206. *Researches on Acetylenic Compounds. Part VIII. Miscellaneous Addition Reactions of Ethynyl Ketones.*

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In connexion with light-absorption studies (see following paper) a variety of addition reactions of the readily available ethynyl ketones (I) (Bowden, Heilbron, Jones, and Weedon, this vol., p. 39) mainly of the type indicated below ($I \longrightarrow II$), has been studied. The adducts employed include ammonia and amines, sulphinic acids, ethylthiol and thiophenol, alcohol and phenol, halogens, hydrogen bromide, and water.

In Part II (Bowden, Braude, Jones, and Weedon, this vol., p. 45) the facile addition of primary and secondary amines to ethynyl ketones (I) was described and, as a consequence of this study, a detailed survey of the auxochromic properties and conjugating power of the amino-group in substituted vinylamines became possible. The marked bathochromic and hyperchromic effects observed in the light-absorption behaviour of these nitrogen compounds suggested that the extension of this survey to include other elements was highly desirable. In partial pursuance of this new objective, addition reactions of ethynyl ketones (I) with sulphinic acids, ethylthiol and thiophenol, alcohol and phenol, halogens, hydrogen bromide, and water have now been studied, addition reactions which in general are of the type :

$$\text{(I.)} \quad R{\cdot}CO{\cdot}C{\equiv}CH + HX \longrightarrow R{\cdot}CO{\cdot}CH{=}CHX \quad \text{(II.)}$$

The light-absorption properties of the adducts (II), from which the auxochromic characteristics of the atom or group X can be ascertained, are reported in detail in the following paper. Certain data bearing upon stereochemical problems, however, are included below.

In order to render more complete our information concerning the light-absorption behaviour of substituted vinylamines, phenyl ethynyl ketone has been caused to react with diethylamine, ethylamine, and ammonia, *e.g.*,

$$Ph{\cdot}CO{\cdot}C{\equiv}CH + NH_3 \longrightarrow Ph{\cdot}CO{\cdot}CH{=}CH{\cdot}NH_2 \quad \text{(III.)}$$

In the last case, isomerism similar to that already encountered with other vinylamines (Bowden, Braude, Jones, and Weedon, *loc. cit.*) has been experienced. The crude product obtained by interaction of the ketone with liquid ammonia at its boiling point had m. p. 82°. Sublimation in a high vacuum yielded the α-*form* of 1-*amino*-3-*phenylpropen*-3-*one* (III), m. p. 70°, and this on boiling with alcohol was extensively converted into the β-*form*, m. p. 90—91°. Both forms were practically unaffected by exposure in alcoholic solutions to ultra-violet light for a few minutes, and their light-absorption properties (cf. Part II, *loc. cit.*) are recorded below :

	M. p.	$\lambda_{max.}$, A.	$\epsilon_{max.}$		M. p.	$\lambda_{max.}$, A.	$\epsilon_{max.}$
(III)	70°	2420	14,000	(III)	90—91°	2420	11,000
		3240	22,000			3240	18,000

These results are somewhat similar to those already obtained with the isomers of 1-anilinobut-1-en-3-one ($Me{\cdot}CO{\cdot}CH{=}CH{\cdot}NHPh$), although the intensity differences between the isomers of (III) are more clearly defined.

With many of the classical examples of geometrical isomerism it has been observed that the more stable, higher m. p. form (the *trans*-isomer) shows the more intense absorption (Henri and Errera, *Compt. rend.*, 1925, **180**, 2049; Castille, *Bull. Acad. roy. Belg.*, 1930, **16**, 81; cf. Koch, *Chem. and Ind.*, 1942, 273); notable exceptions, however, include the nitriles of crotonic and *iso*crotonic acids (Bruylants and Castille, *Bull. Acad. roy. Belg.*, 1927, **13**, 767) and the amides of geranic acid (Caldwell and Jones, this vol. p. 599). The light-absorption properties of the isomeric amines (III) are thus also exceptional when related to their melting points, as are the sulphones referred to later in this paper.

The preparation of 1-diethylaminohex-1-en-3-one ($Pr{\cdot}CO{\cdot}CH{=}CH{\cdot}NEt_2$) from propyl ethynyl ketone and diethylamine was reported in Part II (*loc. cit.*) and it seemed desirable to complete the series of aliphatic vinylamines by the reaction of this ethynyl ketone with both ethylamine and ammonia. In the former case 1-*ethylaminohex*-1-*en*-3-*one* was readily isolated, but with liquid ammonia only a poor yield of a highly unstable substance, which failed to show the expected light-absorption properties, was obtained.

The addition of a sulphinic acid to the triple bond of a substituted $\alpha\beta$-acetylenic ketone has been described by Kohler and Barrett (*J. Amer. Chem. Soc.*, 1924, **46**, 748) who treated benzoylphenylacetylene ($Ph{\cdot}CO{\cdot}C{\equiv}C{\cdot}Ph$) with *p*-toluenesulphinic acid, obtaining two stereoisomeric sulphones. Phenyl ethynyl ketone has been found to react smoothly with this acid in alcoholic solution giving two isomeric *sulphones* of structure (IV). Kohler

$$p\text{-}Me{\cdot}C_6H_4{\cdot}SO_2H + HC{\equiv}C{\cdot}CO{\cdot}Ph \longrightarrow p\text{-}Me{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH{=}CH{\cdot}CO{\cdot}Ph \quad \text{(IV.)}$$

and Larsen (*ibid.*, 1935, **57**, 1448) prepared the sulphone, $Ph{\cdot}SO_2{\cdot}CH{=}CH{\cdot}CO{\cdot}Ph$, in stereoisomeric forms, by a roundabout route. A mixture of the isomers, which can be resolved by crystallisation, is readily obtained by interaction of benzenesulphinic acid and phenyl ethynyl ketone and, as was shown by Kohler and Larsen (*loc. cit.*), the form with m. p. 113—115° is converted into the other form (m. p. 148—149°) by irradiation with ultra-violet light, the reverse change being catalysed by traces of hydrogen chloride or sodium methoxide.

$$Ph{\cdot}SO_2{\cdot}CH{=}CH{\cdot}CO{\cdot}Ph,\ \underset{(\text{“ \textit{trans} ”})}{\text{m. p. }113\text{—}115°} \ \xrightleftharpoons[\text{HCl or NaOMe}]{h\nu} \ \underset{(\text{“ \textit{cis} ”})}{\text{m. p. }148\text{—}149°}$$

In the classical cases of geometrical isomerism the more unstable, lower melting *cis*-forms (*e.g.*, maleic acid) are usually produced from the more stable, higher melting *trans*-forms (*e.g.*, fumaric acid) by irradiation, the reverse conversion being effected in the presence of halogens, halogen acids, etc., at ordinary temperatures. Kohler and Larsen (*loc. cit.*) therefore suggested that, in spite of the melting-point indications, the lower m. p. sulphone had the *trans*-configuration. On the same basis the lower m. p. form of the tolyl sulphone (IV) can also be assigned a *trans*-configuration. The light-absorption data for these four substances (in alcoholic solutions) are indicated below.

	" *cis* "			" *trans* "		
Sulphone.	M. p.	$\lambda_{max.}$, A.	$\epsilon_{max.}$	M. p.	$\lambda_{max.}$, A.	$\epsilon_{max.}$
$\mathrm{Ph{\cdot}SO_2{\cdot}CH{=}CH{\cdot}CO{\cdot}Ph}$	148—149°	2370	16,000	113—115°	2280	12,000
		2420	16,000		2450	13,000
		2480	16,000		2510	13,500
		2510	16,000		2570	16,500
		2800	4,000		2650	16,500
					2800	11,500
					2900	9,500
p-$\mathrm{Me{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH{=}CH{\cdot}CO{\cdot}Ph}$	129	2450	29,000	98	2510	16,500
		2520	27,000		2560	16,500
		2800	7,000		2800	12,000

It will be noted that, in agreement with the suggestion of Kohler and Larsen (*loc. cit.*), the so-called *trans*-forms absorb at 2800 A. (the shorter wave-length absorption is probably due to the partial chromophore $\mathrm{Ph{\cdot}CO{\cdot}CH{=}CH}$) with appreciably greater intensities than the *cis*-forms (see above). The marked diminution in fine structure, consequent upon the introduction of the methyl group into the benzene nucleus, is well illustrated in the above examples.

Although thiophenol has been combined with phenylacetylene (Kohler and Potter, *J. Amer. Chem. Soc.*, 1935, **57**, 1316), little work seems to have been done on addition reactions with acetylenic ketones. By using

$$\mathrm{PhSH + HC{\equiv}C{\cdot}CO{\cdot}Ph \longrightarrow PhS{\cdot}CH{=}CH{\cdot}CO{\cdot}Ph} \qquad \text{(V.)}$$

piperidine (cf. Ruhemann, *J.*, 1905, **87**, 467) or sodium methoxide as catalysts, good yields of vinyl sulphides (*e.g.*, V) are obtainable when thiophenol and ethylthiol react with ethynyl ketones.

Reactions with phenols in the presence of sodium phenoxide (cf. Moureu and Brachin, *Bull. Soc. chim.*, 1905, **33**, 134) take a similar course, vinyl ethers, *e.g.*, $\mathrm{PhO{\cdot}CH{=}CH{\cdot}CO{\cdot}Ph}$, being formed in good yields. The employment of alcohols in such addition reactions with ethynyl ketones, on the other hand, leads to unexpected results. With substituted acetylenic ketones of type (VI), where R and R_1 are aryl groups, β-alkoxyvinyl

$$\text{(VI.)} \qquad \mathrm{R{\cdot}CO{\cdot}C{\equiv}CR_1 + EtOH \longrightarrow R{\cdot}CO{\cdot}CH{=}CR_1{\cdot}OEt} \qquad \text{(VII.)}$$

ketones (*e.g.*, VII) are usually formed as the result of mono-addition (cf. Claisen, *Ber.*, 1903, **36**, 3665; 1911, **44**, 1165; Viguier, *Ann. Chim.*, 1913, **28**, 503; Weygand, *Ber.*, 1925, **58**, 1478; Moureu and Brachin, *Bull. Soc. chim.*, 1922, **31**, 1299). When phenyl ethynyl ketone is treated with alcohol and sodium ethoxide, the *di-adduct* (VIII), with light absorption properties ($\lambda_{max.}$ 2390, 2420 A., $\varepsilon_{max.}$ 15,000 and 15,000) similar to those of

$$\mathrm{Ph{\cdot}CO{\cdot}C{\equiv}CH + 2EtOH \longrightarrow Ph{\cdot}CO{\cdot}CH_2{\cdot}CH(OEt)_2} \qquad \text{(VIII.)}$$

acetophenone [$\lambda_{max.}$ 2400 A.; $\varepsilon_{max.}$ 13,000 (Ley and Wingchen, *Ber.*, 1934, **67**, 501)] is obtained. In the same way propyl ethynyl ketone gives the *diethoxy-ketone* (IX) and the *triethoxyhexanone* (X) is isolated from

$$\text{(IX.)} \quad \mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH(OEt)_2} \qquad \mathrm{CH_3{\cdot}CH(OEt){\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH(OEt)_2} \quad \text{(X.)}$$

propenyl ethynyl ketone. Purification of (IX) and (X) is rendered extremely difficult by their persistent contamination with small quantities of unsaturated ketones which are not easily eliminated by fractional distillation. Moureu and Lazennac (*Bull. Soc. chim.*, 1906, **35**, 528) found that by the interaction of αβ-acetylenic nitriles with methyl alcohol and sodium methoxide inseparable mixtures of mono- and di-adducts were produced, but when potassium hydroxide was employed as catalyst only mono-addition occurred. Even in the presence of potassium hydroxide, however, only di-adducts can be obtained from the ethynyl ketones. Attempts to split off alcohol from these di-adducts by heating with *p*-toluenesulphonic acid (cf. Killian, Hennion, and Nieuwland, *J. Amer. Chem. Soc.*, 1935, **57**, 544; Nazarov, *Bull. acad. sci. U.R.S.S.*, 1940, 545) results in extensive decomposition. It would appear that the presence of the ethynyl hydrogen atom is an important factor in stabilising these di-adducts in the acetal form.

The addition of bromine to ethynyl ketones (cf. Grard, *Ann. Chim.*, 1930, **13**, 363; Dufraisse, *ibid.*, 1922, **17**, 141, who employed substituted acetylenic ketones) proceeds smoothly at 15—20° in chloroform solution. Judging from the wide b. p. range and variations in refractive indices, the *dibromide* from propyl ethynyl ketone is a mixture of the two possible stereoisomerides. Addition of chlorine to the same ketone gave a product boiling over a wide range and, although an arbitrary cut had the anticipated light-absorption properties, satisfactory analytical data could not be obtained. The reaction of propyl ethynyl ketone with hydrogen bromide in acetic acid solution gave the somewhat unstable 1-*bromohexen*-3-*one*.

Many examples of the hydration of substituted acetylenic ketones to β-diketones are to be found in the literature. Nef (*Annalen*, 1899, **308**, 277) obtained dibenzoylmethane by treating benzoylphenylacetylene with concentrated sulphuric acid, and this method has been employed by a number of other workers (Yvon, *Compt. rend.*, 1925, **180**, 748; Moureu and Delange, *Bull. Soc. chim.*, 1901, **25**, 306; *Ann. Chim.*, 1914, **2**, 277; Fuson, Ullyot, and Huckson, *J. Amer. Chem. Soc.*, 1939, **61**, 410; Morton, Hassan, and Calloway, *J.*, 1934, 899). Phenyl ethynyl ketone remains unchanged after dissolution in concentrated sulphuric acid at 20° followed by dilution with water, and at higher temperatures decomposition occurs. However, with dilute sulphuric acid containing mercuric sulphate at 80—100°, hydration occurs smoothly giving 1-phenylpropane-1 : 2-dione (XI), characterised as its α-semicarbazone. Thus, in common with all compounds containing the ethynyl group, and in spite of the presence of the α-carbonyl group, hydration of the triple bond results in the formation of a ketone and not an aldehyde.

$$\mathrm{Ph{\cdot}CO{\cdot}C{\equiv}CH \longrightarrow Ph{\cdot}CO{\cdot}CO{\cdot}CH_3} \qquad \text{(XI.)}$$

EXPERIMENTAL.

(The preparation of the ethynyl ketones is described by Bowden, Heilbron, Jones, and Weedon, this vol., p. 39.)

1-*Amino*-3-*phenylpropen*-3-*one* (III).—Finely powdered phenyl ethynyl ketone (1 g.) was added during 5 minutes to boiling liquid ammonia (25 c.c.), care being taken to exclude moisture. The solvent was then allowed to evaporate during an hour, and removal of the last traces under diminished pressure gave a pale yellow solid (1·1 g.), m. p. 82°. Sublimation at 50° (bath temp.)/10^{-4} mm. gave the *α-form* of 1-*amino*-3-*phenylpropen*-3-*one* (0·9 g.) as colourless needles, m. p. 70° (Found : N, 9·35. C_9H_9ON requires N, 9·5%). The *picrate*, prepared in methanol, crystallised from alcohol in long yellow needles, m. p. 174—175° (Found : N, 15·1. $C_{15}H_{12}O_8N_4$ requires N, 14·9%).

The *β-form* was prepared by refluxing the α-form in alcohol for 10 minutes, removing the solvent under reduced pressure, and washing the residual solid with cold ether. It forms rosettes of needles, m. p. 90—91° (Found: N, 9·35%).

1-*Ethylamino*-3-*phenylpropen*-3-*one*.—Phenyl ethynyl ketone (6·5 g.) in ether (25 c.c.) was treated at 0° with ethylamine (4 c.c.) in ether (25 c.c.). Next day the solvent was evaporated, and distillation gave 1-*ethylamino*-3-*phenylpropen*-3-*one* (6·5 g.), b. p. 109°/0·4 mm. (Found : C, 75·6; H, 7·6. $C_{11}H_{13}ON$ requires C, 75·4; H, 7·5%).

1-*Diethylamino*-3-*phenylpropen*-3-*one*.—Prepared from the ketone (6·5 g.) and diethylamine (5·5 g.) in ether (40 c.c.) at 20—30°. Distillation gave an oil (8·1 g.), b. p. 147°/0·5 mm., which solidified, and crystallisation from light petroleum (b. p. 40—60°) gave the *amino-ketone* (7·5 g.) as pale yellow needles, m. p. 52—53° (Found : C, 77·2; H, 8·65. $C_{13}H_{17}ON$ requires C, 76·8; H, 8·4%).

1-*Ethylaminohex*-1-*en*-3-*one*.—The *amino-ketone* (3·5 g.) prepared by interaction of propyl ethynyl ketone (3·2 g.) with ethylamine (1·5 g.) in ether (20 c.c.) at 20° had b. p. 114—115°/20 mm., $n_D^{17°}$ 1·5236 (Found : N, 9·7. $C_8H_{15}ON$ requires N, 9·9%).

1-p-*Toluenesulphonyl*-3-*phenylpropen*-3-*one* (IV).—A solution of phenyl ethynyl ketone (2·6 g.) in alcohol (40 c.c.) was heated with *p*-toluenesulphinic acid (3·6 g.) on a steam-bath for 10 minutes. The solid separating on cooling was crystallised from alcohol and gave the *α-form* of 1-p-*toluenesulphonyl*-3-*phenylpropen*-3-*one* (5·1 g.) as needles, m. p. 129° (Found : C, 67·25; H, 5·2. $C_{16}H_{14}O_3S$ requires C, 67·1; H, 4·95%).

From the filtrates, by crystallisation from aqueous methanol, the *β-form* (0·5 g.) was obtained as long needles, m. p. 98—99° (Found : C, 67·1; H, 5·1%).

1-*Benzenesulphonyl*-3-*phenylpropen*-3-*one*.—The ketone (2·6 g.) and benzenesulphinic acid (3·2 g.) were heated in alcohol (40 c.c.) for 10 minutes on a steam-bath. After an hour at 0° the crystals (2·8 g., m. p. 146—148°) which separated were filtered off and crystallised from methanol giving "*cis*"-1-benzenesulphonyl-3-phenylpropen-3-one (2·05 g.), m. p. 148—149° (Kohler and Larsen, *loc. cit.*, give m. p. 149°).

The solid obtained from the mother liquors was crystallised from methanol giving the "*trans*"-form, m. p. 113—115° (Kohler and Larsen, *loc. cit.*, give m. p. 114°). This "*trans*"-form was also prepared from the "*cis*"-form by refluxing for 20 minutes in methanol containing a trace of alkoxide.

1-*Phenylthio*-3-*phenylpropen*-3-*one* (V).—Thiophenol (2·2 g.) in ether (10 c.c.) to which three drops of piperidine had been added was dropped into phenyl ethynyl ketone (2·6 g.) in ether (10 c.c.) at 20° during 15 minutes. Removal of the solvent and crystallisation from petroleum (b. p. 80—100°) gave 1-*phenylthio*-3-*phenylpropen*-3-*one* (4·6 g.) as pale yellow needles, m. p. 82—83° (Found : C, 74·85; H, 4·95. $C_{15}H_{12}OS$ requires C, 75·0; H, 5·05%).

1-*Ethylthio*-3-*phenylpropen*-3-*one*.—Ethylthiol (4 c.c.) in ether (15 c.c.) was caused to react with phenyl ethynyl ketone (6·5 c.c.) in ether (25 c.c.) at 20—30°, using a trace of sodium methoxide as catalyst. Distillation of the residue obtained after removal of the solvent gave 1-*ethylthio*-3-*phenylpropen*-3-*one* (6·5 g.), b. p. 125—126°/0·5 mm. (Found: C, 69·0; H, 6·65. $C_{11}H_{12}OS$ requires C, 68·7; H, 6·3%).

1-*Ethylthiohex*-1-*en*-3-*one*.—Ethylthiol (7·5 c.c.) in ether (50 c.c.) was added dropwise to propyl ethynyl ketone (9·6 g.) in ether (50 c.c.) to which a trace of sodium methoxide had previously been added. After the addition, carried out at 20°, was complete, the mixture was kept for 12 hours. Evaporation and distillation gave 1-*ethylthiohex*-1-*en*-3-*one* (10 g.), b. p. 130—131°/20 mm., $n_D^{20°}$ 1·5288 (Found : C, 60·45; H, 8·9. $C_8H_{14}OS$ requires C, 60·7; H, 8·9%).

1-*Phenoxy*-3-*phenylpropen*-3-*one*.—A solution of sodium phenoxide was prepared from sodium (1·15 g.) and molten phenol (50 g.), and phenyl ethynyl ketone (6·5 g.) was added in portions at 80°. During the addition the temperature rose to 90° and the mixture darkened. After cooling, the product was isolated with ether giving a pale yellow oil (9 g.), b. p. 150—155°/0·5 mm. Redistillation at 90° (bath temp.)/10^{-4} mm. gave a solid (6·9 g.), m. p. 46—48°, which after crystallisation from light petroleum (b. p. 60—80°) gave 1-*phenoxy*-3-*phenylpropen*-3-*one* (4 g.), m. p. 49·5—50·5° (Found : C, 80·4; H, 5·45. $C_{15}H_{12}O_2$ requires C, 80·35; H, 5·4%). A small quantity of material, m. p. 27—29°, presumably a stereoisomer, was also isolated.

1 : 1-*Diethoxy*-3-*phenylpropan*-3-*one* (VIII).—To a solution of sodium ethoxide, prepared from sodium (1·15 g.) and alcohol (50 c.c.), phenyl ethynyl ketone (6·5 g.) in alcohol (25 c.c.) was added with stirring during 1 hour, the temperature being kept at 0—5°. After acidification with acetic acid (3 g.), isolation by means of ether gave 1 : 1-*diethoxy*-3-*phenylpropan*-3-*one* (7·9 g.), b. p. 111—112°/1 mm., $n_D^{15°}$ 1·5032 (Found : C, 70·55; H, 8·2. $C_{13}H_{18}O_3$ requires C, 70·2; H, 8·15%).

1 : 1-*Diethoxyhexan*-3-*one* (IX).—(*a*) Propyl ethynyl ketone (9·6 g.) in alcohol (50 c.c.) was added at 0—5° with stirring during 90 minutes to a solution of sodium (2·3 g.) in alcohol (100 c.c.). After a further 30 minutes the mixture was acidified with acetic acid; isolation with ether gave, after prolonged fractionation, 1 : 1-*diethoxyhexan*-3-*one* (10 g.), b. p. 96°/10 mm., $n_D^{19.5°}$ 1·4211 (Found : C, 64·05; H, 10·85. $C_{10}H_{20}O_3$ requires C, 63·75; H, 10·7%). The urethane

derivative was prepared from the diethoxy-ketone (1·5 g.) by stirring with urethane (5 g.) dissolved in N-hydrochloric acid (50 c.c.) at 20°. The sparingly soluble product crystallised from water in long needles (1·1 g.), m. p. 133—134° (Found: N, 10·0. $C_{12}H_{22}O_5N_2$ requires N, 10·2%).

(*b*) To a solution of potassium hydroxide (11·2 g.) in alcohol (90 c.c.), kept at 0—5°, propyl ethynyl ketone (9·6 g.) in alcohol (20 c.c.) was added with stirring during 30 minutes. The deep red solution was stirred for a further 30 minutes, and after acidification with acetic acid the product was isolated by means of ether. This procedure gave after repeated fractionation 1 : 1-diethoxyhexan-3-one (7 g.), b. p. 98—99°/14 mm., $n_D^{14.5°}$ 1·4250.

1 : 1 : 5-*Triethoxyhexan*-3-*one* (X).—To a solution of sodium (4·6 g.) in alcohol (200 c.c.) kept at 0—5°, propenyl ethynyl ketone (18·8 g.) in alcohol (50 c.c.) was added with stirring during 30 minutes. The mixture was then acidified with acetic acid; isolation with ether gave 1 : 1 : 5-*triethoxyhexan*-3-*one* (21·4 g.), b. p. 74—75°/0·3 mm., $n_D^{18.5°}$ 1·4279 (Found: C, 62·7, 62·7; H, 10·15, 10·55. $C_{12}H_{24}O_4$ requires C, 62·05; H, 10·4%).

1-*Bromohex*-1-*en*-3-*one*.—A solution of hydrogen bromide in acetic acid (16·2 c.c.; 50% w/v) was added to propyl ethynyl ketone (9·6 g.) in acetic acid (20 c.c.) at 5—10°. After dilution with water, isolation with chloroform gave 1-*bromohex*-1-*en*-3-*one* (4·7 g.), b. p. 80°/18 mm., $n_D^{16°}$ 1·5021 (Found: Br, 45·35. C_6H_9OBr requires Br, 45·15%). The ketone rapidly decomposes and it assumes a red colour after being kept for 30 minutes at 0°.

1 : 2-*Dibromohex*-1-*en*-3-*one*.—Bromine in chloroform (80 g.; 20% w/w) was added during 30 minutes to propyl ethynyl ketone (9·6 g.) in chloroform (25 c.c.) at such a rate that any appreciable excess of free bromine was avoided. The 1 : 2-*dibromohex*-1-*en*-3-*one* (20 g.) had b. p. 102—108°/17 mm., and $n_D^{18°}$ (of the various fractions) 1·5282—1·5365. After two fractionations a middle cut, b. p. 104·5—105°/17 mm., $n_D^{17°}$ 1·5340 was taken and used for analysis (Found: Br, 62·45. $C_6H_8OBr_2$ requires Br, 62·45%). The 2 : 4-*dinitrophenylhydrazone* formed bright yellow leaflets, m. p. 176°, from ethyl acetate (Found: N, 12·8. $C_{12}H_{12}O_4N_4Br_2$ requires N, 12·85%). Light absorption in chloroform: Maxima, 2560, 2820, 2900, 3650 A.; ϵ = 13,500, 10,500, 8000, and 25,500 respectively.

1-*Phenylpropane*-1 : 2-*dione* (XI).—2N-Sulphuric acid (50 c.c.) containing mercuric sulphate (0·25 g.) was added to phenyl ethynyl ketone (6·5 g.) in alcohol (100 c.c.). The mixture was stirred under reflux on a steam-bath for 6 hours, a further quantity of mercuric sulphate (0·25 g.) in 2N-sulphuric acid (50 c.c.) being added in portions during this time. Isolation with ether gave 1-phenylpropane-1 : 2-dione (4·1 g.) as a yellow oil, b. p. 88°/17 mm., $n_D^{17°}$ 1·5350 (von Auwers, *Ber.*, 1918, **51**, 1122, gives $n_D^{10°}$ 1·537). The α-semicarbazone crystallised from alcohol in leaflets, m. p. 208° (von Auwers and Ludewig, *Annalen*, 1936, 526, 130, give m. p. 208—209°).

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