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THE PROTOTROPIC REARRANGEMENT OF SECONDARY PROPARGYLIC AMINES

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Abstract—Secondary and tertiary propargylic amines of types 3 and 4 were synthesized. On prototropic isomerization amines **3a–f** isomerized to α,β-unsaturated aldimines of type **6** while **3g** and **3h** isomerized to conjugated aldimines **18** and **19** respectively. The diyne-diamine **27** isomerized to a fully conjugated diene-diimine **28**. Amine **3i** on treatment with base yielded aniline. Alkyl-substituted dipropynylamines **29b–d** were prepared and on prototropic isomerization aromatized to alkyl-substituted pyridines. The unsubstituted dipropynylamine **29a** however underwent under the above conditions two types of skeletal rearrangement to yield nitriles **44a** and **b** in high yield and oximes **45a** and **b** in low yield.

The base-catalyzed rearrangement of acetylenic compounds is by now well documented.[1] In the case of acetylenic hydrocarbons it afforded difficultly accessible conjugated polyenes,[2] polyenynes[3a,c] and polyynes[3b] from readily obtainable acetylenes, but its most impressive utilization was in the preparation of a large series of annulenes by Sondheimer and his group.[4] Among heterosubstituted acetylenes investigated were propargylic ethers, propargylic thioethers and tertiary propargylic amines.[1a,c] These yielded equilibrated mixtures containing starting materials and the corresponding allenes and internal acetylenes in which the heteroatom was bound directly to the allenic or acetylenic moiety.

Secondary propargylic amines are one group of compounds to which the base-catalyzed isomerization has practically not yet been applied. In contrast to the above mentioned tertiary propargylic amines this group contains a hydrogen atom on nitrogen and therefore there exists the possibility, that on prototropic rearrangement it would yield systems with nitrogen as part of the conjugated skeleton, i.e. it would give conjugated imines. If this could be realized, these secondary amines could serve as potential precursors in the preparation of heteroannulenes containing unsaturated nitrogen in the ring. To test this possibility, a series of secondary propargylic amines was submitted to base-catalyzed treatment.

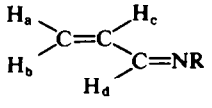
Starting secondary propargylic amines **3a–g** were prepared by the alkylation of the corresponding amines **2** with propargyl bromide (**1**), using an excess of amine **2** (3 equivs). This alkylation also furnished in low yield the corresponding tertiary amines **4** (Tables 1 and 2).

$$\underset{\mathbf{1}}{HC{\equiv}CCH_2Br} + \underset{\mathbf{2}}{RNH_2} \rightarrow \underset{\mathbf{3}}{HC{\equiv}CCH_2NHR} + \underset{\mathbf{4}}{(HC{\equiv}CCH_2)_2NR}$$

2–4a: R = n–C_7H_{15}; **b**: R = n–C_6H_{13}; **c**: R = n–C_5H_{11}; **d**: R = n–Pr;
e: R = t–Bu; **f**: R = cyclohexyl; **g**: R = $CH_2CH{=}CH_2$; **h**: R = $PhCH_2$;
i: R = Ph

On treating the secondary amines **3a–f** with saturated solutions of t-BuOK in t-BuOH for *ca* 20 min at *ca* 100° they afforded the corresponding α,β-unsaturated aldimines **6a–f** in moderate yields.

$$\underset{\mathbf{3}}{HC{\equiv}CCH_2NHR} \longrightarrow \underset{\mathbf{5}}{[CH_2{=}C{=}CHNHR]} \longrightarrow$$



6

Additional isomerization experiments with **3f** showed that with satd t-BuOK in t-BuOH at room temperature or with 10% KOH solution in abs EtOH under reflux for 4 hr no rearrangement took place and the starting amine was recovered unchanged. With refluxing EtONa in abs EtOH isomerization of **3f** to **6f** was slow. With t-BuOK in diglyme at 0° isomerization of **3f** was moderately fast and afforded **6f** in high yield. It was also observed that injection of a solution of **3f** in satd t-BuOK in t-BuOH on a VPC column at 144° yielded mixtures of **3f** and **6f** in 1:2 ratio and both were eluted from the column preparatively.

The above isomerization may serve as a synthetic route to N-allylidenealkylamines **6** because the direct condensation of acrolein with a primary amine leads to products other than the desired imine.[5] The early assumption that imines **6** had been formed on dehydrohalogenation of N-(2-bromoallyl)alkylamines with sodamide in liquid ammonia[5] proved incorrect and it was shown that the obtained products were N-alkylmethyleneaziridines.[6] Russian workers also reported that in the prototropic isomerization of N-(2-vinyloxyethyl)propargylamine with powdered KOH in anisole at 130° only a dark brown polymeric mass had been obtained.[7] On the other hand it was reported that aldimines **6** were prepared by the pyrolysis of anthracene adducts.[8] The parent compound, acraldehyde imine (**6**, R=H) was also synthesized and its NMR spectrum recorded.[9]

The aldimines **6a–f** distil as colorless liquids and are severe lachrymators with a characteristic odor. When kept neat at room temperature or for a longer time in a refrigerator they polymerize to colored viscous oils. With maleic anhydride in benzene solution in the cold they precipitate at once brown polymers.

When a solution of 10% $AgNO_3$ in EtOH—H_2O (10:1) is added to aldimines **6a–f** a silver mirror is obtained within a few minutes. This served as a qualitative test for their detection during isomerization. Presumably the silver nitrate catalyzes the hydrolysis of the imine to the aldehyde and then oxidizes the latter while being reduced to metallic silver, thus acting as a Tollens reagent.

The UV spectra of aldimines **6a–f** have a single maximum at *ca* 214–15 nm ($\epsilon > 20{,}000$). α,β-Unsaturated imines of type **6** with a single additional alkyl substitution on the vinyl group have a single maximum at *ca* 220 nm (ϵ *ca* 23,000).[8,10,11] This corresponds to the 5 nm bathochromic shift for each alkyl substituent on 1,3-dienes but not to the shifts in 1,3-enones.[12]

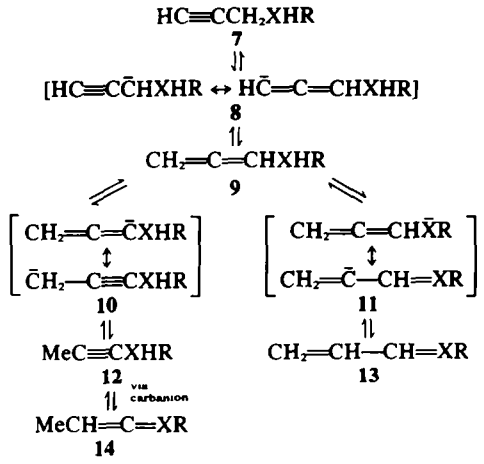
In the IR aldimines **6a–f** show two strong peaks in the ranges of 1653–1637 and 1610–1603 cm^{-1} which are assigned to the C=N and C=C stretching vibrations respectively in the conjugated chromophore. Both are bathochromically shifted with respect to the nonconjugated vibrations. The CH and CH_2 out-of-plane deformations occur at *ca* 995 and 925 cm^{-1} respectively. A weak peak appears consistently in all the aldimines at exactly the double frequency of the CH_2 out-of-plane deformation and is generally assigned to an overtone of this absorption.[13,8,14]

In the NMR at 60 MHz aldimines **6a–f** show complex multiplets in the δ 5·3–5·9 region (H_a and H_b) and in the δ 6·1–6·9 region (H_c) as well as a doublet at *ca* δ 7·8 (H_d). Compound **6e** was further investigated at 90 MHz: the H_c multiplet then afforded a practically first order octet with J_{bc} = 17·4, J_{ac} = 10·4 and J_{cd} = 8·3 Hz. On intense double irradiation of H_d, H_c collapsed to a symmetrically spaced sextet in which the outer two peaks were very weak and the inner intense quartet leaned heavily towards the CH_2 multiplet. This quartet had by a first order analysis the same coupling constants mentioned above. The spectral pattern however indicated that the vinylic group (after decoupling from H_d) was still an ABC system from which the exact parameters could only be obtained by computer analysis.[8]

From the limited amount of data of this study it is evident that the imine grouping in conjugation with the vinylic group diminishes the shielding of the *gem*-proton (H_c) of the latter to approximately the same extent as do the ethylenic and carbonyl groups. On the other hand the decrease in the shielding of the *cis*- and *trans*-protons (H_a and H_b) caused by the imine group is intermediate between that caused by the above two groups.[15] At room temperature the aldimines **6a–f** gave no indication of *syn–anti* isomerism in their NMR spectra.[16] The peaks of the H_d doublet and of the NCH_2 triplet in compounds **6a–d** were broader (hhw 3·0–3·5 Hz) than those of the H_d doublet of **6e** (hhw 1·8 Hz) which may point to allylic coupling through nitrogen.[16]

It is well established that the first intermediate in the prototropic rearrangement of 1-alkynes **7C** is the allene **9C** formed via the carbanion **8C** (Scheme 1).[17] When R = alkyl the isomerization proceeds further to the 2-alkyne **12C** by the route indicated in Scheme 1. The equilibrated mixture then contains predominantly the 2-alkyne **12C** and very little of the 1-alkyne **7C** and allene **9C**.[18] When strong base is used, such as satd t-BuOK in t-BuOH the isomerization proceeds further via the 2,3-diene **14C** to give an equilibrated mixture of 2- (**12C**) and 3-alkynes.[19*] 1,3-Dienes **13C** are not formed under the above conditions. That proton abstraction occurs only at the internal allenic carbon of **9C** and not at the saturated carbon is due to the greater acidity at the sp^2-hybridized carbon. However when R is an electron-withdrawing group such as aryl, carbonyl, carboxyl, vinyl or ethynyl, the abstraction of a proton from CH_2 in **9C** is facilitated and may compete with proton abstraction from the internal allenic carbon, thus leading to 1,3-dienes **13C** via carbanion **11C**. In fact such dienes are formed either exclusively or predominantly in such isomerizations.[2,3a,c,20] By contrast, in the present investigation we have observed that secondary propargylic amines **7N** isomerize to azadienes **13N** even when R is an alkyl group, i.e. when R is not electron-withdrawing. The NH proton in **9N** is relatively much more acidic than the proton of CH_2 in

*In certain cases, as with sodamide in liquid ammonia the sodium salt of **7C** is insoluble and precipitates from solution, thus shifting the equilibrium towards the 1-alkyne **7C**.



SCHEME 1[a]

9C and is therefore closer in acidity to that of the internal allenic proton in 9N, and as a result it is abstracted much more effectively to yield aldimines 13N instead of ynamines 12N. If the latter were formed, they might have further isomerized to ketenimines 14N, but neither 14N nor any products resulting from them were isolated. It should also be pointed out that basic isomerization of tertiary propargylic amines 15 leads to allenamines 16 and ynamines 17:[21,22]

$$HC{\equiv}CCH_2NR_2 \rightarrow CH_2{=}C{=}CHNR_2 + MeC{\equiv}CNR_2$$
15 16 17

To probe the feasibility of further extending conjugation by prototropic isomerization of secondary propargylic amines additional amines were investigated. First amines 3g and 3h were isomerized to yield respectively aldimines 18 and 19 of extended conjugation. On acid hydrolysis 19 yielded benzaldehyde.

$$HC{\equiv}CCH_2NHCH_2CH{=}CH_2 \longrightarrow \mathbf{6g} \longrightarrow MeCH_f{=}CH_eN{=}CH_dCH_c{=}C(H_a)(H_b)$$
3g 18

$$HC{\equiv}CCH_2NHCH_2Ph \rightarrow \mathbf{6h} \rightarrow MeCH_f{=}CH_e{-}N{=}CH_d{-}Ph$$
3h 19 (*cis* and *trans*)

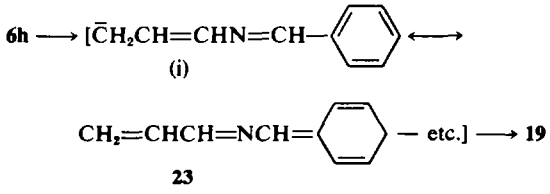
That the first step in this isomerization is the formation of the allylideneamines 6g and 6h which then rearrange to 18 and 19 respectively is supported by the report that ketimines 20 (obtained from α,β-unsaturated ketones and benzylamine) rearrange with base to aldimines 21.[23] The further isomerization

$$R'CH{=}CHCR{=}NCH_2Ph \rightarrow R'CH_2CH{=}CRN{=}CHPh$$
20 21

of 6g, 6h and 20 is a result of the presence of electron-withdrawing groups (vinyl and phenyl) which increase the acidity of the protons of the saturated CH_2 group. This is supported by the finding that the prototropic isomerization of azomethines is slowed down considerably with increase in the electron-donating effect of alkyl substituents at the saturated carbon which is bonded to nitrogen.[24] In fact no further isomerization was observed with aldimines 6a–d,f where hydrogens are still available on the saturated carbon bonded to nitrogen.

The further rearrangement of 6g and 6h occurs via proton abstraction to yield a carbanion. The carbanion 22* derived from 6g is symmetrical and

$$\mathbf{6g} \rightarrow [\bar{C}H_2CH{=}CHN{=}CHCH{=}CH_2 \leftrightarrow CH_2{=}CHCH{=}NCH{=}CH\bar{C}H_2] \rightarrow \mathbf{18}$$
22



therefore yields on protonation one product, namely 18. Of the resonance structures of the carbanion 23* derived from 6h, evidently (i) affords the predominant contribution to resonance and as a result protonation of 23 yields 19 only.

Russian workers[25] also reported that the condensation of aldehydes and ketones with allylamine afforded equilibrated mixtures of imines 24, 25 and 26 and that 24 isomerized to 26 on treatment with 3–6% K_2O on Al_2O_3 at 135–250°.

$$RR'C{=}O + H_2NCH_2CH{=}CH_2 \rightarrow RR'C{=}NCH_2CH{=}CH_2$$
24, 70–90%
$$+ RR'CHN{=}CHCH{=}CH_2 + RR'C{=}NCH{=}CHMe$$
25, 10–25% 26, ~ 5%

Although on analytical VPC 18 showed a single peak it may be a mixture of the *cis* and *trans* isomers. The IR spectrum showed a band at 966 cm^{-1} assigned to a *trans* double bond, however the *cis* isomer may also be present. The NMR spectrum

[a] X=CH or N; the numbered formulas of this Scheme are marked in the text C or N to indicate if X=CH or N respectively.

*Resonance structures of the carbanion which on protonation will regenerate nonconjugated products are not shown.

was of no use in configurational assignment because of overlapping multiplets.

Imine **19** was formed as a mixture of *cis* and *trans* isomers. The configurational assignment is based upon the larger coupling constant of the *trans* relative to the *cis* double bond but the IR spectra showed no differentiating features in this respect. In contrast to *cis*-**19** in which the Me group is a double doublet, each of the two peaks of the Me-doublet in *trans*-**19** is a quartet with 0·75 Hz spacings. This may be due to *syn–anti* isomerism and is supported by the observation that in contrast to *cis*-**19** where H_f can be analyzed as a first order quintet, H_f in *trans*-**19** is a complex multiplet which does not show a first order pattern. This is now being further investigated since recently such isomerism has been observed in N-(9-anthranylidene)alkylamines.[16]

To obtain even more extended conjugation, **3e** was oxidatively coupled to give the diyne–diamine **27**. This on prototropic isomerization with

$$\mathbf{3e} \rightarrow (\text{t-BuNHCH}_2\text{C}{\equiv}\text{C})_2 \xrightarrow{\text{base}} \underset{\mathbf{27}}{} \qquad (\text{t-BuN}{=}\text{CHCH}{=}\text{CH})_2 \quad \mathbf{28}$$

ethanolic KOH afforded the fully conjugated diene–diimine **28**. The colorless crystals, m.p. 155–158°, obtained by recrystallization and sublimation gave a single spot on TLC and a single peak on VPC. Because of the strong band in the IR at relatively high frequency (993 cm^{-1}), absence of a *cis* band at 700–850 cm^{-1} and the high melting point it is assigned the *trans–trans* configuration.[26]

The only thorough report of base treatment of a secondary propargylic amine is that of N-phenylpropargylamine **3i**.[27] When heated with piperidine at 140° for 42 hr it afforded aniline in 20% yield and trace yields of three isoindoline derivatives.[28] Aniline (1·6% yield) and one of the three isoindoline derivatives (2·7% yield) were also isolated on heating **3i** at 140° for *ca* 70 hr without base.[28] We have found that when **3i** was heated with satd t-BuOK in t-BuOH at 90° for 13 min aniline (17% yield) was the only product isolated. A mechanism to rationalize the isomerization results in piperidine was advanced.[28]

The base treatment of dipropynylamines **29a–d** leads to rearrangements which differ considerably from those of amines **3a–i**. We shall first discuss

$$\text{RC}{\equiv}\text{CCH}_2\text{NHCHR}'\text{C}{\equiv}\text{CR}^2$$

29a: R=R'=R²=H
b: R=R'=H, R²=Me
c: R=R²=H, R'=Me
d: R=R²=Me, R'=H

29b–d which afford aromatized products (alkylpyridines) and then the unsubstituted amine **29a** which gives nitriles and oximes by skeletal rearrangements.

Amines **29b–d** were prepared by the following alkylation reactions which also yielded amines **30**, **31** and **32**:

$$\text{MeC}{\equiv}\text{CCH}_2\text{Br} + \text{NH}_3 \rightarrow \underset{\mathbf{30}}{\text{MC}{\equiv}\text{CCH}_2\text{NH}_2} +$$

$$\underset{\mathbf{29d}}{(\text{MeC}{\equiv}\text{CCH}_2)_2\text{NH}} + \underset{\mathbf{31}}{(\text{MeC}{\equiv}\text{CCH}_2)_3\text{N}}$$

$$\text{MeC}{\equiv}\text{CCH}_2\text{Br} + \underset{\mathbf{29b}}{\text{HC}{\equiv}\text{CCH}_2\text{NH}_2} \rightarrow \text{MeC}{\equiv}\text{CCH}_2\text{NHCH}_2\text{C}{\equiv}\text{CH} + \underset{\mathbf{32}}{(\text{MeC}{\equiv}\text{CCH}_2)_2\text{NCH}_2\text{C}{\equiv}\text{CH}}$$

$$\text{HC}{\equiv}\text{CCHMeBr} + \text{HC}{\equiv}\text{CCH}_2\text{NH}_2 \rightarrow \underset{\mathbf{29c}}{\text{HC}{\equiv}\text{CCHMeNHCH}_2\text{C}{\equiv}\text{CH}}$$

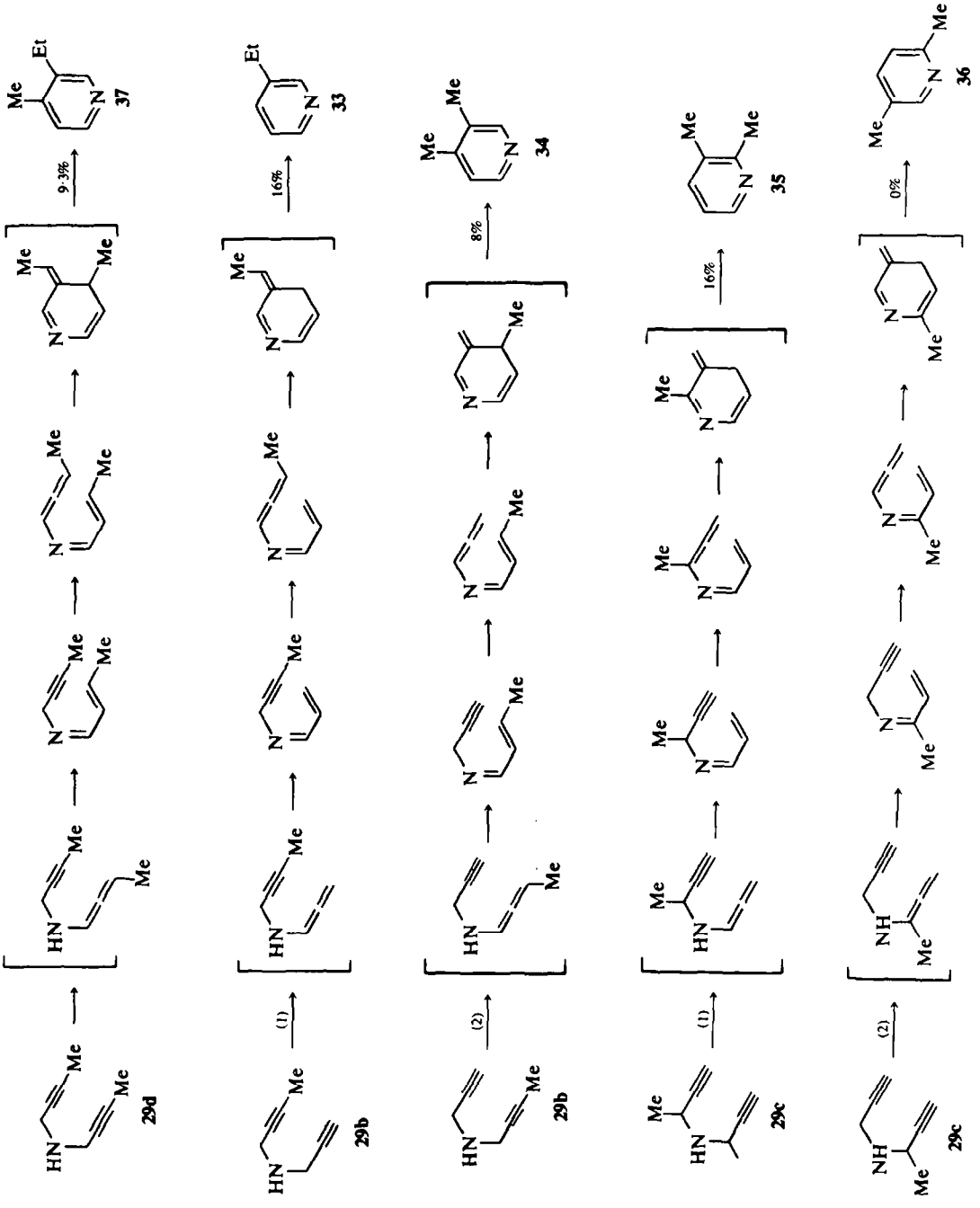
When **29b** and **c** were heated with satd t-BuOK in t-BuOH to *ca* 90° an exothermic reaction occurred: **29b** afforded 3-ethylpyridine (**33**) (16% yield), 3,4-lutidine (**34**) (8% yield) and two unidentified products of higher molecular weights; **29c** afforded only 2,3-lutidine (**35**) (16% yield) and none of 2,5-lutidine (**36**). Isomerization of **29d** proceeded slowly and only after many hours reflux with satd t-BuOK in t-BuOH it gave 3-ethyl-4-picoline (**37**) (9·3% yield) (Scheme 2).

The aromatization of diacetylenic hydrocarbons on heating with strong base has been reported: thus diynes of types **38** (n = 3–6, 10, 17) and **39** (n = 12)[29,3c] and *cis*-4-octene-1,7-diyne[30] yielded aromat-

$$\underset{\mathbf{38}}{\text{HC}{\equiv}\text{C(CH}_2)_n\text{C}{\equiv}\text{CH}} \qquad \underset{\mathbf{39}}{\text{Me(CH}_2)_n(\text{C}{\equiv}\text{C})_2(\text{CH}_2)_n\text{Me}}$$

ized as well as other products. It was proposed that aromatization occurred by way of prototropic isomerization to a *cis* diene–allene followed by an intramolecular Diels Alder reaction.[29,3c] Some doubt was cast on this mechanism when Hopf[31] reported that 1,5-hexadiyne on heating with t-BuOK in boiling diglyme cyclized to benzene, an aromatization which could not occur by the above mechanism. We however apply the above mechanism as it predicts correctly the aromatized products and their relative yields (Scheme 2).

The hydrogens of the saturated carbon atom of an unsubstituted propargylic group are more acidic than those of alkyl-substituted propargylic groups because of the electron-donating effect of alkyl groups. Therefore **29b** and **c** which still contain an unsubstituted propargylic group will isomerize faster than **29d** which has only substituted propargylic groups: in fact **29b** and **c** isomerized fast and exo-



SCHEME 2

thermically whereas **29d** required many hours for isomerization as indicated above. Furthermore, in **29b** and **c** isomerization by route (1) will be faster than by route (2) because in the former the *cis*-1-aza-1,3-diene moiety **40** is generated from the unsubstituted propargylic group and therefore higher yields are expected via that route.

40

That **29b–d** do not isomerize in the manner of **3g** and **3h** to yield linear conjugated products **41*** is in accord with the above mechanism. Thus it has been indicated that the first product in all the amine

MeCH=CHN=CHC≡CH

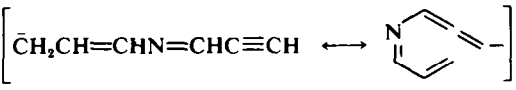
41

CH_2=CHCH=NCH$_2$C≡CH

42

isomerizations treated here is the α,β-unsaturated imine (e.g. **6g**, **6h**, **42**). The next step is a proton abstraction to yield a carbanion. In the case of carbanion **43**† derived from **42**, resonance structure (ii) is more important than (i) because the negative charge resides on an sp^2-hybridized carbon. Structure (ii)

42 ⟶



(i) **43** (ii)

can however undergo at once an intramolecular Diels–Alder closure and thus yield alkylpyridines. It is conceivable that some alkyl-substituted type **41** products were formed from **29b–d** but they may have polymerized under the severe reaction conditions as indicated by the large polymeric residues obtained on distilling the isomerization mixtures of **29b–d**.

When the unsubstituted dipropynylamine **29a** was heated with satd t-BuOK in t-BuOH at 70° it led to skeletal rearrangements totally different from those of all the other amines described until now. The reaction was exothermic and yielded a mixture which on chromatography gave the *cis*- and *trans*-5-t-butoxy-2-methyl-4-pentenenitriles (**44a** and **b**) (5:19; 40% yield), small amounts of the *cis*- and *trans*-6-t-butoxy-4-hexen-3-one oximes (**45a** and **b**) and 4-cyano-n-valeraldehyde (**46**) (Scheme 3). Aldehyde **46** had not been present in the crude isomerization mixture and was formed by hydrolysis from nitriles **44a** and **b** during chromatography on Kieselgel. By analogy with the substituted dipropynylamines **29b–d**, 3-picoline is the expected product of rearrangement. It was however not formed at all in this isomerization. Also as with all the amines described until now, no isomerization took place at room temperature with satd t-BuOK in t-BuOH and **29a** was recovered unchanged. Slow isomerization to the *cis*- and *trans*-nitriles **44a** and **b** occurred with t-BuOK in diglyme at 5° and then at room temperature, the conditions used to isomerize **3f** to **6f** at 0°. No oximes were formed during the isomerization in diglyme.

The structures of nitriles **44a** and **b** were elucidated from their UV, IR, NMR and mass spectra as well as from their degradation via cyanoaldehyde **46** and 4-cyano-n-valeric acid (**48**) to α-methylglutaric acid (**49**) (Scheme 3). Hydrolysis of the vinyl moiety in **44a** and **b** with 2N H_2SO_4 in dioxane afforded only the aldehyde **46** whereas hydrolysis of **44b** in MeOH gave an equilibrated mixture of **46** and its dimethyl acetal **47** (3:7). The same equilibrium mixture was obtained from **46** and 2N H_2SO_4 in MeOH. The configurational assignments of **44a** and **b** are derived from their out-of-plane deformations in their IR spectra (**44a**: 735 cm^{-1}; **44b**: 929 cm^{-1}) and the larger coupling constant between the ethylenic protons in **44b** as compared to that in **44a**.

The oximes **45a** and **b** were obtained in low yields as impure materials, possibly contaminated by hydroxylated components since the elemental analysis of **45a** showed a low value for carbon and the NMR spectra of both isomers on shaking with D_2O have lost impurity absorptions and have thus become amenable to first order analysis (these impurity absorptions were regenerated after shaking with H_2O). The constitutions of the isomers **45** were therefore elucidated from their first order NMR spectra and double irradiation experiments after having been shaken with D_2O (Experimental). An alternative structure **50** is excluded since the NH proton of α,β-unsaturated secondary amides resonates

t-BuOCH$_2$CH=CHCONHEt

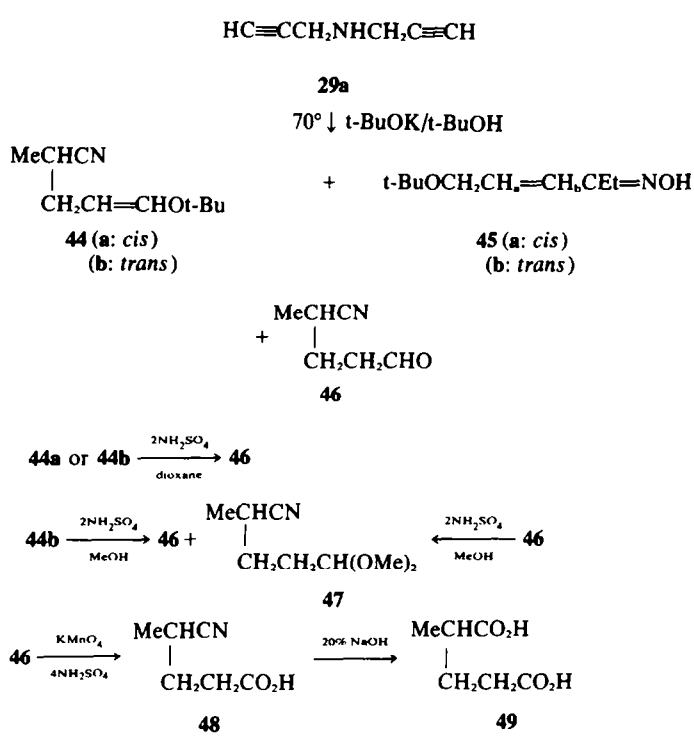
50

at much higher field (by *ca* 3-4 ppm)[32a] than the NOH proton of α,β-unsaturated ketoximes,[33] while the methylene protons of alkyl groups attached to NH in the former resonate at lower fields (by *ca* 1·5–2 ppm)[32b] than the methylene protons of alkyl groups bonded to carbon of the carbon-nitrogen double bond in ketoximes.[33] Also the UV spectra of the two types of compound support the structure of an α,β-unsaturated ketoxime[34] and not that of an α,β-unsaturated secondary amide.[35]

The configurational assignments of the ethylenic

*For simplicity the following arguments are exemplified with **29a** instead of **29b–d**, although only the latter amines gave aromatized products.

†See footnote page 4113.



SCHEME 3

bond of **45a** and **b** are based upon the IR out-of-plane deformation which in the *trans* isomer **45b** appears at 964 cm^{-1} but is absent in the *cis* isomer **45a**. Further support for these assignments is the larger coupling constant between the ethylenic protons in **45b** than in **45a**. The larger allylic coupling constant in the *cis* isomer (1·5 Hz) relative to that in the *trans* isomer (0·75 Hz) is also indicative of the correct configurational assignment.[36]

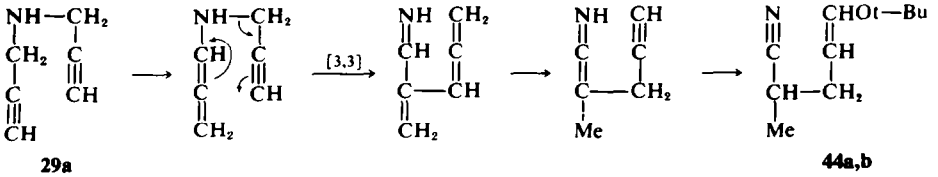
The *trans* oxime **45b** shows in the NMR two broad hydroxylic peaks as well as doublet fine structure in the Me and CH_2 peaks of the Et group. The *cis* oxime **45a** has a very broad hydroxylic peak (hhw 20 Hz) and also shows as **45b** the doublet splittings in the Et group. These observations indicate that both oximes may exist as mixtures of *syn-anti* isomers. In this respect it is interesting to note that whereas in cyclic α,β-unsaturated ketoximes[33a,b] the α-ethylenic proton and α-methylene protons have well separated resonances for their *syn* and *anti* isomers, the peaks of the multiplets of both ethylenic protons in **45a** and **b** are sharp.

An attractive but tentative mechanism for the overall isomerization of **29a** to nitriles **44a** and **b** involves a Cope—(or Claisen)—type [3, 3] sigmatropic rearrangement concomitant with several prototropic shifts. One such pathway is depicted in Scheme 4. The mechanism may be modified so that the sigmatropic rearrangement and the addition of t-BuOH take place at other stages of the sequence of prototropic shifts. Nontheless the sigmatropic rearrangement seems to take place at the stage given in Scheme 4; otherwise the next step which would have involved formation of **51** would have led to aromatization as in the cases of **29b-d**, but as has been indicated no 3-picoline was formed.

CH_2=CHCH=NCH$_2$C≡CH

51

Such Cope-like rearrangements occur in 1,5-



SCHEME 4

diynes[37] and 1-en-5-ynes[38] at *ca* 350–400° but propargyl vinyl ethers,[39] propargyl vinyl thioethers[40a,b] and ketenemercaptals[40c] undergo Claisen-like rearrangements at lower temperatures (200–300°, 100–120°, and room temperature respectively). It is therefore conceivable that rearrangement may take place at lower temperatures as in the case of **29a**. There remains the question why the substituted **29b–d** do not undergo this type of rearrangement but aromatize. It has been observed that in the case of the 1,5-diyne and 1-en-5-yne hydrocarbons[37,38,41] alkyl substitution at the triple bond retarded the [3, 3] sigmatropic rearrangement and it has been argued that this might be due to the greater stabilization of the sp- versus sp^2-hybridized carbon by alkyl, or else also to steric effects. This may explain the lack of sigmatropic rearrangement in the cases of **29b** and **d** but not in the case of **29c** because 2-methyl-1-hexen-5-yne rearranged faster than both 1-hexen-5-yne and 1-hepten-5-yne.[38]

The reaction leading from **29a** to the oximes **45** involves a 1,2-shift of carbon from nitrogen to carbon as well as the addition of t-BuOH and H_2O molecules. It therefore may proceed by a mechanism different from that leading to the nitriles **44**.

The results of this investigation indicate that the prototropic isomerization of secondary propargylic amines imitates to a large extent the isomerizations of acetylenic hydrocarbons and therefore should be useful in the preparation of more complex conjugated cyclic hetero-systems, such as hetero-annulenes.

EXPERIMENTAL

M.p.s (Fisher-Jones apparatus) and b.p.s are uncorrected. IR spectra: on Perkin-Elmer Infracord spectrophotometers Models 137 and 237 (only significant bands are given). UV spectra: on a Cary Model 14 spectrophotometer. NMR spectra: on a Varian Model A-60 spectrometer (unless otherwise stated) and on a Bruker Model HFX-10 spectrometer operating at 90 MHz. Mass spectra: on an Atlas CH-4 spectrometer. TLC on glass plates coated with Kieselgel G (Merck AG, Darmstadt) and on TLC cards SIF coated with Kieselgel with fluorescenting indicator (Riedel–de Haen AG, Seelze-Hannover) using UV fluorescence, iodine and a $KMnO_4$–$Cu(OAc)_2$ spray as indicators. Column chromatography on Kieselgel 60 (mesh 70–230) for column chromatography (from Merck). Analytical and preparative VPC on an Aerograph Autoprep Model A-700 instrument, using a column of 20% silicon GE SF-96 on firebrick (mesh 60–80), 5 ft×0·25 in. Elemental analyses of the unsaturated aldimines were done immediately after distillation and elution by preparative VPC.

N-n-Heptyl-2-propynylamine (**3a**) *and* *N-n-heptyldi-2-propynylamine* (**4a**). Propargyl bromide **1** (31·2 g, 0·26 mole) was added dropwise to a stirred and ice-water-cooled mixture of n-heptylamine (90 g, 0·78 mole) and water (30 ml) in 70 min. The mixture was stirred overnight at room temp, NaOH pellets (18 g) were added and the mixture was extracted with ether. The ether extracts were washed with satd NaCl aq and dried (K_2CO_3). The solvent was evaporated and the residue distilled. A fraction of **3a** b.p. 67–69°/2 mm, (13·4 g, 95% pure, 34% yield) was collected. The residue after several redistillations yielded finally on bulb-to-bulb distillation a cut of pure **4a**, bath temp 70–90°/0·2 mm (0·6 g, 2·4% yield).

The other amines **3b–g** and **4b–g** were prepared in similar fashion and in similar yields from **1** and the appropriate amine **2** and were purified by several distillations. Analytical samples were obtained by preparative VPC. Table 1 records their b.p.s (and m.p.s of hydrochlorides) and analytical data and Table 2 their IR and NMR spectra.

2-Butynylamine (**30**), *di-2-butynylamine* (**29d**) *and tri-2-butynylamine* (**31**). 1-Bromo-2-butyne[46] (144 g, 1·08 mole) was added dropwise in 70 min to a stirred and ice-cooled soln of ammonia (55 g, 3·2 mole) in EtOH (1·44 l). The cold soln was stirred for 2 days. Most of the solvent was distilled and the concentrated soln was filtered. Aqueous NaOH (47 g, 200 ml H_2O) was added, the mixture was extracted with ether and the ether extracts dried (K_2CO_3). After distilling the solvent the residue was fractionated to give the following fractions as colorless liquids: **30** (1·8 g, 2·4%), b.p. 52–55°/60 mm (lit.[47] b.p. 112°); **29d** (2·2 g, 3·3%), b.p. 138–141°/60 mm; and **31** (10·0 g, 16%), b.p. 135–138°/3·5 mm. Analytical samples of **29d** and **31** were obtained by preparative VPC. Amine **29d**, colorless liquid; IR ($CHCl_3$) 2212w (C≡C) cm^{-1}; NMR ($CDCl_3$) δ 1·68 (s, 1H, NH); 1·82 (t, J=2·5 Hz, 6H, Me); 3·46 (q, J=2·5 Hz, 4H, CH_2). (Found: C, 79·45; H, 8·89; N, 11·53. Calc. for $C_8H_{11}N$: C, 79·29; H, 9·15; N, 11·56%). Amine **31** colorless liquid; IR (neat) 2222w (C≡C) cm^{-1}; NMR ($CDCl_3$) δ 1·82 (t, J=2·5 Hz, 9H, Me); 3·38 (q, J=2·5 Hz, 6H, CH_2). (Found: C, 83·38; H, 8·58; N, 7·82. Calc. for $C_{12}H_{15}N$: C, 83·19; H, 8·73; N, 8·09%).

N-(2-Butynyl)-2-propynylamine (**29b**) *and* *N-(2-propynyl)-di-2-butynylamine* (**32**). 1-Bromo-2-butyne[46] (9·6 g, 72 mmole) was added dropwise in 3 hr to a stirred and ice-cooled mixture of 2-propynylamine (Aldrich Chemical Co.) (12·3 g, 223 mmole) and water (4 ml). The mixture was stirred overnight at room temp, NaOH pellets (10 g) were added and the mixture was extracted with ether and the ether extracts dried (K_2CO_3). After distilling the solvent the residue was fractionated *in vacuo* to give **29b** (2·2 g, 29%) as a colorless liquid, b.p. 99–102°/30 mm. The residue was distilled to give a colorless fraction (1·7 g), b.p. 90–112°/4 mm which was a mixture (*ca* 1 : 1) of **32** and a component which was not identified and which on VPC had a longer retention time than **32**. Analytical samples of **29b** and **32** were obtained by preparative VPC. Amine **29b**, colorless liquid; IR ($CHCl_3$) 3289s and 2179w (HC≡C); 2222vw (MeC≡C) cm^{-1}; NMR ($CDCl_3$) δ 1·62 (s, 1H, NH); 1·82 (d, J=2·5 Hz, 3H, Me); 2·24 (t, J= 2·5 Hz, 1H, HC≡C); 3·45–3·60 (m, 4H, $2CH_2$). Amine **29d**.HCl, colorless crystals (MeOH–ether), m.p. 128–131°. (Found: C, 58·04; H, 6·78. Calc. for $C_7H_{10}NCl$: C, 58·54; H, 7·02%). Amine **32**, colorless liquid; IR (neat) 3257s and 2208vw (HC≡C); 2268vw (MeC≡C) cm^{-1}; NMR ($CDCl_3$) δ 1·82 (t, J=2·5 Hz, 6H, Me); 2·24 (t, J=2·5 Hz, 1H, HC≡C); 3·35–3·55 (m, 6H, $3CH_2$). (Found: C, 82·88; H, 8·18; N, 8·81. Calc. for $C_{11}H_{13}N$: C, 82·97; H, 8·23; N, 8·80%).

N-(1-Methyl-2-propynyl)-2-propynylamine (**29c**). 3-Bromo-1-butyne[46] (2·99 g, 23 mmole) was added dropwise in 85 min to a stirred and ice-cooled mixture of 2-propynylamine (5 g, 91 mmole) and water (1·5 ml). The mixture was stirred overnight at room temp, NaOH pellets (4 g) were added and the mixture extracted with ether, and the ether extracts dried (K_2CO_3). After distilling the solvent the residue was distilled to give **29c** (1·9 g, 79%) as

Table 1. B.P.s and M.P.s (of Hydrochlorides) and Analytical Data of Amines **3a–g** and **4a–g**

Compd	B.p./mm (or M.p.)	Formula	Calculated (%)			Found (%)		
			C	H	N	C	H	N
3a	67–69/2 colorless crystals	$C_{10}H_{19}N$	78·37	12·50	9·14	77·98	12·20	9·50
3a.HCl	175–177 (dec.) (MeOH–ether)	$C_{10}H_{20}NCl$	63·30	10·63	7·38	63·20	10·51	7·54
4a	70–90/0·2[f]	$C_{13}H_{21}N$	81·61	11·06	7·32	81·42	10·90	7·50
3b	48–50/0·8 colorless crystals	$C_9H_{17}N$	77·63	12·31	10·06	77·19	12·02	9·89
3b.HCl	174–176 (MeOH–ether)	$C_9H_{18}NCl$	61·52	10·33	7·97	61·57	10·13	8·10
4b	60–62/0·6	$C_{12}H_{19}N$	81·30	10·80	7·90	81·53	10·76	7·78
3c[a]	78–81/24 colorless crystals	$C_8H_{15}N$	76·74	12·08	11·19	76·50	12·13	11·27
3c.HCl	176–178 (MeOH–ether)	$C_8H_{16}NCl$	59·43	9·98	8·66	59·62	9·96	8·73
4c[b]	57–58/0·8	$C_{11}H_{17}N$	80·92	10·50	8·58	80·71	10·38	8·73
3d[c]	127–129							
4d[d]	95–98/65							
3e[e]	37–39/26 needles	$C_7H_{13}N$	75·61	11·79	12·60	75·40	11·60	12·76
3e.HCl[f]	215–217 (MeOH–ether)							
4e[g]	78–79/22	$C_{10}H_{15}N$	80·48	10·13	9·39	80·69	9·94	9·23
3f[h]	48–50/1·5							
4f	66/0·5	$C_{12}H_{17}N$	82·23	9·78	7·99	81·81	9·46	7·66
3g[i]	38–40/26							
4g	73/24	$C_9H_{11}N$	81·16	8·33	10·52	80·99	8·25	10·30

[a] Lit.[42] b.p. 55–56°/0·1 mm; [b] lit.[42] b.p. 68–70°/0·1 mm; [c] lit.[43] b.p. 123°; [d] lit.[44] b.p. 90–92°/55 mm; [e] lit.[45a] b.p. 127–129° and [45b] b.p. 125–126°; [f] lit.[45b] m.p. 202–203°; [g] lit.[44] b.p. 74–76°/18 mm; [h] lit.[45a] b.p. 98–100°/30 mm; [i] lit.[45a] b.p. 123°; [f] bulb-to-bulb distillation (bath temp).

a colorless liquid, b.p. 60–62°/33 mm; IR (neat) 3226s and 2101vw (HC≡C) cm^{-1}; NMR (CCl_4) δ 1·12 (s, 1H, NH); 1·37 (d, J=6·5 Hz, 3H, Me); 2·08 (t, J=2·5 Hz, 1H, $HC{\equiv}CCH_2$); 2·17 (d, J=2·5 Hz, 1H, $HC{\equiv}CCHMe$); 3·49 (d, J=2·5 Hz, CH_2) and 3·65 (qd, J_{Me-CH}=6·5 Hz, $J_{CH-C\equiv CH}$=2·5 Hz, C*H*Me, the high-field doublet of the quartet of doublets is overlapped by the CH_2 doublet) (multiplets at 3·49 and 3·65 integrate to 3H). (Found: C, 78·14; H, 8·25; N, 12·77. Calc. for C_7H_9N: C, 78·46; H, 8·47; N, 13·07%).

N,N'-*Di-t-butyl*-2,4-*hexadiyne*-1, 6-*diamine* (**27**). A soln of **3e** (4·83 g) in 2N HCl (26 ml) was added to a mixture of NH_4Cl (26 g), powdered CuCl (8·5 g) and water (25 ml). The mixture was heated to 55°, vigorously stirred and O_2 was bubbled in for 6 hr. Concentrated ammonia (25 ml) was added to the cooled mixture which was then extracted with ether. The ether extracts were washed with satd NaCl aq and dried (K_2CO_3). The solvent was evaporated and the residue was submitted to a bulb-to-bulb distillation (bath temp 110–125°/0·25 mm) to give **27** (3·9 g, 81%) as a pale yellow liquid which soon solidified to pale yellow crystals. For elemental analysis a sample was sublimed (bath temp 113–120°/0·25 mm) to furnish **27** as colorless crystals, m.p. 54–55°. IR ($CHCl_3$) 2257w (C≡C) cm^{-1}; UV (EtOH) λ_{max} 257, 243 nm (ϵ 422, 715) and end absorption (at λ 220 nm, ϵ 2, 130); NMR (CCl_4) δ 0·80 (s, 2H, NH); 1·08 (s, 18H, t-Bu); 3·38 (s, 4H, CH_2). (Found: C, 76·10; H, 10·70; N, 12·91. Calc. for $C_{14}H_{24}N_2$: C, 76·31; H, 10·98; N, 12·71%). **27**.HCl, colorless crystals (MeOH), m.p. (placed on block at 253°) 260–265° (decomposition). (Found: C, 57·59; H, 8·82; N, 9·63. Calc. for $C_{14}H_{26}N_2Cl_2$: C, 57·33; H, 8·94; N, 9·55%).

N-*Allylidene-n-heptylamine* (**6a**). A mixture of **3a** (5·97 g) and satd t-BuOK in t-BuOH (60 ml) was stirred and heated under moisture exclusion at 100° for 15 min: the mixture became dark brown. It was cooled, taken up in pentane, washed with satd NaCl aq and dried (K_2CO_3). Analytical VPC showed the soln to contain **6a** (3·15 g, 53%) but no **3a**. The solvent was evaporated and the residue distilled at bath temp 120–140°/2·5 mm to give **6a** (2·7 g, 45%) as a pale yellow liquid and a dark brown viscous oil (2·07 g) as residue. The distillate was redistilled to give **6a** (1·4 g, 23%) as a very pale yellow liquid, b.p. 50–53°/1·2 mm. It is a severe lachrymator and possesses a characteristic odor. With 10% $AgNO_3$ in EtOH—H_2O (10:1) a silver mirror is formed within 1–2 min. On standing at room temp in the dark or for a longer time in a refrigerator it polymerizes to an orange-colored viscous oil. It also decomposes on standing in $CHCl_3$ soln. Pure colorless samples were obtained by preparative VPC and were submitted at once to spectral and elemental analysis. IR (neat) 1645s and 1605s (C=C—C=N); 995s and 925s (CH_2=CH); 1825w (CH_2 = overtone) cm^{-1}; UV (EtOH) λ_{max} 214 nm (ϵ 24,100); NMR ($CDCl_3$) δ 3·46 (t, J = 6·5 Hz, 2H, NCH_2); 5·4–5·9 (m, 2H, H_a and H_b); 6·15–6·85 (m, 1H, H_c); 7·88 (d, J_{cd} = 8 Hz, 1H, H_d). (Found: C, 77·93; H, 11·92; N, 9·21. Calc. for $C_{10}H_{19}N$: C, 78·36; H, 12·50: N, 9·14%).

Table 2. NMR and IR Spectra of Amines **3a–g** and **4a–g**

	Protons, δ ppm					*Hz*			IR (cm $^{-1}$)
Compd	Sol.[a]	HC≡C	HC≡CCH_2	NCH_2CH$_2$	NH	$J_{HC\equiv CCH_2}$	$J_{NCH_2CH_2}$	Sol.[b]	
3a	C	2·07t	3·34d	2·65t		2.5	7	C	3310vs, 2110vw (HC≡C)
4a	D	2·23t	3·47d	2.55t		2·5	7	C	3320vs, 2100vw (HC≡C)
3b	C	2·07t	3·34d	2·65t		2·5	7	C	3311vs, 2119vw (HC≡C)
4b	D	2·21t	3·43d	2·53t		2·5	7	C	3295vs, 2105vw (HC≡C)
3c	C	2·06t	3·31d	2·65t		2·5	7	C	3296vs, 2091vw (HC≡C)
4c	D	2·26t	3·43d	2·53t		2·5	7	C	3289vs, 2110vw (HC≡C)
3d	D	2·22t	3·42d	2·67t 0·93t (Me); 1·45m (CH_2Me); J_{MeCH_2}=6 Hz	1·25s	2·5	7	C	3289vs, 2110vw (HC≡C)
4d	D	2·22t	3·40d	2·50t 0·92t (Me); 1·50m (CH_2Me) J_{MeCH_2}=7 Hz		2·5	8	C	3311vs, 2110vw (HC≡C)
3e	C	2·04t	3·30d	1·08s (t-Bu)	0·75br,s	2·5		C	3279vs, 2110vw (HC≡C)
4e	C	2·04t	3·55d	1·17s (t-Bu)		2·5		C	3247vs, 2105w (HC≡C)
3f	C	2·07t	3·37d	2·63(br,m,CH of cyclohexyl)		2·5		C	3289vs, 2110vw (HC≡C)
4f	D	2·22t	3·55d	2·53(br,m,CH of cyclohexyl)		2·5		C	3300vs, 2110vw (HC≡C)
3g	C	2·11t	3·33d	allylic CH_2;[c] 4·9–5·4m (CH_2=); 5·5–6·2m (CH=)	1·04s	2·5		N	3311vs, 2080vw (HC≡C); 999s, 917s,br (CH_2=CH)
4g	C	2·11t	3·35d	3·12d (allylic CH_2); J_{CH_2CH}=6 Hz; 5·0–5·5m (CH_2=) 5·55–6·2m (CH=)		2·5	6	N	3315vs, 2083vw (HC≡C); 993m, 922s (CH_2=CH)

[a]NMR: C—CCl_4; D—$CDCl_3$; [b]IR: C—$CHCl_3$; N—neat; [c]the allylic CH_2 is on the higher field side of the propargylic CH_2 and is partly overlapped by the latter.

The following amines were similarly isomerized with satd t-BuOK in t-BuOH and worked up as above:

(a) Amine **3b** (4·1 g) and t-BuOK in t-BuOH (40 ml) at 110° in 27 min yielded on distillation *N-allylidene-n-hexylamine* (**6b**) (0·45 g, 11%) as a pale yellow liquid, b.p. 46–49°/3 mm. Colorless spectral and analytical samples by preparative VPC: IR (neat) 1653s and 1610s (C=C—C=N); 994s and 926s (CH_2=CH); 1854w (CH_2 = overtone); UV (EtOH) λ_{max} 215 nm (ϵ 19,400); NMR ($CDCl_3$) δ 3·47 (t, J = 6·5 Hz, 2H, NCH_2); 5·4–5·9 (m, 2H, H_a and H_b); 6·2–6·85 (m, 1H, H_c); 7·86 (d, J_{cd} = 8 Hz, 1H, H_d). (Found: C, 76·98; H, 12·40; N, 10·68. Calc. for $C_9H_{17}N$: C, 77·63; H, 12·31; N, 10·06%).

(b) Amine **3c** (6·2 g) and t-BuOK in t-BuOH (62 ml) at 110° in 20 min yielded on distillation N-*allylidene-n-pentylamine* (**6c**) (2·4 g, 39%) as a colorless liquid, b.p. 40–42°/24 mm. Colorless spectral and analytical samples by preparative VPC: IR (neat) 1642s and 1605s (C=C—C=N); 995s and 925s (CH_2=CH); 1848w (CH_2 = overtone) cm^{-1}; UV (EtOH) λ_{max} 214 nm (ϵ 21,900); NMR (CCl_4) δ 3·40 (t, J = 6 Hz, 2H, NCH_2); 5·30–5·85 (m, 2H, H_a and H_b); 6·15–6·80 (m, 1H, H_c); 7·78 (d, J_{cd} = 8·5 Hz, 1H, H_d). (Found: C, 76·36; H, 11·80. Calc. for $C_8H_{15}N$: C, 76·74; H, 12·08%).

(c) Amine **3d** (0·4 g) and t-BuOK in t-BuOH (1·2 ml) at 100° in 23 min gave after work-up a solution which on preparative VPC yielded N-*allylidene-n-propylamine* (**6d**) as a colorless liquid. IR ($CHCl_3$); 1647s and 1603m (C=C—C=N); 994s and 935s (CH_2=CH); 1869w (CH_2 = overtone) cm^{-1}; UV (EtOH) λ_{max} 211–215 nm (ϵ 6,800); NMR (CCl_4) δ 0·92 (t, J = 7 Hz, 3H, Me); 1·25–1·95 (m, 2H, CH_2Me); 3·38 (t, J = 6·5 Hz, 2H, NCH_2); 5·3–5·8 (m, 2H, H_a and H_b); 6·1–6·8 (m, 1H, H_c); 7·78 (d, J_{cd} = 8 Hz, 1H, H_d). The compound was too volatile and polymerized too fast to be submitted for elemental analysis.

(d) Amine **3e** (4·08 g) and t-BuOK in t-BuOH (12 ml) at 110° in 30 min gave after work-up a soln which contained as determined by analytical VPC *N-allylidene-t-butylamine* (**6e**) (1·33 g, 33%). Preparative VPC gave **6e** as a colorless liquid. IR (neat) 1637s and 1605s (C=C—C=N); 996s and 929s (CH_2=CH); 1855w (CH_2 = overtone); UV (EtOH) λ_{max} 214 nm (ϵ 24,000). NMR ($CDCl_3$) δ 1·15 (s, 9H, t-Bu); 5·3–5·8 (m, 2H, H_a and H_b); 6·1–6·8 (m, 1H, H_c); 7·78 (d, J_{cd} = 8 Hz, 1H, H_d); NMR (CCl_4; locked on t-Bu of **6e**) at 90 MHz gave H_c as a practically first order octet at δ 5·26 downfield from the t-Bu singlet with J_{bc} = 17·4, J_{ac} = 10·4 and J_{cd} = 8·3 Hz. On double irradiation of H_d, H_c collapsed to a symmetrically spaced sextet in which the 2 outer peaks were very weak while the inner intense quartet retained the above chemical shift and coupling constants of a first order pattern.

(e) Amine **3g** (3·23 g) and t-BuOK in t-BuOH (2·2 ml) at 85° in 17 min gave after work-up a solution which by VPC was a mixture of **3g** (0·67 g, 21%) and *N-allylidene-1-propenylamine* (**18**) (0·21 g, 6·5%). Preparative VPC gave **18** as a colorless liquid which was not pure by analytical VPC and which was too volatile and polymerized too fast to be submitted to elemental analysis. IR ($CHCl_3$) 1721m (impurity?); 1656m and 1570m (C=C—N=C—C=C); 994s and 927s (CH_2=CH); 966m (*trans* CH=CH); 1859w (CH_2 = overtone) cm^{-1}; UV (EtOH) λ_{max} 235 nm and shoulder at 250 nm (rel. opt. dens. 0·93 and 0·86) and intense end absorption; NMR (at 90 MHz) (CCl_4) δ 1·79 (dd, J_{Me-H_f} = 7 Hz, J_{Me-H_e} = 1 Hz, 3H, Me); 4·7–6·1 (m, 3H, H_a, H_b and H_f); 6·25–6·80 (m, 2H, H_c and H_e); 7·63 (d, J_{cd} = 8 Hz, 1H, H_d); impurity centered at *ca* 5·26 (*ca* 1H).

(f) Amine **3h** (Aldrich Chemical Company) (10 g) and t-BuOK in t-BuOH (100 ml) was stirred and heated at 100° for 23 min and worked up as usual to give a solution containing by analytical VPC cis-*N-benzylidene-1-propenylamine* (*cis*-**19**) (1·89 g, 18·9%) and trans-*N-benzylidene-1-propenylamine* (*trans*-**19**) (2·15 g, 21·5%) but no **3h**. The solvent was evaporated in vacuo and the residue was distilled to give a mixture of *cis*- and *trans*-**19** (2·5 g, 25%) as a pale yellow liquid, b.p. 66–72°/1 mm and a glassy hard residue (5·0 g). Preparative VPC of the distillate afforded a colorless liquid of a mixture of *cis*- and *trans*-**19** for elemental analysis. (Found: C, 82·57; H, 7·57; N, 9·64. Calc. for $C_{10}H_{11}N$: C, 82·72; H, 7·64; N, 9·65%). Preparative VPC also gave the *cis* and *trans* isomers separately (the *cis* isomer being eluted first) as colorless liquids.

cis-**19**: IR (neat) (significant peaks only) 1595m, 1565m, 980m, 968m, 932w, 734s, 685s cm^{-1}; UV (EtOH) λ_{max} 217, 223, 231 and 281 nm (ϵ 13,800, 13,200, 8,100 and 17,200). NMR ($CDCl_3$) δ 2·05 (dd, J_{Me-H_f} = 7 Hz, J_{Me-H_e} = 1·5 Hz, 3H, Me); 5·52 (quintet, J_{Me-H_f} = 7 Hz, J_{ef} = 7·5 Hz, 1H, H_f); 6·80 (dq, J_{ef} = 7·5 Hz, J_{Me-H_e} = 1·5 Hz, 1H, H_e); 7·25–7·50 (m, 3H) and 7·60–7·95 (m, 2H) (aromatic); 8·19 (s, 1H, H_d).

trans-**19**: IR (neat) (significant peaks only) 1650m, 1595m, 1563m, 976m, 969s, 935s, 751s, 688s cm^{-1}; UV (EtOH) λ_{max} 217, 223, 229 and 281 nm (ϵ 16,000, 15,300, 9,200 and 20,600); NMR ($CDCl_3$) δ 1·83 (d, J_{Me-H_f} = 7 Hz with each peak of the doublet split into a quartet with 0·75 Hz spacings, 3H, Me); 5·76–6·55 (m, 1H, H_f); 6·90 (dq, J_{ef} = 12·5 Hz, J_{Me-H_e} = 1·5 Hz, 1H, H_e); 7·30–7·55 (m, 3H) and 7·55–7·95 (m, 2H) (aromatic); 8·16 (s, 1H, H_d).

Samples of mixtures of *cis*- and *trans*-**19** on standing in a refrigerator for over a month hydrolyzed slowly to yield benzaldehyde (identified by analytical VPC).

A mixture of *cis*- and *trans*-**19** (2:1) (80 mg), MeOH (1 drop) and 2N HCl (5 drops) was stirred at room temp for 88 min. The mixture was extracted with ether. The ether soln was washed with satd NaCl aq and dried ($MgSO_4$). The liquid residue on evaporation of the solvent was identical with authentic benzaldehyde by analytical VPC and IR spectrum.

(g) *Isomerization of* **3f**. (i) *with* t-BuOK *in* t-BuOH *at 100°*. Amine **3f** (4·0 g) in t-BuOK in t-BuOH (40 ml) at 100° in 25 min afforded a soln containing by analytical VPC *N-allylidenecyclohexylamine* (**6f**) (3·3 g, 83%) and no **3f**. Distillation gave **6f** as a colorless liquid (1·7 g, 42%), b.p. 50°/3·5 mm (lit.[8] b.p. 67–68°/20 mm) and a glassy brown residue (1·8 g). Samples for elemental analysis and spectral data were obtained by preparative VPC of the distillate. IR (neat)[8,14] 1639m and 1608m (C=C—C=N); 995m and 925s (CH_2=CH); 1859w (CH_2 = overtone) cm^{-1}; UV (EtOH) λ_{max} 215 nm (ϵ 24,600) NMR ($CDCl_3$)[8] δ 1·0–2·0 (m, 10H, 5 methylenes of cyclohexyl); 2·99 (br, m, 1H, CH of cyclohexyl); 5·4–5·9 (m, 2H, H_a and H_b); 6·15–6·90 (m, 1H, H_c); 7·89 (d, J_{cd} = 8·5 Hz, 1H, H_d). (Found: C, 78·47; H, 10·91; N, 10·62. Calc. for $C_9H_{15}N$: C, 78·77; H, 11·02; N, 10·21%).

(ii) *With* t-BuOK *in* t-BuOH *on a VPC column*. Injection of an aliquot of a mixture of **3f** (0·4 g) and t-BuOK in t-BuOH (4 ml) on a column of 20% silicon GE SF-96 on firebrick (mesh 60–80) at 144° showed **3f** to isomerize partly on the column to **6f**; **3f**–**6f** ratio 1:2 (retention times of **3f** 5 min 53 sec and of **6f** 4 min 53 sec). Both components were eluted preparatively from the column.

(iii) *With* EtONa *in* EtOH. A mixture of **3f** (0·25 g) and a EtONa soln in abs EtOH (0·1 g Na, 5 ml) was refluxed 3 hr and worked up as usual. The reaction product contained by VPC analysis **3f** (75 mg, 26%) and **6f** (26 mg, 9%).

(iv) *With* t-BuOK *in diglyme at* o°. Satd t-BuOK in

t-BuOH (2·5 ml) was evaporated to dryness *in vacuo* and dried at 160° for 15 min and then suspended in freshly distilled diglyme (5 ml). The suspension was added dropwise in 3 min to a stirred solution of **3f** (0·27 g) in diglyme (2·5 ml) cooled to 0°. The mixture was stirred at 0° for 25 min, worked up as usual and dried (K_2CO_3). By analytical VPC the mixture contained **3f** (50 mg, 18%) and **6f** (166 mg, 61%).

Treatment of **6f** *with maleic anhydride.* Powdered maleic anhydride (0·19 g, 1·9 mmole) was added slowly in small portions to a stirred solution of **6f** (0·27 g, 2 mmole) in benzene (2 ml) cooled to 12°. Within 1 min the mixture became yellow and then a brown ppt formed. Filtration and washing with pentane furnished a brown powder (309 mg), insoluble in benzene, ethanol and ethyl acetate and moderately soluble in $CHCl_3$.

Treatment of **3i** *with* t-BuOK *in* t-BuOH.[27,28] A mixture of **3i**[27] (1·1 g) and satd t-BuOK in t-BuOH (9 ml) was heated at 90° for 13 min when it became dark brown. It was diluted with pentane to give a large brown polymeric precipitate. The pentane soln was decanted, washed with satd NaCl aq and dried (K_2CO_3). Analytical VPC showed that **3i** was absent from the soln but that it contained aniline (*ca* 133 mg, 17%). The soln was concentrated, extracted with 2N HCl when more solid precipitated. The acidic layer was made basic with 2N NaOH and extracted with ether. The ether extract was washed with satd NaCl aq and dried (K_2CO_3). On evaporation it afforded aniline (96 mg, 12%), identical with an authentic sample by IR and VPC.

Isomerization of **27**. A mixture of **27** (0·9 g) and a solution of KOH in abs EtOH (0·56 g KOH, 6 ml EtOH) was stirred and heated at 90° for 40 min. A dark brown soln resulted. On addition of pentane a large black polymeric ppt formed. The pentane soln was decanted, washed with satd NaCl aq and dried (K_2CO_3). The filtered solution contained 2,4-*hexadien*-1,6-*dial*-*di*-t-*butylimine* (**28**) (0·6 g, 67% yield as determined by UV). Concentration of the solution in vacuo in the cold gave on filtration a batch of **28** (85 mg, 8·6% yield, 91% pure by UV) as a crystalline yellow solid. The filtrate was then evaporated to dryness and on a bulb-to-bulb distillation at bath temperature 70-95°/0·2 mm yielded additional diimine **28** (0·28 g, 17·3% yield, 88% pure by UV) as a mixture of pale yellow crystals and oil. For elemental and spectral analysis a sample of the above distillate was crystallized from pentane to furnish colorless crystals which were sublimed at bath temperature 110–130°/0·2 mm to furnish **28** as colorless crystals (with very faint yellow tinge), m.p. 155–158° (placed on block at 148°) and giving a single spot on TLC and a single peak on VPC; IR ($CHCl_3$) 2865s, 1613s, 1567w, 1445m, 1351s, 1122s, 994s, 901–881 br, m cm^{-1}; IR (CS_2) 2890s, 1618s, 1350s, 1203s, 1122s, 993s, 899-870 br, m cm^{-1}; UV (EtOH) λ_{max} 280, 290, 302 nm (ϵ 49,500, 62,600, 48,500); NMR (CCl_4) (at 90 MHz) δ 1·22 (s, 18H, t-Bu); 6·2–6·7 (m, 4H, CH=CHCH=CH); 7·93 (d, J = 7·5 Hz, 2H, N=CH); intense double irradiation at the 6·2–6·7 region caused collapse of the N=C*H* doublet to a fine-structured singlet (hhw 3·5 Hz) and intense double irradiation at the N=C*H* doublet only caused changes in the appearance of the multiplet at the 6·2–6·7 region but did not reduce its complexity. (Found: C, 75·77; H, 10·78; N, 12·36. Calc. for $C_{14}H_{24}N_2$: C, 76·31; H, 10·98; N, 12·71%). The diimine is converted very fast at room temperature to a brown polymer.

Isomerization of **29d**. A mixture of **29d** (1·39 g) and satd t-BuOK in t-BuOH (60 ml) was refluxed for 7 hr. Aliquots removed after 25 min, 4 and 7 hr reflux showed by analytical VPC the following ratios of **29d**–**37**: 9:1; 2·4:1 and 1·1:1 respectively. The reaction mixture was poured on satd NaCl aq and extracted with ether. The ether extracts were dried (K_2CO_3), filtered and the solvent evaporated. The residue was submitted to a bulb-to-bulb distillation to furnish a colorless liquid (0·28 g) of a mixture (1·1:1) of **29d** and **37** (9·3% yield of **37**) as determined by analytical VPC as well as a large brown polymeric residue. Pure samples of **29d** and **37** were obtained by preparative VPC from the distillate and their structures were verified by analytical VPC and spectral comparison (IR, NMR, UV) with authentic samples.

Isomerization of **29b**. A mixture of **29b** (1·8 g), dry t-BuOH (2 ml) and satd t-BuOK in t-BuOH (15 ml) was stirred and heated. When bath temp reached 95° (after 10 min heating) the reaction became exothermic. The bath was removed at once and the dark brown mixture poured on satd NaCl aq, extracted with ether, and the ether extracts were dried (K_2CO_3) and filtered. Most of the solvent was distilled and the residue was shown by VPC to contain **33** (285 mg, 16% yield), **34** (145 mg, 8% yield) (both being eluted from the VPC column at 80°), a component *A* (*ca* 150 mg) eluted at 130° and a component **B** (*ca* 45 mg) eluted at 170°. The reaction mixture contained no **29b**. The above residue on vacuum distillation yielded a distillate (0·49 g) composed of **33**, **34** and **A**, as well as a black polymeric residue. Compounds **33** and **34** were eluted by preparative VPC and their structures were verified by analytical VPC and spectral comparison (IR, NMR, UV) with authentic samples. The two other products (**A** and **B**) have not yet been obtained pure.

Isomerization of **29c**. A mixture of **29c** (1·25 g), dry t-BuOH (1 ml) and satd t-BuOK in t-BuOH (13 ml) was stirred and heated. After 15 min the bath temp reached 90° and the reaction became exothermic. The bath was removed at once and the dark brown mixture was cooled. It was poured on satd NaCl aq and extracted with ether, the ether extracts dried and filtered. Most of the solvent was distilled and the residue contained as determined by analytical VPC **35** (200 mg, 16% yield) as sole product of the same molecular weight as **29c** (no **29c** was present in the mixture). The residue yielded on vacuum distillation **35** (120 mg) and a black polymeric residue. The structure of **35** was verified by analytical VPC and spectral comparison (IR, NMR, UV) with an authentic sample.

Isomerization of di-2-propynylamine (**29a**) *with* t-BuOK *on* t-BuOH *at* 70°. A mixture of **29a** (from Aldrich Chemical Company; 5·02 g), dry t-BuOH (10 ml) and satd t-BuOK in t-BuOH (40 ml) was stirred and heated. At 70° the reaction became exothermic and the mixture turned black. The bath was removed at once, the mixture was cooled, diluted with ether, washed with satd NACl aq and dried ($MgSO_4$). Analytical VPC of the filtered soln indicated that it was composed mainly of nitriles **44a** and **b** (1:3·8) and very small amounts of oximes **45a** and **b** (1:1).* The soln was concentrated and chromatographed on Kieselgel (230 g). Elution with pentane-ether (11:1) furnished a mixture of nitriles **44a** and **b** as a pale yellow liquid (3·6 g, 40%; 5:19 by VPC) and elution with ether gave an oily mixture (1·23 g) composed (as determined by

*In a separate experiment in which the cooled mixture (before work-up) was injected directly on a VPC column it was verified that no 3-picoline was formed (although a yield of *ca* 0·5% could have been detected).

VPC) of oximes **45a** and **b**, the cyanoaldehyde **46** and other minor components which were not identified. Rechromatography of the nitrile mixture (3·6 g) on Kieselgel (250 g) and elution with pentane-ether (12:1) afforded **44a** (0·72 g, 8%) and elution with pentane-ether (12:1 to 9:1) gave **44b** (2·65 g, 29%) as pale yellow liquids which were homogeneous by TLC and VPC. For elemental analysis and physical properties pure samples were obtained by preparative VPC.

cis-*Nitrile* **44a**, colorless liquid, b.p. 229° (determined by the micromethod of Garcia[49]); IR (neat) 2227w (CN); 1656vs (C=C); 1258s, 1189vs, 1124br, s and 1075s (t-BuOC=C); 735br, m(*cis* CH=CH) cm^{-1}; UV (EtOH) end absorption only; NMR ($CDCl_3$) δ 1·28 (s, 9H, t-Bu); 1·30 (d, J = 7·5 Hz, 3H, Me, the 2 peaks of the Me doublet flank the t-Bu singlet*); 2·15–3·00 (m, 3H, CH_2CHCN); 4·46 (quartet with broad inner peaks resulting from a first order A_2MX pattern: J_{CH-CH} = 6 Hz, J_{CH_2CH-} = 7·5 Hz, 1H, CH_2CH=); 6·38 (dt, J_{CH-CH} = 6 Hz, J_{CH_2CH-CH} = 1 Hz, 1H, =CHO). (Found: C, 71·80; H, 10·33; N, 8·20; mass spectrum, M^+ at m/e 167. Calc. for $C_{10}H_{17}ON$; C, 71·81; H, 10·25; N, 8·38%; M^+ 167).

trans-*Nitrile* **44b**, colorless liquid, b.p. 241–242° (determined by the micro-method of Garcia[49]); IR (neat) 2232w (CN); 1661vs (C=C); 1245s, 1189m, and 1152vs (t-BuOC=C); 929s (*trans* CH=CH); 875m cm^{-1}; UV (EtOH) end absorption only; NMR ($CDCl_3$) δ 1·28 (s, 9H, t-Bu); 1·28 [d, J = 6·5 Hz, 3H, Me, the 2 peaks of the Me doublet flank the t-Bu singlet (see footnote to the NMR of **44a**)]; 2·0–3·0 (m, 3H, CH_2CHCN); 4·96 (sextet resulting from a first order A_2MX pattern: J_{CH-CH} = 12 Hz, J_{CH_2CH-} = 7 Hz, 1H, CH_2CH=); 6·43 (dt, J_{CH-CH} = 12 Hz, J_{CH_2CH-CH} = 1 Hz, 1H, =CHO); at 90 MHz: 2·25 (triplet resulting from a first order AM_2X system: J_{CH_2CH-} = 7 Hz, J_{CH_2CHCN} = 6·5 Hz, 2H, CH_2); 2·60 (sextet resulting from a first order A_3MX_2 system: J_{MeCH} = 6·5 Hz, J_{CH_2CHCN} = 6·5 Hz, 1H, CHCN); the other signals show the same patterns as in the 60 MHz spectrum; double irradiation at CH_2 caused collapse of the CH=CHO sextet to a doublet, verifying that J_{CH-CH} = 12 Hz; double irradiation at CHO caused collapse of the CH=CHO sextet to a triplet, thus affording J_{CH_2CH} = 7 Hz. (Found: C, 71·83; H, 10·13; N, 8·20; mass spectrum M^+ at m/e 167. Calc. for $C_{10}H_{17}ON$: C, 71·81; H, 10·25; N, 8·38; M^+ 167).

Chromatography of the mixture containing the oximes (1·23 g) on Kieselgel (100 g) and elution with ether afforded fraction **A** (oil) composed of the aldehyde **46** and the *cis*-oxime **45a** (0·63 g, 1:2·5 by VPC) and fraction **B** containing the *trans*-oxime **45b** (0·5 g, 5%) as a yellow oil which crystallized in the cold.

A pure sample of **46** was obtained by preparative VPC from fraction **A** as a colorless liquid and was identical by IR, NMR, TLC and VPC with a sample obtained by hydrolysis of nitriles **44a** and **b** (*vide infra*).

Fraction **A** also afforded on preparative TLC (developed with hexane-ether, 5:95) followed by distillation (bath temperature 90–110°/0·9 mm) and preparative VPC the cis-*oxime* **45a** as a colorless liquid, homogeneous by TLC and VPC but still impure by elemental analysis. (Found: C, 62·73; H, 10·10. Calc. for $C_{10}H_{19}O_2N$: C, 64·83; H, 10·34%); mass spectrum m/e (relative intensity) 185 (29, M^+), 129 (43), 128 (20), 112 (16), 100 (43), 82 (4), 73 (24), 72 (96), 57 (100), 56 (84), 55 (11), 54 (11), 44 (70), 43 (17), 41 (37), 40 (46), 39 (13); metastable peaks m^*/e 90·1 (185→129), 88·8 (185→128), 77·4 (129→100); UV (EtOH) λ_{max} 229 nm (ϵ 19,500); IR (neat) 3356 m and 3279 m (OH); 2976 s; 2882 m, sh; 1686 sh and 1656 vs (C=C—C=N); 1490 s; 1385 w; 1361 m; 1245 m; 1193 s; 1134 m and 1070 s (t-Bu—O—CH_2); 1019 m; 885 br, m cm^{-1}; NMR ($CDCl_3$) (at 60 and 90 MHz) δ 9·13 (very br, hhw 20 Hz, 1H, OH) which on shaking with D_2O does not disappear at once but after longer time; the D_2O also removes an impurity multiplet centered at δ 6·70 to give the following spectrum: δ 1·18 (t, lower-field peak of triplet overlapped by t-Bu singlet, J_{MeCH_2}=7 Hz, Me; each of the 2 exposed peaks of the triplet possesses doublet fine structure with ca. 1 Hz spacings); 1·28 (s, t-Bu)(Me+t-Bu: 12 H); 2·28 (9, J_{MeCH_2}=7 Hz, 2 H, $MeCH_2$, each of the 4 peaks of the quartet is split into doublets with *ca* 1·5 Hz spacings); 4·18 (dd, $J_{CH_2\text{-}H_a}$=4 Hz, $J_{CH_2\text{-}H_b}$=1·5 Hz, 2H, CH_2O); 4·72 (dt, $J_{CH_2\text{-}H_a}$=4 Hz, J_{ab}=9 Hz, 1H, H_a); 6·88 (dt, J_{ab}=9 Hz, $J_{CH_2\text{-}H_b}$ = 1·5 Hz, 1H, H_b); double irradiation at CH_2O caused collapse of H_a and of H_b to sharp doublets, J_{ab}= 9 Hz; double irradiation at H_a caused collapse of CH_2O to a doublet, $J_{CH_2\text{-}H_b}$=1·5 Hz and of H_b to a broad singlet (hhw 4 Hz); double irradiation at H_b caused collapse of CH_2O to a doublet, $J_{CH_2\text{-}H_a}$=4 Hz and of H_a to a triplet, $J_{CH_2\text{-}H_a}$ = 4 Hz; shaking with H_2O recovered the OH peak as well as the impurity multiplet at δ 6·70.

Fraction **B** was rechromatographed on Florisil and eluted with hexane-ether (2:3) to yield several fractions of the trans-*oxime* **45b** as colorless crystals, homogeneous by TLC and VPC (same R_fs and retention times respectively) but of different m.p. (e.g. 28–35°, 34–37°, 36–38°, 37–53°). The fractions of m.p. 37–53° were combined and had the following spectral properties: mass spectrum m/e (rel int) 185 (5, M^+), 129 (12), 128 (5), 112 (8), 100 (10), 73 (6), 72 (32), 59 (32), 57 (100), 56 (58), 55 (21), 54 (26), 44 (42), 43 (53), 41 (58), 39 (26); metastable peaks m^*/e 90·1 (185→129), 88·8 (185→128), 77·4 (129→100); UV (EtOH) λ_{max} 233 nm (ϵ 19,000); IR (KBr) 3426 m and 3247 m (OH); 3021 sh; 2941 m; 2890 sh; 1689 sh and 1656 vs (C=C—C=N); 1529 m; 1381 w; 1353 w; 1235 m; 1190 m; 1124 w and 1045 m (t-Bu—O—CH_2); 1015 w; 964 s (*trans* CH=CH); 878 m cm^{-1}; NMR ($CDCl_3$) (at 60 and 90 MHz) δ 8·56 and 8·73 (2 broad peaks, hhw 5 Hz each, 1H, OH) which on shaking with D_2O do not not disappear at once but after longer time; the D_2O also causes a quartet centered at δ 7·00 to collapse to a doublet to give the following spectrum δ 1·13 (t, lower-field peak of triplet overlapped by t-Bu singlet, J_{MeCH_2}=7·5 Hz, Me; each of the 2 exposed peaks of the triplet possesses doublet fine structure with *ca* 1 Hz spacings); 1·20 (s, *t*-Bu) (Me + t-Bu: 12H); 2·28 (q, J_{MeCH_2} = 7·5 Hz, 2H, $MeCH_2$, each of the 4 peaks of the quartet is split into doublets with *ca* 1·5 Hz spacings); 3·92 (dd, $J_{CH_2H_a}$ = 7 Hz, $J_{CH_2\text{-}H_b}$ = 0·75 Hz, 2H, CH_2O); 5·32 (first order quintet, $J_{CH_2\text{-}H_a}$=7 Hz, J_{ab}= 14 Hz, 1H, H_a); 7·00 (d, br, J_{ab}=14 Hz, 1H, H_b); double irradiation at CH_2Me caused collapse of the Me triplet to a singlet; double irradiation at CH_2O caused collapse of H_a and H_b to doublets, J_{ab}=14 Hz; double irradiation at H_a caused collapse of CH_2O and of H_b to broad singlets; double irradiation at H_b caused collapse of CH_2O to a doublet, $J_{CH_2\text{-}H_a}$ = 7 Hz and of H_a to a triplet, $J_{OCH_2\text{-}H_a}$ = 7 Hz; shaking with H_2O recovered the OH peaks as well as the quartet centered at δ 7·00.

Cyanoaldehyde **46** (*a*) *trans-Nitrile* **44b** (0·97 g), dioxane (10 ml) and 2N H_2SO_4 (2 ml) were heated at bath

*When **29a** was rearranged in satd $(CD_3)_3COK$ in $(CD_3)_3COH$ the reaction mixture showed the Me signal of the nitrile mixture as a doublet with J = 7 Hz, the t-Bu signal being absent.

temperature 110° for 20 min. After work-up the solvent was evaporated to give aldehyde **46** (276 mg) as a light yellow liquid. For spectral and elemental analysis samples were purified by preparative VPC to give **46** as a colorless liquid, b.p. 205–208° (determined by micro-method of Garcia[49]); IR (neat) 2801 w and 2710 w (CHO); 2238 w (CN); 1712 vs (CO) cm^{-1}; NMR ($CDCl_3$) δ 1·37 (d, J_{Me-CH} = 7 Hz, 3H, Me); 1·75–2·15 (m, 2H, $CHCH_2$); 2·4–3·0 (m, 3H, CH and CH_2CHO); 9·88 (s, 1H, CHO). (Found: C, 64·65; H, 7·95; N, 12·35; mass spectrum: molecular peak absent; *m/e* M—CO:83. Calc. for C_6H_9ON: C, 64·84; H, 8·16; N, 12·60%).

(b) *From* cis-*nitrile* **44a**. Hydrolysis of **44a** under the conditions of (a) afforded **46**, identical in every respect with that obtained from **44b**.

4-Cyano-n-valeraldehyde dimethyl acetal (**47**). Cyanoaldehyde **46** (0·1 g), MeOH (2 ml) and 2N H_2SO_4 (10 drops) were stirred 1 hr at room temp. After work-up the solvent was evaporated to yield an oil (0·09 g) consisting of **46** and **47** (3:7) (by analytical VPC). The acetal **47** was obtained from this mixture by preparative VPC as a colorless liquid: IR (neat) 2232 w (CN); 1124 s and 1066 s (C—O—C); NMR ($CDCl_3$) δ 1·33 (d, J_{Me-CH} = 7 Hz, 3H, Me); 1·55–1·90 (m, 4H, CH_2CH_2); 2·4–2·9 (m, 1H,MeCH); 3·37 (s, 6H, OMe); 4·43[t, $J_{CH_2CH(OMe)_2}$ = 5 Hz; 1H, $CH(OMe)_2$]. [Found: C, 60·98; H, 9·50; N, 8·79; mass spectrum *m/e* 157 (M^+), 156 (M^+-1), 126 (M^+-MeO). Calc. for $C_8H_{15}O_2N$: C, 61·12; H, 9·62; N, 8·91%].

Hydrolysis of **44b** with 2N H_2SO_4 in MeOH also furnished the above mixture of **46** and **47** (3:7).

α-Methylglutaric acid (**49**). To a stirred mixture of **46** (0·26 g) and 4N H_2SO_4 (2·5 ml) $KMnO_4$ (0·26 g) was added at room temp during 5 min and stirring was continued for another 10 min. The mixture was then decolorized with $NaHSO_3$ (0·3 g). It was then extracted with $CHCl_3$ and the extract washed with satd NaCl aq and dried ($MgSO_4$). The solvent was evaporated to yield crude *4-cyano-n-valeric acid* (**48**) as a yellow oil. It was taken up in 20% NaOH (2 ml) and after washing with ether and $CHCl_3$, the aqueous layer was diluted with H_2O (15 ml) and refluxed 2 hr. The cooled soln was washed again with ether and $CHCl_3$ and then acidified with 8N H_2SO_4. The acid soln was extracted with $CHCl_3$ and ether and combined organic extracts washed with satd NaCl aq and dried ($MgSO_4$). Evaporation of the solvent furnished the crude diacid **49** as colorless crystals (62 mg), m.p. 70–73°. Recrystallization from ether-pentane gave the diacid (51 mg) as colorless crystals, m.p. 76–78° (lit.[50] m.p. 77–78°; 79°); IR (KBr) 2639 w, br (OH); 1690 vs (CO); 1215 s (C—O); NMR ($CDCl_3$) δ 1·23 (d, J_{Me-CH} = 6·5 Hz, 3H, Me); 1·7–2·2 (m, 2H, $CHCH_2CH_2$); 2·25–2·90 (m, 3H, CH and CH_2CO_2H); 11·21 (s, 1H, CO_2H).

Isomerization of **29a** *with t-BuOK in diglyme.* Satd t-BuOK in t-BuOH (3 ml) was evaporated to dryness *in vacuo* and dried at 160°. It was suspended in dry diglyme (5 ml) and the suspension filtered through a sintered glass funnel under N_2. The filtrate was added dropwise to a stirred soln of **29a** (0·27 g) in diglyme (7·5 ml) which was cooled to bath temp 5°. The mixture became dark brown and was further stirred at 5° for 7 min and then at room temp for 23 min. Water was added and the mixture was extracted with ether, the ether extracts washed with satd NaCl aq and dried ($MgSO_4$) to furnish on evaporation a viscous brown oil which by analytical VPC was a mixture of **29a** and nitriles **44a** and **44b** (*ca* 4:1:15) but the oximes were absent. The total yield of the two nitriles was *ca* 12%.

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