Olefin Synthesis by Two-fold Extrusion Processes. Part 3.[1] Synthesis and Properties of Hindered Selenoketones (Selones)

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Monomeric selenoketones (selones) have been prepared from di-t-butyl ketone and (−)-1,3,3-trimethylnorbornan-2-one through heating their triphenylphosphoranylidenehydrazones with selenium. Although selones show greater reactivity towards diazo-compounds than thiones it was still not possible to prepare the elusive tetra-t-butylethylene. However, (−)-1,1',3,3,3',3'-hexamethyl-2,2'-binorbornylidene, which is a ' tied back ' tetra-t-butylethylene, was obtained without difficulty and is stable to oxygen.

The chemistry of selones has been briefly explored and compared with that of thiones. An improved preparation of di-t-butylketen is reported.

TWO-FOLD extrusion of stable moieties X and Y from a suitable cyclic precursor of general formula (I) provides a powerful method for the synthesis of hindered olefins (II).[1-3] We[3] and, independently, Kellogg and his colleagues,[3] have emphasized the particular utility of

Δ^3-1,3,4-thiadiazolines (III) in this respect. Pyrolysis of these compounds furnished episulphides, which in turn gave the desired olefins upon treatment with

[1] Part 2, D. H. R. Barton, F. S. Guziec, jun., and I. Shahak, J.C.S. Perkin I, 1974, 1794.

[2] T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziec, jun., J.C.S. Chem. Comm., 1975, 539.

[3] D. H. R. Barton and B. J. Willis, J.C.S. Perkin I, 1972, 305; Chem. Comm., 1970, 1225; D. H. R. Barton, E. H. Smith, and B. J. Willis, ibid., p. 1226; R. M. Kellogg and S. Wassenaar, Tetrahedron Letters, 1970, 1987; R. M. Kellogg, S. Wassenaar, and J. Buter, ibid., p. 4689; J. Buter, S. Wassenaar, and R. M. Kellogg, J. Org. Chem., 1972, 37, 4045.

phosphines. In this way, the very hindered olefins 2-diphenylmethylenebornane (IV), 2-diphenylmethylene-1,3,3-trimethylnorbornane (V), 1,1-di-t-butyl-2,2-diphenylethylene (VI), and 2-di-t-butylmethylenebornane (VII) were prepared in good yield. However, our inability to obtain tetra-t-butylethylene (VIII) or 2-di-t-butylmethylene-1,3,3-trimethylnorbornane (IX) indicates the steric limitations of this technique.

Our desire to extend the scope of the method prompted us to examine the possibility of using Δ^3-1,3,4-selenadiazolines (X) in lieu of their sulphur analogues as precursors of hindered olefins. The radius of the selenium atom is greater than that of sulphur;[4] hence, the hindered carbon centres would be held further apart in compounds of type (X) than in those of type (III), thereby reducing steric interactions during the formation of (X). Expulsion of nitrogen from a 1,3,4-selenadiazoline would generate the corresponding episelenide and thus provide access to the olefin by ready loss of selenium from the latter species,[5] as depicted in Scheme 1.

The most promising route to the heterocycles (X) appeared to be the cycloaddition of selenoketones (selones) to diazo-compounds. Δ^3-1,3,4-Thiadiazolines bearing bulky substituents are best prepared by reacting thiones with diazo-compounds.[1] However, the only selenoketones reported are those which are ligand-stabilized or resonance-stabilized by conjugation with an

electric-donating heteroatom.[6] To our knowledge, saturated, monomeric selenoketones had not been described until our recent communication[2] on the synthesis of di-t-butyl selenoketone (XI) and (—)-1,3,3-trimethyl-
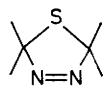
norbornane-2-selone (XII). Subsequently, Ingold and his collaborators[7] prepared the former selone by a modification of our method and in improved yield. We
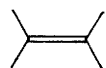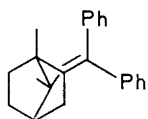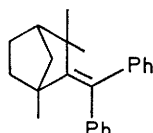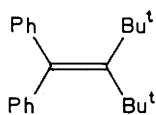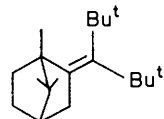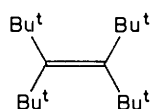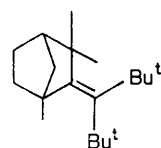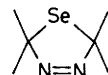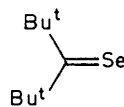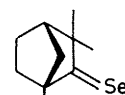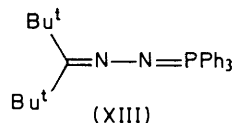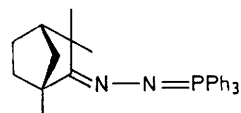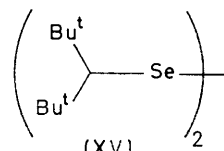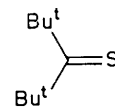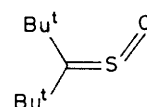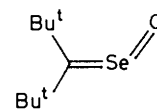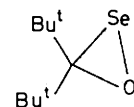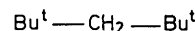

now describe the synthesis and properties of these novel compounds, particularly with regard to their utility as precursors of hindered olefins.

SCHEME 1

Di-t-butyl selenoketone (XI) was obtained (35%) by heating di-t-butyl ketone triphenylphosphoranylidenehydrazone (XIII) with selenium and a trace of tri-n-butylamine. The product was a distillable blue liquid with a mild, slightly unpleasant odour. Similar treatment of (—)-1,3,3-trimethylnorbornan-2-one triphenylphosphoranylidenehydrazone (XIV) afforded (—)-1,3,3-trimethylnorbornane-2-selone (XII), which was continuously distilled from the reaction mixture and isolated in

[4] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, London, 1972, p. 421.

[5] T. H. Chan and J. R. Finkenbine, *Tetrahedron Letters*, 1974, 2091.

[6] R. B. Silverman, 'Organic Selenium Compounds: Their Chemistry and Biology,' eds. D. L. Klayman and W. H. H. Günther, Wiley–Interscience, London, 1973, ch. 7.

[7] K. U. Ingold, personal communication; see also J. C. Scaiano and K. U. Ingold, *J.C.S. Chem. Comm.*, 1976, 205.

28% yield as bright blue crystals possessing a camphoraceous odour. The phosphoranylidenehydrazones were in turn readily obtained from the corresponding hydrazones by the method of Bestmann and Fritzsche.[8] The ylidenehydrazones used must be free of hydrazone, or the selones are reduced to selenols as fast as they are formed.

Both selones are remarkably stable thermally and were recovered intact after prolonged heating under nitrogen at 150 °C. Their inertness is attributed to the absence of enolisable hydrogen and to the steric protection of the selenocarbonyl group.

Di-t-butyl selenoketone (XI) underwent rapid aerial oxidation in the presence of light to form di-t-butyl ketone and selenium. No oxidation was observed in the dark; thus an excited state of the selone is implicated in the oxidation. The selone (XI) was inert to irradiation by visible light under nitrogen, but was smoothly reduced to the diselenide (XV) with u.v. light. The detailed photochemistry of the selenoketone (XI) is under investigation by de Mayo and his colleagues.[9]

Oxidation of thiones with peroxy-acids is a well known method for preparing thioketone S-oxides (sulphines).[10] When di-t-butyl thioketone [1] (XVI) was treated with 1 equiv. of m-chloroperbenzoic acid in ether, a quantitative yield of crystalline di-t-butyl thioketone S-oxide (XVII) was obtained. The ability of bulky substituents to impart unusual stability to otherwise reactive functional groups was again demonstrated by the high thermal stability of the sulphine (XVII), which survived prolonged heating at 150 °C. It was thus of interest to attempt the preparation of di-t-butyl selenoketone Se-oxide (XVIII), in order to investigate the nature of the novel C=Se=O grouping. On treatment of the selone (XI) with m-chloroperbenzoic acid at −80 °C the selone was consumed as evidenced by the discharge of the blue colour. On warming slowly to room temperature, precipitation of selenium and formation of di-t-butyl ketone occurred. N.m.r. experiments indicated that the oxidation product was stable at −80 °C but decomposed rapidly at −20 °C. We believe that the selenine (XVIII) is formed at low temperature, but on warming decomposes spontaneously to the ketone. It is, therefore, considerably more labile than its sulphine analogue. Decomposition of the selenine may occur via a three-membered cyclic intermediate (XIX). A mechanism of this type has been proposed for the decomposition of sulphines.[11]

When di-t-butyl selenoketone (XI) was heated with tris(dimethylamino)phosphine or tri-n-butylphosphine, 2,2,4,4-tetramethylpentane (XX) was obtained as the chief product. This hydrocarbon was also formed by reduction of the selone with sodium–potassium alloy. Alternatively, treatment of the selone (XI) with ethanolic sodium borohydride effected quantitative reduction to the diselenide (XV). The intermediate selenol was not isolated and underwent rapid oxidation to compound (XV) on work-up in air.

A competition experiment was devised to confirm our belief that selones would react more readily than analogous thiones in forming cycloadducts with diazo-compounds. Equimolar amounts of di-t-butyl selenoketone (XI) and di-t-butyl thioketone (XVI) were treated with a limited quantity of diazodiphenylmethane.[1] The greater reactivity of the selone was clearly demonstrated by immediate formation of 2,2-diphenyl-5,5-di-t-butyl-Δ^3-1,3,4-selenadiazoline (XXI) and the complete absence of the analogous 1,3,4-thiadiazoline [1] (XXII). The selenadiazoline (XXI) was an isolable solid which readily extruded nitrogen and selenium on mild heating to provide the olefin (VI).

Contrary to our previous report,[1] compound (VI) displayed normal olefinic behaviour. For example, it formed the epoxide in high yield on treatment with m-chloroperbenzoic acid.
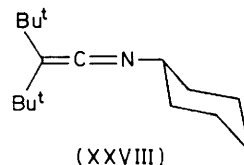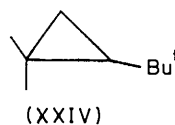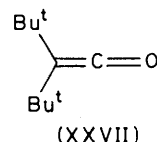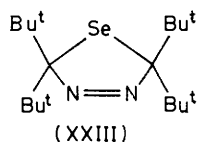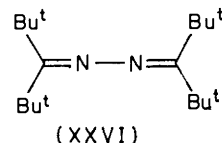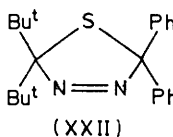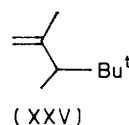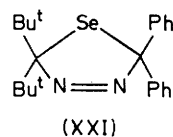
In view of the ready formation of the selenadiazoline (XXI), the reaction of the selone (XI) with a more hindered diazo-compound was investigated. Diazo-di-t-butylmethane [1] was selected, as the resulting cycloadduct (XXIII) would be a potential precursor of tetra-t-butylethylene (VIII). Diazodi-t-butylmethane was prepared by a new, more convenient method. Pyrolysis of di-t-butyl ketone triphenylphosphoranylidenehydrazone (XIII) under continuous vacuum caused the pure diazo-compound to distil into a cold trap in quantitative yield. Attempts to prepare the selenadiazoline (XXIII) by heating the diazo-compound with

[10] B. F. Bonini, G. Maccagnani, A. Wagenaar, L. Thijs, and B. Zwanenburg, *J.C.S. Perkin I*, 1972, 2490; G. Opitz, *Angew. Chem. Internat. Edn.*, 1967, **6**, 107; J. F. King and T. Durst, *J. Amer. Chem. Soc.*, 1963, **85**, 2676.

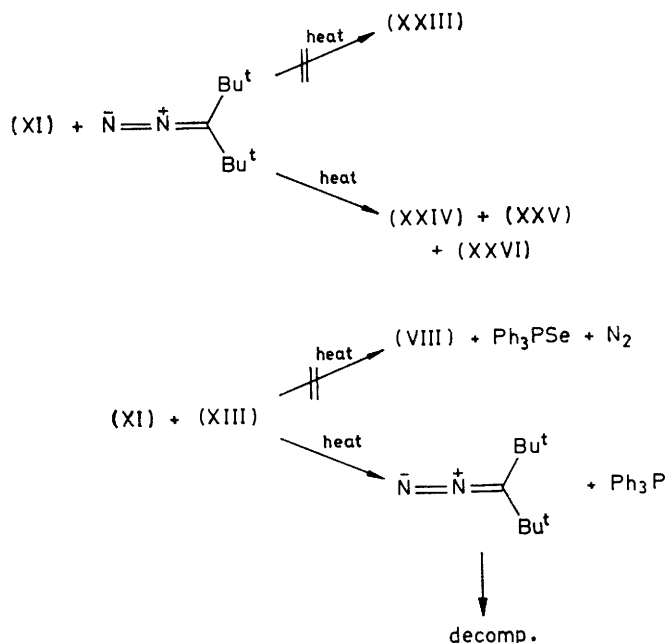[11] J. P. Snyder, *J. Amer. Chem. Soc.*, 1974, **96**, 5005.

[8] H. J. Bestmann and H. Fritzsche, *Chem. Ber.*, 1961, **94**, 2477.

[9] P. de Mayo, personal communication.

di-t-butyl selenoketone resulted in 1,1-dimethyl-2-t-butylcyclopropane (XXIV), 2,3,4,4-tetramethylpent-1-ene (XXV), and a small amount of di-t-butyl ketone azine (XXVI). The presence of unchanged selone and the absence of both the adduct (XXIII) and tetra-t-butylethylene indicate that cyclization is not a favoured process in this case. The hydrocarbons (XXIV) and (XXV) are clearly identified as decomposition products of the diazo-compound (presumably *via* a unimolecular mechanism involving a carbene) by their formation during pyrolysis of the pure diazo-compound in a blank experiment.

Increased pressure is sometimes effective remedy for cases where unwelcome unimolecular reactions pre-dominate over a desired bimolecular process. Thus, it was hoped that elevated pressure would permit cyclo-addition to compete more favourably with decomposi-tion of the diazo-compound. When the selone (XI) and diazodi-t-butylmethane were heated at 150 atm, the reaction followed its usual course. At 8 500 atm, formation of di-t-butyl ketone azine (XXVI) pre-dominated. Hence, high pressure did favour a bimole-cular reaction as expected, but not the desired one affording the selenadiazoline (XXIII)

Hindered olefins have also been prepared by the reaction of thiones directly with phosphoranylidene-hydrazones.[1] The preparation of tetra-t-butylethylene was also attempted by heating di-t-butyl ketone tri-phenylphosphoranylidenehydrazone (XIII) with di-t-butyl selenoketone (XI). Again, unchanged selone was observed, along with the formation of the hydrocarbons (XXIV) and (XXV). Hence, the phosphoranylidene-hydrazone (XIII) dissociates on heating to form diazo-di-t-butylmethane, which in turn decomposes in the

aforementioned manner. When compound (XIII) was pyrolysed in a blank experiment, the cyclopropane derivative (XXIV) was the chief product. These processes are shown in Scheme 2.

The possibility of using di-t-butyl selenoketone (XI) to form cycloadducts (I) other than 1,3,4-selenadiazolines

SCHEME 2
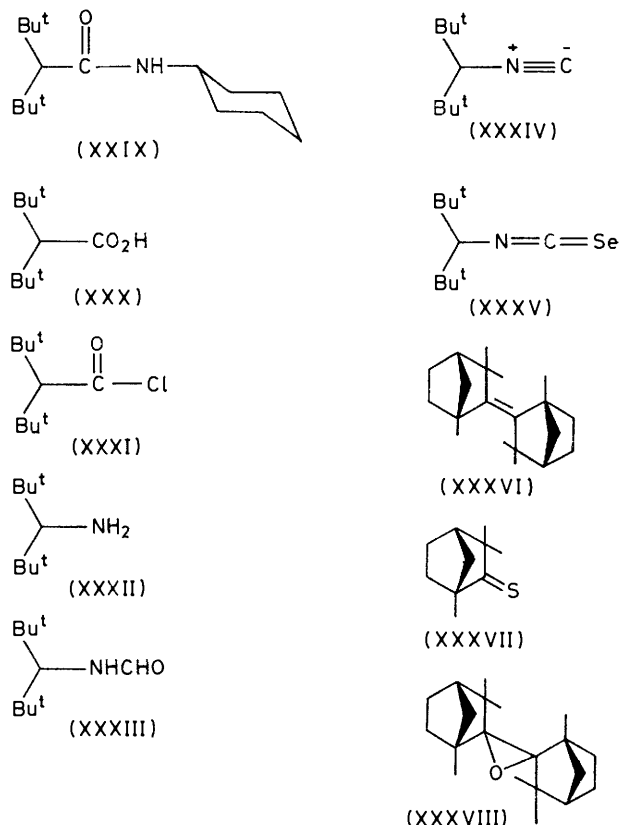
was also investigated in our attempts to prepare tetra-t-butylethylene. The reaction of the selone (XI) with di-t-butyl thioketone *S*-oxide (XVII) did not form a cycloadduct, but resulted in oxidation of the selone to generate di-t-butyl ketone and di-t-butyl thioketone. The reaction progressed slowly at 185 °C, but went to completion within 4 h on irradiation with u.v. light.

The reaction of di-t-butylketen (XXVII) with the selone (XI) was also studied. The only reported pre-paration of this keten involves a six-step synthesis developed by Newman and his co-workers[12] which affords the product in an overall yield of 16% from di-t-butyl ketone. We have developed an alternative route in which a yield of *ca.* 60% is obtained, from diazodi-t-butylmethane. Cyclohexyl isocyanide reacted with diazodi-t-butylmethane to provide the ketenimine (XXVIII), which underwent mild acidic hydrolysis to furnish the amide (XXIX) in 86% yield. Further hydrolysis to the acid (XXX) was accomplished by heating the amide with orthophosphoric acid at 150 °C. The crude carboxylic acid was converted into the acyl chloride (XXXI) in 81% yield by the method of New-

[12] M. S. Newman, A. Arkell, and T. Fukunaga, *J. Amer. Chem. Soc.*, 1960, **82**, 2498.

man,[12] and treatment of the latter with tri-n-butylamine at 90 °C afforded an 86% yield of the desired keten.

When di-t-butyl selenoketone (XI) and di-t-butylketen (XXVII) were heated together, the selone was reduced to the diselenide (XV), but no sign of cycloaddition was observed. Early reports by Staudinger [13] indicate that mixtures of diphenylketen and certain thioketones exist in equilibrium with the corresponding thietan-2-one, with formation of the latter species being favoured by low temperatures. However, di-t-butylketen and the selone (XI) showed no evidence of cycloaddition when cooled to −80 °C. Furthermore, no reaction occurred when a solution of the ketene and the selone in benzene was irradiated in a Pyrex apparatus with u.v. light. The keten also failed to react with di-t-butyl thioketone when irradiated through Pyrex with u.v. light.

Finally, a mixture of di-t-butyl selenoketone and di-t-butyl thioketone was irradiated with u.v. light. Once again, there was no sign of a cycloadduct, and reduction of the selone and the thione to the diselenide (XV) and the corresponding disulphide occurred.

with n-butyl-lithium or with lithium di-isopropylamide, followed by addition of selenium gave the isoselenocyanate (XXXV) in high yield.

We have shown that selones are more reactive towards diazo-compounds than are thiones. Despite this fact, we were unable to prepare tetra-t-butylethylene. In an effort to determine more precisely the steric limitations of our method, we turned our attention to the synthesis of the hexamethyl-2,2′-binorbornylidene which can be regarded as the product of (XXXVI), joining three methyl groups of each pair of geminal t-butyl substituents of tetra-t-butylethylene into a bicyclic structure. The steric hindrance in structure (XXXVI) is therefore lower than in tetra-t-butylethylene. The trimethylnorbornanone triphenylphosphoranylidene-hydrazone (XIV) was heated with selenium to give the olefin (XXXVI) in 24% yield as a single isomer, presumed to have the *trans*-configuration. The selone (XII) was an intermediate in this process; it can be isolated from the mixture under these conditions by vacuum distillation. When the phosphoranylidenehydrazone (XIV) was heated with the thione (XXXVII), the same

SCHEME 3
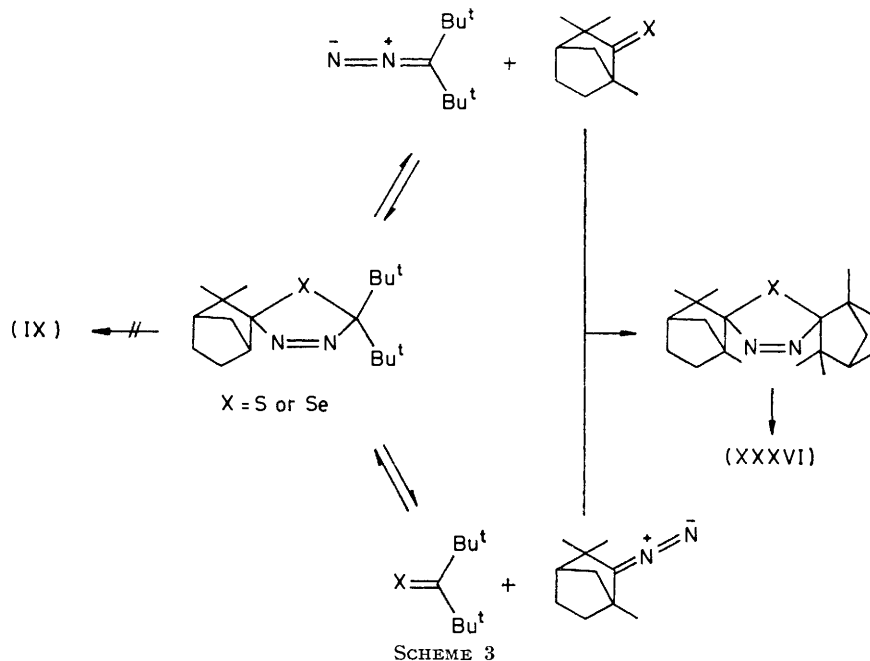
Di-t-butyl selenoketone (XI) reacted with pentacarbonyliron at elevated temperatures. The complex $Fe_3Se_2(CO)_9$[14] was isolated in low yield and identified by its i.r. and mass spectra. Volatile products were not identified.

2,2,4,4-Tetramethylpentane-3-imine [1] was smoothly reduced to the amine (XXXII) by lithium aluminium hydride, and the amine was formylated with formic acid–acetic anhydride to give a high yield of the formamide (XXXIII). Dehydration of the latter with phosgene afforded the isocyanide (XXXIV). Treatment

isomer of the olefin (XXXVI) was obtained in high yield. Hence, the use of the selone (XII) instead is not advantageous in this preparation. The olefin (XXXVI) undergoes ozonolysis to form 1,3,3-trimethylnorbornan-2-one and reacts with m-chloroperbenzoic acid to afford the corresponding epoxide (XXXVIII) in high yield.

The properties of the olefin (XXXVI) are of particular interest for several reasons. It is the most hindered olefin yet prepared. Nevertheless, it exhibits at least some aspects of typical olefinic behaviour. Recent calculations have shown [15,16] that bulky substituents on

[13] H. Staudinger and H. Freudenberger, *Ber.*, 1928, **61**, 1576; H. Staudinger, *Helv. Chim. Acta*, 1920, **3**, 862.
[14] W. Hieber and J. Gruber, *Z. anorg. Chem.*, 1958, **296**, 91.

[15] M. Simonetta, personal communication.
[16] O. Ermer and S. Lifson, *Tetrahedron*, 1974, **30**, 2425.

olefins result in departure from planarity and a concomitant decrease in π-overlap. Ultimately, diradical rather than olefinic behaviour is expected when the torsion angle about the double bond is too large for effective π-overlap. This may occur in tetra-t-butylethylene, where the torsion angle has been calculated as close to 80°.[15,16] Evidently, the torsion angle of the hexamethylbinorbornylidene is not great enough to impart significant diradical character, for the compound is stable in solution at room temperature to a stream of oxygen for 1 week. The structure of the olefin (XXXVI) is being studied by X-ray diffraction by Simonetta and his co-workers.[15] The chiroptical properties of the olefin (XXXVI) are also of current interest.[17]

Attempts were made to prepare 2-di-t-butylmethylene-1,3,3-trimethylnorbornane (IX) *via* the reactions of (i) the triphenylphosphoranylidenehydrazone (XIV) with di-t-butyl thioketone (XVI); (ii) compound (XIV) with di-t-butyl selenoketone (XI); and (iii) di-t-butyl ketone triphenylphosphoranylidenehydrazone (XIII) with 1,3,3-trimethylnorbornane-2-thione. In each case, the binorbornylidene (XXXVI) was the only olefin isolated. Hence, 1,3,4-selena- and thia-diazolines are intermediates in these reactions and must exist in equilibrium with both possible pairs of diazo-compounds and seleno- or thioketones, as illustrated in Scheme 3.

The synthesis of other selenoketones was also attempted. When benzophenone triphenylphosphoranylidenehydrazone (XXIX) or adamantanone triphenylphosphoranylidenehydrazone (XL) was heated with

(XXXIX)

(XLII)

(XL)

(XLIII)

(XLI)
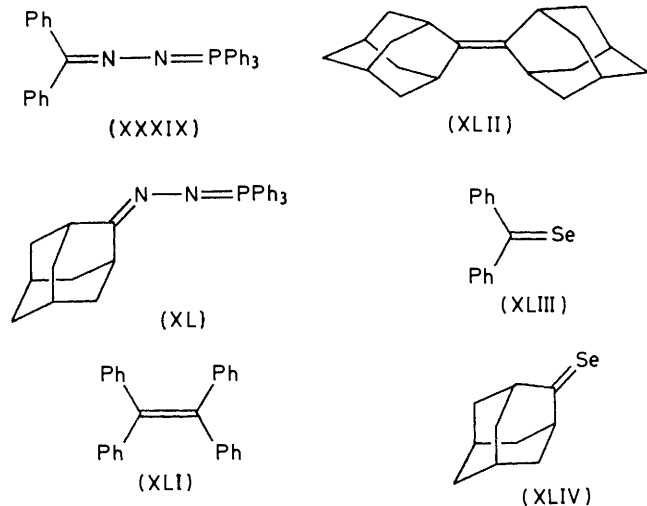
(XLIV)

selenium in the usual manner, the respective products were tetraphenylethylene (XLI) and biadamantylidene (XLII). Selenobenzophenone (XLIII) and selenoadamantanone (XLIV) may be postulated as intermediates in the formation of these olefins.

We note that the physical constants for (+)-2-diphenylmethylene-1,3,3-trimethylnorbornane (V) as reported in Part 2[1] are for a sample of very low optical

[17] H. Wynberg, K. Lammertsma, and L. A. Hulshof, *Tetrahedron Letters*, 1975, 3749.
[18] E. S. Gould, *Analyt. Chem.*, 1951, **23**, 1502.

purity. Correct values are reported in the Experimental section for the (−)-, (+)-, and (±)-isomers of this compound.

EXPERIMENTAL

M.p.s were determined with a Reichert hot-stage apparatus. I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer and u.v. spectra with a Unicam SP 800B spectrometer. [1]H N.m.r. spectra were recorded with a Varian T60 instrument (tetramethylsilane as an internal reference) and ^{13}C spectra were obtained with a Varian XL-100 spectrometer through the cooperation of Dr. L. Phillips (Department of Chemistry, Imperial College). Mass spectra were recorded with an A.E.I. MS9 instrument. Rotations were measured on a Perkin-Elmer 141 polarimeter. The high-pressure experiment (8500 atm) was conducted by Dr. K. E. Weale (Department of Chemical Engineering, Imperial College). Selenium analyses were performed by the method of Gould.[18] ' Light petroleum ' refers to the fraction b.p. 40—60 °C, and ' petroleum ' to the fraction b.p. 60—80 °C.

Di-t-butyl Ketone Hydrazone.—2,2,4,4-Tetramethylpentane-3-imine[1] (30.8 g) and hydrazine hydrate (42.0 g) were refluxed for 18 h in 2,2'-oxydiethanol (50 ml). The mixture was then cooled to room temperature and poured into cold water (300 ml). The resulting solid was filtered off, dried, and recrystallized from methanol–water to provide the hydrazone as plates (88%), m.p. 67—68.5° (lit.,[19] 68—69°).

Di-t-butyl Ketone Azine.—Diazodi-t-butylmethane (154 mg) and copper(I) iodide (10 mg) were stirred for 0.5 h. The orange colour was rapidly discharged and the white solid residue was taken up in dichloromethane (10 ml). The solution was washed with water (10 ml), dried (MgSO$_4$), and concentrated, and the residue crystallized from ether to give white needles of the *azine* (50%), m.p. 67.5—69.5°, $\nu_{max.}$ (CHCl$_3$) 1 565, 1 480, 1 390, 1 370, and 1 000 cm^{-1}, $\nu_{max.}$ (CCl$_4$) 1 480, 1 390, 1 370, 1 215, and 1 060 cm^{-1}, δ (CCl$_4$) 1.30 (s) and 1.26 (s), $\lambda_{max.}$ (cyclohexane) 242 (ε 5 900) and 260 nm (600), *m/e* 280 (M^+) and 223 (M − C$_4$H$_9$) (Found: C, 77.3; H, 12.9; N, 9.9. C$_{18}$H$_{36}$N$_2$ requires C, 77.1; H, 12.9; N, 10.0%).

Adamantanone Hydrazone.—The title compound, prepared (57%) from adamantanone by the method of Newkome and Fishel,[20] had m.p. 68.5—69° δ (CCl$_4$) 5.0—4.5br (2 H, s, exch. D$_2$O), 3.05 (1 H, m), 2.45 (1 H, m), and 1.88br (12 H, s), *m/e* 164 (M^+).

Di-t-butyl Ketone Triphenylphosphoranylidenehydrazone (XIII) *and Congeners.*—A modification of the procedure of Bestmann and Fritzsche[8] was employed. Bromine (12.8 g) in dry benzene (100 ml) was added over 30 min to a stirred, cooled (ice–water) solution of triphenylphosphine (21.0 g) in dry benzene (250 ml). After stirring for 30 min, di-t-butyl ketone hydrazone (12.5 g) and triethylamine (17.8 g) in dry benzene (80 ml) were added over 1 h. After 5 h at room temperature, the mixture was filtered and evaporated *in vacuo*. The resulting yellow oil was crystallized from chloroform–petroleum to afford *compound* (XIII) as two crops of yellow crystals (82%), m.p. 109—110°, $\nu_{max.}$ (CHCl$_3$) 1 485, 1 445, 1 390, and 1360 cm^{-1}, δ (CDCl$_3$) 7.9—7.3 (15 H, complex), 1.60 (9 H, s), and 1.12 (9 H, s) (Found: C, 77.7; H, 7.8; N, 6.6; P, 7.5. C$_{27}$H$_{33}$N$_2$P requires C, 77.9; H, 8.0; N, 6.7; P, 7.4%).

[19] H. D. Hartzler, *J. Amer. Chem. Soc.*, 1971, **93**, 4527.
[20] G. R. Newkome and D. L. Fishel, *J. Org. Chem.*, 1966, **31**, 677.

Similarly, the following were prepared from the corresponding hydrazones: (−)-1,3,3-*trimethylnorbornan-2-one triphenylphosphoranylidenehydrazone* (XIV) (90%), m.p. (from) 123—137°, $[\alpha]_D^{23}$ −41.1° (c 0.6 in $CHCl_3$), δ (CCl_4) 7.50—7.05 (15 H, complex) and 2.0—0.9 (16 H, complex, singlets at δ 1.50, 1.42, and 1.05), m/e 426 (M^+) and 262 ($M - C_{10}H_{16}N_2$) (Found: C, 79.2; H, 7.15; N, 6.9; P, 7.2. $C_{28}H_{31}N_2P$ requires C, 78.85; H, 7.3; N, 6.6; P, 7.25%); *adamantanone triphenylphosphoranylidenehydrazone* (XL) (55%), m.p. (from) 143—145°, δ (CCl_4) 7.9—7.2 (15 H, complex), 2.5br (2 H, s), and 1.9br (12 H, s), m/e 424 (M^+).

Di-t-butyl Selenoketone (XI).—(a) A vigorously stirred mixture of di-t-butyl ketone triphenylphosphoranylidenehydrazone (9.99 g), selenium (3.78 g), and tri-n-butylamine (12 drops) was heated for 21 h at 120 °C under nitrogen. Gas was evolved. The mixture was cooled to room temperature, triturated with light petroleum, and filtered through a short column of silica gel. The light petroleum was evaporated off under reduced pressure at room temperature and the resulting oil was distilled *in vacuo* into a solid CO_2–acetone trap to provide *di-t-butyl selenoketone* (XI) as a blue liquid (35%), b.p. 83—85° at 30 mmHg, $\nu_{max.}$ (film) 2 970, 1 490, 1 395, 1 365, 1 055, 970, and 785 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 230 (ε 2 800), 268 (7 200), and 710 nm (21), δ (CCl_4) 1.53 (s) (Found: C, 53.2; H, 9.0; Se, 38.2%; M^+, 206.057 8. $C_9H_{18}Se$ requires C, 52.7; H, 8.8; Se, 38.5%; M, 206.057 3).

(b) The preceding procedure was followed except that volatile material was distilled from the reaction vessel into a solid CO_2–acetone trap every 90 min by reducing the pressure (to 20 mmHg). When no more distillate was obtained, the temperature was raised to 150 °C and the procedure was continued at 1 mmHg. The combined volatile material was redistilled to provide four fractions. The first afforded pure 2,3,4,4-tetramethylpent-1-ene (XXV), b.p. 57—58° at 90 mmHg, $\nu_{max.}$ (film) 3 075, 1 785, 1 640, and 890 cm^{-1} (lit.,[21] 3 076, 1 785, and 891 cm^{-1}), δ (CCl_4) 4.72 (1 H, s), 4.62 (1 H, s), 1.87 (1 H, q, J 7 Hz), 1.70 (3 H, s), 1.00 (3 H, d, J 7 Hz), and 0.88 (9 H, s), m/e 126 (M^+). The second contained additional olefin of lower purity, b.p. 64—67° at 110 mmHg, redistilled with b.p. 124—126° (lit.,[22] 125—126°) at 754 mmHg (32% total). The third furnished diazodi-t-butylmethane [1] (12%) containing a significant amount of the olefin and a trace of the selone. The last fraction afforded pure selone (23%), b.p. 83—85° at 30 mmHg.

(c) Di-t-butyl ketone triphenylphosphoranylidenehydrazone (2.08 g) and selenium (0.79 g) were heated at 165 °C and 5 mmHg. Volatile material was continuously distilled into a solid CO_2–acetone trap at 5 mmHg. Diazodi-t-butylmethane was collected first (40%), followed by the selone (20%). N.m.r. analysis revealed the purity of the products as ca. 90 and 85%, respectively.

Stability of Di-t-butyl Selenoketone (XI).—(a) The selone (52 mg) was placed in a sealed glass tube under argon and heated for 24 h at 150 °C. No reaction was observed.

(b) The selone (20 mg) was exposed to air and irradiated with a medium-pressure mercury lamp. A precipitate (selenium) formed within 45 min, and after 18 h complete conversion into di-t-butyl ketone was observed (i.r., n.m.r.).

(c) The selone (20 mg) was exposed to air in the absence of

light for 48 h at room temperature. No change was observed. After 20 h at 80 °C, the selone had turned from blue to green but no significant quantities of new products were observed (n.m.r.).

Pyrolysis of Di-t-butyl Ketone Triphenylphosphoranylidenehydrazone (XIII).—The phosphoranylidenehydrazone (3.00 g) was heated for 5 h under nitrogen at 135 °C. The mixture was then distilled *in vacuo* into a solid CO_2–acetone trap to provide 1,1-dimethyl-2-t-butylcyclopropane (XXIV) (84%) containing a trace of diazodi-t-butylmethane. The product was redistilled twice to furnish the pure cyclopropane (XXIV) as a liquid, $\nu_{max.}$ (film) 3 050, 2 950, 1 480, 1 465, 1 380, 1 365, 1 195, 1 025, and 880 cm^{-1}, δ (CCl_4) 1.17 (3 H, s), 1.02 (3 H, s), 0.93 (9 H, s), and 0.4—0.1 (3 H, complex), m/e 126 (M^+), n_D^{21} 1.412 0 (lit.,[23] 1.416 0).

Pyrolysis of Diazodi-t-butylmethane.—The diazo compound (350 mg) was heated for 14 h at 120 °C in a sealed glass tube. After this time, n.m.r. analysis showed nearly total conversion into a mixture of the cyclopropane (XXIV) and a smaller amount of 2,3,4,4-tetramethylpent-1-ene (XXV).

Attempted Preparation of Tetra-t-butylethylene.—(a) Di-t-butyl selenoketone (XI) (205 mg) and di-t-butyl ketone triphenylphosphoranylidenehydrazone (XIII) (416 mg) were heated for 17 h in a sealed glass tube at 135 °C to afford a complex mixture (n.m.r., t.l.c.) containing large quantities of unchanged selone and 2,3,4,4-tetramethylpent-1-ene (XXV) as well as unidentified materials. Chromatography on silica gel under argon gave no tetra-t-butylethylene.

(b) The selone (XI) (113 mg) and diazodi-t-butylmethane (85 mg) were heated in a sealed glass tube at 125 °C for 24 h. Analysis (n.m.r.) then revealed unchanged selone and 1,1-dimethyl-2-t-butylcyclopropane (XXIV) as well as smaller amounts of the olefin (XXV) and di-t-butyl ketone azine. Similar results were obtained when the reactants were refluxed for 9 days in tetrahydrofuran or for 41 h in carbon tetrachloride. No reaction was observed after 6 days in the latter solvent at room temperature.

(c) The selone (205 mg) and the diazo-compound (154 mg) were heated under nitrogen during 17 h at 90 °C and 150 atm. Analysis (n.m.r.) showed the product to contain unchanged selone, bis-(2,2-dimethyl-1-t-butylpropyl) diselenide and decomposition products of the diazo-compound.

(d) (With Dr. K. E. Weale.) The selone (103 mg) and the diazo-compound (77 mg) were heated at 65 °C and 8 500 atm in a Teflon tube for 24 h. The product then contained (i.r., n.m.r.) unchanged selone, di-t-butyl ketone azine, and smaller amounts of di-t-butyl ketone and unchanged diazo-compound.

Di-t-butyl Selenoketone Se-*Oxide.*—(a) Freshly purified [24] m-chloroperbenzoic acid (172 mg) in methylene chloride (2 ml) was added dropwise to a solution of the selone (205 mg) in methylene chloride (8 ml) at −80 °C. The blue colour disappeared towards the end of the addition to furnish a clear solution. On warming to room temperature, a red precipitate (selenium) formed and the presence of di-t-butyl ketone was observed (i.r., n.m.r.).

(b) The oxidation was repeated and decomposition of the selone Se-oxide was monitored by n.m.r. It was stable at −70 °C, but converted slowly into the ketone at −40 °C and rapidly (quantitative in ca. 5 min) at −20 °C.

[21] M. S. Kharasch, Y. C. Liu, and W. Nudenberg, *J. Org. Chem.*, 1954, **19**, 1150.
[22] M. S. Kharasch, Y. C. Liu, and W. Nudenberg, *J. Org. Chem.*, 1955, **20**, 680.
[23] H. E. Simmons, jun., U.S.P. 3,074,984/1963 (*Chem. Abs.*, 1963, **58**, 13820a).
[24] N. N. Schwartz and J. H. Blumbergs, *J. Org. Chem.*, 1964, **29**, 1976.

2,2-Diphenyl-5,5-di-t-butyl-Δ³-1,3,4-selenadiazoline (XXI).—Di-t-butyl selenoketone (410 mg) in tetrahydrofuran (10 ml) was added to a cooled (ice–water bath) solution of diazodiphenylmethane (388 mg) in tetrahydrofuran (10 ml). After stirring and cooling for an additional 0.5 h, the solvent was evaporated off under reduced pressure at 0 °C. The residue was triturated with methylene chloride; the solid was filtered off and crystallized by addition of light petroleum at −80 °C to furnish a light brown solid (44%), m.p. 111—117° (decomp.). A second crop was obtained by evaporation of the filtrate at 0 °C, followed by crystallization of the residue from methylene chloride–light petroleum (29%, 73% total); m.p. 112—118° (decomp.). The product was recrystallized twice more in this manner to provide *compound* (XXI), m.p. 114—118° (decomp.), $v_{max.}$ (CCl$_4$) 3 060, 2 960, 2 030, 1 600, 1 485, 1 445, 1 390, 1 365, 1 110, 950, and 860 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 226 (ε 10 200), 325 (3 000), and 356 nm (2 800) (changes in the spectrum were observed within 1 h at room temperature), δ (CCl$_4$) 7.8—7.0 (10 H, complex) and 1.10 (18 H, s) (Found: C, 66.1; H, 7.1; N, 7.3. C$_{22}$H$_{28}$N$_2$Se requires C, 66.1; H, 7.1; N, 7.0%).

3,3-Dimethyl-1,1-diphenyl-2-t-butylbut-1-ene.— 2,2-Diphenyl-5,5-di-t-butyl-Δ³-1,3,4-selenadiazoline (XXI) (200 mg) was refluxed for 15 h in carbon tetrachloride (2 ml), during which time a red precipitate (selenium) formed. Absence of starting material and formation of the olefin, along with small amounts of di-t-butyl selenoketone and 2,3,4,4-tetramethylpent-1-ene (XXV) were indicated by n.m.r. The solution was filtered through Celite and evaporated *in vacuo*, and the residue was crystallized from ethanol to afford the olefin [1] (67%).

Competitive Reaction of Di-t-butyl Thioketone and Di-t-butyl Selenoketone with Diazodiphenylmethane.—Diazodiphenylmethane (58 mg) in carbon tetrachloride (2 ml) was added over 10 min to a cooled (0 °C) solution of di-t-butyl thioketone [1] (47 mg) and di-t-butyl selenoketone (62 mg) in carbon tetrachloride (1 ml). After stirring for 15 min at room temperature, n.m.r. demonstrated the presence of the thioketone and 2,2-diphenyl-5,5-di-t-butyl-Δ³-1,3,4-selenadiazoline (XXI). Only a trace of selone and no 2,2-diphenyl-5,5-di-t-butyl-Δ³-1,3,4-thiadiazoline [1] (XXII) were observed.

Reaction of Di-t-butyl Selenoketone with Phosphines.—(a) The selone (422 mg) and tris(dimethylamino)phosphine (336 mg) were heated for 16 h at 140 °C in a sealed glass tube. Volatile material was then distilled at 15 mmHg into a solid CO$_2$–acetone trap to provide 2,2,4,4-tetramethylpentane (XX) (50%), having ¹H and ¹³C n.m.r. spectra identical with those reported.[25, 26] The distillation residue contained chiefly tris(dimethylamino)phosphine selenide, as well as unidentified material (n.m.r.).

(b) The selone (205 mg) and tri-n-butylphosphine (202 mg) were heated for 24 h at 140 °C in a sealed glass tube. N.m.r. analysis showed 2,2,4,4-tetramethylpentane (XX) to be the main product.

Di-t-butyl Thioketone S-Oxide.—m-Chloroperbenzoic acid (1 equiv.) in ether was added over 15 min to a stirred solution of di-t-butyl thioketone (1.59 g) in ether (40 ml) at −20 to −30 °C. After 0.5 h at −20 °C and 1 h at room temperature, the colourless mixture was washed with sodium hydrogen sulphite solution and sodium hydrogen carbonate solution, and dried. Concentration of the solution at

5 mmHg afforded the crude *thioketone* S-*oxide* (XVII) as crystals (*ca.* 100%), m.p. 42—45° (subl.). A sample obtained by recrystallization from light petroleum at −30 °C followed by sublimation at 38 °C and 1 mmHg had m.p. 45—46° (subl.), $v_{max.}$ (CCl$_4$) 1 400, 1 370, and 1 075 cm^{-1}, $\lambda_{max.}$ (EtOH) 264 nm (ε 9 000), δ (CCl$_4$) 1.51 (9 H, s) and 1.38 (9 H, s), *m/e* 174 (*M*$^+$) (Found: C, 61.9; H, 10.5; S, 18.6. C$_9$H$_{18}$SO requires C, 62.0; H, 10.4; S, 18.4%).

The thioketone S-oxide (20 mg) was heated at 150 °C for 18 h in a sealed glass tube. No new products were detected (i.r., n.m.r.).

Reaction of Di-t-butyl Thioketone S-*Oxide with Di-t-butyl Selenoketone.*—(a) The thioketone S-oxide (XVII) (52 mg) and the selone (XI) (62 mg) were heated in a sealed glass tube at 185 °C for 18 h, to give di-t-butyl thioketone and di-t-butyl ketone (i.r., n.m.r.). Unchanged thioketone S-oxide was also detected. When the reaction was performed at 85 °C for 24 h, only starting material was present (n.m.r.).

(b) The thioketone S-oxide (XVII) (87 mg) and the selone (XI) (103 mg) were placed in a stoppered u.v. cell under nitrogen and irradiated with a medium-pressure mercury lamp. A precipitate (selenium) formed within 15 min, and after 4 h conversion into thioketone and ketone was complete (i.r., n.m.r.).

Photolysis of Di-t-butyl Selenoketone.—(a) The selone (205 mg) in cyclohexane (20 ml) was irradiated under nitrogen with a 300 W lamp (tungsten filament). After 40 h the solution was still blue and no new products were detected (i.r., n.m.r.) after removal of solvent under reduced pressure.

(b) The selone (205 mg) in redistilled benzene (30 ml) was irradiated under nitrogen in a quartz apparatus with a medium-pressure mercury lamp. The blue solution had turned orange within 1 h, and after 22 h the solvent was removed under reduced pressure to furnish bis-(2,2-dimethyl-1-t-butylpropyl) diselenide (93%) as a red oil containing a small amount of unchanged selone (n.m.r.). The i.r. and mass spectra were identical with those of authentic diselenide.

Diazodi-t-butylmethane.—Di-t-butyl ketone triphenylphosphoranylidene hydrazone (8.00 g) was heated for 2 h at 160 °C and 0.3 mmHg. Volatile material was continuously distilled into a solid CO$_2$–acetone trap to provide the pure diazo-compound (100%), as an orange liquid with i.r. and n.m.r. spectra identical with those of an authentic sample.[1]

N-(*Cyclohexyl*)-3,3-*dimethyl-2-t-butylbutyramide* (XXIX). —Diazodi-t-butylmethane (3.08 g) and cyclohexyl isocyanide [27] (2.70 g) were heated for 8·h at 80 °C to provide crude N-(cyclohexyl)-3,3-dimethyl-2-t-butylbut-1-enylideneamine (XXVIII) as a liquid, $v_{max.}$ (film) 2 020 cm^{-1}, *m/e* 235 (*M*$^+$). The product was then poured into dilute hydrochloric acid (50 ml) and, after stirring for 2 h, the resulting precipitate was filtered off, washed with water, and recrystallized from ethanol–water to afford two crops of the *amide* (XXIX) (86%), m.p. 176—177°. A sample obtained by sublimation at 100 °C and 0.3 mmHg, followed by recrystallization from ethanol–water, had m.p. 176.5—177°, *m/e* 253 (*M*$^+$) (Found: C, 76.0; H, 12.2; N, 5.65. C$_{16}$H$_{31}$NO requires C, 75.8; H, 12.3; N, 5.5%).

Di-t-butylketen.—The foregoing amide (3.80 g) and orthophosphoric acid (30 ml) were heated at 150 °C for 23 h.

[25] K. W. Bartz and N. F. Chamberlain, *Analyt. Chem.*, 1964, **36**, 2151.

[26] L. P. Lindeman and J. Q. Adams, *Analyt. Chem.*, 1971, **43**, 1245.

[27] R. Appel, R. Kleinstück, and K. D. Ziehn, *Angew. Chem. Internat. Edn.*, 1971, **10**, 132.

The mixture was poured into water (100 ml) and extracted with ether (3 × 30 ml); the extracts were filtered through Celite, dried (Na_2SO_4), and evaporated *in vacuo* to provide the crude acid. Direct treatment of the latter with thionyl chloride *via* the method of Newman [12] provided the acid chloride (81% based on amide); $\nu_{max.}$ (film) 1 800 cm^{-1} (lit.,[12] 5.57 μm). Purity was confirmed by n.m.r.: δ (CCl_4) 2.81 (1 H, s) and 1.17 (18 H, s).

3,3-Dimethyl-2-t-butylbutyryl chloride (266 mg) and tri-n-butylamine (257 mg) were heated for 3 h at 80 °C. Di-t-butylketen (XXVII) was then distilled at an oil-bath temperature of 90 °C and 5 mmHg into a solid CO_2–acetone trap (86%), $\nu_{max.}$ (film) 2 090 cm^{-1} (lit.,[12] 4.80 μm), δ (CCl_4) 1.18 (s).

Attempted Reaction of Di-t-butylketen (XXVII) *with Di-t-butyl Selenoketone* (XI).—(a) The keten (77 mg) and the selone (103 mg) were heated in a sealed glass tube at 125 °C for 23 h. The mixture then contained unchanged keten (i.r., n.m.r.) and bis-(2,2-dimethyl-1-t-butylpropyl) diselenide (n.m.r. and mass spectra). No significant quantities of other products were observed.

(b) No new products were observed when the selone and ketene were cooled to −80 °C in methylene chloride, or when irradiated for 41 h in benzene (Pyrex apparatus) with a high-pressure mercury lamp.

Attempted Reaction of Di-t-Butylketen with Di-t-butyl Thioketone.—A mixture of the keten (77 mg) and the thioketone (79 mg) was irradiated under nitrogen (Pyrex apparatus) with a medium-pressure mercury lamp. After 14 h, no new products were detected (n.m.r.).

Attempted Reaction of Di-t-butyl Selenoketone with Di-t-butyl Thioketone.—The selone (103 mg) and the thione (79 mg) were placed in a stoppered u.v. cell under nitrogen and irradiated for 22 h with a medium-pressure mercury lamp. N.m.r. then showed the presence of the thioketone, bis-(2,2-dimethyl-1-t-butylpropyl) diselenide, and the corresponding disulphide, as well as several unidentified components. A small sample of the disulphide was obtained for comparison by reduction (sodium borohydride) of the thioketone, followed by oxidation of the resulting thiol with iodine; δ (CCl_4) 2.53 (2 H, s) and 1.17 (36 H, s), *m/e* 318 (M^+).

Reduction of Di-t-butyl Selenoketone.—(a) *With sodium borohydride.* The selone (103 mg) in ethanol (25 ml) was added to sodium borohydride (38 mg) in ethanol (25 ml). The blue colour rapidly changed to pale yellow, and after 20 h the ethanol was removed under reduced pressure. The residue was taken up in petroleum (100 ml), washed with water (100 ml), dried, concentrated *in vacuo*, and crystallized from petroleum–methanol to provide bis-(2,2-*dimethyl*-1-*t*-*butylpropyl*) *diselenide* (99%), m.p. 56.5°, $\nu_{max.}$ ($CHCl_3$) 1 480, 1 390, and 1 370 cm^{-1}, δ (CCl_4) 3.08 (2 H, s) and 1.25 (36 H, s), *m/e* 414 (M^+) (Found: C, 52.85; H, 9.3. $C_{18}H_{38}Se_2$ requires C, 52.4; H, 9.3%).

(b) *With sodium–potassium alloy.* Freshly prepared sodium–potassium alloy (1 : 5) (180 mg) was covered with dry ether (1 ml) under nitrogen. The selone (204 mg) was added in dry ether (1 ml) over 5 min. An immediate exothermic reaction was observed and a red colour appeared. After stirring for 3 days at room temperature, water was cautiously added, followed by concentrated hydrochloric acid (several drops). A red precipitate (selenium) formed upon acidification and was filtered off (33%). The ether layer was separated, dried, and evaporated at room temperature and 300 mmHg. The remaining oil was distilled at 1

mmHg into a solid CO_2–acetone trap to provide 2,2,4,4-tetramethylpentane (XX) (45%), identical (g.l.c., n.m.r.) with the sample prepared by the reaction of the selone with tris(dimethylamino)phosphine.

The reaction was performed in a similar fashion with sodium and sodium amalgam (1% and 10%). The chief product in each case was bis-(2,2-dimethyl-1-t-butyl-propyl) diselenide (*ca.* 50%). Volatile products were not examined.

The selone was unchanged when treated with copper powder in refluxing tetrahydrofuran (21 h) or with zinc dust in ether at room temperature (24 h).

Reaction of Di-t-butyl Selenoketone with Pentacarbonyl-iron.—The selone (205 mg) and pentacarbonyliron (0.5 ml) were stirred in benzene (2 ml) for 26 h at room temperature. The solution was filtered and found to contain only starting material (n.m.r.).

The reaction was repeated at reflux for 30 h; more pentacarbonyliron (0.5 ml) was added after 6 h. The mixture was then filtered through Celite and evaporated under reduced pressure to afford the complex $Fe_3Se_2(CO)_9$ (19%) as a homogeneous (t.l.c.), dark purple crystalline solid, m.p. 115—120° (decomp.), $\nu_{max.}$ (CCl_4) 2 090, 2 060, 2 040, 2 020, and 1 985 cm^{-1} (lit.,[14] 2 087, 2 058, 2 040, 2 018, and 1 984 cm^{-1}), *m/e* 580 (M^+), 552, 524, 496, 468, 440, 412, 384, 356, and 328 (M^+ − 9CO). Volatile products were not identified.

N-(2,2-*Dimethyl*-1-*t*-*butylpropyl*)*formamide*.—2,2,4,4-Tetramethylpentane-3-imine (14 g) in dry ether (50 ml) was added to a suspension of lithium aluminium hydride (1.7 g) in dry ether (50 ml). The mixture was stirred at room temperature for 24 h and refluxed for 2 h. After cooling, water (1.7 ml), 15% sodium hydroxide (5 ml), and water (5 ml) were cautiously added in succession, and the mixture was filtered, concentrated, and distilled to give the amine (83%), b.p. 79—81° at 40 mmHg, δ (CCl_4) 2.15 (1 H, s) and 1.00 (18 H, s).

Formic acid (60 ml) was added dropwise to acetic anhydride (60 ml) at 0 °C, followed by 3-amino-2,2,4,4-tetramethylpentane (10.7 g). The solution was stirred for 0.5 h, heated on a steam-bath for a further 0.5 h, and concentrated under reduced pressure. The residual oil was taken up in dichloromethane (100 ml) and stirred vigorously with 10% sodium hydrogen carbonate (150 ml) for 3.5 h. The layers were separated, and the aqueous layer washed with dichloromethane (2 × 50 ml). The combined organic fractions were dried and concentrated to a solid, which was crystallized from ether at −30 °C to give the *formamide* (93%), m.p. 89—91°, $\nu_{max.}$ (CCl_4) 3 450, 1 680, 1 375, and 1 250 cm^{-1}, δ (CCl_4) 8.16 (1 H, d, *J* 2 Hz, collapses to singlet upon D_2O exch.), 8.0 (1 H, m, exch. D_2O), 3.87 (2 H, d, *J* 11 Hz, collapses to singlet upon D_2O exch.), and 1.03 (18 H, s), *m/e* 171 (M^+) (Found: C, 70.15; H, 12.3; N, 8.2. $C_{10}H_{21}NO$ requires C, 70.1; H, 12.35; N, 8.2%).

3-*Isocyano*-2,2,4,4-*tetramethylpentane* (XXXIV).— The foregoing formamide (3.4 g) in pyridine (10 ml) and dichloromethane (25 ml) was treated with phosgene (4 g) in dichloromethane (20 ml) at 0 °C. After stirring for 0.5 h and refluxing for 0.5 h, dichloromethane (50 ml) was added, and the mixture was washed with water (100 ml), N-hydrochloric acid (50 ml), and 10% sodium hydrogen carbonate (50 ml), dried ($MgSO_4$), and concentrated. Distillation afforded the *isocyanide* (72%), b.p. 60—62° at 5 mmHg, $\nu_{max.}$ (CCl_4) 2 120, 1 470, 1 400, and 1 375 cm^{-1}, δ (CCl_4) 3.07 (1 H, t, J_{NH} 2 Hz) and 1.10 (18 H, s), *m/e* 138

$(M - CH_3)$ (Found: C, 77.9; H, 12.3; N, 9.1. $C_{10}H_{19}N$ requires C, 78.4; H, 12.5; N, 9.1%).

3-*Isoselenocyanato*-2,2,4,4-*tetramethylpentane* (XXXV).—3-Isocyanato-2,2,4,4-tetramethylpentane (0.3 g) in tetrahydrofuran at -80 °C was treated with n-butyl-lithium (2.4 mmol) in pentane under argon. After 5 min, selenium (0.4 g) was added with stirring, and the mixture allowed to warm to room temperature overnight. Removal of solvent, followed by preparative t.l.c. (silica) afforded di-n-butyl diselenide (54%) and the *isoselenocyanate* (XXXV) (75%), m.p. 45°, $\nu_{max.}$ (CCl$_4$) 2 140 vs, 1 400, and 1 275 cm^{-1}, δ (CCl$_4$) 3.30 (1 H, s) and 1.15 (18 H, s), $\lambda_{max.}$ (cyclohexane) 250 nm (ϵ 9 400), m/e 233 (M^+) (Found: C, 51.9; H, 8.1; N, 6.0. $C_{10}H_{19}NSe$ requires C, 51.7; H, 8.25; N, 6.0%). The use of lithium di-isopropylamide instead of n-butyllithium gave a 72% yield of the isoselenocyanate.

1,3,3-*Trimethylnorbornane*-2-*selone* (XII).—(—)-1,3,3-Trimethylnorbornan-2-one triphenylphosphoranylidenehydrazone (XIV) (3.41 g) and selenium (1.62 g) were heated at 160 °C with stirring at 5 mmHg pressure. A bright blue liquid was distilled into a solid CO$_2$–acetone cold trap. Redistillation and recrystallization from ether at -30 °C gave the blue crystalline *selone* (XII) (28%), m.p. 41—47°, $\nu_{max.}$ (CCl$_4$) 1 470, 1 450, 1 380, 1 360, 1 080, and 1 050 cm^{-1}, δ (CCl$_4$) 2.6—1.0 (complex, singlets at δ 1.43, 1.22, and 1.13), $\lambda_{max.}$ (cyclohexane) 616 (ϵ 42), 272 (9 600), and 224 nm (3 700), m/e 216 (M^+) (Found: C, 56.15; H, 7.5; Se, 36.7. $C_{10}H_{16}Se$ requires C, 55.8; H, 7.5; Se, 36.7%).

A sample of the selone (XII) was heated in a sealed tube under argon at 150 °C for 24 h without decomposition (n.m.r.).

(—)-1,1′,3,3,3′,3′-*Hexamethyl*-2,2′-*binorbornylidene* (XXXVI).—(a) (—)-1,3,3-Trimethylnorbornan-2-one triphenylphosphoranylidene hydrazone (XIV) (3.41 g) and selenium (1.62 g) were heated at 160 °C with stirring under dry nitrogen for 24 h. The cooled residue was extracted with hot petroleum and the extract concentrated and chromatographed on silica (100 g). Elution with petroleum gave an oil (0.5 g). Repeated recrystallization from petroleum at -30 °C gave a single isomer of the olefin (XXXVI) (24%), m.p. 125—127°, $[\alpha]_D^{23}$ $-240.0°$ (c 0.3 in EtOH), $\nu_{max.}$ (CCl$_4$) 1 470, 1 450, 1 390, and 1 365 cm^{-1}, δ (CCl$_4$) 2.1—0.9 (complex, singlets at δ 1.50, 1.32, and 1.25), m/e 272 (M^+), 257 ($M - CH_3$), and 242 ($M - C_2H_6$) (Found: C, 87.8; H, 12.1. $C_{20}H_{32}$ requires C, 88.2; H, 11.8%).

(b) The hydrazone (XIV) (2.13 g) and (—)-1,3,3-trimethylnorbornane-2-thione[1] (0.84 g) were treated (24 h) and worked up as in (a). Elution with petroleum gave the olefin (XXXVI) (72%), m.p. 110—115°, $[\alpha]_D^{23}$ $-174°$ (c 0.6 in EtOH), n.m.r. and i.r. spectra identical with those for the single isomer. Repeated recrystallization from hot ethanol gave material of m.p. 120—125° and $[\alpha]_D^{23}$ $-225.0°$ (c 0.6 in EtOH).

Ozonolysis of the Binorbornylidene (XXXVI).—Ozone was bubbled through a solution of the olefin (0.54 g) in dry dichloromethane (10 ml) at -25 °C. After 2.5 h, the starting material was entirely consumed (t.l.c.). The solution was washed with 5% sodium iodide and 5% sodium thiosulphate, dried (MgSO$_4$), and concentrated to an oil (0.7 g). T.l.c. indicated the presence of a complex mixture containing 1,3,3-trimethylnorbornanone (identified by i.r. and n.m.r.).

1,1″,3,3,3″,3″-*Hexamethyldispiro*[*norbornane*-2,2′-*oxiran*-3′,2″-*norbornane*] (XXXVIII).—The olefin (0.54 g)

was added with stirring to a solution of m-chloroperbenzoic acid (0.69 g) in chloroform (10 ml). After 1 h, the solution was washed with aqueous potassium carbonate, dried (MgSO$_4$), and concentrated, and the residue was crystallized from carbon tetrachloride to give the *epoxide* (XXXVIII) ($>90%$), m.p. 117—118°, $[\alpha]_D^{23}$ $+65.0°$ (c 0.5 in cyclohexane), $\nu_{max.}$ (CCl$_4$) 1 465, 1 455, 1 390, 1 370, 1 210, 950, 910, and 870 cm^{-1}, δ (CCl$_4$) 2.2—0.9 (complex, singlets at δ 1.17, 1.13, and 1.05), m/e 288 (M^+) and 273 ($M - CH_3$) (Found: C, 83.05; H, 11.45. $C_{20}H_{32}O$ requires C, 83.3; H, 11.2%).

2,2-*Diphenyl*-3,3-*di-t-butyloxiran*.— 1,1-Diphenyl-2,2-di-t-butylethylene (0.29 g) was added with stirring to a solution of m-chloroperbenzoic acid (0.69 g) in chloroform (10 ml). After 16 h at room temperature, the solution was refluxed for 4 h, washed with aqueous potassium carbonate, dried (MgSO$_4$), and concentrated, and the residue was crystallized from ethanol to give the *epoxide* ($>90%$), m.p. 152—153°, $\nu_{max.}$ (CCl$_4$) 1 480, 1 455, 1 395, 1 370, 1 240, 1 230, 950, 885, and 865 cm^{-1}, δ (CCl$_4$) 7.5—6.8 (10 H, complex) and 1.02 (18 H, s), m/e 308 (M^+) and 251 ($M - C_4H_9$) (Found: C, 85.8; H, 9.25. $C_{22}H_{28}O$ requires C, 85.7; H, 9.15%).

Attempted Preparation of 2-*Di-t-butylmethylene*-1,3,3-*trimethylnorbornane* (IX).—(a) The hydrazone (XIV) (2.13 g) and di-t-butyl thioketone (0.79 g) were treated (24 h) and worked up as for the preparation of the olefin (XXXVI). Elution with petroleum gave the olefin (XXXVI) (isomeric mixture) [59% based on (XIV)], m.p. 70—75°, $[\alpha]_D^{23}$ $-189.6°$ (c 0.6 in EtOH), i.r. and mass spectra identical with those for the single isomer, δ (CCl$_4$) 2.1—0.9 (complex, singlets at δ 1.50, 1.42, 1.32, 1.25, and 1.18) (Found: C, 88.2; H, 11.8. Calc. for $C_{20}H_{32}$: C, 88.2; H, 11.8%).

A portion was recrystallised from hot ethanol to m.p. 82—87° and $[\alpha]_D^{23}$ $-231.3°$ (c 0.6 in EtOH). A further portion was recrystallized from petroleum at $-30°$ to m.p. 120—125°, $[\alpha]_D^{23}$ $-230.8°$ (c 0.6 in EtOH), n.m.r. data identical with those for the single isomer.

(b) Di-t-butyl ketone triphenylphosphoranylidenehydrazone (XIII) (2.08 g) and (—)-1,3,3-trimethylnorbornane-2-thione (0.84 g) were treated (24 h) and worked up as in (a). Elution with petroleum gave the olefin (XXXVI) (isomeric mixture) [28% based on (XXXVII)], di-t-butyl thioketone (30%), and the starting thione (36%).

(c) Di-t-butyl selenoketone (XI) (205 mg) and (—)-1,3,3-trimethylnorbornan-2-one triphenylphosphoranylidenehydrazone (XIV) (426 mg) were heated for 19 h at 185 °C in a sealed glass tube. Chromatography on silica gel (petroleum) furnished the binorbornylidene (XXXVI) as a mixture of isomers (76%), identical (i.r., n.m.r., and t.l.c.) with an authentic sample. Further elution (chloroform) afforded crude triphenylphosphine selenide (75%), which was recrystallized from chloroform–methanol; m.p. 188—189° (lit.,[28] 184—185°). The presence of a large amount of 1,1-dimethyl-2-t-butylcyclopropane (XXIV) was also observed (n.m.r.). When the reaction was performed for 15 h at 120 °C, starting material was detected (n.m.r. and t.l.c.).

Attempted Preparation of Selenobenzophenone (XLIII).—Benzophenone triphenylphosphoranylidenehydrazone [8] (3.8 g) and selenium (1.3 g) were treated under the conditions used for trimethylnorbornane-2-selone. No distillate was observed, and the evolution of nitrogen ceased after 2 h. The cooled mixture was taken up in chloroform; the solu-

[28] N. N. Mel'nikov and M. S. Rokitskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1938, **8**, 834.

tion was filtered, and concentrated and the residue chromatographed on silica (200 g). Elution with 50% benzene–petroleum gave tetraphenylethylene (84%), m.p. 227° (lit.,[29] 223—224°), identical with an authentic sample.

Attempted Preparation of Selenoadamantanone (XLIV).—Adamantanone triphenylphosphoranylidenehydrazone (XL) (1.7 g) and selenium (0.63 g) were treated under the conditions used for trimethylnorbornane-2-selone. No distillate was observed. After 4 h the mixture was cooled and taken up in chloroform; the solution was filtered and concentrated to an oil (0.32 g). Preparative t.l.c. (silica; petroleum) gave adamantylideneadamantane (24%), m.p. 189—190° (lit.,[30] 184—187°), m/e 268 (M^+).

2-Diphenylmethylene-1,3,3-trimethylnorbornane [1]   (V).—The reaction of (−)-1,3,3-trimethylnorbornane-2-thione {prepared from the (−)-2-ketone, $[\alpha]_D^{23}$ −48.3° (neat) (lit.,[31] $[\alpha]_D^{20}$ −65°)} with diazodiphenylmethane gave,[1]

[29] J. E. Mackenzie, *J. Chem. Soc.*, 1922, 1695.
[30] H. W. Geluk, *Synthesis*, 1970, 652.
[31] J. V. Braun and A. Jacob, *Ber.*, 1933, **66**, 1461.

upon work-up, (−)-2-diphenylmethylene-1,3,3-trimethylnorbornane (42%), m.p. 140—142°, $[\alpha]_D^{23}$ −326.9° (c 0.9 in EtOH). A portion was recrystallized to m.p. 156—157.5° and $[\alpha]_D^{23}$ −360.2° (c 0.7 in EtOH).

Similarly, (+)-1,3,3-trimethylnorbornane-2-thione {prepared from the (+)-2-ketone, $[\alpha]_D^{23}$ + 35.6° (neat)} gave (+)-2-diphenylmethylene-1,3,3-trimethylnorbornane (90%), crystallized to m.p. 153—157° and $[\alpha]_D^{23}$ +367.2° (c 0.9 in EtOH) (previously reported as m.p. 137—139°, $[\alpha]_D^{23}$ +37.7°).

(±)-2-Diphenylmethylene-1,3,3-trimethylnorbornane had m.p. 140—141.5°, $[\alpha]_D^{23}$ 0°.