132. *Researches on Acetylenic Compounds. Part XVIII. The Addition of Thiolacetic Acid to Acetylenic Hydrocarbons. The Conversion of Monosubstituted Acetylenes into Aldehydes and 1 : 2-Dithiols.*

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Hitherto, methyl ketones or their derivatives have invariably resulted from hydration reactions with monosubstituted acetylenes. A method of converting such acetylenes into aldehydes has now been discovered.

When thiolacetic acid reacts with monosubstituted acetylenes, either alone or under the influence of organic peroxides or irradiation with ultra-violet light, mono- and di-adducts are produced by "abnormal" addition reactions. The mono-adducts, on treatment with the usual carbonyl reagents, are converted into derivatives of the corresponding aldehydes, while, under rather more acidic conditions, the di-adducts yield 1 : 2-dithiols.

Light-absorption data for the $C{=}C{\cdot}S{\cdot}CO{\cdot}CH_3$ chromophore are recorded for the first time; they throw further light on the chromolatory properties of the sulphur atom.

Although the hydration of monosubstituted acetylenes has been effected in a variety of ways, particularly by employing sulphuric acid with mercuric sulphate as catalyst, addition of water has always been found to occur in the "normal" manner, *i.e.*, according to Markownikoff's rule, leading to the formation of methyl ketones and not aldehydes :

$$R{-}C{\equiv}CH \xrightarrow{H_2O} R{-}CO{-}CH_3$$

Other addenda, such as alcohols and carboxylic acids, add on readily under the influence of the mercuric oxide–boron trifluoride catalyst of Hennion and Nieuwland (for summary see Spring, *Ann. Reports*, 1942, **39**, 131) with production of derivatives of methyl ketones. Only in the case of hydrogen bromide has "abnormal" addition been observed (for summary see Mayo and Walling, *Chem. Reviews*, 1940, **27**, 351) :

$$R{-}C{\equiv}CH \xrightarrow[\text{peroxides}]{HBr} R{-}CH{=}CHBr$$

but the 1-bromoalkenes so produced cannot readily be converted into aldehydes.

The value of acetylenic compounds in organic synthesis would clearly be enormously enhanced if methods of converting monosubstituted acetylenes into aldehydes or aldehydic derivatives could be found. With this object we have been studying addition reactions with thiols of various types, since, from what is known of the behaviour of olefins with such addenda, there was every prospect that "abnormal" reactions could be induced under the influence of peroxides or irradiation. (The literature on the addition of thiols to olefins has been reviewed recently by Cunneen, *J.*, 1947, 36, 134.) The only mention of the reaction of substituted acetylenes with thiols is by Kohler and Potter (*J. Amer. Chem. Soc.*, 1935, **57**, 1316) who added thio-*p*-cresol to phenylacetylene and described, without comment, the *cis*- and *trans*-forms of the "abnormal" adduct.

In trial experiments with hex-1-yne and a variety of thiols we obtained the most promising results with thiolacetic acid. The reaction between this substance and olefins has been shown to proceed "abnormally" (Holmberg, *Arkiv Kemi, Min. Geol.*, 1938, **12**, *B*, No. 47; Holmberg and Schjånberg, *ibid.*, 1940, **14**, *A*, No. 7; Ipatieff and Friedmann, *J. Amer. Chem. Soc.*, 1939, **61**, 71), and, while our work was in progress, Cunneen (*loc. cit.*) reported a detailed study of additions of this type. He observed that the activity of thiols in addition reactions with olefins follows the order of their acidities, *i.e.*, thiolacetic acid reacts more readily than thiophenols and thiols, and he also investigated the catalytic influence of irradiation and of peroxides such as ascaridole.

Thiolacetic acid readily undergoes addition reactions with monosubstituted acetylenic hydrocarbons; mono- and di-adducts have been isolated, usually in reasonable yields. In some cases the yields can be increased by ultra-violet irradiation or by addition of peroxides such as ascaridole or benzoyl peroxide. It has been found possible to convert the mono-adducts into derivatives of the corresponding aldehydes; the di-adducts lead to 1 : 2-dithiols.

A vigorous reaction occurs when thiolacetic acid is added to an equimolecular amount of hex-1-yne, and by fractional distillation of the mixture, a mono- and a di-adduct can be isolated. The latter can be prepared by heating the mono-adduct with thiolacetic acid. By employing ascaridole as a catalyst, slight improvements in yields are observed, but the advantage of this procedure lies mainly in the improved reproducibility of the experiments.

Various methods have been employed in attempts to prove the structure of the mono-adduct. Ozonolysis was unsatisfactory, as it led to complex oxidation products, and the thiolacetate was found to be stable towards alkalis and dilute acids. However, a method originally used by Sen (*J. Indian Chem. Soc.*, 1936, **13**, 268) to investigate *cyclo*hexenyl thiolacetate was found to be eminently suited to our purpose. Sen treated his thiolacetate with phenylhydrazine, and obtained the phenylhydrazone of *cyclo*hexanone together with acetylphenylhydrazine, hydrogen sulphide being evolved. When the mono-adduct from hex-1-yne was heated with 2 : 4-dinitrophenylhydrazine sulphate in alcoholic solution, hydrogen sulphide was evolved and the 2 : 4-dinitrophenylhydrazone of hexoic aldehyde was formed. This is clear evidence that the mono-adduct must be *hex-1-enyl thiolacetate* (I), as the only conceivable alternative structure would be expected to lead to the derivative of methyl butyl ketone. When semicarbazide acetate was used for the hydrolysis, the semicarbazone of hexoic aldehyde (III) was isolated in almost 60% yield, together with acetylsemicarbazide (II).

$$\underset{\text{(I.)}}{C_4H_9{\cdot}CH{:}CH{\cdot}S{\cdot}CO{\cdot}CH_3} + NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2 \longrightarrow [C_4H_9{\cdot}CH{:}CH{\cdot}SH] + \underset{\text{(II.)}}{CH_3{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2}$$

$$[C_4H_9{\cdot}CH_2{\cdot}CHS] + NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2 \longrightarrow \underset{\text{(III.)}}{C_4H_9{\cdot}CH_2{\cdot}CH{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2} + H_2S$$

When the di-adduct was treated with the usual carbonyl reagents no appreciable evolution of hydrogen sulphide was observed, and no crystalline derivatives, such as would be expected from a di-adduct of the thioacetal type (IV), were formed. After treatment with semicarbazide

$$\text{(IV.)}\quad C_4H_9{\cdot}CH_2{\cdot}CH(SAc)_2 \qquad\qquad C_4H_9{\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc\quad \text{(V.)}$$

acetate the residue obtained on evaporation was hydrolysed under reflux with 2N-hydrochloric acid in the presence of petroleum, giving a 40% yield of *hexane-1 : 2-dithiol,* exhibiting the characteristic dithiol colour reaction with ferric chloride and condensing readily with acetone. The formulation of the di-adduct as *hexane-1 : 2-dithiol diacetate* (V) is in accord with the experience of Young, Vogt, and Nieuwland (*J. Amer. Chem. Soc.*, 1936, **58**, 1806) who obtained 1-bromohexene and 1 : 2-dibromohexane by the peroxide-catalysed addition of hydrogen bromide to hex-1-yne. It was found later that the diacetate (V) could be hydrolysed most conveniently by heating it with semicarbazide hydrochloride in aqueous alcohol, an 82% yield of the dithiol being obtained. This procedure compares favourably with those hitherto employed (cf. Owen *et al.*, *J.*, 1949, 244, 248) for the hydrolysis of esters of 1 : 2-dithiols.

Hexenyl thiolacetate (I) and other compounds of the same type have been found to exhibit maximal light absorption in the region of 2540 A. ($\varepsilon = 8500$); this must be regarded as being typical of the chromophore, $C{=}C{-}S{-}C{=}O$. The di-adduct (V) absorption spectrum (max. 2310 A.) is similar to those previously observed for other unconjugated thiolacetates (Sjöberg, *Z. physikal. Chem.*, 1942, *B*, **52**, 909; Cunneen, *loc. cit.*).

The effect of peroxide catalysis or ultra-violet irradiation was most marked in the addition of thiolacetic acid to phenylacetylene, *styryl 2-thiolacetate* (VI) being obtained in 60—70%

$$\text{(VI.)}\quad Ph{\cdot}CH{:}CH{\cdot}S{\cdot}CO{\cdot}CH_3 \longrightarrow Ph{\cdot}CH_2{\cdot}CHO\quad \text{(VII.)}$$

yield by using these devices but only in 25% yield in an uncatalysed reaction. However, with *p*-methoxyphenylacetylene a 70% yield of p-*methoxystyryl 2-thiolacetate* was obtained without the use of added catalysts. In neither of these cases could any di-adducts be isolated. Both (VI) and the corresponding *p*-methoxy-compound were converted by treatment with carbonyl reagents into derivatives of phenylacetaldehyde (VII).

An addition reaction employing the diacetylenic hydrocarbon, octa-1 : 7-diyne (VIII), led to the isolation of three products. The formulation of these three substances

$$\text{(VIII.)}\quad HC{\vdots}C{\cdot}[CH_2]_4{\cdot}C{\vdots}CH \qquad\qquad HC{\vdots}C{\cdot}[CH_2]_4{\cdot}CH{:}CH{\cdot}SAc\quad \text{(IX.)}$$

$$\text{(X.)}\quad HC{\vdots}C{\cdot}[CH_2]_4{\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc \qquad\qquad AcS{\cdot}CH{:}CH{\cdot}[CH_2]_4{\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc\quad \text{(XI.)}$$

as the *mono-*, *di-*, and *tri-adducts* (IX), (X), and (XI) respectively, was facilitated by the determination of their absorption spectra and comparison with the data already obtained for the hexyne adducts. The mono-adduct exhibited absorption corresponding to that of hexenyl thiolacetate (I), the maximum in the case of the di-adduct at 2330 A. corresponded to that of (V), and the tri-adduct furnished a curve of the type expected to result from the superposition of the curves of (IX) and (X) (see Table I). No appreciable alteration in the proportions of these three products was produced by employing ascaridole as catalyst, and no indications of the presence of any of the symmetrical di-adduct, from which it was hoped to obtain derivatives of the dialdehyde, octane-1 : 8-dial, were forthcoming.

Methyl propargyl ether gave rise to *addition products* to which the structures (XII) and (XIII)

(XII.) $MeO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}SAc$ $MeO{\cdot}CH_2{\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc$ (XIII.)

are assigned. The yields, particularly of (XII), were not satisfactory, peroxides and irradiation only serving to increase the yield of the di-adduct.

TABLE I.

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$		$\lambda_{max.}$, A.	$\varepsilon_{max.}$
$C_4H_9{\cdot}CH{=}CH{\cdot}S{\cdot}CO{\cdot}CH_3$	2540	8,500	$C_4H_9{\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc$	2310	9,500
$HC{\equiv}C{\cdot}[CH_2]_4{\cdot}CH{=}CH{\cdot}S{\cdot}CO{\cdot}CH_3$	2530	8,500	$HC{\equiv}C{\cdot}[CH_2]_4{\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc$	2330	10,500
$MeO{\cdot}CH_2{\cdot}CH{=}CH{\cdot}S{\cdot}CO{\cdot}CH_3$	2510	7,000	$MeO{\cdot}CH_2{\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc$	2300	7,500
			cf. $C_6H_{11}{\cdot}SAc$ [1]	2300	4,000
$C_6H_5{\cdot}CH{=}CH{\cdot}S{\cdot}CO{\cdot}CH_3$	2220	9,000			
	2810	16,500	$AcS{\cdot}CH{=}CH{\cdot}[CH_2]_4{\cdot}CH(SAc){\cdot}CH_2{\cdot}SAc$	2355	13,500
	2910	17,000		2470*	9,500
	2990*	13,500		2560*	8,500
p-$MeO{\cdot}C_6H_4{\cdot}CH{=}CH{\cdot}S{\cdot}CO{\cdot}CH_3$	2220	11,000			
	2800*	16,000			
	2900	23,500			

* Inflexion. [1] Cunneen, *loc. cit.*

TABLE II.

	$\lambda_{max.}$ (approx.), A.		
	$X = O$.	$X = S$.	$X = CH{=}CH$.
$R{\cdot}CH_2{\cdot}X{\cdot}COMe$	2050	2300	2300
$R{\cdot}CH{=}CH{\cdot}X{\cdot}COMe$	—	2500	2600
$R{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}X{\cdot}COMe$ [1]	—	2700	3050
$Ph{\cdot}CH{=}CH{\cdot}X{\cdot}COMe$	—	2900	3200
	2100	2350	2550

[1] Compound where $X = S$ to be described in forthcoming publication.

Unfortunately it has not been found possible to obtain simple adducts from reactions between thiolacetic acid and conjugated vinylacetylenes. As was observed by Cunneen (*loc. cit.*) thiolacetic acid adds very readily to olefins, and in the cases which we have examined vinylacetylenes gave complex mixtures which could not be resolved. Consequently this route to unsaturated aldehydes, *i.e.*, addition of thiolacetic acid to vinylacetylenes followed by

$$H_2C{=}CH{-}C{\equiv}CH \longrightarrow H_2C{=}CH{-}CH{=}CH{\cdot}SAc \longrightarrow CH_3{-}CH{=}CH{-}CHO$$

hydrolysis, has been abandoned, and we have turned our attention to the addition reaction with ethynylcarbinols as an alternative method. The results of this work will be published later.

$$Me_2C(OH){-}C{\equiv}CH \longrightarrow Me_2C(OH){-}CH{=}CH{\cdot}SAc \longrightarrow Me_2C{=}CH{-}CHO$$

The light-absorption data of the various addition compounds described in this paper are given in Table I. The data for the substances containing the $CH{=}CH{-}S{-}CO{-}CH_3$ chromophore are closely similar, both in location and in intensity of the maxima. A similar uniformity is seen in the data for the dithiol diacetates, the intensities being approximately twice that of a typical monothiolacetate.

The sulphur atom in the chromophore, $CH{=}CH{-}S{-}CO{-}CH_3$, thus exerts a powerful chromolatory effect, and a comparison of the new data with those already available (Table II) indicates that in these respects the sulphur atom produces effects intermediate between those of oxygen and the ethylenic bond (cf. Bowden, Braude, and Jones, *J.*, 1946, 948).

EXPERIMENTAL.

(All light-absorption data were determined in alcoholic solution.)

Addition of Thiolacetic Acid to Hex-1-*yne. Formation of Hex*-1-*enyl Thiolacetate* (I) *and Hexane*-1 : 2-*dithiol Diacetate* (V).—(*a*) When thiolacetic acid (15·2 g.; 0·2 mol.) was added to hex-1-yne (16·4 g.; 0·2 mol.) a vigorous reaction ensued which, after the mixture had boiled, was moderated by external cooling (ice–salt). The mixture was finally heated for 10 minutes on the steam-bath, and fractionation gave (i) *hex*-1-*enyl thiolacetate* (16·8 g.; 53%) as a slightly yellowish liquid, b. p. 83°/20 mm., $n_D^{20°}$ 1·4899

(Found: C, 60·6; H, 9·0; S, 20·8. $C_8H_{14}OS$ requires C, 60·7; H, 8·9; S, 20·25%). Light absorption: see Table I; (ii) *hexane*-1 : 2-*dithiol diacetate* (8·3 g.; 18%), b. p. 85°/0·05 mm., $n_D^{21^\circ}$ 1·5070 (Found: C, 52·5; H, 7·9; S, 27·8. $C_{10}H_{18}O_2S_2$ requires C, 52·2; H, 7·75; S, 27·4%). Light absorption: see Table I.

(*b*) To hex-1-yne (16·4 g.) and ascaridole (0·17 g.), cooled in ice, a mixture of thiolacetic acid (15·2 g.) and ascaridole (0·17 g.) was added dropwise during 30 minutes with continual shaking. After 24 hours at 20°, distillation yielded hex-1-enyl thiolacetate (12·25 g.; 40%) and the dithiol diacetate (11·8 g.; 25%).

(*c*) A solution of thiolacetic acid (15·2 g.) in ether (30 c.c.) was added dropwise during 10 minutes to hex-1-yne (16·4 g.) contained in a silica tube provided with an internal glass spiral through which cold water was circulated. The tube and its contents were exposed at a distance of about 15 cm. to the radiation of a mercury vapour lamp both during the addition and for a further 2 hours. The ether was removed, and distillation gave the thiolacetate (13·45 g.; 42%) and the dithiol diacetate (4·1 g.; 9%).

(*d*) Thiolacetic acid (30·4 g.) was added rapidly to a mixture of hex-1-yne (16·4 g.) and ascaridole (0·34 g.) at 0°. The cooling bath was removed as soon as the addition was complete, and the mixture boiled. After the spontaneous reaction had subsided, refluxing was continued for an hour, and distillation gave the thiolacetate (16·95 g.; 54%) and the dithiol diacetate (8·5 g.; 18%).

Addition of Thiolacetic Acid to Hex-1-*enyl Thiolacetate*.—When thiolacetic acid (1·2 g.) and hex-1-enyl thiolacetate (2·4 g.) were mixed, no heat was evolved. After 1 hour's heating on the steam-bath distillation gave 0·5 g. of recovered thiolacetate and hexane-1 : 2-dithiol diacetate (2·15 g.; 60%), b. p. 158°/2 mm., $n_D^{19^\circ}$ 1·5071.

Conversion of Hex-1-*enyl Thiolacetate* (I) *into Derivatives of Hexoic Aldehyde*.—(a) 2 : 4-*Dinitrophenylhydrazone*. The thiolacetate (1 g.) was added to a solution of 2 : 4-dinitrophenylhydrazine (2·4 g.) in alcohol (40 c.c.) containing concentrated sulphuric acid (1·6 g.), and the mixture was refluxed for 5 hours on the steam-bath, hydrogen sulphide being evolved. Orange-yellow needles (1·63 g.), m. p. 97°, separated on cooling, and two crystallisations from alcohol gave hexoic aldehyde 2 : 4-dinitrophenylhydrazone (1·1 g.; 52%), m. p. 104°, undepressed on admixture with an authentic specimen.

(b) *Semicarbazone*. The thiolacetate (1·58 g.) was added to a solution of semicarbazide acetate (from 2·44 g. of the hydrochloride) in alcohol (10 c.c.) and water (0·5 c.c.), and the mixture was refluxed (24 hours) until hydrogen sulphide evolution ceased. Evaporation under reduced pressure and crystallisation of the residue from benzene–light petroleum (b. p. 40—60°) gave prisms of hexoic aldehyde semicarbazone (0·9 g.; 57%), m. p. 106°, undepressed on admixture with an authentic specimen.

The initial benzene-insoluble residue was recrystallised thrice from alcohol–ether to yield β-acetylsemicarbazide (0·76 g.; 65%) as prismatic needles, m. p. 163°, undepressed when mixed with an authentic sample, m. p. 165°, prepared according to Widman and Cleeve (*Ber.*, 1898, **31**, 381).

Hexane-1 : 2-*dithiol from the Diacetate* (V).—The diacetate (8·9 g.) was refluxed on a steam-bath in nitrogen for 9 hours in an alcoholic solution (70 c.c.; 60%) of semicarbazide hydrochloride (8·5 g.). The yellow oil which separated was isolated with light petroleum (b. p. 40—60°), and fractionation gave *hexane*-1 : 2-*dithiol* (4·7 g.; 82%), b. p. 99°/14 mm., $n_D^{19^\circ}$ 1·5071, as a colourless oil, with a putrid odour, which gave a blue precipitate with an alcoholic solution of ferric chloride [Found: C, 48·3; H, 9·7; S, 42·1; SH, 44·35. $C_6H_{14}S_2$ requires C, 47·9; H, 9·4; S, 42·7; SH, 44·0%].

A solution of the dithiol (1 g.) in dry acetone (10 c.c.) was saturated with dry hydrogen chloride and set aside overnight. Isolation by means of ether gave 2 : 2-*dimethyl*-4-n-*butyl*-1 : 3-*dithiolan* (1·1 g.), b. p. 110°/12 mm., $n_D^{22\cdot5^\circ}$ 1·5052, as a colourless liquid with a fruity odour (Found: C, 57·2; H, 9·4; S, 33·25. $C_9H_{18}S_2$ requires C, 56·8; H, 9·5; S, 33·65%).

Addition of Thiolacetic Acid to Phenylacetylene.—Thiolacetic acid (15 g.; 0·2 mol.) was added dropwise to a mixture of phenylacetylene (20 g.; 0·2 mol.) and benzoyl peroxide (0·2 g.) at 20° during 30 minutes. After 16 hours the mixture was heated on the steam-bath for 2 hours, and the product was isolated with ether, excess of thiolacetic acid being washed out with sodium carbonate solution. Evaporation and distillation of the residue gave *styryl* 2-*thiolacetate* (24·5 g.; 70%), b. p. 142°/16 mm., $n_D^{17^\circ}$ 1·6215, which crystallised in long needles, m. p. 32° (Found: C, 67·0; H, 5·5; S, 17·85. $C_{10}H_{10}OS$ requires C, 67·4; H, 5·65; S, 18·0%). Light absorption: see Table I. No homogeneous product could be isolated from the higher-boiling material.

In the absence of benzoyl peroxide, the yield of the thiolacetate was only 25%, but irradiation, as described above, during the addition of the acid and for a further 3 hours gave a 60% yield of the thiolacetate.

Conversion of Styryl Thiolacetate (VI) *into Derivatives of Phenylacetaldehyde*.—(a) *Semicarbazone*. A solution of the thiolacetate (1·8 g.) and semicarbazide hydrochloride (2·44 g.) in pyridine (13 c.c.) and water (5 c.c.) was heated on the steam-bath for 5 minutes; a rapid evolution of hydrogen sulphide occurred. After standing overnight at 20° the separated solid was crystallised from water, giving phenylacetaldehyde semicarbazone (1·05 g.; 60%), m. p. (and mixed m. p.) 156° (Henle, *Ber.*, 1905, **38**, 1366, gives m. p. 156°).

(b) *Oxime*. A solution of the thiolacetate (1·8 g.), hydroxylamine hydrochloride (1·54 g.), and potassium acetate (2·16 g.) in alcohol (5 c.c.) and water (10 c.c.) was heated under reflux on the steam-bath for 30 hours. The residue obtained on evaporation was crystallised from water, giving phenylacetaldoxime (0·54 g.; 40%), m. p. 102° (Harris and De Osa, *Ber.*, 1904, **37**, 843, give m. p. 103°).

Addition of Thiolacetic Acid to p-*Methoxyphenylacetylene*.—When a mixture of thiolacetic acid (7·6 g.) and *p*-methoxyphenylacetylene (13·2 g.; Manchot, *Annalen*, 1912, **387**, 278; Weltzien *et al.*, *ibid.*, 1923, **433**, 257) was heated, a vigorous reaction set in at about 40°. After this had subsided, refluxing was continued for 3 hours, and distillation then gave a product which crystallised on standing. Recrystallisation from light petroleum (b. p. 40—60°) gave long colourless needles of p-*methoxystyryl* 2-*thiolacetate*, m. p. 46·5° (15·4 g.; 75%) (Found: C, 63·2; H, 5·8; S, 15·55. $C_{11}H_{12}O_2S$ requires C, 63·45; H, 5·8; S, 15·4%). Light absorption: see Table I.

Conversion of p-*Methoxystyryl* 2-*Thiolacetate into Derivatives of* p-*Methoxyphenylacetaldehyde*.—(a) *Oxime*. The thiolacetate (1 g.) was added to a solution of hydroxylamine acetate (from the hydrochloride, 1·2 g.) in alcohol (8 c.c.) and water (2 c.c.). Hydrogen sulphide was evolved in the cold, but in order to complete the reaction the mixture was heated under reflux for 16 hours. After evaporation to dryness under reduced pressure, the residue was treated with benzene (50 c.c.) and water (5 c.c.), and the benzene layer was washed with water, dried, and evaporated. [The aqueous layer gave a cherry-red coloration with ferric chloride, characteristic of acethydroxamic acid (Jones and Oesper, *J. Amer. Chem. Soc.*, 1909, **42**, 518).] The residue was crystallised from light petroleum (b. p. 60—80°) and then twice from *cyclo*hexane, giving *p*-methoxyphenylacetaldoxime (0·3 g., 38%), m. p. 111—113°, as long needles [this is probably a mixture of geometrical isomers, since Rosenmund and Dornsaft, *Ber.*, 1919, **52**, 1740, give m. p. 120°) (Found : N, 8·1. Calc. for $C_9H_{11}O_2N$: N, 8·5%).

(b) *Semicarbazone.* The thiolacetate (1·04 g.) was added to a solution of semicarbazide acetate (from the hydrochloride, 1·2 g.) in alcohol (12 c.c.) and water (1 c.c.), and after 1 day at 20° the mixture was heated under reflux for 44 hours by which time hydrogen sulphide evolution had ceased. After evaporation, the dried residue was crystallised from benzene from which the semicarbazone of *p*-methoxyphenylacetaldehyde (0·57 g.; 52%) separated in needles, m. p. 173° (Weerman, *Rec. Trav. chim.*, 1917, **37**, 4, gives m. p. 173—174°; Harries and Adam, *Ber.*, 1916, **49**, 1033, give m. p. 175—176°).

Octa-1 : 7-*diyne* (VIII) (with B. C. L. Weedon).—To a solution of sodium acetylide, prepared from sodium (118 g.) in liquid ammonia (1800 c.c.) by using the ferric nitrate catalyst of Vaughn, Vogt, and Nieuwland (*J. Amer. Chem. Soc.*, 1934, **56**, 2120) to catalyse the formation of sodamide, a solution of tetramethylene dibromide (270 g.) in dry ether (500 c.c.) was added during 1 hour with cooling (alcohol–solid carbon dioxide) and stirring. More ether (100 c.c.) was then added, and the mixture was cooled and stirred overnight, during which time most of the ammonia evaporated. More ether was added, and the solid residue was decomposed by the careful addition of water. The ethereal layer was washed successively with sulphuric acid (2N), saturated sodium carbonate solution, and water, and dried ($CaCl_2$). The ether was removed through a column, and distillation of the residual liquid gave octa-1 : 7-diyne (78·3 g.), b. p. 93—95°/190 mm., $n_D^{18^\circ}$ 1·4521 (Lespieau and Deluchat, *Compt. rend.*, 1926, **183**, 889, give b. p. 135—136°, $n_D^{21^\circ}$ 1·453).

Addition of Thiolacetic Acid to Octa-1 : 7-*diyne.*—Thiolacetic acid (15·2 g.; 0·2 mol.) was added dropwise during 10 minutes to octadiyne (10·6 g., 0·1 mol.) cooled in ice–salt. After being allowed to warm to room temperature, the mixture was heated on the steam-bath for 1 hour. Careful fractionation of the mixture resulted in the separation of three products, *viz.* : (a) *oct*-1-*en*-7-*ynyl thiolacetate* (IX) (4·8 g.; 26% based on octadiyne) as a yellow liquid, b. p. 61—62°/0·1 mm., $n_D^{19^\circ}$ 1·5115 (Found : S, 17·6. $C_{10}H_{14}OS$ requires S, 17·6%). Light absorption : see Table I; (b) *oct*-7-*yn*-1 : 2-*dithiol diacetate* (X) (3·05 g.; 12% based on octadiyne), a yellow liquid, b. p. 98—100°/10^{-3} mm., $n_D^{18^\circ}$ 1·5324 (Found : S, 24·8. $C_{12}H_{18}O_2S_2$ requires S, 25·2%). Light absorption : see Table I; (*c*) *oct*-1-*en*-1 : 7 : 8-*trithiol triacetate* (XI) (12·1 g.; 36% based on octadiyne), a yellow liquid, b. p. 146°/2 × 10^{-4} mm., $n_D^{20^\circ}$ 1·5458 (Found : S, 28·6. $C_{14}H_{22}O_3S_3$ requires S, 28·8%). Light absorption : see Table I.

Conversion of Oct-1-*en*-7-*ynyl Thiolacetate* (IX) *into the Oxime of Oct*-7-*yn*-1-*al.*—The thiolacetate (0·9 g.) was added to a solution of hydroxylamine acetate (from the hydrochloride, 0·8 g.) in alcohol (10 c.c.) and water (0·5 c.c.), and, although hydrogen sulphide was evolved in the cold, the mixture was heated under reflux for 24 hours in order to complete the reaction. Evaporation to dryness under reduced pressure and crystallisation of the residue from boiling water gave the *oxime* (0·35 g.; 50%) as needles, m. p. 86·5° (Found : C, 69·2; H, 9·4. $C_8H_{13}ON$ requires C, 69·0; H, 9·4%).

Addition of Thiolacetic Acid to Methyl Propargyl Ether.—The methyl ether (7·0 g.; 0·1 mol.) was treated with thiolacetic acid (7·5 g.; 0·1 mol.), added dropwise during 20 minutes, with or without a catalyst, and the resultant solution was allowed to stand or was heated on the steam-bath as indicated in the table below. Fractionation of the product gave (i) 3-*methoxyprop*-1-*enyl thiolacetate* (XII) as a straw-coloured liquid, b. p. 96—97°/14 mm., $n_D^{20^\circ}$ 1·4997 (Found : S, 22·6. $C_6H_{10}O_2S$ requires S, 21·95%), and (ii) 3-*methoxypropane*-1 : 2-*dithiol diacetate* (XIII) as a deep yellow viscous liquid, b. p. 158—159°/13 mm., $n_D^{25^\circ}$ 1·5143 (Found : S, 28·6. $C_8H_{14}O_3S_2$ requires S, 28·85%). Light-absorption data for both compounds are given in Table I.

Expt.	Temp.	Time (hrs.).	Conditions.	Mono-adduct (% yield).	Di-adduct (% yield).
1	20°	2	No catalyst	15	10
2	20	18	,,	15	50
3	100	1	,,	15	15
4	20	2	With 1% of benzoyl peroxide	15	15
5	20	3	With 1% of ascaridole	15	15
6	20	30	,, ,,	15	35
7	20	3	No catalyst; ultra-violet irradiation	15	30

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