

Olefin Synthesis by Two-fold Extrusion Processes. Part I Preliminary Experiments

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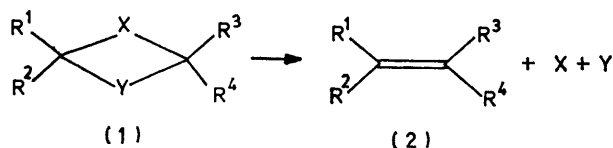
The principle of olefin synthesis by two-fold extrusion processes is enunciated. Seven possible systems have been examined, the two most promising involving the extrusion of carbon dioxide and sulphur and of nitrogen and sulphur. A novel system containing azo and lactone functions afforded nitrogen, keten, and ketone instead of nitrogen, carbon dioxide, and olefin.

CONVENTIONAL olefin-forming reactions are seriously affected by steric hindrance, and there is need for a general reaction which will afford highly hindered olefins in good yield from readily available reagents. The Wittig reaction has been widely used in the preparation of disubstituted olefins, but yields are lower in the case of trisubstituted olefins, and generally very low (often not reported) in the case of tetrasubstituted olefins. Elimination reactions have provided an im-

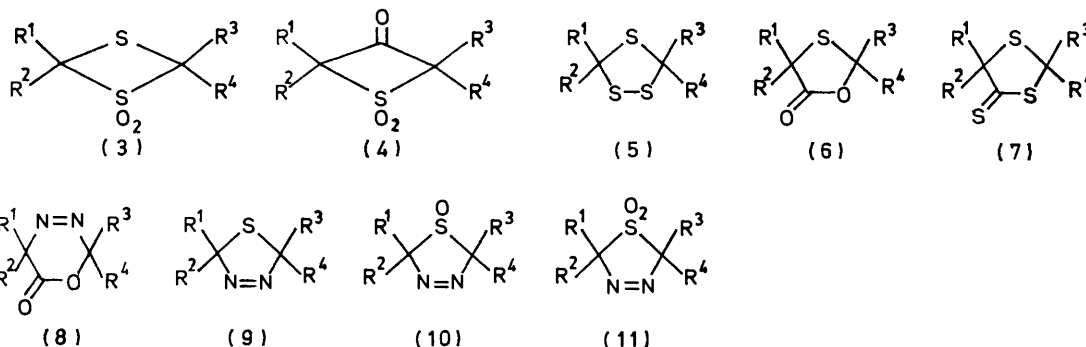
portant synthetic route to olefins, but intermediates become progressively less accessible with increasing

outlined¹ which should be particularly applicable to highly hindered olefins. In principle, the two-fold extrusion process [(1) → (2)], where R¹ *etc.* are alkyl, aralkyl, aryl *etc.* and X and Y are easily extrudable fragments, would enable highly hindered olefins to be synthesised, since both olefin bonds would be formed intramolecularly, and the nature of X and Y can be chosen to avoid problems of steric compression. A large number of systems might in principle undergo the two-fold extrusion process, and the choice of X, Y, and the terminal substituents R¹ *etc.* would be expected to govern the extrusion conditions. Amongst many other possible systems we have examined the series (3)–(11).

It is reported that the 1,3-dithietan 1,1-dioxide [(3); R¹ = R² = R³ = R⁴ = CF₃] extrudes sulphur dioxide at 600° to give a thiiran,² and that flash



become progressively less accessible with increasing



substitution. Nevertheless, they provide a useful route to otherwise inaccessible compounds, although yields are low.

Recently a new approach to olefin synthesis was

* D. H. R. Barton and B. J. Willis, *Chem. Comm.*, 1970, 1225; D. H. R. Barton, E. H. Smith, and B. J. Willis, *ibid.*, p. 1226.

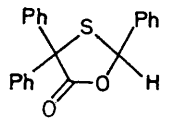
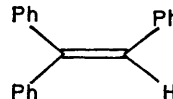
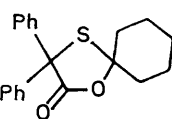
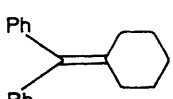
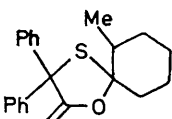
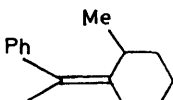
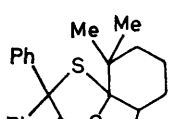

thermolysis of thietan-3-one 1,1-dioxides (4) at 930–950° yields olefins,³ but clearly neither system is likely to provide a useful olefin synthesis.

² W. J. Middleton, Abstracts XIXth I.U.P.A.C. Congress, 1963, A5–77; Du Pont, U.S.P. 3,136,781/1964.

³ C. L. McIntosh and P. de Mayo, *Chem. Comm.*, 1969, 32.

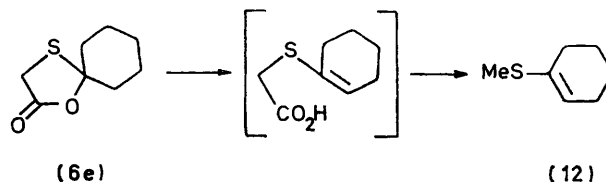
1,2,4-Trithiolans (5) are well known, and those derived from ketones are reported to be very stable.⁴ The readily available⁵ trithiolan (5; $R^1R^2 = R^3R^4 = [CH_2]_5$) was prepared, and found to resist attack by many trivalent phosphorus reagents [triethyl phosphite, triphenylphosphine, tris(diethylamino)phosphine], and although it was slowly desulphurised with tributylphosphine at 200° a complex and intractable mixture resulted.

The acid-catalysed condensation of thiobenzilic acid⁶ [$Ph_2C(SH) \cdot CO_2H$] with various carbonyl compounds gave the oxathiolan-5-ones (6a—d). Toluene-*p*-sulphonic acid, hydrogen chloride gas-glacial acetic acid,

Oxathiolan-5-one	Pyrolysis (T/°C; t/h)	Olefin formed	Yield (%)
	(6a) 150—160; 2		95
	(6b) 160—200; 5		82
	(6c) 215—225; 4		88
	(6d) 180—230; 4		80

and boron trifluoride gas were the three catalysts investigated. The n.m.r. spectra of compounds (6c) and (6d) indicated that each was a mixture of two isomers, which were not separated. Heating these

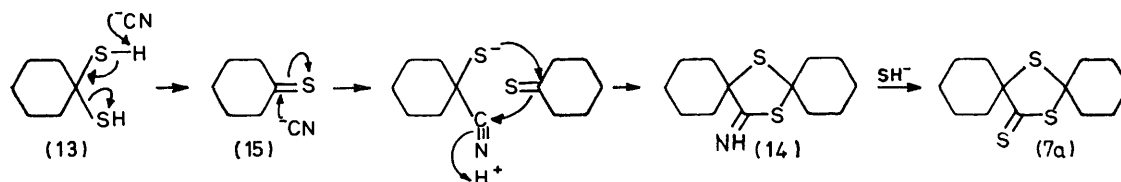
in the absence of trivalent phosphine gave a mixture containing diphenylmethylenecyclohexane, the corresponding thiiran, and triphenylmethane. It has previously been reported⁷ that pyrolysis of oxathiolan-5-ones derived from aliphatic carbonyl compounds and thiobenzilic acid affords complex mixtures containing up to ten components, which were not characterised.



Benzaldehyde derivatives gave thiirans, which afforded olefins (and sulphur) in relatively low yields. That compound (6a) expels carbon dioxide at a lower temperature than (6b), (6c), or (6d) is a result of the presence of the extra terminal phenyl group. Although this type of two-fold extrusion affords highly hindered olefins with ease, it is not applicable unless phenyl or other conjugating groups are present to facilitate the loss of carbon dioxide. Thus pyrolysis of compound (6e) at 220° in the presence of triphenylphosphine gave only 1-methylthiocyclohex-1-ene (12).

The 1,3-dithiolan-4-thione system (7) is new. Treatment of the readily available⁸ cyclohexane-1,1-dithiol (13) with potassium cyanide in dioxan-water gave two products, identified as the 1,3-dithiolan-4-imine (14) and the 1,3-dithiolan-4-thione (7a). The pink colour observed during the reaction is attributed to the thio-carbonyl compound (15). As expected the imine (14) was converted into the thione (7a) when treated with hydrogen sulphide. Heating compound (7a) with tris(diethylamino)phosphine did not give any bis-cyclohexylidene.

An apparently attractive olefin synthesis would result if X were (-N=N-) and Y were (-CO-O-) in (1), as in system (8). Now the more ready loss of nitrogen might be the expected first step of the two-fold extrusion process, followed by the expulsion of carbon dioxide to afford olefins. Condensation of cholestanone



oxathiolan-5-ones in the presence of tris(diethylamino)phosphine gave good yields of the corresponding olefins (see Table). Pyrolysis of compound (6b) at 210°

⁴ D. S. Breslow and H. Skolnik, 'Multi-sulfur and Sulfur and Oxygen Five- and Six-membered Heterocycles,' Interscience, New York, 1966, p. 70.

⁵ F. Asinger, M. Thiel, G. Lipfert, R. E. Plessmann, and J. Mennig, *Angew. Chem.*, 1958, **70**, 372; F. Asinger and M. Thiel, *ibid.*, p. 667; F. Asinger, M. Thiel, and G. Lipfert, *Annalen*, 1959, **627**, 195.

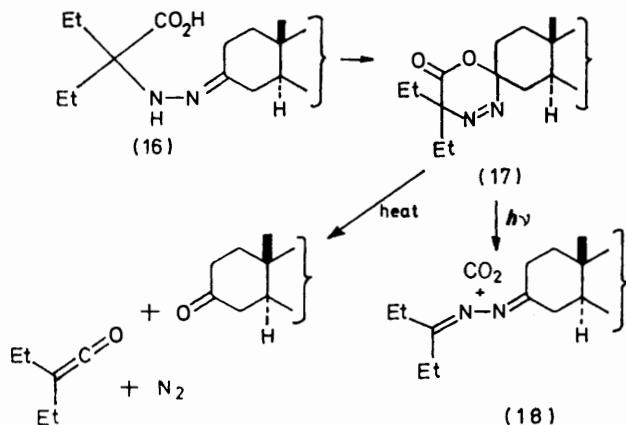
⁶ H. Becker and A. Bistrzycki, *Ber.*, 1914, **47**, 3149.

⁷ C. T. Pedersen, *Acta Chem. Scand.*, 1968, **22**, 247.

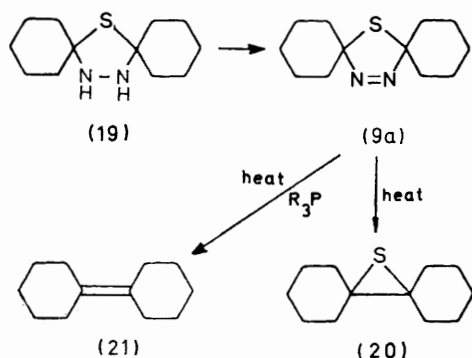
⁸ J. Jentzsch, J. Fabian, and R. Mayer, *Ber.*, 1962, **95**, 1764.

⁹ A. Carmi, G. Pollak, and H. Yellin, *J. Org. Chem.*, 1960, **25**, 44.

trapping with ethanol and with cyclohexylamine and by its i.r. spectrum) and cholestanone. There was no trace of the expected olefin. Photolysis of the azo-lactone in cyclohexane gave smoothly the mixed azine (18) and carbon dioxide.



One might expect the azo-sulphide system (9) to be susceptible to the two-fold extrusion process. Treatment of cyclohexanone with hydrazine hydrate and hydrogen sulphide affords¹⁰ the thiadiazolidine (19). The latter was oxidised with lead tetra-acetate or dichlorodicyanobenzoquinone (DDQ) to the azo-sulphide (9a). Heating this azo-sulphide at 100° gave the thiiran (20), whereas bis-cyclohexylidene (21) was formed in high yield when triphenylphosphine or tris(diethylamino)phosphine was also present. The thiadiazolidine (19) was also prepared by treating solutions of cyclohexanone azine with hydrogen sulphide. Quantitative yields of essentially pure thiadiazolidine were obtained when solutions of cyclohexanone azine were treated with hydrogen sulphide in a converted atmospheric hydrogenation apparatus. Photolysis of the azo-sulphide (9a) in cyclohexane gave cyclohexanone azine and sulphur, but no bis-cyclohexylidene.



Oxidation of the azo-sulphide (9a) with hydrogen peroxide in acetic acid gave the corresponding azo-

sulphoxide. Further oxidation of the latter with peracetic acid in dichloromethane gave the corresponding azo-sulphone. Pyrolysis of the azo-sulphoxide or azo-sulphone gave only poor yields of bis-cyclohexylidene (21). Photolysis of the azo-sulphoxide or azo-sulphone again afforded cyclohexanone azine, but no olefin.

While this work was in progress, the synthesis of the azo-sulphide (9a) and its conversion into bis-cyclohexylidene (21) was also reported by Kellogg and Wassenaar.^{11a} Kellogg and his colleagues have also reported an elegant synthesis of *cis*- and of *trans*-di-*t*-butylethylene based on analogous extrusion reactions.^{11b}

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were recorded with a Unicam SP 200 or a Perkin-Elmer 257 spectrometer and u.v. spectra with a Unicam SP 800B spectrometer. ¹H n.m.r. spectra were recorded with a Varian A60 or T60 instrument (tetramethylsilane as internal reference). Mass spectra were recorded with an A.E.I. MS9 or a Perkin-Elmer 270 machine.

The phrase 'worked-up in the usual way' implies repeated washing with saturated sodium hydrogen carbonate or 2% sodium carbonate solution followed by washing with water to neutrality, and drying. Organic solutions were dried over anhydrous sodium sulphate before evaporation of the solvent. Solids were dried *in vacuo*.

Silica gel MFC and alumina grade III were used for column chromatography. Unless otherwise stated 'light petroleum' refers to the fraction b.p. 40–60°.

2,4,4-Triphenyl-1,3-oxathiolan-5-one (6a).—Mercapto(diphenyl)acetic acid (3.00 g), toluene-*p*-sulphonic acid (0.42 g), and benzaldehyde (1.23 g) in benzene (50 ml) were heated under reflux for 5 h, with azeotropic removal of water and under nitrogen. Work-up in the usual way gave a white solid. Crystallisation from acetone-hexane, afforded the *oxathiolan-5-one* (94%), m.p. 96.5–97.5° (lit.,¹² 94–95°), ν_{\max} (hexachlorobutadiene) 1755 cm⁻¹.

Triphenylethylene.—2,4,4-Triphenyl-1,3-oxathiolan-5-one (1.50 g) and tris(diethylamino)phosphine (1.23 g) were heated at 150–160° under nitrogen for 2 h, by which time i.r. monitoring showed the reaction to be complete. Column chromatography (silica gel; benzene) gave *triphenylethylene* (95%), m.p. 67–68°. One crystallisation from methanol afforded rods, m.p. 70–71° (lit.,¹³ 68–69°).

4',4'-Diphenylcyclohexanespiro-2'-1',3'-oxathiolan-5'-one (6b).—This compound was prepared by the procedure described for 2,4,4-triphenyl-1,3-oxathiolan-5-one. Crystallisation from acetone-light petroleum afforded the *oxathiolan-5-one* as rhombs (83%), m.p. 82–83° (lit.,¹² 80–82°), ν_{\max} (hexachlorobutadiene) 1755 cm⁻¹.

Diphenylmethylenecyclohexane.—The spiro-oxathiolan (6b) (0.40 g) and tris(diethylamino)phosphine (0.35 g) were heated between 160 and 200° under nitrogen for 5 h. Chromatography gave *diphenylmethylenecyclohexane* (82%), m.p. 79–80°. Crystallisation from light petroleum afforded rhombs m.p. 83–83.5° (lit.,¹⁴ 83–83.5°).

¹² A. Romo de Vivar and J. Romo, *J. Org. Chem.*, 1959, **24**, 1490.

¹³ H. Adkins and W. Zartman, *Org. Synth.*, 1937, **17**, 89; Coll. Vol. 2, p. 606.

¹⁴ R. E. Lyle, N. B. Martin, and H. L. Fielding, *J. Amer. Chem. Soc.*, 1953, **75**, 4089.

¹⁰ K. Rühlmann, *J. prakt. Chem.*, 1959, **8**, 285.

¹¹ (a) R. M. Kellogg and S. Wassenaar, *Tetrahedron Letters*, 1970, 1987; (b) R. M. Kellogg, S. Wassenaar, and J. Buter, *Tetrahedron Letters*, 1970, 4689.

2-Methyl-4',4'-diphenylcyclohexanespiro-2'-1',3'-oxathiolan-5'-one (6c).—Dry hydrogen chloride was passed into a mixture of potassium mercapto(diphenyl)acetate (6.00 g), glacial acetic acid (12.0 ml), and 2-methylcyclohexanone (2.47 g) at 65–75° for 5 h. Ice-water was added and the organic products were extracted with diethyl ether. Work-up in the usual way gave an oil which was triturated with light petroleum. The solid was collected and dried (74%); m.p. 66.5–68.5°. Crystallisation from light petroleum afforded the mixture of two isomers as conglomerates, m.p. 70–71.5°, ν_{\max} (CHCl₃) 1750 cm⁻¹, τ (CDCl₃) 8.9 (3H, m), 8.3 (9H, m), and 2.5 (10H, m), m/e 338 (M^+) (Found: C, 74.4; H, 6.5; S, 9.4. Calc. for C₂₁H₂₂O₂S: C, 74.5; H, 6.55; S, 9.5%).

1-Diphenylmethylene-2-methylcyclohexane.—The spiro-oxathiolan (6c) (0.60 g) and tris(diethylamino)phosphine (0.48 g) were heated at 215–225° under nitrogen for 4 h. Chromatography gave the olefin (88%), m.p. 68–70°. Crystallisation from light petroleum afforded rods m.p. 73.5–74°, ν_{\max} (hexachlorobutadiene) 3080, 3060, 3025, 1600, 1490, 1445, and 755 cm⁻¹, λ_{\max} (EtOH) 243 nm (ϵ 13,300), τ (CCl₄) 8.8 (3H, d, J 15 Hz), 8.6–7.0 (9H, m), and 2.9 (10H, s), m/e 262 (M^+) (Found: C, 91.4; H, 8.3. C₂₀H₂₂ requires C, 91.55; H, 8.45%).

2,2,6-Trimethyl-4',4'-diphenylcyclohexanespiro-2'-1',3'-oxathiolan-5'-one (6d).—Boron trifluoride gas was passed into a solution of mercapto(diphenyl)acetic acid (644 mg) and 2,2,6-trimethylcyclohexanone (230 mg) in dry dichloromethane–hexane (ca. 10 ml) at 25°. Further quantities of acid (490 mg) were added after 2.5 h and again after 4 h. After 6 h excess of hexane was added and the passage of gas was discontinued shortly afterwards. The upper (colourless) layer was removed and dichloromethane–hexane was added to the red oily residue until it had dissolved. The passage of gas was continued and the process of precipitating the red oil and removing the upper layer was repeated after 1 h. The upper layers were combined and worked up in the usual way. Chromatography (silica gel; light petroleum–benzene, 1:1 v/v) afforded the mixture of two isomers as an oil (34%), ν_{\max} (CHCl₃) 1745 cm⁻¹, τ (CDCl₃) 9.0–7.5 (16H, m) and 2.7 (ca. 10H, m), m/e 366 (M^+). Preparative t.l.c. gave a sample of m.p. 23–26° (Found: C, 75.6; H, 7.4; S, 8.8. Calc. for C₂₃H₂₆SO₂: C, 75.4; H, 7.15; S, 8.7%).

1-Diphenylmethylene-2,2,6-trimethylcyclohexane.—The spiro-oxathiolan (6d) (302 mg) and tris(diethylamino)phosphine (302 mg) were heated at 210–230° under nitrogen for 4 h. Chromatography afforded the olefin as an oil (80%), ν_{\max} (film) 3080, 3060, 3025, 1600, 1495, 1445, and 760 cm⁻¹, λ_{\max} (EtOH) 242 nm (ϵ 12,100), τ (CDCl₃) 9.1 (3H, s), 8.9 (6H, s and superimposed d), 8.5 (6H, m), 7.7 (1H, m), and 2.9 (10H, s), m/e 290 (M^+) (Found: C, 90.9; H, 9.0. C₂₂H₂₆ requires C, 91.0; H, 9.0%).

Cyclohexanespiro-2'-1',3'-oxathiolan-5'-one (6e).—Thioglycolic acid (23.35 g), toluene-*p*-sulphonic acid (5.0 g), and cyclohexanone (24.75 g) in benzene (100 ml) were heated under reflux for 3 h, with azeotropic removal of water and under nitrogen. Work-up in the usual way and distillation under reduced pressure gave one main fraction which solidified (43%; one experiment only); b.p. 131–134° at 10 mmHg. Crystallisation from light petroleum gave a sample of m.p. 26.5–27°, ν_{\max} (CCl₄) 1780 cm⁻¹, τ (CDCl₃) 8.7–7.8 (10H, m) and 6.3 (2H, s) (Found: C, 55.6; H, 6.8; S, 18.7. C₈H₁₂O₂S requires C, 55.8; H, 7.0; S, 18.6%).

Pyrolysis of the Spiro-oxathiolan (6e) in the Presence of Triphenylphosphine.—The spiro-oxathiolan (4.30 g) and triphenylphosphine (9.79 g) were heated at 220° under nitrogen for 1.5 h. Distillation gave no methylenecyclohexane (b.p. 103° at 760 mmHg. Distillation under reduced pressure gave one main fraction, b.p. 89–91° at 30 mmHg (1.89 g), identified as 1-methylthiocyclohexene (12), n_D^{27} 1.5249, ν_{\max} (film) 3050 and 1635 cm⁻¹, τ (CDCl₃) 8.4 (4H, m), 7.8 (7H, m), and 4.6br (1H, s), m/e 128 (M^+) (lit.¹⁵ b.p. 75.5–77° at 16 mmHg, n_D^{20} 1.5252).

Cyclohexanespiro-2'-1',3'-dithiolan-4'-spirocyclohexan-5'-thione (7a) and the Corresponding 5'-Imine (14).—Potassium cyanide (2.60 g) in water (20 ml) and dioxan (10 ml) was added dropwise during 20 min to a stirred solution of cyclohexane-1,1-dithiol⁸ (5.92 g) in dioxan (5 ml) at 23°. Monitoring by t.l.c. (silica gel; benzene) indicated the formation of two products. After 6 h water was added and the organic products were extracted with chloroform. The combined extracts were washed with water and dried. Evaporation left an orange oil (5.32 g). Chromatography afforded the 1,3-dithiolan-5-thione as a solid (45%), which crystallised from light petroleum as orange plates, m.p. 53.5–54°, ν_{\max} (CCl₄) 1165, 1120, 1065, 1040, 970, and 885 cm⁻¹, λ_{\max} (cyclohexane) 321 nm (ϵ 10,700), m/e 272 (M^+) (Found: C, 57.4; H, 7.5; S, 35.35. C₁₃H₂₀S₃ requires C, 57.4; H, 7.4; S, 35.3%). The more polar 5-imine was obtained as a solid (52%), which crystallised from light petroleum as needles, m.p. 85.0–85.5°, ν_{\max} (CCl₄) 3400, 1600, 1230, 1070, 1020, 960, 910, and 900 cm⁻¹, λ_{\max} (cyclohexane) 225 nm (ϵ 3300), τ (CCl₄) ca. –4.0br (1H, s, exchanged with deuterium oxide), m/e 255 (M^+) (Found: C, 61.2; H, 8.3; N, 5.4; S, 25.2. C₁₃H₂₁NS₂ requires C, 61.1; H, 8.3; N, 5.5; S, 25.1%).

2-(Cholestan-3-ylidenehydrazino)-2-ethylbutyric Acid (16).—2-Ethyl-2-hydrazinobutyric acid⁹ (0.59 g), cholestanone (1.16 g), and absolute ethanol (20 ml) were heated at reflux under nitrogen for 6 h. The ethanol was evaporated off, dichloromethane was added, and the solution was washed with water to remove unchanged hydrazino-acid before drying. Evaporation afforded the hydrazone as a foam, which crystallised from light petroleum (yield 76%), m.p. 122–125°. A sample of m.p. 128–131° had $[\alpha]_D^{+31}$ (CHCl₃), ν_{\max} (CHCl₃) 1730 cm⁻¹, τ (CDCl₃) ca. –3.1br (2H, both exchanged with deuterium oxide), m/e 514 (M^+) (Found: C, 76.8; H, 11.2; N, 5.2. C₃₃H₅₈N₂O₂ requires C, 77.0; H, 11.4; N, 5.4%).

5',5'-Diethyl-5',6'-dihydrocholestan-3-spiro-2'-2H-1',3',4'-oxadiazin-6'-one (17).—Lead tetra-acetate (1.33 g) in dry dichloromethane (15 ml) was added dropwise during 10 min to 2-ethyl-2-(cholestan-3-ylidenehydrazino)butyric acid (1.55 g) in dichloromethane (80 ml) at –18° with stirring. After a further 4 min at this temperature, cold (0°) saturated sodium hydrogen carbonate solution (75 ml) was added, and the product was allowed to warm to 0°. Any solid present was removed by filtration through Celite. The organic layer was separated, washed once with ice-water, and dried at 0°. Evaporation of the solvent (0°) afforded an unstable solid (1.46 g). The azo-lactone was purified by gel-filtration (Sephadex LH20; tetrahydrofuran; u.v. monitoring) (yield 65%; m.p. 88–91°). A sample gave needles from chloroform–methanol, m.p. 95–96° (solution with evolution of gas), $[\alpha]_D^{+14}$ (tetrahydrofuran), ν_{\max} (CHCl₃) 1740 and 1590 cm⁻¹, λ_{\max} (tetra-

¹⁵ A. R. Katritzky, R. Mayer, J. Morgenstern, and M. J. Sewell, *J. Chem. Soc.*, 1965, 5953.

hydrofuran) 368 nm (ϵ 130) (Found: C, 77.5; H, 10.9; N, 5.3. $C_{33}H_{56}N_2O_2$ requires C, 77.3; H, 11.0; N, 5.5%).

Pyrolysis of the Spiro-oxadiazine (17).—The spiro-oxadiazine (31 mg) was heated at 105–110° for 50 min. Volatile diethylketen was flushed from the pyrolysis vessel by a stream of nitrogen and trapped in chloroform. The chloroform solution had ν_{\max} 2100 cm^{-1} . After addition of absolute ethanol (3 drops) the solution had ν_{\max} 1720 cm^{-1} . Ethyl 2-ethylbutyrate was prepared and shown to be identical with the ester from the trapping experiment. The pyrolysis residue was essentially pure cholestanone.

In a second experiment the azo-lactone (98 mg) was heated at 115° for 8 min and the diethylketen was trapped with an ethereal solution of cyclohexylamine. The amide precipitated as a white solid, which was collected and dried (29.5 mg). Crystallisation from ethyl acetate afforded long needles, m.p. 125.5–126.5° (sealed tube), identical with an authentic sample of *N*-cyclohexyl-2-ethylbutyramide. The pyrolysis residue (79 mg) was essentially pure cholestanone and contained no trace of the required olefin.

N-Cyclohexyl-2-ethylbutyramide.—2-Ethylbutyric acid (5.8 g) in tetrahydrofuran (50 ml) containing triethylamine (5.1 g) was cooled to 0°, and ethyl chloroformate (5.4 g) in tetrahydrofuran (10 ml) was added with stirring. After 20 min cyclohexylamine (5.3 g) in tetrahydrofuran (25 ml) was added and stirring was continued for 2 h at 0°, then for 12 h at 20°. The solid was removed by filtration. The solvent was evaporated from the mother liquor and the residue was dissolved in dichloromethane and worked up in the usual way to give a solid (8.4 g). Chromatography (silica gel; ethyl acetate–benzene, 1 : 3 v/v) afforded the pure *amide*, which crystallised from ethyl acetate as long needles m.p. 126–126.5° (sealed tube), ν_{\max} ($CHCl_3$) 3450, 1655, and 1520 cm^{-1} , m/e 197 (M^+) (Found: C, 72.8; H, 11.8; N, 7.0. $C_{12}H_{23}NO$ requires C, 73.0; H, 11.75; N, 7.1%).

Photolysis of the Spiro-oxadiazine (17).—The spiro-oxadiazine (48 mg) was photolysed in cyclohexane (15 ml) at 19° with a medium-pressure mercury arc lamp and Pyrex apparatus. The photolysis was monitored by observing the disappearance of the u.v. absorption band at 368 nm, and was complete in 1.5 h. The extrusion of carbon dioxide was illustrated by passing a slow stream of nitrogen through the apparatus and into lime-water. Evaporation of the cyclohexane and crystallisation of the residue from chloroform–ethyl acetate afforded the unsymmetrical azine (18) derived from cholestanone and pentan-3-one as conglomerates (43 mg), m.p. 210–212°, $[\alpha]_D + 58^\circ$ ($CHCl_3$), ν_{\max} ($CHCl_3$) 1635 cm^{-1} (Found: M^+ , 468.44238. Calc. for $C_{32}H_{56}N_2$: M , 468.44433). No ions were present in the mass spectrum at higher m/e . A mixed m.p. with symmetrical cholestanone azine showed a depression of 13°.

Cyclohexanone Azine.—Hydrazine hydrate (98%; 6.2 g) in ethanol (15 ml) was added dropwise during 20 min to cyclohexanone (25.0 g) in ethanol (60 ml) heated under gentle reflux. After 3 h the heating was discontinued and the solution was stored at 17° for 16 h. The solvent was evaporated off and the residue poured into water (150 ml). The azine was extracted with diethyl ether and the combined extracts were dried. Evaporation gave an oil which crystallised from light petroleum (74%); m.p. 32–32.5°.

Cyclohexanespiro-2'-1',3',4'-thiadiazolidine-5'-spirocyclohexane (19).—An atmospheric pressure hydrogenation apparatus, with facilities for shaking, was converted for use with hydrogen sulphide gas. Cyclohexanone azine (2.51 g) in acetone–benzene (1 : 1 v/v; 9.1 g) absorbed 537 ml of gas (at 17° and 767 mmHg) in 170 min (*cf.* 170 ml for a solvent only experiment). Evaporation afforded essentially pure *thiadiazolidine* (100%), m.p. 91–93°, which was used without further purification.

2',5'-Dihydrocyclohexanespiro-2'-1',3',4'-thiadiazine-5'-spirocyclohexane (9a) (With E. H. SMITH).—(a) Powdered calcium carbonate (6.0 g) was suspended in light petroleum (b.p. 60–80°; 100 ml) and lead tetra-acetate (6.0 g) was added. The suspension was stirred at 0° for 15 min. Compound (19) (2.0 g) in light petroleum (b.p. 60–80°; 100 ml) was added dropwise during 45 min at 0°. The reactants were allowed to warm to 18° and stirred for a further 1.5 h. The product was decomposed with saturated sodium hydrogen carbonate solution and any solid present was removed by filtration. Work-up in the usual way gave the *azo-sulphide* as an off-white solid (99%), m.p. 65–70°. Crystallisation from light petroleum afforded needles, m.p. 80–81° (sealed tube), ν_{\max} (KBr) 1575 cm^{-1} , λ_{\max} (EtOH) 325 and 286 nm (ϵ 225 and 330) (Found: C, 64.1; H, 8.8; N, 12.6; S, 14.5. $C_{13}H_{20}N_2S$ requires C, 64.2; H, 9.0; N, 12.5; S, 14.3%).

(b) 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.30 g) in diethyl ether (75 ml) was added dropwise during 35 min to compound (19) (0.25 g) in diethyl ether (10 ml) at 0° with stirring. After 30 min the solution was allowed to warm to 17° and stirred for a further 30 min. The product was washed several times with saturated sodium hydrogen sulphite, then with saturated sodium hydrogen carbonate solution, and finally with water, before drying. Evaporation afforded the *azo-sulphide* (91%), m.p. 76–79.5°.

Cyclohexanespiro-2'-thiiran-3'-spirocyclohexane (20) (With E. H. SMITH).—Compound (9a) (0.85 g) was heated at 110–115° for 1 h, after which evolution of gas had ceased. The residue solidified on cooling. Crystallisation from methanol afforded plates (76%), m.p. 72–74° (Found: C, 73.5; H, 10.3; S, 16.25. $C_{12}H_{20}S$ requires C, 73.5; H, 10.2; S, 16.3%).

Bis-cyclohexylidene (21) (With E. H. SMITH).—(a) Compound (9a) (1.22 g) and triphenylphosphine (1.58 g) were heated together at 100° for 2 h. Chromatography afforded bis-cyclohexylidene (75%), as a white solid, m.p. 53–54° (lit.,¹⁶ 54.5–55.5°).

(b) Similarly, tris(diethylamino)phosphine afforded bis-cyclohexylidene (77%), m.p. 53.5–54.5°.

(c) Bis-cyclohexylidene was obtained in an overall yield of 73% from cyclohexanone azine when the whole reaction sequence was repeated without purification of the intermediates.

Photolysis of Compound (9a).—Compound (9a) (354 mg) was photolysed in cyclohexane (60 ml) at 19° with a medium-pressure mercury arc lamp and under nitrogen. The photolysis was monitored by t.l.c. (alumina; benzene) and was complete in 24 h. A deposit of elemental sulphur was present inside the photolysis vessel. The solvent was evaporated off and the residue chromatographed. The major product was cyclohexanone azine (52%). The non-polar material contained some cyclohexanespiro-2'-thiiran-3'-spirocyclohexane, but no bis-cyclohexylidene.

¹⁶ S. D. Koch, R. M. Kliss, D. V. Lopicke, and R. J. Wineman, *J. Org. Chem.*, 1961, **26**, 3122.

2',5'-Dihydrocyclohexanespiro-2'-1',3',4'-thiadiazine-5'-spirocyclohexane 1'-Oxide.—Compound (9a) (9.60 g), glacial acetic acid (75 ml), dichloromethane (40 ml), and hydrogen peroxide (100 vols; 10.0 ml) were stirred together at 20° for 20 h, after which monitoring by t.l.c. (alumina; benzene-acetone, 50 : 1 v/v) indicated that the reaction was complete. Work-up in the usual way afforded the *azo-sulphoxide*, which crystallised from diethyl ether as long needles (94%), m.p. 146–147° (decomp.), ν_{\max} (Nujol) 1570 and 1040 cm^{-1} (Found: C, 60.0; H, 8.4; N, 11.7; S, 13.1. $\text{C}_{12}\text{H}_{20}\text{N}_2\text{OS}$ requires C, 60.0; H, 8.4; N, 11.7; S, 13.3%).

Pyrolysis of the Azo-sulphoxide.—The foregoing *azo-sulphoxide* (480 mg) and triphenylphosphine (614 mg) were heated at 140° under nitrogen for 30 min. Chromatography afforded bis-cyclohexylidene (11%).

Photolysis of the Azo-sulphoxide.—The foregoing *azo-sulphoxide* (321 mg) was photolysed in cyclohexane (80 ml) at 19° under nitrogen. The photolysis was monitored by t.l.c. (alumina; benzene) and was complete in 2.5 h. The solvent was evaporated off and the residue chromatographed. The major product was cyclohexanone azine (54%). Olefinic material (14 mg) containing traces of bis-cyclohexylidene was isolated.

2',5'-Dihydrocyclohexanespiro-2'-1',3',4'-thiadiazine-5'-spirocyclohexane 1',1'-Dioxide.—The foregoing *azo-sulphoxide* (2.30 g), dichloromethane (50 ml), and 5*N*-peracetic acid (6.25 ml) were stirred at 21° for 48 h. A further quantity of peracid (0.50 ml) was added and stirring was continued for a further 4 h, whereupon monitoring by t.l.c. (alumina; benzene) indicated that the oxidation

was complete. Work-up in the usual way gave essentially pure *azo-sulphone* (98%), m.p. 141–143°. Chromatography (alumina; light petroleum) and crystallisation from light petroleum afforded plates, m.p. 146–147° (sintering 132°), ν_{\max} (Nujol) 1310 and 1130 cm^{-1} , λ_{\max} (cyclohexane) 366 nm (ϵ 140) (Found: C, 56.1; H, 7.8; N, 10.7; S, 12.4. $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$ requires C, 56.2; H, 7.9; N, 10.9; S, 12.5%).

Pyrolysis of the Azo-sulphone.—The foregoing *azo-sulphone* (192 mg) was pyrolysed under nitrogen. Gas evolution did not become apparent until the temperature had risen to 205° (14 min). The pyrolysis was stopped after a further 30 min, by which time the temperature had risen to 230°. Chromatography gave bis-cyclohexylidene (12%).

Photolysis of the Azo-sulphone.—The foregoing *azo-sulphone* (194 mg) was photolysed in cyclohexane (50 ml) at 19° under nitrogen. The photolysis was monitored by observing the disappearance of the u.v. absorption band at 366 nm and was complete in 30 min. The solvent was evaporated and the residue chromatographed. Cyclohexanone azine (18%) was isolated. No olefinic material was observed.

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