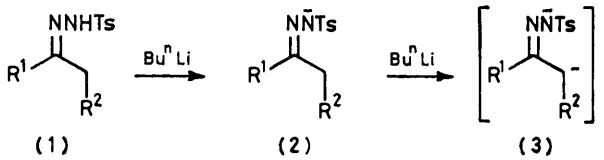
Concise Syntheses of 3-Methylenetetrahydrofuran-2-one Derivatives and Related Systems

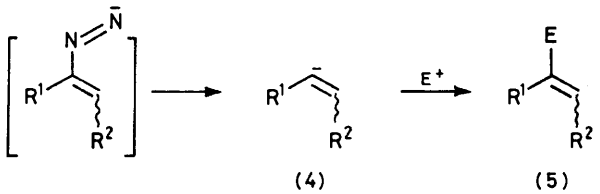
By **Robert M. Adlington** and **Anthony G. M. Barrett,*** Department of Chemistry, Imperial College, London SW7 2AY

Using the Shapiro reaction, the title compounds were prepared in 'one pot' from the condensation of two ketones, or an aldehyde and a ketone, with carbon dioxide. For example, acetone 2,4,6-tri-isopropylbenzenesulphonylhydrazone was treated in sequence with n-butyl-lithium (−50 °C), acetone (−50 °C), n-butyl-lithium (−78 to 0 to −78 °C), carbon dioxide (−78 °C), and trifluoroacetic acid (25 °C) to give 5,5-dimethyl-3-methylenetrahydrofuran-2-one. The reaction was extended to prepare derivatives of 3-methylenetetrahydropyran-2-one and 3,5-dimethylenetetrahydrofuran-2-one.

THE 3-methylenetetrahydrofuran-2-one unit occurs widely in diverse sesquiterpene systems noted for their cytotoxicity. Elegant total syntheses of vernolepin, vernomenin, *etc.* rely on late α-methylenylation of preformed lactones or the oxidation of α-methyl-γ-lactones.[1] Alternative synthetic methods exist,[2] many of which are synthetically less versatile. Herein, we report the application of the Shapiro reaction as a concise synthetic method for the construction of both α-methylenetetrahydro-furan-2-one and -pyran-2-one systems.

On reaction with alkyl-lithium reagents, ketone toluene-4-sulphonylhydrazones (1) form the *CN*-dianion (3).† The subsequent facile elimination of the toluene-4-sulphinate anion and nitrogen provides the vinyl carbanion (4) (Scheme 1). This transformation, the

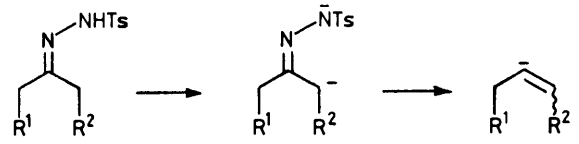


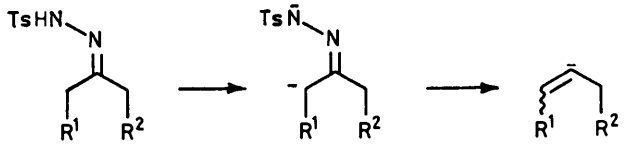


SCHEME 1 E^+ = electrophile

Shapiro reaction,[3] of ketone into vinyl carbanion is the most convenient known. The intermediates (2), (3), and (4) have all been confirmed by capture with electrophiles.[3,4] Thus, for example, vinyl carbanions may be converted into deuterio-olefins,[4,5] α,β-unsaturated aldehydes (with *NN*-dimethylformamide),[6] or vinyl silanes.[7] Paquette *et al.*[7] have emphasised the versatility of the Shapiro reaction as a route to vinyl silanes.

With an unsymmetrical ketone, the regioselectivity of the Shapiro reaction depends on the geometry of the initial tosylhydrazone and on the choice of solvent. Clearly (Scheme 1), the position of the final olefinic bond depends solely on the site of initial C–H deprotonation in the formation of the dianion (3). In hydrocarbons or





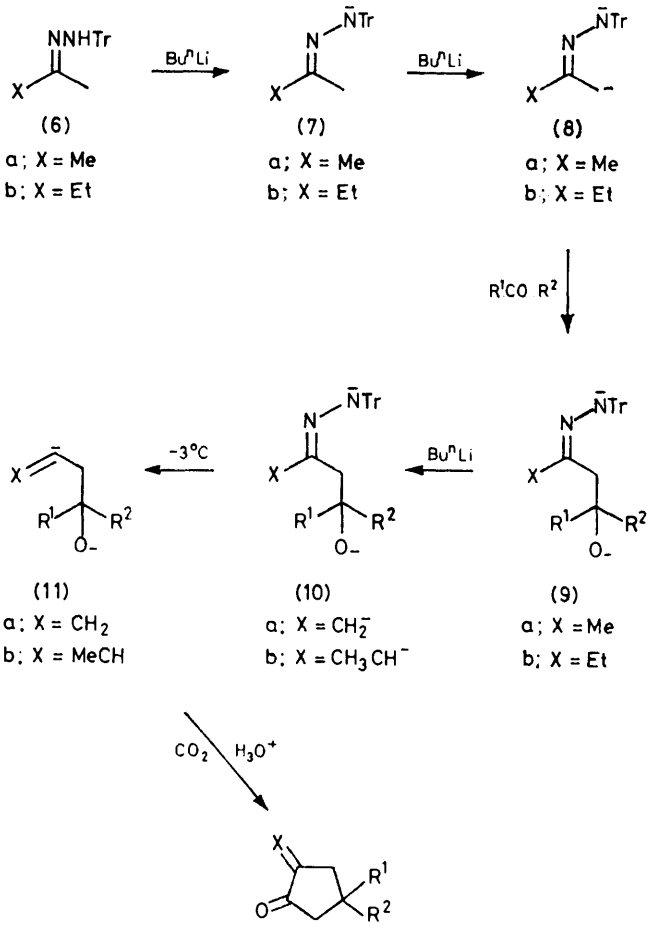
SCHEME 2

ethers the dianion (3) which is formed is exclusively *syn*. This *syn*-dianion effect [3,4,8] results from the monoanion (2) which co-ordinates and directs the incoming alkyllithium to deprotonate the anion (2) on the same flank of the C=N bond. Thus, in hydrocarbons or ethers the geometry of the tosylhydrazone alone controls the regioselectivity. The two geometrically pure tosylhydrazones each give different vinyl carbanions regiospecifically (Scheme 2). In the solvent *NNN'N'*-tetramethylethylenediamine (TMEDA) [9] the directional influence of the nitrogen atom in intermediate (2) is overwhelmed; TMEDA is a more powerful ligand for lithium(I). In TMEDA the least substituted dianion (3) is formed preferentially. Thus, for example, in TMEDA methyl ketone tosylhydrazones give rise to terminal vinyl carbanions irrespective of the tosylhydrazone geometry. The suppression of the *syn*-dilithio-effect in TMEDA, especially in β-substituted ketone tosylhydrazones,[10] requires further study.

The Shapiro reaction, however, has one severe limitation. The fragmentation of the dianion (3) to form the vinyl carbanion (4) is slow. Thus, protonation of

† In all the formulae given herein Ts = 4-$MeC_6H_4SO_2$; Tr = 2,4,6-$Pr^i_3C_6H_2SO_2$.

(4) by the solvent is a complication. In addition, the toluene-4-sulphonate ring is partially *ortho*-metallated by the alkyl-lithium reagent.[9] Thus, on the addition of electrophiles other than water, the products (5; E ≠ H) are often difficult to isolate and are formed only in poor yield. Bond *et al.* introduced ketone 2,4,6-tri-isopropylbenzenesulphonylhydrazones (hereafter trisyl = 2,4,6-tri-isopropylbenzenesulphonyl) to overcome these disadvantages.[9] Clearly, *ortho*-metallation is prevented and the fragmentation [of type (3) into (4)] is more facile on account of the reduction of steric congestion. Prior to the work of Bond *et al.*, Reese *et al.*[11,12] utilised trisylhydrazones in a most elegant reductive cyanation of ketones.

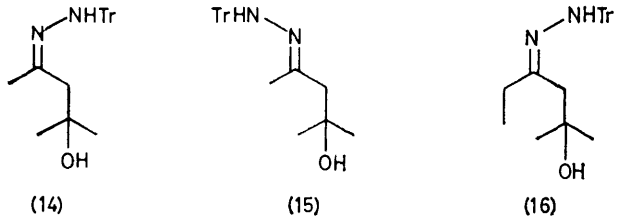


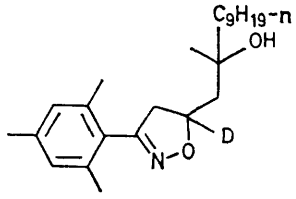
(12) X = CH_2 a; R^1 = Me, R^2 = C_9H_{19}-n
b; R^1, R^2 = -$[CH_2]_5$
c; R^1 = Me, R^2 = C_6H_{13}-n
d; R^1 = Me, R^2 = Et
e; R^1 = H, R^2 = Pr^n
f; R^1 = H, R^2 = Et
g; R^1 = Me, R^2 = Bu^i
h; R^1 = R^2 = Me

(13) X = MeCH a; R^1 = Me, R^2 = Bu^i
b; R^1 = R^2 = Me

SCHEME 3

We considered that the Shapiro reaction should provide a convenient ' one-pot ' reaction for the condensation of two ketones and carbon dioxide to produce derivatives of 3-methylenetetrahydrofuran-2-one (Scheme 3). Prior to our preliminary publication,[13] Lipton and Shapiro described the preparation af homo-





(17)

allylic alcohols from tosylhydrazones.[8] The addition of n-butyl-lithium to acetone trisylhydrazone (6a) in 1,2-dimethoxyethane (DME) at −70 °C gave the dianion (8) as a golden yellow solution which was stable at low temperature. Completion of the reaction was obvious since the monoanion (7) is colourless and complete formation of this was indicated by a golden end-point. To the golden solution was added acetone until it became colourless (reaction end-point). Work-up gave the β-hydroxy-trisylhydrazone, initially as the *Z*-isomer (14) (95%). In solution this equilibrated to generate the more stable *E*-isomer (15). Thus the dianion (9) must be geomtrically stable in solution.[14] Trisylhydrazone geometry is most conveniently assigned using n.m.r. spectroscopy.[8] Analogously, butanone trisylhydrazone (6b) (predominantly the *E*-isomer) was converted into the *Z*-hydroxy-trisylhydrazone (16) (90%).

Reaction of the dianion (8a) with undecan-2-one gave a solution of the dianion (9a; R^1 = Me, R^2 = n-C_9H_{19}). Further addition of n-butyl-lithium gave the trianion (10a; R^1 = Me, R^2 = n-C_9H_{19}), *vide infra*, as an orange-yellow solution which is stable at low temperature. When the solution was warmed to −3 °C, the orange colour faded, nitrogen was evolved, and the alkoxy-vinyl dianion (11a; R^1 = Me, R^2 = n-C_9H_{19}) was formed. Again, completion of this reaction was obvious from the colour changes. The dianion (11a; R′ = Me, R^2 = n-C_9H_{19}) was quenched with D_2O and subsequent reaction with 2,4,6-trimethylbenzonitrile oxide gave the isoxazoline (17) (85%). Both n.m.r. and mass spectral

data were consistent with a 90% D incorporation. Clearly, the dianion (11a) was stable to the solvent. When the Shapiro reaction was repeated using tetrahydrofuran (THF) as solvent, the isoxazoline (17) was formed in lower yield (80%) with less D-incorporation (84%).

Since the anions (8a), (9a), (10a), and (11a) were efficiently produced, the 'one-pot' synthesis of the methylene-lactones (12) and (13) was examined. Typically, n-butyl-lithium and acetone were added, in sequence, to acetone trisylhydrazone (6a) in DME at −70 °C to give compound (9a; $R^1 = R^2 = Me$). Further metallation gave compound (10a; $R^1 = R^2 = Me$) which decomposed at −3 °C to give the alkoxy-vinyl dianion (11a; $R^1 = R^2 = Me$). Subsequently, carboxylation at −78 °C and acidification with trifluoroacetic acid gave 5,5-dimethyl-3-methylenetetrahydrofuran-2-one (12h) (57%).[15] The reaction was applied to several aldehydes and ketones (see the Table). Clearly, the Shapiro reaction provides a highly convenient synthesis of diverse α-methylene-γ-lactones. All except the ultimate step in the 'one-pot' reaction had obvious colour-change end-points.

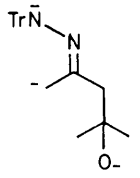
Alternatively, the α-methylene-γ-lactones were available *via* β-hydroxy-trisylhydrazones. 4-Hydroxy-4-methylpentan-2-one and trisylhydrazine gave the expected hydrazones (14) and (15), $E > Z$. Metallation with n-butyl-lithium at −78 °C gave a mixture of the trianions (10a; $R^1 = R^2 = Me$) and (18). These trianions were warmed to −3 °C, carboxylated at −78 °C, and acidified to give the expected methylene-lactone (12h) (74%). Similarly, the trisylhydrazone (16) gave the lactone (13b) ($E : Z$, 9 : 32, 41%). The predominance of the *Z*-geometry in the Shapiro reaction has ample precedent.[3]

The formation of the trianion (10) *via* deprotonation of the dianion (9) deserves further comment. In contrast with Shapiro's observations [8] we found that the trianion (10a) was trapped by electrophiles. The addition of acetone to (10a; $R^1 = R_2 = Me$) gave the expected ββ′-dihydroxy-trisylhydrazone (19), albeit in poor yield (31%). Clearly the third metallation step [(9a)→(10a)], which involved deprotonation *anti* to the arylsulphonyl group, was incomplete at −78 °C. It is most reasonable that the deprotonation was forced *anti* for two reasons. The oxy-anion in the dianion (9a) firstly must suppress the acidity of the adjacent C–H protons and, secondly, should be able to direct the incoming n-butyl-lithium to *anti*-deprotonate and so give the chelated trianion (20). Consistent with incomplete deprotonation at −70 °C we found that when n-butyl-lithium was added to the trisylhydrazone mixture of (15) and (14) ($E > Z$) at −78 °C and the solution was quenched with [$^2H_6$]acetone, the trisylhydrazone (21) (16%) and deuterium-free starting material (14) and (15) (80%) were obtained. The two geometric isomers (14) and (15) were easily separable by chromatography. Each was separately converted into the respective trianions (10a; $R^1 = R^2 = Me$) (orange-yellow) and (18) (golden yellow). The trianion (18) was more easily formed since reaction with acetone gave the trisylhydrazone (19) (43%). With the geometric isomer (10a; $R^1 = R^2 = Me$) the yield of compound (19) was less (29%). In addition, the geometrically pure trianions were converted into the lactone (12h). The respective yields from (15) and (14) were (78%) and 49%).

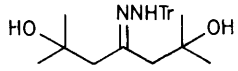
TABLE

Entry	Compound/mmol	B_1/mmol	T_1/°C	R^1·CO·R^2 R^1	R^2	mmol	B_2/mmol	M_1/min	T_2/°C	M_2/min	Acid, g [a]	Product
1	(6a), 1.41	2.94	−50	Me	C_9H_{19}-n	1.55	1.54	15	0	60	A, 0.2	(12a), 33
2	(6a), 1.00	3.00	−60	$-C_5$	$-[CH_2]_5$	2.14	3.60	3	−3	60	B, 1.5	(12b), 40
3	(6a), 1.28	3.00	−50	Me	C_6H_{13}-n	1.92	2.40	5	−3	120	B, 0.5	(12c), 61
4	(6a), 1.01	2.40	−66	Me	Et	1.70	2.40	5	−3	60	B, 1.0	(12d), 61
5	(6a), 1.01	2.40	−70	H	Pr^n	1.62	3.00	5	−3	50	B, 1.3	(12e), 62
6	(6a), 0.99	2.40	−70	H	Et	2.76	2.40	5	−3	60	B, 1.3	(12f), 45
7	(6a), 1.15	2.16	−65	Me	Bu^i	1.36	2.16	10	−4	50	B, 1.2	(12g), 66
8	(6a), 1.00	2.40	−50	Me	Me	1.77	1.80	8	−5	40	B, 0.4	(12h), 57
9	(6b), 1.02	2.64	−65	Me	Bu^i	1.68	2.97 [b]	3	−3	180	B, 1.5	*E*-(13a), 5; *Z*-(13a), 12
10	(6b), 1.00	2.40	−65	Me	Me	2.04	3.60	15	−5	60	B, 1.3	*E*-(13b), 2; *Z*(13b), 35

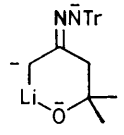
[a] A, AcOH; B, CF_3CO_2H. [b] s-Butyl-lithium was used.



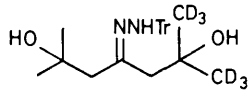
(18)



(19)



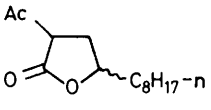
(20)



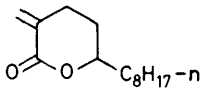
(21)

Since the α-methylene-γ-lactones (12) and (13) were readily prepared from β-hydroxy-trisylhydrazones we sought a route from γ-hydroxy-trisylhydrazones to α-methylene-δ-lactones. Such units also occur in cytotoxic

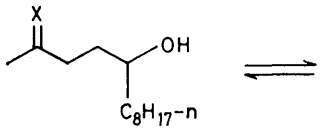
sesquiterpenes.[1] n-Octyloxiran was converted,[16] *via* the lactone (22), into 5-hydroxytridecan-2-one (23a). In contrast with the β-hydroxy-trisylhydrazones, the derived trisylhydrazone (23b) was unstable. However, without



(22)



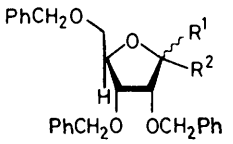
(24)



(23)

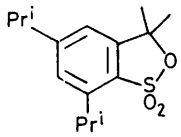
a; X = O
b; X = NNHTr
c; X = NNH.$C_6H_3(NO_2)_2$-2,4

characterisation, the crude trisylhydrazone (23b) was treated with n-butyl-lithium and carbon dioxide in the usual way. Work-up gave the lactone (24) in poor yield (23%). We considered that this low yield resulted from the facile decomposition of the hydrazone (23b) *via* cyclisation and loss of 2,4,6-tri-isopropylbenzenesulphinic acid and nitrogen. However, the reaction mixture obtained from decomposition of the hydrazone (23b) was intractable. In a related decomposition the ribose derivative (25a)[17] and trisylhydrazine gave the ribolactone (25b)[18] and sultone (26).[19] In contrast to the hydrazone (23b), the less hindered tosylhydrazone (27) was stable.

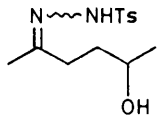


(25)

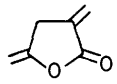
a; R^1=H, R^2=OH
b; R^1, R^2=O



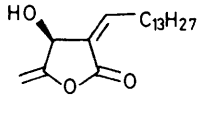
(26)



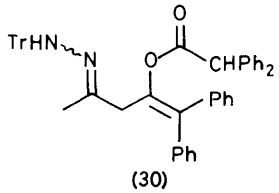
(27)



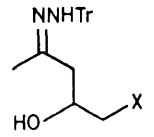
(28)



(29)

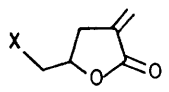


(30)



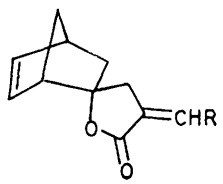
(31)

a; X = SPh
b; X = SePh



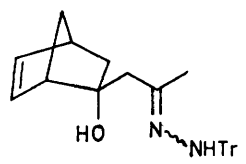
(32)

a; X = SPh
b; X = SePh
c; X = $SeBu^n$
d; X = SeMe

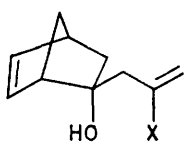


(33)

a; R = H
b; R = C_5H_{11}-n

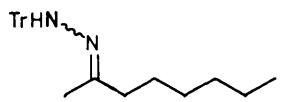


(34)



(35)

a; X = D
b; X = CO_2H



(36)

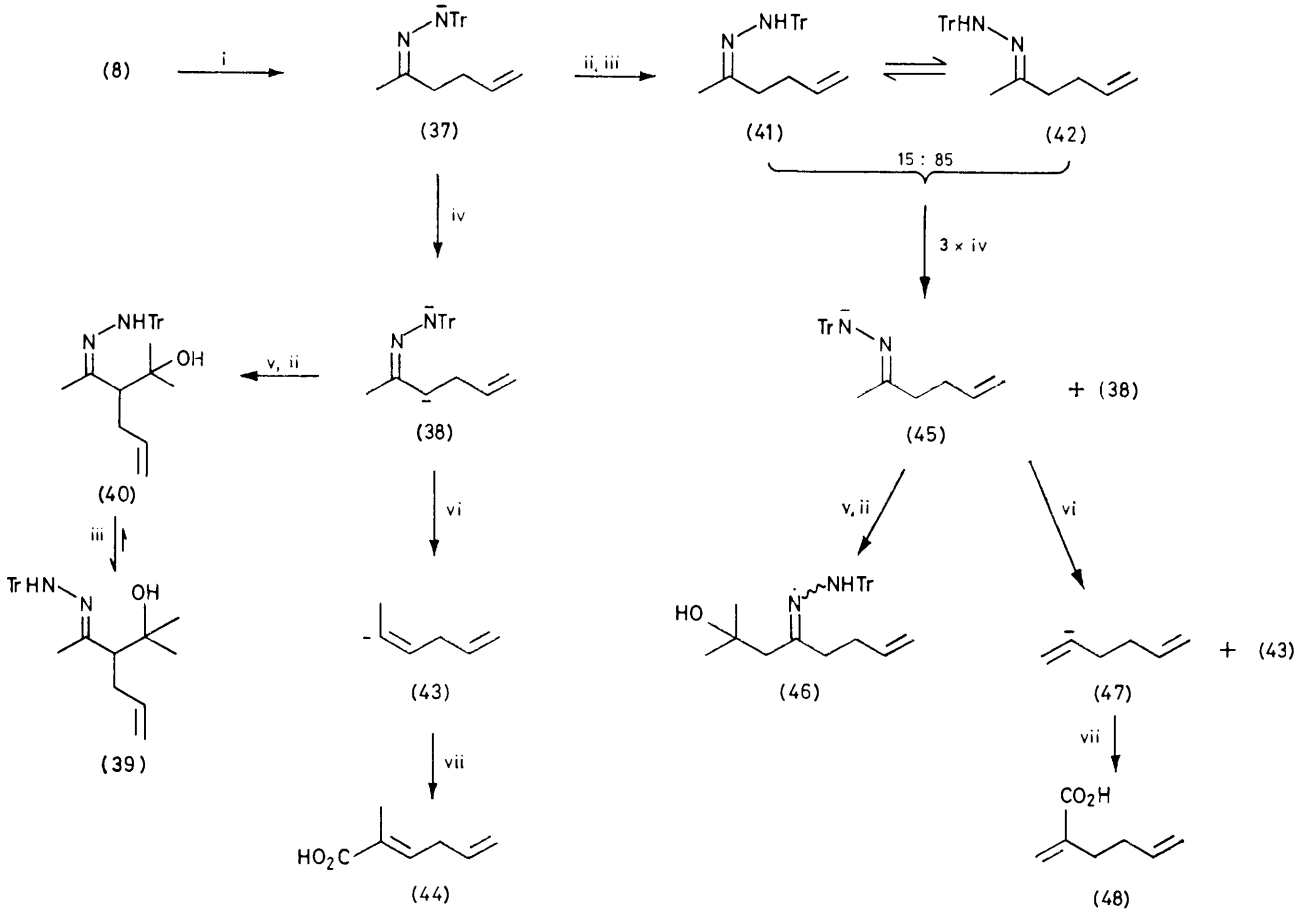
The 3,5-dimethylenetetrahydrofuran-2-one unit (28) occurs naturally in the obtsusilactones, *etc.* [*e.g.* compound (29)].[20] We considered that such systems should be available by the Shapiro reaction from a ketone, a keten, and carbon dioxide. Initially, we sought a concise route to the parent lactone (28). In a model reaction for keten, the reaction between the golden dianion (8a) and diphenylketen was examined. The only product isolated was the *CO*-diacylated system (30) (25%). Clearly, masked ketens must be employed.

Phenylthioacetaldehyde or selenium analogues are potential keten equivalents *via* late oxidation. The golden dianion (8a) was treated with phenylthio- and

phenylseleno-acetaldehyde to give the expected adducts (31a) and (31b). Neither could be converted efficiently into the derived α-methylene-γ-lactones (32a) or (32b). The β-hydroxy-trisylhydrazone (31b) was treated with n-butyl-lithium and carbon dioxide in sequence to give an abysmal yield of the lactone (32c) (1—2%). That this was formed *via* transmetallation at selenium was established by the isolation of benzoic acid (17%), formed *via* phenyl-lithium. An attempt to prepare the lactone (32d) from the dianion (8a) and methylseleno-acetaldehyde using methyl-lithium as base gave only fetid, intractable mixtures. Hetero-substituted keten equivalents were abandoned as reactants.

Reaction of the golden dianion (8a) with norborn-2-en-5-one,[21] n-butyl-lithium, and carbon dioxide in the usual way gave the spiro-lactone (33a) (61%). *exo*-Attack on norborn-2-en-5-one has ample precedent.[22] In separate experiments the intermediacy of the usual anions was confirmed by the isolation of the hydroxy-trisylhydrazone (34) and the deuterio-olefin (35a) (70%, with a 91% D incorporation). The lactonisation of the hydroxy-acid (35b) using trifluoroacetic acid was unsatisfactory. Acetic acid, however, was efficient and, additionally, attractive in that formation of the sultone (26) [19] was suppressed. Chromatographic purification of the methylene-lactones was sometimes complicated by the sultone (26).

Flash-vacuum pyrolysis [23] of the lactone (33a) at 550 °C and 10^{-4} mmHg gave the analytically pure lactone (28). This reaction, *via* the retro-Diels–Alder loss of cyclopentadiene, has precedent.[24] Octan-2-one trisylhydrazone [predominantly the isomer (36)] was treated with n-butyl-lithium, norborn-2-en-5-one, n-butyl-lithium, carbon dioxide, and acetic acid to give the lactone (33b). The low yield (16%) of the lactone (33b) precluded flash-vacuum pyrolytic studies.

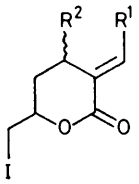


SCHEME 4 *Reagents:* i, CH_2=$CHCH_2Br$; ii, AcOH; iii, 25 °C; iv, Bu^nLi; v, Me_2CO; vi, −3 °C; vii, CO_2, H_3O^+.

Herein, we have demonstrated that the golden dianion (8) is highly versatile *via* hydroxy-alkylation reactions. As an alternative route to 3-methylenetetrahydropyran-2-one derivatives, the allylation of the dianion (8a) was examined (Scheme 4). The golden dianion (8a) was treated with allyl bromide at −65 °C in DME for 1 h and gave the anion (37). This was geometrically stable in solution. In accord with the *syn*-dilithio-effect further reaction of the anion (37) with n-butyl-lithium gave the golden dianion (38). Compound (38) was quenched with acetone to a colourless end-point to give the expected (*E*)-hydroxy-trisylhydrazone (39) (88%) on acidification and

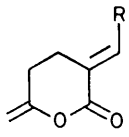
equilibration. The dianion (38) decomposed at −3 °C to give the vinyl carbanion (43). Subsequent carboxylation gave (*E*)-methylhexa-2,5-dienoic acid (44).

Alternatively, the hydrazones (41) and (42) (15 : 85) were formed on the acidification of the anion (37) and equilibration. The hydrazone mixture (41) and (42) (15 : 85) was treated with n-butyl-lithium to give, in accord with the *syn*-dilithio-effect, the dianions (45) and



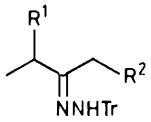
(49)

a; $R^1=R^2=H$
b; $R^1=Me$, $R^2=H$
c; $R^1=H$, $R^2=Me$



(50)

a; R = H
b; R = Me



(51)

a; $R^1=H$, $R^2=CH_2CH=CH_2$
b; $R^1=CH_2CH=CH_2$, $R^2=H$

(38), with the former predominant.* This was confirmed when the dianions were trapped with acetone to give the β-hydroxy-trisylhydrazone (46) (69%) as the principal product. The mixture of dianions (45) and (38) at − 3 °C gave the vinyl carbanions (47) and (43). As expected, on carboxylation, the principal product formed was 2-methylenehex-5-enoic acid (48). The acid (48) was treated with iodine to give the expected iodolactone (49a) [50% based on compounds (41) and (42)]. On treatment with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in benzene at 74 °C, smooth elimination of hydrogen iodide took place which gave the stable 3,6-dimethylenetetrahydropyran-2-one (50a) (64%).

The iodo-lactones (49b) (39%) and (49c) (6%) were prepared from butanone trisylhydrazone (*E* > *Z*) *via* the mixture of the hydrazones (51a) (major) and (51b) (minor). The predominant formation of the iodolactone (49b) was fully consistent with the *syn*-dilithio-effect [*E*-(6b) > *Z*-(6b), and *E*-(51a) > *Z*-(51a) after equilibration]. The reaction of iodo-lactone (49b) with DBU in benzene at reflux gave the expected lactone (50b) (71%).

Clearly, the Shapiro reaction provides a most convenient and concise route to the construction of α-methylene-lactones.

* The minor carboxylic acid product (44), derived from compound (38), is unable to iodolactonise.

EXPERIMENTAL

M.p.s were determined on a Kofler hot stage. I.r. spectra were recorded as Nujol mulls (solids) or films (oils). N.m.r. spectra were recorded in deuteriochloroform using tetramethylsilane as an internal reference. Reagents and solvents were purified by standard techniques.[25] TMEDA was distilled from potassium diphenylketyl onto sodium wire. DME was purified by reflux over sodium wire and distillation from potassium onto sodium wire. Aldehydes were freshly distilled from anhydrous calcium or magnesium sulphate. Acetone and butanone were freshly redistilled from phosphorus pentoxide. Reactions were carried out under dry, oxygen free [Cr^{II}] argon. Alkyl-lithium reagents (Aldrich) were added in drops for 5—10 min at low (bath) temperatures. Work-up refers to the following procedures. (A) The solution was evaporated and the residue, in solvent (given below), was washed with brine (×2), dried (Na_2SO_4), and evaporated. (B) The solution was evaporated and the residue, in water, was extracted (×2) with solvent (given below). The organic phase was dried (Na_2SO_4) and evaporated. (C) The solution was evaporated and the residue, in water, was extracted with solvent (×2) (given below). The aqueous phase was acidified and saturated with sodium chloride or sodium sulphate and re-extracted with the solvent. The combined organic phase was dried (Na_2SO_4) and evaporated.

Chromatography was carried out on Merck Kieselgel-GF_{254} [preparative layer chromatography (p.l.c.) with the eluants given in parentheses] or -H (flash chromatography) [26] using solvent gradients. Eluted compounds are listed in order of increase in polarity.

Preparation of Butanone 2,4,6-*Tri-isopropylbenzenesulphonylhydrazone* (6b).—2,4,6-Tri-isopropylbenzenesulphonylhydrazine [12] (373 mg) was dissolved in butanone (5 ml). After 25 min evaporation and re-evaporation from dichloromethane (5 ml) and toluene (5 ml) gave the *butanone trisylhydrazone* (6b) (408 mg, 93%), m.p. 115—121 °C (from aqueous ethanol); $\nu_{max.}$ 3 250s, 1 605m, 1 325s, 1 300m, 1 170s, 1 155s, and 660s, cm^{-1}; δ_H 0.95 (3 H, 2 overlapping t, *J* 7 Hz, *Me*CH_2), 1.30 (18 H, 4 overlapping d, *J* 7 Hz, CH*Me*$_2$), 1.77 and 1.82 (3 H, 2 s, MeC=N), 2.10 (2 H, 2 overlapping d, *J* 7 Hz, MeCH_2), 2.83 (1 H, 2 overlapping septets, *J* 7 Hz, *p*-C*H*Me_2), 4.24 (2 H, 2 overlapping septets, *J* 7 Hz, *o*-C*H*Me_2), 7.10 (2 H, s, aryl-H), and 7.50—8.40 (1 H, br, NH); *m/e* 352 ($M^{+\cdot}$), 267, 203, 86, 85, 72, and 56 (base) (Found: C, 64.7; H, 9.15; N, 7.95. $C_{19}H_{32}N_2O_2S$ requires C, 64.75; H, 9.15; N, 7.95%).

Preparation of Acetone 2,4,6-*Tri-isopropylbenzenesulphonylhydrazone* (6a).—The trisylhydrazone (6a) (92%) prepared by a similar route to the hydrazone (6b), was recrystallised from aqueous methanol, m.p. 136—138 °C (lit.,[9] 130—132 °C) (Found: C, 63.8; H, 8.95; N, 8.25. Calc. for $C_{18}H_{30}N_2O_2S$: C, 63.85; H, 8.95; N, 8.25%).

Preparation of Octan-2-one 2,4,6-*Tri-isopropylbenzenesulphonylhydrazone* (36).—2,4,6-Tri-isopropylbenzenesulphonylhydrazine (1.52 g), octan-2-one (0.692 g), Amberlite IR 120H (catalyst), and dichloromethane (30 ml) were stirred for 2 h. Filtration, evaporation, and recrystallisation from aqueous ethanol gave the trisylhydrazone (36) (2.0 g, 96%), m.p. 87—89 °C (lit.,[9] 87—88 °C) (Found: C, 67.6; H, 10.1; N, 6.9. Calc. for $C_{23}H_{40}N_2O_2S$: C, 67.6; H, 9.85; N, 6.85%).

Preparation of (E)- *and* (Z)-4-*Hydroxy*-4-*methylpentan*-2-*one* 2,4,6-*Tri-isopropylbenzenesulphonylhydrazones* (15) *and*

(14).—A mixture of 2,4,6-tri-isopropylbenzenesulphonylhydrazine (0.742 g) and 4-hydroxy-4-methylpentan-2-one (0.289 g) in dichloromethane (10 ml) was refluxed for 30 min. Evaporation and recrystallisation from aqueous ethanol gave a mixture of the (E)- *and* (Z)-*trisylhydrazones* (15) and (14) (*ca.* 2 : 1) (0.92 g, 93%), m.p. 125—127 °C; $\nu_{max.}$ 3 580—3 350m (OH), 3 255m (NH), 1 320m (SO_2N), 1 265m (OH), 1 165 and 1 155s (SO_2N), 1 135m (C–O), and 670m cm^{-1}; δ_H 1.05 and 1.30 (6 H, 2 s, 4-Me), 1.24 (18 H, 4 overlapping d, *J* 7 Hz, $CHMe_2$), 1.85 and 1.97 (3 H, 2 s, 1-Me), 2.34 and 2.45 (2 H, 2 s, 3′-CH_2), 2.83 (1 H, overlapping septets, *J* 7 Hz, *p*-$CHMe_2$), 4.25 (2 H, overlapping septets, *J* 7 Hz, *o*-$CHMe_2$), 7.15 and 7.17 (2 H, 2 s, aryl-H), and 7.40—7.55 and 9.75—9.85 (1 H, 2 br, NH); *m/e* 396 ($M^{+\cdot}$, weak), 381 ($M^{+\cdot}$ – Me), 379 (M^+ – OH), 378 ($M^{+\cdot}$ – H_2O) 269, 267, 189, 111 [M^+ – (H_2O + $ArSO_2$), base], and 59 (Found: C, 63.5; H, 9.3; N, 7.05; S, 7.95. $C_{21}H_{36}N_2O_3S$ requires C, 63.6; H, 9.15; N, 7.05, S, 8.1%).

The *Z*-(14) and *E*-(15) isomers were readily separated by chromatography on Kieselgel H (eluant: diethyl ether–dichloromethane, 0 : 1—1 : 4) to give the (Z)-*hydrazone*(14) (R_F 0.6 on t.l.c., diethyl ether–dichloromethane, 1 : 9); δ_H 1.28 (18 H, d, *J* 7 Hz), 1.30 (6 H, s), 1.97 (3 H, s), 2.45 (2 H, s), 2.60 (1 H, br m), 2.95 (1 H, septet, *J* 7 Hz), 4.28 (2 H, septet, *J* 7 Hz), 7.2 (2 H, s), and 9.8 (1 H, s, NH); *m/e* 396 ($M^{+\cdot}$), 378, 338, 282, 267 (100%), 241, 236, 221, 204, 189, 161, 111, 97, 91, 59, 43, and 41; and the (E)-*hydrazone* (15) (R_F 0.2 on t.l.c., diethyl ether–dichloromethane, 1 : 9); δ_H 1.05 (6 H, s), 1.2—1.35 (18 H, 2 d, *J* 7 Hz), 1.85 (3 H, s), 2.34 (2 H, s), 2.80 (1 H, br m), 2.84 (1 H, septet, *J* 7 Hz), 4.27 (2 H, septet, *J* 7 Hz), 7.2 (2 H, s), and 7.6 (1 H, s, NH); *m/e* 396 ($M^{+\cdot}$), 381, 338, 282, 267 (100%), 236, 221, 204, 189, 161, 91, 59, 43, and 41.

Reaction of the Dianion (8a) *with Acetone*.—The sulphonylhydrazone (6a) (466 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.40M; 2.2 ml) was added and gave a golden solution which was stirred for 15 min, warmed to −50 °C over 20 min, quenched with acetone (0.14 ml) until colourless, and warmed to 25 °C. General work-up [(A) diethyl ether, glacial acetic acid] gave the (*Z*)-hydrazone (14) (520 mg, 95%), m.p. 95—98 °C, initially exclusively as the less-polar *Z*-isomer by t.l.c. The product partially isomerised with time into the *E*-isomer (15).

Preparation of (Z)-5-*Hydroxy*-5-*methylhexan*-3-*one* 2,4,6-*Tri-isopropylbenzenesulphonylhydrazone* (16).—The (*E*)- and (*Z*)-butanone hydrazones (6b) (1.06 g) were dissolved in DME (8 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.20M; 6.0 ml) was added to give an orange solution which was warmed to −65 °C over 10 min. Acetone (0.5 ml) was added as drops for 2 min to give a solution which was quenched with glacial acetic acid (0.50 ml) in water (2 ml) at −60 °C, and warmed to 25 °C. General work-up [(A) diethyl ether], chromatography on Kieselgel H (20 g) [eluant: dichloromethane], and recrystallisation from methanol and water gave the (Z)-*hydrazone* (16) (1.11 g, 90%), m.p. 132—134 °C; $\nu_{max.}$ 3 470s (OH), 3 080m (NH), 1 325s (SO_2N), 1 165 and 1 155s (SO_2N), 1 125m (C–O), 1 035m, 912m, 885m, and 655m cm^{-1}; δ_H 1.00 (3 H, t, *J* 7 Hz, 1-Me), 1.25 (18 H, overlapping d, *J* 7 Hz, $CHMe_2$), 1.32 (6 H, s, Me_2C), 2.22 (2 H, q, *J* 7 Hz, 2-CH_2), 2.44 (2 H, s, 4-CH_2), 3.00 (1 H, overlapping septets, *J* 7 Hz, *p*-$CHMe_2$), 4.20 (2 H, overlapping septets, *J* 7 Hz, *o*-$CHMe_2$), 7.10 (2 H, s, aryl-H), and 10.10 (1 H, br, NH); *m/e* 410 ($M^{+\cdot}$), 395 (M^+ – Me), 352 [$M^{+\cdot}$ – (C_3H_6O)], 204, 189 (base), and 161 (Found: C, 64.5; H, 9.4; N, 6.85. $C_{22}H_{38}N_2O_2S$ requires C, 64.35; H, 9.35; N, 6.8%).

Preparation of 5-(2-*Hydroxy*-2-*methylundecyl*)-3-(2,4,6-*trimethylphenyl*)-2-[5-$^2H_1$]*isoxazoline* (17) *from the Sulphonylhydrazone* (6a) *using DME as Solvent*.—The sulphonylhydrazone (6a) (399 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.20M; 2.0 ml) was added to give an orange solution which was stirred for 10 min and then warmed to −50 °C over 20 min. Undecan-2-one (0.30 ml) was added to give a clear solution which was recooled to −78 °C and treated with further n-butyl-lithium (1.20M; 1.3 ml). The resultant red solution was stirred for 10 min, warmed to −3 °C over 1 h, and quenched with deuterium oxide (0.50 ml). General work-up [(B) diethyl ether] and chromatography on Kieselgel H (20 g) (eluant: dichloromethane) gave crude 4-hydroxy-4-methyl[2-$^2H_1$]tridec-1-ene (340 mg) [*m/e* 213 ($M^{+\cdot}$)], a sample of which (171 mg) was dissolved with 2,4,6-trimethylbenzonitrile oxide [27] (129 mg) in THF (5 ml). The resultant solution was stirred for 10 d. Evaporation and chromatography on Kieselgel H (20 g) [eluant: dichloromethane–diethyl (1 : 0—4 : 1)] gave the *isoxazoline* (17) (189 mg, 85%) as an oil; $\nu_{max.}$ 3 430m (OH), 2950s, 2 850s, 1 615m (C=N), 1460s, 1 435m, 1 380m (OH), 1 330m, 910m, 850m, and 730m cm^{-1}; δ_H 0.70—1.00 (3 H, br, $MeCH_2$), 1.05—1.70 [19 H, br, Me(CH_2)$_8$, MeCO], 1.70—3.40 (5 H, m, 4-CH_2), 1′-CH_2, OH), 2.20 (6 H, s, *o*-Me), 2.23 (3 H, s, *p*-Me), and 6.80 (2 H, s, aryl-H); *m/e* 374 ($M^{+\cdot}$), 359 (M^+ – Me), 247 (M^+ – n-C_9H_{19}), 188 ($M^{+\cdot}$ – $C_{12}H_{26}O$, base), 159, and 145, (90% monodeuteriated) (Found: C, 76.7; H, 10.65; N, 3.65. $C_{24}H_{38}{}^2H_1NO_2$ requires C, 76.95; H, 10.75; N, 3.75%).

Preparation of the Isoxazoline (17) *from the Sulphonylhydrazone* (6a) *using THF as Solvent*.—The sulphonylhydrazone (6a) (344 mg) was dissolved in THF (10 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.20M; 2.5 ml) was added and gave a yellow solution which was warmed to −65 °C over 10 min. Undecan-2-one (0.45 ml) was added and gave a clear solution which was recooled to −78 °C. n-Butyl-lithium (1.20M; 3.0 ml) was again added which gave an orange solution which was warmed to 0 °C over 75 min and to 15 °C over a further 80 min. Deuterium oxide (2.0 ml) was added and the solution was warmed to 25 °C. A similar work-up and reaction with 2,4,6-trimethylbenzonitrile oxide gave the isoxazoline (17) (80%) identical [t.l.c., n.m.r., and *m/e* (84% monodeuteriated)] with an authentic sample.

General Preparation of the α-*Methylene*-γ-*lactones* (12) *and* (13).—The ketone hydrazone (6a) or (6b) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (B_1, Table) was added, the solution was warmed to T_1 (Table) and treated with ketone or aldehyde. (Table). The solution was recooled to −78 °C, treated with n-butyl-lithium (B_2, Table), stirred for M_1 min, warmed to T_2 over M_2 min (Table), and recooled to −78 °C. After the mixture had been quenched with carbon dioxide gas for 1 min it was warmed to 25 °C; general work-up [(C), CH_2Cl_2], chromatography on Kieselgel H, and p.l.c., in sequence, gave the α-methylene-γ-lactones (12) or (13) (see the Table). The spectral and analytical data of these compounds are given below.

5-*Methyl*-3-*methylene*-5-*nonyltetrahydrofuran*-2-*one* (12a). Compound (12a) (111 mg, 33%) was obtained as an *oil*; $\nu_{max.}$ 2 925s, 2 860s, 1 770s (C=O), 1 470m, 1 385m, 1 285s (C–O), 1 120m, 1 100m, 1 065m, 940s, (CH_2=), and

905m cm^{-1}; δ_H 0.75—1.05 (3 H, br, *Me*CH_2), 1.15—1.50 (16 H, br, $[CH_2]_8$), 1.35 (3 H, s, 5-Me), 2.70 (2 H, q, *J* 2.5 Hz, 4-CH_2), 5.50 (1 H, dd, *J* 3,3 Hz, =CH_2), and 6.13 (1 H, dd, *J* 3.3 Hz, =CH_2); *m/e* 239 ($M^{+\cdot}$ + H), 223 (M^+ − Me), 195 (M^+ − Pr), 154 [(M^+ + H) − n-C_6H_{13}], 126 [(M^+ + H) − C_8H_{17}], 111 [M^+ − n-C_9H_{19}, base], and 55 (Found: C, 75.15; H, 10.95. $C_{15}H_{26}O_2$ requires C, 75.6; H, 11.0%).

3-*Methylene*-1-*oxaspiro*[4,5]*decan*-2-*one* [28] (12b). Compound (12b) (66 mg, 40%) was obtained as an oil; $\nu_{max.}$ 2 940s, 2 875m, 1 765s (C=O), 1 290s, 1 280s (C–O), 1 265m, 1 240m, 1 193s (C–O), 1 130m, 1 104s, 1 033s, 961s, and 938m cm^{-1}; δ_H 1.10—2.10 (10 H, br, $[CH_2]_5$), 2.64 (2 H, t, *J* 2.5 Hz, 4-CH_2), 5.40—5.60 (1 H, m, =CH_2), and 5.96—6.14 (1 H, m, =CH_2); *m/e* 166 ($M^{+\cdot}$), 123, 111, 97 (base), and 68 (Found: C, 72.35; H, 8.7. Calc. for $C_{10}H_{14}O_2$: C, 72.25; H, 8.5%).

5-*Hexyl*-5-*methyl*-3-*methylenetetrahydrofuran*-2-*one* (12c). Compound (12c) (154 mg, 61%) was obtained as an *oil*; $\nu_{max.}$ 2 925s, 2 855m, 1 762s, (C=O) 1 280s (C–O), and 940m cm^{-1} (=CH_2); δ_H 0.75—1.10 (3 H, br, *Me*CH_2), 1.10—1.80 (10 H, br, $[CH_2]_5$), 1.32 (3 H, s, 5-Me), 2.58—2.76 (2 H, br 4-CH_2), 5.58 (1 H, m, =CH_2), and 6.05 (1 H, m, =CH_2); *m/e* 197 (M^+ + H), 181 (M^+ − Me), 111 (M^+ − n-C_6H_{13}, base), 68, 55, and 43 (Found: C, 73.2; H, 10.25. $C_{10}H_{20}O_2$ requires C, 73.45; H, 10.25%).

5-*Ethyl*-5-*methyl*-3-*methylenetetrahydrofuran*-2-*one* [29] (12d). Compound (12d) (86 mg, 61%) was obtained as an oil; $\nu_{max.}$ 1 760s (C=O), 1 285s, 1 270s (C–O), 1 095m, 1 085m, and 940m cm^{-1} (=CH_2); δ_H 0.96 (3 H, t, *J* 7 Hz, *Me*CH_2), 1.36 (3 H, s, 5-Me), 1.70 (2 H, q, *J* 7 Hz, MeC*H*$_2$), 2.60—2.76 (2 H, m, 4-CH_2), 5.50 (1 H, m, =CH_2), and 6.10 (1 H, t, *J* 3 Hz =CH_2); *m/e* 140 ($M^{+\cdot}$), 126, 111 (M^+ − Et, base), 97, 69, and 68 (Found: C, 68.45; H, 8.85. Calc. for $C_8H_{12}O_2$: C, 68.55; H, 8.6%).

3-*Methylene*-5-*propyltetrahydrofuran*-2-*one* [30] (12e). Compound (12e) (87 mg, 62%) was obtained as an oil; $\nu_{max.}$ 2 965s, 2 940s, 2 880m, 1 760s (C=O), 1 670m (C=C), 1 400m, 1 340m, 1 270s (C–O), 1 255s, 1 155s, 1 115s (C–O), 1 105s, 1 000s, and 940m cm^{-1} (=CH_2); δ_H 0.70—2.00 (7 H, br, Pr^n), 2.40—3.50 (2 H, m, 4-CH_2), 4.28—4.80 (1 H, m, 5-CH), 5.52 (1 H, t, *J* 2.5 Hz, =CH_2), and 6.12 (1 H, t, *J* 2.5 Hz, =CH_2); *m/e* 140 ($M^{+\cdot}$), 111 (M^+ − Et), 97 (M^+ − Pr^n, base), 69, and 68 (Found: C, 68.5; H, 8.85. Calc. for $C_8H_{12}O_2$: C, 68.55; H, 8.6%).

5-*Ethyl*-3-*methylenetetrahydrofuran*-2-*one* (12f). Compound (12f) (56 mg, 45%) was obtained as an *oil*; $\nu_{max.}$ 2 970s, 2 940s, 2 880m, 1 765s (C=O), 1 670m (C=C), 1 465m, 1 440m, 1 400m, 1 350s, 1 275s (C–O), 1 250s, 1 190m, 1 160s, 1 115s (C–O), 1 090s, 1 000s, 985m, 960s (=CH_2), and 815m cm^{-1}; δ_H 1.00 (3 H, t, *J* 7 Hz, *Me*CH_2), 1.70 (2 H, dq, *J* 7 Hz, MeC*H*$_2$), 2.30—3.40 (2 H, m, 4-CH_2), 4.50 (1 H, *ca.* quintet, *J* 7 Hz, 5-CH), 5.60 (1 H, t, *J* 2.5 Hz, =CH_2), and 6.10 (1 H, t, *J* 2.5 Hz, =CH_2); *m/e* 126 ($M^{+\cdot}$), 111 (M^+ − Me), 97 (M^+ − Et, base) 69, 68, 44, and 40 (Found: C, 66.55; H, 8.1. $C_7H_{10}O_2$ requires C, 66.65; H, 8.0%).

5-*Isobutyl*-5-*methyl*-3-*methylenetetrahydrofuran*-2-*one* [29] (12g). Compound (12g) (129 mg, 66%) was obtained as an oil; $\nu_{max.}$ 2 960m, 2 930m, 1 765s (C=O), 1 670m (C=C), 1 470m, 1 420m, 1 382m, 1 370m, 1 285s (C–O), 1 270m, 1 202m, 1 170m, 1 100m, 1 090m, 1 045m, 940s (=CH_2), and 812m cm^{-1}; δ_H 0.99 (6 H, dd, *J* 6, 1 Hz, CH*Me*$_2$), 1.42 (3 H, s, 5-Me), 1.64 (3 H, m, C*H*$_2$C*H*Me$_2$), 2.75 (2 H, t, *J* 2.5 Hz, 4-CH_2), 5.60 (1 H, t, *J* 2.5 Hz, =CH_2), and 6.18 (1 H, t, *J* 2.5 Hz, =CH_2); *m/e* 168 ($M^{+\cdot}$), 153 (M^+ − Me), 111 (M^+ − Bu^i, base), 97, and 58 (Found: C, 71.2; H, 9.75. Calc. for $C_{10}H_{16}O_2$: C, 71.35; 9.6%).

5,5-*Dimethyl*-3-*methylenetetrahydrofuran*-2-*one* [15] (12h). Compound (12h) (72 mg, 57%) was obtained as an oil; $\nu_{max.}$ 2 980m, 2 937m, 1 760s (C=O), 1 670m (C=C), 1 403m, 1 392m, 1 380m, 1 280s (C–O), 1 188m, 1 127m, 1 087s (C–O), and 942s cm^{-1} (=CH_2); δ_H (CCl_4), 1.40 (6 H, s, 5-Me), 2.70 (2 H, t, *J* 2.5 Hz, 4-CH_2), 5.52 (1 H, t, *J* 2.5 Hz, =CH_2), and 6.08 (1 H, t, *J* 2.5 Hz, =CH_2); *m/e* 126 ($M^{+\cdot}$), 111 (M^+ − Me, base), 83, 68, 43, and 40 (Found: C, 66.4; H, 8.05. Calc. for $C_7H_{10}O_2$: C, 66.6; H, 8.0%).

(E)-3-*Ethylidene*-5-*isobutyl*-5-*methyltetrahydrofuran*-2-*one* (13a). Compound *E*-(13a) (9 mg, 5%) was obtained as an *oil*; $\nu_{max.}$ (CCl_4) 2 970m, 2 930m, 1 765s (C=O), 1 690m (C=C), 1 290m, 1 275m, 1 230m (C–O), 1 125m (C–O), 1 020m, and 950m cm^{-1}; δ_H (CCl_4) 0.95 (6 H, 2 overlapping d, *J* 6.5 Hz, CH*Me*$_2$), 1.20—1.70 (3 H, br, C*H*$_2$C*H*Me$_2$), 1.32 (3 H, s, 5-Me), 1.76 (3 H, dt, *J* 7, 1 Hz, *Me*C=), 2.44—2.68 (2 H, m, 4-CH_2), and 6.40—6.90 (1 H, br, HC=); *m/e* 182($M^{+\cdot}$), 167 (M^+ − Me), 125 (M^+ − Bu^i, base), 111, 97, and 81 (Found: C, 72.35; H, 10.2. $C_{11}H_{18}O_2$ requires, C, 72.5; H, 9.95%).

(Z)-3-*Ethylidene*-5-*isobutyl*-5-*methyltetrahydrofuran*-2-*one* (13a). Compound *Z*-(13a) (22 mg, 12%) was obtained as an *oil*; $\nu_{max.}$ (CCl_4) 2 960m, 2 930m, 2 880m, 1 760s, (C=O), 1 680m (C=C), 1 470m, 1 445m, 1 385m, 1 355m, 1 215s (C–O), 1 115s (C–O), 1 095m, and 955m cm^{-1}; δ_H (CCl_4) 0.96 (6 H, 2 overlapping d, *J* 6.5 Hz, *Me*$_2$CH), 1.20—1.80 (3 H, br, Me$_2$C*H*C*H*$_2$), 1.30 (3 H, s, 5-Me), 2.14 (3 H, dt, *J* 7, 2.5 Hz, *Me*C=), 2.50—2.70 (2 H, m, 4-CH_2), and 5.90—6.40 (1 H, m, HC=); *m/e* 182 ($M^{+\cdot}$), 167 (M^+ − Me), 125 (M^+ − Bu^i, base), 111, 97, and 83 (Found: C, 72.25; H, 10.3. $C_{11}H_{18}O_2$ requires C, 72.5; H, 9.95%.

(Z)-3-*Ethylidene*-5,5-*dimethyltetrahydrofuran*-2-*one* (13b). Compound *Z*-(13b) (49 mg, 35%) was obtained as an *oil*; $\nu_{max.}$ 2 980m, 2 930m, 1 750s (C=O), 1 680m (C=C), 1 445m, 1 390m, 1 375m, 1 355m, 1 302s, 1 267m, 1 250s, and 1 210s (C – O), 1180m 1 127s, 1 096s, 963m, and 927m cm^{-1}; δ_H 1.40 (6 H, s, 5-Me), 2.14 (3 H, dt, *J* 7, 2.5 Hz, *Me*C=), 2.56—2.80 (2 H, m, 4-CH_2), and 5.90—6.50 (1 H, m, HC=); *m/e* 140 ($M^{+\cdot}$, base), 125 (M^+ − Me), 95, 84, 82, 55, and 49 (Found: C, 68.4; H, 8.75. $C_8H_{12}O_2$ requires C, 68.55; H, 8.6%).

(*E*)-3-*Ethylidene*-5,5-*dimethyltetrahydrofuran*-2-*one* (13b). Compound *E*-(13b) (3 mg, 2%) was obtained as an *oil*; $\nu_{max.}$ 2 980m, 2 935m; 1 755s (C=O), 1 670m (C=C), 1445m, 1 390m, 1377m, 1 274s (C–O), 1 200s, 1 177m, 1 120m (C–O) 1 030m, 981m, 923m, and 714m cm^{-1}; δ_H (CCl_4) 1.40 (6 H, s, 5-Me), 1.84 (3 H, dt, *J* 7, 1.5 Hz, *Me*C=) 2.50—2.72 (2 H, br, 4-CH_2), and 6.40—6.84 (1 H, br, HC=); *m/e* 140 ($M^{+\cdot}$), 125 (M^+ − Me), 82 (base), 55, 44, and 43 (Found: C, 68.45; H, 8.75. $C_8H_{12}O_2$ requires C, 68.55; H, 8.6%).

Preparation of the α-*Methylene*-γ-*lactone* (12h) *from the* (E)- *and* (Z)-*hydroxysulphonylhydrazones* (15) *and* (14).—A mixture of the (*E*)- and (*Z*)-hydroxy-sulphonylhydrazones [(14) < (15)] (436 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.20M,; 3.7 ml) was added and gave a yellow solution which was warmed to −3 °C over an hour, recooled to −78 °C, quenched with carbon dioxide gas for 1 min, and warmed to 25 °C. General work-up [(C) dichloromethane, trifluoroacetic acid (1 g)] afforded a crude residue which was dissolved in dichloromethane (10 ml) and left at 0 °C overnight. Chromatography on Kieselgel H (12 g) [eluant: light petroleum–diethyl ether (1 : 0—1 : 1)] and p.l.c. [three

developments with light petroleum–diethyl ether (13 : 7)] gave the α-methylene-γ-lactone (12h) (102 mg, 74%) identical (t.l.c. and n.m.r.) with an authentic sample.

Preparation of the α-Ethylidene-γ-lactone (13b) *from the Hydroxysulphonyl-hydrazone* (16).—Mainly the *Z*-hydroxy-sulphonylhydrazone (16) (408 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.34M; 3.0 ml) and s-butyl-lithium (0.78M; 2.0 ml) were added, the solution was warmed to −3 °C over 95 min, recooled to −78 °C, quenched with carbon dioxide gas until colourless, and then warmed to 25 °C. General work-up [(C) dichloromethane, trifluoroacetic acid (1.0 g)], chromatography on Kieselgel H (20 g) (eluant: dichloromethane), and p.l.c. [three developments with light petroleum–diethyl ether (3 : 1)] gave the (*Z*)-ethylidene-γ-lactone *Z*-(13b) (44 mg, 32%) and the (*E*)-ethylidene-γ-lactone *E*-(13b) (12 mg, 9%), both identical (t.l.c. and n.m.r.) with authentic samples.

Preparation of 2,6-*Dihydroxy*-2,6-*dimethylheptan*-4-*one* 2,4,6-*Tri-isopropylbenzenesulphonylhydrazone* (19).—The sulphonylhydrazone (6a) (366 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.2M; 2.1 ml) was added and gave a golden solution which was quenched with acetone (90 μl). n-Butyl-lithium (1.2M; 1.0 ml) was added and gave an orange-yellow solution which was quenched with acetone (120 μl). Glacial acetic acid (0.33 g) was added and the solution was warmed to 25 °C. General work-up [(A) dichloromethane], chromatography on Kieselgel H (20 g) [eluant: dichloromethane–diethyl ether (1 : 0—7 : 3)], and p.l.c. [three developments with dichloromethane–diethyl ether (9 : 1)] gave a mixture of the (*E*)- and (*Z*)-hydroxy-hydrazones (15) and (14) (152 mg, 35%), identical (t.l.c. and n.m.r.) with an authentic sample, and the *hydroxy-hydrazone* (19) (153 mg, 31%), m.p. 151—153 °C (from dichloromethane and diethyl ether); $\nu_{max.}$ 3 300m (OH, NH), 3 080m (OH, NH), 1 330m (SO_2-N), 1 168m and 1 158m (SO_2-N), 910m, and 880m cm^{-1}; δ_H 1.10—1.50 (30 H, m, Me), 2.40 (2 H, s, CH_2), 2.50 (2 H, s, CH_2), 2.86 (1 H, septet, *J* 7 Hz, *p*-C*H*Me$_2$), 3.44 (2 H, br, OH), 4.17 (2 H, septet, *J* 7 Hz, *o*-C*H*Me$_2$), 7.10—7.25 (1 H, br, NH), and 7.20 (2 H, s, aryl-H); *m/e* 454 ($M^{+\cdot}$), 438, 381, 332, 267, 251, 233, 204, 189 (base), 161, and 127 (Found: C, 63.35; H, 9.35; N, 6.15. $C_{24}H_{42}N_2O_4S$ requires C, 63.4; H, 9.3; N, 6.15%).

Preparation of 2,6-*Dihydroxy*-2-([$^2H_3$]*methyl*)-6-*methyl*-[1-$^2H_3$]*heptan*-4-*one* 2,4,6-*Tri-isopropylbenzenesulphonylhydrazone* (21).—The hydroxy-sulphonylhydrazones (14) and (15) (423 mg) were dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.1M; 3.6 ml) was added and gave an orange-yellow solution which was warmed to −70 °C over 20 min and quenched with [$^2H_6$]acetone (0.25 ml). The solution was warmed to −60 °C, treated with buffer (pH 6.5), and warmed to 25 °C. General work-up [(B) diethyl ether], chromatography on Kieselgel H (20 g) [eluant: dichloromethane–diethyl ether (1 : 0—4 : 1)], p.l.c. [three developments with dichloromethane–diethyl ether (9 : 1)], and recrystallisation from methanol and water at 25 °C gave a mixture of (*E*)- and (*Z*)-hydroxy-sulphonyl-hydrazones (15) and (14) (340 mg, 80%), identical (t.l.c. and n.m.r.) with an authentic sample, and the *deuterio-hydroxy-sulphonylhydrazone* (21) (78 mg, 16%), m.p. 141.5—142.5 °C; $\nu_{max.}$ 3 300s, (NH), 3 090s (OH), 2230m (C–^{2}H), 1 625m (C=N), 1 602s (C=C), 1 565m, 1 410s, 1 340s (SO_2-N), 1 295m, 1 270m, 1 255m, 1 230m, 1 205m, 1 195m, 1 180m, 1 165 and 1 155s (SO_2-N), 1 105m, 1 065m, 1 050m, 1 040m, 975m, 940m, 930m, 920m, 905s, 890m, 845m, 820m, 765m, 670s, and 655m cm^{-1}; δ_H 1.12 and 1.35 (6 H, 2 s, 6-Me), 1.24 (18 H, overlapping d, *J* 7 Hz, CH*Me*$_2$), 2.37 and 2.48 (4 H, 2 s, 3,5-CH_2), 2.92 (1 H, septet, *J* 7 Hz, *p*-C*H*Me$_2$), 3.25 (1 H, br s, OH), 4.25 (2 H, septet, *J* 7 Hz, *o*-C*H*Me$_2$), and 7.25 (2 H, s, aryl-H); *m/e* 461 ($M^{+\cdot}$ + H), 445 (M^+ − Me), 402 ($M^{+\cdot}$ − C_3H_6O), 396 ($M^{+\cdot}$ − $C_3{}^2H_6O$), 267 (base), 135, and 129 (Found: C, 62.45; H, 9.35; N, 6.05. $C_{24}H_{36}{}^2H_6N_2O_4S$ requires C, 62.55; H, 10.51; N, 6.1%).

Preparation of the Hydroxy-sulphonylhydrazone (19) *from the* (E)-*Hydroxy-sulphonylhydrazone* (15).—The (*E*)-hydroxy-sulphonylhydrazone (15) (398 mg) was dissolved in DME (5 ml) and the solution was cooled to −76 °C; n-butyl-lithium (1.3M; 4.0 ml) was added to it and the solution was warmed to −65 °C over 20 min. The golden trianion (18) was quenched with acetone (0.30 ml), warmed to −60 °C, treated with glacial acetic acid (0.4 g), and warmed to 25 °C. General work-up [(B) diethyl ether], chromatography on Kieselgel H (20 g) [eluant: dichloromethane–diethyl ether (1 : 0—3 : 1)], and p.l.c. [three developments with dichloromethane–diethyl ether (9 : 1)] gave a mixture of (*E*)- and (*Z*)-hydroxy-sulphonylhydrazones (15) and (14) (116 mg, 29%), identical (t.l.c. and n.m.r.) with an authentic sample, and the hydroxy-sulphonylhydrazone (19) (233 mg, 51%), identical (t.l.c. and n.m.r.) with an authentic sample. An identical sequence applied to the (*Z*)-hydroxy-sulphonylhydrazone (14) (400 mg) gave, *via* the orange trianion (10a; R^1 = R^2 = Me), a mixture of the (*E*)- and (*Z*)-hydroxy-sulphonylhydrazones (15) and (14) (173 mg, 43%), and the hydroxy-sulphonylhydrazone (19) (140 mg, 30%), all identical (t.l.c. and n.m.r.) with authentic samples.

Preparation of the α-Methylene-γ-lactone (12h) *from the* (E)-*Hydroxy-sulphonylhydrazone* (15).—The (*E*)-hydroxy-sulphonylhydrazone (15) (378 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C; n-butyl-lithium (1.30M; 4.4 ml) was then added to it. The solution was warmed to −3 °C over 80 min, recooled to −78 °C, quenched with carbon dioxide gas, and warmed to 25 °C. General work-up [(C) dichloromethane, trifluoroacetic acid (1.0 g)], chromatography on Kieselgel H (14 g) [eluant: dichloromethane], and p.l.c. [one development with dichloromethane] gave the α-methylene-γ-lactone (12h) (94 mg, 78%), identical (t.l.c. and n.m.r.) with an authentic sample.

An identical sequence applied to the (*Z*)-hydroxy-sulphonylhydrazone (14) (417 mg) gave the α-methylene-γ-lactone (12h) (65 mg, 49%), identical (t.l.c. and n.m.r.) with an authentic sample.

Preparation of 3-*Acetyl*-5-*octyltetrahydrofuran*-2-*one* (22).—Sodium (0.66 g) was dissolved in ethanol and the solution was cooled to 0 °C; ethyl acetoacetate (3.25 g) was then added to it. This was followed by 1,2-epoxydecane (4.5 g) after which the solution was warmed to 25 °C, stirred for 5 d, evaporated, and quenched with glacial acetic acid (1.82 g) in ice–water (5 g). The excess acid was neutralised with solid sodium hydrogencarbonate. General work-up [(B) diethyl ether] and chromatography on Kieselgel H [(i) 35 (ii) 30 g; eluant (i) dichloromethane, (ii) light petroleum–dichloromethane (1 : 0—0 : 1)] gave the impure lactone (22) (5.08 g), *ca.* 75% pure by n.m.r. spectroscopy. A sample was purified by p.l.c. [one development with light petroleum–dichloromethane (1 : 2)] to yield the *lactone* (22) as an oil; $\nu_{max.}$ 2 930s, 2 865s, 1 775s (O–C=O), 1 730s (C=O), 1 470m, 1 367m, 1 235s, and 1 165s (C–O); δ_H 0.73—1.05 (3 H, br, *Me*CH_2), 1.15—2.20 (14 H, br, $[CH_2]_7$), 2.20—2.30 (2 H, m, 4-CH_2), 2.41 and 2.45 (3 H, 2 s, *Me*C=O), 3.60—3.90 (1 H,

m, 3-CH), and 4.30—4.70 (1 H, br, 5-CH); *m/e* 240 ($M^{+\cdot}$), 212 ($M^{+\cdot}$ − CO), 138, 114, 97, 81, and 55 (base) (Found: C, 69.75; H, 10.2. $C_{14}H_{24}O_3$ requires C, 69.95; H, 10.05%).

Preparation of 5-*Hydroxytridecan*-2-*one* (23a).—The impure keto-lactone (22) (4.6 g), concentrated hydrochloric acid (2 ml), and water (11 ml) were heated at 50 °C for 5 d. Diethyl ether (50 ml) was added and the aqueous phase was neutralised and saturated with potassium carbonate. General work-up [(B) diethyl ether] and chromatography on Kieselgel H (30 g) [eluant: dichloromethane–diethyl ether (1 : 0—0 : 1)] gave 5-hydroxytridecan-2-one (23a) (2.06 g, 39% from ethyl acetoacetate) as an oily solid; $\nu_{max.}$ 3 050m (OH), 1 710s (C=O), and 1100s (C–O) cm^{-1}; *m/e* 214 ($M^{+\cdot}$), 197 (M^+ − OH), 101 (M^+ − n-C_8H_{17}), 83, and 62. Treatment of the ketone (23a) (105 mg) with 2,4-dinitrophenylhydrazine (103 mg) gave 5-*hydroxytridecan*-2-*one* 2,4-*dinitrophenylhydrazone* (23c) (168 mg, 87%), m.p. 61.5—63.0 °C (from methanol and water at 0 °C); $\nu_{max.}$ (CCl_4) 1 625s (C=N), 1 600m (C=C), 1 345s (CNO_2), and 1 320m cm^{-1}, δ_H 0.80—1.06 (3 H, br, 12-Me), 1.15—2.00 (16 H, br, 4-CH_2, $[CH_2]_7$), 2.10 and 2.17 (3 H, 2 s, 1′-Me), 2.65 (2 H, *ca.* t, *J* 7.5 Hz, 3′-CH_2), 3.55—3.90 (1 H, br, 5-CH), 7.96—8.50 (3 H, m, aryl 5-, 6-H, HC=N), 9.20 (1 H, d, *J* 2.5 Hz, aryl 3-H), and 10.95 (1 H, br, NH); *m/e* 394 ($M^{+\cdot}$), 377 (M^+ − OH), 281 (M^+ − n-C_8H_{17}), 196 (base), 83, 71, and 55 (Found: C, 57.7; H, 7.6; N, 14.4. $C_{19}H_{30}N_4O_5$ requires C, 57.85; H, 7.65; N, 14.2%).

Preparation of 3-*Methylene*-6-*octyltetrahydropyran*-2-*one* (24).—5-Hydroxytridecan-2-one (23a) (214 mg) and 2,4,6-tri-isopropylbenzenesulphonylhydrazine (298 mg) were dissolved in dry diethyl ether. Activated 4 Å molecular sieves (0.5 g) and Amberlite IR-120H resin catalyst were added and the mixture was stirred for 30 min. T.l.c. analysis indicated the presence of a product, presumably the hydrazone (23b) (*ca.* 90%). The solution was filtered and after evaporation of the filtrate the residue was dissolved in toluene (3 × 5 ml), and then re-evaporated. The residue was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.2 M, 4.0 ml) was added to it to give a yellow solution which was warmed to −3 °C over 75 min, recooled to −78 °C, quenched with carbon dioxide gas, and warmed to 25 °C. General work-up [(C) dichloromethane, trifluoroacetic acid (1.20 g)] gave a crude residue which was dissolved in dichloromethane (10 ml) and was left for 40 min. Chromatography on Kieselgel H (17 g) [eluant: light petroleum–diethyl ether (1 : 0–4 : 1) and p.l.c. (six developments with light petroleum–diethyl ether (4 : 1)] gave the *tetrahydropyran*-2-*one* (24) (51 mg, 23%) as an oil; $\nu_{max.}$ 2 960s, 2928s, 2858s, 1 726s (C=O), 1630m (C=C), 1 398m, 1 300m, 1 180m (C–O), 1 165m (C–O), 1 130m, and 940m cm^{-1} (CH_2=); δ_H 0.70—1.00 (3 H, br, *Me*CH_2), 1.05—2.20 (18 H, br, $[CH_2]_7$, 5-CH_2), 2.40—2.80 (2 H, br, 4-CH_2), 4.04—4.62 (1 H, br, 6-CH), 5.40—5.58 (1 H, m, CH_2=), and 6.26—6.42 (1 H, m, CH_2); *m/e* 224 ($M^{+\cdot}$), 179, 111 (M^+ − n-C_8H_{17}, base), 83, 55, 43, and 41 (Found: C, 74.8; H, 10.95. $C_{14}H_{24}O_2$ requires C, 74.95; H, 10.8%).

Reaction of the Ribofuranose (25a) *with* 2,4,6-*Tri-isopropylbenzenesulphonylhydrazine*.—2,3,5-Tri-*O*-benzyl-D-ribofuranose [17] (25a) (96 mg), 2,4,6-tri-isopropylbenzenesulphonylhydrazine (72 mg), and Amberlite IR-120H resin catalyst were stirred in carbon tetrachloride (5 ml) for 1 h. T.l.c. analysis indicated the presence of a hydrazone derivative. The mixture was stirred for 28 d and evaporated. Purification by p.l.c. (two developments with dichloromethane) gave the sultone (26) (20 mg, 30%), identical (t.l.c. and n.m.r.) with authentic material,[19] and 2,3,5-tri-*O*-benzyl-D-ribofuranolactone (25b) (56 mg, 59%) as an oily solid, $[\alpha]_{589}^{29}$ + 75° (*c* 0.99, $CHCl_3$) [lit.,[18] m.p. 54—55 °C, +74.8 (*c* 3, $CHCl_3$)]; $\nu_{max.}$ 2 875m, 1 790s (C=O), 1 695m, 1 500m, 1 458s, 1 368m, 1 210m, 1 180m, 1 150s, 1 100s (C–O), 1 040s, 1 028s, 735s (aryl-H), and 698 s cm^{-1} (aryl-H); δ_H 3.50—3.64 (2 H, br, OCH_2CH), 3.90—4.90 (9 H, br), and 7.16—7.40 (15 H, m, aryl-H); *m/e* 417 (M^+ − H), 341, 327 (M^+ − $PhCH_2$), 253, 205, 181, 107, and 91 (base) (Found: C, 74.45; H, 6.45. Calc. for $C_{26}H_{26}O_5$: C, 74.6; H, 6.25%).

Preparation of 5-*Hydroxyhexan*-2-*one Toluene*-4-*sulphonylhydrazone* (27).—5-Hydroxyhexan-2-one (2.00 g) and toluene-4-sulphonylhydrazine (3.13 g) were dissolved in THF (20 ml) and the solution was stirred overnight. Evaporation and recrystallisation from chloroform at 0 °C gave the *hydroxy-sulphonylhydrazone* (27) (3.82 g, 80%), m.p. 128—129.5 °C; $\nu_{max.}$ 3 350m (OH, NH), 3 040m, 1 600m (C=C), 1 415, 1 340m (SO_2–N), 1 310m (OH), 1 227m, 1 187m, 1 167s (SO_2–N), 1 072m, 1 040m, (C–O), 925m, 905m, 875m, 810m (aryl-H), 750m, 745s, and 660m cm^{-1}; δ_H {[$^2H_6$]dimethyl sulphoxide DMSO)} (0.90 (3 H, d, *J* 6 Hz, 6-Me), 1.10—1.60 (2 H, m, 4-CH_2), 1.70 (3 H, s, 1-Me), 2.10 (2 H, t, *J* 8 Hz, 3-CH_2), 2.30 (3 H, s, aryl-Me), 3.40—4.00 (2 H, br, 5-CH, OH), 7.30—7.90 (4 H, m, aryl-H), and 9.60 (1 H, br, NH); *m/e* 285 ($M^{+\cdot}$ + H), 284 ($M^{+\cdot}$, weak), 267, 139, 111 (base), 99, and 91 [Found: C, 55.0; H, 7.15; N, 9.95; S, 11.6; (M^+ + H), 285.1264. $C_{13}H_{20}N_2O_3S$ requires C, 54.9; H, 7.1; N, 9.85; S, 11.3%; (M^+ + H), 285.1273].

Reaction of the Dianion (8a) *with Diphenylketen*.—The sulphonylhydrazone (6a) (335 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.37M; 1.6 ml) was added to it to give a golden solution which was warmed to −65 °C over 20 min, and recooled to −78 °C. Diphenylketen (0.35 ml) was added, the suspension was warmed to −66 °C over 10 min, quenched with glacial acetic acid (0.20 ml) in water (1 ml), and warmed to 25 °C. General work-up [(A) diethyl ether], chromatography on Kieselgel H (20 g) [eluant (i) light petroleum–dichloromethane (1 : 0—0 : 1) (ii) dichloromethane–diethyl ether (1 : 0—0 : 1)], and p.l.c. [one development with dichloromethane] gave 1,1-*diphenyl*-2-(*diphenylacetoxy*)*pent*-1-*en*-4-*one* 2,4,6-*tri-isopropylbenzenesulphonylhydrazone* (30) (181 mg, 25%), m.p. 165—166 °C (from dichloromethane and diethyl ether); $\nu_{max.}$ (CCl_4) 3 065 and 3 035m (aryl-H), 2 965s, 2 930m, 2 870m, 1 760s (C=O), 1 600m (C=C), 1 497m, 1 465m, 1 457m, 1 447m, 1 430m, 1 385m, 1 366m, 1 333m (SO_2–N), 1 260m, 1 195m, 1 168, and 1 155s (SO_2–N), 1 115s (C–O), 1 072m, 1 060m, 1 040m, 1 034m, 963m, 940m, 910m, 882m, 696s (aryl-H), and 660m cm^{-1}; δ_H 1.21 (18 H, overlapping d, *J* 7 Hz, $CHMe_2$), 1.55 (3 H, s, 5-Me), 2.90 (1 H, *ca.* septet, *p*-$CHMe_2$), 3.30 (2 H, s, 3-CH_2), 4.30 (2 H, *ca.* septet, *o*-$CHMe_2$), 4.94 (1 H, s), and 7.00—7.40 (23 H, br, aryl-H, NH); *m/e* 726 (M^+, weak), 236, 234, 221, 189, 167 (base), and 165 (Found: C, 75.95; H, 6.9; N, 3.7. $C_{46}H_{50}N_2O_4S$ requires C, 76.0; H, 6.95; N, 3.85%).

Preparation of 4-*Hydroxy*-5-*phenylthiopentan*-2-*one* 2,4,6-*Tri-isopropylbenzenesulphonylhydrazone* (31a).—The sulphonylhydrazone (6a) (360 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.56M; 2.0 ml) was added to it to give a golden solution which was warmed to − 65 °C over 20 min, quenched with phenylthioacetaldhyde [31] (0.30 ml), and then warmed to 25 °C. General work-up [(B) diethyl ether], chromatography on Kieselgel H (13 g) [eluant: dichloromethane–diethyl ether (1 : 0—9 : 1)], and p.l.c. [(i) one development

with dichloromethane–diethyl ether (20 : 1), (ii) four developments with dichloromethane] gave a mixture of the (E)- *and* (Z)-*sulphonylhydrazones* (31a) (124 mg, 24%) as an oily solid; $\nu_{max.}$ 3 480m,br (O–H), 3 220m,br (NH), 3 050m (ArH), 2 955s, 2 920s, 2 875s, 1 600m (C=C), 1 592m, 1 480m, 1 460s, 1 438s, 1 423s, 1 380s, 1 360s, 1 320s (SO_2–N), 1 165 and 1 150s (SO_2–N), 1 070s (C–O), 1 038s, 1 030s, 1 023m, 938m, 910m, 880m, 735s (Ph), 687s (Ph), and 660s cm^{-1}; δ_H 1.24 (18 H, overlapping d, *J* 6 Hz, $CHMe_2$), 1.80 (3 H, s, 1-Me), 2.30—2.60 (2 H, br, 3-CH_2), 2.60—3.20 (3 H, br, *p*-$CHMe_2$, SCH_2), 3.70—4.45 (3 H, br, *o*-$CHMe_2$ and 4-CH), 7.10—7.60 (5 H, br, Ph), and 7.16 (2 H, s, aryl-H); *m/e* 490 (M^+), 472 ($M^{+\cdot} - H_2O$), 363 [($M^+ - H_2O$) – PhS·], 251, 204, 189 (base), 95, and 43 (Found: C, 63.65; H, 7.65; N, 5.55. $C_{26}H_{38}N_2O_3S_2$ requires C, 63.65; H, 7.8; N, 5.7%).

Attempted Preparation of 3-Methylene-5-(phenylthiomethyl)-tetrahydrofuran-2-one (32a).—The sulphonylhydrazone (6a) (338 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.56M; 1.6 ml) was added to it to give a golden solution which was warmed to −65 °C and quenched with phenylthioacetaldehyde (0.20 ml). The resultant clear solution was recooled to −78 °C and n-butyl-lithium (1.56M; 2.0 ml) was added. The resultant solution was warmed to −3 °C over 90 min and gave a deep red solution which was recooled to −78 °C, quenched with carbon dioxide gas, and warmed to 25 °C. General work-up [(C) dichloromethane, trifluoroacetic acid (1.0 g)] and chromatography on Kieselgel H (17 g) [eluant: light petroleum–diethyl ether (1 : 0—0 : 1)] gave no detectable methylene-lactone (32a).

A similar sequence, performed with the thiohydrazone (31a) (132 mg) and n-butyl-lithium (1.56M; 0.75 ml), gave no detectable methylene-lactone (32a).

Preparation of 1,1-*Diethoxy-2-phenylselenoethane*.—Diphenyl diselenide (6.00 g) was suspended in ethanol (70 ml) at 0 °C, sodium borohydride (1.60 g) was added slowly over 30 min to give a clear solution which was warmed to 25 °C and recooled to 0 °C; 1-bromo-2,2-diethoxyethane (5.80 ml) was then added to it. The solution was warmed to 58 °C for 4 h, filtered, and general work-up [(B) dichloromethane] gave crude 1,1-diethoxy-2-phenylselenoethane. Repeated chromatography on Kieselgel H [(i) 35 g, and (ii) and (iii) 30 g; eluant : light petroleum–dichloromethane (1 : 0—0 : 1)] gave the title selenoacetal [32] (10.0 g, 95%) as a liquid; $\nu_{max.}$ 2 980s, 2 932s, 2 900s, 2 880s, 1 583m (C=C), 1 482s, 1 440s, 1 374m, 1 345m, 1 196m, 1 157m, 1 120s (C–O), 1 056s (C–O), 1 023s, 1 002s, 981m, 735s (Ph), and 690m cm^{-1} (Ph); δ_H 1.20 (6 H, t, *J* 7 Hz, $MeCH_2$), 3.10 (2 H, d, *J* 5.5 Hz, $SeCH_2$), 3.60 (4 H, dq, *J* 2.5, 7 Hz, CH_2Me), 4.70 (1 H, t, *J* 5.5 Hz, 1-CH), and 7.14—7.70 (5 H, m, aryl-H); *m/e* 274 and 272 ($M^{+\cdot}$), 229 and 227 (M^+ – OEt), 183 and 181, 157 and 155 ($PhSe^+$), 103 (M^+ – $PhSeCH_2$, base), and 75 (Found: C, 52.95; H, 6.9. Calc. for $C_{12}H_{18}O_2Se$, C, 52.75; H, 6.65%).

Preparation of Phenylselenoacetaldehyde.—1,1-Diethoxy-2-phenylselenoethane (5.05 g), hydrochloric acid (2.5 ml), and water (47.5 ml) were stirred at 50 °C for 4.5 h and cooled to 25 °C. General work-up [(A) diethyl ether, sodium hydrogencarbonate], and distillation gave phenylselenoacetaldehyde [32] (2.92 g, 79%), b.p. 84 °C at 0.2 mmHg; $\nu_{max.}$ 1 710s (C=O), 1 580m (C=C), 1 480m, 1 440m, 1 150m, 1 025m, 740m, and 690m (Ph), and 670m cm^{-1}; δ_H 3.60 (2 H, d, *J* 4 Hz, $SeCH_2$), 7.40—8.00 (5 H, m, Ph), and 9.80 (1 H, t, *J* 4 Hz, CHO); *m/e* 200 and 198 ($M^{+\cdot}$, base), 171 and 169 (M^+ – CHO), 157 and 155 ($PhSe^+$), 91, 77 (Ph^+), and 51 (Found: C, 48.15; H, 4.2; Calc. for C_8H_8OSe: C, 48.25; H, 4.05%). Phenylselenoacetaldehyde (180 mg) was treated with 2,4-dinitrophenylhydrazine (198 mg) to give *phenylselenoacetaldehyde 2,4-dinitrophenylhydrazone* (261 mg, 77%), m.p. 151—152 °C; $\nu_{max.}$ 3 300m (NH), 1 620s (C–N), 1 596s (C=C), 1 513s (CNO_2), 1 497s, 1 330s (CNO_2), 1 310s, 1 275m, 1 265m, 1 220m, and 740m cm^{-1} (Ph); δ_H 3.74 (2 H, d, *J* 6 Hz, $SeCH_2$), 7.10—7.90 (7 H, m, Ph, aryl 6-H, HC=N), 8.14 (1 H, dd, *J* 2.5, 10 Hz, aryl 5-H), 9.16 (1 H, d, *J* 2.5 Hz, aryl 3-H), and 10.90—11.20 (1 H, br, NH); *m/e* 380 and 378 ($M^{+\cdot}$), 314 and 312, 266 and 264, 223 (M^+ – PhSe, base), 157 and 155 ($PhSe^+$), 75, and 55 (Found: C, 44.6; H, 3.15; N, 14.75. $C_{14}H_{12}N_4O_4Se$ requires C, 44.35; H, 3.2; N, 14.75%).

Preparation of 4-*Hydroxy-5-phenylselenopentan-2-one* 2,4,6-*Tri-isopropylbenzenesulphonylhydrazone* (31b).—The sulphonylhydrazone (6a) (338 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.4M; 1.8 ml) was added to it to give a golden solution which was warmed to −65 °C over 15 min and recooled to −78 °C. Phenylselenoacetaldehyde (0.25 ml) was added to the mixture which was then warmed to −68 °C, quenched with glacial acetic acid (0.18 ml), and warmed to 25 °C. General work-up [(A) diethyl ether], chromatography on Kieselgel H (18 g) [eluant : dichloromethane–diethyl ether (1 : 4—4 : 1)], and p.l.c. [two developments in dichloromethane–diethyl ether (9 : 1)] gave a mixture of the (E)- *and* (Z)-*hydroxy-sulphonylhydrazones* (31*b*) (319 mg, 59%), as an unstable oil; $\nu_{max.}$ 3 490m,br (OH), 3 205m,br (NH), 3 070 and 3 058m (aryl-H), 2 960s, 2 930s, 2 890s, 2 870s, 1 600s, (C=C), 1 580m, 1 565m, 1 478s, 1 460s, 1 438s, 1 425s, 1 382s, 1 362s, 1 350m 1 323s (SO_2–N), 1 300s, 1 256m, 1 216m, 1 194m 1 170, and 1 153s (SO_2–N), 1 135s, 1 105s (C–O), 1 072s, 1 060s, 1 040s, 1 022s, 1 012m, 1 000m, 940s, 932s, 923s, 910s, 882s, 865m, 842m, 735, and 690s (Ph), 668s, 663s, and 652s cm^{-1}; δ_H 1.28 (18 H, overlapping d, *J* 7 Hz, $CHMe_2$), 1.80 and 1.92 (3 H, 2 s, 1-Me), 2.36—2.68 (2 H, br, 3-CH_2), 2.80—3.30 (4 H, br, *p*-$CHMe_2$, $SeCH_2$, and OH), 3.80—4.60 (3 H, br, *o*-$CHMe_2$ and 4-CH), and 7.20—7.80 (8 H, m, aryl-H); *m/e* 538/536 ($M^{+\cdot}$. weak), 392 and 390, 360 and 358, 314 and 312, 236, 221, 204, 189 (base), and 161 (Found: C, 57.9; H, 7.35; N, 4.9. $C_{26}H_{38}N_2O_3SSe$ requires C, 58.1; H, 7.1; N, 5.2%).

Attempted Preparation of 3-*Methylene-5-(phenylselenomethyl)tetrahydrofuran-2-one* (32b).—The sulphonylhydrazone (6a) (352 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.4M; 1.9 ml) was added to it to give a golden solution which was warmed to −65 °C over 25 min and recooled to −70 °C. Phenylselenoacetaldehyde (0.25 ml) was added to give a clear solution which was recooled to −78 °C. n-Butyl-lithium (1.4M; 1.3 ml) was added to it to give a golden solution which was warmed to −3 °C over 90 min. The resultant red solution was recooled to −78 °C, quenched with carbon dioxide gas, and warmed to 25 °C. General work-up [(C) dichloromethane, trifluoroacetic acid (0.62 g)], chromatography on Kieselgel H (18 g) [eluant : light petroleum–diethyl ether (1 : 0—0 : 1)], and p.l.c. [two developments in dichloromethane] gave 5-(*butylselenomethyl*)-3-*methylenetetrahydrofuran-2-one* (32c) (3 mg, *ca.* 1%) as an oil, $\nu_{max.}$ ($CHCl_3$) 1 765s (C=O), 1 335m, 1 280m, 1 155m, 1 120m, 995m, and 945m cm^{-1} (CH_2=); δ_H (weak) 0.80—1.70 (7 H, br, Pr^n), 2.50—3.10 (6 H, br, CH_2Se, 4-CH_2), 4.50—5.00 (1 H, br, 5-CH), 5.70 (1 H, *ca.* t, HC=), and 6.30

(1 H, *ca.* t, HC=); *m/e* 248 and 246 ($M^{+\cdot}$) (Found: $M^{+\cdot}$ 249.0300. $C_{10}H_{16}O_2{}^{80}Se$ requires $M^{+\cdot}$ 248.0315) and benzoic acid (21 mg, 17%), m.p. 121—122 °C (lit.,[33] 122 °C), identical with authentic material.

The sequence was repeated with the sulphonylhydrazone (6a) (341 mg) *except* that the solution was warmed to −30 °C over 1 h and maintained between −30 and −25 °C for 30 min before it was recooled to −78 °C and quenched with carbon dioxide gas. A similar work-up gave the selenolactone (32c) (5 mg, *ca.* 2%), identical (t.l.c., i.r., and n.m.r.) with the previous sample, and benzoic acid (21 mg, 17%).

Preparation of 1,1-*Diethoxy*-2-*methylselenoethane*.—Dimethyl diselenide [34] (4.00 g) was dissolved in ethanol (50 ml) at 0 °C and sodium borohydride (1.61 g) was added to it slowly over 30 min. The clear solution was then warmed to 25 °C and recooled to 0 °C. 2-Bromo-1,1-diethoxyethane (6.40 ml) was added to the solution which was then warmed to 50 °C for 3.5 h; t.l.c. analysis indicated an incomplete reaction. Further sodium methylselenide [prepared from dimethyl diselenide (4.00 g) and sodium borohydride (1.60 g) in ethanol (30 ml) at 0 °C] was added to the solution which was then cooled to 25 °C, and filtered. General work-up [(A) diethyl ether] and repeated chromatography on Kieselgel H [(i) 30 g, (ii) 35 g; eluant : light petroleum–dichloromethane (1 : 0—0 : 1)] gave the *seleno-acetal* (7.26 g, 81%), as a liquid; $\nu_{max.}$ 2 980s, 2 930s, 2 900s, 2 880s, 2 830m 1 448m, 1 425m, 1 410m, 1 392m, 1 375m, 1 346m, 1 202m, 1 160s, 1 125, 1 100, and 1 052s (C–O), 1 004s, and 745m cm^{-1}; δ_H 1.22 (6 H, t, *J* 7 Hz, $MeCH_2$), 2.10 (3 H, s, SeMe), 2.72 (2 H, d, *J* 6 Hz, CH_2Se), 3.68 (4 H, dq, *J* 2.5, 7 Hz, CH_2Me), and 4.72 (1 H, t, *J* 6 Hz, 1-CH); *m/e* 212 and 210 ($M^{+\cdot}$), 167 and 165 (M^+ − EtO), 139 and 137, 103 (base), 75, and 48 (Found: C, 39.65; H, 7.65. $C_7H_{16}O_2Se$ requires C, 39.8; H, 7.65%).

Preparation of Methylselenoacetaldehyde.—1,1-Diethoxy-2-methylselenoethane (5.90 g), concentrated hydrochloric acid (5 ml), water (95 ml), and THF (50 ml) were stirred together at 40 °C for 4 d after which the solution was cooled to 25 °C. General work-up [(A) dichloromethane, sodium hydrogencarbonate solution] and distillation gave *bis(methylseleno)acetaldehyde* (0.55 g, 17%), b.p. 70—72 °C at 0.45 mmHg; $\nu_{max.}$ 2 925m, 2 820m, 1 695s (C=O), 1 420m, 1 370m, 1 277m, 1 204m, 1 095m, 1 050m, 1 018m, and 910m cm^{-1}; δ_H 2.04 (6 H, s, MeSe), 4.40 (1 H, d, *J* 4 Hz, HCSe), and 9.30 (1 H, d, *J* 4 Hz, HC=O); *m/e* 232, 230, and 228 ($M^{+\cdot}$, base), 203, 201, and 199 (M^+ − CHO), 175, 173, and 171, 137 and 135 (M^+ − MeSe), 109 and 107, and 93 and 91, and crude methylselenoacetaldehyde, isolated from the cold trap.

Bis(methylseleno)acetaldehyde (133 mg) was treated with 2,4-dinitrophenylhydrazine (115 mg) to yield *bis(methylseleno)acetaldehyde* 2,4-*dinitrophenylhydrazone* (174 mg, 73%), m.p. 133—134 °C; $\nu_{max.}$ (CCl_4) 1 622s (C=N), 1 598m (C=C), 1 508m (CNO_2), 1 432m, 1 340s and 1 327s (CNO_2), 1 309m, 1 276m, and 1 140m cm^{-1}; δ_H 2.12 (6 H, s, MeSe), 4.72 (1 H, d, *J* 7 Hz, SeCH), 7.40—8.70 (3 H, m, HC≡N, aryl 5,6-H), 9.24 (1 H, d, *J* 3 Hz, aryl 3-H), and 11.35 (1 H, br, NH); *m/e* 412, 410, and 408 ($M^{+\cdot}$, weak), 395, 393, and 391 (M^+ − OH), 317 and 315 (M^+ − MeSe), 301 and 299 (base), 233, 190, and 95 and 93 ($MeSe^+$) (Found: C, 29.45; H, 2.8; N, 13.65. $C_{10}H_{12}N_4O_4Se_2$ requires C, 29.3; H, 2.95; N, 13.65%).

The crude methylselenoacetaldehyde was purified by chromatography on Kieselgel H (24 g) [eluant : light petroleum–dichloromethane (1 : 0—0 : 1)] to yield *methylselenoacetaldehyde* (1.03 g, 27%) as an oil; $\nu_{max.}$ 2 935m, 2 825m, 2 720m, 1 710s (C=O), 1 425m, 1 410m, 1 385m, 1 282m, 1 158s, 1 030m, 970m, 910m, and 833m cm^{-1}; δ_H 2.00 (3 H, s, MeSe), 3.25 (2 H, d, *J* 4 Hz, $SeCH_2$), and 9.60 (1 H, t, *J* 4 Hz, HC=O); *m/e* 138 and 136 ($M^{+\cdot}$), 109 and 107 (M^+ − CHO), 95 and 93 ($MeSe^+$), 83, 57, and 43. A sample of methylselenoacetaldehyde (70 mg) was treated with 2,4-dinitrophenylhydrazine (105 mg) to yield *methylselenoacetaldehyde* 2,4-*dinitrophenylhydrazone* (102 mg, 63%), m.p. 134—135 °C; $\nu_{max.}$ (CCl_4) 1 623s (C=N), 1 598m (C=C), 1 510m (CNO_2), 1 340 and 1 330m (CNO_2), 1 312m, and 1 140m cm^{-1}; δ_H 2.10 (3 H, s, MeSe), 3.50 (2 H, d, *J* 7 Hz, CH_2Se), 7.50—8.60 (3 H, m, HC=N, aryl 5,6-H), 9.24 (1 H, d, *J* 2.5 Hz, aryl 3-H), and 11.30 (1 H, br, NH); *m/e* 318 and 316 ($M^{+\cdot}$), 223 (M^+ − MeSe, base) 196, 176, and 122 (Found: C, 34.1; H, 3.05; N, 17.9. $C_9H_{10}N_4O_4Se$ requires C, 34.1; H, 3.2; N, 17.65%).

Attempted Preparation of 3-*Methylene*-5-*(methylselenomethyl)tetrahydrofuran*-2-*one* (32d).—The sulphonylhydrazone (6a) (340 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. Methyl-lithium (1.09M; 3.0 ml) was added to it to give a yellow solution which was warmed to −65 °C over 15 min and then recooled to −78 °C. Methylselenoacetaldehyde (386 mg) in DME (1 ml) was added and the solution was treated with methyl-lithium (1.09M; 3.5 ml). The solution was warmed to −35 °C over 70 min, then to −3 °C over 30 min, recooled to −78 °C, quenched with carbon dioxide gas, and warmed to 25 °C. General work-up [(C) dichloromethane, trifluoroacetic acid (1.10 g)] gave a crude residue. N.m.r. analysis indicated the absence of any significant amount of the methylene-lactone (32d) or selenomethyl compounds.

Preparation of 5-endo-*Hydroxy*-5-exo-[2-(2,4,6-*tri-isopropylbenzenesulphonyl(hydrazone)propyl]bicyclo*[2.2.1]*hept*-2-*ene* (34).—The sulphonylhydrazone (6a) (323 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.31M; 2.1 ml) was added to it and the resultant golden solution was warmed to −68 °C over 15 min and then recooled to −78 °C. Bicyclo[2.2.1]hept-2-en-5-one [21] (0.20 ml) was added to the solution which was then warmed to −65 °C, quenched with glacial acetic acid (0.25 ml), and warmed to 25 °C. General work-up [(A) diethyl ether] and chromatography on Kieselgel H (17 g) [eluant : diethyl ether–light petroleum (0 : 1—1 : 3)] gave (*a*) the crude (*Z*)-hydrazone *Z*-(34) (323 mg) and (*b*) the crude (*E*)-hydrazone *E*-(34) (152 mg). Purification of (*b*) by p.l.c. [two developments with dichloromethane–diethyl ether (3 : 1)] and recrystallisation from ethanol and water gave mainly the (E)-*sulphonylhydrazone E*-(34) (72 mg, 17%), m.p. 120—124 °C; $\nu_{max.}$ 3 550s (OH), 3 265s (NH), 1 604s (C=C), 1 335m (SO_2–N), 1 318m, 1 258m, 1 168m, and 1 158s (SO_2–N), 1 147s, 1 125m, 1 108m, 1 085m, 1 075m, 1 065m, 722m, 674m, and 660m cm^{-1}; δ_H 1.25 (18 H, overlapping d, *J* 7 $CHMe_2$), 1.30—1.70 (4 H, m, 6-, 7-CH_2), 1.90 (3 H, s, 3′-Me), 2.45—2.80 (2 H, br, 1-, 4-CH), 2.60 (2 H, s, 1′-CH_2), 2.90 (1 H, overlapping septets, *J* 7 Hz, *p*-$CHMe_2$), 4.28 (2 H, overlapping septets, *J* 7 Hz, *o*-$CHMe_2$), 5.95—6.20 (1 H, m, HC=), 6.30—6.50 (1 H, m, HC=), 7.15 (2 H, s, aryl-H), and 7.50 (1 H, br, NH); *m/e* 446 ($M^{+\cdot}$), 267, 204, 189 (base), 161, and 66 ($C_5H_6{}^+$) (Found: C, 67.4; H, 8.75; N, 6.3. $C_{25}H_{38}N_2O_3S$ requires C, 67.25; H, 8.55; N, 6.25%). Double recrystallisation of crude (*a*) from methanol and water gave mainly the (*Z*)-sulphonylhydrazone (34) (165 mg, 39%); δ_H 1.30 (18 H, overlapping d, *J* 7 Hz, $CHMe_2$), 1.30—3.40 (12 H, br), 4.25 (2 H, overlapping septets, *J* 7 Hz,

o-C*H*Me$_2$), 6.10 (1 H, br, HC=), 6.30 (1 H, br, HC=), and 7.20 (2 H, s, aryl-H).

Preparation of 5-endo-*Hydroxy*-5-exo-[(2-^{2}H$_1$]*prop*-2-*enyl*)*bicyclo*[2.2.1]*hept*-2-*ene* (35a).—Acetone trisylhydrazone (6a) (331 mg) was dissolved in DME (5 ml) and the solution cooled to −78 °C. n-Butyl-lithium (1.3M; 2.3 ml) was added and the resultant yellow solution was then warmed to −66 °C over 25 min and recooled to −78 °C. Bicyclo-[2.2.1]hept-2-en-5-one (0.21 ml) was then added to the solution which was warmed to −66 °C over 5 min, and recooled to −78 °C. n-Butyl-lithium (3.90 mmol) was added to the resultant yellow solution which was warmed to −3 °C over 130 min, recooled to −10 °C, quenched with deuterium oxide (0.60 ml), and warmed to 25 °C. General work-up [(B) dichloromethane] and repeated chromatography on Kieselgel H (4 × 25 g) [eluant : light petroleum–diethyl ether (1 : 0—4 : 1)] gave the *deuterio-olefin* (35a) (104 mg, 70%) as an oil; $\nu_{max.}$ 3 450m (OH), 3 075m (CH_2=), 2 970s, 2 878m, 1 618m (C=C), 1 432m, 1 354m, 1 335s (OH), 1 275m, 1 255m, 1 245m, 1 200m, 1 185m, 1 172m, 1 120s, 1 105m, 1 087m, 1 078m, 1 055s (C–O), 956m (CH_2=), 910s, and 720s cm^{-1} (CH=CH); δ_H 1.50 (2 H, br s, 7-CH_2), 1.72 (2 H, m, 6-CH_2), 2.50 (2 H, br s, 1-, 4-CH), 2.70—3.00 (2 H, m, 1′-CH_2), 5.00—5.30 (2 H, m, CH_2=), and 6.10—6.56 (2 H, 2 m, 2-, 3-CH); *m/e* 151 ($M^{+\cdot}$), 109 ($M^+ - C_3H_4{}^2H_1$, base), 81, 79, and 66 ($C_5H_6{}^+$), 91% mono-deuteriated (Found: C, 79.35; H, 10.2. $C_{10}H_{13}{}^2H_1O$ requires C, 79.4; H, 10.0%).

Preparation of (1S,4S,5R)- *and* (1R,4R,5S)-4′-*methylene-bicyclo*[2.2.1]*hept*-2-*ene*-5-*spiro*-2′-*tetrahydrofuran*-5′-*one* (33a).—The sulphonylhydrazone (6a) (677 mg) was dissolved in DME (8 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.3M; 3.4 ml) was added and the resultant golden solution was warmed to −68 °C over 25 min, and recooled to −72 °C. Bicyclo[2.2.1]hept-2-en-5-one (0.40 ml) was added and the solution was stirred for 10 min, and then recooled to −78 °C. n-Butyl-lithium (1.3M; 3.5 ml) was added and the resultant orange-red solution was warmed to −3 °C over 85 min, recooled to −78 °C, quenched with carbon dioxide gas, warmed to 25 °C, and then evaporated. The residue was extracted with water (100 ml) and dichloromethane (80 ml), the aqueous layer was separated, re-extracted with dichloromethane (2 × 60 ml), saturated with sodium chloride, filtered, diluted to 122 ml, and divided into fraction (i) (64 ml) and fraction (ii) (58 ml). Fraction (i) was acidified with glacial acetic acid (0.351 g) and stirred at 25 °C for 3 d. General work-up [(B) dichloromethane, diethyl ether] gave a crude residue. T.l.c. analysis indicated a *ca.* 20% conversion of the intermediate hydroxy-acid into the lactone (33a). The residue was dissolved in dichloromethane (10 ml), acidified with glacial acetic acid (2 drops), and stirred at 25 °C. Evaporation and chromatography on Kieselgel H (16 g) [eluant: dichloromethane) and p.l.c. [one development with light petroleum–diethyl ether (1 : 1)] gave the *bicyclospirolactone* (33a) (113 mg, 61%) as an oil; $\nu_{max.}$ 2 970m, 1 765s (C=O), 1 670m (C=C), 1 290m, 1 273m (C–O), 1 215m, 1 165m, 1 138m, 1 124m, 1 093m, 1 028m, 966m, 938m (CH_2=), and 718m (HC=CH) cm^{-1}; δ_H 1.20—2.00 (4 H, m, 6-, 7-CH_2), 2.70 (1 H, s, 1-CH), 2.90 (1 H, s, 4-CH), 2.95—3.20 (2 H, m, 3′-CH_2), 5.60 (1 H, t, *J* 1 Hz, α-CH, and 6.10—6.50 (3 H, m, α-CH, 2-, 3-H); δ_C 41.2 (m, 6-C), 42.9 (m, 7-C), 43.2 (d, 1-C), 48.9 (d, 4-C), 56.2 (m, 3′-C), 89.7 (s, 5-C), 121.4 (m, α-C), 133.2 (d, 2-C), 135.8 (s, 4′-C), 138.4 (d, 3-C), and 170.2 (s, 5′-C); *m/e* 176 ($M^{+\cdot}$), 111, 68, 67, 66 ($C_6H_5{}^+$, base) and 40 (Found: C, 74.85; H, 7.05. $C_{11}H_{12}O_2$ requires C, 75.0; H, 6.85%). The lactonisation of intermediate (35b) using trifluoroacetic acid was less satisfactory (29%).

Preparation of 3,5-*Dimethylenetetrahydrofuran*-2-*one* (28).—The spirolactone (33a) (58 mg) was suspended on glass wool and subjected to flash-vacuum pyrolysis [23] under the following conditions: substrate temperature, −78—55 °C over 6 h; furnace temperature, 550 °C; operating pressure, 10^{-4} mmHg. Extraction of the cold finger with dichloromethane and evaporation at 0 °C gave the *dimethylene-lactone* (28) (30 mg, 83%) as a volatile oil; $\nu_{max.}$ 1 795s (C=O), 1 765m, 1 682, and 1 670s, (C=C–O), 1 403m, 1 279s (C–O), 1 262m, 1 232m, 1 085s (C–O), 975m (CH_2=), 877m, and 840m cm^{-1}; $\lambda_{max.}$ 249 nm (ε 1 900); δ_H 3.44—3.68 (2 H, m, 4-CH_2), 4.34 (1 H, q, *J* 2 Hz, 5-C=CH_2), 4.76 (1 H, q, *J* 2 Hz, 5-C=CH_2), 5.68 (1 H, t, *J* 2.5 Hz, 3-C=CH_2), and 6.28 (1 H, t, *J* 3.0 Hz, 3-C=CH_2); *m/e* 110 ($M^{+\cdot}$), 68 [$M^+ - (C_2H_2O)$, base], and 40 [$M^+ - (C_3H_2O_2)$] (Found: C, 65.3; H, 5.75%; $M^{+\cdot}$, 110.0368. $C_6H_6O_2$ requires C, 65.45; H, 5.5%; $M^{+\cdot}$, 110.0368).

Preparation of (1S,4S,5R)- *and* (1R,4R,5S)-(Z)-3′-*Pentylidenebicyclo*[2.2.1]*hept*-2-*ene*-5-*spiro*-2′-*tetrahydrofuran*-5′-*one* (33b).—The sulphonylhydrazone (36) (417 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.3M; 2.0 ml) was added to it and the solution was warmed to −66 °C over 15 min and then recooled to −78 °C. Bicyclo[2.2.1]hept-2-en-5-one (0.20 ml) was added to the solution which was then warmed to −66 °C over 7 min and recooled to −78 °C. n-Butyl-lithium (1.3M; 3.0 ml) was added to the solution which was warmed to −3 °C over 150 min, recooled to −78 °C, quenched with carbon dioxide gas, and warmed to 25 °C. After general work-up [(C) dichloromethane, glacial acetic acid (0.51 g)], the residue was stirred in dichloromethane (10 ml) for 2 d. Chromatography on Kieselgel H (16 g) [eluant: dichloromethane] and p.l.c. [one development with light petroleum–diethyl ether (3 : 7)] gave the *alkylmethylene-lactone* (33b) (41 mg, 16%) as an oil; $\nu_{max.}$ 2 960s, 2 930s, 2 860s, 1 755s (C=O), 1 675m (C=C), 1 462m, 1 442m, 1 370m, 1 337m, 1 318m, 1 265m, 1 235m, 1 218s (C–O), 1 176m, 1 137s, 1 127m, 1 104m, 1 085m, 1 063m, 1 026s (C–O), 1 008m, 965m, and 712m cm^{-1}; δ_H 0.80—1.85 (13 H, br), 2.30—3.30 (6 H, m, allylic-H), and 5.80—6.50 (3 H, m, HC=); *m/e* 246 ($M^{+\cdot}$), 181 ($M^+ - C_5H_5$, base), 180 ($M^{+\cdot} - C_5H_6$), 137, 95, and 66 ($C_5H_6{}^{+\cdot}$) (Found: C, 77.95; H, 9.0. $C_{16}H_{22}O_2$ requires C, 78.0; H, 9.0%).

Preparation of (E)- *and* (Z)-*Hex*-5-*en*-2-*one* 2,4,6-*Tri-isopropylbenzenesulphonylhydrazones* (41) *and* (42).—The sulphonylhydrazone (6a) (1.342 g) was dissolved in DME (14 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.35M; 6.5 ml) was added and the resultant golden solution was warmed to −67 °C over 25 min, and recooled to −78 °C. Allyl bromide (0.70 ml) was added to it and the suspension was warmed to −65 °C over 1 h, stirred for 30 min, and warmed to −60 °C over 30 min. Glacial acetic acid (0.66 ml) was added and the solution was warmed to 25 °C. General work-up [(A) diethyl ether] and recrystallisation from ethanol and water at 25 °C gave a mixture of the *sulphonylhydrazones* (41) and (42) (1.405 g, 94%), m.p. 113—115 °C; $\nu_{max.}$ 3 265s (NH), 1 605m (C=C) 1 330s (SO_2–N), 1 305m, 1 262m, 1 170, and 1 158s (SO_2–N), 1 107m, 938m, 913m (CH=CH_2), 884m, and 666s cm^{-1}; δ_H 1.28 (18 H, overlapping d, *J* 7 Hz, CH*Me*$_2$), 1.78 and 1.92 (3 H, 2 s, 1-*Me*), 2.16—2.32 (4 H, br, 3-, 4-CH_2), 2.95 (1 H, septet, *J* 7 Hz, *p*-C*H*Me$_2$), 4.30 (2 H, septet, *J* 6.5 Hz, *o*-C*H*Me$_2$), 4.60—5.80 (3 H, m, CH=CH_2), 7.20 (2 H, s, aryl-H), and

7.70 (1 H, br, NH), *E* : *Z* *ca.* 85 : 15 by n.m.r.; *m/e* 379 ($M^{+\cdot}$ + H), 236, 221, 204, 189 (base), 161, and 67 (Found: C, 66.5; H, 9.15; N, 7.4. $C_{21}H_{31}N_2O_2S$ requires C, 66.65; H, 9.05; N, 7.4%).

Preparation of (E)- *and* (Z)-3-(2-*Hydroxypropan*-2-*yl*)*hex*-5-*en*-2-*one* 2,4,6-*Tri-isopropylbenzenesulphonylhydrazones* (39) *and* (40).—The sulphonylhydrazone (6a) (680 mg) was dissolved in DME (7 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.35M; 3.6 ml) was added to the solution which was then warmed to −68 °C over 20 min, and recooled to −78 °C. Allyl bromide (0.25 ml) was added to the solution which was then warmed to −65 °C over 1 h and stirred at this temperature for 20 min; it was then recooled to −78 °C. Further n-butyl-lithium (1.35M; 2.6 ml) was added to the solution which was warmed to −68 °C over 20 min, recooled to −78 °C, and quenched with acetone (0.50 ml). The suspension was warmed to −50 °C, quenched with glacial acetic acid (0.40 ml) in water (1 ml), and warmed to 25 °C. General work-up [(A) diethyl ether], chromatography on Kieselgel H (20 g) [eluant: dichloromethane–diethyl ether (1 : 0—4 : 1)], and p.l.c. [two developments with dichloromethane–diethyl ether (9 : 1)] gave the *hydroxy-sulphonylhydrazones* (39) and (40) (772 mg, 88%), m.p. 129—130 °C (from ethanol and water) mainly as the *E*-isomer (39); $\nu_{max.}$ 3 530m (OH), 3 260m, (NH), 1 605m (C=C), 1 317m (SO_2–N), 1 300m, 1 167 and 1 150s (SO_2–N), 1 105m, 1 040m, 940m, 910m (CH_2=), 900m, and 667m cm^{-1}; δ_H 1.08 and 1.14 (6 H, 2 s, *Me*CO), 1.30 (18 H, overlapping d, CH*Me*$_2$), 1.80 (3 H, s, 1-Me), 2.28 (2 H, d, *J* 4 Hz, 4-CH_2), 2.40 (1 H, s, OH), 2.60—3.10 (1 H, br. *p*-C*H*Me$_2$), 3.90—4.60 (3 H, br, *o*-C*H*Me$_2$, 3-CH), 4.60—5.90 (3 H, m, CH_2=CH), 7.28 (2 H, s, aryl-H), and 7.68 (1 H, br, NH); *m/e* 436 ($M^{+\cdot}$), 421 (M^+ − Me), 267, 204, 189 (base), 161, and 111 (Found: C, 66.25; H, 9.35; N, 6.45. $C_{24}H_{40}N_2O_3S$ requires C, 66.0; H, 9.25; N, 6.4%).

Preparation of (E)-2-*Methylhexa*-2,5-*dienoic Acid* (44).—The sulphonylhydrazone (6a) (681 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.03M; 5.0 ml) was added and the resultant golden solution was warmed to −66 °C over 17 min, and recooled to −78 °C. Allyl bromide (0.30 ml) was added, and the suspension was warmed to −65 °C over 30 min, stirred for 30 min, and recooled to −78 °C. TMEDA (1.0 ml) and n-butyl-lithium (1.03M; 4.0 ml) were added and the resultant golden solution was warmed to −3 °C over 110 min, recooled to −78 °C, quenched with carbon dioxide gas, and warmed to 25 °C. General work-up [(C) dichloromethane, trifluoroacetic acid (1.50 g)], chromatography on Kielselgel H (16 g) [eluant: dichloromethane], and p.l.c. [two developments with dichloromethane] gave the (E)-*acid* (44) (65 mg, 26%) as an oil; $\nu_{max.}$ 3 500—2 400mbr (OH), 1 690s (CO_2H), 1 640m (C=C), 1 420m, 1 285m (C–O), and 915m cm^{-1} (CH_2=CH); δ_H 1.90 (3 H, d, *J* 1 Hz, Me), 3.05 (2 H, t, *J*, 7 Hz, 4-CH_2), 5.00—6.50 (3 H, m, CH_2=CH), 7.10 (1 H, br t, *J* 7 Hz, 3-CH), and 10.50—11.0 (1 H, br, OH); *m/e* 126 ($M^{+\cdot}$), 111 (M^+ − Me), 87, 81 (M^+ − CO_2H, base), 55, and 41 (Found: C, 66.85; H, 8.15. $C_7H_{10}O_2$ requires C, 66.65; H, 8.0%).

Preparation of 2-*Hydroxy*-2-*methyloct*-7-*en*-4-*one* 2,4,6-*Tri-isopropylbenzenesulphonylhydrazone* (46).—A mixture of the (*E*)- and (*Z*)-sulphonylhydrazones (42) and (41) (85 : 15; 430 mg) was dissolved in DME (4.5 ml) and TMEDA (0.5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.35M; 2.5 ml) was added and the resultant golden solution was warmed to −65 °C over 10 min, quenched with acetone (0.20 ml), and warmed to 25 °C. General work-up [(A) glacial acetic acid (0.30 g), diethyl ether (150 ml)] and chromatography on Kieselgel H (20 g) [eluant: (i) light petroleum–dichloromethane (1 : 0—0 : 1); (ii) dichloromethane–diethyl ether (1 : 0—3 : 1)] gave the (Z)-*hydroxy-sulphonylhydrazone* (46) (344 mg, 69%), m.p. 102—105 °C (from ethanol and water at 25 °C as the *Z*-isomer); $\nu_{max.}$ 3 480s (OH), 3 108m (NH), 1 647m (C=N), 1 605m (C=C), 1 330s (SO_2–N), 1 165 and 1 155s (SO_2–N), 1 133m, 1 104m, 1 060m, 1 039m, 923m, 910s (CH_2=CH), 883m, 676s, and 652m cm^{-1}; δ_H 1.28 (18 H, overlapping d, *J* 7 Hz, CH*Me*$_2$), 1.34 (6 H, s, 2-Me), 2.20—2.50 (6 H, m, 2,5,6-CH_2), 2.70 (1 H, br, OH), 2.95 (1 H, septet, *J* 7 Hz, *p*-C*H*Me$_2$), 4.28 (2 H, septet, *J* 7 Hz, *o*-C*H*Me$_2$), 4.75—5.10 (2 H, br, 8-CH_2), 5.50—6.00 (1 H, m, 7-CH), 7.25 (2 H, s, aryl-H), and 10.60 (1 H, br, NH); *m/e* 436 ($M^{+\cdot}$), 267, 251, 204, 189 (base), 161, 112, 91, and 59 (Found: C, 66.2; H, 9.4; N, 6.5. $C_{24}H_{40}N_2O_3S$ requires C, 6.60; H, 9.25; N, 6.4%).

Preparation of 6-*Iodomethyl*-3-*methylenetetrahydropyran*-2-*one* (49a).—A mixture of the (*E*)- and (*Z*)-sulphonylhydrazones (42) and (41) (85 : 15, 1.188 g) was dissolved in DME (10 ml) and TMEDA (1.5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.31M; 5.6 ml) was added and the solution was warmed to −3 °C over 2 h, recooled to −78 °C, quenched with carbon dioxide gas, and warmed to 25 °C. General work-up [(C) trifluoroacetic acid (1.4 g), dichloromethane] and chromatography on Kieselgel H (20 g) [eluant: dichloromethane–diethyl ether (1 : 0—19 : 1)] gave slightly impure 2-methylenehex-5-enoic (48) (270 mg, <68%) as an oil; $\nu_{max.}$ 3 500—2 400br (OH), 1 700s (CO_2H), 1 633m (C=C), 950m (CH_2=C), and 915m cm^{-1} (CH_2=CH); δ_H 2.10—2.60 (4 H, m, 3-, 4-CH_2), 4.95—5.25 (2 H, m, 6-CH), 5.65—6.15 (1 H, m, 5-CH), 5.75 (1 H, t, *J* 1 Hz, 2-C=CH_2), 6.43 (1 H, t, *J* 1 Hz, 2-C=CH_2), and 11.60 (1 H, br, OH); *m/e* 126 ($M^{+\cdot}$), 111 (M^+ − Me), 108 ($M^{+\cdot}$ − H_2O), and 81 (M^+ − CO_2H, base). The acid (48) was dissolved in water (20 ml) and dichloromethane (20 ml). Sodium hydrogencarbonate (180 mg) was added and the mixture was stirred for 15 min. A solution of iodine (544 mg) in saturated potassium iodide (10 ml) was added as drops for 30 min and the mixture was then stirred for 1 h. General work-up [(A) sodium thiosulphate solution, dichloromethane] and chromatography on Kieselgel H (21 g) [eluant: dichloromethane] gave the *iodo-lactone* (49a) (396 mg, 50%) as an oil; $\nu_{max.}$ 1 728s (C=O), 1 625m (C=C), 1 378m, 1 297s, 1 228m, 1 210m, 1 155 and 1 140s (C–O), 1 075m, 1 043m, 1 020m, 1 010m, 950m (CH_2=), 933m, and 804m cm^{-1}; δ_H 1.54—2.55 (2 H, m, 5-CH_2), 2.60—3.00 (2 H, m, 4-CH_2), 3.46 (2 H, d, *J* 5 Hz, CH_2I), 4.28—4.60 (1 H, m, 6-CH), 5.72 (1 H, q, *J* 1.5 Hz, CH_2=), and 6.47 (1 H, q, *J* 1.5 Hz, CH_2=); *m/e* 252 (M^+), 125 (M^+ − I, base), 111 (M^+ − ICH_2), 97, 83, 55, 43, and 41 (Found: C, 33.5; H, 3.8. $C_7H_9IO_2$ requires C, 33.35; H, 3.6%).

Preparation of 3,6-*Dimethylenetetrahydropyran*-2-*one* (50a).—The iodo-lactone (49a) (169 mg) was dissolved in benzene (4 ml) and DBU (0.15 ml) was added to it; the solution was then heated to 74 °C for 2.75 h after which it cooled to 25 °C. General work-up [(B) diethyl ether] and p.l.c. [one development with dichloromethane] gave the *dimethylene-lactone* (50a) (53 mg, 64%) as an oily solid; $\nu_{max.}$ 1 740s (C=O), 1 660s (CH=C–O), 1 635m (C=C), 1 440m, 1 325m, 1 296s, 1 265m, 1 135s (C–O), 990m, 946 (CH_2=), 850m, and 800m cm^{-1}; δ_H 2.62 (4 H, br s, 4-, 5-CH_2), 4.38 (1 H, br s, 6-C=CH_2), 4.72 (1 H, t, *J* 1 Hz, 6-C=CH_2),

5.72 (1 H, t, *J* Hz, 3-C=CH_2), and 6.54 (1 H, t, *J* 1 Hz, 3-C=CH_2); *m/e* 124 ($M^{+\cdot}$), 96, 95, 86, 84 (base), and 39 (Found: C, 67.5; H, 6.55. $C_7H_8O_2$ requires C, 67.75; H, 6.5%).

Preparation of Hept-6-en-3-one 2,4,6-*Tri-isopropylbenzenesulphonylhydrazone* (51a).—The butanone trisylhydrazone (6b) (971 mg) was dissolved in DME (5 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.31M; 5.0 ml) was added and the resultant golden solution was warmed to −66 °C over 20 min and recooled to −78 °C. Allyl bromide (0.40 ml) was added to give a cloudy solution which was warmed to −65 °C over 40 min, stirred for 20min, quenched with glacial acetic acid (0.50 ml) in water (2 ml). and warmed to 25 °C. General work-up [(A) diethyl ether] and recrystallisation from ethanol and water gave an inseparable mixture of the (E)- *and* (Z)-*sulphonylhydrazones* (51a) (major) and the (E)- *and* (Z)-3-*methylhex-5-en-2-one* 2,4,6-*tri-isopropylbenzenesulphonylhydrazones* (51b) (minor) (810 mg, 75%) homogeneous on t.l.c., m.p. 78—82 °C; $\nu_{max.}$ 3 270m (NH), 1 603m (C=C), 1 328m (SO_2–N), 1 163s and 1 154s (SO_2–N), 1 305m, 942m, 907m (CH_2=CH), 882m, and 665s cm^{-1}; δ_H (51a) 1.05 (3 H, *ca.* t, *J* 8 Hz, 1-*Me*), 1.26 (18 H, overlapping d, *J* 7 Hz, CH*Me*$_2$), 1.95—2.40 (6 H, m, 2-, 4-, 5-CH_2), 2.95 (1 H, overlapping septets, *J* 7 Hz, *p*-C*H*Me$_2$), 4.30 (2 H, overlapping septets, *J* 7 Hz, *o*-C*H*Me$_2$), 4.70—5.25 (2 H, m, 7-CH_2), 5.40—5.95 (1 H, m, 6-CH), and 7.15 (2 H, s, aryl-H); *m/e* 394 ($M^{+\cdot}$), 267 (base), 189, 161, 55, and 43. Recrystallisation from methanol and water gave material with m.p. 87—95 °C (Found: C, 67.35; H, 9.5; N, 7.1. $C_{22}H_{36}N_2O_2S$ requires C, 67.3; H, 9.25; N, 7.15%).

Preparation of 3-*Ethylidene*-6-*iodomethyltetrahydrofuran*-2-*one* (49b).—A mixture of the sulphonylhydrazones (51a) (major) and (51b) (minor) (693 mg), m.p. 78—82 °C, was dissolved in DME (6 ml) and the solution was cooled to −78 °C. n-Butyl-lithium (1.31M; 4.3 ml) was added and the resultant brown-red solution was warmed to −70 °C over 45 min; it was then warmed to −4 °C over 2 h, recooled to −78 °C, quenched with carbon dioxide gas, and warmed to 25 °C. General work-up [(C) dichloromethane, trifluoroacetic acid (0.70 g)] and chromatography on Kieselgel H (19 g) [eluant: dichloromethane–diethyl ether (1 : 0—19 : 1)] gave crude 2-ethylidenehex-5-enoic acid (202 mg); $\nu_{max.}$ 1 690s (CO_2H), 1 645m (C=C), and 910s cm^{-1} (CH_2=). Sodium hydrogencarbonate (132 mg) and water (14 ml) were added and the solution was stirred for 10 min. Dichloromethane (20 ml) was added and a solution of iodine (367 mg) in saturated potassium iodide (10 ml) was added as drops for 25 min. The solution was stirred for 1 h and treated with solid sodium thiosulphate until colourless. General work-up [(B) diethyl ether], chromatography on Kieselgel H (18 g) [eluant: dichloromethane], and p.l.c. [one development with dichloromethane] gave the *iodo-lactone* (49b) (182 mg, 39%) as an oil; $\nu_{max.}$ 1 720s (C=O), 1 640s (C=C) 1 385m, 1 320m, 1 262s (C–O), 1 232m, 1 200m, 1 150s (C–O), 1 090m, 1 065m, 1 050m, 965m, and 726m cm^{-1}; δ_H 1.50—1.70 (4 H, m, 4-, 5-CH_2), 1.83 (3 H, dt, *J* 7, 1 Hz, Me), 3.34—3.70 (2 H, m, CH_2I), 4.14—4.47 (1 H, m, 6-CH), and 7.06 (1 H, qt, *J* 7, 2 Hz, HC=); *m/e* 266 ($M^{+\cdot}$), 139 (M^+ − I), 125 (M^+ − CH_2I, base), 97, and 53 (Found: C, 36.4; H, 4.3. $C_8H_{11}IO_2$ requires C, 36.1; H, 4.15%) and 6-*iodomethyl*-4-*methyl*-3-*methylenetetrahydropyran*-2-*one* (49c) (28 mg, 6%) as an oil; $\nu_{max.}$ 2 958m, 1 723s (C=O), 1 618m (C=C), 1 400m, 1 376m, 1 292m, 1 253s, 1 148s, 1 110m, 1 033m, 950m (CH_2=), and 800m cm^{-1}; δ_H 1.28 (3 H, d, *J* 7 Hz, 4-Me), 1.30—3.60 (3 H, m, 4-CH, 5-CH_2), 3.30—3.35 (2 H, m, CH_2I), 4.15—4.75 (1 H, m, 6-CH), 5.65—5.85 (1 H, m, CH_2=), and 6.50—6.70 (1 H, m, =CH_2); *m/e* 266 ($M^{+\cdot}$), 139 (M^+ − I, base) 125 (M^+ − CH_2I), 97, 67, and 53 (Found: C, 36.25; H, 4.35. $C_8H_{11}IO_2$ requires C, 36.1; H, 4.15%).

Preparation of (E)-3-*Ethylidene*-6-*methylenetetrahydropyran*-2-*one* (50b).—The methylene-lactone (49b) (104 mg) was dissolved in benzene (4 ml) and DBU (0.07 ml); the solution was heated to 80 °C for 3 h and cooled to 25 °C. General work-up [(B) diethyl ether], chromatography on Kieselgel H (11 g) [eluant: dichloromethane], and p.l.c. [one development with dichloromethane] gave the (E)-*dimethylene-lactone* (50b) (38 mg, 71%) as an oil; $\nu_{max.}$ 1 740s (C=O), 1 670s (C=C–O), 1 645s (C=C), 1440m, 1 326m, 1 315m, 1 277m, 1 250s, 1 174s, 1 158s, 1 140s (C–O), 1 062m, 1 020m, 968m, and 736m cm^{-1}; δ_H 1.86 (3 H, d, *J* 7 Hz, Me), 2.55 (4 H, br s, 4-, 5-CH_2), 4.37 (1 H, br s, CH_2=), 4.70 (1 H, d, *J* 1.5 Hz, CH_2=), and 7.10 (1 H, q, *J* 7 Hz, 3-C=CH); *m/e* 138 ($M^{+\cdot}$, base), 96, 95, 68, and 67 (Found: C, 69.6; H, 7.65. $C_8H_{10}O_2$ requires C, 69.55; H, 7.3%).

We thank the S.R.C. for support and Professor C. W. Rees for advice on the technique of flash-vacuum pyrolysis.

1/559 *Received*, 8*th April*, 1981]

REFERENCES

[1] For example, see: R. D. Clark and C. H. Heathcock, *Tetrahedron Lett.*, 1974, 1713; P. A. Grieco, Y. Ohfune, and G. Majetich, *J. Am. Chem. Soc.*, 1977, **99**, 7393; P. A. Grieco, M. Nishizawa, T. Oguri, S. D. Burke, and N. Marinovic, *ibid.*, p. 5773; S. Danishefsky, P. F. Schuda, T. Kitahara, and S. J. Etheredge, *ibid.*, p. 6066; G. R. Kieczykowski and R. H. Schlessinger, *ibid.*, 1978, **100**, 1938; M. Isobe, H. Iio, T. Kawai, and T. Goto, *ibid.*, p. 1940; P. A. Grieco, J. A. Noguez, and Y. Masaki, *J. Org. Chem.*, 1977, **42**, 495; P. A. Grieco and M. Nishizawa, *ibid.*, p. 1717; A. E. Greene, J-C. Muller, and G. Ourisson, *ibid.*, 1974, **39**, 186; F. Zutterman, H. DeWilde, R. Mijngheer, P. DeClercq, and M. Vanderwalle, *Tetrahedron*, 1979, **35**, 2389.

[2] For example, see: P. A. Grieco, *Synthesis*, 1975, 67; N. Petragnani and H. M. C. Ferraz, *ibid.*, 1978, 476; A. Hassner, H. W. Pinnick, and J. M. Ansell, *J. Org. Chem.*, 1978, **43**, 1774, S. Torii, T. Okamoto, and T. Oida, *ibid.*, p. 2294; R. M. Carlson and A. R. Oyler, *ibid.*, 1976, **41**, 4065; J. R. Norton, K. E. Shenton, and J. Schwartz, *Tetrahedron Lett.*, 1975, 51; R. M. Carlson, *ibid.*, 1978, 111; T. F. Murray, V. Varma, and J. R. Norton, *J. Chem. Soc., Chem. Commun.*, 1976, 907; M. F. Semmelhack and E. S. C. Wu, *J. Am. Chem. Soc.*, 1976, **98**, 3384; C. P. Casey and W. R. Brunsvold, *J. Organomet. Chem.*, 1975, **102**, 175.

[3] R. H. Shapiro, *Org. React.*, 1975, **23**, 405.

[4] R. H. Shapiro, M. F. Lipton, K. J. Kolonko, R. L. Buswell, and L. A. Capuano, *Tetrahedron Lett.*, 1975, 1811.

[5] J. E. Stemke and F. T. Bond, *Tetrahedron Lett.*, 1975, 1815.

[6] J. E. Stemke, A. R. Chamberlin, and F. T. Bond, *Tetrahedron Lett.*, 1976, 2947.

[7] L. A. Paquette, W. E. Fristad, D. S. Dime, and T. R. Bailey, *J. Org. Chem.*, 1980, **45**, 3017.

[8] M. F. Lipton and R. H. Shapiro, *J. Org. Chem.*, 1978, **43**, 1409.

[9] A. R. Chamberlin and F. T. Bond, *Synthesis*, 1979, 44; A. R. Chamberlin, J. E. Stemke, and F. T. Bond, *J. Org. Chem.*, 1978, **43**, 147.

[10] T. Mimura and T. Nakai, *Chem. Lett.*, 1980, 931; T. Nakai and T. Mimura, *Tetrahedron Lett.*, 1979, 531.

[11] D. M. Orere and C. B. Reese, *J. Chem. Soc., Chem. Commun.*, 1977, 280.

[12] J. Jiricny, D. M. Orere, and C. B. Reese, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1487.

[13] R. M. Adlington and A. G. M. Barrett, *J. Chem. Soc., Chem. Commun.*, 1978, 1071; 1979, 1122.

[14] W. G. Dauben, G. T. Rivers, and W. T. Zimmerman, *J. Am. Chem. Soc.*, 1977, **99**. 3414.

[15] E. Öhler, K. Reininger, and U. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 457.

[16] R. M. Adams and C. A. Vanderwelf, *J. Am. Chem. Soc.*, 1950, **72**, 4386.
[17] R. Barker and H. G. Fletcher, *J. Org. Chem.*, 1961, **26**, 4605, and references therein.
[18] W. Timpse, K. Dax, N. Wolf, and H. Weidmann, *Carbohydr. Res.*, 1975, **39**, 53.
[19] R. M. Adlington and A. G. M. Barrett, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1076.
[20] J. C. Martinez, V. M. Yoshida, and O. R. Gottlieb, *Tetrahedron Lett.*, 1979, 1021, and references therein.
[21] P. K. Freeman, D. M. Balls, and D. J. Brown, *J. Org. Chem.*, 1968, **33**, 2211, and reference therein.
[22] H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, 1975, **97**, 7442.
[23] D. J. Anderson, D. C. Horwell, E. Stanton, T. G. Gilchrist, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1317.
[24] J. Haslouin and F. Rouessac, *Tetrahedron Lett.*, 1976, 4651.
[25] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, ' Purification of Laboratory Chemicals,' Pergamon Press, London, 1966.
[26] W. C. Still, M. Kahn, and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.
[27] C. Grundmann and J. M. Dean, *J. Org. Chem.*, 1965, **30**, 2809.
[28] S. Torii, T. Oida, and T. Okamoto, *Japan Kokai Tokyo Koho*, 78 108964 (*Chem. Abstr.*, 1979, **90**, 87243m).
[29] Y. Hirose, K. Ishikawa, N. Iida, Y. Nakazawa, T. Toyama, H. Tachibana, Y. Enomoto, Y. Funakoshi, and T. Fujita, *Japan Kokai Tokyo Koho*, 79 84564 (*Chem. Abstr.*, 1979, **91**, 174843w).
[30] S. Huneck, K. Schrieber, C. Schulze, and G. Sembdner, Ger. Dem. Rep. P., 112884 (*Chem. Abstr.*, 1976, **84**, 116942x).
[31] K. Toyoshima, T. Okuyama, and T. Fueno, *J. Org. Chem.*, 1978, **43**, 2789; Badische Anilin-und Soda Fabrik Akt.-Ges., *Ger. p.*, 9600095 (*Chem. Abstr.*, 1958, **52**, 16296i).
[32] F. C. McIntire and E. P. Painter, *J. Am. Chem. Soc.*, 1947, **69**, 1834; R. Baudat and M. Petrzilka, *Helv. Chim. Acta.*, 1979, **62**, 1406.
[33] Heilbron's ' Dictionary of Organic Compounds,' Eyre and Spottiswoode Ltd., London, 1965, 4th Edn.
[34] W. H. H. Gunther, *J. Org. Chem.*, 1966, **31**, 1202.