Base-catalysed Prototropic Isomerisations. Part I. Preparation of *NN*-Dialkylprop-1-ynylamines and Allenamines from *NN*-Dialkylprop-2-ynylamines (a Novel Method for the Preparation of Ynamines)

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A dispersion of potassium amide on alumina is a very active catalyst for the prototropic isomerisation of *NN*-di-alkylprop-2-ynylamines into allenamines and ynamines. *NN*-dialkylmethyl ynamines are readily obtained in large amounts by a simple continuous process.

DURING work on macrocyclic dienes it was found that a dispersion of potassium on alumina had interesting properties,[1] and it was thought that the special properties of this system could perhaps help to solve the problem of preparing aliphatic ynamines in large quantities by catalysing the migration of triple bonds. The ynamines are stable compounds which can be distilled easily and have an interesting chemistry.[2-6] It was expected that the equilibrium between *NN*-diethylprop-2-ynylamine (I) and *NN*-diethylprop-1-ynylamine (III) by way of the allenic compound (II) would be almost entirely on the side of (III).

$HC{:}C{\cdot}CH_2{\cdot}NEt_2$ (I) $H_2C{:}C{:}CH{\cdot}NEt_2$ (II) $MeC{:}C{\cdot}NEt_2$ (III)

An alkali metal has been used as a catalyst for the isomerisation of the triple bond of a substituted prop-2-ynylamine:[7] the dienamine (IV) was prepared by the following reaction:

$$HC\vdots C{\cdot}CHMe{\cdot}NEt_2 \longrightarrow CH_2{:}CH{\cdot}C({:}CH_2){\cdot}NEt_2$$
(IV)

A low yield of ynamine (III) (13%) (Table I, example 5) was obtained in a preliminary experiment from *NN*-diethylprop-2-ynylamine with potassium on alumina as catalyst. The use of a solvent increased the yield slightly but it was obvious that potassium was too reactive and side-products were formed. Potassium amide on alumina gave a much better yield (*ca.* 60%) but carefully controlled conditions were necessary; the use of a solvent such as benzene or hexane was required to get a good yield of ynamine. A large amount of catalyst was also necessary; when a small quantity was used, almost no ynamine was obtained, and dimers and polymers were formed.

The ynamine was not obtained with alumina; potassium amide alone reacted sluggishly and olefinic material (dimers and polymers) was obtained. Use of sodium or sodamide proved much less effective.

Temperature was not very important; reaction in refluxing benzene was rapid (complete within 15 minutes) but it was easier to work with a temperature of 65° and hexane as solvent. The solvent was more easily removed than benzene and the rate of the reaction was high enough (*ca.* 30 minutes for completion). The best results were obtained with a small column filled with the catalyst and heated at 65° (near the boiling point of hexane). The solution was filtered slowly through the column so that the amine (I) was always in contact with a large excess of catalyst, and the rate of elution could be controlled to give the best yield of ynamine (III). The reaction was easily followed by i.r. spectroscopy; the amine (I) absorbed at 3·0 μ (C≡CH), the allene (II) at 5·2 μ (C=C=C), the ynamine (III) at 4·5 μ (C≡C), and the olefinic dimers and polymers at 6·1 μ. The allenamine (II) was the intermediate in the isomerisation. It appeared in large quantities (i.r. spectrum) in the early stages of the reaction. With a low reaction temperature (65%) and high rates of flow a mixture which contained no amine (I), a little ynamine

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(III), much allenamine (II), and olefinic dimers was obtained. The band at 5·2 μ [allenamine (II)] disappeared when the product was left at room temperature overnight.

These experiments showed that the allenamine (II) was the intermediate in the isomerisation and that it was the species which gave the olefinic by-products.

With a well controlled moderate rate of flow a small amount of allenamine (II) was always present, but the ynamine (III) was obtained in large amounts (i.r. spectrum) together with varying quantities of olefinic dimers and polymers. The allenamine was much less stable than the ynamine: the small amount of allenamine which was present in these cases (Table 2) was destroyed during the distillation and could be detected only by spectroscopy.

TABLE 1

Isomerisation of *NN*-diethylprop-2-ynylamine in batch

	Catalyst	Amine/Catalyst (molar ratio)	Catalyst/Alumina (mole/ml.)	Amine/Benzene (v/v)	Yield of (III) (%)
1	KNH_2	4	0·003	2	60
2	KNH_2	2	0·004	2	40
3	KNH_2	5	0·003	2	30
4	KNH_2	11	0·002	2	0
5	K	11	0·0015	No solvent	13
6	K	3	0·003	1	20
7	Na	2	0·004	No solvent	0
8	$NaNH_2$	4	0·003	2	Trace (i.r.)

TABLE 2

Preparation of $MeC{\vdots}C{\cdot}NR_2$ by the flow technique [catalyst KNH_2 (from 2 g. K) on 20 ml. Al_2O_3; solvent hexane (50—60% solution); temperature 65°; time of contact *ca.* 40 min.]

R_2	B. p.	Yield (%)	Dimers (and polymers) (%)	Maximum quantity of amine isomerised by column (g.)
Me_2 *	95—100°/760 mm.	25		200
Et_2	80—85/100	65	20	1600
$\cdot[CH_2]_4\cdot$	80—85/100	35	65	160
$\cdot[CH_2]_5\cdot$	90—100/30	38	60	1000
$(CH_2{\cdot}CH_2)_2O$	80—90/20	25	70	80

* Prepared in n-decane because its b. p. is too close of that of hexane.

The method did not seem to be useful for the preparation of aliphatic ynamines with R ≠ H. Isomerisation of (V; $R^1 = R^2 = R^3 = Et$) gave only traces of ynamine (VII, $R^1 = R^2 = R^3 = Et$), much allene (VI; $R^1 = R^2 = R^3 = Et$), and some olefins. Allene (VI) was the main product.

$$\underset{(V)}{R^1C{\vdots}C{\cdot}CH_2{\cdot}NR^2R^3} \rightleftharpoons \underset{(VI)}{R^1CH{:}C{:}CH{\cdot}NR^2R^3} \rightleftharpoons \underset{(VII)}{R^1CH_2{\cdot}C{\vdots}C{\cdot}R^2R^3}$$

Distillation of the material gave a mixture of allene (VI), olefin, and a little ynamine (VII). Heating at 100° for 10 minutes gave a mixture of olefinic material and ynamine (VII) (which was already present in the initial mixture). This was additional evidence that the allenamine was the species which gave olefinic dimers. Compound (V; $R^1 = Ph$, $R^2 = R^3 = Et$)* polymerised violently under the conditions of isomerisation.

Various ynamines (VII) with $R^1 = H$ and various amino-substituents (Table 2) were prepared without difficulty. The rate of elution through the column required careful control, and was determined by the i.r. spectra of aliquot portions.

An attempt to isomerise *N*-ethyldiprop-2-ynylamine into *N*-ethyldiprop-1-ynylamine failed: violent polymerisation was observed on the catalyst.

The mechanism of the reaction is not very clear, but it is probably a classical base-catalysed prototropic rearrangement of the acetylenic group; the catalyst is very active because of the high dispersion of the base but some specific action of the alumina support is probable. The presence of much ynamine at equilibrium is easily explained. It is well known that a disubstituted triple bond is more stable than a monosubstituted one, and the overlap between the electron pair on nitrogen and the triple bond also makes the ynamine more stable than the prop-2-ynylamine.

The high reactivity of the catalyst explains the success of the isomerisation which failed under other conditions. It was necessary that the unstable allene (II) was isomerised quickly and that equilibrium with the ynamine (III) was established with a few minutes. If this was not the case, the allene had time to dimerise before isomerisation was complete. For instance (Table 1, example 4) when a small amount of catalyst was used, no ynamine was formed, only small amounts of allene were detected, and dimers and polymers were formed extensively. The dilution of the prop-2-ynylamine (I) with a solvent greatly increased the yield (Table 1), since isomerisation is a monomolecular process, whereas the dimerisation of allene is bimolecular. However, a fairly concentrated solution *ca.* 40—50% of amine (I)] was used because it was easier to remove the solvent, and the yields were still acceptable.

In the case of *NN*-diethylprop-2-ynylamine, olefinic dimers were obtained in at least 30% yield when a small amount of catalyst was used. They boiled at 90—100°/0·1 mm., were unstable, and darkened rapidly in the presence of oxygen. A solution in carbon disulphide

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* Sample provided by Dr. R. Fuks.

rapidly turned deep red; a benzene solution turned red more slowly. Analysis and molecular weight measurement agreed well with a dimeric structure. The strong band at 6·1 μ in the infrared showed the presence of C=C. Two bands were observed in the u.v. spectrum: at 318 (ε 7200) and 278 mμ (ε 8100). The mixture of dimers absorbed two moles of hydrogen with a palladium–charcoal catalyst. The diamine thus obtained was more stable. The olefins were probably formed by a thermal dimerisation of the allene (II). It is well known that allene itself dimerises on heating and gives divinylcyclobutane. We have probably obtained bis(diethylaminoethylene)cyclobutanes.

Some ynamines were recently obtained by the isomerisation of *NN*-disubstituted prop-2-ynylamine with t-butylpotassium in dimethyl sulphoxide[8] but the method was limited to compounds with aromatic *N*-substituents and is much less convenient than the flow technique, especially for the preparation of large quantities of ynamine. Dumont[8] also observed the formation of allenes. In the case of *N*-prop-2-ynylcarbazole, for instance, he observed the formation of allenamine (95%) and traces of ynamine. The same compound gave a mixture containing 30% ynamine and 70% allenamine on the dispersion of potassium amide on alumina. This example shows the high activity of our catalyst. The base-catalysed isomerisation of substituted prop-2-ynylamines into conjugated dienes[9] was also recently investigated by Farmer and Kurtz.[12]

Further investigation of our system, *e.g.*, its use for the isomerisation of other unsaturated compounds is in progress.

EXPERIMENTAL

NN-*Disubstituted Prop*-2-*ynylamines* (V).—These amines were prepared by standard procedures[10] (2 moles of secondary amine and 1 mole of prop-2-ynyl bromide in ether).

Preparation of the Catalyst.—(*a*) Potassium and sodium were dispersed on alumina by standard techniques.[11]

(*b*) Potassium and sodium amides were prepared by dissolving the metal (2 g.) in ammonia (100 ml.) and adding a crystal of ferric nitrate. When the blue colour of the metal solution had vanished, the solution was evaporated in the presence of alumina [Woelm, basic (20 ml.)] with stirring. The powder thus obtained was dried at 65°.

Isomerisation of NN-*Disubstituted Prop*-2-*ynylamines by the Flow Technique.*—The potassium amide catalyst [from potassium (2 g.)] on alumina (20 ml.) was poured under nitrogen into the reactor. The system was heated at 65° with a furnace (or by running hot water or oil around the column). The temperature was controlled with a thermocouple and a regulator device (Elnik-Regler REZ 21 eZ, 20—300°, 220 v, 50 Hz).

A solution of the *NN*-diethylprop-2-ynylamine (I) (190 ml., 157 g.) in hexane (250 ml.) was poured on to the column and filtered very slowly through the catalyst. The optimum rate of elution was determined by i.r. spectroscopy (Beckmann IR 5); absorption of aliquot portions was measured at 3·0, 4·5, 5·1 and 6·1 μ in a cell (0·025 mm.). The rate which gave the highest absorption at 4·5 μ and no absorption at 3·0 μ was adopted. A time of contact of about 40 min. was best for the amines investigated except for the 2-pyrrolidin-1-ylprop-1-yne, which required a slightly higher rate than the others (time of contact *ca.* 20—30 min.). The solution was then distilled under reduced pressure. The catalyst was still active after the compound had passed through.

A deep brown zone which always remained at the top of the column was considered to be catalyst destroyed by impurities in the starting material. Below this coloured zone the catalyst was grey. The thickness of this dark zone was used to evaluate the maximum amount of amine which could be isomerised before the catalyst was completely destroyed (see Table 2). In some cases large amounts of ynamine can be prepared with a very small quantity of catalyst. Use of pure starting material improved the life of the catalyst.

The ynamines were identified by their i.r. spectra (comparison with those of authentic samples from R. Buyle), by g.l.c. (R. Buyle's samples of *NN*-diethylprop-1-ynylamine were used to identify this ynamine), and by analysis (for the previously unknown ynamines): 1-*pyrrolidin*-1-*ylprop*-1-*yne* (Found: C, 76·6; H, 10·4; N, 12·5. $C_7H_{11}N$ requires C, 77·0; H, 10·2; N, 12·8%); 1-*morpholinoprop*-1-*yne* (Found: C, 65·7; H, 8·91; N, 11·44. $C_7H_{11}NO$ requires C, 67·2; H, 8·85; N, 11·2%).

Isomerisation of NN-*Disubstituted Prop*-2-*ynylamine in Batch.*—The catalyst was prepared as described above and the amine or its solution in benzene was added. The mixture was refluxed under nitrogen on an oil-bath at 180° and the reaction was followed by i.r. spectroscopy (see above). This method was used only for the preliminary attempts in order to study the influence of various factors. The results are summarised in Table 1.

Preparation of Olefinic Dimers.—These dimers were obtained by distillation of the residue from the preparation of ynamine (III). However the best yield of dimers was obtained by boiling the prop-2-ynylamine (I) with a small amount of catalyst.

NN-diethylprop-2-ynylamine (80 ml.) in benzene (40 ml.) was boiled with potassium amide [from potassium (2 g.)] on alumina (25 ml.). The isomerisation was followed by i.r. spectroscopy (see above). The reaction was sluggish and starting material was still present after 40 min. Traces of ynamine (III) and allene (II) were detected. The main product was olefinic dimer. Distillation gave 34% of product, b. p. 110—120°/1 mm. (Found: C, 74·8; H, 12·05; N, 12·65%; *M*, 231. $C_{14}H_{26}N_2$ requires C, 75·6; H, 11·8; N, 12·6%; *M*, 222).

At least 10% of the starting material was recovered. A residue of polymer (*ca.* 10%) remained in the distillation flask.

Dimers were not eluted by g.l.c. Hydrogenation over palladium–charcoal gave an amine (70%) which did not absorb at 6·1 μ, b. p. 100—110°/1 mm. (Found: C, 73·25; H, 13·35; N, 12·5%; *M*, 230. $C_{14}H_{30}N_2$ requires C, 73·2; H, 13·4; N, 12·5%; *M*, 226).

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