205. *Researches on Acetylenic Compounds. Part VII. Reactions of 2-Chlorohex-3-en-5-yne and Related Compounds with Ammonia and Amines. Reversed Anionotropic Rearrangements accompanying Replacement.*

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In systems of the type (A), such as is present in 2-chlorohex-3-en-5-yne, replacement reactions with amines either proceed normally (giving B) or else are accompanied by anionotropic rearrangements when amines of type

$$\underset{\text{(B)}}{\mathrm{—CHX{\cdot}CH{=}CH{\cdot}C{\equiv}C—}} \longleftarrow \underset{\text{(A)}}{\mathrm{—CHCl{\cdot}CH{=}CH{\cdot}C{\equiv}C—}} \longrightarrow \underset{\text{(C)}}{\mathrm{—CH{=}CH{\cdot}CHX{\cdot}C{\equiv}C—}}$$

(C) result. The structures of these abnormal products have been ascertained from light-absorption data and ozonolysis experiments. It has been shown that increasing base strength of the substituting amine (XH) tends to promote the formation of isomerised products, which tendency is also favoured by the presence of substituents known to enhance the mobility of the hydroxyl group in the parent oxotropic systems, *e.g.*:

$$\mathrm{—CH{=}CH{\cdot}CH(OH){\cdot}C{\equiv}C—} \longrightarrow \mathrm{—CH(OH){\cdot}CH{=}CH{\cdot}C{\equiv}C—}$$

In a previous publication (Heilbron, Jones, Lacey, McCombie, and Raphael, *J.*, **1945**, 77) the simultaneous rearrangement and replacement chlorination which occurs when acetylenic carbinols and glycols derived from $\alpha\beta$-ethylenic aldehydes are treated with concentrated hydrochloric acid at room temperature has been described. Thus propenylethynylcarbinol readily yields 2-chlorohex-3-en-5-yne (I) under these conditions, whereas on shaking with dilute sulphuric or other acids, the corresponding alcohol, hex-3-en-5-yn-2-ol (II) (Jones and McCombie, *J.*, **1943**, 261) is produced.

$$\mathrm{CH_3{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH} \xrightarrow{\text{conc. HCl}} \mathrm{CH_3{\cdot}CHCl{\cdot}CH{=}CH{\cdot}C{\equiv}CH} \qquad \text{(I.)}$$
$$\mathrm{CH_3{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH} \xrightarrow{\text{dil. } \mathrm{H_2SO_4}} \mathrm{CH_3{\cdot}CH(OH){\cdot}CH{=}CH{\cdot}C{\equiv}CH} \qquad \text{(II.)}$$

The behaviour of compounds of the type (I) on treatment with ammonia and amines has now been studied. Replacement reactions occur readily in every case and, as would be expected, the best yields are obtained with secondary amines, whereas ammonia and primary amines give rise to considerable quantities of undistillable secondary and/or tertiary amines. Simple replacement, however, is not the only reaction which has been encountered, and the products obtained can be differentiated sharply into two groups, depending both upon the nature of the chloro-compound and upon the particular base employed.

Normal Reactions.—When 2-chlorohex-3-en-5-yne (I) is treated with ammonia, ethylamine, or aniline, the expected *amines* (III, IV, or V respectively) are obtained.

$$\text{(I.)}\ \mathrm{HC{\equiv}C{\cdot}CH{=}CH{\cdot}CHCl{\cdot}CH_3} \xrightarrow{\mathrm{NH_3}} \mathrm{HC{\equiv}C{\cdot}CH{=}CH{\cdot}CH(NH_2){\cdot}CH_3} \qquad \text{(III.)}$$
$$\text{(I.)}\ \mathrm{HC{\equiv}C{\cdot}CH{=}CH{\cdot}CHCl{\cdot}CH_3} \xrightarrow{\mathrm{EtNH_2}} \mathrm{HC{\equiv}C{\cdot}CH{=}CH{\cdot}CH(NHEt){\cdot}CH_3} \qquad \text{(IV.)}$$
$$\text{(I.)}\ \mathrm{HC{\equiv}C{\cdot}CH{=}CH{\cdot}CHCl{\cdot}CH_3} \xrightarrow{\mathrm{PhNH_2}} \mathrm{HC{\equiv}C{\cdot}CH{=}CH{\cdot}CH(NHPh){\cdot}CH_3} \qquad \text{(V.)}$$

The light-absorption properties of these bases and their *hydrochlorides* are typical of those of conjugated vinylacetylene systems (Table I) (cf. Jones and McCombie, *loc. cit.*, and later papers in the same series) and the assigned structures received further confirmation from Zerewitinoff determinations.

The reaction between the same chloro-compound (I) and the stronger base, diethylamine, is anomalous, however, and is discussed in detail below. On the other hand, even with this base, the chloro-compounds (VII; R = H or *n*-Bu), derived from acraldehyde carbinols (VI) by hydrochloric acid treatment, behave in the normal manner, giving *amines* (VIII; R = H or *n*-Bu) which, as well as their *hydrochlorides*, exhibit typical vinylacetylene absorption (Table I).

$$\text{(VI.)}\quad \mathrm{RC{\equiv}C{\cdot}CH(OH){\cdot}CH{=}CH_2}$$
$$\Big\downarrow \text{conc. HCl}$$
$$\text{(VII.)}\quad \mathrm{RC{\equiv}C{\cdot}CH{=}CH{\cdot}CH_2Cl} \xrightarrow{\mathrm{Et_2NH}} \mathrm{RC{\equiv}C{\cdot}CH{=}CH{\cdot}CHNEt_2} \qquad \text{(VIII.)}$$

The dichloro-compound (IX) obtained from crotonaldehyde acetylene glycol reacts with both methyl- and ethyl-amines giving *amines* (*e.g.*, X), which show light absorption similar to that of the parent compound (IX), characteristic of the conjugated divinylacetylene chromophore (Table I).

$$\text{(IX.)}\quad \mathrm{CH_3{\cdot}CHCl{\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CHCl{\cdot}CH_3} \xrightarrow{\mathrm{MeNH_2}}$$
$$\mathrm{CH_3{\cdot}CH(NHMe){\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH(NHMe){\cdot}CH_3} \qquad \text{(X.)}$$

Abnormal Reactions.—The chloro-compound (I) reacts smoothly with diethylamine either at 100° or at 20° for a much longer time giving a tertiary *amine* in excellent yield, but the product, unlike the amines described

TABLE I.

	$\lambda_{max.}$, A.	$\epsilon_{max.}$.
$NHPh{\cdot}CHMe{\cdot}CH{=}CH{\cdot}C{\equiv}CH$	2260	17,500
	2400	17,500
Hydrochloride	2280	19,000
$NHEt{\cdot}CHMe{\cdot}CH{=}CH{\cdot}C{\equiv}CH$	2230	13,000
Hydrochloride	2230	15,000
$NH_2{\cdot}CHMe{\cdot}CH{=}CH{\cdot}C{\equiv}CH$	2235	11,000
	2280 *	9,500
Hydrochloride	2230	14,000
	2340 *	9,500
$NEt_2{\cdot}CH_2{\cdot}CH{=}CH{\cdot}C{\equiv}CH$	2230	12,500
Hydrochloride	2250	15,500
	2340 *	12,000
$NEt_2{\cdot}CH_2{\cdot}CH{=}CH{\cdot}C{\equiv}CBu$ (*n*)	2280	16,000
	2370 *	15,500
$CHMeCl{\cdot}CH{=}CH{\cdot}C{\equiv}CH$ [1]	2260	14,000
$CH_3{\cdot}CH(OH){\cdot}CH{=}CH{\cdot}C{\equiv}CH$ [2]	2230	13,500
	2300 *	9,500
$CH_3{\cdot}CH(NHR){\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH(NHR){\cdot}CH_3$		
(R = Me)	2200	10,000
	2290	10,000
	2660	16,500
	2750 *	14,500
(R = Et)	2650	17,000
	2730 *	15,500
$CH_3{\cdot}CHCl{\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CHCl{\cdot}CH_3$ [1]	2210	11,500
	2700	19,500
	2760	18,500

[1] Heilbron, Jones, Lacey, McCombie, and Raphael, *loc. cit.*
[2] Jones and McCombie, *loc. cit.*
* Inflexion.

above, shows no high-intensity absorption in the ultra-violet and its hydrochloride is similarly transparent. Consequently it cannot contain any conjugated system, either of the vinylacetylene type or of the type ($C{=}C{-}N$) which, as recently demonstrated (Bowden, Braude, Jones, and Weedon, this vol., p. 45) absorbs strongly in the 2200A. region. Further, since an ethynyl hydrogen atom is still present (silver derivative and Zerewitinoff) the only reasonable structure for this compound is (XI), its formation from the chloro-compound thus involving substitution together with a reversal of the well established anionotropic rearrangement by which

(I.)  (XI.)

$$CH_3{\cdot}\underset{Cl}{CH}{\cdot}CH{=}CH{\cdot}C{\equiv}CH \xrightarrow[NHEt_2]{} CH_3{\cdot}CH{=}CH{\cdot}\underset{NEt_2}{CH}{\cdot}C{\equiv}CH$$

(XII.) $CH_3{\cdot}CHCl{\cdot}CH{=}CH{\cdot}C{\equiv}CBu(n) \longrightarrow CH_3{\cdot}CH{=}CH{\cdot}CH(NEt_2){\cdot}C{\equiv}CBu(n)$ (XIII.)

the conjugated vinylacetylene system is originally formed. The *amine* (XIII), obtained from the halogeno-compound (XII) also in excellent yield, is analogously formulated in view of its light absorption properties and those of its hydrochloride.

Further confirmation of the structures (XI and XIII) assigned to these anomalous products is afforded by the results of ozonolysis experiments. Yields of acetaldehyde (estimated as its dimedon derivative) of 40 and 25% respectively are obtained, comparing favourably with a 45% yield resulting from the application of an identical procedure to propenylethynylcarbinol. Also, the behaviour of the amine (XI) on hydrogenation in the presence of a platinum catalyst appears to be typical of the location of the amino-group between the two unsaturated centres. In methanol solution four molecular equivalents of hydrogen are absorbed and an almost quantitative yield of diethylamine (as hydrochloride) results. Less fission of the carbon–nitrogen bond occurs in *cyclo*hexane solution. Mannich, Handke, and Roth (*Ber.*, 1936, **69**, 2112) observed similar fissions and variations according to the polar nature of the solvent employed while hydrogenating some diamines of the type $-\overset{\alpha}{C}H(NR_2){\cdot}CH{=}CH{\cdot}NR_2$ (cf. also Meisenheimer and Link, *Annalen*, 1930, **479**, 211). Hydrogenolysis was confined to the amino-group attached to the α-carbon atom.

When the divinylacetylene chloro-compound (XIV) reacts with diethylamine the *product* (XV) exhibits light absorption (Table II) indicative of the presence of only a simple conjugated vinylacetylene system.

(XIV.) $CH_3{\cdot}CHCl{\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}CMe{=}CHMe \longrightarrow CH_3{\cdot}CH{=}CH{\cdot}CH(NEt_2){\cdot}C{\equiv}C{\cdot}CMe{=}CHMe$ (XV.)

$CH_3{\cdot}CH(NMe_2){\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH(NMe_2){\cdot}CH_3$ (XVI.)

$CH_3{\cdot}CH{=}CH{\cdot}CH(NR_2){\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH(NR_2){\cdot}CH_3$ (XVII.)

$CH_3{\cdot}CH{=}CH{\cdot}CH(NEt_2){\cdot}C{\equiv}C{\cdot}CH(NEt_2){\cdot}CH{=}CH{\cdot}CH_3$ (XVIII.)

According to light-absorption data (Table II) the product of the reaction of the dichloro-compound (IX) with dimethyl- or diethyl-amine is a mixture of (XVI) and (XVII; R = Me), or (XVII; R = Et) and (XVIII) respectively, the use of the stronger base resulting in the formation of none of the normal product. Ozonolysis of the mixture of (XVII; R = Et) and (XVIII) gave about 20% of the theoretical yield of acetaldehyde.

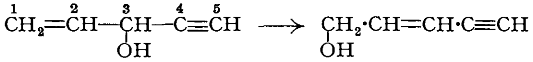
TABLE II.

	$\lambda_{max.}$, A.	$\epsilon_{max.}$
$CH_3{\cdot}CH{=}CH{\cdot}CH(NEt_2){\cdot}C{\equiv}C{\cdot}CMe{=}CHMe$	2280	13,000
$CH_3{\cdot}CH{=}CH{\cdot}CH(NMe_2){\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH(NMe_2){\cdot}CH_3$	2290	9,500
$CH_3{\cdot}CH(NMe_2){\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH(NMe_2){\cdot}CH_3$	2670	8,000

Discussion.—A sufficient number of examples of both normal and anomalous replacement reactions has been encountered in the present study to enable certain general conclusions to be drawn concerning the factors involved in determining the nature of the final product.

With ammonia, and also the weak primary amines, ethylamine and aniline, 2-chlorohex-3-en-5-yne (I) undergoes simple replacement, but with the stronger base, diethylamine, rearrangement accompanies the substitution reaction. Similarly, the dichloro-compound (XIV) behaves normally with both methylamine and ethylamine, some isomerisation occurs with dimethylamine, and this is considerably more extensive with diethylamine. Increasing base strength thus tends to promote the formation of abnormal products.

In oxotropic systems of the type:



$$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\underset{OH}{\overset{3}{C}H}{-}\overset{4}{C}{\equiv}\overset{5}{C}H \longrightarrow \underset{OH}{C}H_2{\cdot}CH{=}CH{\cdot}C{\equiv}CH$$

kinetic studies (Braude and Jones, this vol., p. 122) have revealed that replacement of the hydrogen atoms at C_1, C_3, and C_5 by alkyl groups has a profound enhancing effect upon the velocity of the acid-catalysed rearrangement. Thus under comparable conditions introduction of a methyl group at C_1 increases the velocity constant by a factor of 3000, at C_3 the factor for this group is 500 whereas a *n*-butyl group at C_5 steps up the velocity constant 300 times. In the present studies it has been observed, in a qualitative fashion, that groups which increase the mobility of the above oxotropic system are apparently similarly effective in promoting the reversed rearrangement during these amine replacement reactions. Thus the rearrangement of the carbinols (VI; R = H and *n*-Bu) to the corresponding primary alcohols with acids is only effected with difficulty (the relative *k*'s are respectively 0·0003 and 0·1 when compared with 1 for propenylethynylcarbinol) and, even with the strongest base used in the present study, amination of the corresponding chloro-compound (VII) proceeds without rearrangement. The chloro-compounds (I, XII, and XIV) derived by hydrochloric acid treatment from much more readily isomerised carbinols all undergo anomalous reactions on heating with diethylamine.

Somewhat similar reversals of anionotropic rearrangements accompanying substitution reactions have been observed by Meisenheimer and Link (*loc. cit.*). On treatment of cinnamyl chloride with both aqueous-alcoholic potassium hydroxide and potassium acetate in acetic acid, mixtures of derivatives of cinnamyl alcohol and phenylvinylcarbinol are obtained.

$$PhCH{=}CH{\cdot}CH_2Cl \longrightarrow PhCH{=}CH{\cdot}CH_2X + PhCHX{\cdot}CH{=}CH_2$$

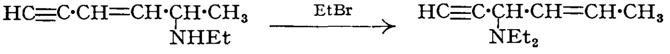
With *alcoholic* potassium hydroxide, on the other hand, no isomerisation occurs, the product consisting entirely of cinnamyl ethyl ether. It may also be noted that prolongation of the treatment of cinnamyl chloride with potassium acetate in acetic acid results in the formation of a greater proportion of cinnamyl acetate, owing to the isomerisation of the phenylvinylcarbinyl acetate under these conditions. This effectively demonstrates that the abnormal product (*i.e.*, phenylvinylcarbinyl acetate) does not result from the isomerisation of an initially formed normal replacement product (*i.e.*, cinnamyl acetate). It suggested therefore that in the amine replacement reactions dealt with in this paper the anomalous products (*e.g.*, XI, XIII, and XV) might be capable of rearrangement to the conjugated vinylacetylenic amines thus:

$$\text{(XI.)}\quad HC{\equiv}C{\cdot}CH(NEt_2){\cdot}CH{=}CH{\cdot}CH_3 \longrightarrow HC{\equiv}C{\cdot}CH{=}CH{\cdot}CH(NEt_2){\cdot}CH_3 \quad\text{(XIX.)}$$

provided that suitable conditions could be found. However with moderately concentrated acids the amine (XI) remains unaffected (under more vigorous conditions hydration of the acetylenic linkage tends to occur), suggesting that (XI) is indeed more stable than the conjugated isomer (XIX).

Note Added in Proof.—This suggestion is apparently borne out by the results of ethylation experiments with the secondary amine,

(IV.)



$$HC{\equiv}C{\cdot}CH{=}CH{\cdot}\underset{NHEt}{C}H{\cdot}CH_3 \xrightarrow{EtBr} HC{\equiv}C{\cdot}\underset{NEt_2}{C}H{\cdot}CH{=}CH{\cdot}CH_3$$

(XI.)

2-ethylaminohex-3-en-5-yne (IV). Treatment with ethyl bromide at 80° gave, after removal of quaternary salt and unchanged secondary amine, a 30% yield of the unconjugated tertiary amine (XI). If the conjugated amine (XIX) is produced initially, as would normally be expected, it must undergo rearrangement under the conditions of the experiment to the apparently more stable unconjugated isomer (XI).

The only amine replacement reaction at all comparable with the present study is that carried out by Meisenheimer and Link (*loc. cit.*) with ethylaniline. Using equimolecular proportions of ethylaniline and cinnamyl chloride, a homogeneous product (*i.e.*, PhCH═CH·CH$_2$·NEtPh), involving no rearrangement, results. From the experiments described above, and also from related studies on the anionotropic rearrangement of phenylvinylcarbinol (Braude, Jones, and Stern, this vol., p. 396), only the normal product would be expected with the weak base employed and, in view of the low mobility of the phenylvinylcarbinol ⟶ cinnamyl alcohol system, it is unlikely that even diethylamine treatment of cinnamyl chloride would effect any appreciable rearrangement. It can be predicted, however, with a fair degree of certainty that styrylmethylcarbinyl chloride (PhCH═CH·CHCl·Me) should readily undergo rearrangement during amine replacements. It is hoped to examine these and allied reactions in the near future in the expectation of throwing further light on the relationship between both base strength and carbinol structure and the reaction mechanism.

EXPERIMENTAL.

Absorption spectra were determined in alcoholic solutions. Light petroleum refers to that fraction with b. p. 40—60° unless otherwise stated. The preparation of most of the chloro-compounds is described by Heilbron, Jones, Lacey, McCombie, and Raphael (*loc. cit.*).

2-*Anilinohex*-3-*en*-5-*yne* (V).—A solution of 2-chlorohex-3-en-5-yne (10 g.) in freshly distilled aniline (40 c.c.) was heated in a sealed tube at 100° for 16 hours. Much aniline hydrochloride separated. The mixture was treated with ether and 2N-sodium hydroxide, the aqueous portion was ether-extracted several times, and the combined ethereal solutions were washed with water, dried, and evaporated. After removal of aniline at 5 mm., a colourless oil (8·8 g.) was obtained, b. p. 85°/0·1 mm., $n_{\rm D}^{19^\circ}$ 1·5845. Cooling and trituration with light petroleum gave a solid product (5·5 g.) which on crystallisation from light petroleum gave 2-*anilinohex*-3-*en*-5-*yne* as prismatic needles, m. p. 57·5° (Found : C, 84·4; H, 7·65; N, 8·45. $C_{12}H_{13}N$ requires C, 84·2; H, 7·65; N, 8·2%). Active hydrogen (Zerewitinoff) : The amine (47 mg.) evolved 12·8 c.c. of methane at 12°/768 mm., after heating to 90° (2·0 active hydrogen atoms per mol.).

A slow stream of dry hydrogen chloride was passed into a dry ethereal solution of the amine (0·3 g.). Scratching with a glass rod soon induced the separation of the derivative which was filtered off at intervals in order to avoid addition of hydrogen chloride to the ethylenic and acetylenic bonds. Crystallisation from acetone–light petroleum gave the *hydrochloride* (0·2 g.) as needles, m. p. 169° (Found : N, 6·95. $C_{12}H_{14}NCl$ requires N, 6·75%).

2-*Ethylaminohex*-3-*en*-5-*yne* (IV).—Prepared by heating ethylamine (90 c.c.) with 2-chlorohex-3-en-5-yne (19 g.) at 80° for 20 hours, followed by isolation in the manner described above, the *amine* (12·3 g.) was obtained with b. p. 72°/30 mm., $n_{\rm D}^{13.5^\circ}$ 1·4788 (Found : C, 77·85; H, 10·5. $C_8H_{13}N$ requires C, 78·0; H, 10·65%). Active hydrogen (Zerewitinoff) : 50 Mg. gave 20·5 c.c. of methane at 20°/765 mm., after heating to 90° (18 c.c. after 1 hour at 20°) (2·1 active hydrogen atoms per mol.).

Prepared as described above from the amine (1 g.) in dry ether (30 c.c.) the *hydrochloride* separated from *iso*propyl alcohol–light petroleum as plates, m. p. 158° (Found : N, 8·7. $C_8H_{14}NCl$ requires N, 8·75%). The α-*naphthylurea*, obtained by adding α-naphthyl *iso*cyanate (0·3 g.) to a solution of the amine (0·3 g.) in petroleum (5 c.c.; b. p. 80—100°), crystallised from aqueous alcohol in needles, m. p. 127° (Found : N, 9·8. $C_{19}H_{20}ON_2$ requires N, 9·6%). Light absorption : Maximum, 2230A.; ϵ = 74,500.

2-*Aminohex*-3-*en*-5-*yne* (III).—Heating the chloro-compound (30 g.) in liquid ammonia (250 c.c.) in an autoclave at 100° for 20 hours gave the primary *amine* (4·5 g.), b. p. 145°, 69—70°/39 mm., $n_{\rm D}^{17^\circ}$ 1·4934 (Found : C, 76·05; H, 9·65. C_6H_9N requires C, 75·75; H, 9·55%). Active hydrogen (Zerewitinoff) : 24·5 Mg. gave 18 c.c. of methane at 18°/762 mm., after heating to 90° (12 c.c. after 1 hour at 18°) (2·95 active hydrogen atoms per mol.). The amine (0·3 g.) gave the *hydrochloride* which on crystallisation from alcohol–light petroleum (b. p. 60—80°) formed plates (0·2 g.), m. p. 171° (Found : N, 10·75. $C_6H_{10}NCl$ requires N, 10·65%). The α-*naphthylurea* crystallised from aqueous alcohol in plates, m. p. 168—169° (decomp.) (Found : N, 10·65. $C_{17}H_{16}ON_2$ requires N, 10·6%). Light absorption : Maxima, 2230 and 2195A.; ϵ = 58,000 in each case. The *picrate* separated from ethyl acetate–light petroleum in yellow plates, m. p. 165° (Found : C, 44·65; H, 4·05. $C_{12}H_{12}O_7N_4$ requires C, 44·45; H, 3·75%).

1-*Diethylaminopent*-2-*en*-4-*yne* (VIII; R = H).—A mixture of 1-chloropent-2-en-4-yne (12 g.) and diethylamine (35 c.c.), heated at 80° for 16 hours (reaction occurs slowly in the cold) gave the *amine* (7·5 g.), b. p. 76°/27 mm., $n_{\rm D}^{18^\circ}$ 1·4730, as a colourless oil which rapidly becomes yellow in air (Found : C, 79·35, 79·65; H, 11·3, 11·3. $C_9H_{15}N$ requires C, 78·75; H, 11·05%). Active hydrogen (Zerewitinoff) : 63 Mg. gave 11 c.c. of methane at 18°/749 mm., no increase after heating to 90° (1·0 active hydrogen atom per mol.). The *hydrochloride* formed plates, m. p. 172°, from chloroform–light petroleum (b. p. 60—80°) (Found : C, 62·25; H, 9·35. $C_9H_{16}NCl$ requires C, 62·25; H, 9·3%). The *picrate* crystallised from water in yellow needles, m. p. 124° (Found : C, 49·3; H, 4·8. $C_{15}H_{18}O_7N_4$ requires C, 49·15; H, 4·95%).

1-*Diethylaminonon*-2-*en*-4-*yne* (VIII; R = *n*-Bu).—1-Hexyne (86 g.) in dry ether (150 c.c.) was added to a solution of ethylmagnesium bromide (from Mg, 24 g.) and the well-agitated mixture was refluxed in nitrogen on a steam-bath for 1½ hours. The solution was cooled and acraldehyde (56 g.) in ether (200 c.c.) was added dropwise during 2½ hours, after which the solution was stirred at 20° for 16 hours. The Grignard complex was decomposed with ammonium nitrate and isolation with ether gave *non*-1-*en*-4-*yn*-3-*ol* (100 g.), b. p. 101—102°/21 mm., 94—95°/13 mm., $n_{\rm D}^{20^\circ}$ 1·4658 (Found : C, 78·25; H, 10·25. $C_9H_{14}O$ requires C, 78·15; H, 10·2%). Active hydrogen (Zerewitinoff) : The carbinol (110 mg.) gave 18·0 c.c. of methane at 18°/761·5 mm. (0·95 active hydrogen atom per mol.). No light absorption with $E_{1\,\rm cm.}^{1\%}$ >40 above 2200A.

The carbinol (12 g.) was shaken with concentrated hydrochloric acid (40 c.c.) at room temperature in nitrogen for 2 hours. Isolation of the product in the usual way gave 1-*chloronon*-2-*en*-4-*yne* (10 g.), b. p. 105—108°/19 mm., $n_{\rm D}^{21.5^\circ}$ 1·4970 (Found : C, 69·3; H, 8·3. $C_9H_{13}Cl$ requires C, 69·0; H, 8·35%). Light absorption : Maximum, 2330A.; ϵ = 15,500.

When the chloro-compound (10 g.) was mixed with diethylamine (30 c.c.), heat was evolved and diethylamine hydrochloride separated rapidly. After 20 hours' heating in a sealed tube at 90°, isolation of the basic product gave 1-*diethylaminonon*-2-*en*-4-*yne* (8·6 g.), b. p. 72—74°/4 mm., $n_{\rm D}^{19^\circ}$ 1·4800 (Found : C, 80·95; H, 11·75. $C_{13}H_{23}N$ requires C, 80·75; H, 12·0%). The hydrochloride, a crystalline solid, was too hygroscopic to be isolated in a pure condition.

4-*Diethylaminohex*-2-*en*-5-*yne* (XI).—Heating a mixture of 2-chlorohex-3-en-5-yne (40 g.) with diethylamine (130 c.c.) at 100° for 20 hours gave the *amine* (28 g.), b. p. 69°/19 mm., $n_{\rm D}^{18^\circ}$ 1·4568 (Found : C, 79·7; H, 11·1. $C_{10}H_{17}N$ requires C, 79·4; H, 11·35%). Active hydrogen (Zerewitinoff) : 88 Mg. gave 13·8 c.c. of methane at 17°/766 mm., after heating to 90° (equivalent to 1·0 active hydrogen atom per mol.). Light absorption : End absorption at 2180A., ϵ = 2500.

Treatment of the amine (5 g.) with hydrogen chloride as described above gave the ***hydrochloride*** (3 g.) as prisms, m. p. 144°, from either ethyl acetate–light petroleum (b. p. 60—80°) or *cyclo*hexanone–light petroleum (b. p. 60—80°) (Found: N, 7·6. $C_{10}H_{18}NCl$ requires N, 7·45%). It shows no absorption of appreciable intensity above 2200A. The ***methiodide***, prepared in ether at 20°, crystallised from acetone–light petroleum as irregular prisms, m. p. 117—118° (decomp.) (Found: C, 44·9; H, 6·8. $C_{11}H_{20}NI$ requires C, 45·05; H, 6·9%).

The base (2·1 g.) regenerated from the hydrochloride (2·7 g.) with 2N-sodium hydroxide had b. p. 68°/19 mm., $n_{D}^{19\cdot5^\circ}$ 1·4552. Light absorption: End absorption only. At 2130A.; ϵ = 3000.

4-*Diethylaminodec*-2-*en*-5-*yne* (XIII).—A mixture of 2-chlorodec-3-en-5-yne (11·5 g.) and diethylamine (20 c.c.) on heating at 100° for 20 hours gave the *amine* (10·5 g.), b. p. 70—71°/4 mm., $n_{D}^{18^\circ}$ 1·4634 (Found: C, 80·9; H, 12·2. $C_{14}H_{25}N$ requires C, 81·05; H, 12·15%). It shows no absorption of $E_{1\,\text{cm.}}^{1\%}$ >100 above 2200A.

The *picrate*, prepared in acetone solution, was crystallised first from methyl alcohol and then from benzene–light petroleum (b. p. 60—80°), from which it separated as yellow prisms, m. p. 88° (Found: C, 54·25; H, 6·2. $C_{20}H_{28}O_7N_4$ requires C, 54·05; H, 6·45%).

4-*Diethylamino*-7-*methylnona*-2 : 7-*dien*-5-*yne* (XV).—2-Chloro-7-methylnona-2 : 7-dien-5-yne (9 g.) was heated with diethylamine (30 c.c.) at 95° for 20 hours in a stainless steel autoclave. Isolation of the basic material in the usual manner gave 4-*diethylamino*-7-*methylnona*-2 : 7-*dien*-5-*yne* (6·5 g.), b. p. 57—59°/0·5 mm., $n_{D}^{19^\circ}$ 1·4855 (Found: C, 82·15; H, 11·25. $C_{24}H_{29}N$ requires C, 81·9; H, 11·3%).

Ozonolysis of Propenylethynylcarbinol.—Ozonised oxygen (3%) was passed into a solution of the carbinol (0·96 g.) in "AnalaR" acetic acid (25 c.c.) at 15° through a fine capillary for twice the time theoretically required for the ozonolysis of the ethenoid linkage. The resulting solution was added dropwise during 15 minutes to a vigorously stirred mixture of zinc dust (10 g.) and boiling water (200 c.c.) to which small quantities of quinol and silver nitrate had been added. The mixture was then distilled in nitrogen, the distillate (about 60 c.c.), collected in a receiver at 0°, was neutralised (phenolphthalein) with dilute sodium hydroxide, and the resulting solution was redistilled, the distillate being passed into an excess of a saturated solution of dimedon in aqueous methanol (10%). The precipitate (1·45 g.) obtained after 24 hours had m. p. 135—138° and after crystallisation from aqueous alcohol yielded needles or plates of the dimedon derivative of acetaldehyde, m. p. 138—139°, undepressed on admixture with an authentic specimen (m. p. 140°).

Ozonolysis of 4-*Diethylaminohex*-2-*en*-5-*yne* (XI).—The amine (1·51 g.), ozonised as described above, gave acetaldehyde dimedon derivative (1·27 g.), m. p. 135—138°, which after one crystallisation from aqueous alcohol had m. p. 139°, undepressed on admixture with an authentic specimen.

Ozonolysis of 4-*Diethylaminodec*-2-*en*-5-*yne* (XIII).—The amine (2·07 g.), treated as indicated above, gave 1·06 g. of dimedon derivative, which softened at *ca.* 80° and had m. p. 105—120°. Crystallisation from pentane gave the acetaldehyde derivative (0·75 g.), m. p. 136—138° (mixed m. p. with authentic specimen, 138—140°). The more soluble, low m. p. impurity may have been the dimedon derivative (m. p. 105°) of *n*-valeraldehyde, arising from ozonolysis of the acetylenic bond.

Reactions of 2 : 9-*Dichlorodeca*-3 : 7-*dien*-5-*yne* (IX) *with Primary Amines.*—(*a*) A mixture of dry methylamine (20 g.) and 2 : 9-dichlorodeca-3 : 7-dien-5-yne (5 g.) was heated at 100° in a sealed tube for 24 hours. The clear liquid was treated with excess of concentrated hydrochloric acid and repeatedly extracted with ether until no more neutral material was extracted. The diamine was liberated from the acid solution with excess of sodium hydroxide solution and isolated by means of ether. Distillation then gave 2 : 9-*bismethylaminodeca*-3 : 7-*dien*-5-*yne* (X) (2·6 g.), as a yellow liquid, b. p. 60° (bath temp.)/10^{-4} mm., $n_{D}^{17^\circ}$ 1·5371 (Found: C 75·0; H, 10·35. $C_{12}H_{20}N_2$ requires C 75·0; H, 10·5%).

(*b*) When the dichloro-compound (5 g.) was treated with ethylamine (20 g.) as described above the product consisted of 2 : 9-*bisethylaminodeca*-3 : 7-*dien*-5-*yne* (2·5 g.), a pale yellow liquid, b. p. 116—118°/10^{-4} mm., $n_{D}^{18^\circ}$ 1·5120 (Found: C, 76·5; H, 11·05. $C_{14}H_{24}N_2$ requires C, 76·3; H, 11·0%).

Reactions of 2 : 9-*Dichlorodeca*-3 : 7-*dien*-5-*yne* (IX) *with Secondary Amines.*—(*a*) The dichloro-compound (5 g.) was caused to react with diethylamine (20 g.) as described above, the reaction tube gradually becoming filled with crystals of diethylamine hydrochloride. The diamine mixture (6 g.; 90%) was isolated as a pale yellow liquid, b. p. 86—88°/10^{-3} mm., 110°/0·1 mm.; $n_{D}^{18^\circ}$ 1·4890 (Found: C, 78·3; H, 11·4. Calc. for $C_{18}H_{32}N_2$: C, 78·2; H, 11·7%). Light absorption: Maximum, 2310A.; ϵ = 7500. Redistillation of 3·5 g. of the mixture gave a product (2·5 g.) with $n_{D}^{17^\circ}$ 1·4815. Light absorption: Maximum, 2200A.; ϵ = 5500. Inflexion, 2420A.; ϵ = 4000. Ozonolysis of this product (2·8 g.) followed by working up in the manner described above gave the dimedon derivative of acetaldehyde (0·9 g.), m. p. 139—140°, undepressed on admixture with an authentic sample.

(*b*) A mixture of the dichloro-compound (5 g.) and dimethylamine (20 g.) treated as above gave the diamine mixture (4·5 g.; 90%) as a yellow liquid, b. p. 50° (bath temp.)/10^{-4} mm., $n_{D}^{20^\circ}$ 1·5146 (Found: C, 76·8; H, 10·75. Calc. for $C_{14}H_{24}N_2$: C, 76·3; H, 11·0%).

Note Added in Proof. Ethylation of 2-*Ethylaminohex*-3-*en*-5-*yne* (IV).—A mixture of the above amine (12·3 g.) and ethyl bromide (10·9 g.) together with a trace of quinol was heated at 80° for 48 hours. Isolation of the amine fraction gave 7 g. of material, b. p. 60—68°/15 mm., $n_{D}^{15^\circ}$ 1·4615. This mixture, dissolved in petrol (20 c.c.; b. p. 100—120°), was treated with α-naphthyl *iso*cyanate until no further precipitate appeared to be formed. After 1 hour the solid was filtered off and on crystallisation from aqueous alcohol gave the α-naphthylurea of (IV) (3 g.), m. p. 127°, undepressed on admixture with an authentic sample. The petrol solution was shaken for some time with an excess of dilute hydrochloric acid, and the small amount of di-α-naphthylurea so formed was removed; treatment of the aqueous layer with alkali followed by isolation with ether gave 4-diethylaminohex-2-en-5-yne (XI) (4·5 g.), b. p. 63—65°/15 mm., $n_{D}^{14^\circ}$ 1·4589. Light absorption in alcohol: End absorption only, $E_{1\,\text{cm.}}^{1\%}$ 90 at 2180A. The hydrochloride, after crystallisation from acetone–ethyl acetate, had m. p. 142—143°, undepressed on admixture with an authentic sample. It showed no absorption of appreciable intensity in the range 2200—4000A. The methiodide, crystallised once from acetone–light petroleum, had m. p. 115—117°, undepressed on admixture with an authentic sample.

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