of alkene substitution pattern.

As expected, treatment of 2-phenylselenocyclohexanone with diazomethylphosphonate anion in the presence of methylenecyclohexane initially afforded an isomeric mixture of (24), (25) and (26). Alkylidenecyclopropanes (24) and (25), however, rearranged on standing to afford the single compound (26) in 65% yield overall. (Scheme 8).



Scheme 8

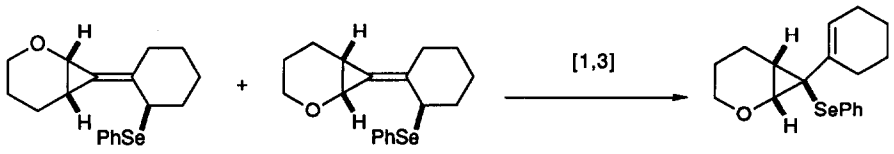
By way of contrast, styrene proved to be an unreactive olefinic partner. The spectral properties of the major product isolated from an attempted reaction using α-phenylselenoacetone are consistent with the labile bis-selenide structure (27), and an analogous product (28) was similarly prepared using phenylselenomethyl isopropyl ketone. In this case, a possible mechanism involving intermolecular trapping of the initially formed α-phenylselenoalkylidene carbene by substrate α-phenylselenoketone may be operating.



(27) R = CH_3

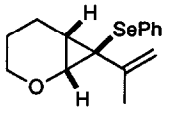
(28) R = $(CH_3)_2CH$

Use of the electron rich enol ether unit of dihydropyran was more rewarding. Thus, trapping of the alkylidene carbene from α-phenylselenocyclohexanone afforded a virtually quantitative yield of isomeric adducts (29) and (30) (99%) which underwent facile allyl selenide rearrangement on standing to afford the desired vinylcyclopropyl selenide (31). (Scheme 9).



(29) (30) **Scheme 9** (31)

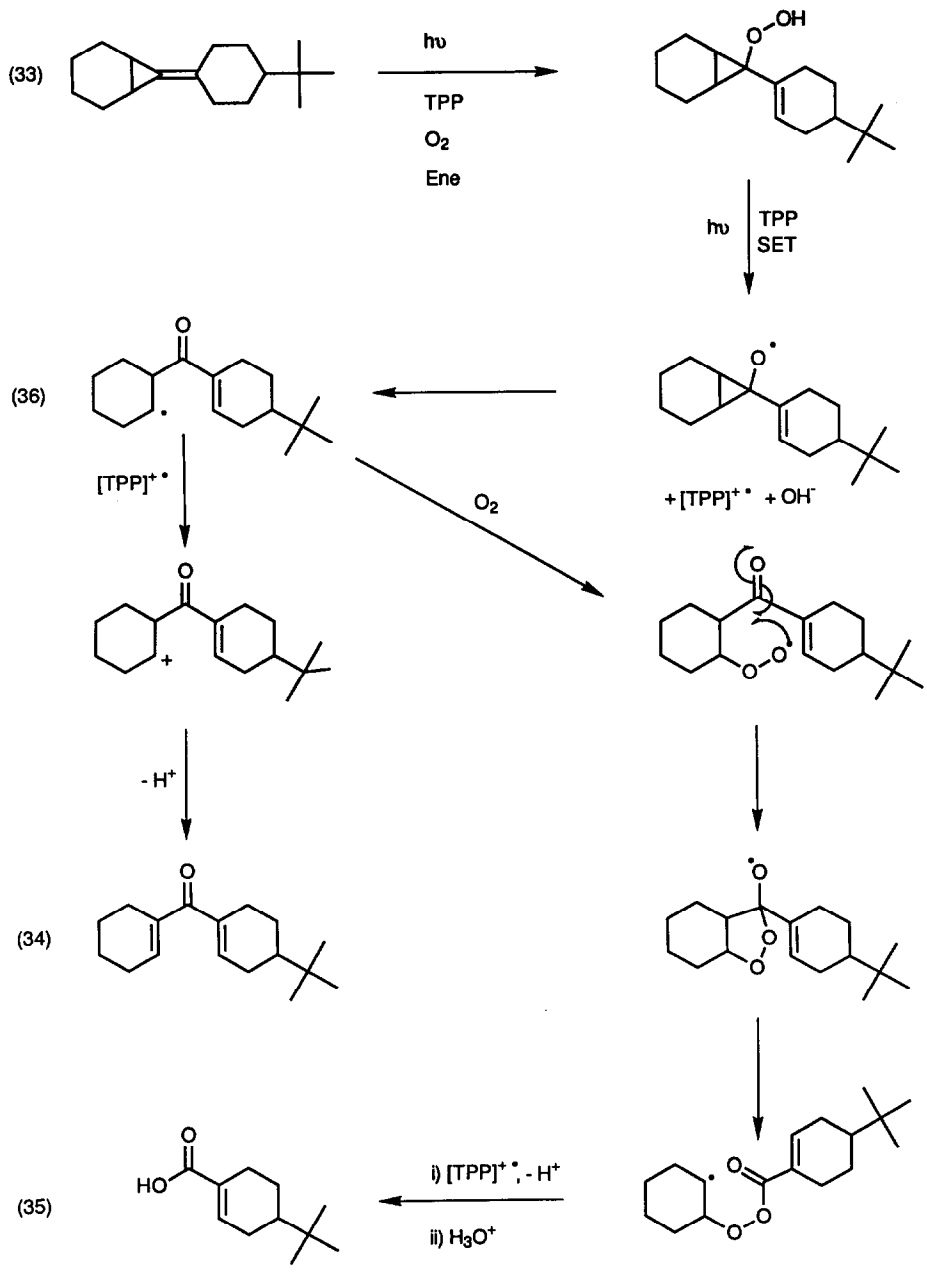
In similar fashion, base induced condensation of α-phenylselenoacetone and diethyldiazomethyl phosphonate in the presence of dihydropyran gave the trapped and rearranged adduct (32) directly, as a result of the increased facility for allylic selenide rearrangement previously noted in experiments using cyclohexene as the carbene trap.



(32)

Finally, in view of the fact that the Gilbert method of trapping simple unfunctionalised alkylidenecarbenes by olefins is a highly efficient process, we have also made a brief study of the allylic oxidation of such substrates as an alternative route to 1-vinyl-1-cyclopropanol derivatives.

Our attention was initially focused on the possibility of using the singlet oxygen ene reaction. Indeed, studies by Conia and coworkers[19] using alkylidene cyclopropanes had not only established the validity of this process, but also shown that the product allylic hydroperoxides, although susceptible to radical rearrangements, were sufficiently stable at low temperature and could be reduced *in situ* with triphenylphosphine to the alcohol. In the case of the alkene (33) (Scheme 10) however, we were unable to detect the presence of the desired vinylcyclopropanol following photooxygenation and reductive work up. Reactions performed at room temperature gave complex mixtures from which the cross conjugated dienone (34) was isolated in low yield, presumably as a result of sensitiser-mediated radical rearrangement of the initial photoproduct as shown in Scheme 10. Contrastingly, at lower temperatures and increased oxygen concentrations, the carboxylic acid (35) was formed in good yield (65%). A possible rationale for the formation of this latter product is shown in Scheme 10, and involves capture of the common carbon centred

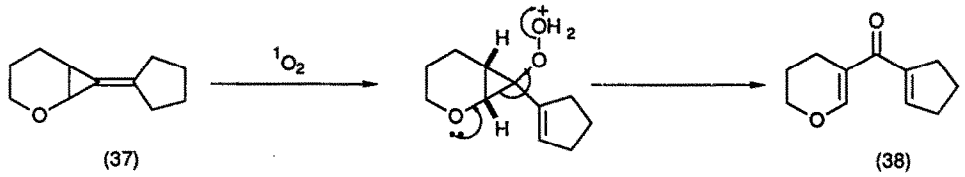


TPP = Tetraphenylporphyrin
SET = Single Electron Transfer

Scheme 10

radical (36) by triplet oxygen, cyclisation of the resultant peroxy radical, and subsequent β-scission of the peroxy lactol derived alkoxyl.

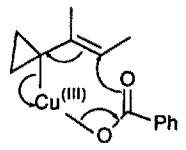
Similarly, the addition of singlet oxygen to alkene (37) gave an analogous dienone (38) in 42% yield. The breakdown of the intermediate hydroperoxide in this instance is undoubtedly facilitated by the presence of the ring oxygen atom and may proceed either *via* the radical pathway or more probably by simple acid catalysis (Scheme 11).



(37) (38)

Scheme 11

As the above observations served to convince us that the addition of singlet oxygen was a method which was sensitive both to substrate structure and to experimental variation, our attention was directed to the copper catalysed allylic oxidation of alkenes by peresters.[20] Recent mechanistic studies by the Beckwith group[20] have suggested that the observed preference for formation of the *less* thermodynamically stable olefin in such reactions may be attributed to a preference for the formation of the more stable allylic organocopper(III) intermediate which then delivers the allylic benzoate functionality by an intramolecular seven-membered cyclic transition state. In terms of alkylidenecyclopropane functionalisation, such an argument would suggest that intermediates such as (39) would be of lower energy than (40).



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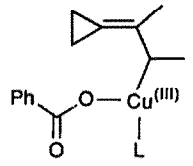
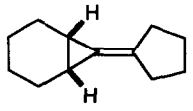


(40)

We reasoned that reinstatement of the strained alkylidene cyclopropane double bond in the rearrangement step from (39) would be a demanding process and that opportunities could exist either for equilibration of allylic organocopper intermediates or for a thermodynamically driven [3,3] sigmatropic rearrangement in the product allylic esters. In the event, treatment of a mixture of 7-cyclopentylidenenorcarane (41) and catalytic cuprous chloride in refluxing benzene with *t*-butylperbenzoate afforded a 1:1 mixture of the two allylic benzoates (42) and (43), while a second experiment involving slow syringe-pump addition of perbenzoate to the alkene and extended heating gave a 70:30 mixture in favour of (42). The indicated stereochemistry is derived from consideration of reagent approach from the convex face of (41). Clearly, although both regioisomers are formed, this stringent test provides additional evidence for the Beckwith mechanism[20] and reflects the importance of intermediates such as (39).



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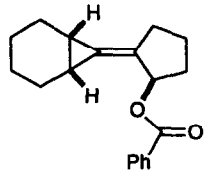

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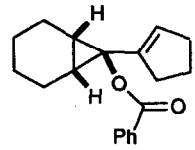

(43)

In summary, the present paper has demonstrated that within the cited limitations of α-phenylselenocarbonyl basicity, α-phenylselenoalkylidene carbenes may be efficiently generated and trapped by both normal and electron rich alkenes. The resultant allylically substituted alkylidenecyclopropanes, either by simple thermal or oxidative sigmatropic rearrangement, then give rise to the important class of 1-heterosubstituted-1-vinylcyclopropanes, thereby formally constituting an equivalent to the direct addition of an allylic α-heterosubstituted carbene to an alkene.

Experimental

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin Elmer 983 G grating infrared spectrophotometer as thin films, or as dichloromethane or carbon tetrachloride solutions. ^{1}H and ^{13}C nmr spectra were recorded at 90 MHz and 22.5 MHz respectively on a Jeol FX 90 Q; at 250 MHz and 62.9 MHz respectively on a Bruker WM-250; and at 500 MHz and 125.8 MHz respectively on a Bruker AM-500, with tetramethylsilane as internal standard. ^{31}P n.m.r. spectra were recorded at 36.2 MHz on a Jeol FX 90 Q with 85% aqueous phosphoric acid in deuterium oxide as external reference. Spectra were recorded in deuteriochloroform, deuteriobenzene, or deuterium oxide as specified. ^{13}C assignments were routinely confirmed by J-modulated spin echo and/or off resonace pulse decoupled experiments as appropriate. Mass spectra were recorded on a VG Micromass 7070B instrument. Elemental microanalysis was performed by the staff of the Imperial College Chemistry department microanalysis laboratory.

Analytical thin layer chromatography was performed on precoated glass-backed plates (Merck Kieselgel 60 F_{254}). Preparative thin layer chromatography was performed on (20 x 20 cm) glass plates coated with Merck Kieselgel 60 GF_{254}. Preparative column chromatography was performed at low positive pressure on Merck Kieselgel 60 (230-400 mesh); "Silica" refers to this grade of Kieselgel.

"Petrol" refers to redistilled light petroleum ether with b.p. 40-60°C unless otherwise indicated. "Ether" refers to diethyl ether. Ether, tetrahydrofuran, dimethoxyethane, toluene, and benzene were distilled from sodium - benzophenone ketyl under argon immediately prior to use. Dimethylformamide was distilled from calcium hydride at reduced pressure, and stored over 4Å molecular sieves under an argon atmosphere prior to use. Dimethylsulphoxide, distilled from 4Å molecular sieves was stored likewise. Dichloromethane was freshly distilled from phosphorus pentoxide under an argon atmosphere prior to use. 1,1-Dichloroethane was passed through a pad of neutral alumina prior to distillation from 4Å sieves under an argon atmosphere. All other solvents and reagents were purified by standard methods.

Unless stated otherwise, all reactions were performed under an atmosphere of dry argon in degassed solutions. Glassware was oven dried at 150°C before use. Solutions were concentrated with a rotary evaporator at water pump pressure, followed by static evaporation at an oil pump. α-Phenylselenoketones were prepared by literature methods.[11]

Preparation of 1,3,5-Tri-N-benzylhexahydro-S-triazine (6).
To benzylamine (41.4g, 386 mmol) at 0°C was added with stirring a 40% solution of formalin (38.8ml, 400 mmol) slowly, such that the temperature remained below 10°C. To the precipitated gum was added 3M aqueous sodium hydroxide (40 ml), and the mixture stirred briefly with a glass rod. After standing in ice for 0.3h, ether (100 ml) was added, and the mixture stirred until all precipitate dissolved. The aqueous phase was separated and extracted with ether. The combined organic layers were washed with brine. The solvents were stripped at reduced pressure to afford the S-triazine as a colourless oil. Crystallisation from ethanol (450 ml per mol) at -10°C by addition of water (in 30 ml portions per 450 ml) afforded, after drying at 0.1 torr, tri-N-benzylhexahydro-S-triazine (6) (39.7g, 86%) as colourless rods. m.p. 50°C (lit 50°C);[21] ν_{max} (film) 2861, 1360, 1168, 1118, 1072, 1016, 982, 739, and 699 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 3.45 (6H, s, N-CH_2-N), 3.7 (6H, s, Ph-CH_2), 7.37 (15H, m, PhH); m/z 357(M^+), 267 (M-Ph-CH_2), 178 (M-2(Ph-CH_2)), 164, 119, 91.

Preparation of N-Benzylaminomethyl diethyl phosphonate hydrochloride (7).
To a solution of S-triazine (6) (39.7 g, 111 mmol) under argon was added diethyl phosphite (46.1g, 43 ml, 334 mmol), and the mixture was heated with stirring at 100°C for 6h. The mixture was then heated at 50°C, 0.1 torr for 18 h to remove volatile impurities. The resulting crude amine was taken up in dry ether (800 ml), cooled to 0°C in an ice/salt bath, and dry HCl gas passed through slowly with stirring, when the colourless hydrochloride salt precipitated. Filtration and drying in vacuo over $CaCl_2$ afforded N-benzylaminomethyl diethyl phosphonate hydrochloride[10] (7) (95 g, 83%) m.p. 89-90°C; δ_P (36.2 MHz; D_2O) 18.82. (Found: C, 49.28; H, 7.32; N, 4.74; Cl, 11.91. $C_{12}H_{21}NO_3PCl$ requires: C, 49.07; H, 7.21; N, 4.77; Cl, 12.07%).

Preparation of Aminomethyl diethyl phosphonate
To a solution of N-benzylaminomethyl phosphate hydrochloride (7) (109g, 379 mmol) in absolute ethanol (500 ml) was added 10%-Pd/carbon catalyst (3 g). The efficiently stirred mixture was exhaustively hydrogenated under a slight positive pressure of hydrogen. Progress was monitored by ^1H and ^{31}P n.m.r.. On completion, the catalyst was filtered, and the solvent stripped at reduced pressure. Aqueous (0.880) ammonia solution was added to the residue until well basic, and the free amine was extracted with DCM. The combined extracts were washed with brine and dried (Na_2SO_4). The solvent was stripped at reduced pressure, and the residual oil distilled to afford aminomethyl diethyl phosphonate[10] (59g, 95%) as a colourless oil b.p. 92°C 0.005 torr; ν_{max} (film) 3370(N-H), 3306,2982, 2907,1606,1443,1390,1233,1164,1054,968, and 775 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.35 (6H, t, J 7Hz, $MeCH_2OP$), 1.52 (2H, br s, NH_2), 3.0 (2H, d, J 10Hz, P-CH_2-NH_2), 4.13 (4H, m $MeCH_2OP$); δ_P (36.2 MHz; $CDCl_3$) 24.53 free amine, (20.73 hydrochloride). Distillation is not normally necessary prior to diazotisation.

Preparation of Diazomethyl diethyl phosphonate (8)
To a solution of aminomethyldiethyl phosphonate (39.0g, 232 mmol), in DCM (217 ml) at -5°C was added with stirring aqueous sodium nitrite (19.33 g, 280 mmol, 108 ml water), followed by glacial acetic acid (28g, 462 mmol) dropwise over 10 min. On stirring at 0°C for 4h the DCM layer became bright yellow. The mixture was transfered to a chilled separating funnel, and the DCM layer run into cold aqueous potassium carbonate (75g in 100 ml water). The aqueous layer was extracted once with DCM, and the combined organic phases shaken with the potassium carbonate until well neutralised. The layers were separated, and the organic phase dried (K_2CO_3), filtered through a short pad of neutral alumina, and the solvent stripped at reduced pressure below 40°C. Distillation of the residual oil afforded diazomethyl diethyl phosphonate[10] (8) as a bright yellow liquid (30.5g, 73%), stable at 4°C under an argon atmosphere. b.p. 86-88°C, 0.2 torr.; ν_{max} (film) 3482,2986,2103 (N=N=C strong), 1298,1247,1025,970, and 826 cm^{-1}; δ_H (250 MHz; $CDCl_3$), 1.32 (6H, t, J 7.5 Hz, $MeCH_2OP$), 3.75 (1H, d, J 11Hz, P-CHN_2), 4.09 (4H, m, $MeCH_2OP$);
δ_P(36.2 MHz; $CDCl_3$) 17.36; *m/z* 178 (M^+), 133 (M-OEt), 121 (M-N_2-Et), 105 (133-N_2), 93,65 (base).

7-(2-Phenylselenocyclohexylidene)bicyclo[4.1.0]heptane (10)
To potassium *t*-butoxide (336 mg, 3 mmol) in DME (5 ml) and cyclohexene (5 ml) at -78°C was added a

solution of 2-phenylselenocyclohexanone[11] (9) (630 mg, 2.37 mmol) in DME (1 ml), followed by DAMP (8) (650 mg, 3.65 mmol) dropwise over 1h, when evolution of nitrogen occurred. The mixture was stirred a further 1h then allowed to stand at -78°C for 18h. Ether (5 ml) was addded, followed by saturated aqueous ammonium chloride (5 ml) and the reaction allowed to warm to room temperature. Extraction from water with petrol, drying ($MgSO_4$), concentration at reduced pressure, and chromatography of the residue (Silica-5% ether/petrol) were performed rapidly to afford 7-(2-phenylselenocyclo-hexylidene)-bicyclo[4.1.0]heptane (10) as a pale yellow oil (678 mg, 82%). ν_{max} (film) 3067, 2928,2852,1576, 1473, 1443,1434,1329,1250,1174, 1155, 1064, 1022, 997, 738, 690 and 653 cm^{-1}; δ_H(90 MHz; $CDCl_3$) 0.72-2.80 (18H, m, all aliphatic-H, except 2'-H), 4.38 (1H, m, 2'-H), 7.25 (3H, m, m, p-Ar-H), 7.53 (2H, m, o-Ar-H); δ_C(22.5 MHz; $CDCl_3$) 12.37, 13.16 (C-1, C-6), 21.10, 21.40 (C-3,C-4), 22.62, 22.74 (C-2, C-5), 27.38, 27.56, 28.72, 30.01 (C-3', 4', 5'), 33.18, 33.49 (C-6'), 48.86, 49.66 (C-2'), 125.76, 126.86 (C-7, C-1'), 130.71 (Se-*C*Ar), 127.05-135.53 (Ar); *m/z* 332 (M^+), 251 (M-C_6H_9), 175 (M-SePh), 157 (SePh), 147, 133, 119, 105, 91,81, 77, 67, 55, 41. (Found: M^+, 332.1049. $C_{19}H_{24}Se$ requires: M+, 332.1043).

Allylselenide Rearrangement of 7-(2-Phenylselenocyclohexylidene)bicyclo[4.1.0]heptane (10).

A solution of 7-(2-phenylselenocyclohexylidene)norcarane (10) (100mg, 0.3 mmol) in $CDCl_3$ (0.5 ml) was stored at 4°C without shielding from stray light sources for a number of weeks. The progress of the allyl selenide rearrangement was followed by ^1H n.m.r. The chemical shift of the 2'-H changes from δ 4.38 to 5.12. The rearrangement proceeds to completion to afford 7-(cyclohexen-1-yl)-7-(phenylseleno)-bicyclo[4.1.0]heptane (11) as a pale yellow oil. ν_{max} (film) 2930, 2856, 1660, 1575, 1473, 1339, 1299, 1174, 1135, 1064, 1022, 737, and 690 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 0.91 (2H, m, 1-H, 6-H), 1.05-2.35 (14H, m, 2-5-H_2, 3'-6'-H_2), 5.15 (1H, m, 2'-H), 7.25 (3H, m, m,p-ArH), 7.53 (2H, m, o-ArH); δ_C(62.9 MHz; $CDCl_3$) 21.39 (C-3, C-4), 21.53 (C-2,C-5), 22.42 (C-1,C-6), 23.13 (C-4', C-5'), 25.48 (C-3'), 27.80 (C-6'), 36.95 (C-7), 131.41 (C-2'), 134.28 (C-1'), 127.28 (p-Ar), 128.17 (m-Ar), 128.55 (Se-CAr), 135.20 (o-Ar); *m/z* 332 (M^+), 251 (M-C_6H_9), 175 (M-SePh), 157 (SePh)., 133, 119, 105, 91, 81, 77, 67, 55. (Found: M^+, 332.1039. $C_{19}H_{24}Se$ requires: M^+, 332.1043).

Oxidative Rearrangement of Allyl Selenides (10) and (11).

To a stirred solution of the allyl selenides (10) and (11) (1.40 g, 4.23 mmol) in THF-pyridine (3:1 v/v) (100 ml) at -25°C was added 30% aqueous H_2O_2 (2.6 ml, 23 mmol, 5.4 equiv.) dropwise over 3 min. The mixture was stirred at -25°C for 2.3h, then diluted with ether (100 ml). The aqueous layer was separated, the organic phase washed with water, brine, dried (Na_2SO_4), and concentrated at reduced pressure. The residue was chromatographed (Silica-20% ether/petrol) to afford in order of elution, the allylic alcohols (12) and (13), (354 mg, 44%) as colourless needles, followed by the epoxide (14) (240 mg, 27%). Epoxide (14) was purified by fractional crystallisation from petrol (40-60 b.p), as colourless rods. The allylic alcohols were inseparable, proton n.m.r. of the mixture indicating a ratio (12): (13) of 1: 1.8 by integration of peaks at δ 5.79, 4.24. The spectroscopic properties were consistent with those of pure materials obtained by other means (*vide infra*).

Data for Dispiro(bicyclo[4.1.0]heptane-7,2'-oxirane-3',1"-(2"-hydroxycyclohexane) (14).

Colourless rods (petrol 40-60 b.p.) m.p. 81-84°C; ν_{max} (DCM) 3550, 2934, 2858, 1448, 1073, 1035, 1004, and 860 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.0-2.2 (19H, m all H except 2"-H), 3.78 (1H, dd, J 9.4 Hz, 4.7 Hz, 2"-H); δ_C(62.9 MHz; $CDCl_3$) 11.74, 13.75 (C-1, C-6), 19.99, 20.65 (C-3, C-4), 21.87, 21.91(C-2,C-5), 23.18 (C-4"), 23.34(C-5"), 31.06 (C-6"), 33.80(C-3"), 66.88(C-7), 68.27(C-2"), 68.39(C-1"); *m/z* 208 (M^+), 190(M-H_2O), 162 (190-C_2H_4 retro D.A), 148, 133, 126 (base), 111, 98($C_6H_{10}O$), 81, 70, 41. (Found: C, 74.97; H, 9.79. $C_{13}H_{20}O_2$ requires: C, 74.96; H, 9.68%).

Oxidative Rearrangement of 7-(Cyclohexen-1-yl)-7-phenylselenobicyclo[4.1.0]heptane (11).

To a solution of the selenide (11) (949mg, 2.87 mmol) in pyridine (20 ml), was added with stirring a 15%

w/w solution of H_2O_2 (14 ml, 20 equiv.), and the mixture stirred for 0.5h. On dilution with ether (20 ml), the mixture was washed with 10% aq. HCl (2 x 40 ml), brine, dried (Na_2SO_4), and concentrated at reduced pressure. Chromatography of the residue (Silica-20% ether/petrol) afforded 7-(2-hydroxocyclo-hexylidine)-bicyclo[4.1.0]heptane (13) (292 mg, 53%) as colourless needles, (petrol 40-60 b.p) m.p. 96-99°C ν_{max} (CCl_4) 3604 (OH), 3470, 2934, 1705 (C=C), 1447, 1379, 1222, 1078, 1034, 1000, and 968 cm^{-1}; δ_H (90 MHz; $CDCl_3$), 4.24 (1H, m, 2'H), 0.8-2.7 (19H, m, all other protons); δ_C (22.5 MHz; $CDCl_3$) 10.11, 12.74 (C-1, C-6), 21.03, 21.22 (C-3, C-4), 22.32, 22.68 (C-2, C-5), 23.35 (C-4'), 27.20 (C-5'), 30.25 (C-6'), 35.81 (C-3'), 71.75 (C-2'), 122.35 (C-7), 129.91 (C-1'); *m/z* 192 (M^+), 174 (M-H_2O), 163, 149, 145, 131, 109, 95 (C_7H_{11}), 81 (C_6H_9), 79 (C_6H_7), 67.41; (Found: M^+, 192.1516. $C_{13}H_{20}O$ requires: M^+, 192.1514).

Preparation of 7-Cyclohexenyl-7-hydroxybicyclo[4.1.0]heptane (12)

To potassium *t*-butoxide (180 mg, 1.60 mmol) in dry DME (2.5 ml) and cyclohexene (2.5 ml) at -78°C was added a solution of 2-phenylselenocyclohexanone[11] (9) (309 mg, 1.21 mmol) in DME (1 ml). To the mixture was added dropwise with stirring over 1h DAMP (8) (320 mg, 1.8 mmol), when evolution of nitrogen occurred. The mixture was stirred a further 2h at -78°C, and then quenched by slow addition of saturated aqueous NH_4Cl (5 ml), and warming to ambient temperature. The mixture was poured into water, and extracted with petrol. After concentration at reduced pressure below room temperature, the crude selenide was taken up in THF: pyridine (3:1) (30 ml), chilled to -25°C (ice/acetone), and 30% aqueous hydrogen peroxide (0.75 ml, 6.6 mmol) added dropwise. After stirring 2h at -25°C, the mixture was allowed to warm to room temperature, poured into water, and extracted with petrol. The extracts were dried ($MgSO_4$) and concentrated at reduced pressure, residual pyridine being removed at 0.1 torr. The residue was chromatographed (Silica -20% ether/petrol) to afford 7-(cyclohexen-1-yl)-7-hydroxy-bicyclo[4.1.0]heptane (12) (138mg, 58%) as colourless needles m.p. 95-98°C; ν_{max} (CCl_4) 3602 (OH), 2934, 2856, 1448, 1379, 1222, 1187, 1078, 1034, 967 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.0-2.5 (18H, m, all aliphatic-H), 4.24 (1H, m, OH), 5.79 (1H, m, 2'-H); δ_C(62.9 MHz; $CDCl_3$) 20.49 (C-3, C-4), 21.28 (C-2, C-5), 21.71 (C-1, C-6), 22.26(C-4'), 22.93 (C-5'), 25.25 (C-3'), 26.22 (C-6'), 63.21 (C-7), 128.69 (C-2'), 136.08 (C-1'); *m/z* 192 (M^+), 174 (M-H_2O), 146 (174-C_2H_4, retro D.A.), 131, 109, 91 (tropylium), 81 (C_6H_9), 41. (Found: M^+, 192.1516. $C_{13}H_{20}O$ requires: M^+, 192.1514).

Oxy-anion Mediated Rearrangement of 7-Cyclohexen-1-yl-7-hydroxybicyclo[4.1.0)]-heptane (12)

To a stirred slurry of sodium hydride (24 mg of 60% oil dispersion, 0.6 mmol, 2 equiv.) in toluene (5 ml) was added a solution of vinylcyclopropanol (12) (58mg, 0.3 mmol) in toluene (15 ml), and the mixture stirred 45 min at room temperature. The mixture was then heated at reflux for 2.25h, cooled, and cautiously quenched with saturated aqueous NH_4Cl. The organic layer was separated, dried (Na_2SO_4), and concentrated at reduced pressure. The residue was chromatographed (Silica-10% ether/petrol) to afford cyclohexyl cyclo-hex-1-enyl ketone (42mg, 72%) as a colourless oil. ν_{max} (film) 2930, 2854, 1662, 1633, 1448, 1244, 1197, and 984 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.05-1.85 (14H, m, 2'-6'H_2,4-H_2, 5-H_2), 2.16(4H, m, 3-H_2, 6-H_2) 2.90, (1H, m, 1'-H), 6.83 (1H, m, 2-H); δ_C(62.9 MHz; $CDCl_3$), 21.69(C-4, C-5), 22.12(C-4'), 23.45(C-3), 25.95(C-3', C-5'), 26.06 (C-6), 29.80(C-2', C-6'), 44.27(C-1'), 138.25(C-2), 138.40 (C-1), 204.80(C=O); *m/z* 192 (M^+), 163, 109 (M-C_6H_{11}, base), 81 (109-CO), 55,41. (Found: M^+, 192.1516. $C_{13}H_{20}O$ requires: M^+, 192.1514.

Preparation of 7-(1-(Phenylselenomethyl)ethylidene)bicyclo[4.1.0]heptane (16).

To freshly sublimed potassium *t*-butoxide (526 mg, 4.7 mmol) at -78°C in DME (4 ml) and cyclohexene (6 ml) was added a solution of DAMP (8) (876 mg, 4.9 mmol, 1.5 equiv) in DME (2 ml) dropwise with stirring. After 20 min, a solution of 2-phenylselenoacetone[11] (15) (678 mg, 3.18 mmol) in DME (5 ml) was added dropwise over 15 min, and the resulting mixture stirred at -78°C for 48h with provision for venting of the nitrogen evolved. The mixture was allowed to warm to room temperature, poured into water, and extracted with petrol. The extracts were dried (Na_2SO_4), concentrated at reduced pressure, and chromatographed (Silica-5% ether/petrol) to afford 7-(1-(phenylselenomethyl)ethylidene)-

bicyclo[4.1.0]heptane (16). (396 mg, 43%) as a pale yellow oil. ν_{max} (film) 2931, 2857, 1576, 1473, 1435, 1369, 1022, 895, 736, and 690 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.0-1.8 (10H, m, 1-H, 6-H, 2-5-H_2), 1.92 (3H, t, J 1.7Hz, 1'-Me), 3.7 (2H, A:B q, J_{gem} 10.6 Hz, CH_2SePh), 7.23 (3H, m, m, p-Ar-H), 7.50 (2H, m, o-ArH); δ_C(62.9 MHz; $CDCl_3$) 12.92, 13.38 (C-1, C-6), 19.04 (C-2'), 21.33, 21.42 (C-3, C-4), 22.59, 22.68 (C-2, C-5), 33.06 (CH_2SePh), 120.87 (C-1'), 130.78 (C-7), 126.81, 128.65, 133.72(p,m,o-ArC), 131.20(SeCAr); *m/z* 292 (M^+), 157 (SePH), 135 (M-SePh), 131, 117, 91, 77, 41. (Found: M^+, 292.0729. $C_{16}H_{20}Se$ requires: M^+, 292.0730). Also in the product distribution were diphenyldiselenide, 2-phenylselenoacetone (15) ν_{max} (film) 3054, 2998, 1700, 1576, 1476, 1435, 1355, 1229, 738, and 690 cm^{-1}; δ_H (90 MHz; $CDCl_3$), 2.22 (3H, s, Me), 3.54 (2H, s, CH_2SePh), 7.23 (3H, m,p-Ar), 7.46 (2H, o-Ar), and 2,2-diphenylselenoacetone (18) ν_{max} (film), 3053, 1695, 1473, 1435, 1352, 1238, 1216, 1021, 740, and 690 cm^{-1}; δ_H (90 MHz; $CDCl_3$), 2.32 (3H, s, Me), 4.95 (1H, s, $CH(SePh)_2$), 7.25 (6H, m, m,p-Ar), 7.52 (4H, m, o-Ar). Aldol products were not detected.

Allyl Selenide Rearrangement of 7-(Phenylselenomethylethylidene)norcarane (16).
Facile allyl selenide rearrangement occurred on standing, or if the reaction mixture was allowed to stand at room temperature for any length of time prior to workup. The 7-phenylseleno-7-(propen-2-yl)-bicyclo[4.1.0]heptane (17) was obtained in quantitative yield when a concentrated solution was stored at 4°C for prolonged periods, as a pale yellow oil. ν_{max} (film) 2934, 2857, 1474, 1446, 895, and 736cm^{-1}; δ_H(90MHz; $CDCl_3$) 0.5-2.0 (10H,m,1-H,6-H,2-5-H_2), 1.93 (3H,s,C-2'-Me), 4.55 (1H,m,1'-H_1), 4.85 (1H,m,1'-H1), 7.02 (3H,m, m,p-ArH), 7.32 (2H,m, o-Ar); δ_C(22.5 MHz; $CDCl_3$) 21.28(C-2,3,4,5), 22.19 (C-1,C-6), 23.41(C-2'-Me), 36.05(C-7), 116.55(C-1'), 141.94(C-2'), 127.23,128.57, 134.18(o,m,p-ArC), 131.39(SeCAr); *m/z* 292(M^+), 157(SePh), 135(M-SePh), 131, 117, 107, 93, 91, 79, 77, 55.
(found : M^+, 292.0734 . $C_{16}H_{20}Se$ requires: M^+, 292.0730).

Oxidative Rearrangement of Allyl Selenides (16) and (17)
To a solution of mixed allyl selenides (16) and (17) (304 mg,1.04 mmol) in pyridine (5 ml) at 0°C, was added dropwise with stirring 15% aqueous hydrogen peroxide (4 ml, 17.5 mmol) over 1 min. After stirring an additional 30 min at room temperature, the mixture was diluted with ether, washed with water, and concentrated at reduced pressure. Residual pyridine was removed at 0.1 torr. The residue was chromatographed (Silica-20% ether/petrol) to afford the transposed allylic alcohol (18) as a colourless oil.
7-(1-Hydroxymethylethylidene)-Bicyclo[4.1.0]Heptane (18) (80.3 mg, 50.7%)
ν_{max}(DCM) 3600, 2930, 2856, 1445, 1378, 1054, 1000, and 969 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.05-1.90 (11H,m,1-H,6-H,2-5-H_2,OH), 1.81 (3H,t,J 1.5Hz, C-1'-Me), 4.17 (2H,br.s,CH_2-OH); *m/z* 151(M^+-H), 137(M-Me), 134(M-H_2O), 119(134-Me), 109,95,93,91,81,67,55,41. (Found: M^+-H,151.1123 . $C_{10}H_{16}O$ requires M^+-H, 151.1123). 7-Hydroxy-7-(Propen-2-yl)-Bicyclo[4.1.0]Heptane (12mg, 7.6%) ν_{max}(DCM) 3575, 2934,2858,1447,1202,1178,1073, and 913 cm^{-1}; δ_H(250 MHz;$CDCl_3$) 1.0-1.9 (11H,m,1-H,6-H,2-5-H_2,OH), 1.84 (3H,t, J 1.1Hz,C-2'Me), 5.03 (2H,t,J 1.1Hz,1'-H2); *m/z* 151(M^+-H), 137(M-Me), 135(M-OH), 119,111(M-C_3H_5), 109,95(C_7H_{11}), 91, 81, 69, 55, 43 (base), 41(C_3H_5).
(Found: M^+-H, 151.1123 . $C_{10}H_{16}O$ requires : M^+-H, 151.1123).

Reaction of Methylenecyclohexane with 2-Phenylselenocyclohexanone
To a suspension of potassium hydride (425 mg,3.7 mmol) in DME (3ml), and dry methylenecyclohexane (2.5 ml, 21 mmol) was added t-butanol (200 µL,2.1 mmol), and the mixture was cooled to -78°C. A solution of DAMP (8) (800 mg, 4.49 mmol) in DME (0.5 ml) was added dropwise with stirring. The mixture was stirred for 10 min then 2-phenylselenocyclohexanone (511 mg, 2.03 mmol) in DME (1 ml) was added dropwise over 15 min when the yellow solution became orange and nitrogen was evolved. The mixture was stirred at -78°C for 14 h then allowed to warm to -40°C before quenching by cautious addition of saturated aqueous NH_4Cl (5 ml). The mixture was poured into water, extracted with ether, and the extracts dried (Na_2SO_4). After concentration at reduced pressure, the residue was chromatographed (Silica-2% ether/petrol) to afford a mixture of allylic selenides (24), (25) and (26), (448 mg, 65%) as a pale yellow oil. The initial ratio was determined to be (24):(25):(26) 1:3:4.4 by ^1H n.m.r integration of the 2'-H of each species at 4.46,

4.33, and 5.12 ppm respectively.
δ_H(250 MHz; $CDCl_3$) 0.08-2.8 (20H,m, all other aliphatics), 4.33 (0.36H,m,*CH*-SePh, assigned as (25) on basis of expected major isomer), 4.46 (0.12H,m,*CH*-SePh, isomer (24)), 5.12 (0.52H,m,2'-H,isomer (26), 7.22 (3H,m, m,p-ArH), 7.5 (2H,m,o-ArH); δ_C(62.9 MHz; $CDCl_3$) 49.48,49.67(C-2',(24),(25)), 65.71(C-2',(26)); *m/z* 346(M^+), 189(M-SePh base), 157(SePh), 121, 107(189-C_6H_{10}), 95,91,79,67,55,41.
(Found: M^+,346.1206 . $C_{20}H_{26}Se$ requires: M^+, 346.1200)
Quantitative rearrangement to isomer (26) occurred on standing.

Reaction of Styrene with Phenylselenomethyl Isopropyl Ketone
To a suspension of potassium hydride (430 mg of 35% oil dispersion, washed with ether, 3.76 mmol) in DME (4 ml) and styrene (5 ml, 44 mol) at -70°C was added t-butanol (200μL,2.12 mmol), followed by a solution of DAMP (8) (890 mg, 5 mmol) in THF (2 ml) dropwise over 5 min, and the mixture cooled to -78°C. After stirring an additional 0.5 h a solution of seleno-ketone (486 mg, 2.01 mmol) in DME (3 ml) was added dropwise over 0.5 h. The mixture was stirred 48 h at -78°C with provision for venting the nitrogen evolved, then allowed to warm to room temperature. After cautious addition of saturated aqueous NH_4Cl (5 ml), the mixture was diluted with ether, poured into water, and extracted with ether. The extracts were washed with brine, dried (Na_2SO_4), and concentrated at reduced pressure. The styrene was removed at 0.1 torr, and the residue chromatographed (Silica-3% ether/petrol) to afford in order of elution:- diphenyldiselenide (44 mg), vinyl selenide (28) (127 mg) as an unstable pale yellow oil, and a mixture of mono and diselenated ketones (250 mg, 51% by wt. of starting material).

3-Methyl-1-phenylseleno-2-(phenylselenomethyl)but-1-ene (28)
ν_{max}(film) 3055,2959,2927,2868,1576,1474,1435,1072,1022,808,736,690 and 668 cm^{-1}; δ_H(250 MHz;$CDCl_3$) 1.10 (6H,d,J 7Hz,Me)2.63 (1H,hept,J 7Hz,3-H), 3.84 (2H,s,CH_2-SePh), 6.35 (1H,s,1-H), 7.25 (6H,m, m,p-ArH), 7.38 (2H,m, o-ArH), 7.60 (2H,m, o-ArH); δ_C(62.9 MHz;$CDCl_3$) 22.05(Me,q), 31.04(CH_2-SePh,t), 34.97(C-3,d), 116.55(C-1,d),126.66, 127.26, 128.91, 129.05, 131.49, 133.92(o,m,p-ArC,d), 130.69, 131.93(SeCAr), 148.63(C-2,s); *m/z* 396(M^+), 239 (M-SePh), 206, 185, 157(SePh), 143, 129, 115, 105, 91, 77, 58, 43(C_3H_7,base), 41.

Reaction of styrene with 2-phenylselenoacetone
Under reaction conditions analagous to those reported above, 2-phenylselenoacetone reacted in the presence of styrene and DAMP (8) to afford unstable 2-methyl-1,3-di(phenylseleno)-prop-1-ene (27) *m/z* 368(M^+), 211(M-SePh), 209,157(SePh), 130,91,77,51; δ_H(250 MHz;$CDCl_3$) 2.0 (3H,d,J 1.4Hz,C-2 Me), 3.80(2H,s,3-H_2),6.25 (1H,d,J 1.4Hz,1-H), 7.2-7.65 (10H,m,Ar).

Preparation of cis,trans 7-(2-phenylselenocyclohexylidene)-2-oxabicyclo[4.1.0]heptane (29) (30)
To potassium hydride (400 mg of 35% oil dispersion, washed with ether, 3.6 mmol) suspended in DME (4 ml) at -78°C was added dihydropyran (5 ml, 55 mmol), and t-butanol(200 μL,2.12 mmol) with stirring. A solution of 2-phenylselenocyclohexanone (660 mg, 2.6 mmol) in DME (2 ml) was prepared, and 0.8 ml added to the reaction mixture, followed by a solution of DAMP (8) (660 mg, 3.7 mmol) in DME (3 ml) dropwise over 30 min, with the rest of the ketone solution being added after 15 min. Evolution of nitrogen was observed from the bright yellow solution. The mixture was stirred at -78°C for a further 4h, quenched by cautious dropwise addition of saturated aqueous NH_4Cl (5 ml), and allowed to warm to room temperature. The mixture was extracted from water with ether, the extracts dried (Na_2SO_4), concentrated at reduced pressure, and the residue chromatographed (Silica-3% ether/petrol), to afford cis, trans 7-(2-phenylselenocyclohexylidene)-2-oxabicyclo[4.1.0]heptane (29) and (30) in ~2:1 ratio. (combined yield 863 mg, 99%) Proton nmr assignments of the isomers in the mixture are as follows: (29) δ_H(250 MHz; $CDCl_3$) 0.8-2.4 (12H,m,4-H_2,5-H_2,6-H,3'-5'-H_2,6-H_{1ax}), 2.65 (1H,m,6-H_{1eq}), 3.01 (1H,dd,J 7.5,1.9Hz,1-H), 3.25 (1H,m,3-H_{1ax}), 3.52 (1H,dt,J 11,3.8Hz,3-H_{1eq}), 4.47 (1H,m,2'-H),7.2 (3H,m, m,p-ArH), 7.47 (2H,m, o-ArH); and (30) δ_H(250 MHz;$CDCl_3$) 0.8-2.8 (13H,m,4-H_2,5-H_2, 6-H,3'-6'-H_2,6-H_1), 3.27

(1H,m,3-H_{1ax}), 3.53 (1H,m,3-H_{1eq}), 3.68 (1H,d,J 7.7Hz,1-H), 4.32(1H,m,2'-H), 7.2 (3H,m, m,p-Ar), 7.54 (2H,m, o-ArH) δ_C(62.9 MHz; $CDCl_3$) 11.12,13.47(C-6), 48.29,48.88(C-1), 49.09(C-2'), 63.44(C-3), 120.97, 121.79, 132.37, 133.43, (C-7,C-1'); *m/z* 334(M^+), 177(M-SePh, base), 159, 133, 108,91,84,79,41. (Found: M^+, 334.0841 . $C_{18}H_{22}OSe$ requires: M^+, 334.0836).

Allyl Selenide Rearrangement of 7-(2-Phenylseleno)-2-oxabicyclo[4.1.0]heptane (29) and (30)

Facile allyl selenide rearrangement occurred cleanly and quantitatively on standing, or under the reaction conditions for preparing the alkylidene cyclopropane if allowed to stand for any length of time at room temperature prior to workup, to afford 7-cyclohexenyl-7-phenylseleno-2-oxabicyclo[4.1.0]heptane (31) as a pale yellow oil. ν_{max}(film) 2926,2853,1434,1136,1072,1016,736, and 691 cm^{-1}; δ_H (250 MHz;$CDCl_3$) 1.2-2.4 (13H,m,4-H_2,5-H_2, 6-H,3'-6'-H_2), 3.25 (1H, ddd,J10.7,10.7,3.0Hz, 3-H_{1ax}), 3.57 (1H,dt,J 10.7,3.6Hz,3-H_{1eq}), 3.87 (1H,d,J 7.4Hz, 1-H), 5.30 (1H,m,2'-H), 7.27 (3H,m, m, p-ArH), 7.50 (2H,m, o-ArH); δ_C(62.9 MHz; $CDCl_3$) 18.66(C-5,t), 22.08, 22.45(C-4,C-5'), 23.07(C-6,d,-ve), 23.18(C-4'), 25.68(C-3',t), 27.33(C-6',t), 35.27(C-7,s), 60.82(C-1,d,discont), 64.12(C-3,t), 129.03(C-2') 133.93(C-1'), 127.61, 128.43(m,p-ArC), 135.28(o-ArC), 130.31(Se-Ar); *m/z* 334(M+), 253(M-C_6H_9), 177(M-SePh), 159, 133, 105, 91,79,41.
(Found: M^+, 334.0841 . $C_{18}H_{22}OSe$ requires: M^+, 334.0836).

Preparation of 7-Phenylseleno-7-(propen-2-yl)-2-oxabicyclo[4.1.0]heptane (32)

To a solution of potassium *t*-butoxide (900 mg,8.0 mmol) in DME (10 ml) at -60°C was added dihydropyran (5 ml, 55 mmol). On cooling to -70°C. DAMP (8) (1.60 g,8.99 mmol) was added dropwise. After stirring for 2.5 h, 2-phenylselenoacetone (15) (400 mg, 1.87 mmol) was added dropwise over 5 min. After stirring for 18 hr at -78°C , the reaction was warmed to room temperature, poured into water, extracted with ether, dried (Na_2SO_4), and concentrated at reduced pressure. The residue was chromatographed (Silica-5% ether/petrol), to afford exclusively 7-phenylseleno-7-(propen-2-yl)-2-oxabicyclo[4.1.0]heptane (32) 161 mg, 28%) as a low melting pale yellow solid (m.p. <23°C) ν_{max}(film) 2954 ,2857, 1474, 1436, 1232, 1147, 1072,1022, 884,738, and 690 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.30 (1H,m,4-H_{1ax}), 1.44 (1H,m,4-H_{1eq}), 1.60 (1H,m,6-H), 1.92 (2H,m,5-H_2), 1.95 (3H,t,J 1.3Hz,C-2'-Me), 3.25 (1H,ddd,J 11,11,2.6Hz,3-H_{1ax}), 3.60 (1H,dt,J 11,3.6Hz, 3-H_{1eq}), 3.90 (1H,d,J 7.6Hz,1-H), 4.68 (1H,m,1'-H_1), 4.88 (1H,m,1'-H_1), 7.27 (3H,m, m,p-Ar), 7.52 (2H,m, o-Ar), assignments checked by decoupling expts.; δ_C(62.9 MHz; $CDCl_3$) 18.34(C-5,t), 21.66(C-2'-Me,q), 21.89(C-4), 23.42(C-6,d), 34.58(C-7,s), 60.92(C-1,d), 64.06(C-3,t), 116.87(C-1',t), 141.81(C-2',s), 127.67, 128.70, 134.6(o,m,p-ArC), 130.25(Se-CAr,s); m/z 294(M^+), 157(SePh), 137(M-SePh), 93(C_6H_6O), 79,67,41(C_3H_5).
(Found: M^+, 294.0536 . $C_{15}H_{18}OSe$ requires : M^+, 294.0523).
In addition a mixture of starting ketone and 2,2-diphenylselenoacetone (152 mg) was recovered.

Preparation of 7-Cyclopentylidene-2-oxabicyclo[4.1.0]heptane (37)

To a suspension of potassium hydride (800 mg of a 35% oil dispersion, washed with ether, 7.0 mmol) in DME (5 ml) at -78°C was added a solution of cyclopentanone (420 mg, 5 mmol) in dihydropyran (5 ml, 55 mmol), followed by DAMP (8) (1.62 g, 8 mmol) dropwise with stirring, when gas evolution occurred. The reaction was stirred for 18h at -78°C, warmed to room temperature, poured into saturated aqueous NH_4Cl, and extracted with ether. The extracts were dried ($MgSO_4$), concentrated at reduced pressure and the residue chromatographed, (Silica-2% ether/petrol (30-40 b.p.), to afford 7-cyclopentylidene-2-oxabicyclo[4.1.0]heptane (37) (247 mg, 30%) as a colourless aromatic oil. ν_{max}(film) 2953, 2860, 1450, 1432, 1226, 1192, 1139, 1106, 1063, and 845 cm^{-1}; δ_H(90MHz; $CDCl_3$) 0.85 (1H, m, 6-H), 1.0-2.0 (8H,m,4-H_2,5-H_2,3'-H_2,4'-H_2), 2.3 (4H,m,2'-H_2,5'-H_2), 3.4 (2H,m,3-H_2), 3.82 (1H,m,1-H); δ_C(22.5 MHz;$CDCl_3$) 14.5(C-6,d), 19.64(C-5,t), 22.56(C-4,t), 26.71(C-3',C-4',t), 31.22(C-5',t), 32.2(C-2'), 49.80(C-1,d), 63.85(C-3,t), 116.21(C-1',s), 136.71(C-7,s); *m/z* 164(M^+), 136,107,97(M-C_5H_7), 91,85,79,67(C_5H_7), 57,41. (Found: M^+, 164.1200 . $C_{11}H_{16}O$ requires : M^+, 164.1201).

Singlet Oxygenation of 7-Cyclopentylidene-2-oxabicyclo[4.1.0]heptane (37)

Dry oxygen was passed through a solution of the alkylidenecyclopropane (37) (168 mg,1.02 mmol) and meso-tetraphenylporphyrin (4 mg) in benzene (20 ml), whilst irradiating with a 650 W tungsten-halogen lamp for 3 h. On cooling in ice, triphenylphosphine (280 mg, 1.07 mmol) in ether (10 ml) was added, and the mixture stirred for 1.5 h. The solvents were stripped at reduced pressure, and the residue chromatographed (Silica - 15% ether/petrol) to afford 3,4-dihydro-2H-pyran-3-yl (1-cyclopentenyl) ketone (38) (77 mg, 42%) the only isolable product, as a colourless oil. ν_{max}(film) 2950, 1618(s,br), 1388, 1343, 1304, 1266, 1230, 1173, 996, 937, 754 and 729 cm^{-1}; δ_H(90 MHz ; $CDCl_3$) 1.8 (4H,m,5-H_2,4'-H_2), 2.4 (6H,m,4-H_2,5'-H_2,3'-H_2), 4.03 (2H,t,J 5.4Hz,6-H_2), 6.14 (1H,m,2'-H), 7.48 (1H,s,2-H): δ_C(22.5 MHz ; $CDCl_3$) 18.41(C-4), 20.91(C-5), 22.56(C-4'), 32.81, 33.49(C-3',C-5'), 66.87(C-6), 116.73(C-3), 138.82(C-2'), 143.65(C-1'), 157.80(C-2), 193.14(C=0) ; *m/z* 178(M^+), 150, 122, 111(M-C_5H_7), 95(M-C_5H_70), 83, 67, 41, 28. (Found: M^+, 178.0990 . $C_{11}H_{14}O_2$ requires : M^+ 178.0994).

Preparation of 7-Cyclopentylidenebicyclo[4.1.0]heptane (41)

To a solution of potassium *t*-butoxide (672 mg,6 mmol) in DME (7 ml) and cyclohexene (7 ml) at -78°C was added cyclopentanone (0.5 g, 6 mmol), followed by DAMP (8) (1.09 g, 6.1 mmol) dropwise with stirring. The mixture was stirred at -78°C for 4 h when gas evolution ceased. On warming to room temperature the mixture was poured into water, and extracted with petrol (30-40 b.p.). The extracts were dried ($MgSO_4$), concentrated at reduced pressure, and the residue chromatographed (Silica-2% ether/petrol (30-40 b.p)), to afford 7-cyclopentylidene-bicyclo[4.1.0]heptane (41) (863 mg, 89%) as a colourless oil. ν_{max}(film) 2930, 2834, 1449, 1340, 1328, 1170, 940, 845, and 690 cm^{-1}; δ_H(90 MHz; $CDCl_3$) 0.90 (2H,m,1-H,6-H), 1.2 (4H,m,3-H_2,4-H_2), 1.70 (8H,m,2-H_2,5-H_2,3'-H_2,4'-H_2), 2.3 (4H,m,2'-H_2,5'-H_2); δ_C(22.5 MHz; $CDCl_3$) 12.86(C-1,C-6), 21.52(C-3,C-4), 22.26(C-2,C-5), 26.71(C-3',C-4'), 31.23(C-2',C-5'), 120.51(C-1') 130.89(C-7); *m/z* 162(M^+), 147, 133, 119, 105, 91, 79, 67(C_5H_7). (Found: M^+, 162.1406 . $C_{12}H_{18}$ requires: M^+, 162.1408).

Synthesis of 7-(4-t-Butylcyclohexylidene)bicyclo[4.1.0]heptane (33)

To a solution of potassium *t*-butoxide (725 mg, 6.5 mmol) in DME (7 ml) and cyclohexene (7 ml, 69 mmol) was added at -78°C a solution of 4-*t*-butyl-cyclohexanone (926 mg, 6 mmol) in DME (1 ml), followed by DAMP (8) (1.09 g, 6.12 mmol) dropwise with stirring when gas was evolved. The mixture was allowed to warm to -70°C, and stirred a further 2 h before warming to room temperature. The reaction was poured into water and extracted with petrol. The extracts were dried($MgSO_4$), concentrated at a reduced pressure, and the residue chromatographed (Silica-2% ether/petrol) to afford 7-(4-t-butylcyclohexylidene)-bicyclo[4.1.0]heptane (33) (996 mg, 67%) as a colourless solid. m.p. 63-65°C; ν_{max}(CCl_4) 2938,2856, 1479,1442,1364,1240, and 1187 cm^{-1}; δ_H(90 MHz; $CDCl_3$) 0.88 (9H,s,^{t}Bu), 1.0-2.7 (19H,m,all other H); δ_C(22.5 MHz;$CDCl_3$) 12.37(C-1,C-6,-ve), 21.52(C-3,C-4), 22.99(C-2,C-5), 27.69(*Me*$_3$C), 28.48, 28.91(C-3',C-5'), 32.81,33.12(C-2',C-6'), 48.32(C-4'), 135.22, 135.35(C-7,C-1'); *m/z* 232(M^+), 217(M-Me), 175(M-^{t}Bu,base), 161, 147, 133, 123, 107, 93, 79, 67, 57(^{t}Bu).
(Found: C,87.60; H,12.26 . $C_{17}H_{28}$ requires: C,87.86; H,12.14%).

Singlet Oxygenation of 7-(4-t-Butylcyclohexylidene)bicyclo[4.1.0]heptane (33)

Dry oxygen was passed through a solution of the olefin (33) (95.5 mg, 0.38 mmol), and meso-tetraphenyl-porphyrin (4 mg) in dry benzene (5 ml) and pyridine (50 µL,0.62 mmol), whilst irradiating with a 650W tungsten halogen lamp for 10 h, further portions of benzene being added periodically to maintain concentration. The mixture was chilled to 4°C and a solution of triphenylphosphine (150 mg, 0.57 mmol, 1.5 eq) in ether (5 ml) was added. After standing 12 h at 4°C, the solvent was stripped at reduced pressure, and the residue chromatographed (Silica-gradient 0-5% ether/petrol), to afford in order of elution, triphenylphosphine (126 mg), and a number of products of total mass 45 mg. No 4-*t*-butyl-cyclohexanone was observed by t.l.c. The major product (20 mg), a colourless oil was identified as (4-*t*-butyl-1-cyclohexenyl) 1-cyclohexenyl ketone (34) ν_{max}(film), 2941,2866,1630(s,br), 1365,1249,919, and 733 cm^{-1}; δ_H(90 MHz;$CDCl_3$) 0.88 (9H,s,Me_3C), 1.0-2.7 (15H,m, all other H), 6.42 (2-H,m,2-H,2'-H); δ_C(22.5 MHz; $CDCl_3$) 21.77, 22.13(C-4',C-5'), 23.60(C-3'), 24.33(C-6), 25.67(C-6'), 25.86(C-3), 27.14(*Me*$_3$C), 27.50(C-5), 32.14(Me$_3$*C*), 43.62(C-4), 138.09, 138.34(C-1,C-1'), 138.70, 139.19(C-2,C-2'),

199.73(C=0); *m/z* 246(M^+), 231(M-Me), 218(M-28,retro D.A), 189(M-^{t}Bu), 162(M-84,retro D.A), 133,109(C_7H_9O), 84,81,57(^{t}Bu). Derivative 2,4-dinitrophenylhydrazone m.p. 144-146°C.
(Found: M^+, 426.2239 . $C_{23}H_{30}O_4N_4$ requires M^+, 426.2267).

Low Temperature Singlet Oxygenation Reaction of 7-(4-t-Butylcyclohexylidene)-bicyclo[4.1.0]heptane (33)

Dry oxygen was passed through a solution of the olefin (33) (68.5 mg, 0.28 mmol) and tetraphenylphorphrin (4 mg) in toluene (4.5 ml) at -78°C whilst irradiating with a 650 W tungsten-halogen lamp for 18 h. (The reaction vessel was immersed in acetone/CO_2, contained in a non-silvered dewar). A solution of triphenylphosphine (80 mg,0.304 mmol,1.1 eq) in toluene (2 ml) at -78°C was then added, the mixture agitated for 0.5 h, then allowed to warm to room temperature. The solvent was stripped at reduced pressure, and the residue chromatographed (Silica-100% ether), to afford in addition to recovered olefin (7 mg), 4-t-butyl-1-cyclohexene carboxylic acid (35) (33 mg, 65%) as colourless plates (hexane) m.p. 189-191°C; ν_{max}(film) 2953, 2925, 2852, 1675, 1639, and 1274 cm^{-1}; δ_H(90 MHz;$CDCl_3$) 0.92 (9H,s,Me_3C), 0.9-2.8 (8H,m,OH,3-H_2, 4-H,5-H_2,6-H_2), 7.13 (1H,m,2-H); δ_C(22.5 MHz; $CDCl_3$) 23.54(C-3), 25.25(C-6), 27.08(Me_3C), 27.75(C-5), 32.08(Me_3C), 43.25(C-4), 129.67(C-1), 142.85(C-2), 172.82(CO_2H); *m/z* 182(M^+), 167(M-Me), 139,126,111,84(C_6H_{12}),57(^{t}Bu,base).
(Found: C,72.50; H,10.11. $C_{11}H_{18}O_2$ requires: C,72.48; H,9.95%)

Copper(I) Catalysed Reaction of Olefin (41) with t-Butylperbenzoate

To a mixture of olefin (41) (145 mg, 0.89 mmol) and cuprous chloride (0.6 mg, 6 μmol) in benzene (10 ml) at reflux was added dropwise over 30 min *t*-butyl perbenzoate (120 mg, 0.62 mmol). After a further 1.5 h at reflux t.l.c. indicated complete consumption of the perbenzoate. On cooling the solvent was stripped at reduced pressure, and the residue chromatographed (Silica-3% ether/petrol), to obtain in order of elution, recovered olefin (60 mg, 41%), and two major products (42) (32 mg, 12.8%), and (43) (23 mg, 9.2%), respectively as colourless oils, with an additional 6 mg, 2.4% of mixture 2-(7-bicyclo[4.1.0]heptylidene)cyclopentyl benzoate (42) ν_{max}(film) 2938,2854,1718,1450,1314,1272,1107, 1069,734, and 712 cm^{-1}; δ_H(250 MHz;$CDCl_3$) 1.0-2.7(16H,m,all other H), 5.88 (1H,m,1-H), 7.45 (3H,m, m,p-Ar), 8.02 (2H,m, o-Ar); δ_C(22.5MHz; $CDCl_3$) 12.31, 13.34(C-1',C-6',-ve), 21.22,21.46(C-3',C-4'), 21.71,22.01(C-2',C-5'), 23.23(C-4), 29.46(C-5), 33.67(C-3), 76.57(C-1), 128.2(Ar,m), 128.75(C-2,+ve), 129.55(Ar,*o*), 132.48 (Ar-CO,+ve), 132.60(Ar,*p*), 134.12(C-7',+ve), 166.35(CO_2R,+ve); *m/z* 282(M^+), 176(M-PhCOH), 160(M-$PhCO_2H$,Mclafferty), 105(PhCO), 95,91,77,67(C_5H_5). (Found: M^+,282.1614 . $C_{19}H_{22}O_2$ requires: M^+,282.1620.) 7-(1-cyclopentenyl)-bicyclo[4.1.0]hept-7-yl benzoate (43) δ_H(90 MHz;$CDCl_3$) 0.8-2.3 (16H,m, all aliphatics), 6.0 (1H,m,2'-H), 7.45 (3H,m, m,p-Ar), 8.02 (2H,m, o-Ar); δ_C(22.5 MHz; CDCl3) 19.56(C-1,C-6), 20.97(C-3,C-4), 21.10(C-2,C-5), 22.87(C-4), 32.69,33.55(C-3'.C-5'), 62.78(C-7), 130.95(C-2'), 137.42(C-1'), 128.08, 129.43, 132.42, 134.55(ArC), 165.56(CO_2R). (Found: M^+, 282.1617 . $C_{19}H_{22}O_2$ requires: M^+,282.1620.)

Copper(I) Catalysed Reaction of Olefin (41) with slow addition of t-Butyl perbenzoate

To a solution of olefin (41) (265 mg, 1.64 mmol) in dry benzene (20 ml) and cuprous chloride (4 mg, 40 μmol), at reflux was added a solution of *t*-butyl perbenzoate (317 mg, 311 μL, 1.64 mmol) in benzene (0.6 ml) dropwise over 40h *via* a syringe pump. The mixture was heated a further 8 h, cooled and poured into saturated aqueous $NaHCO_3$. The organic phase was dried ($MgSO_4$), the solvent stripped, and the residue chromatographed (Silica-4% ether/petrol) to afford in order of elution, recovered olefin (118 mg,44%), and the allylic benzoate isomers (42) and (43) (191 mg, 41%) in a ratio (42):(43) of 70:30, identical in all respects with materials prepared previously.

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