Thermal and Photochemical Studies of Symmetrical and Unsymmetrical Dihydro-1,3,4-selenadiazoles

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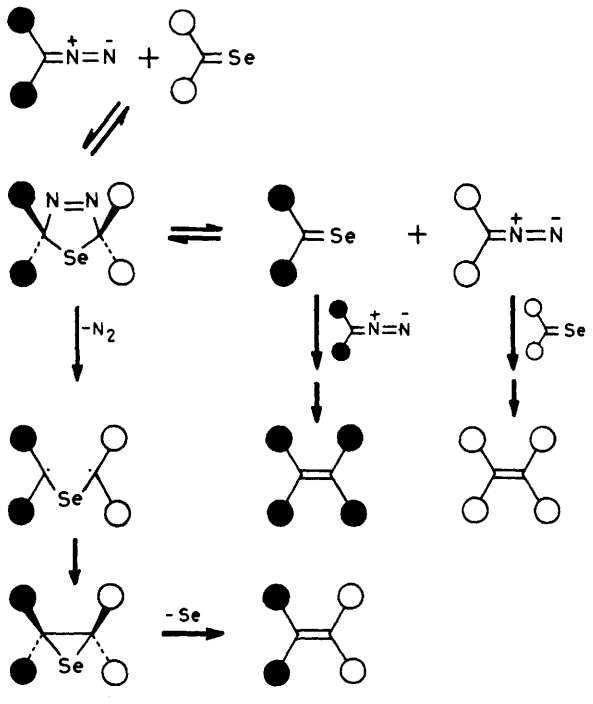
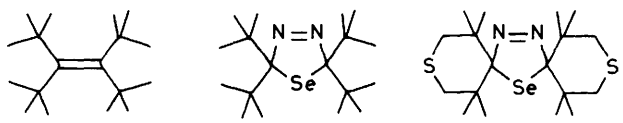
The thermal and photochemical reactivities of very sterically hindered dihydroselenadiazoles were investigated. The symmetrical tied-back dihydroselenadiazoles (**4**)—(**6**), and unsymmetrical fenchane (1,3,3-trimethylnorbornane) derived dihydroselenadiazoles (**10**)—(**12**) proved to be relatively thermally stable and could be used as intermediates in the preparation of the symmetrical olefins (**7**)—(**9**) and fenchane-derived olefins (**15**)—(**17**). The di-t-butylmethylene-derived dihydroselenadiazoles (**28**)—(**30**) were isolable, but underwent complete retrocyclization on thermolysis. Photolysis of symmetrical and unsymmetrical dihydroselenadiazoles afforded the corresponding azines in good yield.

Two-fold extrusion reactions have been widely used in the preparation of very sterically hindered alkenes.[1,2] Dihydro-1,3,4-selenadiazoles have proved to be particularly useful intermediates in these reactions.[2,3] Sterically hindered dihydroselenadiazoles can be readily prepared *via* a dipolar cycloaddition of a sterically hindered selone with a sterically hindered diazo compound; subsequent thermal extrusion of selenium and nitrogen affords the desired olefin (Scheme). In



Scheme.

the course of our work on approaches to tetra-t-butylethylene (**1**) *via* tied-back functionalized hindered alkenes,[3] we thought it necessary to investigate the thermal and photochemical reactivity of sterically hindered dihydroselenadiazoles. We were especially interested in developing methods of preparing unsymmetrical hindered olefins using two-fold extrusion reactions (*vide infra*), since we had previously observed retrocyclization–recombination affording the least hindered of the possible olefins formed in other attempted unsymmetrical two-fold extrusion procedures (Scheme).[2,4]



(1) (2) (3)

Table 1. Pyrolysis of symmetrical dihydroselenadiazoles at 190 °C

Dihydro-selenadiazole	Products	Pyrolysis time and product yield (%) 2 min	24 h (only olefin reported)
(**4**)	(**7**)	40	70
(**4**)	(**24d**)	40	
(**4**)	(**4**)	20	
(**5**)	(**8**)	40	47
(**5**)	(**25d**)	40	
(**5**)	(**5**)	20	
(**6**)	(**9**)	50	71
(**6**)	(**26d**)	40	
(**6**)	(**6**)	10	

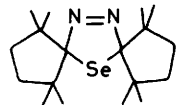
Results and Discussion

As previously reported neither of the dihydroselenadiazoles (**2**) and (**3**) can be isolated from reactions of the corresponding selones and diazoalkanes. Apparently, significant non-bonded interactions across the heterocyclic system destabilize the dihydroselenadiazole. There is no spectroscopic evidence for the existence of even small amounts of the dihydroselenadiazole (**2**) or (**3**) in equilibrium with the corresponding selone and diazoalkane.[2,4] In contrast to these results, more tied-back derivatives (**4**)—(**6**) have been readily prepared, and show remarkable thermal stability. These nicely crystalline, characterizable dihydroselenadiazoles are stable indefinitely at room temperature if protected from light. The dihydroselenadiazoles (**4**) and (**5**) did not thermally decompose until they were heated above their melting points (*ca.* 130 °C); the dihydroselenadiazole (**6**) was thermally stable up to *ca.* 170 °C. Pyrolysis of these compounds at 190 °C gave the expected olefins (**7**)—(**9**) in good yield (Table 1). The fact that significant olefin formation occurred within 2 min, and relatively minor increases in yield took place during 24 h, suggests that retrocyclization–recombination was a minor pathway in this symmetrical olefin formation.

The unsymmetrical fenchone (1,3,3-trimethylnorbornan-2-one) derivatives (**10**)—(**12**) also proved to be easily prepared

Table 2. Pyrolysis of unsymmetrical dihydroselenadiazoles at 190 °C

Dihydroselenadiazole	Product	Olefin yield (%)
(10)	(7)	6
(10)	(15)	29
(10)	(20)	23
(11)	(8)	18
(11)	(16)	40
(11)	(20)	22
(12)	(9)	15
(12)	(17)	25
(12)	(20)	10



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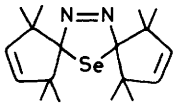

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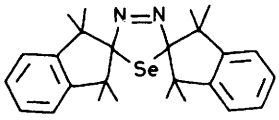

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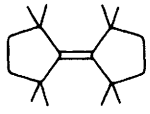
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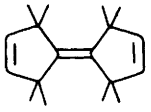
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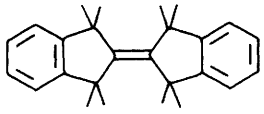
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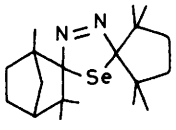

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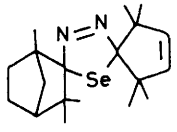

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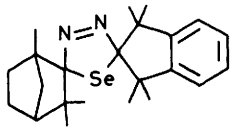

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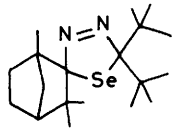

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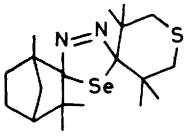

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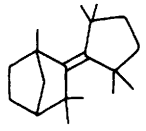
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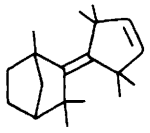
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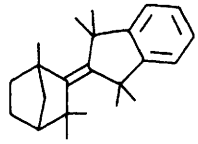
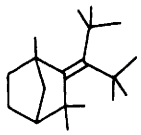

(17)

and readily isolated in contrast to the less tied-back compounds (**13**) and (**14**) which were not isolable nor detectable spectroscopically.[2,4] Compound (**10**)—(**12**) proved to be inseparable diastereoisomeric mixtures which were stable up to their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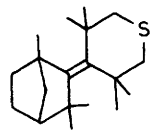

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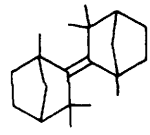
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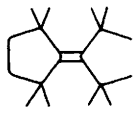
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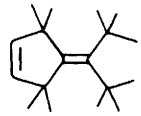
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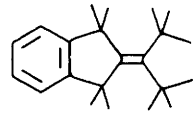
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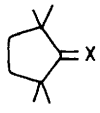

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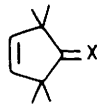

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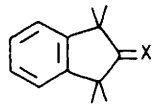

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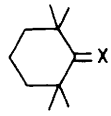


(27)

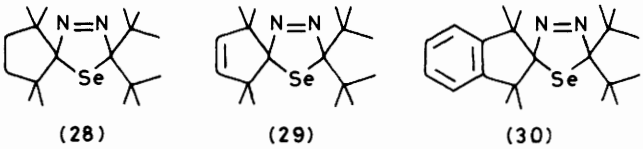
a; X = NNH_2 **c**; X = N_2
b; X = $NNPPh_3$ **d**; X = Se

melting points (*ca.* 130 °C). Pyrolysis of these dihydroselenadiazoles at 190 °C gave mixtures of three possible alkenes (Table 2). While the major product in each case was the unsymmetrical olefin (**15**)—(**17**), considerable amounts of the symmetrical olefins formed *via* retrocyclization–recombination.

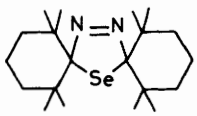
This success in forming unsymmetrical olefins is in marked contrast to attempts to prepare the olefins (**18**) and (**19**) *via* the dihydroselenadiazoles (**13**) and (**14**) where the only olefinic product isolated was 2,2′-bifenchylidene (**20**). This complete retrocyclization–recombination in the cases of compounds (**13**) and (**14**) indicates that there are increased steric interactions in these dihydroselenadiazoles relative to the more tied-back species (**10**)—(**12**). The modest success in preparing unsymmetrical fenchane-derived olefins such as (**15**)—(**17**) led us to concentrate on the attempted preparation of unsymmetrical di-t-butylmethylene substituted olefins such as (**21**)—(**23**). If such compounds could be prepared, the difficulties in the functionalization necessary for the conversion into (**1**)[4,5] could be considerably lessened. First, the central double bond would be more hindered, lessening the likelihood of reactions at this site. Secondly, only one tied-back site would be untied and reduced, limiting the possible side reactions previously observed in attempted functionalization of the olefins (**7**) and (**9**).

The reactions of di-t-butyldiazomethane with the selones[6] (**24d**), (**25d**), and (**26d**) without solvent at −30 °C led to reasonable yields of crystalline dihydroselenadiazoles (**28**)—(**30**). While these compounds appeared to be quite stable in the crystalline form, rapid retrocyclization occurred upon attempted recrystallization from warm solvents. An n.m.r. investigation of the solution stability of dihydroselenadiazoles in deuteriochloroform or carbon tetrachloride confirmed this instability. One interesting point worth noting is the preponderance of tied-back selone formed upon these retrocyclizations relative to di-t-butylselone (Table 3). The pyrolysis of the dihydroselenadiazoles (**28**)—(**30**) afforded the symmetrical olefins (**7**)—(**9**) as the only olefinic products.

When 2,2,5,5-tetramethylcyclohexaneselone (**27**) was treated with the corresponding diazoalkane at −30 °C, a colourless crystalline product was formed, presumably the dihydroselenadiazole (**31**). Attempted dissolution of this compound at −30 °C or warming of the compound to room temperature led to complete retrocyclization. No spectroscopic identification of



(28) (29) (30)



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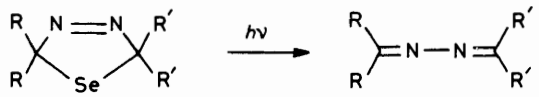


(4),(32) R,R = R′,R′ =

(5),(33) R,R = R′,R′ =

(6),(34) R,R = R′,R′ =

(10),(35) R,R = , R′,R′ =

(11),(36) R,R = , R′,R′ =

(12),(37) R,R = , R′,R′ =

(28),(38) R,R = , R′,R′ = Bu^t

(29),(39) R,R = , R′ R′ = Bu^t

(30),(40) R,R = , R′ R′ = Bu^t

Table 3. Solution stability of unsymmetrical dihydroselenadiazoles at 21 °C

Dihydroselenadiazole	Half-life (min)	Selone:di-t-butyl selone
(28)	184	30:1
(29)	264	25:1
(30)	21	25:1

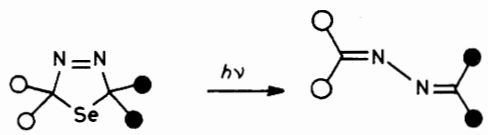
Table 4. Dihydroselenadiazole photolysis at 3 000 Å

Dihydroselenadiazole	Azine	Isolated (g.c.) yield (%)
(4)	(32)	78 (90)
(5)	(33)	80 (95)
(6)	(34)	52 (70)
(10)	(35)	82
(11)	(36)	88
(12)	(37)	76
(28)	(38)	40 (50)
(29)	(39)	47 (70)
(30)	(40)	50 (70)

this compound was possible. If this material was in fact the dihydroselenadiazole (**31**), this suggests a limit in the stability of dihydroselenadiazoles because of the increased steric interactions due to the fact that the tetramethylcyclohexanylidene moiety is less tied-back in (**31**) compared with dihydroselenadiazoles (**4**)—(**6**) or (**28**)—(**30**). In addition, no dihydroselenadiazole was observed upon the attempted reaction of dimesityldiazomethane[7] with compound (**26**) or (**27**), showing another steric limitation to dihydroselenadiazole formation.

The recent successes in the use of high pressure to overcome steric constraints[8,9] led us to investigate the effect of pressure on dihydroselenadiazole thermolyses. While the thermolysis of di-t-butyldiazomethane and di-t-butyl selone at 8.5 kbar led only to di-t-butylketazine,[2] it was hoped that with an isolable selenadiazole retrocyclization would be retarded allowing a 'normal' extrusion to take place. Warming the dihydroselenadiazole (**29**) at temperatures of 30—80 °C in dichloromethane–tetrahydrofuran at 15 kbar gave mixtures containing mainly starting dihydroselenadiazole as well as small amounts of the symmetrical dihydroselenadiazole (**5**), the selone (**25**), and the olefin (**8**). No unsymmetrical olefin (**22**) could be detected in the mixture. It is likely from these results that extrusion of nitrogen from a dihydroselenadiazole occurs with a net increase in volume as has been reported for typical azo compound pyrolyses.[10]

Finally, photolyses of dihydroselenadiazoles were attempted. If the photochemical extrusion of nitrogen from dihydroselenadiazoles could be induced, it would provide a useful alternative to pyrolysis, potentially avoiding problems associated with thermal retrocyclization. Photolysis of dihydroselenadiazoles under a variety of conditions led only to selenium extrusion affording azines in moderate to good yield (Table 4). Only traces of the olefin (**8**) could be detected in the photolyses of the dihydroselenadiazoles (**5**) presumably because of a competing thermal reaction. Photolysis of the unsymmetrical dihydro-



selenadiazoles (**28**)—(**30**) proceeded with some retrocyclization leading to photoreduction of the thermally generated selone. The diselenides resulting from this process complicated the work-up of the reaction mixtures, lowering the isolated azine yields.

These photochemical results parallel those described for moderately hindered dihydrothiadiazoles.[11,12] Azine formation in these cases was explained by the absence of an orbital symmetry-allowed pathway for the extrusion of nitrogen, where an allowed pathway was available for the loss of sulphur.[11] While these reactions did not provide a route to olefins,

dihydroselenadiazole photolyses may be useful for the preparation of sterically hindered azines, and especially for the synthesis of unsymmetrical azines which can not be easily prepared using other procedures.

Experimental

General Methods.—G.l.c. analyses were performed with a GOW-MAC 550P gas chromatograph and a stainless steel column filled with 8% OV-17 or 5% OV-101 on Chromosorb W-HP (80—100 mesh). ^{1}H N.m.r. spectra were recorded with a Jeol CO PS 100 (100 MHz) spectrometer using tetramethylsilane as an internal standard. ^{13}C N.m.r. spectra were recorded with a Varian XL 200 spectrometer using tetramethylsilane as an internal standard. I.r. spectra were recorded with a Perkin-Elmer 382 spectrophotometer. U.v. spectra were recorded with a Perkin-Elmer 320 UV-VIS spectrophotometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-GL or a Hewlett-Packard 5995A GC-MS. Elemental analyses were performed by Baron Analytical, Orange, CN, and by MHW Laboratories, Phoenix, Arizona. Tetrahydrofuran was dried by distillation from benzophenone–sodium. Diethylene glycol and hydrocarbon solvents were dried over sodium wire. Triethylamine was distilled from barium oxide. Solvents were removed with a rotary evaporator under reduced pressure. M.p.s were recorded on a Mel-temp melting point apparatus and are uncorrected. Ether refers to diethyl ether. The preparations of the sebones have been reported previously.[6]

1,1,3,3-*Tetramethylindan*-2-*one Hydrazone* (**26a**).—1,1,3,3-Tetramethylindan-2-one[13] (18 g, 96 mmol) and an excess of hydrazine hydrate (25 ml) in diethylene glycol (35 ml) were stirred and heated to reflux for 4 days. The reaction mixture was cooled, added to water (50 ml) and extracted with ether (4 × 50 ml). The combined organic layers were washed with water, saturated brine, and dried (Na_2SO_4). Evaporation of solvent gave white crystals of the hydrazone. Two crops of colourless needles were obtained from hexane (15.1 g, 78%); m.p. 106—106.5 °C; $\nu_{max.}$($CHCl_3$) 3 540, 1 682, 1 640, 1 510, 1 482, 1 478, 1 390, and 1 335 cm^{-1}; δ(CCl_4) 7.18 (4 H, s), 5.2 (2 H, br s), 1.60 (6 H, s), and 1.35 (6 H, s) (Found: C, 77.2; H, 8.9; N, 13.85. Calc. for $C_{13}H_{18}N_2$: C, 77.19; H, 8.97; N, 13.85%).

1,1,3,3-*Tetramethylindan*-2-*one Triphenylphosphoranylidenehydrazone* (**26b**).—Bromine (24.6 g, 154 mmol) in dry benzene (180 ml) was added during 30 min to a stirred, ice-cooled solution of triphenylphosphine (37.4 g, 144 mmol) in dry benzene (440 ml). After an additional 30 min of stirring, 1,1,3,3-tetramethylindan-2-one hydrazone (**26a**) (30.2 g, 149 mmol) and triethylamine (44 ml, 32.4 g, 320 mmol) in dry benzene (160 ml) were added during 1 h. After 5 h at room temperature the mixture was filtered and concentrated to give yellow crystals. Recrystallization from chloroform–hexane gave the phosphazine (**26b**) (61.2 g, 89%) as three crops of yellow needles: m.p. 165 °C; $\nu_{max.}$(CCl_4) 3 070, 1 490, 1 258, 1 118, and 1 030 cm^{-1}; δ(CCl_4) 8.0—7.3 (15 H, complex), 7.15 (4 H, s), 1.82 (6 H, s), and 1.20 (6 H, s) (Found: C, 80.6; H, 6.9; N, 6.1. Calc. for $C_{31}H_{31}N_2P$: C, 80.49; H, 6.76; N, 6.06%).

2-*Diazo*-1,1,3,3-*tetramethylindan* (**26c**).—(*a*) 1,1,3,3-Tetramethylindan-2-one hydrazone (**26a**) (0.22 g), barium manganate[14] (700 mg), and calcium oxide (700 mg) in dichloromethane (4 ml) were stirred for 2 h at room temperature. The mixture was filtered through Celite, concentrated *via* a rotary evaporator and purified by Kugelrohr distillation at 50 °C (0.5 Torr) to give the pure diazo compound (**26c**) (0.180 g, 82%) as red crystals, m.p. 67 °C, $\nu_{max.}$(film) 2 030, 1 480, 1 380, 1 360, and 750 cm^{-1}; $\lambda_{max.}$(cyclohexane) 257 (ε 9 700), 502 nm (5); δ(CCl_4) 7.13 (4 H, m), and 1.50 (12 H, s).

(*b*) Phosphoranylidene hydrazone (**26b**) (8.0 g, 173 mmol) was heated in an oil bath at 195 °C while the volatile compounds were distilled off at 1 Torr into a dry ice–acetone trap until no more diazo compound was produced. Kugelrohr distillation afforded material identical with that obtained in (*a*) in 20% yield.

1,1,3,3-*Tetramethylindan*-2-*selone* (**26d**).—Phosphoranylidene hydrazone (**26b**) (20 g, 43 mmol) and an excess of selenium powder (12 g) were heated at 185 °C (1 Torr) while the volatile compounds were distilled off into a dry ice–acetone trap affording a blue oil which contained the selone, small amounts of diazo compound, and rearrangement products. Bulb-to-bulb distillation gave the pure selone (9.5 g, 88%) as dark blue crystals, m.p. 40—43 °C; $\nu_{max.}$(neat) 1 590, 1 485, 1 455, 1 355, 1 050, and 755 cm^{-1}; δ($CDCl_3$) 7.32 (4 H, s), 1.51 (12 H, s), identical with that previously reported.[15]

1,1,1′,1′,3,3,3′,3′-*Octamethyl*-2,2′-*bi-indanylidene* (**9**).—(*a*) 1,1,3,3-Tetramethylindan-2-selone (**26d**) (4.50 g, 18 mmol) and phosphoranylidene hydrazone (**26b**) (8.25 g, 18 mmol) were heated to 185 °C under argon with stirring. After 5 days, dichloromethane (10 ml) was added to the cooled reaction mixture. Filtration gave white crystals which upon recrystallization from chloroform–methanol afford the pure olefin (4.0 g, 65%) as colourless plates, m.p. 255 °C; $\nu_{max.}$(KBr) 1 600, 1 490, 1 450, 1 380, 1 360, and 750 cm^{-1}; δ($CDCl_3$) 7.15 (8 H, br s), 1.77 (24 H, s); δ_C($CDCl_3$) 154.4, 151.0, 126.6, 121.9, 50.3, and 33.1 p.p.m. *m/z* 344 (M^+) (Found: C, 90.6; H, 9.45. Calc. for $C_{26}H_{32}$: C, 90.64; H, 9.36%).

(*b*) To a stirred solution of the selone (**26d**) (146 mg, 0.58 mmol) in tetrahydrofuran (2 ml) was added dropwise 2-diazo-1,1,3,3-tetramethylindan (**26c**) (116 mg, 0.58 mmol). Solvent removal afforded a white crystalline material (261 mg). This intermediate dihydroselenadiazole was heated under N_2 for 24 h at 190 °C. Upon cooling the residue was dissolved in hot chloroform and filtered. Removal of the solvent and recrystallization of the residue from chloroform–methanol afforded the pure olefin (**9**) (141 mg, 71%), identical with that obtained in part (*a*).

1,1,1″,1″,3,3,3″,3″-*Octamethyl*-2′,5′-*dihydroindan*-2-*spiro*-2′-[1,3,4]*selenadiazole*-5′-*spiro*-2″-*indan. General Procedure.*—2-Diazo-1,1,3,3-tetramethylindan (**26c**) (0.4 g, 2 mmol) was slowly added, with stirring, to a solution of 1,1,3,3-tetramethylindan-2-selone (**26d**) (0.5 g, 2 mmol) in anhydrous tetrahydrofuran (2 ml). The blue colour of the selone was slowly discharged during the course of the reaction and, when equimolar amounts of each reagent were present, the solution became colourless and the dihydroselenadiazole precipitated out of solution. Removal of the solvent with a stream of nitrogen followed by drying at 0.1 Torr afforded yellow crystals of the dihydroselenadiazole (0.89 g, 99%). Recrystallization from tetrahydrofuran gave light yellow crystals, m.p. 170 °C; $\nu_{max.}$(KBr) 1 590, 1 580, 1 485, 1 450, 1 380, 1 365, 1 310, 976, and 855 cm^{-1}; $\lambda_{max.}$(cyclohexane) 306 nm (ε 750); δ($CDCl_3$) 7.15 (8 H, s), 1.48 (12 H, s), and 1.16 (12 H, s); δ_C($CDCl_3$) 148.4, 131.3, 127.4, 122.6, 52.8, 34.3, and 24.4 p.p.m. (Found: C, 69.7; H, 7.15; N, 6.2. Calc. for $C_{26}H_{32}N_2Se$: C, 69.16; H, 7.14; N, 6.20%).

Preparation of 2,2,5,5-*Tetramethylcyclopentaneselone* (**24d**).—(*a*) 2,2,5,5-Tetramethylcyclopentanone triphenylphosphoranylidenehydrazone[16] (7.7 g, 18.6 mmol) and an excess of selenium powder (4 g) were heated to 180 °C, with stirring, while the volatile compounds were continually distilled off at 0.5 mmHg into a dry ice trap. The resulting blue selone was purified by

Kugelrohr distillation (60 °C, 0.5 Torr) affording the crystalline blue selone (1.0 g, 30%), m.p. 74—77 °C; $\nu_{max.}$($CHCl_3$) 1 460, 1 380, 1 360, 1 220, and 1 060 cm^{-1}; δ($CDCl_3$) 1.94 (4 H, s), 1.22 (12 H, s) (Found: C, 53.0; H, 7.9. Calc. for $C_9H_{16}Se$: C, 53.20; H, 7.94%).

(*b*) This selone, identical with that described in (*a*), could also be prepared from the hydrazone and selenium(I) bromide in 67% yield as previously reported.[6]

Diazo-2,2,5,5-tetramethylcyclopentane (**24c**).—(*a*) 2,2,5,5-Tetramethylcyclopentanone hydrazone[16] (300 mg, 1.9 mmol), barium manganate[14] (800 mg, 2.1 mmol), calcium oxide (800 mg), and sand (1 g) in dichloromethane (3 ml) were vigorously stirred for 2 h. Filtration through Celite, removal of the solvent, and Kugelrohr distillation (40 °C, 0.5 Torr) gave the pure diazo compound (**24c**) (150 mg, 50%) as a red oil; $\nu_{max.}$(neat) 2 030, 1 460, 1 385, 1 365, and 1 255 cm^{-1}; δ($CDCl_3$) 1.64 (4 H, s), 1.21 (12 H, s).

(*b*) 2,2,5,5-Tetramethylcyclopentane triphenylphosphoranylidenehydrazone (**24b**) (10.1 g, 24.4 mmol) was heated at 175 °C, with stirring, while the volatile compounds collected in a dry ice–acetone trap at 0.5 Torr. The total yield of red diazo compound collected was 1.5 g (40%) which was identical with that obtained in part (*a*).

2,2,2″,2″,5,5,5″,5″-Octamethyl-2′,5′-dihydrocyclopentanespiro-2′-[1,3,4]selenadiazole-5′-spirocyclopentane (**4**).—Preparation following the general procedure from the selone (**24**) and the corresponding diazo compound gave this dihydroselenadiazole in 97% yield. Recrystallization from tetrahydrofuran gave an analytical sample, m.p. 126—127 °C; $\nu_{max.}$(KBr) 1 585, 1 460, 1 382, 1 365, 1 250, 980, and 860 cm^{-1}; $\lambda_{max.}$(cyclohexane) 302 nm (ε 745); δ($CDCl_3$) 2.26—1.68 (8 H, complex), 1.16 (12 H, s), and 0.81 (12 H, s); δ_C($CDCl_3$) 127.99, 46.6, 39.2, 32.0, and 26.2 (Found: C, 60.6; H, 9.2; N, 7.8. Calc. for $C_{18}H_{32}N_2Se$: C, 60.83; H, 9.08; N, 7.88%).

Preparation of 2,2,2′,2′,5,5,5′,5′-Octamethyl-1,1′-bicyclopentanylidene (**7**).—The dihydroselenadiazole (**4**) (243 mg, 0.68 mmol) was heated under nitrogen at 170 °C for 16 h then at 190 °C for 2 h. The cooled reaction mixture was distilled *via* Kugelrohr (40 °C, 0.5 Torr) to remove selone and the residue was filtered and recrystallized from ethanol, giving the olefin (**7**) as three crops of colourless crystals (116 mg, 70%); m.p. 126—128 °C. The spectra were identical with those previously reported.[17]

Pyrolysis of the Dihydroselenadiazoles (**4**)—(**6**) *at* 190 °C *for* 2 min.—The dihydroselenadiazole (*ca.* 25 mg) was placed in an ^1H n.m.r. tube under N_2 and immersed $\frac{1}{2}$ in. into an oil-bath which had been preheated to 190 °C. After 2 min the tube was removed. Deuteriochloroform with 3% Me_4Si was added and an n.m.r. spectrum (100 MHz) was taken. The peak areas were integrated to determine the product distribution. Because of the instability of the diazo compounds the relative amounts of selones and olefins were used as markers for the degree of extrusion and retrocyclization in these reactions. These results are listed in Table 1.

Pyrolysis of the Dihydroselenadiazoles (**4**)—(**6**) *at* 190 °C *for* 24 h.—The dihydroselenadiazole (*ca.* 100 mg) in a 10-ml round-bottomed flask, equipped with a water-cooled condenser, was heated at 190 °C for 24 h under nitrogen. The mixture was cooled, taken up in chloroform, and filtered. The solvent was removed and the mixture allowed to stand at reduced pressure (0.1 Torr) to remove any volatile components. The essentially pure olefin was weighed and the % yield was calculated.

1″,2,2,3″,3″,5,5-Heptamethyl-2′,5′-dihydrocyclopentanespiro-2′-[1,3,4]selenadiazole-5′-spiro-2″-norbornane (**10**).—Preparation from selenofenchone[2] and the diazo compound (**24b**), following the procedure for (**6**), gave this dihydroselenadiazole in 95% yield. Recrystallization from ether–chloroform gave yellow needles, m.p. 130—133 °C; $\nu_{max.}$(KBr) 1 590, 1 470, 1 455, 1 380, 1 370, 990, and 870 cm^{-1}; $\lambda_{max.}$(cyclohexane) 306 nm (ε 660); δ($CDCl_3$) 2.76 (1 H, br s), 2.28—0.66 (31 H, complex).

1″,2,2,3″,3″,5,5-Heptamethyl-2′,5′-dihydrocyclopent-3-enespiro-2′-[1,3,4]selenadiazole-5′-spiro-2″-norbornane (**11**).—Preparation following the general procedure from selenofenchone and the diazo compound (**25b**) gave this dihydroselenadiazole in 99% yield. Recrystallization from ether at −20 °C afforded the dihydroselenadiazole as yellow needles, m.p. 131—132 °C; $\nu_{max.}$(CCl_4) 1 630, 1 595, 1 470, 1 455, and 900 cm^{-1}; $\lambda_{max.}$(cyclohexane) 301 nm (ε 620); δ(CCl_4) 5.63 (2 H, s), 2.76 (1 H), 2.00—0.54 (27 H, complex).

1,1,1″,3,3,3″,3″-Heptamethyl-2′,5′-dihydroindan-2-spiro-2′-[1,3,4]selenadiazole-5′-spiro-2″-norbornane (**12**).—Preparation from selenofenchone[2] and the diazo compound (**26b**) following the general procedure gave this dihydroselenadiazole in 95% yield. Recrystallization from tetrahydrofuran gave yellow needles, m.p. 125—128 °C; $\nu_{max.}$(KBr) 1 595, 1 485, 1 450, 1 380, 1 360, 990, and 755 cm^{-1}; $\lambda_{max.}$(cyclohexane) 303 nm (ε 450); δ(CCl_4) 7.2—6.85 (4 H, complex), 2.80 (1 H, br s), 2.04—0.8 (27 H, complex).

1,3,3-Trimethyl-2-(2,2,5,5-tetramethylcyclopent-3-ylidene)-norbornane (**15**).—The dihydroselenadiazole (**10**) (135 mg, 0.37 mmol) was heated to 190 °C for 12 h under nitrogen. The cooled reaction mixture was dissolved in pentane and filtered. The residue contained the olefins (**7**), (**20**), and (**15**) in a ratio of 1:4:5. Preparative gas chromatography (g.c.) gave the analytically pure olefin (**15**) (28.6 mg, 30%); m.p. 90—91 °C; $\nu_{max.}$(KBr) 1 465, 1 390, 1 360, 1 195, and 1 020 cm^{-1}; δ($CDCl_3$) 2.0—0.94 (32 H, complex, s at δ 1.60, 1.36, 1.29, 1.24); δ_C($CDCl_3$) 149.5, 148.3, 52.7, 52.6, 49.3, 48.0, 45.7, 45.6, 45.0, 44.9, 37.4, 32.5, 31.8, 31.1, 30.2, 29.4, 28.8, and 26.2 p.p.m. *m/z* 260 (M^+), 245 ($M^+ - 15$) (Found: C, 87.5; H, 12.4. Calc. for $C_{19}H_{32}$: C, 87.62; H, 12.38%).

1,3,3-Trimethyl-2-(3,3,5,5-tetramethylcyclopenten-4-ylidene)-norbornane (**16**).—The dihydroselenadiazole (**11**) (1.40 g, 3.84 mmol) was heated at 135 °C under nitrogen for 2 days, and then the temperature was raised to 170 °C for 4 h. Dichloromethane was added to the cooled reaction mixture which was then filtered and concentrated. The residue contained the olefins (**8**), (**20**), and (**16**) in a ratio of 1:1:2. Flash chromatography[18] (silica–hexane) followed by Kugelrohr distillation (65 °C, 0.1 Torr) afforded the olefin (**16**) (417 mg, 42%). Multiple Kugelrohr distillations gave an analytical sample; m.p. 70—73 °C; $\nu_{max.}$($CHCl_3$) 3 040, 3 015, 1 390, and 1 365 cm^{-1}; δ($CDCl_3$) 5.15 (2 H, AB q), 2.05—0.9 (28 H, complex); *m/z* 258 (M^+), 343 ($M^+ - CH_3$) (Found: C, 88.2: H, 11.6. Calc. for $C_{19}H_{30}$: C, 88.30; H, 11.70%).

1,3,3-Trimethyl-2-(1,1,3,3-tetramethylindan-2-ylidene)norbornane (**17**).—Triphenylphosphoranylidene hydrazone (**26b**) (2.5 g, 5.4 mmol) and (−)-selenofenchone (**2**) (1.75 g, 8.1 mmol) were stirred and heated to 195 °C under argon for 42 h. The crude reaction mixture containing 2,2′-bifenchylidene (**20**), 1,1,1′,1′,3,3,3′,3′-octamethyl-2,2′-bi-indanylidene (**9**), and the unsymmetrical olefin (**17**) in a ratio of 2:3:5 was triturated with cyclohexane, and the soluble material was fractionated using flash chromatography[18] (silica–cyclohexane). The unsymmetrical olefin was recrystallized from chloroform–methanol,

affording the pure olefin (**17**) (0.33 g, 20%), m.p. 103 °C; $\nu_{max.}$($CHCl_3$) 1 600, 1 490, 1 395, 1 370, and 1 030 cm^{-1}; δ($CDCl_3$) 7.10 (4 H, br s), 2.1—0.9 (30 H, complex); δ_C($CDCl_3$) 153.7, 151.0, 150.4, 150.1, 127.1, 126.5, 122.1, 122.0, 54.6, 52.5, 50.1, 49.5, 48.3, 48.2, 36.9, 34.7, 33.7, 32.5, 30.2, 29.8, 29.7, and 27.1 p.p.m.; *m/z* 308 (M^+), 293 ($M - CH_3$) (Found: C, 89.7; H, 10.5. Calc. for $C_{23}H_{32}$: C, 89.54; H, 10.46%).

2′,2′,5′,5′-*Tetramethyl*-2,2-*di-t-butyl*-2,5-*dihydro*[1,3,4]-*selenadiazole*-5-*spirocyclopentane* (**28**).—Preparation from the selone (**24**) and di-t-butyldiazomethane[2] followed the general procedure, with the following modifications. The reagents were mixed neat and cooled to −30 °C for 48 h. The crystalline dihydroselenadiazole was filtered and quickly washed with cold (−30 °C) pentane affording the crystalline dihydroselenadiazole in 60% yield, m.p. 72—74 °C (decomp.); $\nu_{max.}$(KBr) 1 575, 1 465, 1 390, 1 360, 955, and 855 cm^{-1}; $\lambda_{max.}$(cyclohexane) 317 nm (ε 325); δ(CCl_4) 2.1—1.6 (4 H, complex), 1.24 (18 H, s), 1.18 (6 H, s), and 0.98 (6 H, s).

2′,2′,5′,5′-*Tetramethyl*-2,2-*di-t-butyl*-2,5-*dihydro*[1,3,4]-*selenadiazole*-5-*spirocyclopent*-3-*ene* (**29**).—Prepared following the general procedure, with the following modifications. Di-t-butyldiazomethane[2] and the selone (**25**) were mixed neat and immediately cooled to −30 °C. The crystals were collected after 48 h by filtration. Recrystallization from dichloromethane at −70 °C afforded the yellow crystalline dihydroselenadiazole in 60% yield, m.p. 66—71 °C (decomp.); $\nu_{max.}$(KBr) 1 655, 1 570, 1 465, 1 390, 1 365, 960, and 765 cm^{-1}; $\lambda_{max.}$(cyclohexane) 293 (ε 2 000); δ(CCl_4) 5.41 (2 H, s), 1.26 (18 H, s), 1.19 (6 H, s), and 1.07 (6 H, s).

1′,1′,3′,3′-*Tetramethyl*-2,2-*di-t-butyl*-2,5-*dihydro*[1,3,4]-*selenadiazole*-5-*spiro*-2-*indan* (**30**).—This dihydroselenadiazole was prepared from the selone (**26**) and di-t-butyldiazomethane[2] following the general procedure, with the following modifications. The reagents were mixed neat and immediately cooled to −30 °C. The crystals were collected after 40 h by suction filtration and quickly washed with cold (−30 °C) pentane affording crude dihydroselenadiazole in 70% yield. Recrystallization from dichloromethane at −70 °C gave yellow crystalline dihydroselenadiazole (65%) m.p. 84—86 °C (decomp.); $\nu_{max.}$(KBr) 1 600, 1 570, 1 490, 1 370, 1 360, 960, and 755 cm^{-1}; $\lambda_{max.}$(cyclohexane) 300 nm (ε 880); δ($CDCl_3$) 7.32 (4 H, s), 1.41 (6 H, s), and 1.32 (24 H, s).

Stability of the Dihydroselenadiazoles in Solution: General Procedure.—The dihydroselenadiazole (*ca.* 20 mg) was placed in a ^1H n.m.r. tube; deuteriochloroform (0.5 ml) was added and the sample was immediately placed in the probe of a 100 MHz n.m.r. instrument. A spectrum was taken immediately and again after appropriate intervals (5 or 10 min). The degree of retrocyclization, giving selones and diazo compounds, was monitored by integration of the peak areas. The relative ratio of the selones was determined as well as the half-life of the retrocyclization reaction (Table 3). Compounds (**4**)—(**6**), and (**10**)—(**12**) were stable indefinitely in solution. No retrocyclization was seen when a chloroform solution was stored at 25 °C in the dark.

Compound (**28**). Retrocyclization was observed giving a selone (**24d**): di-t-butyl selone ratio of 30:1. ^1H N.m.r. spectra were taken after 5, 15, 35, 50, 70, 85, 145, and 180 min. The half-life of this compound was 184 min at 21 °C.

Compound (**29**). Retrocyclization was observed giving a selone (**25d**): di-t-butyl selone ratio of 25:1. ^1H N.m.r. spectra were taken after 15, 35, 95, 130, 160, 195, and 280 min. The half-life of this compound was 264 min at 21 °C.

Compound (**30**). Retrocyclization was observed giving a selone (**26d**): di-t-butyl selone ratio of 25:1. ^1H N.m.r. spectra were taken after 10, 15, 20, 30, and 60 min. The half-life of this compound was 21 min at 21 °C.

High-pressure Thermolyses of the Dihydroselenadiazole (**29**) (**with R. A. Bunce**).—The dihydroselenadiazole (**29**), *ca.* 0.5M in dichloromethane–tetrahydrofuran, was heated at 30, 50, and 80 °C at 15 kbar for 36 h. Only small amounts of nitrogen were liberated. Rapid n.m.r. analyses showed the major product to be in each case the starting dihydroselenadiazole (66—86%) with increased amounts of selone (6—9%) and symmetrical olefin (4—7%) at higher temperatures. No unsymmetrical olefin could be detected.

Preparation of Diazo-2,2,6,6-*tetramethylcyclohexane* (**27b**).—2,2,6,6-Tetramethylcyclohexanone hydrazone, m.p. 46—47 °C (300 mg, 1.79 mmol), barium manganate (700 mg, 1.87 mmol), calcium oxide (700 mg), and sand (1 g) in carbon tetrachloride (3 ml) were vigorously stirred for 2 h. Filtration through Celite, removal of the solvent, and Kugelrohr distillation (50 °C, 0.5 Torr) gave the pure diazo compound as an orange oil (250 mg, 83%); δ(CCl_4) 1.46 (6 H, m), 1.14 (12 H, s).

2,2,2″,2″6,6,6″,6″-*Octamethyl*-2′,5′-*dihydrocyclohexanespiro*-2′-[1,3,4]*selenadiazole*-5′-*spirocyclohexane* (**31**).—The attempted preparation of compound (**31**) followed the general procedure with the following modifications. 2,2,6,6-Tetramethylcyclohexaneselone and the diazo compound (**27b**) were mixed neat and immediately cooled to −30 °C. Colourless crystals formed after 48 h but could not be isolated because the compound retrocyclized below 15 °C.

Attempted Preparation of 2,2-*Dimesityl*-1′,1′,3′,3′-*tetramethyl*-2,5-*dihydro*[1,3,4]*selenadiazole*-5-*spiro*-2′-*indan*.—This attempted preparation followed the general procedure with the following modifications. The selone (**26**) and dimesityldiazomethane[7] were mixed neat and cooled to −30 °C. After 48 h no crystalline material had separated and only starting material was observed in the n.m.r. spectrum.

Photolysis (3 000 Å) *of Dihydroselenadiazoles: General Procedure.*—The dihydroselenadiazole (*ca.* 0.4 mmol) in pentane (40 ml) was placed in a Pyrex tube (30-mm inside diameter, 2-mm walls) and the apparatus was placed in a Rayonet photochemical reactor equipped with a cooling fan and 14 Rayonet photochemical reactor lamps (3 000 Å). The sample was photolysed for 12 h at ambient temperatures with occasional agitation to dislodge precipitated selenium from the reaction vessel walls. After the reaction was complete (n.m.r.) the reaction mixture was filtered through Celite. Upon removal of the solvent a green crystalline material was obtained, containing azine, selone, and rearrangement products from diazo decomposition. Purification by Kugelrohr distillation (0.5 mmHg, 50—70 °C) and then recrystallization from MeOH gave the respective azines in the specified yield (n.m.r. or g.c. yield in parentheses). No olefinic product was observed in any of the reaction mixtures.

2,2,5,5-*Tetramethylcyclopentanone azine* (**32**). The azine was obtained as yellow needles in 78% yield (90% by n.m.r.), m.p. 64 °C; $\nu_{max.}$(KBr) 1 645, 1 455, 1 380, 1 360, and 1 045 cm^{-1}; δ($CDCl_3$) 1.64 (8 H, s), 1.28 (12 H, s), and 1.16 (12 H, s); δ_C($CDCl_3$) 177.7, 44.4, 43.3, 39.4, 37.3, 27.5, and 25.4 p.p.m.; *m/z* (M^+), 261, 138 (Found: C, 78.4; H, 11.7; N, 10.3. Calc. for $C_{18}H_{32}N_2$: C, 78.20; H, 11.67; N, 10.13%).

3,3,5,5-*Tetramethylcyclopenten*-4-*one azine* (**33**). The azine was obtained as yellow needles in 80% yield (95% by g.c.), m.p. 87—88 °C; $\nu_{max.}$(KBr) 1 660, 1 455, 1 380, 1 355, and 760 cm^{-1}; δ($CDCl_3$) 5.61 (2 H, d), 5.44 (2 H, d), 1.37 (12 H, s), and 1.27 (12

H, s); $\delta_C(CDCl_3)$ 177.4 138.0, 135.9, 48.9, 48.7, 28.5, and 24.9 p.p.m.; *m/z* 272 (M^+), 257, 136 (Found: C, 79.2; H, 10.3; N, 10.2. Calc. for $C_{18}H_{28}N_2$: C, 79.36; H, 10.36; N, 10.28%).

1,1,3,3-*Tetramethylindan-2-one azine* (**34**). This azine was obtained as yellow needles in 52% yield (70% by n.m.r.), m.p. 172—173 °C; $\nu_{max.}$(KBr) 1 650, 1 480, 1 450, 1 370, 1 355, and 745 cm^{-1}; $\delta(CDCl_3)$ 7.24 (8 H, s), 1.66 (12 H, s), and 1.55 (12 H, s); $\delta_C(CDCl_3)$ 179.0, 148.9, 127.4, 127.2, 122.6, 122.5, 47.5, 47.2, 30.1, and 26.6 p.p.m.; *m/z* 372 (M^+) (Found: C, 84.0; H, 8.7; N, 7.4. Calc. for $C_{26}H_{32}N_2$: C, 83.82; H, 8.66; N, 7.53%).

1,3,3-*Trimethyl*-2-(*tetramethylcyclopentanylidenehydrazono*)-*norbornane* (**35**). The azine was obtained as yellow needles in 82% yield, m.p. 47 °C; $\nu_{max.}$(KBr) 1 655, 1 460, 1 380, 1 360, and 1 040 cm^{-1}; $\delta(CDCl_3)$ 2.0—1.12 (complex, s at δ 1.62, 1.29, 1.26, 1.16); *m/z* 288 (M^+), 273, 150 (Found: C, 78.9; H, 11.1; N, 9.75. Calc. for $C_{19}H_{32}N_2$: C, 79.11; H, 11.18; N, 9.71%).

1,3,3-*Trimethyl*-2-(3,3,5,5-*tetramethylcyclopenten*-4-*ylidene-hydrazono*)*norbornane* (**36**). The azine was obtained as yellow needles in 88% yield, m.p. 64 °C; $\nu_{max.}$(KBr) 1 660, 1 460, 1 380, 1 360, and 760 cm^{-1}; $\delta(CDCl_3)$ 5.6—5.5 (1 H, m), 5.46—5.38 (1 H, m), and 1.92—1.04 (28 H, complex); *m/z* 286 (M^+), 271, 136 (Found: C, 79.7; H, 10.6; N, 9.9. Calc. for $C_{19}H_{30}N_2$: C, 79.66; H, 10.56; N, 9.78%).

1,3,3-*Trimethyl*-2-(1,1,3,3-*tetramethylindan*-2-*ylidenehydra-zono*)*norbornane* (**37**). The azine was obtained as yellow needles in 76% yield, m.p. 99—100.5 °C; $\nu_{max.}$(KBr) 1 660, 1 485, 1 450, 1 375, 1 355, and 750 cm^{-1}; $\delta(CDCl_3)$ 7.3—7.1 (4 H, m), 1.9—1.13 (28 H, complex); *m/z* 336 (M^+), 321, 186 (Found: C, 82.1; N, 9.55; N, 8.25. Calc. for $C_{23}H_{32}N_2$: C, 82.09; H, 9.59; N, 8.32%).

1-(*Di-t-butylmethylenehydrazono*)-2,2,5,5-*tetramethylcyclo-pentane* (**38**). The azine was obtained as light yellow crystals in 40% isolated yield (50% by g.c.); m.p. 56—58 °C; $\nu_{max.}$(KBr) 1 620, 1 460, 1 385, 1 355, 1 220, and 1 050 cm^{-1}; $\delta(CDCl_3)$ 1.64 (4 H, s), 1.38 (9 H, s), 1.30 (9 H, s), 1.26 (6 H, s), and 1.18 (6 H, s); *m/z* 278 (M^+), 124 (Found: C, 77.5; H, 12.2; N, 10.2. Calc. for $C_{18}H_{34}N_2$: C, 77.63; H, 12.31; N, 10.06%).

4-(*Di-t-butylmethylenehydrazono*)-3,3,5,5-*tetramethylcyclo-pentene* (**39**). The azine was obtained as a light yellow oil in 47% isolated yield (70% by g.c.); $\nu_{max.}$(neat) 1 640, 1 455, 1 390, 1 360, 1 355, and 760 cm^{-1}; $\delta(CDCl_3)$ 5.58 (1 H, d), 5.44 (1 H, d), and 1.60—1.20 (30 H, complex); *m/z* 276 (M^+), 136 (Found: M^+, 276.256 54. Calc. for $C_{18}H_{32}N_2$: *M*, 276.256 536).

2-(*Di-t-butylmethylene hydrazono*)-1,1,3,3-*tetramethylindan* (**40**). The azine was obtained as light yellow crystals in 50% isolated yield (70% by g.c.); m.p. 60—61 °C; $\nu_{max.}$(KBr) 1 635, 1 480, 1 375, 1 365, 1 310, 975, and 750 cm^{-1}; $\delta(CDCl_3)$ 7.32 (4 H, s), 1.63 (3 H, s), 1.60 (9 H, s), 1.50 (6 H, s), 1.43 (6 H, s), and 1.28 (6 H, s); *m/z* 326 (M^+), 186 (Found: C, 81.0; H, 10.4; N, 8.65. Calc. for $C_{22}H_{34}N_2$: C, 80.92; H, 10.50; N, 8.58%).

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