Syntheses using Monoketals of cyclo*Hexane*-1 : 2-*dione. Part I.* 2-*Oxo*cyclo*hexane*-1-spiro-2′-1′ : 3′-*Dioxolan and the corresponding Oxathiolan and Dithiolan.*

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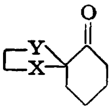
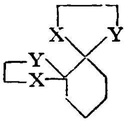
Treatment of *cyclo*hexane-1 : 2-dione with ethylene glycol, 2-mercaptoethanol, and ethane-1 : 2-dithiol by Salmi's procedure (*Ber.*, 1938, **71**, 1803) gave the mono- and di-ketals. 2-Hydroxy*cyclo*hexanone and ethylene glycol gave a monoketal. Observations are made on the structure of solid 2-hydroxy*cyclo*hexanone. Reductive desulphurization with Raney nickel of the hemithioketals (I*b*), (III), and (IV) is recorded. The mechanism of these reactions is discussed. With boiling Brady's reagent 2-ethyl-2-hydroxy*cyclo*hexanone gave 2-ethyl*cyclo*hex-2-enone 2 : 4-dinitrophenylhydrazone.

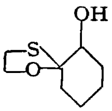
The present communication begins a series in which we shall describe the use of *cyclo*hexane-1 : 2-dione as a source for intermediates capable of forming the basis of rings C and D in D-homo-18-norsteroid systems. The compounds we require are certain 2-substituted *cyclo*hex-2-enones or their derivatives in which the carbonyl group is protected against anionoid reagents. It appeared that an obvious route to these would involve the protection of one of the carbonyl groups of *cyclo*hexane-1 : 2-dione whilst developing a side chain based on the other. The formation of cyclic ethylene ketals as a means of protecting carbonyl groups has recently found wide application in steroid syntheses (*inter al.*, Poos, Arth, Beyler, and Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422; Wilds *et al.*, *ibid.*, p. 4878), and in 1952 we independently demonstrated the usefulness of the method in a synthesis of 5-acetyl-1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-octahydro-10-methylnaphthalene-2-*spiro*-2′-1′ : 3′-dioxolan (Jaeger, Robinson, and Smith, unpublished work). Our experience in this field led us to investigate the same method with *cyclo*hexane-1 : 2-dione; accordingly we first investigated the preparation of 2-oxo*cyclo*hexane-1-*spiro*-2′-1′ : 3′-dioxolan (I*a*). The observation that a carbonyl group can be regenerated from an oxathiolan by treatment with Raney nickel (Romo, Rosenkrantz, and Djerassi, *J. Amer. Chem. Soc.*, 1951, **73**, 4961; Djerassi and Gorman, *ibid.*, 1953, **75**, 3704) prompted us to prepare also the corresponding oxathiolan (I*b*) and to treat it and the derived alcohols (III) and (IV) with Raney nickel. To complete the series we have also synthesized 2-oxo*cyclo*hexane-1-*spiro*-2′-1′ : 3′-dithiolan (I*c*).



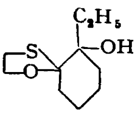
(I*a*); X = Y = O
(I*b*); X = O, Y = S
(I*c*); X = Y = S



(II*a*); X = Y = O
(II*b*); X = O, Y = S
(II*c*); X = Y = S



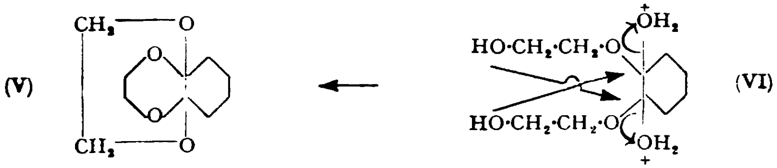
(III)



(IV)

Reaction of *cyclo*hexane-1 : 2-dione with one mol. of ethylene glycol in benzene in the presence of toluene-*p*-sulphonic acid by Salmi's method (*loc. cit.*) gave a mixture of the monoketal (I*a*) and the diketal (II*a*), together with unchanged dione. The monoketal was obtained in low but reproducible yield (15—18%) and could only be satisfactorily separated from the diketal by chromatography on alumina. Reaction with an excess of ethylene glycol (2 mols.) under the same conditions gave only the diketal. Evidently ketal formation is easier with the monoketal than with the enolic *cyclo*hexane-1 : 2-dione. It is noteworthy that when the latter preparation was carried out with a much larger amount of catalyst there was also obtained a small quantity (*ca.* 2%) of a second diketal which is isomeric with the first and probably has the benzo-1 : 4-dioxan structure (V). This ketal could not be obtained by treatment of its isomer (II*a*) with toluene-*p*-sulphonic acid monohydrate under conditions of its formation from *cyclo*hexane-1 : 2-dione. The formulation (V) is in accord with the experimental conditions observed to produce the second diketal; for if formation of the ketal is discussed in terms of a conventional mechanism (Waters, " Physical Aspects of Organic Chemistry," Routledge and Kegan Paul Ltd., London, 1950, p. 336; Djerassi and Gorman, *loc. cit.*) the production of (V) from *cyclo*hexane-1 : 2-dione probably depends on the formation of an ion of the type (VI) and this would be expected to occur, although to a small extent only, under the influence of a high proton concentration.

The keto-ketal (I*a*) is hydrolysed by acid to *cyclo*hexane-1 : 2-dione comparatively slowly; this behaviour can be understood when it is realized that the strongly electron-attracting carbonyl group is bound directly to the carbon atom which must become cationic if hydrolysis is to proceed (cf. Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953, p. 334). The reverse effect has been observed in the case of the acid hydrolysis of the acetals of pentaerythritol with formaldehyde, acetaldehyde, and acetone, increase in the number of electron-releasing substituents resulting in large increases in the reaction rate (Skrabal and Zlatewa, *Z. physikal. Chem.*, 1926, **122**, 349). The rates of hydrolysis of the ketals (II*a*) and (V) are extremely low; apart from purely steric effects, here again the co-ordination of a proton to a possible position of attack is inhibited by the inductive effect of an accumulation of electron-attracting *O*-alkyl substituents at the adjacent carbon atom.



Because of the low yield of (I*a*) obtained from *cyclo*hexane-1 : 2-dione we attempted to find an alternative method of preparation and investigated the reaction between 2-hydroxy*cyclo*hexanone and ethylene glycol, which proceeded in toluene in the presence of concentrated sulphuric acid to give 2-hydroxy*cyclo*hexane-1-*spiro*-2′-1′ : 3′-dioxolan whose structure follows from its identity with the lithium aluminium hydride reduction product of (I*a*). This could not be oxidized by Oppenauer's method or by treatment with the chromium trioxide–pyridine complex (Sarett *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 1708). For the foregoing work a quantity of 2-hydroxy*cyclo*hexanone (adipoin) was prepared by alkaline hydrolysis of 2-chloro*cyclo*hexanone as recommended by Kötz *et al.* (*Annalen*, 1913, **400**, 62). The solid adipoin had properties similar to those described by Sheehan, O'Neill, and White (*J. Amer. Chem. Soc.*, 1950, **72**, 3376) who assigned to it a bimolecular lactolid structure on the basis of the infra-red spectrum and a Rast molecular-weight determination in camphor. Although our sample had been purified in a manner closely resembling that of Sheehan *et al.* we did not observe their value for the molecular weight. Rast determinations under a variety of conditions, in camphor or in *cyclo*pentadecanone (m. p. *ca.* 80°), gave a value of around 140, whilst cryoscopic measurements in water gave 107. Solid adipoin in pyridine at room temperature yielded a 3 : 5-dinitrobenzoate corresponding to monomeric 2-hydroxy*cyclo*hexanone; a solution obtained by boiling solid adipoin with chloroform for a short time had, after separation from the chiefly undissolved material, an infra-red maximum of appreciable intensity at 5·84 μ. The melting point and insolubility of solid adipoin in common non-polar organic solvents favours a polymeric structure but the evidence we have presented indicates that disaggregation is so easy that any measurement involving dissolution or heat cannot reveal the true molecular weight. Supporting this view is our observation that when solid adipoin, previously showing no carbonyl band in the infra-red, is melted, a powerful carbonyl band appears, which disappears on crystallization and reappears on remelting. It seems likely, as suggested by Sheehan *et al.*, that the solid is mainly dimeric, but the presence of variable amounts of higher aggregates cannot be ruled out. This, and variations in the partial disaggregation on heating, may explain the different values obtained for the melting point of solid adipoin.

Reaction of *cyclo*hexane-1 : 2-dione with 2-mercaptoethanol by Salmi's method (*loc. cit.*) gave the monohemithioketal (I*b*) in about 40% yield, together with a mixture of diketals probably consisting mainly of the stereoisomers of (II*b*); one of these was obtained crystalline. With lithium aluminium hydride and ethylmagnesium bromide the ketonic derivative (I*b*) gave the alcohols (III) and (IV) respectively. These oxathiolans were each desulphurized under the same conditions with Raney nickel (Romo, Rosenkrantz, and Djerassi, *loc. cit.*); the ketone (I*b*) containing a powerfully electron-attracting group adjacent to the site of reaction gave none of the expected *cyclo*hexane-1 : 2-dione but a mixture consisting largely of 2-ethoxy*cyclo*hexanone and 2-ethoxy*cyclo*hexanol, with a little 2-hydroxy*cyclo*hexanone. The alcohol (III) containing a weaker electron-attracting group adjacent to the C–S bond gave *cyclo*hexane-1 : 2-diol and some 2-hydroxy*cyclo*hexanone, whilst the tertiary alcohol (IV) having adjacent electron-attracting and electron-repelling groups gave mainly 2-ethyl-2-hydroxy*cyclo*hexanone and only a trace of the corresponding diol. The products from the alcohols (III) and (IV) are consistent with a " normal " desulphurization accompanied by some reduction of a carbonyl group; that from (I*b*) apparently is anomalous.

Kenner, Lythgoe, and Todd (*J.*, 1948, 957), recalling that treatment of hydrazobenzene with Raney nickel in ethanol gave *N*-ethylaniline (Mozingo, Spencer, and Folkers, *J. Amer. Chem. Soc.*, 1944, **66**, 1859), suggested that desulphurization by this reagent involves attack by atomic hydrogen with the intermediate formation of free radicals, and this view has been supported by Hauptmann and Wladislaw (*J. Amer. Chem. Soc.*, 1950, **72**, 707, 711) and Bonner (*ibid.*, p. 1034; 1952, **74**, 1034). To account for the regeneration of a parent ketone from a hemithioketal Djerassi *et al.* (*loc. cit.*) invoked the intermediate formation of a 1 : 4-diradical, *e.g.*, $\cdot CR_2\cdot O\cdot CH_2\cdot CH_2\cdot$, which stabilizes itself by the elimination of ethylene ($\longrightarrow R_2CO + C_2H_4$). Now almost any substituent in place of hydrogen stabilizes the amphoteric unpaired electron (references cited by Birch, *Quart. Reviews*, 1950, **4**, 72), and so if reductive desulphurization by Raney nickel is a free-radical process, it might be expected that alterations in the substitution at the position β to the sulphur atom should not affect the product. It may be, however, that the nature of the product is decided by the relative rates with which the diradical rearranges to a ketone or adds hydrogen to give an ethyl ether. In the compound (I*b*) the carbonyl group may so stabilize an adjacent unpaired electron that addition of hydrogen atoms to the diradical becomes the principal, but not the sole, reaction. Desulphurization by a heterolytic mechanism would give an ethyl ether and not a ketone, and the possibility that the powerful electron-attraction of the carbonyl group can call into play this type of mechanism (Hey, *Ann. Reports*, 1948, **45**, 139) in (I*b*) should also be noted.

When 2-ethyl-2-hydroxy*cyclo*hexanone was boiled for several minutes with Brady's reagent the 2 : 4-dinitrophenylhydrazone of 2-ethyl*cyclo*hex-2-enone was obtained. Similar dehydrations were observed with 2-hydroxy-2-methyl*cyclo*hexanone 2 : 4-dinitrophenylhydrazone and semicarbazone in hot mineral acid (Butz, Davis, and Gaddis, *J. Org. Chem.*, 1947, **12**, 122). This may be contrasted with the difficulty of dehydrating the α-ketol or its acetate by direct means (Butz *et al.*, *loc. cit.*). This type of reaction is probably quite general for 2-alkyl-2-hydroxyalkanones and is evidently related to the rapid dehydrobromination which occurs when α-bromo-ketones are treated with 2 : 4-dinitrophenylhydrazone in the presence of acid (Mattox and Kendall, *J. Amer. Chem. Soc.*, 1948, **70**, 882; Djerassi, *ibid.*, 1949, **71**, 1003).

Acid hydrolysis of the ketals (I*b*), (III), and (IV) was slow—in that order of increasing speed, in accordance with the expected electronic effects.

The dithioketal (I*c*) was best prepared from *cyclo*hexane-1 : 2-dione and ethane-1 : 2-dithiol by Salmi's method, the catalyst being toluene-*p*-sulphonic acid. Reaction at room temperature in the presence of zinc chloride and a dehydrating agent gave an unsatisfactory result.

EXPERIMENTAL

Light petroleum without further definition means the fraction of b. p. 60—80°. Infra-red spectra of solids were determined for Nujol mulls except where stated otherwise; approximate intensities of bands are given as: s = strong; m = medium; w = weak. Spectra were determined by Dr. F. B. Strauss with the technical assistance of Mr. F. Hastings.

2-*Oxo*cyclo*hexane*-1-spiro-2′-1′ : 3′-*dioxolan* (I*a*).—A solution of *cyclo*hexane-1 : 2-dione (15·8 g.) (Butz *et al., loc. cit.*) and ethylene glycol (9 c.c.) in dry benzene (175 c.c.) was refluxed for 6 hr. with toluene-*p*-sulphonic acid (50 mg.), under a Dean–Stark water separator. Ether (150 c.c.) was added, unchanged diketone extracted with aqueous sodium hydroxide, and the organic layer washed, dried, and evaporated. The dark oil (14·5 g.) was adsorbed from light petroleum on alumina. Elution with light petroleum and light petroleum–benzene (1 : 1) gave cyclo*hexane*-1 : 2-*di*(spiro-2′-1′ : 3′-*dioxolan*) (II*a*) (6·5 g.) as a colourless oil, b. p. 130—133°/18 mm. [Found: C, 60·2; H, 7·9%; *M* (Rast), 190. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%; *M*, 200]; elution with benzene and benzene–ether (up to 1 : 4) yielded pure 2-*oxo*cyclo*hexane*-1-spiro-2′-1′ : 3′-*dioxolan* (3·5 g.) as a colourless oil, b. p. 115—116°/22 mm. (Found: C, 61·5; H, 7·8. $C_8H_{12}O_3$ requires C, 61·5; H, 7·7%). The infra-red spectrum had a band at 5·78 μ (s). Light absorption in MeOH: Max. = 295 mμ (ε = 38); compared with *cyclo*hexanone: Max. = 280 mμ (ε = 19). The 2 : 4-*dinitrophenylhydrazone*, prepared in pyridine (cf. Braude and Timmons, *J.*, 1953, 3131), separated from ethyl acetate–ethanol as orange-red prisms, m. p. 171° (Found: C, 49·9; H, 4·8; N, 16·7. $C_{14}H_{16}O_6N_4$ requires C, 50·0; H, 4·8; N, 16·7%).

The diketal (II*a*) was obtained in quantitative yield when *cyclo*hexane-1 : 2-dione was treated with ethylene glycol (2 mols.) under the above conditions. In one experiment *cyclo*hexane-1 : 2-dione (26·7 g.) and ethylene glycol (26 c.c.; 2 mols.) in dry benzene (260 c.c.) were refluxed as above with an unusually large amount of toluene-*p*-sulphonic acid (0·75 g.). Elimination of water was rapid and two non-ketonic products were obtained: (i) the normal diketal (II*a*) (33·6 g.) and (ii) a colourless oil (1 g.), b. p. 134—138°/18 mm., which crystallized from light petroleum (b. p. 40—60°) in prisms, m. p. 102—103°, to which the structure 1 : 2-1 : 2-*bisethylenedioxy*cyclo*hexane* (V) has been assigned [Found: C, 60·1; H, 8·0%; *M* (Rast), 223]. The infra-red spectrum of the liquid (II*a*) in CS_2 (17·4 mg./c.c.) had bands at 3·43s, 3·45s, 7·39m, 7·42m (infl.), 7·50m, 7·90m, 8·43s, 8·86s, 9·10s, 9·26s, 9·61s, 9·90m, 10·22s, 10·55s, 10·85w, 11·20w, 11·42w, 12·61w, and 13·07w μ. The infra-red spectrum of the solid (V) in CS_2 (17·4 mg./c.c.) had bands at 3·43s, 3·46s, 7·25w, 7·40s, 7·86s, 7·98s, 8·45s, 8·75s, 9·10s, 9·57s, 9·63s, 9·95s, 10·32s, 10·41s, 10·87s, 11·13s, 11·20s, 11·65w, 11·99s, 12·71w, and 13·20m μ.

The compounds (I*a*), (II*a*), and (V) were each refluxed with 50% acetic acid for 30 min. under nitrogen, and the products isolated by means of ether. Most of the starting materials (*ca.* 80—90%) were recovered. A small quantity of *cyclo*hexane-1 : 2-dione was identified by a ferric chloride test and by its characteristic odour; the amounts [*ca.* 20% from (I*a*) and *ca.* 5—10% from (II*a*) and (V)] were estimated from the infra-red spectra.

2-*Hydroxy*cyclo*hexane*-1-spiro-2′-1′ : 3′-*dioxolan*.—Reduction of the above *cyclo*hexanone-*spiro*dioxolan (2 g.) with lithium aluminium hydride in ether in the known manner gave 2-*hydroxy*cyclo*hexane*-1-spiro-2′-1′ : 3′-*dioxolan* as a colourless oil (1·5 g.), b. p. 115°/15 mm. (Found: C, 61·1; H, 9·1. $C_8H_{14}O_3$ requires C, 60·8; H, 8·9%). The 3 : 5-*dinitrobenzoate* separated from methanol as needles, m. p. 136—137° (Found: C, 51·3; H, 4·7; N, 7·8. $C_{15}H_{16}O_8N_2$ requires C, 51·2; H, 4·6; N, 8·0%).

2-*Hydroxy*cyclo*hexanone*.—This was prepared by Kötz's method (*loc. cit.*). It distilled at 98—100°/20 mm. and on recrystallization from acetone had m. p. 117—119° (softening at 100°) [Found: C, 63·2; H, 8·8; active H, 1·2%; *M* (Rast in camphor; Pyrex tube), 139, 144; *M* (Rast in *cyclo*pentadecanone), 141; *M* (cryoscopically in water), 107. Calc. for $C_6H_{10}O_2$: C, 63·2; H, 8·8; active H, 0·9%; *M*, 114]. The infra-red spectrum of the crystalline form exhibited a hydroxyl band at 3·0 μ and no carbonyl band in the 5·8 μ region. The freshly distilled oil showed a hydroxyl band at 2·99 μ and a carbonyl band at 5·86 μ The latter disappeared on solidification but reappeared on remelting.

The 3 : 5-*dinitrobenzoate* crystallized from methanol in cream-coloured prisms, m. p. 146—148° [Found: C, 50·9; H, 4·0; N, 8·7%; *M* (Rast in camphor), 285. $C_{13}H_{12}O_7N_2$ requires C, 50·6; H, 3·9; N, 9·1%; *M*, 308]. The infra-red spectrum had strong bands of equal intensity at 5·76 μ and 5·84 μ.

The methyl ether of dimeric adipoin was prepared from the solid and methanolic hydrogen chloride (cf. Bergmann and Gierth, *Annalen*, 1926, **448**, 50) [Found: C, 65·7; H, 9·4; *M* (Rast in camphor), 224. Calc. for $C_{14}H_{24}O_4$: C, 65·5; H, 9·4%; *M*, 256].

*Reaction of 2-Hydroxy*cyclo*hexanone with Ethylene Glycol*.—2-Hydroxy*cyclo*hexanone (15 g.) and ethylene glycol (14·64 c.c.) were refluxed in toluene (250 c.c.) containing concentrated sulphuric acid (9 drops) for 3 hr., under a Dean–Stark water separator. The cooled mixture was washed with 2N-sodium hydroxide (2 × 100), and then water, and dried (Na_2SO_4). Distillation gave 2-hydroxy*cyclo*hexane-1-*spiro*-2′-1′ : 3′-dioxolan (9·0 g.), b. p. 62—64°/0·3 mm. (Found: C, 61·4; H, 9·0. Calc. for $C_8H_{14}O_3$: C, 60·8; H, 8·9%), probably containing some unchanged hydroxy*cyclo*hexanone which could not be entirely removed by fractionation. The infra-red spectrum shows bands at 2·88s, 5·85w μ and in the 8—10-μ region (s).

The 3 : 5-dinitrobenzoate, obtained in excellent yield, formed needles from ethanol, m. p. 136—137°, undepressed by the same derivative described above and possessing an identical infra-red spectrum (Found: C, 51·1; H, 4·5; N, 7·8%).

The hydroxy*cyclo*hexane*spiro*dioxolan was recovered unchanged after 6 hours' refluxing with aluminium *iso*propoxide and acetone in toluene; it also could not be oxidized by chromium trioxide–pyridine (Sarett *et al.*, *loc. cit.*).

*2-Oxo*cyclo*hexane*-1-spiro-2′-1′ : *3′-oxathiolan* (I*b*).—A mixture of *cyclo*hexane-1 : 2-dione (20 g.), 2-mercaptoethanol (16 g.), toluene-*p*-sulphonic acid (100 mg.), and benzene (400 c.c.) was refluxed in an inert atmosphere for 6 hr. (Dean–Stark head) and worked up as described for the corresponding dioxolan. Fractionation of the crude product gave 2-*oxo*cyclo*hexane*-1-spiro-2′-1′ : 3′-*oxathiolan* (12·3 g.) as a colourless oil, b. p. 78—82°/0·3 mm. (Found: C, 56·0; H, 7·0; S, 18·4. $C_8H_{12}O_2S$ requires C, 55·8; H, 7·0; S, 18·6%). The infra-red spectrum had a strong band at 5·80 μ. The 2 : 4-*dinitrophenylhydrazone*, prepared with Brady's reagent, separated from ethyl acetate–ethanol as orange prisms, m. p. 178° (Found: C, 47·8; H, 4·4. $C_{14}H_{16}O_5N_4S$ requires C, 47·7; H, 4·5%). The fraction, b. p. 125—135°/0·3 mm., a colourless non-ketonic oil (8 g.), partly solidified. It was adsorbed from light petroleum on alumina and eluted with light petroleum. From the first eluate what is probably a stereoisomer of cyclo*hexane*-1 : 2-*di*(spiro-2′-1′ : 3′-*oxathiolan*) (II*b*) was obtained as a colourless, viscous oil, b. p. 130°/0·2 mm. (Found: C, 52·0; H, 6·9; S, 27·3. $C_{10}H_{16}O_2S_2$ requires C, 51·7; H, 6·9; S, 27·6%); further eluates contained an *isomer* which crystallized from light petroleum (b. p. 40—60°) as prisms, m. p. 135° (Found: C, 51·9; H, 6·9; S, 27·6%).

*2-Hydroxy*cyclo*hexane*-1-spiro-2′-1′ : *3′-oxathiolan* (III).—The hemithioketal (I*b*) (1·3 g.) was refluxed with lithium aluminium hydride (0·85 g.) in ether (30 c.c.) for 30 min. "Celite 545" was added, followed by damp ether and water. Working up in the known manner gave 2-*hydroxy*cyclo*hexane*-1-spiro-2′-1′ : 3′-*oxathiolan* (1·1 g.), b. p. 80° (bath-temp.)/0·15 mm. (Found: C, 55·5; H, 7·9; S, 18·3. $C_8H_{14}O_2S$ requires C, 55·2; H, 8·05; S, 18·4%). The 3 : 5-*dinitrobenzoate* crystallized from ethanol in off-white needles, m. p. 144° (Found: C, 47·8; H, 4·4; N, 7·9; S, 8·7. $C_{14}H_{16}O_7N_2S$ requires C, 47·2; H, 4·5; N, 7·9; S, 9·0%).

*2-Ethyl-2-hydroxy*cyclo*hexane*-1-spiro-2′-1′ : *3′-oxathiolan* (IV).—An ethereal solution of (I*b*) (3·5 g.) was added gradually with stirring to an ice-cold one of ethylmagnesium bromide (from 2·1 g. of magnesium and 10·6 g. of ethyl bromide in nitrogen). After 12 hr. at room temperature the mixture was refluxed for 7 hr., then decomposed with aqueous ammonium chloride, and the product was isolated with ether. The *spiran* distilled as a pale yellow, mobile oil (3·4 g.), b. p. 100°/0·1 mm. (Found: C, 59·6; H, 8·9; S, 15·9. $C_{10}H_{18}O_2S$ requires C, 59·5; H, 8·9; S, 15·8%). The infra-red spectrum had bands at 2·88m, 8·7s, and 9·35s μ.

Desulphurization of the Hemithioketals (I*b*), (III), *and* (IV) (cf. Romo, Rosenkrantz, and Djerassi, *loc. cit.*).—(i) A solution of the spiran (I*b*) (1 g.) in acetone (200 c.c.) was refluxed for 3 hr. with W-2 Raney nickel (10 g.), the catalyst filtered off, and the solvent evaporated. The pleasant-smelling, colourless oil (0·6 g.), b. p. 90°/24 mm., which gave no ferric chloride reaction (absence of *cyclo*hexane-1 : 2-dione), was a mixture of, chiefly, 2-ethoxy*cyclo*hexanone, 2-ethoxy*cyclo*hexanol, and very little 2-hydroxy*cyclo*hexanone (Found: C, 67·2; H, 10·4; OEt, 30·2. Calc. for $C_8H_{14}O_2$: C, 67·6; H, 9·9; OEt, 31·6. Calc. for $C_8H_{16}O_2$: C, 66·7; H, 11·1; OEt, 31·2%). The infra-red spectrum had bands at 2·95, 5·82, and 9·05 μ. Boiling this mixture (0·15 g.) for 3 min. with Brady's reagent gave *cyclo*hexane-1 : 2-dione bis-2 : 4-dinitrophenylhydrazone (*ca.* 50 mg.) which crystallized from ethyl acetate in bright red prisms, m. p. 233—235°

(decomp.) (cf. Campbell and McCall, *J.*, 1950, 2870) (Found: C, 46·1; H, 3·6; N, 24·0. Calc. for $C_{18}H_{16}O_8N_8$: C, 45·9; H, 3·4; N, 23·8%). Light absorption in $CHCl_3$: Max. = 350 (ε 32,000) and 395 mμ (ε 25,000).

Another portion of the above mixture (0·15 g.) was boiled for 3 min. with pyridine (1 c.c.) and 2 : 4-dinitrophenylhydrazone (0·25 g.) (cf. Braude and Timmons, *loc. cit.*); benzene (20 c.c.) was added and the solution adsorbed on alumina. Elution with benzene gave 2-*ethoxy*cyclo*hexanone* 2 : 4-*dinitrophenylhydrazone*, which crystallized from benzene–light petroleum as yellow needles, m. p. 130° (Found: C, 52·3; H, 5·5; N, 17·2. $C_{14}H_{18}O_5N_4$ requires C, 52·2; H, 5·6; N, 17·4%). Elution with benzene–ethyl acetate (9 : 1) yielded a second 2 : 4-*dinitrophenylhydrazone* of 2-ethoxy*cyclo*hexanone, which separated from light petroleum as orange needles, m. p. 116°, depressed on admixture with the higher-melting derivative (Found: C, 52·2; H, 5·7; N, 17·1%). These two derivatives are probably *syn*- and *anti*-forms.

A third portion of the desulphurization product yielded 2-*ethoxy*cyclo*hexyl* 3 : 5-*dinitrobenzoate* which, after chromatography on "Florex," crystallized from light petroleum (b. p. 40—60°) in almost colourless prisms, m. p. 77—78° (Found: C, 53·8; H, 5·4; N, 8·5. $C_{15}H_{18}O_7N_2$ requires C, 53·3; H, 5·3; N, 8·3%).

(ii) The alcohol (III) (0·45 g.) was treated with Raney nickel as described above. The resultant liquid (0·3 g.), b. p. 120°/20 mm., consisted of *cyclo*hexane-1 : 2-diol accompanied by a little 2-hydroxy*cyclo*hexanone (Found: C, 62·5; H, 9·9. Calc. for $C_6H_{12}O_2$: C, 62·1; H, 10·0%). The infra-red spectrum had bands at 3·0s and 5·85w μ. *cyclo*Hexane-1 : 2-diol bis-3 : 5-dinitrobenzoate, crystallized from ethanol, had m. p. 177° (Wilson and Read, *J.*, 1935, 1269, give m. p. 179° for the derivative from the *trans*- and m. p. 169° for that of the *cis*-diol) (Found: C, 47·7; H, 3·4; N, 10·8. Calc. for $C_{20}H_{16}O_{12}N_4$: C, 47·7; H, 3·2; N, 11·1%). Boiling a sample of the desulphurization product with Brady's reagent yielded a small quantity of 2-hydroxy*cyclo*hexanone 2 : 4-dinitrophenylosazone, m. p. 234—235° (decomp.), undepressed on admixture with a previously prepared specimen.

(iii) Treatment of the alcohol (IV) (1 g.) with Raney nickel as above gave 2-*ethyl*-2-*hydroxy*cyclo*hexanone* (0·65 g.), b. p. 115—120°/20 mm. (Found: C, 67·2; H, 10·1. $C_8H_{14}O_2$ requires C, 67·5; H, 9·9%). The infra-red spectrum showed bands at 2·93s and 5·85s μ. This α-ketol, on 5 minutes' boiling with Brady's reagent, yielded 2-*ethyl*cyclo*hex*-2-*enone* 2 : 4-*dinitrophenylhydrazone*, dark red elongated prisms (from ethyl acetate), m. p. 229—231° (Found: C, 55·3; H, 5·4; N, 18·4. $C_{14}H_{16}O_4N_4$ requires C, 55·3; H, 5·3; N, 18·4%). Light absorption in chloroform: Max. = 385 mμ (ε = 25,600). The 3 : 5-*dinitrobenzoate* of the α-ketol crystallized, after chromatography on "Florex" and elution with light petroleum–benzene (3 : 1), in cream-coloured prisms (from methanol), m. p. 127° (Found: C, 53·8; H, 4·9; N, 8·4. $C_{15}H_{16}O_7N_2$ requires C, 53·6; H, 4·8; N, 8·3%).

Acid Hydrolysis of the Hemithioketals (I*b*), (III), *and* (IV).—The compounds were refluxed with aqueous-ethanolic hydrogen chloride for 3—5 hr. in nitrogen (cf. Djerassi, *J. Amer. Chem. Soc.*, 1953, **75**, 3704). In each case most of the starting material was recovered. The spiran (I*b*) yielded less than 5% of *cyclo*hexane-1 : 2-dione, identified by ferric chloride reaction and estimated from the infra-red spectrum. The spiran (III) gave 5—10% and (IV) *ca.* 15—20% of the dione, which was converted into the bis-2 : 4-dinitrophenylhydrazone, m. p. 235°.

2-*Oxo*cyclo*hexane*-1-spiro-2′-1′ : 3′-*dithiolan* (I*c*).—*cyclo*Hexane-1 : 2-dione (3·6 g.) was refluxed (Dean–Stark water separator) for 6 hr. under nitrogen with ethanedithiol (3·3 g.), dry benzene (80 c.c.), and toluene-*p*-sulphonic acid (20 mg.), and the mixture worked up as described for (I*b*). After fractionation the distillate, b. p. 94°/0·2 mm., consisting of 2-*oxo*cyclo*hexane*-1-spiro-2′-1′ : 3′-*dithiolan*, crystallized from light petroleum in colourless needles (2·2 g.), m. p. 57·5° (Found: C, 51·3; H, 6·5; S, 33·8. $C_8H_{12}OS_2$ requires C, 51·0; H, 6·4; S, 34·0%). The infra-red spectrum had a strong band at 5·87 μ. The fraction, b. p. 155—165°/0·2 mm. yielded cyclo*hexane*-1 : 2-*di*(spiro-2′-1′ : 3′-*dithiolan*) (II*c*) which separated from ethyl acetate as colourless prisms, m. p. 156° (Found: C, 45·7; H, 5·9; S, 48·1. $C_{10}H_{16}S_4$ requires C, 45·5; H, 6·1; S, 48·5%).

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