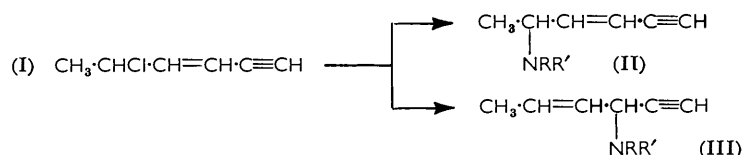


648. *Researches on Acetylenic Compounds. Part LXII.\* The Interaction of Amines and the Stereoisomers of 5-Chlorohex-3-en-1-yne.*

By IAN BELL, R. MADROÑERO, and M. C. WHITING.

*trans*-5-Chlorohex-3-en-1-yne reacts with a number of amines to give normal and abnormal (*i.e.*, non-conjugated) substitution products in proportions which vary widely from case to case and are much influenced by the solvent used and by the presence of small amounts of water. Earlier mechanistic suggestions are revised, and the results are correlated with differential solvent effects upon  $S_N1$ ,  $S_N2$ , and  $S_N2'$  processes. The *cis*-chloride behaves differently, giving either pyrroles by cyclisation of the products of normal substitution, or unconjugated amines by abnormal substitution.

REACTIONS between 5-chlorohex-3-en-1-yne (I) and a number of amines were described by Jones, Lacey, and Smith.<sup>1</sup> While ammonia, aniline, and ethylamine behaved normally, giving the expected conjugated vinylacetylenic amines (II), diethylamine gave instead



3-diethylaminohex-4-en-1-yne (III;  $R = R' = \text{Et}$ ). Similar results were obtained with some related chlorides; they were explained on the assumptions that the products were in each case the most stable isomers, and that rearrangement was promoted by high basicity of the amine used and by the presence in the allylic chloride of substituents tending to increase the mobility of the anionotropic system.

These assumptions have seemed less plausible in recent years, and re-investigation of the reaction by Dr. J. B. Armitage in 1949<sup>2</sup> revealed some discrepancies with the original experimental findings. The work of Young, Webb, and Goering,<sup>3</sup> amplified by Young, Clement, and Shih,<sup>4</sup> has provided the basis for a more acceptable rationalisation of the results of Jones *et al.*,<sup>1</sup> which have now been extended and generalised. Reactions between 5-chlorohex-3-en-1-yne—now known<sup>5</sup> to be a 3 : 1 mixture of stereoisomers—and amines were originally carried out in metal autoclaves; these experiments have given inconsistent results—usually lower yields—on attempted repetition, probably because corrosion introduced small amounts of metal halides which influenced the reaction. Working at lower temperatures with glass apparatus, we have examined the reactions of the pure *cis*- and *trans*-5-chlorohex-3-en-1-yne isomers with ethylamine and diethylamine, the amines mainly used by Jones *et al.*,<sup>1</sup> and also with several others. Higher yields were obtained; but the composition of the products was influenced by the presence of quite small quantities of water, so we controlled this factor also. It was possible at an early stage to identify products which were essentially homogeneous, and these were purified as crystalline salts and regenerated. With pure specimens of all the conjugated and two representative unconjugated amines available (see Table), quantitative analysis of total reaction products by spectrophotometry became straightforward.

The case of *trans*-5-chlorohex-3-en-1-yne will be considered first. All amines, under

\* Part LXI, *J.*, 1958, 1313.

<sup>1</sup> Jones, Lacey, and Smith, *J.*, 1946, 940.

<sup>2</sup> Armitage, unpublished work at Manchester.

<sup>3</sup> Young, Webb, and Goering, *J. Amer. Chem. Soc.*, 1951, **73**, 1076.

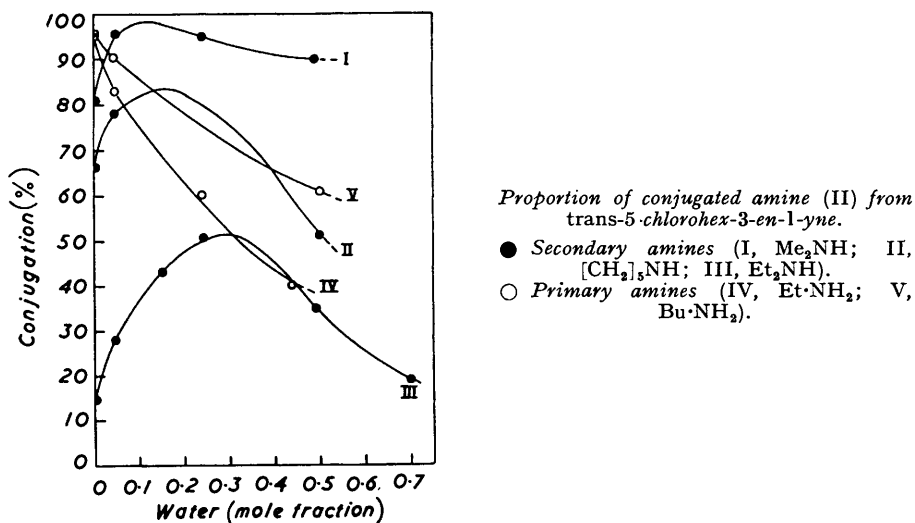
<sup>4</sup> Young, Clement, and Chih-Hua Shih, *ibid.*, 1955, **77**, 3061.

<sup>5</sup> Bell, Jones, and Whiting, *J.*, 1957, 2597.

Amine	B. p./mm.	$n_D$	$\epsilon_{2230}$	Amine	B. p./mm.	$\epsilon_{2230}$ *
(I; R = H, R' = Et)	61.5°/20	1.4756 (18°)	13,400	(I; R = R' = Me)	41°/15	13,600
(II; R = H, R' = Et)	54°/20	1.4570 (20°)	170	(I; RR' = [CH <sub>2</sub> ] <sub>6</sub> )	94°/15	13,400
(I; R = R' = Et) .....	75°/15	1.4738 (22°)	13,400	(I; R = H, R' = Bu)	85°/15	13,400
(II; R = R' = Et)	68°/22	1.4530 (21.5°)	560			

\* Spectra were determined in EtOH; the conjugated, but not the unconjugated, amines showed maxima at  $2230 \pm 10 \text{ \AA}$ .

the conditions used, gave vinylacetylenic amines in total yields of up to 90%. The Figure shows the variation in the proportions of the two isomers formed when ethylamine, dimethylamine, *n*-butylamine, diethylamine, and piperidine were treated with the chloride in the presence of varying amounts of water. The two primary amines gave, under anhydrous conditions, almost pure conjugated amines, whereas addition of water resulted in the formation of mixtures, quite small quantities, especially when calculated on a weight or volume basis, having a marked effect. Qualitatively, it was clear that the addition of water was increasing the reaction rate. It is possible to explain these results simply by assuming that bimolecular substitution by primary amines proceeds without significant



rearrangement [*i.e.*,  $k(S_N2) \gg k(S_N2')$  in solvent amine], but that unimolecular substitution becomes more important as the reaction medium becomes more polar and gives a mixture in which the amount of unconjugated amine slightly outweighs that of its isomer. Acceleration of both reactions, but of  $S_N1$  more than  $S_N2$ , would be predicted as the polarity of the medium is increased.<sup>6</sup> The unconjugated and conjugated isomers (I and II; R = H, R' = Et) were both stable in the presence of ethylamine hydrochloride under the conditions used, and indeed under the more drastic conditions which were applied in unsuccessful attempts to effect anionotropic rearrangements.

The secondary amines behaved quite differently. Dimethylamine, piperidine, and diethylamine gave, in the absence of water, products containing respectively 81%, 66%, and 18% of the conjugated isomers. In each case, addition of water resulted in, first, an increase, to maxima of about 97%, 84%, and 50%, then a decrease to less than 90%, 50%, and 20%, respectively. The amounts of water required to give the maximal proportion of conjugated amine increased in the same order: dimethylamine, piperidine, diethylamine. Now, this order is not related to the basicity of the three amines used (dimethylamine < diethylamine < piperidine); it is that of decreasing polarity, considered as solvents. We believe that in the anhydrous amines, reactions  $S_N2$  and  $S_N2'$  proceed side by side; in

<sup>6</sup> Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 345 *et seq.*

dimethylamine, as in the primary amines studied,  $k(S_N2) > k(S_N2')$ , whereas in diethylamine the relation is inverted. This seems a reasonable assumption; the transition state for the  $S_N2$  reaction shows considerable dipolar character, and its potential energy will be much affected by the ability of solvent molecules to stabilise the developing charges by dipole compensation and intermolecular hydrogen-bond formation. In  $S_N2'$  substitution, however, the attacking nucleophil almost certainly enters from the same side of the planar allylic system as that on which the chloride ion leaves;<sup>3,7</sup> the two centres of opposite charge are then close together, and the dipole moment is correspondingly smaller, while the formation of an intra-complex hydrogen bond<sup>3</sup> between the arriving and the departing group will, in this case, further reduce the need for solvation. Addition of water to the reaction mixture would be expected to stabilise the  $S_N2$  transition state relative to that for  $S_N2'$  reaction, and so to increase the proportion of conjugated form; ultimately, however, it will accelerate unimolecular substitution to the point where this process becomes of greater importance, and the ratio of products will then approximate to that typical of the allylic carbonium ion, and varying to some extent, of course, with the amine.

When the *trans*-chloride was treated with "50%" aqueous acetonitrile under the conditions used for the reactions with amines it did in fact suffer hydrolysis; on distillation of the product, no chloride was recovered, but the hexenynol produced was heavily contaminated with higher-boiling compounds and showed strong bands in the C=O stretching region. Hydration of acetylenic compounds and addition of hydrogen chloride are possible under such conditions.

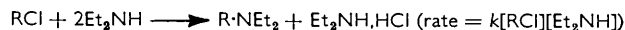
This interpretation is not, of course, rigorously proved; while the complete description of simple "carbonium ions" is still a matter of controversy, that of allylic and vinyl-acetylenic analogues is beyond the range of useful discussion. If, however, ion-pair or covalently solvated intermediates were postulated, their behaviour would presumably be similar as far as the present studies are concerned.

Except that products treated as individual isomers by the earlier workers are now seen to have contained about 4% (ethylamine) and 18% (diethylamine) of the unconjugated and conjugated amines, respectively, the above experimental results agree well with those earlier reported. The conversion of 5-ethylaminohex-3-en-1-yne into 3-diethylaminohex-4-en-1-yne on ethylation, which was described (30% yield) by Jones *et al.*<sup>1</sup> only in a footnote, would not be consistent with the present conclusions, since it would imply thermodynamic control of the reaction and an unexpected stability relation for the tertiary amines. This experiment was therefore repeated, both with neat reactants, as described<sup>1</sup> [but in glass apparatus (29% yield)], and in acetonitrile (58% yield). In each case the tertiary amine obtained consisted *entirely* (by spectrophotometry  $\pm$  96%) of the *conjugated* form. We can only assume that the actual specimen of the conjugated ethylamino-compound used in this experiment by the earlier workers had been prepared under non-anhydrous conditions and had contained enough of the unconjugated isomer to allow the isolation of 30% of its ethylated analogue after preferential destruction of the conjugated amine (which is in fact more easily resinified) under the vigorous conditions used.

The essence of the explanation just given for the striking difference between the behaviour of ethylamine and diethylamine is that as solvents they are of different polarity. If this is correct, it follows that in a medium of which the amine constitutes only a small part, the two amines will give much more similar products. This is apparently true for aqueous solutions (see Figure); although immiscibility prohibits the continuation of the curves, these do approach comparable values for the percentage of conjugated isomers in the two cases. Choice of alternative solvents is not easy, as when alcohols are used considerable quantities of alkoxyhexenynes result; acetone rapidly self-condenses in the reaction conditions used, while in light petroleum, benzene, or ether a second liquid phase, consisting of the amine and amine hydrochloride, separates. Acetonitrile proved satisfactory; in it ethylamine gave, in 82% yield, a product containing at least 99% of the

<sup>7</sup> Stork and White, *J. Amer. Chem. Soc.*, 1953, **75**, 4119.

conjugated isomer, while diethylamine gave, in 46% yield, a product containing 84% of the conjugated isomer. A molar ratio 1 : 4 : 30 for chloride : amine : acetonitrile was used in each case. These reactions were also investigated kinetically at 35°; diethylamine gave good second-order rate constants up to 85% completion, providing that the equation used was that calculated for the reaction:

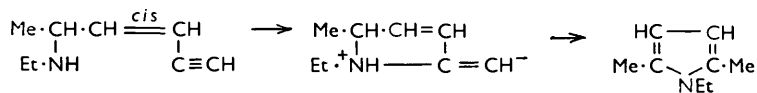


Evidently the acetylenic amines formed are much less basic than diethylamine (or ethylamine).<sup>8</sup> The rate constants in this case rose steadily during the reaction from  $2.26 \times 10^{-4}$  to  $2.48 \times 10^{-4}$  l. mole<sup>-1</sup> min.<sup>-1</sup>, presumably because of the expected primary salt effect. For ethylamine, the second-order rate constants fell rapidly, then rose slowly; the initial drop was greater when the initial chloride concentration was halved, and was almost certainly due to the presence, in the ethylamine used, of a trace of impurity (presumably ammonia or methylamine) which reacted more rapidly. The best estimates for the initial rate constants for ethylamine and diethylamine were  $(4.0 \pm 0.2) \times 10^{-4}$  and  $(2.25 \pm 0.05) \times 10^{-4}$  l. mole<sup>-1</sup> min.<sup>-1</sup>, respectively. If these results, obtained for 2M- and M-solutions, respectively, at 35°, are applicable relatively to the 2.5M-solutions at 50° used in the preparative experiments, it follows that the S<sub>N</sub>2' reaction for diethylamine in acetonitrile is at least seven times faster than that for ethylamine in the same solvent, since 16%, as against <1%, of the unconjugated amine was formed. Evidently, then, the above explanation is not entirely adequate; diethylamine shows an intrinsic tendency to react by mechanism S<sub>N</sub>2', for which the explanation is not obvious.

The use of acetonitrile in preparative work involving halide-amine reactions in allylic systems when normal replacement is required is clearly advantageous. Nitromethane, used as solvent in the reaction with ethylamine, gave, in 71% yield, a product containing only 83% of the conjugated isomer, and so is much less satisfactory.

In a system containing diethylamine, water, and acetonitrile (molar ratio about 1 : 8 : 3) a 71% yield of a product containing only 10% of the conjugated form was obtained; on the other hand ethylamine under similar conditions gave an essentially (78%) conjugated product. Though too complicated for mechanistic discussions, the former conditions may have preparative value for promoting abnormal substitution (see below).

Attention was next directed to the reactions of the *cis*-chloride. In acetonitrile, less than a 2% yield of basic material was obtained; the main product was 1-ethyl-2:5-dimethylpyrrole (62%). In anhydrous ethylamine the same product was obtained in smaller yield (18%), together with much recovered chloride (46%) and a little (~9%) 3-ethylaminohex-4-en-1-yne, under the same conditions as those in which the *trans*-chloride gave a 77% yield of amine. In aqueous acetonitrile (1 : 8 : 3) the main product (37% yield) was basic, and of this only 4% was the conjugated isomer. A little ethyldimethylpyrrole was present, with a larger quantity of *cis*-hex-3-en-5-yn-2-ol (total ca. 8%). Apparently use of acetonitrile again gives a clean, normal bimolecular substitution reaction, the product then undergoing cyclisation to the pyrrole. In excess of amine as solvent the S<sub>N</sub>2



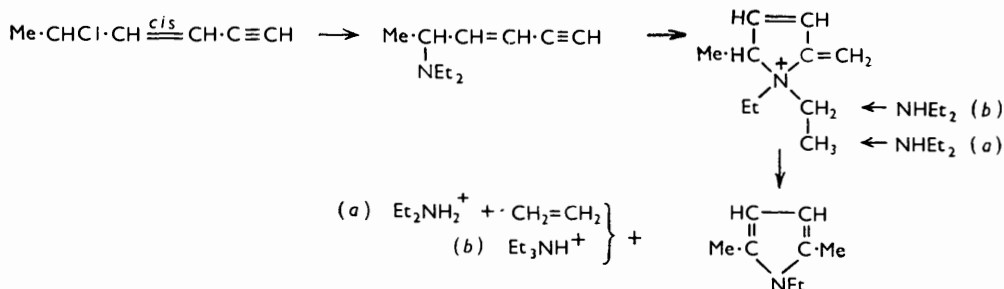
reaction is slower than that involving the *trans*-isomer, and the S<sub>N</sub>2' process is able to compete fairly effectively. Under S<sub>N</sub>1 conditions a carbonium ion is formed which for the most part reacts before equilibrating with its *trans*-isomer,<sup>9</sup> giving mainly the non-conjugated product.

The reaction between the *cis*-chloride and diethylamine in acetonitrile took an unexpected course; the product was again 1-ethyl-2:5-dimethylpyrrole. Presumably

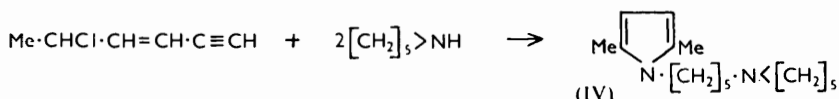
<sup>8</sup> Wolff and Ramin, *Annalen*, 1957, **610**, 67.

<sup>9</sup> Waters and de la Mare, *Ann. Reports*, 1953, **50**, 141.

the first formed *cis*-tertiary amine underwent cyclisation to a 1:1-dimethylpyrrolium ion (or its prototropic isomer), which lost an ethyl group by either (a) an elimination or (b) a substitution involving a second molecule of diethylamine:



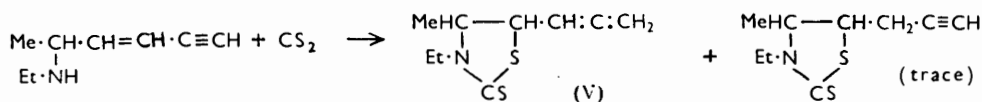
Rather than try to distinguish between these possibilities, we substituted piperidine for diethylamine, when (a) would lead to 2:5-dimethyl-1-pent-4'-enylpyrrole, and (b) to 1-(2:5-dimethyl-1-pyrrolyl)-5-piperidinopentane (IV). The product was clearly the latter, forming an unstable monohydrochloride and showing ultraviolet and infrared absorption spectra suggestive of a trisubstituted pyrrole.



In acetonitrile, diethylamine and the *cis*-chloride also gave a very small (2%) yield of basic material, largely (90%) unconjugated. This is less than the yield of unconjugated amine obtained from the *trans*-isomer (7%); evidently the  $S_N2'$  reaction with diethylamine is also inhibited by the *cis*-configuration. In contrast, the reaction in "50%" aqueous acetonitrile (1:8:3) gave almost as large a yield (66%) of basic product as did that of the *trans*-form, and it contained a mere 1.5% of the conjugated amine. This clear-cut result encourages the belief that in this case, at least, a genuine unimolecular reaction was being observed; the products bore no resemblance to those obtained in anhydrous acetonitrile, the pyrrole yield being below 1.5%.

The *cis*-chloride reacted rather sluggishly with aniline to give the known crystalline 2:5-dimethyl-1-phenylpyrrole.

Infrared spectra for the amines prepared were consistent with the structures proposed. 3-Ethylaminohex-4-en-1-yne was examined in carbon disulphide solution without complications due to reaction between the  $>\text{NH}$  and carbon disulphide groupings—presumably because of its relatively low basicity<sup>8</sup>—but when the conjugated isomer was similarly treated it gave a spectrum which included a strong band at 1951  $\text{cm}^{-1}$ . This band was



traced to the rapid formation of the allenic thiothiazolidone (V), which was isolated after distillation and separated by crystallisation from a small quantity of the acetylenic isomer formed concurrently.

#### EXPERIMENTAL

*Preparation of Pure Amines.*—5-Ethylaminohex-3-en-1-yne. *trans*-5-Chlorohex-3-en-1-yne<sup>5</sup> (90 g.), ethylamine (200 c.c.), and acetonitrile (1200 c.c.) were heated to 50° for 40 hr., under a water-condenser surmounted by a "cold-finger" condenser containing acetone and solid carbon dioxide (the latter was probably unnecessary, since there was no evidence of condensation in it). The ethylamine and about 900 c.c. of acetonitrile were distilled off, water was added, and the

basic fraction was isolated with ether. Distillation gave the amine (78.5 g., 81%), b. p. 61—62°/20 mm.,  $n_D^{18}$  1.4756, m. p.  $-5.5^\circ$  to  $-4.5^\circ$  (Jones *et al.*<sup>1</sup> report b. p. 72°/30 mm.,  $n_D^{13.5}$  1.4788). The  $\alpha$ -naphthylurea formed needles, m. p. 126—127°, from aqueous ethanol, and the hydrochloride, prepared in dry ether, formed plates, m. p. 159.5—160.5°, from propan-2-ol-light petroleum (Jones *et al.*<sup>1</sup> give m. p. 127° and 158°, respectively).

**3-Ethylaminohex-4-en-1-yne.** *trans*-5-Chlorohex-3-en-1-yne (91 g.), ethylamine (200 c.c.), water (72 c.c.), and acetonitrile (72 c.c.) were mixed; the temperature rose to 60°. The mixture was kept for 24 hr. at 40°, then worked up, giving a basic product (72.5 g.), b. p. 66—75°, which was redistilled through a 50 × 1.8 cm. column filled with 1/16" gauze rings<sup>10</sup> and fitted with a total-condensation still-head with manual control of reflux ratio. The first group of fractions (20 g.), b. p. 58—59°/18 mm.,  $n_D^{19}$  1.4594—1.4608, probably contained 90—95% of the unconjugated amine; a portion was converted into the *hydrochloride*, which separated from propan-2-ol-light petroleum as needles, m. p. 179—180° (Found: C, 60.4; H, 8.85.  $C_8H_{14}NCl$  requires C, 60.15; H, 8.85%). Regeneration gave the *amine*, b. p. 54°/20 mm.,  $n_D^{20}$  1.4570 (Found: C, 77.7; H, 10.75.  $C_8H_{13}N$  requires C, 78.0; H, 10.65%).

**5-Diethylaminohex-3-en-1-yne.** (a) 5-Ethylaminohex-3-en-1-yne (12.3 g.), ethyl bromide (21.8 g.), and acetonitrile (150 c.c.) were heated under reflux (internal temperature about 85°) for 24 hr. Isolation of the basic fraction with ether and distillation gave a liquid (11.25 g.), which was treated with light petroleum and phenyl *isocyanate* (10 g.). The phenylurea was separated by filtration, and the basic fraction again isolated and distilled, giving 5-*diethylaminohex-3-en-1-yne* (8.8 g.), b. p. 74—76°/15 mm.,  $n_D^{21.5}$  1.4736—1.4740; after redistillation it had  $n_D^{22}$  1.4738, m. p.  $-6^\circ$  to  $-4^\circ$  (Found: C, 79.15; H, 11.15.  $C_{10}H_{17}N$  requires C, 79.4; H, 11.35%). The hydrochloride formed prisms, m. p. 147—148°, from ethyl acetate; the *methiodide* formed prisms, m. p. 183—184° (decomp.), from acetone (Found: C, 44.9; H, 6.7.  $C_{11}H_{20}NI$  requires C, 45.05; H, 6.9%).

(b) The secondary amine (12.3 g.) and ethyl bromide (43.6 g.) were heated under reflux (internal temperature 53°) for 24 hr. The tertiary amine formed was isolated as above (4.35 g.), having b. p. 88—90°/27 mm.,  $n_D^{26}$  1.4704—1.4708, with an extinction coefficient at 2230 Å almost equal to that of the above specimen.

**3-Diethylaminohex-4-en-1-yne.** 3-Ethylaminohex-4-en-1-yne (2.25 g.), ethyl bromide (10 g.), and acetonitrile (75 c.c.) were heated under reflux for 24 hr. (internal temperature 75°). Isolation of the tertiary amine as above gave 3-*diethylaminohex-4-en-1-yne* (1.35 g.), b. p. 68°/22 mm.,  $n_D^{21.5}$  1.4530—1.4532 (Found: C, 79.3; H, 11.2%). The hydrochloride formed prisms, m. p. 146—147°, from benzene (Jones *et al.*<sup>1</sup> report b. p. 68°/19 mm.,  $n_D^{19.5}$  1.4552 for the amine and m. p. 144° for the hydrochloride).

The other conjugated amines (I = NMe<sub>2</sub>, NHBu, N[CH<sub>2</sub>]<sub>5</sub>) were isolated from the products of analytical experiments as described below.

**Analytical Experiments.**—Ethylamine and dimethylamine were stored over potassium hydroxide and dried with sodium and lithium; there was some evidence that the deep blue colour of the metal solution was obtained most quickly when both metals were used. They were distilled directly into the cooled reaction vessel. Diethylamine was fractionated under partial reflux. *n*-Butylamine and piperidine were distilled over sodium. Results are tabulated and, in part, discussed further below.

**Reactions of *cis*-5-Chlorohex-3-en-1-yne.**—(a) The *cis*-chloride (11.4 g.), ethylamine (26 c.c.), and acetonitrile (200 c.c.) were heated to 50° for 48 hr. under reflux. The basic fraction obtained was less than 0.2 g.; distillation of the neutral fraction gave 1-ethyl-2:5-dimethylpyrrole (7.6 g., 62%), b. p. 56—58°/9 mm.,  $n_D^{21}$  1.4904—1.4908 (Found: C, 77.85; H, 10.75; N, 11.25. Calc. for  $C_8H_{13}N$ : C, 78.0; H, 10.65; N, 11.35%). The pyrrole showed no absorption maximum above 2000 Å, but at that wavelength had  $\epsilon$  9000 (Hazelwood *et al.*<sup>11</sup> give b. p. 102°/79 mm.).

(b) Experiments 1, 5, 7, 8, and 15 were repeated with the *cis*-chloride, and are numbered with asterisks:

Expt. 1\* gave unchanged chlorohexenyne (2.6 g., 46%), ethyldimethylpyrrole (1.12 g., 18%), and an amine fraction (0.5 g., 9%), mainly unconjugated but difficult to free from a little pyrrole.

Expt. 5\* gave a basic fraction (2.27 g., 37%) which contained only 4% of the conjugated isomer (derived from 1—2% of *trans*-chloride as impurity?). The neutral fraction (0.41 g.),

<sup>10</sup> Dixon, *J. Soc. Chem. Ind.*, 1949, **68**, 88, 119.

<sup>11</sup> Hazelwood, Hughes, and Lions, *Proc. Roy. Soc. New South Wales*, 1937, **71**, 92.

Analytical experiments with *trans*-5-chlorohex-3-en-1-yne.

Expt.	Amine (c.c.)	Water (c.c.)	MeCN (c.c.)	Temp.	Time (hr.)	Yield (%)	Conjugn.* (%)	Remarks	
1	EtNH <sub>2</sub>	13	6	0	20°	96	77	95	a
2	"	75	1.1	0	20	96	82	83	a
3	"	75	7.1	0	20	96	81	60	a
4	"	75	21.5	0	20	96	76	40	a
5	"	13	37.5	37.5	50	24	36	93	b
6	"	50	7.1	20.5	20	96	83	78	a
7	Et <sub>2</sub> NH	21	0	0	65	24	59	14	c
8	"	42	0	150	50	24	46	84	d
9	"	75	0.6	0	60	24	51	28	
10	"	75	2.5	0	60	24	63	43	a
11	"	75	4.4	0	60	24	73	51	a
12	"	75	13.1	0	60	24	76	35	a
13	"	50.4	22.1	0	60	24	71	19	e
14	"	75	4.4	12.7	60	24	76	53	a
15	"	21	37.5	37.5	50	24	71	10	a
16	Me <sub>2</sub> NH	15	0	0	20	96	81	81	a
17	"	75	1.0	0	20	96	73	96	a
18	"	75	6.5	0	20	96	76	95	a
19	"	75	19.6	0	20	96	76	90	
20	BuNH <sub>2</sub>	21	0	0	65	24	55	96	
21	"	75	0.65	0	65	24	74	91	
22	"	75	13.8	0	65	24	16	61	
23	(CH <sub>2</sub> ) <sub>5</sub> NH	30	0	0	65	24	63	66	
24	"	75	0.5	0	65	24	61	78	
25	"	75	4.6	0	65	24	61	83	
26	"	75	14.5	0	65	24	63	52	

\* The percentages of conjugated isomer were obtained spectrophotometrically, by using the listed  $\epsilon_{\max}$  values for the conjugated amines and the  $\epsilon_{2230}$  values (no maximum) of the ethylamino- and diethylamino-compounds (III) for secondary and tertiary unconjugated amines, respectively. Results are, of course, quite insensitive to small variations in the latter.

(a) Neutral fraction  $>100$  mg., not investigated; (b) neutral fraction yielded 1.7 g. (35%) of an alcohol, b. p. 92°/60 mm.,  $n_D^{20}$  1.4846,  $\lambda_{\max}$  2230 Å,  $\epsilon$  13,000, evidently essentially (~93%) *trans*-hex-3-en-5-yn-2-ol; (c) neutral fraction yielded 0.31 g. (5.5%) of unchanged chloride; (d) in expt. 8, 11.4 g. of the chlorohexenyne were used; (e) in expt. 13, 3.84 g. of the chlorohexenyne were used.

b. p. 65—69°/18 mm.,  $n_D^{19}$  1.4762—1.4798, was shown by its infrared spectrum to be a mixture of *cis*-hex-3-en-4-yn-2-ol and some ethyldimethylpyrrole. 2:5-Dimethylfuran was sought but not found.

Expt. 7\* was continued for 72 hr. instead of 24 hr. The basic fraction (2.5 g., 33%) contained 9% of the conjugated form. The neutral fraction (0.23 g.), b. p. 100—120° (bath temp.)/76 mm.,  $n_D^{21}$  1.4802, was a mixture of ethyldimethylpyrrole and unchanged chloride.

Expt. 8\* gave a basic fraction (0.33 g., 2%), containing 12% of the conjugated tertiary amine, the remainder being 3-diethylaminohex-4-en-1-yne. The neutral fraction yielded 1-ethyl-2:5-dimethylpyrrole (3.6 g., 29%), b. p. 58°/13 mm.,  $n_D^{22}$  1.4880—1.4892, with ultraviolet and infrared spectra identical with those of the specimen obtained from ethylamine.

Expt. 15\* was carried out at 65° instead of 50°. The basic fraction (5.0 g., 66%) contained only 1.5% of the conjugated amine; it had b. p. 66—68°/16 mm.,  $n_D^{21}$  1.4522—1.4524, and showed the same infrared spectrum as did the amine obtained by ethylation of the secondary amine. The neutral fraction contained less than 100 mg.

(c) 1-(2:5-Dimethyl-1-pyrrolyl)-5-piperidinopentane (IV). *cis*-2-Chlorohex-3-en-5-yne (11.4 g.), piperidine (40 c.c.), and acetonitrile (150 c.c.) were heated to 50° for 48 hr. Distillation of the basic fraction gave a fore-run (2.55 g.; b. p. ca. 50°/0.05 mm.,  $n_D^{21}$  1.4890—1.4896), apparently mainly 3-piperidinohex-4-en-1-yne, then the expected *pentane* (4.7 g., 19%), b. p. 110—112°/0.05 mm.,  $n_D^{21}$  1.5070 (after redistillation) (Found: C, 77.25; H, 11.15; N, 11.1. C<sub>16</sub>H<sub>28</sub>N<sub>2</sub> requires C, 77.35; H, 11.35; N, 11.3%),  $\lambda_{\max}$  2160 Å ( $\epsilon$  6800 in EtOH). The *hydrochloride* formed unstable prisms, m. p. 179—180°, from benzene (Found: C, 66.95; H, 9.95. C<sub>16</sub>H<sub>28</sub>N<sub>2</sub>Cl requires C, 67.45; H, 10.3%).

(d) 2:5-Dimethyl-1-phenylpyrrole. The *cis*-chloride (5.73 g.), aniline (18.5 c.c.), and acetonitrile (75 c.c.) were heated to 55° for 75 hr. Distillation of the neutral fraction gave a liquid (0.83 g., 10%), b. p. 60—61°/0.05 mm.,  $n_D^{19}$  1.5650—1.5658, which yielded prisms, m. p. 50.5—51.5° (from pentane at -30°) (Hazlewood *et al.*<sup>11</sup> give m. p. 51—52°).

*Isolation of Pure Products from Analytical Experiments.*—5-Dimethylamino-hex-3-en-1-yne. The product from expt. 17 was dissolved in dry ether, and a solution of hydrogen chloride in ether was added slowly. The precipitate crystallised from isopropyl alcohol–light petroleum, giving hygroscopic plates (1.6 g.), m. p. 122–123°, of the *hydrochloride* (Found: C, 60.9; H, 9.0; N, 8.3; Cl, 21.7.  $C_8H_{14}NCl$  requires C, 60.2; H, 8.75; N, 8.75; Cl, 22.2%). The *amine*, obtained by regeneration, had b. p. 45°/15 mm. (Found: C, 78.05; H, 10.8; N, 11.1.  $C_8H_{13}N$  requires C, 78.05; H, 10.55; N, 11.4%).

5-n-Butylamino-hex-3-en-1-yne. The product from expt. 20 gave the *hydrochloride* as needles, m. p. 137–138°, from ethyl acetate (Found: C, 64.4; H, 9.6; N, 7.45; Cl, 18.5.  $C_{10}H_{18}NCl$  requires C, 64.0; H, 9.6; N, 7.45; Cl, 18.9%). After regeneration the *amine* had b. p. 85–86°/15 mm. (Found: C, 78.6; H, 11.0; N, 9.45.  $C_{10}H_{17}N$  requires C, 79.4; H, 11.3; N, 9.25%).

5-Piperidinohex-3-en-1-yne. The products from expts. 24 and 25 were combined and fractionated; although the b. p. did not vary sensibly from 31°/0.02 mm., the  $E_{1\text{cm}}^{1\%}$  values varied from 470 to 800. Those with  $E_{1\text{cm}}^{1\%} > 670$  were combined and converted into the *hydrochloride*, which after crystallisation from ethanol had m. p. 178–179° (Found: C, 65.9; H, 9.1; N, 7.15; Cl, 18.0.  $C_{11}H_{18}NCl$  requires C, 66.1; H, 9.05; N, 7.05; Cl, 17.8%). After regeneration, the *amine* had b. p. 94°/15 mm. (Found: C, 80.7; H, 10.35; N, 9.0.  $C_{11}H_{17}N$  requires C, 81.0; H, 10.35; N, 8.6%).

1-Ethyl-4-propadienylthiazolin-2-thione. To a solution of carbon disulphide (25 c.c.) in dry ether (50 c.c.), 5-ethylamino-hex-3-en-1-yne (10 g.) was added dropwise with cooling to 10°. After 24 hr. at 20° the ether was evaporated and the product was distilled at 120° (bath temp.)/10<sup>-4</sup> mm., a good yield of a liquid,  $n_D^{25}$  1.6190, being obtained; it solidified and had m. p. ca. 31°, raised after four crystallisations from ether to 50–51° (Found: C, 54.35; H, 6.5.  $C_9H_{13}NS_2$  requires C, 54.25; H, 6.6%). (The distilled product showed weak absorption at 3300 cm.<sup>-1</sup>, evidently due to a trace of the prop-2'-ynyl analogue and removed by recrystallisation.) A light-absorption maximum was at 2770 Å ( $\epsilon$  16,000).

*Kinetic Measurements.*—*Procedure.* The chloride (5.73 g.) was weighed into a 100 c.c. volumetric flask, and pure acetonitrile (30 c.c.) was added, followed by a cold solution of the dried amine in acetonitrile; the mixture was made up to 100 c.c. and at once immersed in the thermostatic bath. Zero time was taken as 4 min. after addition of amine, or 3 min. after immersion in the bath. Aliquot parts (approx. 5 c.c.) were run into ether (25 c.c.) and shaken with water (25 c.c.). The aqueous layer was twice more extracted with ether (25 c.c.), and 7M-nitric acid was added to neutrality (phenolphthalein), followed by an additional 3 c.c. An excess of standard silver nitrate solution, followed by nitrobenzene (2 c.c., A.R.) and 40% ferric ammonium sulphate solution (1 c.c., containing a little nitric acid), was added, and the solution was titrated with potassium thiocyanate solution.

The rate constant  $k$  (see Table) was calculated from the equation:

$$k = \frac{2.303}{t(2a - b)} \log \frac{b(a - x)}{a(b - 2x)}$$

where  $a$  and  $b$  were the original molar concentrations of chlorohexenyne and amine, and  $x$  was the chloride-ion concentration after  $t$  minutes.

(i) Ethylamine; $b = 2.035M$ ; $35.1^\circ \pm 0.1^\circ$ .						(ii) Diethylamine; $a = 0.1016M$ ; $b = 0.9565M$ ; $35.1^\circ \pm 0.1^\circ$ .		
$a = 0.500M$		$a = 0.250M$		$t$	$x$	$t$	$x$	$10^4k$
(min.)	$x$ (M)	$10^4k$ (min. <sup>-1</sup> )	$t$ (min.)	$x$ (M)	$10^4k$ (min. <sup>-1</sup> )	(min.)	(M)	(min. <sup>-1</sup> )
120	0.0581	5.23	120	0.0307	5.48	480	0.0098	2.26
240	0.0892	4.24	230	0.0481	4.70	1320	0.0249	2.29
470	0.1514	4.10	475	0.0863	4.60	1925	0.0340	2.30
1440	0.3173	4.25	1205	0.1548	4.33	2780	0.0455	2.36
1830	0.3588	4.38	1887	0.1942	4.45	3360	0.0518	2.36
3000	0.4252	4.37	2650	0.2174	4.42	4200	0.0596	2.37
4335	0.4645	4.53	3300	0.2290	4.39	4840	0.0650	2.40
						6120	0.0732	2.41
						7740	0.0818	2.48

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