23. *The Addition of Thiolacetic Acid to Ethynylcarbinols and the Conversion of the Adducts into Aldols and αβ-Unsaturated Aldehydes.*

By Henry Bader.

"Abnormal" addition (cf. *J.*, 1949, 619) of thiolacetic acid to α- and β-ethynylcarbinols produces hydroxyalkenyl thiolacetates or alkadienyl thiolacetates ($\mathrm{R{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}SAc}$) and diacetylthioalkanols. The monoadducts are converted by the usual carbonyl reagents into derivatives of the corresponding aldols or αβ-unsaturated aldehydes, while under the same conditions the dienyl thiolacetates yield the derivatives of αβ-unsaturated aldehydes.

Bader, Cross, Heilbron, and Jones (*J.*, 1949, 619; cf. Behringer, *Annalen*, 1949, **564**, 219) described the addition of thiolacetic acid to monosubstituted acetylenic hydrocarbons alone and under the influence of organic peroxides or irradiation with ultraviolet light. The addition was shown to proceed "abnormally," yielding mono- and di-adducts (I) and (II). The monoadducts were converted by the usual carbonyl reagents into the derivatives of the corresponding saturated aldehydes, while the diadducts under similar conditions yielded 1 : 2-dithiols. Simple adducts of thiolacetic acid and conjugated vinylacetylenes could not be obtained. Consequently, in pursuit of an alternative route to αβ-unsaturated aldehydes, attention was turned to the addition reaction with the readily available ethynylcarbinols. Rearrangement of the latter by formic acid (Rupe and

$$\underset{\text{(I)}}{\mathrm{R{\cdot}CH{:}CH{\cdot}SAc}} + \mathrm{2NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2} \longrightarrow \mathrm{R{\cdot}CH_2{\cdot}CH{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 + Ac{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2 + H_2S}$$

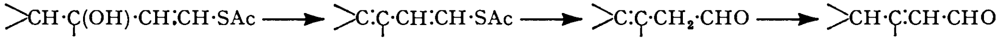
$$\text{(II)}\quad \mathrm{R{\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc} \longrightarrow \mathrm{R{\cdot}CH(SH){\cdot}CH_2{\cdot}SH}$$

Kambli, *Helv. Chim. Acta*, 1926, **9**, 672; 1928, **11**, 449; Rupe and Kuenzy, *ibid.*, 1931, **14**, 708), originally claimed to yield αβ-unsaturated aldehydes, was finally proved to give mostly unsaturated ketones with only traces of the aldehydes (Chanley, *J. Amer. Chem. Soc.*, 1948, **70**, 244; see also McGregor, *ibid.*, p. 3953, and Bergmann, *ibid.*, 1951, **73**, 1218, for special cases where appreciable conversion into the aldehyde did occur). A more indirect, but for the time being the only practical, route for the conversion of ethynylcarbinols into αβ-unsaturated aldehydes is the sequence of reactions employed by Dimroth (*Ber.*, 1938, **71**, 1333, 1346), which however is limited to tertiary α-ethynylcarbinols.

In the present approach a monoadduct resulting from the addition of thiolacetic acid to an α-ethynylcarbinol is hydrolysed to the corresponding aldol which can be easily

$$>\mathrm{C(OH){\cdot}C{:}CH} \longrightarrow >\mathrm{C(OH){\cdot}CH{:}CH{\cdot}SAc} \longrightarrow >\mathrm{C(OH){\cdot}CH_2{\cdot}CHO} \longrightarrow >\mathrm{C{:}CH{\cdot}CHO}$$

dehydrated to an αβ-unsaturated aldehyde; the adduct may be dehydrated before hydrolysis and the resulting βγ-unsaturated aldehyde rearranged to the αβ-isomer. Unlike the previous attempts, the present method is applicable to primary and secondary, as well as to the tertiary, alcohols.



$$>\mathrm{CH{\cdot}\underset{|}{C}(OH){\cdot}CH{:}CH{\cdot}SAc} \longrightarrow >\mathrm{C{:}\underset{|}{C}{\cdot}CH{:}CH{\cdot}SAc} \longrightarrow >\mathrm{C{:}\underset{|}{C}{\cdot}CH_2{\cdot}CHO} \longrightarrow >\mathrm{CH{\cdot}\underset{|}{C}{:}CH{\cdot}CHO}$$

Since thiolacetic acid and hex-1-yn-3-ol at first gave small yields of adduct, the effects of various factors were studied in detail (>30 experiments). Occasionally experiments under apparently identical conditions gave different results, but some broad generalisations may be made. In all these experiments the yield of the monoadduct was of primary interest, so equimolecular proportions of the reactants were used; in every case practically all the carbinol not converted into adducts was recovered. In general, a low temperature (0°) during the addition favoured formation of the monoadduct. Rapid addition, allowing the thermal effect, favoured formation of the diadduct. Irradiation by ultraviolet light during the addition increased the yield of the monoadducts (from 32·5 to 51%) at low temperature, or of the diadduct (from 14·5 to 22·5%) at the reflux temperature. Addition of as little as 1 mole % of ascaridole increased the yield of the monoadduct (from 34 to 64%) at room temperature; but benzoyl peroxide had no effect though it catalysed the addition of thiolacetic acid to phenylacetylene (Bader *et al.*, *loc. cit.*) [Cunneen (*J.*, 1947, **36**, 134), while this work was in progress, reported similar difference in the action of the two peroxides in the addition of thiolacetic acid to olefins].

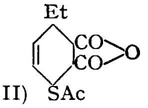
The two products from hex-1-yn-3-ol were identified as 3-hydroxyhex-1-enyl thiolacetate (III) and 1 : 2-diacetylthiohexan-3-ol (IV). Fission of the former adduct with semicarbazide acetate gave the semicarbazone of 3-hydroxyhexanal (V) rather than the derivative of the αβ-unsaturated aldehyde.

$C_3H_7\cdot CH(OH)\cdot CH{:}CH\cdot SAc$ (III) $C_3H_7\cdot CH(OH)\cdot CH(SAc)\cdot CH_2\cdot SAc$ (IV) $C_3H_7\cdot CH(OH)\cdot CH_2\cdot CHO$ (V)

In attempts to dehydrate the thiolacetate (III), it was recovered unchanged after pyrolysis at 350°, potassium hydrogen sulphate at 100° caused no dehydration, and oxalic acid gave only 6—10% of an impure product. Finally, shaking the ester in benzene with phosphoric oxide at room temperature gave a mixture which on fractionation yielded *ca.* 30% of hexa-1 : 3-dienyl thiolacetate (VII) exhibiting the expected light absorption with a maximum at 2690 Å, together with recovered carbinol and a polymer. The dienyl thiolacetate (VII) was characterised by a maleic anhydride adduct which showed maximal ultraviolet absorption at 2280 Å, in agreement with the structure (VIII).

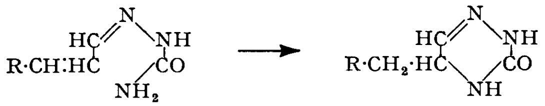
$C_2H_5\cdot CH{:}CH\cdot CH{:}CH\cdot SAc \longrightarrow C_2H_5\cdot CH{:}CH\cdot CH_2\cdot CHO \longrightarrow C_3H_7\cdot CH{:}CH\cdot CHO$

(VII) (VI)



(VIII)

When the dienyl thiolacetate (VII) was treated with cold aqueous-ethanolic semicarbazide acetate, an immediate crystalline precipitate slowly redissolved. Separation of the solid afforded 20% of the semicarbazone of hex-2-enal (VI); redissolution of this semicarbazone in its mother-liquor agrees with an observation by Delaby [*Ann. Chim.* (*France*), 1923, **20**, 211] that the semicarbazones of crotonaldehyde and pent-2-enal redissolve in their mother-liquors owing to ring closure to ketotriazines.



With 1-phenylprop-2-yn-1-ol there were greater difficulties in preparation of the adducts: fission of the monoadduct occurred very readily and was accompanied by dehydration. The yields of monoadduct never exceeded 25%, and of diadduct 18%. Furthermore, separation of products was tedious owing to their high and similar boiling points. Although 3-hydroxy-3-phenylprop-1-enyl thiolacetate (IX) was obtained

(IX) $Ph\cdot CH(OH)\cdot CH{:}CH\cdot SAc$ $Ph\cdot CH(OH)\cdot CH(SAc)\cdot CH_2\cdot SAc$ (X)

pure, the diadduct (X) was not, though its light absorption properties leave no doubt as to its constitution. The effect of the conditions of addition was not the same as for hex-1-yn-3-ol: *e.g.*, addition at a higher temperature increased the yield of the monoadduct, irradiation in the cold favoured the formation of both the di- and the mono-adduct, and addition of ascaridole in the cold increased the yield of the diadduct.

Treatment of the monothiolacetate (IX) with a solution of semicarbazide acetate at room temperature gave instantaneously a precipitate of cinnamaldehyde semicarbazone by fission and simultaneous dehydration. The low yield (40%) of the semicarbazone was undoubtedly due to presence of a small amount of impurities in the thiolacetate employed, since in general the yields of the isolated derivatives were markedly decreased by even slight impurities in the thiolacetates.

For a study of tertiary α-ethynylcarbinols (cf. Rupe and Dimroth, *locc. cit.*), ethynyl*cyclo*hexanol was chosen. Addition of thiolacetic acid in the presence of ascaridole gave a 55—60% yield of crude product, which on slow distillation was dehydrated to a mixture of isomers of 2-*cyclo*hex-1′-enylvinyl thiolacetate (XII), from which one form was isolated as a solid, m. p. 35·5—36·5°, exhibiting the expected light absorption. Attempts to isolate the alcohol (XI) failed, but 4% of the impure diadduct was obtained; this was formulated as (XIII) on the basis of its ultraviolet absorption (see Table).

	$\lambda_{\max.}$ (Å)	ε
$\mathrm{C_3H_7{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}SAc}$	2510	8000
$\mathrm{C_6H_5{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}SAc}$	2500	6000
$\mathrm{CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH{:}CH{\cdot}SAc}$	2280	4000
	2520 2560	7000
$\mathrm{CH_3{\cdot}CH(OAc){\cdot}CH_2{\cdot}CH{:}CH{\cdot}SAc}$	2510	7000
$\mathrm{C_2H_5{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}SAc}$	2690	14,500
$\mathrm{C_6H_9{\cdot}CH{:}CH{\cdot}SAc}$, m. p. 35·5—36·5°	2700	10,500
	2780	10,000
$\mathrm{C_6H_9{\cdot}CH{:}CH{\cdot}SAc}$, liquid	2690	10,500

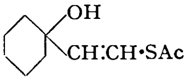
	$\lambda_{\max.}$ (Å)	ε
$\mathrm{C_3H_7{\cdot}CH(OH){\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc}$	2280	7500
$\mathrm{C_6H_5{\cdot}CH(OH){\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc}$	2400	11,500
$\mathrm{HO{\cdot}C_6H_{10}{\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc}$	2300	8500
	2380 *	8000
$\mathrm{CH_3{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc}$	2330	7500
	2420 *	6500
$\mathrm{CH_3{\cdot}CH(SAc){\cdot}CH_2{\cdot}CH(OH){\cdot}C{\vdots}CH}$	2300	3500
	2370 *	3500
Adduct (VIII)	2280	5000
Adduct (XIV)	2330	7000

* Inflexion.

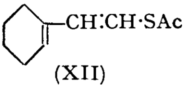
For other compounds containing the chromophores SAc and CH:CH·SAc see Bader, Cross, Heilbron, and Jones (*loc. cit.*).

The dienyl thiolacetate (XII) was also prepared in good yield by dehydration of the crude addition product with anhydrous oxalic acid at 90°, again as a mixture. The ratio of the solid and the liquid product varied but the light absorptions of the two were so similar (see Table) that the oil must be a mixture of geometrical isomers.

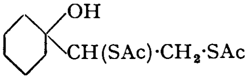
The solid thiolacetate was characterised by a maleic anhydride adduct (XIV) exhibiting an absorption maximum at 2330 Å.



(XI)



(XII)



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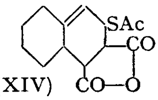


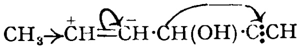
(XIV)

By the action of semicarbazide on the monothiolacetate (XII) a derivative, m. p. 167°, was obtained in 78% yield. Its absorption maxima indicated that it was a constant-melting 2 : 3 mixture of the semicarbazones of *cyclo*hexylideneacetaldehyde and *cyclo*-hexenylacetaldehyde.

Thiolacetic acid added readily to pent-4-yn-2-ol and gave only 4-hydroxypent-1-enyl thiolacetate (XV; R = H), formed in 44% yield when the reaction was carried out under controlled conditions at 0° and in absence of catalysts. Even under vigorous conditions only the monoadduct was formed, its yield being thus raised to 60%. The thiolacetate (XV; R = H) reacted easily with semicarbazide acetate, but the expected semicarbazone of 4-hydroxypentanal (XVI; R = H) could not be isolated, as its solubility was very similar to that of the by-product, β-acetylsemicarbazide, a difficulty experienced to some degree with all the hydroxysemicarbazones. However, the diacetate (XV; R = Ac) gave the semicarbazone of 4-acetoxypentan-1-al (XVI; R = Ac) on treatment with semicarbazide acetate.

$$\text{(XV)}\quad \mathrm{CH_3{\cdot}CH(OR){\cdot}CH_2{\cdot}CH{:}CH{\cdot}SAc} \longrightarrow \mathrm{CH_3{\cdot}CH(OR){\cdot}CH_2{\cdot}CH_2{\cdot}CHO}\quad \text{(XVI)}$$

The complexity of the addition of thiols to vinylacetylenes was referred to above. However, it was of interest to effect the reaction with hex-4-en-1-yn-3-ol (XVII), in which the double and the triple bond are not conjugated and thus to compare directly the reactivities of the two groups. The addition occurred in comparatively small yields and under all conditions tried only two of the possible products were obtained, which on the basis of analysis were shown to be a mono- and a di-adduct. The monoadduct showed light absorption (see Table) characteristic of unconjugated thiolacetates (for a discussion of the absorption of thiolacetates see Bader *et al.*, *loc. cit.*) and did not evolve hydrogen sulphide on treatment with ethanolic semicarbazide acetate (which can be considered as a test for vinyl thiolacetates) and so is formulated as (XVIII), formed by addition of thiolacetic acid to the double bond. The suggested orientation of the addition is based on the general observation that, in additions to unsymmetrical unsaturated systems, radicals attack preferentially at points of high differential electron density with respect to the unsubstituted ethylene (cf. Barton, *Nature*, 1948, **162**, 182). In the alcohol (XVII) $C_{(5)}$ has a higher differential electron density than $C_{(4)}$ and would be expected to be attacked by the thiol radical.

(XVII) 

$CH_3{\rightarrow}\overset{+}{C}H{=}\overset{-}{C}H{\cdot}CH(OH){\cdot}C{:}CH$

$CH_3{\cdot}CH(SAc){\cdot}CH_2{\cdot}CH(OH){\cdot}C{:}CH$ (XVIII)

$CH_3{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc$ (XIX)

The absorption of the diadduct (see Table), corresponding to two saturated thiolacetate groups, is compatible only with the structure (XIX).

EXPERIMENTAL

Light absorptions were determined for EtOH solutions.

Addition of Thiolacetic Acid to Hex-1-*yn*-3-*ol*.—(*a*) To the alcohol (9·8 g., 0·1 mol.; Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 45), cooled in ice and salt, thiolacetic acid (7·6 g., 0·1 mol.) was added dropwise during 50 min. with shaking. The mixture was heated for 1 hr. on the steam-bath, unchanged thiolacetic acid removed under reduced pressure, and the residue fractionated, yielding (i) recovered hex-1-yn-3-ol (4·7 g. 48%), b. p. 45°/13 mm., (ii) 3-*hydroxyhex*-1-*enyl thiolacetate* (6·0 g., 34·5%), a slightly yellowish oil of unpleasant odour, b. p. 76°/5 × 10^{-4} mm., n_D^{16} 1·5050 (Found: S, 18·45. $C_8H_{14}O_2S$ requires S, 18·4%) (light absorption: see Table) (even in great dilution inhalation of the vapours caused violent headaches), and (iii) 1 : 2-*diacetylthiohexan*-3-*ol* (1·0 g., 4%) as a viscous yellowish oil of unpleasant odour, b. p. 80°/10^{-3} mm., n_D^{20} 1·5208 (Found: S, 25·65. $C_{10}H_{18}O_3S_2$ requires S, 25·6%) (light absorption: see Table).

(*b*) When thiolacetic acid (15·2 g., 0·2 mol.) was added rapidly to hex-1-yn-3-ol (19·6 g., 0·2 mol.) a vigorous reaction ensued. After this has subsided, refluxing was continued for 2 hr. Distillation of the product gave recovered hexynol (7·3 g., 37%), the monothiolacetate (8·0 g., 23%), and the di(thiolacetate) (7·2 g., 14·5%).

(*c*) To hex-1-yn-3-ol (4·9 g., 0·05 mol.) and ascaridole (0·05 g., 0·00025 mol.), cooled in ice, a mixture of thiolacetic acid (3·8 g., 0·05 mol.) and ascaridole (0·05 g.) was added during 10 min. After 26 hr. at room temperature distillation yielded the recovered acetylene (1·5 g., 31%) and the monothiolacetate (5·85 g., 67%).

(*d*) A solution of thiolacetic acid (3·8 g.) in ether (30 c.c.) was added dropwise during 20 min. to hex-1-yn-3-ol (4·9 g.) contained in a silica tube provided with an internal glass spiral through which cold water was circulated, and exposed at about 15 cm. to a mercury-vapour lamp during the addition and for a further 3 hr. The ether was removed and distillation gave recovered hexynol (1·95 g., 40%) and the monothiolacetate (4·45 g., 51%).

(*e*) As in (*d*) but without ether. After the addition, the mixture was refluxed for 7½ hr. during further irradiation. Distillation gave recovered hexynol (0·5 g., 10%), the monoadduct (0·5 g., 6%), and the diadduct (2·8 g., 22·5%).

Conversion of 3-*Hydroxyhex*-1-*enyl Thiolacetate* (III) *into the Semicarbazone of* 3-*Hydroxyhexanal* (V).—To a solution of semicarbazide acetate (from the hydrochloride, 1·2 g., in 80% alcohol, 6·5 c.c.), 3-hydroxyhex-1-enyl thiolacetate (0·87 g.) was added and the mixture was warmed to 50° and set aside at room temperature for 30 hr. The yellow oil obtained by evaporation under reduced pressure crystallised in contact with ether (2 c.c.). It was extracted with hot chloroform, and the residue on crystallisation from alcohol gave 3-*hydroxyhexanal semicarbazone* (0·5 g., 60%), prisms, decomp. 149° (Found: N, 24·55. $C_7H_{15}O_2N_3$ requires N, 24·25%), having no intense light absorption above 2150 Å.

Hexa-1 : 3-*dienyl Thiolacetate* (VII).—Phosphoric oxide (3·5 g.) was added to a solution of 3-hydroxyhex-1-enyl thiolacetate (2·9 g.) in dry benzene (40 c.c.). After 19 hours' shaking in nitrogen at 20° the mixture was treated with water. The aqueous layer was extracted with benzene, and the combined benzene extracts were washed with sodium hydrogen carbonate solution and dried. Fractionation of the residue obtained on evaporation yielded slightly impure hexa-1 : 3-dienyl thiolacetate (0·73 g., 30%), b. p. 66°/10^{-3} mm., $n_D^{28·5}$ 1·5330, having a faintly unpleasant odour (Found: S, 19·25. Calc. for $C_8H_{12}OS$: S, 20·5%) (light absorption: see Table), recovered alcohol (0·55 g., 19%), b. p. 78°/10^{-3} mm., and a liquid (0·60 g., 23%), b. p. 102—109°/10^{-3} mm., $n_D^{28·5}$ 1·5228.

The diene thiolacetate (0·31 g.) and maleic anhydride (0·20 g.) were refluxed in benzene (0·5 c.c.) for 15 min. After 3 days at 0° the *adduct* (VIII) (0·06 g.), m. p. 108—109·5°, separated as prisms. It crystallised from aqueous ethanol in plates, m. p. 113° (Found : S, 12·6. $C_{12}H_{14}O_4S$ requires S, 12·6%) (light absorption : see Table).

*Conversion of Hexa-*1 : 3*-dienyl Thiolacetate* (VII) *into Hex-*2*-enal Semicarbazone.*—The thiolacetate (0·78 g.) was added to a solution of semicarbazide acetate (from the hydrochloride, 1·2 g.) in 90% ethanol (13 c.c.), causing a precipitation of fine crystals. After 20 min. at room temperature the solid was separated, then dried *in vacuo*. Hex-2-enal semicarbazone (0·155 g., 20%), m. p. 172—174°, crystallised from 1 : 1 aqueous ethanol (1 c.c.) in needles, m. p. 174° [Kroper and Pinkernelle, *Ber.*, 1934, **67**, 269, give m. p. 173°; Delaby and Guillot, *Bull. Soc. chim.* (*France*), 1933, **53**, 30, give m. p. 175—176°].

Addition of Thiolacetic Acid to 1*-Phenylprop-*2*-yn-*1*-ol.*—(*a*) Thiolacetic acid (7·6 g., 0·1 mol.) in ether (20 c.c.) was added during 15 min. to the propynol (13·2 g., 0·1 mol.; Jones and McCombie, *J.*, 1942, 733) contained in an internally cooled silica tube, exposed to ultraviolet irradiation during the addition and for a further 3 hr. Then the mixture was set aside for 7 days at 20°. Fractionation of the residue gave : (i) recovered phenylpropynol (4·95 g., 37·5%), b. p. 74—76°/10^{-3} mm.; (ii) 3*-hydroxy-*3*-phenylprop-*1*-enyl thiolacetate* (4·95 g., 23·8%), a yellow, viscous oil with a sweet, nauseating odour, b. p. 120—122°/10^{-3} mm., $n_D^{30\cdot5}$ 1·5670—1·5750, which after two redistillations had b. p. 115°/10^{-3} mm., n_D^{20} 1·5730 (Found : S, 15·35. $C_{11}H_{12}O_2S$ requires S, 15·4%) ; and (iii) 1 : 2*-diacetylthio-*3*-phenylpropan-*3*-ol* (3·05 g., 10·7%) as a reddish, viscous oil with nauseating odour, b. p. 123—128°/10^{-3} mm., n_D^{20} 1·5857—1·5904 (Found : S, 21·0. $C_{13}H_{16}O_3S_2$ requires S, 22·5%). Light absorption data for both compounds are given in the Table.

(*b*) The following yields were obtained under other conditions :

	Monoadduct (%)	Diadduct (%)
Slow addition at 0°, then reflux	3	5
Rapid addition, then reflux	17	0
With 1% of ascaridole	6	18

Conversion of 3*-Hydroxy-*3*-phenylprop-*1*-enyl Thiolacetate* (IX) *into Cinnamaldehyde Semicarbazone.*—The thiolacetate (1·04 g.) was added to a solution of semicarbazide acetate (from the hydrochloride, 1·2 g.) in 85% ethanol (7 c.c.). Hydrogen sulphide was at once evolved at room temperature and a crystalline precipitate formed. After 1 day at 20° the semicarbazone (0·39 g., 40%) was isolated as plates, which after recrystallisation from ethanol melted at 207°, undepressed on admixture with cinnamaldehyde semicarbazone (m. p. 208°).

Addition of Thiolacetic Acid to 1*-Ethynyl*cyclo*hexanol.*—A mixture of thiolacetic acid (7·6 g., 0·1 mol.) and ascaridole (0·1 g.) was added dropwise during 30 min. with stirring to 1-ethynyl*cyclo*hexanol (12·4 g., 0·1 mol.) and ascaridole (0·1 g.), cooled in ice. After 2 days at 20° the mixture was neutralised with a saturated solution of sodium hydrogen carbonate and extracted several times with ether. Isolation in the usual manner and distillation gave recovered ethynyl*cyclo*hexanol (3·7 g., 30%), b. p. 69—72°/15 mm., (ii) a colourless liquid with a pleasant odour, b. p. 95—122°/10^{-4} mm., n_D^{22} 1·5328—1·5390 (a mixture of a monoadduct and its dehydration product) (10·3 g., *ca.* 57%), and impure 1-(1 : 2-diacetylthioethyl)*cyclo*hexanol (XIII) (1·1 g., 4%), a colourless liquid with a pleasant odour, b. p. 95°/5 × 10^{-3} mm., n_D^{18} 1·5460 (Found : S, 21·6. $C_{12}H_{20}O_3S_2$ requires S, 23·6%). This product was not obtained pure even after repeated distillation. For light absorption, see Table.

Dehydration. (*a*) The crude monoadduct (16·15 g.) was heated at 95° for 2 hr. at 15 mm. in presence of anhydrous oxalic acid (16·0 g.) activated by entrainment distillation with carbon tetrachloride immediately before use. Water was added and the product isolated by use of light petroleum (b. p. 40—60°). Removal of the solvent and distillation gave an oil, b. p. 85—89°/5 × 10^{-3} mm., n_D^{17} 1·5700 (8·6 g., 55%), which solidified almost completely. Recrystallisation from light petroleum (b. p. 40—60°) at −30° gave 2-cyclo*hex-*1′*-enylvinyl thiolacetate* (5·55 g.) as colourless prismatic needles, m. p. 35·5—36·5°, which very readily darkened and liquefied in air and light (Found : S, 17·45. $C_{10}H_{14}OS$ requires S, 17·6%). Absorption max. at 2700 and 2780 Å (ε 10,500 and 10,000 respectively). After removal of the solid, the residual oil distilled at 85°/0·05 mm. (n_D^{19} 1·5575), but did not yield any more solid : its absorption max. was at 2690 Å (ε 10,400). The overall yield of the isomeric mixture, based on ethynyl*cyclo*hexanol, was 31%.

(*b*) The crude monoadduct (3·95 g.) was twice slowly redistilled through a 10-cm. Vigreux column. A homogeneous liquid was obtained, having b. p. 79°/10^{-3} mm., n_D^{22} 1·5729 (3·75 g., 95%), which in ice and salt solidified partly, giving a mixture of isomers as in (*a*).

The solid diene thiolacetate (0·91 g.) and maleic anhydride (0·49 g.) were refluxed for 15 min.

in benzene (0·5 c.c.). After 24 hr. at 0° a brown solid was deposited. It was extracted with hot *cyclo*hexane and the extract decolorised over charcoal and kept at 0° for 12 hr. 3-*Acetylthio*-1 : 2 : 3 : 5 : 6 : 7 : 8 : 9-*octahydronaphthalene*-1 : 2-*dicarboxylic anhydride* (XIV) (0·445 g., 32%) separated as needles, m. p. 103—103·5° (Found : C, 60·0; H, 5·75; S, 11·2. $C_{14}H_{16}O_4S$ requires C, 60·0; H, 5·75; S, 11·45%) (light absorption, see Table).

Conversion of 2-cyclo*Hex*-1′-*enylvinyl Thiolacetate* (XII) *into* cyclo*Hexenylacetaldehyde and* cyclo*Hexylideneacetaldehyde Semicarbazones.*—The thiolacetate (0·91 g.) was heated under reflux for 2½ hr. with ethanolic semicarbazide acetate (from the hydrochloride, 1·2 g.). By slow addition of water with simultaneous trituration a solid mixture was precipitated (0·71 g., 78%; m. p. 157—158°). Recrystallisation from water gave the mixed semicarbazones as needles, m. p. 167° (Found : C, 60·1; H, 8·7; N, 22·85. Calc. for $C_9H_{15}ON_3$: C, 59·7; H, 8·3; N, 23·2%). The absorption max. were at 2290 and 2720 Å (ε 10,900 and 11,300 respectively), indicating about 60% of *cyclo*hexenylacetaldehyde and 40% of *cyclo*hexylideneacetaldehyde semicarbazones [Aldersley and Burkhardt (*loc. cit.*) reported maximum at 2720 Å (ε 28,000); Dimroth (*loc. cit.*) gave 2740 Å (ε 32,300); Chanley (*loc. cit.*) gave 2690 Å (ε 33,800)].

Addition of Thiolacetic Acid to Pent-4-*yn*-2-*ol.*—(*a*) When thiolacetic acid (15·2 g., 0·2 mol.) was quickly added to a mixture of pent-4-yn-2-ol (16·6 g., 0·2 mol.) (Haynes and Jones, *J.*, 1946, 956) and ascaridole (0·34 g., 0·002 mol.) an extremely violent reaction ensued after an induction period (3—5 min.). After the mixture had boiled, the refluxing was continued for another 3 hr. The unchanged thiolacetic acid was then removed under reduced pressure and the residue fractionated, yielding recovered pentynol (5·8 g., 35%), b. p. 52°/27 mm., and 4-*hydroxypent*-1-*enyl thiolacetate* (19·0 g., 60%), a colourless liquid with a faint sweet odour, b. p. 76°/5 × 10^{-4} mm., $n_{\rm D}^{22\cdot5}$ 1·5158 (Found : S, 19·75. $C_7H_{12}O_2S$ requires S, 20·0%) (light absorption, see Table).

(*b*) Under the same conditions but in absence of ascaridole a yield of 44% of the monoadduct was obtained with recovery of 39% of the acetylene.

4-*Acetoxypent*-1-*enyl Thiolacetate* (XV; R = Ac).—To a mixture of 4-hydroxypent-1-enyl thiolacetate (15·9 g.) and pyridine (9·2 c.c.), cooled in ice and salt, acetic anhydride (9·5 c.c.) was added and the mixture kept at 20° for 60 hr. Water (100 c.c.) and ether (100 c.c.) were then added, and the product isolated in the usual manner. Distillation gave 4-*acetoxypent*-1-*enyl thiolacetate* (18·7 g., 93%), a colourless liquid with a sweet fruity smell, b. p. 83°/0·05 mm., $n_{\rm D}^{19\cdot5}$ 1·4910 (Found : C, 53·55; H, 7·35; S, 16·3. $C_9H_{14}O_3S$ requires C, 53·45; H, 7·0; S, 15·9%) (light absorption, see Table).

Conversion of 4-*Acetoxypent*-1-*enyl Thiolacetate into* 4-*Acetoxypentan*-1-*al Semicarbazone* (cf. XVI; R = Ac).—The diacetate (1·0 g., 0·005 mol.) was refluxed for 13 hr. with semicarbazide acetate (from the hydrochloride, 1·2 g., 0·011 mol.) in 90% ethanol (13 c.c.). Evaporation under reduced pressure left a gum which solidified on prolonged trituration with ether and was then extracted with hot benzene. To the partly evaporated extract light petroleum (b. p. 40—60°) was added until precipitation commenced. At 0° the *semicarbazone* (0·28 g., 28%) separated in prisms, m. p. 86·5° (Found : C, 47·9; H, 7·65; N, 20·6. $C_8H_{15}O_3N_3$ requires C, 47·75; H, 7·5; N, 20·9%).

Addition of Thiolacetic Acid to Hex-4-*en*-1-*yn*-3-*ol.*—The alcohol (9·6 g., 0·1 mol.) (Heilbron, Jones, and Weedon, *J.*, 1945, 81) was treated with thiolacetic acid (7·6 g., 0·1 mol.), added during 20—30 min. at 0° (see Table below), and the resultant solution was kept for 24 hr. at 20°. Fractionation of the product gave recovered hexenynol, b. p. 60—61°/15 mm., 3-*hydroxy*-1-*methylpent*-4-*ynyl thiolacetate* (XVIII), b. p. 67°/10^{-4} mm., $n_{\rm D}^{26\cdot5}$ 1·5007 (Found : S, 18·8. $C_8H_{12}O_2S$ requires S, 18·6%), and 1 : 2-*diacetylthiohex*-4-*en*-3-*ol* (XIX), a mobile liquid with a nauseating odour, b. p. 100°/10^{-4} mm., $n_{\rm D}^{23\cdot5}$ 1·5407 (Found : S, 25·45. $C_{10}H_{16}O_3S_2$ requires S, 25·8%). Light absorption data for both compounds are given in the Table. The yields obtained under varied conditions are :

	Monoadduct (%)	Diadduct (%)
No catalyst	6	6
With 1% of ascaridole	25	11
No catalyst; ultraviolet irradiation	12	13·5

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