Synthesis and Some Reactions of 2-Imino-2,5-dihydro-1,3,4-thiadiazoles. Formation of β-Lactams

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The title compounds, 2-imino-2,5-dihydro-1,3,4-thiadiazoles (2a—c), were prepared by oxidation of thiosemicarbazones. The reactions of (2a—c) with ketenes gave the spiro-β-lactams (7a—d), *via* [2 + 2] cycloaddition. On the other hand, the reaction of (2a) with phenyl isocyanate gave the thiohydantoins (9) and (10). The reactions of compound (2) with some other nucleophiles are also described.

Thiadiazolines (dihydrothiadiazoles) and oxadiazolines (dihydro-oxadiazoles) are useful reagents for carbon–carbon bond formation,[1-4] and for synthesis of other types of heterocycles.[5-7] In our preliminary study[8] we demonstrated a synthesis and some reactions of the dihydrothiadiazoles (2a—c) with ketenes. In this paper we will describe in l the reactions of the dihydrothiadiazoles (2a—c) with ν s nucleophiles.

Synthesis of 2,5-Dihydro-1,3,4-thiadiazoles (2a—c).—2-Phenylimino-2,5-dihydro-1,3,4-thiadiazoles (2a—c) were prepared in good yield by a modified procedure for the synthesis of thiadiazoles[9] by oxidation of thiosemicarbazones (1a—c) with iron(III) chloride in benzene–water at room temperature (Table 1). Characterization of the thiadiazoles (2a—c) was by spectral data and elemental analysis. In particular, the ^{13}C n.m.r. spectra contain singlets at δ_C 106.88 and 174.32 p.p.m. which were assignable to the quaternary and imino carbon, respectively.

Thiadiazoles (2a—c) were also obtained from an oxidation of the thiosemicarbazones (1a—c) by Collins reagent in pyridine, but the yields were not so good (Table 1).

Reactions with Nucleophiles.—Treatment of thiadiazoles (2a—c) with methylmagnesium iodide in diethyl ether at room temperature gave 3-methylated-2,3-dihydrothiadiazoles (3a—c), and not the 5-methylated isomers, suggesting that compound (3) may arise *via* conjugate addition of the Grignard reagent.

Furthermore, reduction of compound (2a) with sodium borohydride in ethanol at room temperature gave a ring-opened product, the thiosemicarbazide (4), in 89% yield, presumably *via* the intermediate (5). The structure of (4) was determined by spectral data as well as by comparison with a sample prepared from the reduction of (1a) with sodium borohydride.

Cycloadditions with Heterocumulenes.—Kellogg and Prins reported that 2,2,5,5-tetra-alkyl-2,5-dihydro-1,3,4-thiadiazoles reacted with various dipolarophiles to give thiophenes along with chelatropic elimination of nitrogen.[4] However, compound (2a) proved to be relatively inert to dipolarophiles, the thiadiazole (2a) being recovered largely unchanged after being refluxed for 5 h in tetrahydrofuran (THF) with dimethyl acetylenedicarboxylate.

On the other hand, compounds (2a—c) reacted smoothly with diphenylketene (6a) in boiling benzene to give 1-thia-4-azaspiro[2.3]hexan-5-ones (7a—c) in excellent yield. Using chloroketone (6b), generated *in situ* from chloroacetyl chloride and triethylamine at −70 °C, instead of compound (6a), the corresponding β-lactam (7d) was obtained in 54% yield (Table 2). These products would be formed *via* [2 + 2] cycloaddition followed by elimination of nitrogen gas.

Structural assignment of compounds (7a—d) was based on satisfactory elemental analyses and i.r., ^1H n.m.r., ^{13}C n.m.r., and mass spectra as well as chemical properties. The i.r. spectrum of (7a), for example, showed a strong absorption at 1 750 cm^{-1} (C=O) and its ^{13}C n.m.r. spectrum contained four singlets at δ_C 168.8, 72.3, 86.8, and 46.8 p.p.m. which are assigned to carbonyl (C-5), C-6, C-3 (spiro), and C-2 carbon atoms, respectively. The mass-spectral fragmentation pattern of (7a) (*m/z* 371, 331, 252, 194, 119, and 74) is also in agreement with the proposed structure.

Furthermore, desulphurization of compounds (7a—c) by Raney-Ni W-2 in boiling ethanol afforded 4-alkylidene β-lactams (8a—c) in excellent yield. In the i.r. spectrum of the isopropylidene lactam (8a), two strong absorptions were observed at 1 780 (C=O) and 1 695 (C=C) cm^{-1} which are comparable to those of 3-methylenecyclobutanone (1 790 cm^{-1} for C=O and 1 675 cm^{-1} for C=C).[7]

The mass spectrum of (8a) exhibited a molecular ion at *m/z* 339.1644 ($C_{24}H_{21}NO$ requires *M*, 339.1627) with principal fragments at *m/z* 311 ($M^+ - CO$), 220, and 145; its ^{13}C n.m.r.

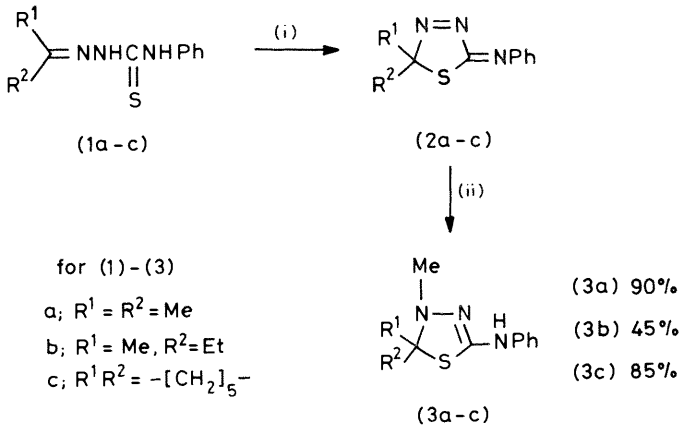
Table 1. 5-Phenylimino-2,5-dihydro-1,3,4-thiadiazoles (2a—c)

Product	Catalyst	Yield [a] (%)	M.p. (°C) [b]	$\nu_{max.}$ (cm^{-1}) C=N	$\nu_{max.}$ (cm^{-1}) N=N	δ_H [c] R¹	δ_H [c] R²	($M^+ - N_2$)
(2a)	$FeCl_3$	90	100—100.5	1 640	1 535	1.80 (s)	1.80 (s)	177
	CrO_3–py [d]	54						
(2b)	$FeCl_3$	85	47.5—49	1 620	1 530	1.84 (s)	1.85 (t), 2.13 (q)	191
	CrO_3–py	45						
(2c)	$FeCl_3$	88	76.5—78	1 630	1 530	0.92—2.76 (m)		217
	CrO_3–py	69						

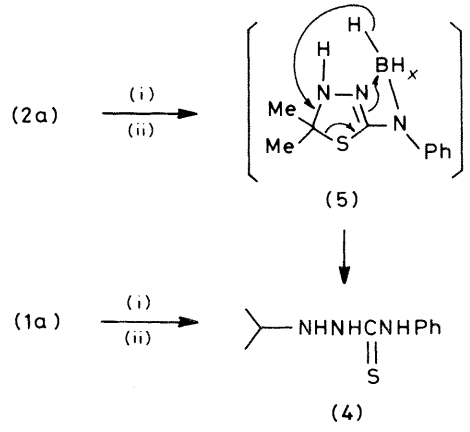
[a] Based on hydrazones. [b] Not corrected. [c] In $CDCl_3$. [d] Py is pyridine.

Table 2. 4-Phenyl-1-thia-4-azaspiro[2.3]hexan-5-ones (7a—d)

Product	R^1	R^2	R^3	R^4	Yield (%)	M.p. (°C)	δ_H R^1	δ_H R^2	δ_H R^3	δ_H R^4	$\nu_{max.}$ (cm^{-1}) C=O	m/z (M^+)
(7a)	CH_3	CH_3	C_6H_5	C_6H_5	100	157—158	1.25	1.50	7.05—7.90		1 750	371
(7b)	CH_3	C_2H_5	C_6H_5	C_6H_5	71	184—187	1.49	0.67—1.70	7.05—7.90		1 760	385
(7c)	$-[CH_2]_5-$		C_6H_5	C_6H_5	100	197.5—199.5	0.70—2.05		7.05—7.90		1 755	411
(7d)	CH_3	CH_3	H	Cl	54	114.5—115.5	1.53	1.65	5.10	—	1 770	253



Reagents and conditions: (i) $FeCl_3 \cdot 6H_2O$, C_6H_6–H_2O, room temperature, 24—68 h; (ii) MeMgI, then water



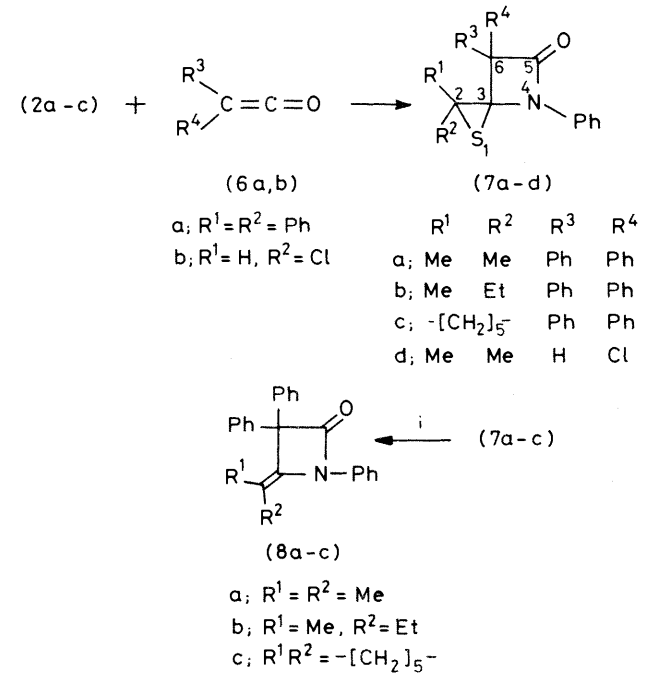
Reagents: (i) $NaBH_4$; (ii) AcOH

spectrum showed signals at δ_C 170.3 (C=O), 72.1 (sp^3 ring carbon), 134.9, and 104.6 p.p.m.

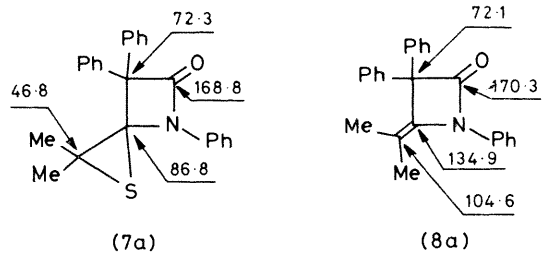
The isopropylidene β-lactam (8a) was also obtained in 66% yield when compound (7a) was refluxed in dimethylformamide.

$$(7a) \xrightarrow[\text{DMF, 2.5 h}]{\text{reflux in}} (8a)\ 66\% + S\ 58\% + (7a)\ 20\%$$

On the other hand, reaction of the dihydrothiadiazole (2a) with phenyl isocyanate proceeded differently from that with ketenes. When an equimolar mixture of (2a) and phenyl isocyanate was refluxed in benzene, two products were isolated; one was 5,5-dimethyl-1,3-diphenyl-2-thiohydantoin (9) [$\nu_{max.}$ 1 750 cm^{-1} (C=O)], and the other was the corresponding 4-thiohydantoin (10) [$\nu_{max.}$ 1 690 cm^{-1} (C=O)]. These carbonyl frequencies are comparable to those of hydantoins.[10]



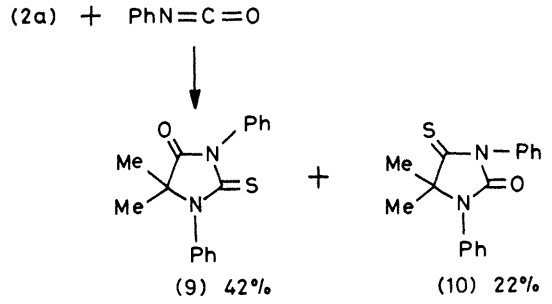
Reagents and conditions: i, Raney-nickel W-2, EtOH, reflux



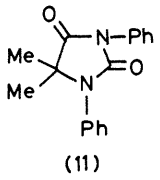
^{13}C N.m.r. chemical shifts (δ_C/p.p.m.) for selected carbon atoms of the spirolactam (7a) and the desulphurized product (8a)

Treatment of the 2-thiohydantoin (9) with hydrogen peroxide in boiling ethanol gave the hydantoin (11) in 89% yield [$\nu_{max.}$ 1 770 and 1 710 cm^{-1} (C=O)].

The proposed pathways for the formation of (9) and (10) is shown in the Scheme. The betaine (12) initially formed would rearrange to give intermediate (13) *via* elimination of nitrogen gas; this intermediate, following cyclization to the thiazolidinone (14) and rearrangement would give product (9) (Path A). Alternatively, the betaine (12) may cyclize to form the spirodiazetidinone (15); subsequent elimination of nitrogen



Conditions: Reflux in benzene



to give the spirothi-iranediazetidinone and ring expansion would then give the 4-thiohydantoin (10) (Path B).

Experimental

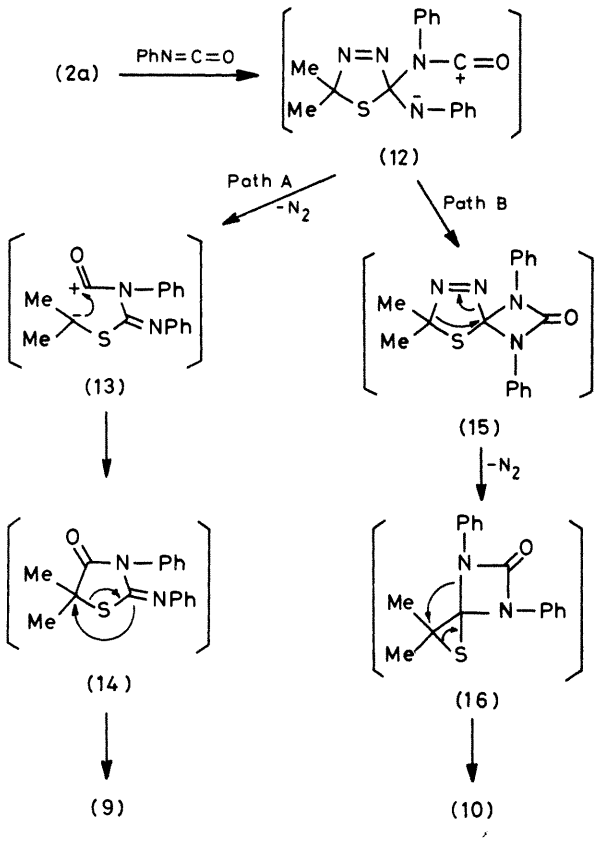
M.p.s were taken with a Mitamura capillary microapparatus. I.r. spectra were obtained using a JASCO IR-E spectrometer. ^{1}H N.m.r. spectra were recorded with a JEOL JNM-C-60HL spectrometer, and ^{13}C n.m.r. spectra with a JNM-FX90Q spectrometer using tetramethylsilane as internal reference. Mass spectra were obtained with a JEOL JMS-01SG-2 spectrometer on-line to a JEOL JEC-6 spectrum computer.

2,2-*Dimethyl*-5-*phenylimino*-2,5-*dihydro*-1,3,4-*thiadiazole* (2a).—(a) *Oxidation by iron*(III) *chloride*. Solutions of 1-isopropylidene-4-phenylthiosemicarbazide (1a) (10.72 g, 52 mmol) in benzene (400 ml) and iron(III) chloride (28.3 g, 105 mmol) in water (100 ml) was stirred together overnight at room temperature. The organic layer was separated and aqueous layer was extracted with benzene (100 ml). The combined organic phases was washed with saturated aqueous sodium chloride, dried (Na_2SO_4), and concentrated to give the *thiadiazole* (2a) (9.63 g, 90%), m.p. 100—100.5 °C (Found: C, 58.45; H, 5.4; N, 20.4; S, 15.5. $C_{10}H_{11}N_3S$ requires C, 58.53; H, 5.40; N, 20.48; S, 15.59%); δ($CDCl_3$) 1.80 (6 H, s, 2 × CH_3) and 6.95—7.50 (5 H, m, Ph). Physical and other spectral data are shown in Table 1.

Similarly prepared were 2-*ethyl*-2-*methyl*-5-*phenylimino*-2,5-*dihydro*-1,3,4-*thiadiazole* (2b) [from the thiosemicarbazone (1b) (13.5 g, 61 mmol) and iron(III) chloride (48.8 g, 181 mmol)] (11.3 g, 85%) (Found: C, 59.9; H, 5.95; N, 19.35. $C_{11}H_{13}N_3S$ requires C, 60.26; H, 5.98; N, 19.15%) and 2,2-*pentamethylene*-5-*phenylimino*-2,5-*dihydro*-1,3,4-*thiadiazole* (2c)* [from the thiosemicarbazone (1c) (14.78 g, 60 mmol) and iron(III) chloride (40.5 g, 150 mmol)] (12.89 g, 88%) (Found: C, 63.6; H, 6.05; N, 16.9; S, 13.05. $C_{13}H_{15}N_3S$ requires C, 63.66; H, 6.16; N, 17.13; S, 13.05%). M.p.s and spectroscopic data for (2b and c) are given in Table 1.

(b) *Oxidation by Collins reagent*. To a solution of pyridinium dichromate [prepared from chromic anhydride (4.2 g, 42 mmol) and anhydrous pyridine (70 ml)] was slowly added the thiosemicarbazone (1a) (5.8 g, 28 mmol) at 0 °C, and the mixture was stirred for 5 h at room temperature. Then the dark brown mixture was poured into ice–water (2 l) and insoluble materials were filtered off and air-dried. The solid collected was extracted with ethyl acetate, and the solvent was evaporated under reduced pressure to give the thiadiazole (2a) (3.1 g, 54%).

Similarly obtained was the thiadiazole (2b) [from chromic anhydride (4.8 g, 48 mmol) and the thiosemicarbazone (1b) (7.1 g, 32 mmol) in pyridine] (3.15 g, 45%).



Scheme.

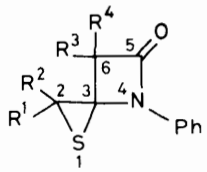
5-*Anilino*-2,2,3-*trimethyl*-2,3-*dihydro*-1,3,4-*thiadiazole* (3a).—To a solution of methylmagnesium iodide (15 mmol) [prepared from magnesium (0.375 g, 15 g-atom) and methyl iodide (2.45 g, 17.5 mmol)] in diethyl ether (90 ml) was added dropwise a solution of the thiadiazole (2a) (2.05 g, 10 mmol) in diethyl ether (50 ml) at room temperature under nitrogen and the mixture was stirred for 1 h at this temperature. Then, water (300 ml) was added, the organic layer was separated, and the aqueous layer was extracted with diethyl ether (100 ml × 2). The combined ethereal phases were washed with brine, dried (Na_2SO_4), and concentrated to give the *thiadiazole* (3a) (1.98 g, 90%), m.p. 158—158.5 °C; $\nu_{max.}$ 3 300 cm^{-1} (NH); δ($CDCl_3$) 1.38 (6 H, s, 2 × CH_3), 2.58 (3 H, s, CH_3), 6.90—7.60 (5 H, m, Ph), and 8.18 (1 H, s, NH); *m/z* 221 (M^+), 206 (Found: M^+, 221.0998. $C_{11}H_{15}N_3S$ requires *M*, 221.0988).

Similarly prepared were 5-*anilino*-2-*ethyl*-2,3-*dihydro*-1,3,4-*thiadiazole* (3b) [from (2b) (2.19 g, 10 mmol) and methylmagnesium iodide (15 mmol)] (1.05 g, 45%), m.p. 152—153 °C; $\nu_{max.}$ 3 140 cm^{-1} (NH); δ($CDCl_3$) 0.93 (3 H, t, CH_3CH_2), 1.31 (3 H, s, CH_3), 1.50—2.20 (2 H, m, CH_2), 2.60 (3 H, s, CH_3), 7.75 (5 H, m, Ph), and 8.93 (1 H, s, NH) (Found: M^+, 235.1127. $C_{12}H_{17}N_3S$ requires *M*, 235.1144) and 5-*anilino*-3-*methyl*-2,2-*pentamethylene*-2,3-*dihydro*-1,3,4-*thiadiazole* (3c)†

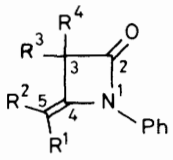
* 3-Phenylimino-4-thia-1,2-diazaspiro[4.5]dec-1-ene.

† 3-Anilino-1-methyl-4-thia-1,2-diazaspiro[4.5]dec-2-ene.

Table 3. Selected ^{13}C n.m.r. data (δ_C/p.p.m.) of β-lactams (7a—d) and (8a—c)



(7a - d)



(8a - c)

Compd.	C-2	C-3	C-4	C-5	C-6
(7a)	46.8	86.8	—	168.8	72.3
(7b)	53.6	87.6	—	169.0	72.4
(7c)	56.4	86.5	—	169.0	71.9
(7d)	46.1	81.2	—	162.0	62.1
(8a)	170.3	72.1	134.9	104.6	—
(8b)	170.2	72.3	135.0	110.0	—
(8c)	170.1	72.1	133.4	112.8	—

[from (2c) (2.45 g, 10 mmol) and methylmagnesium iodide (15 mmol)] (2.22 g, 85%), m.p. 158—158.5 °C; $\nu_{max.}$ 3 140 cm^{-1} (NH); δ($CDCl_3$) 0.45—2.35 (10 H, m, 5 × CH_2), 2.60 (3 H, s, CH_3), 6.85—7.55 (5 H, m, Ph), and 8.70 (1 H, s, NH) (Found: M^+, 261.1274. $C_{14}H_{19}N_3S$ requires M, 261.1330).

Reduction of Compound (2a) *by Sodium Borohydride.*—To a solution of $NaBH_4$ (0.38 g, 10 mmol) in THF (10 ml) was added dropwise a solution of compound (2a) (2.05 g, 10 mmol) in THF (30 ml) at room temperature. The mixture was stirred for 5 h at room temperature, then acetic acid (5 ml) was added and the solvent was evaporated off. To the residue was added saturated aqueous sodium hydrogencarbonate (300 ml) and the mixture was extracted with benzene (100 ml × 3). The combined extracts were dried (Na_2SO_4) and concentrated to give 1-*isopropyl*-4-*phenylthiosemicarbazide* (4) (1.85 g, 89%), m.p. 108—109 °C; $\nu_{max.}$ 3 200 cm^{-1} (NH); δ($CDCl_3$) 1.13 (6 H, d, 2 × CH_3), 2.8—3.48 (1 H, m, CH), 3.85 (1 H, d, NH), 7.09—7.84 (5 H, m, Ph), 7.93 (1 H, s, NH), and 9.34 (1 H, s, NH); *m/z* 209 (M^+) (Found: C, 57.15; H, 7.1; N, 20.15. $C_{10}H_{15}N_3S$ requires C, 57.40; H, 7.23; N, 20.08%).

The thiosemicarbazide (4) was also obtained from compound (1a) (2.07 g, 10 mmol) and $NaBH_4$ (0.38 g, 10 mmol) in THF in a similar manner as above (1.88 g, 88%).

2,2-*Dimethyl*-4,6,6-*triphenyl*-1-*thia*-4-*azaspiro*[2.3]*hexan*-5-*one* (7a).—A mixture of the thiadiazole (2a) (2.5 g, 12 mmol) and diphenylketene (6a) (2.4 g, 12 mmol) in benzene (50 ml) was refluxed for 3 h under nitrogen and then the solvent was removed under reduced pressure to give the *title compound* (7a) (4.5 g, 100%), m.p. 157—158 °C (Found: C, 77.75; H, 5.4; N, 3.75. $C_{24}H_{21}NOS$ requires C, 77.60; H, 5.70; N, 3.77%). Physical and spectral data are shown in Tables 2 and 3.

Similarly prepared were 2-*ethyl*-2-*methyl*-4,6,6-*triphenyl*-1-*thia*-4-*azaspiro*[2.3]*hexan*-5-*one* (7b) [from (2b) (2.19 g, 10 mmol) and diphenylketene (6a) (1.94 g, 10 mmol)] (2.9 g, 75%) (Found: C, 78.05; H, 5.85; N, 3.55. $C_{25}H_{23}NOS$ requires C, 77.90; H, 6.01; N, 3.63%) and 2,2-*pentamethylene*-4,6,6-*triphenyl*-1-*thia*-4-*azaspiro*[2.3]*hexan*-5-*one* (7c) * [from (2c) (2.45 g, 10 mmol) and (6a) (1.94 g, 10 mmol)] (4.3 g, 100%) (Found: C, 79.0; H, 6.0; N, 3.45. $C_{27}H_{25}NOS$ requires C, 78.81; H, 6.12; N, 3.40%).

* 1,3,3-Triphenyl-11-thia-1-azadispiro[3.0.5.1]undecan-2-one.

6-*Chloro*-2,2-*dimethyl*-4-*phenyl*-1-*thia*-4-*azaspiro*[2.3]-*hexan*-5-*one* (7d).—To a solution of compound (2a) (2.05 g, 10 mmol) and triethylamine (2.02 g, 20 mmol) in dry diethyl ether (100 ml) was slowly added dropwise a solution of chloroacetyl chloride (1.7 g, 15 mmol) in dry diethyl ether (20 ml) at −70 °C under nitrogen. After the mixture had been stirred for 1 h at this temperature, warmed to room temperature, and kept overnight, water (100 ml) was added to the mixture, the organic layer was separated, and the aqueous layer was extracted with diethyl ether (50 ml × 2). The combined ethereal phases were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure to give the *title compound* (7d) (1.37 g, 54%) (Found: C, 56.6; H, 4.55; N, 5.5. $C_{12}H_{12}ClNOS$ requires C, 56.80; H, 4.77; N, 5.52%).

4-*Isopropylidene*-1,3,3-*triphenylazetidin*-2-*one* (8a).—A mixture of the spiroazetidine (7a) (1.3 g, 3.5 mmol) and Raney-nickel W-2 (3.4 ml) in ethanol was refluxed for 1 h. After the mixture had cooled, insoluble materials were removed by filtration and the filtrate was concentrated under reduced pressure to give the *azetidinone* (8a) (1.15 g, 97%) (Found: M^+, 339.1644. $C_{24}H_{21}NO$ requires M, 339.1627). Physical and spectral data are given in Tables 3 and 4.

Similarly prepared were 4-*s-butylidene*-1,3,3-*triphenylazetidin*-2-*one* (8b) [from (7b) (2.0 g, 5.2 mmol) and Raney-nickel W-2 (5 ml)] (1.65 g, 90%) (Found: M^+, 353.1759. $C_{25}H_{23}NO$ requires M, 353.1783) and 4-*cyclohexylidene*-1,3,3-*triphenylazetidin*-2-*one* (8c) [from (7c) (2.0 g, 4.9 mmol) and Raney-nickel W-2 (5 ml)] (1.65 g, 89%) (Found: M^+, 379.1937. $C_{27}H_{25}NO$ requires M, 379.1940).

Thermolysis of the Spiroazetidine (7a).—A solution of compound (7a) (1 g, 2.7 mmol) in DMF (15 ml) was refluxed for 2.5 h and kept overnight at room temperature. A crystalline product (sulphur) (yellow needles; 0.05 g, 58%) was then filtered off and brine (100 ml) was added to the filtrate and the mixture was extracted with benzene (50 ml × 3). The combined extracts were dried, concentrated under reduced pressure, and the residue was triturated with diethyl ether to give starting material (7a) (0.2 g, 20% recovery). From the ethereal filtrate was obtained compound (8a) (0.6 g, 66%).

Reaction of Compound (2a) *with Phenyl Isocyanate.*—A mixture of compound (2a) (2.05 g, 10 mmol) and phenyl isocyanate (1.19 g, 10 mmol) in benzene (40 ml) was refluxed for 7.5 h. After the solvent had been removed under reduced pressure the residue was chromatographed on activated alumina with benzene as eluant to give 4,4-*dimethyl*-1,3-*diphenyl*-5-*thioxoimidazolidin*-2-*one* (10) (0.65 g, 22%) and 5,5-*dimethyl*-1,3-*diphenyl*-2-*thioxoimidazolidin*-4-*one* (9) (1.25 g, 42%). Compound (10) has m.p. 188—191 °C; $\nu_{max.}$ 1 690 cm^{-1} (C=O); δ($CDCl_3$) 1.75 (6 H, s, 2 × CH_3) and 7.0—7.8 (10 H, m, 2 × Ph); δ_C ($CDCl_3$) 27.52 (CH_3), 94.534 quaternary (C-4), 123.409—144.375 (aromatic carbons), 149.142 (C=O), and 206.513 p.p.m. (C=S); *m/z* 296 (M^+) (Found: C, 68.8; H, 5.3; N, 9.3. $C_{17}H_{16}N_2OS$ requires C, 68.90; H, 5.44; N, 9.45%). Compound (9) has m.p. 138—140 °C; $\nu_{max.}$ 1 750 cm^{-1} (C=O); δ($CDCl_3$) 1.62 (6 H, s, 2 × CH_3) and 7.20—7.60 (10 H, m, 2 × Ph); δ_C ($CDCl_3$) 28.116 (CH_3), 72.322 (quaternary C-5), 127.743—134.677 (aromatic carbons), 154.180 (C=O), and 208.842 p.p.m. (C=S); *m/z* 296 (M^+) (Found: C, 68.9; H, 5.4; N, 9.45%).

Oxidation of the 2-*Thiohydantoin* (9).—To a solution of the 2-thiohydantoin (9) (1.0 g, 3.4 mmol) in ethanol (60 ml) was added 30% aqueous hydrogen peroxide (30 ml) at room temperature, then the solution was refluxed for 1 h. After

Table 4. 4-Alkylidene-β-lactams (8a—c)

Product	R^1	R^2	Yield (%)	M.p. (°C)	δ_H R^1	δ_H R^2	$\nu_{max.}$ (cm^{-1}) C=O	$\nu_{max.}$ (cm^{-1}) C=C	*m/z* (M^+)
(8a)	CH_3	CH_3	97	105—106	1.55 (s)	1.55 (s)	1 780	1 695	339
(8b)	CH_3	C_2H_5	90	107—109	1.54 (s)	0.55 (t), 1.95 (q)	1 780	1 690	353
(8c)	$-[CH_2]_5-$		89	153—155	0.83—2.25 (m)		1 775	1 685	379

removal of ethanol, brine (100 ml) was added to the residue and the mixture was extracted with benzene. The extract was dried (Na_2SO_4) and concentrated under reduced pressure to give *5,5-dimethyl-1,3-diphenylimidazolidine-2,4-dione* (11) (0.85 g, 89%) m.p. 129.5—130.5 °C; $\nu_{max.}$ 1 770 and 1 710 (C=O) cm^{-1}; δ ($CDCl_3$) 1.53 (6 H, s, 2 × CH_3) and 7.3—7.7 (10 H, m, 2 × Ph); *m/z* 280 (M^+) (Found: C, 72.75; H, 5.8; N, 9.85. $C_{17}H_{16}N_2O_2$ requires C, 72.84; H, 5.75; N, 9.99%).

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