# *Syntheses using Monoketals of* cyclo*Hexane*-1 : 2-*dione. Part II.** 2-*Ethynyl-2-hydroxy*cyclo*hexane*-1-spiro-2'-(1' : 3'-*dioxolan*), *the Corresponding Oxathiolan and Dithiolan, and Some Transformation Products thereof.*

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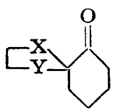
2-Ethynyl-2-hydroxy*cyclo*hexane-1-*spiro*-2'-(1' : 3'-dioxolan) (II*a*) and the corresponding oxathiolan (II*b*) and dithiolan (II*c*) have been prepared by the action of lithium acetylide in liquid ammonia on 2-oxo*cyclo*hexane-1-*spiro*-2'-(1' : 3'-dioxolan) and the corresponding oxathiolan and dithiolan. Treatment of (II*a*), (II*b*), and (II*c*) with formic acid and mercuriacetamide is described. The dehydration of the alcohols (II*b* and *c*) and the reaction of the resulting enynes with methanol in the presence of the boron trifluoride–mercuric oxide–trichloroacetic acid catalyst are recorded.

In Part I* we described the synthesis and some features of the chemistry of the mono-ethylene ketals derived from *cyclo*hexane-1 : 2-dione. We now present an account of the preparation of the corresponding ethynylcarbinols and of some transformation products obtained from them.

Reaction of the oxo-ketals (I*a*, *b*, and *c*) with lithium acetylide in liquid ammonia was slow, but satisfactory yields of the ethynylcarbinols (II*a*, *b*, and *c*) were obtained at room temperature and increased pressure, (I*a*) giving the lowest and (I*c*) the highest yield. The alcohol (II*b*) was obtained in both possible stereoisomeric forms. The infra-red spectrum of the minor, higher-melting isomer in solution in carbon tetrachloride has the hydroxyl band at the longer wave-length (2·92 as against 2·86 μ), indicating a greater degree of hydrogen bonding in this isomer which probably has the hydroxyl group *cis* to the oxygen atom of the oxathiolan ring.



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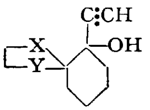

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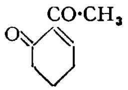

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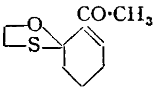

(IV)

Treatment of the ethynylcarbinol (II*a*) with boiling formic acid, a reagent used for the dehydration of ethynylcarbinols and their rearrangement to αβ-unsaturated methyl

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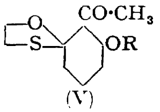
* Part I, *J.*, 1955, 160.

ketones (cf., *e.g.*, Hamlet, Henbest, and Jones, *J.*, 1951, 2657), afforded as the chief recognizable product 2-ethynyl*cyclo*hexanone, formed by hydrolysis of the ketal group. None of the desired product (III) was identified. Heating the carbinols (II*b* and *c*) with formic acid produced intractable tars.

Mercuriacetamide in methanol or ethanol, reagents which normally transform ethynylcarbinols into αβ-unsaturated methyl ketones (Aeschbacher and Goldberg, *Helv. Chim. Acta*, 1939, **29**, 1185; Birch and Robinson, *J.*, 1944, 503), gave no αβ-unsaturated ketone with the carbinols (II*a*, *b*, and *c*). Instead, the carbinol (II*b*), either as a mixture or in its pure lower-melting form, was converted in ethanol into a saturated ketone whose analysis corresponded to a compound formed by the addition of ethanol to the expected acetyl*cyclo*hexenone derivative (IV). The participation of the solvent in the reaction was confirmed when a similar experiment in methanol afforded a different ketone whose analysis indicated addition of methanol to (IV). By analogy with the known mode of addition of weak acids to conjugated mono-olefinic carbonyl compounds (Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, Ltd., London 1953, p. 690) the structures (V; R = Et and Me) were assigned to these ketones. The results of some desulphurization experiments also seem to support these formulations: when the compound (V; R = Me) was desulphurized with Raney nickel (Romo, Rosenkrantz, and Djerassi, *J. Amer. Chem. Soc.*, 1951, **73**, 4961) no product could be isolated even after washing the nickel with ether containing acetic acid—a result consistent with the initial production in the reaction of an enolic β-diketone; when, however, the lithium aluminium hydride reduction product of (V; R = Me) was desulphurized in the same manner a saturated hydroxy-ketone was obtained which, on short treatment with Brady's reagent, gave a derivative having the correct analysis for the 2 : 4-dinitrophenylhydrazone of 2-1′-hydroxyethyl*cyclo*hex-2-enone. The major product of the action of mercuriacetamide in methanol or ethanol on the carbinol (II*c*) was an oxygen-free oil $C_{10}H_{14}S_2$ which, on the basis of its ultra-violet and infra-red absorption spectra, is a heteroannular conjugated diene not containing a terminal vinyl group. If, as seems most probable, no change in ring structure has occurred, this can only be (VI). A small amount of an acetoxy-ketone, formulated as (VII) by analogy with (V), was also isolated from the reaction. The alcohol (II*a*) gave with mercuriacetamide in ethanol a low yield of a hydroxy-ketone which is either (VIII) or, since it is in accord with the behaviour of the reagent with (II*b* and *c*), more probably (IX). The hydroxy-ketone reacted with thionyl chloride in pyridine at room temperature but no satisfactory product resulted.



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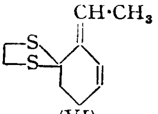

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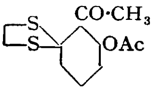

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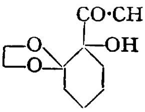

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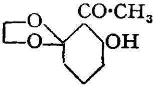
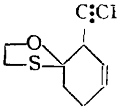


(IX)

Dehydration of the alcohols (II*b* and *c*) could not be achieved with phosphorus oxychloride in pyridine (Hamlet *et al.*, *loc. cit.*) even at reflux temperature, and was finally effected with the same reagent in collidine at 120—140°. The enyne from (II*b*) exhibited in the infra-red absorption spectrum a maximum at 6·0 μ consistent with an unconjugated double bond, and showed no selective light absorption in the range 220—320 mμ; it must therefore be (X). That from (II*c*) had an infra-red absorption maximum at 6·20 μ (conjugated double bond) and a light absorption maximum at 250 mμ, and is therefore (XI). The latter maximum is at a longer wave-length than would be expected for a vinylacetylene (cf. Hamlet *et al.*, *loc. cit.*) but the displacement to longer wave-length could be explained by steric strain in the chromophore (Lewis and Calvin, *Chem. Reviews*, 1939, **25**, 273). We have advanced elsewhere (*Chem. and Ind.*, 1954, 1106) a tentative steric explanation for the different behaviour of the alcohols (II*b* and *c*) on dehydration. The demonstrated instability and therefore high reactivity of a double bond αβ to an oxathiolan ring may be used to explain why (II*b*) does not give an αβ-unsaturated ketone with mercuriacetamide in alcohols. It is predictable that such a ketone, if formed, would tend to add a suitable available weak acid, in this case an alcohol.

The enyne (X) on treatment with methanol in the presence of the boron trifluoride–mercuric oxide–trichloroacetic acid catalyst (Hamlet *et al.*, *loc. cit.*) gave three products. Two of these were isomeric ethynes resulting from the addition of methanol to (X); they formed mixed crystals and were separable by chromatography on alumina. We offer no proof of their structure, but in view of the experimentally demonstrated instability of a double bond αβ to an oxathiolan ring and the known electronic effect of the ethynyl group which is electron-attracting relative to the vinyl group (Ingold, *op. cit.*, p. 71), it is reasonable to predict that they are isomers of (XII) formed by the addition of methanol to (XIII). The latter, under the acid conditions of the reaction, would be in equilibrium with (X). The third product was a methoxy-ketone possessing an infra-red absorption spectrum closely resembling that of (V; R = Me) and an indefinite melting point undepressed by (V; R = Me) from which it appears to be a mixture of stereoisomers of that compound. As might be expected from the observed greater stability of a double bond αβ to the dithiolan ring, the conjugated enyne (XI) added methanol under similar conditions much less readily than (X). Most of (XI) was recovered unchanged, but a small quantity of a compound $C_{11}H_{18}O_2S_2$, possibly (XIV), was obtained.



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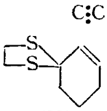

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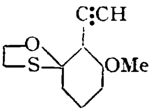

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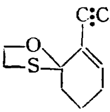

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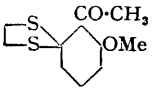

(XIV)

Treatment of the alcohols (II*a*, *b*, and *c*) in acetic acid with Dowex-50 in its acid cycle (Newman, *J. Amer. Chem. Soc.*, 1953, **75**,4740) failed in each case to give a useful product; (II*a* and *b*) gave complex mixtures, and (II*c*), though mostly unchanged, yielded some of the enyne (XI).

## 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. Spectra were determined by Dr. F. B. Strauss with the technical assistance of Mr. F. Hastings.

2-*Ethynyl*-2-*hydroxy*cyclo*hexane*-1-spiro-2′-(1′ : 3′-*dioxolan*) (II*a*).—2-Oxo*cyclo*hexane-1-*spiro*-2′-(1′ : 3′-dioxolan) (7·16 g.) in tetrahydrofuran (50 c.c.) was added to a solution of lithium acetylide (from the metal, 2·9 g.) in liquid ammonia (600 c.c.) contained in a stainless-steel autoclave which was then closed. After 20 hr. the autoclave was cooled in solid carbon dioxide–methanol and opened. Ammonium chloride (22 g.) was added in small portions, followed by ether (200 c.c.) and water (500 c.c.). The ethereal layer was separated, and the aqueous layer thoroughly extracted with ether (4 × 400 c.c.). The extracts were combined, washed with water (200 c.c.), treated with small pieces of solid carbon dioxide, and dried ($Na_2SO_4$). Evaporation under reduced pressure afforded an oil (6·0 g.) which gave a copious precipitate with ammoniacal silver nitrate solution. It was dissolved in benzene–light petroleum (1 : 1; 50 c.c.) and adsorbed on activated alumina (180 g.). Elution with benzene–light petroleum (1 : 1; 500 c.c.) and benzene (1000 c.c.) gave unchanged ketone (2·5 g.); elution with benzene–ether (9 : 1; 1000 c.c.) gave a mixture of unchanged ketone and acetylenic material (0·63 g.); and elution with benzene–ether (2 : 3; 500 c.c.), benzene–ether (1 : 4; 500 c.c.), and ether (500 c.c.) gave the 2-*ethynyl*-2-*hydroxy*cyclo*hexane*-1-spiro-2′-(1′ : 3′-*dioxolan*) (II*a*) (2·4 g.), b. p. 95—100° (bath-temp.)/0·2 mm. (Found: C, 65·7; H, 7·9. $C_{10}H_{14}O_3$ requires C, 66·0; H, 7·7%). The infra-red spectrum had bands at 2·88, 3·08, and 4·77 μ. With Brady's reagent the oil gave a 2 : 4-dinitrophenylhydrazone, m. p. 212—213° after recrystallisation from tetrahydrofuran.

2-*Ethynyl*-2-*hydroxy*cyclo*hexane*-1-spiro-2′-(1′ : 3′-*oxathiolan*) (II*b*).—2-Oxo*cyclo*hexane-1-*spiro*-2′-(1′ : 3′-oxathiolan) (6·45 g.) in tetrahydrofuran (100 c.c.) was added to a solution of lithium acetylide (from the metal, 1·43 g.) in liquid ammonia (500 c.c.) contained in a rocking autoclave. The mixture was shaken for 48 hr., the autoclave cooled as before and opened, and after the addition of ammonium chloride (11 g.) the product was worked up as under (II*a*). The oily product (6·4 g.) was taken up in benzene–light petroleum (1 : 1; 30 c.c.) and adsorbed on activated alumina (150 g.). Elution with benzene–light petroleum (1 : 1; 1000 c.c.) gave unchanged ketone; elution with benzene–light petroleum (3 : 1; 500 c.c.), benzene (500 c.c.), benzene–ether (9 : 1; 500 c.c.) and benzene–ether (7 : 3; 500 c.c.) gave 2-*ethynyl*-2-*hydroxy*-

cyclo*hexane*-1-spiro-2'-(1' : 3'-*oxathiolan*) (II*b*) (2·35 g.), obtained from light petroleum as rhombs, m. p. 68° (Found : C, 60·7; H, 6·9; S, 16·0. $C_{10}H_{14}O_2S$ requires C, 60·6; H, 6·9; S, 16·2%). The infra-red spectrum had bands at 2·89, 3·09, and 4·75 μ; the spectrum in carbon tetrachloride had bands at 2·86 and 3·03 μ. Elution with benzene–ether (1 : 1; 500 c.c.) and ether (500 c.c.) gave a mixture of stereoisomers of (II*b*) as a viscous oil (0·94 g.), b. p. 110° (bath-temp.)/0·25 mm. (Found : C, 60·4; H, 6·9; S, 16·3%).

When the oily mixture of stereoisomers was treated with the Newman catalyst (*loc. cit.*) in acetic acid, and the product chromatographed on " Florex," light petroleum–benzene (3 : 1) eluted the remaining *stereoisomer* which crystallized from light petroleum as needles, m. p. 109—111° (Found : C, 60·3; H, 7·0; S, 16·2%). The infra-red spectrum had bands at 2·98, 3·06, and 4·76 μ; the spectrum in $CCl_4$ had bands at 2·92 and 3·03 μ.

2-*Ethynyl*-2-*hydroxy*cyclo*hexane*-1-spiro-2'-(1' : 3'-*dithiolan*) (II*c*).—2-Oxo*cyclo*hexane-1-2-*spiro*-2'-(1' : 3'-dithiolan) (8·2 g.) in tetrahydrofuran (100 c.c.) was treated with lithium acetylide (from the metal, 1·6 g.) in liquid ammonia (600 c.c.) in an autoclave as before. After 48 hr. the autoclave was cooled and opened, and ammonium chloride (14 g.) was added followed by ether (250 c.c.) and water (500 c.c.). The ethereal solution was separated, and the aqueous layer extracted with benzene–ether (1 : 1; total 2 l.). The combined extracts after evaporation under reduced pressure afforded an oil (8·16 g.) which was dissolved in boiling light petroleum (b. p. 80—100°). On cooling, the solution deposited the 2-*ethynyl*-2-*hydroxy*cyclo*hexane*-1-spiro-2'-(1' : 3'-*dithiolan*) (II*c*) as rhombs (4·6 g.), m. p. 79·5° after recrystallisation from light petroleum (b. p. 80—100°) (Found : C, 55·8; H, 6·1; S, 30·25. $C_{10}H_{14}OS_2$ requires C, 56·1; H, 6·5; S, 29·9%). The infra-red spectrum had bands at 2·93, 3·08, and 4·76 μ.

2-*Ethynyl*-2-*hydroxy*cyclo*hexan*-1-*one*.—The ethynylcarbinol (II*a*) (0·87 g.) was refluxed with formic acid (10 c.c.; 90%) in an atmosphere of nitrogen for 1 hr. The dark mixture was poured on crushed ice, and the product collected in ether. The resulting brown oil was chromatographed in benzene–light petroleum (1 : 4; 10 c.c.) on acid-washed alumina (20 g.). Elution with light petroleum gave a partially crystalline oil A, and elution with mixtures of benzene–light petroleum (1 : 4 to 1 : 1) yielded the 2-*ethynyl*-2-*hydroxy*cyclo*hexane*-1-*one*, obtained from light petroleum as needles (0·16 g.), m. p. 50—52° (micro-hot stage), b. p. 130° (bath-temp.)/18 mm. (Found : C, 69·4; H, 7·6. $C_8H_{10}O_2$ requires C, 69·5; H, 7·3%). The partially crystalline oil A was rechromatographed in benzene–light petroleum on acid-washed alumina (4 g.). Elution with light petroleum gave an oil which on treatment with Brady's reagent yielded a 2 : 4-dinitrophenylhydrazone as a brick-red powder, m. p. 285° (decomp.) (Found : C, 41·1; H, 2·8%). Light absorption (in dioxan) : Max. 410 mμ; $\varepsilon \gg 26{,}000$ (substance only partially dissolved). Elution with mixtures of benzene and light petroleum (1 : 4 and 2 : 3) gave a further quantity (0·09 g.) of 2-ethynyl-2-hydroxy*cyclo*hexan-1-one.

*Reaction of Mercuriacetamide in Alcohols with the Alcohols* (II*a*, *b*, and *c*).—(i) The ethynylcarbinol (II*a*) (0·7 g.) was refluxed in 95% ethanol (25 c.c.) with mercuriacetamide (2·56 g.) for 6 hr. A little " Celite 545 " was added, and a stream of hydrogen sulphide passed through the suspension for 30 min. The solvent was removed under reduced pressure, and the residue repeatedly extracted with boiling ether. The combined extracts were washed with water to remove acetamide, dried ($Na_2SO_4$), and evaporated under reduced pressure to an oil (0·39 g.) which was taken up in light petroleum–benzene (3 : 1; 10 c.c.) and adsorbed on activated alumina (10 g.). The column was washed with light petroleum–benzene (2 : 1; 150 c.c.), then with light petroleum containing increasing proportions of benzene. Elution with benzene (150 c.c.) and benzene–ether (9 : 1; 300 c.c.) gave what is probably 2-*acetyl*-3-*hydroxy*cyclo*hexane*-1-spiro-2'-(1' : 3'-*dioxolan*) (IX), obtained from light petroleum as needles (105 mg.), m. p. 82° (Found : C, 60·3; H, 8·1. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%). The infra-red absorption spectrum had bands at 2·90 and 5·88 μ. When the above experiment was carried out in commercial absolute ethanol a smaller yield of (IX) was obtained.

(ii) The ethynylcarbinol (II*b*), m. p. 68° (0·52 g.), was refluxed in ethanol (20 c.c.) with mercuriacetamide (0·91 g.) for 5·5 hr. Working up in the above manner gave an oil (0·49 g.) which was taken up in light petroleum (5 c.c.)–benzene (5 c.c.) and adsorbed on activated alumina (20 g.). The column was first washed with light petroleum (50 c.c.) and eluted with the same solvent (250 c.c.), then with light petroleum containing increasing amounts of benzene, and finally with pure benzene (100 c.c.). These eluates contained the same crystalline material, which was recrystallised from light petroleum to give 2-*acetyl*-3-*ethoxy*cyclo*hexane*-1-spiro-2'-(1' : 3'-*oxathiolan*) (V; R = Et) (0·19 g.), m. p. 119·5° (Found : C, 58·9; H, 7·9; S, 13·1. $C_{12}H_{20}O_3S$ requires C, 59·0; H, 8·2; S, 13·1%). The infra-red spectrum had a band at 5·88 μ. The alcohol (II*b*) (0·5 g.) in boiling methanol (30 c.c.) with mercuriacetamide (1·75 g.) (5·5 hr.)

gave similarly 2-*acetyl*-3-*methoxy*cyclo*hexane*-1-spiro-2′-(1′ : 3′-*oxathiolan*) (V; R = Me) (0·255 g.), m. p. 138° (Found: C, 57·4; H, 7·6; S, 13·9. $C_{11}H_{18}O_3S$ requires C, 57·4; H, 7·8; S, 13·9%). The infra-red spectrum had a band at 5·90 μ.

(iii) The ethynylcarbinol (II*c*) (0·5 g.) was refluxed in ethanol (25 c.c.) with mercuriacetamide (1·55 g.) for 3·5 hr. Working up in the usual way gave an oil (0·39 g.) which was taken up in light petroleum (15 c.c.) and adsorbed on "Florex" (15 g.). Elution with light petroleum (50 c.c.) gave 2-*ethylidene*cyclo*hex*-3-*ene*-1-spiro-2′-(1′ : 3′-*dithiolan*) (VI) as an oil (0·24 g.), b. p. 150—160° (bath-temp.)/15 mm. (Found: C, 60·1; H, 6·6; S, 32·9. $C_{10}H_{14}S_2$ requires C, 60·6; H, 7·1; S, 32·9%). Light absorption (in MeOH): Max. 235 mμ (ε 8600). The infra-red spectrum had bands at 6·06 and 6·17 μ; there was no band in the 5·5 or 11 μ region. The column was eluted with a further quantity of light petroleum (50 c.c.) and with light petroleum containing increasing amounts of benzene. Elution with pure benzene (50 c.c.) gave what is probably 3-*acetoxy*-2-*acetyl*cyclo*hexane*-1-spiro-2′-(1′ : 3′-*dithiolan*) (VII), obtained from light petroleum as needles (0·06 g.), m. p. 110° (Found: C, 52·7; H, 6·5; S, 23·65. $C_{12}H_{18}O_3S_2$ requires C, 52·6; H, 6·6; S, 23·4%). The infra-red spectrum had bands at 5·76 and 5·85 μ. The same mixture was obtained when the above reaction was carried out in methanol.

2-1″-*Hydroxyethyl*-3-*methoxy*cyclo*hexane*-1-spiro-2′-(1′ : 3′-*oxathiolan*).—The spiran (V; R = Me) (0·44 g.) was reduced with lithium aluminium hydride (0·22 g.) in pure ether (30 c.c.). The oily product (0·44 g.) was taken up in light petroleum (10 c.c.) and adsorbed on alumina (8 g.). Elution with light petroleum (100 c.c.), light petroleum containing increasing amounts of benzene, benzene (50 c.c.), and benzene–ether (9 : 1; 50 c.c.) all gave the 2-1″-*hydroxyethyl*-3-*methoxy*cyclo*hexane*-1-spiro-2′-(1′ : 3′-*oxathiolan*) (130 mg.) which after recrystallisation from light petroleum had m. p. 135° (Found: C, 57·1; H, 8·6; S, 13·8. $C_{11}H_{20}O_3S$ requires C, 56·9; H, 8·6; S, 13·8%). The infra-red absorption spectrum had a band at 2·91 μ. Elution with benzene–ether (1 : 1; 100 c.c.) and ether (100 c.c.) gave a mixture of the above hydroxy-compound and an oil which was not identified. Light absorption for the mixture (in MeOH): Max. 230 and 277 mμ (ε 10,000 and 2000).

The above hydroxyethylmethoxy*cyclo*hexane-*spiro*-oxathiolan (100 mg.) was refluxed with W-2 Raney nickel (1·2 g.) in acetone (30 c.c.) for 3·5 hr. The product was an oil, the infra-red spectrum of which had bands at 2·90, 5·80, 8·22, and 8·45 μ. On treatment with Brady's reagent for 2 min. on the steam-bath it gave 2-1′-*hydroxyethyl*cyclo*hex*-2-*en*-1-*one* 2 : 4-*dinitrophenylhydrazone*, m. p. 194—196° after recrystallisation from ethyl acetate (Found: C, 52·5; H, 5·1. $C_{14}H_{16}O_5N_4$ requires C, 52·5; H, 5·0%). Light absorption (in $CHCl_3$): Max. 390 mμ (ε 31,000).

2-*Ethynyl*cyclo*hex*-3-*ene*-1-spiro-2′-(1′ : 3′-*oxathiolan*) (X).—The ethynylcarbinol (II*b*) (1·22 g.) in collidine (10 c.c.) was stirred with phosphorus oxychloride (1 c.c.) at 120—130° under nitrogen for 1·25 hr. The mixture was cooled in ice, and ether (30 c.c.) was added followed by crushed ice. The ethereal layer was separated, and the aqueous layer extracted with ether (total 100 c.c.). The combined extracts were washed with 2N-sulphuric acid (200 c.c.), sodium hydrogen carbonate solution, and water, and dried ($Na_2SO_4$). The oily product was taken up in light petroleum (15 c.c.) and adsorbed on activated alumina (36 g.). Elution with light petroleum (400 c.c.) gave the 2-*ethynyl*cyclo*hex*-3-*ene*-1-spiro-2′-(1′ : 3′-*oxathiolan*) (X), obtained from light petroleum as needles (0·49 g.), m. p. 59° (Found: C, 66·8; H, 6·7; S, 17·8. $C_{10}H_{12}OS$ requires C, 66·7; H, 6·7; S, 17·8%): no selective light absorption in the range 220—320 mμ. The infra-red spectrum had bands at 3·08, 4·76, and 6·0 μ.

2-*Ethynyl*cyclo*hex*-2-*ene*-1-spiro-2′-(1′ : 3′-*dithiolan*) (XI).—The ethynylcarbinol (II*c*) (3 g.) in collidine (25 c.c.) was stirred at 130—140° with phosphorus oxychloride under nitrogen for 1·5 hr. Working up as above gave a partially crystalline product (2·26 g.) which was dissolved in light petroleum–benzene (4 : 1; 25 c.c.) and adsorbed on activated alumina (25 g.). Elution with light petroleum (b. p. 40—60°; 250 c.c.) gave 2-*ethynyl*cyclo*hex*-2-*ene*-1-spiro-2′-(1′ : 3′-*dithiolan*) (XI) (1·62 g.), m. p. 78° after recrystallisation from light petroleum (b. p. 40—60°) (Found: C, 61·3; H, 6·0; S, 32·6. $C_{10}H_{12}S_2$ requires C, 61·3; H, 6·1; S, 32·6%). Light absorption: Max. 250 mμ (ε 7800). The infra-red spectrum had bands at 3·07 and 6·22 μ.

*Reaction of the Enynes* (X) *and* (XI) *with Methanol in the Presence of a Boron Trifluoride–Mercuric Oxide–Trichloroacetic Acid Catalyst.*—(i) The catalyst was prepared in methanol (5 c.c.) from mercuric oxide (0·6 g.), trichloroacetic acid (0·45 g.), and the boron trifluoride–ether complex (0·2 c.c.) as described by Hamlet, Henbest, and Jones (*loc. cit.*), and 0·5 c.c. of this mixture was added to the enyne (X) (0·39 g.) in methanol (5 c.c.) which was then refluxed for 5 hr. and left at room temperature overnight. The solution was poured into 2N-hydrochloric acid (50 c.c.) and extracted with ether (total 150 c.c.). The ethereal solution was washed with sodium hydrogen carbonate solution, and water, and dried ($Na_2SO_4$) and evaporated under reduced pressure to an oil which was dissolved in light petroleum (10 c.c.) and adsorbed on activated alumina (12 g.). Elution with light petroleum (200 c.c.) and light petroleum–benzene (4 : 1; 50 c.c.) gave what is probably a stereoisomer of 2-*ethynyl*-3-*methoxy*cyclo*hexane*-1-spiro-2′-(1′ : 3′-*oxathiolan*) (XII), obtained from light petroleum as needles (85 mg.), m. p. 95° (Found: C, 62·0; H, 7·4; S, 15·1. $C_{11}H_{16}O_2S$ requires C, 62·3; H, 7·6; S, 15·1%). The infra-red spectrum had bands at 3·08 and 4·76 μ. Elution with light petroleum–benzene (1 : 1; 50 c.c.), light petroleum–benzene (1 : 3; 50 c.c.), and benzene (50 c.c.) gave what is probably another *stereoisomer* of (XII), obtained from light petroleum as needles and plates (77 mg.), m. p. 118° (Found: C, 62·3; H, 7·4; S, 14·8%). The infra-red spectrum had bands at 3·11 and 4·77 μ. Elution with benzene–ether (9 : 1; 100 c.c.) gave what is probably a mixture of stereoisomers of 2-acetyl-3-methoxy*cyclo*hexane-1-*spiro*-2′-(1′ : 3′-oxathiolan) (V; R = Me) (53 mg.), which after recrystallisation from light petroleum had m. p. 110—118° (softening at *ca.* 90°) undepressed on admixture with the sample of (V; R = Me) prepared as above by the action of mercuriacetamide in methanol on (II*b*) (Found: C, 57·4; H, 7·5; S, 13·7. Calc. for $C_{11}H_{18}O_2S$: C, 57·4; H, 7·8; S, 13·9%). The infra-red spectrum had a band at 5·88 μ.

(ii) The enyne (XI) (0·3 g.) was refluxed for 5 hr. in methanol (5 c.c.) containing 0·4 c.c. of the above catalyst mixture. On cooling, the solution was added to 2N-hydrochloric acid and worked up as in (i). The oily product was taken up in light petroleum (10 c.c.) and adsorbed on activated alumina (7 g.). Elution with light petroleum (250 c.c.) gave unchanged (XI), obtained from light petroleum as needles (0·21 g.), m. p. 77°. Elution with light petroleum–benzene (3 : 1; 100 c.c.) gave an ill-defined oil, and elution with benzene–light petroleum (1 : 1; 100 c.c.) gave what is possibly 2-*acetyl*-3-*methoxy*cyclo*hexane*-1-spiro-2′-(1′ : 3′-*dithiolan*) (XIV), obtained from light petroleum (b. p. 40—60°) as needles (37 mg.), m. p. 52·5° (Found: C, 53·5; H, 7·2. $C_{11}H_{18}O_2S_2$ requires C, 53·7; H, 7·3%). The infra-red spectrum had a band at 5·89 μ.

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