Base-catalysed Prototropic Isomerization. Part V.[1] A Novel Method for the Preparation of Enamines

By **A. J. Hubert,** Union Carbide European Research Associates, s.a., 95, rue Gatti de Gamond, Brussels 18, Belgium

Allylamines (I) have been isomerized cleanly to prop-1-enylamines (II) on a dispersion of potassium amide on alumina.

$$\underset{\text{(I)}}{(CH_2{=}CH{\cdot}CH_2)_xR_{3-x}N} \longrightarrow \underset{\text{(II)}}{(CH_3{\cdot}CH{=}CH_xR_{3-x}N}$$

$$(x = 1,\ 2,\ 3)$$

The method has many advantages over older ones for the preparation of some of the lower enamines, and for the preparation of di- and tri-(prop-1-enyl)amines (II; $x = 2$ and 3). The yields are good and the recovery of the product of isomerization is easier than with older techniques. However, the method is not general and is useful only for the preparation of propenylamines.

ENAMINES are very reactive species which are widely used in synthesis. The most general method of preparation is the dehydration of a mixture of a ketone and a secondary amine.[2] The base-catalysed isomerization of allylamines to propenylamines was used by Price and Snyder.[3] These authors used a solution of potassium t-butoxide in dimethyl sulphoxide as catalyst. This method had disadvantages in that the isomerized material had to be extracted from the solvent dimethyl sulphoxide and the yields were not good, and the reaction was incomplete and a relatively large amount of starting material was still present after several days at room temperature. The great effectiveness of the recently

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[1] Part III, A. J. Hubert, *Chem. and Ind.*, 1968, in the press; Part IV, A. J. Hubert and A. J. Anciaux, *Bull. Soc. chim. belges*, in the press.

[2] I. Fleming and M. H. Karger, *J. Chem. Soc.* (*C*), 1967, 226; G. Opitz and E. Tempel, *Annalen*, 1966, **699**, 74; K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, 1961, **26**, 625; F. W. Heyl, and M. E. Herr, *J. Amer. Chem. Soc.*, 1953, **75**, 1918; C. Mannich and H. Davidsen, *Ber.*, 1936, **69**, 2106.

[3] C. C. Price and W. H. Snyder, *Tetrahedron Letters*, 1962, 69.

described[1] catalyst for the isomerization of acetylenic compounds prompted us to use it for the isomerization of allylamines to propenylamines.

$$\underset{\text{(I)}}{(CH_2{=}CH{\cdot}CH_2)_xR_{3-x}N} \longrightarrow \underset{\text{(II)}}{(CH_3{\cdot}CH{=}CH)_xR_{3-x}N}$$

A dispersion of potassium amide on alumina was effective at room temperature. The reaction was clean in most cases, and high yields of enamines were obtained (Table). However, the catalyst could not be used indefinitely; it lost its activity when it remained for a long time (24 hours) in contact with the products of reactions. A relatively large sample of enamine (*ca.* 50 grams) could be prepared with a small amount of potassium amide (1·8 grams) on alumina (20 grams).

Isomerization of $CH_2{=}CH{\cdot}CH_2{\cdot}NRR'$ to $CH_3{\cdot}CH{=}CH{\cdot}NRR'$; catalyst, KNH_2 (1·8 g.) on alumina (20 g.); temp. 25°

Group MRR′	Reaction time (min.)	B.p./mm.	Yield (%)
$N(CH_3)$	30	37/70	70
$N(C_2H_5)_2$	30	35/15	94—100 *
$N(CH_2{=}CH{\cdot}CH_2)_2$	60 †	28/1	76
N-Pyrrolidinyl	15	55/20	65
N-Piperidinyl	60	20/1	52
N-Morpholinyl	30	25/1	57—100 *
N-Carbazolyl	60	160/1	60

* Measured by g.l.c. by using an internal standard. † Reaction run at 50°.

The propenylamines were identified by analysis and infrared spectroscopy. In some cases n.m.r. spectroscopy showed that a rather large amount of *cis*-isomer was present. This fits with the observations of different authors[3-6] for the base-catalysed isomerization of allylamines and allyl ethers.

The n.m.r. spectrum of tri(prop-1-enyl)amine showed that it probably contained the four possible isomers. The *trans*-isomers gave a doublet at τ 6·16 and 5·92 p.p.m. The *cis*-isomers absorbed at 5·92 and 5·8 p.p.m. The relative amounts of the double bonds were about 65% *cis* to 35% *trans*.

Gas chromatography of *N*-prop-1-enylcarbazole showed that it contained two isomers, which were easily separated. The n.m.r. spectra showed that the first eluted was the *trans*-isomer (33%) and the second peak the *cis*-olefin (67%). The coupling constant, *J*, of the two olefinic hydrogens was 14 c./sec. in the case of the *trans*-isomer and 8 c./sec. for the *cis*. The coupling constant of the α-olefinic hydrogen and the methyl protons of the propenyl group was 1·5 c./sec. in the case of the *trans*-isomer and 1·7 for the *cis*.

Gas chromatography gave one single peak in the case of *NN*-diethylpropenylamine. The n.m.r. spectrum showed that the compound was probably homogeneous and contained mainly the *trans*-isomer. The coupling constant was 13·5 c./sec. for the olefinic hydrogens and 1·3 c./sec. for the coupling of the α-olefinic hydrogen with the methyl group.

EXPERIMENTAL (in collaboration with L. Kumps)

Preparation of Allylamines.—They were prepared as usual by reaction of allyl bromide (1 mol.) on secondary amine (2 mol.) in ether.

Preparation of the Catalyst.—The catalyst was prepared as previously described[1] from potassium (1·2 g.) and alumina (20 g.) in liquid ammonia.

Technique of Isomerization.—A solution of the allylamine (15 g.) in hexane or pentane (25 g.) was added to the catalyst under nitrogen, and stirred at the required temperature (25° in most cases). The reaction was followed by infrared spectroscopy; the absorption of the vinyl groups at 10·06 and 10·94 μ disappeared progressively and the reaction was stopped when no more absorption could be detected at these wavelengths. The catalyst was removed by filtration. The solvent was distilled under reduced pressure and the residue was fractionated *in vacuo*. The infrared spectrum showed the typical bands of an enamine at 6·03 μ. Some absorption occurred also at about 10·7 μ.

Preparation of NN-*Diethylprop*-1-*enylamine* (II; $x = 1$, R = Et).—*NN*-Diethylallylamine (15 g.) in pentane (25 ml.) was added to the catalyst. The reaction was complete within 30 min. Another amount (15 g.) of diethylallylamine was added, and the reaction was also complete within 30 min. The reaction worked well also when a third portion of allylamine was added. The total amount of isomerized material was 45 g. The mixture was kept overnight and the catalyst was no more effective for the isomerization of diethylallylamine. Pure NN-*diethylprop*-1-*enylamine*[7] was obtained by distillation under reduced pressure. (Found: C, 73·95; H, 13·5; N, 12·1. $C_7H_{15}N$ requires C, 74·3; H, 13·4; N, 12·4%). The i.r. spectrum showed that the typical absorption for the vinyl group at 10·06 and 10·94 μ had disappeared and the characteristic absorption of C=C was observed at 6·03 μ. Absorption occurred also at 10·7 μ.

Preparation of NN-*Dimethylprop*-1-*enylamine*[3,7] (II; $x = 1$, R = CH_3).—The isomerization of *NN*-dimethylallylamine was made under the same conditions as above. The results are summarized in the Table.

Preparation of N-*Prop*-1-*enylpyrrolidine*.[7]—This enamine was obtained as described above. A large amount of high-boiling material was formed together with the enamine.

Preparation of N-*Prop*-1-*enylpiperidine*.[7]—The isomerization was made under the same conditions as above.

Each of the above three enamines was easily identified by its i.r. spectrum, which was very similar to that of *NN*-diethylprop-1-enylamine.

Preparation of N-*Prop*-1-*enylmorpholine*.—The isomerization was made as above. It was checked that the catalyst remained active after two additions of *N*-allylmorpholine (Found: C, 65·7; H, 10·5; N, 11·2. $C_7H_{13}NO$ requires C, 66·2; H, 10·2; N, 11·0%).

Preparation of NN-*Di(prop*-1-*enyl)cyclohexylamine* (II; $x = 2$, R = C_6H_{11}).—The isomerization was performed as above. It was complete within 30 min. The expected

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[4] C. C. Price and W. H. Snyder, *J. Amer. Chem. Soc.*, 1961, **83**, 1773.

[5] T. J. Prosser, *J. Amer. Chem. Soc.*, 1961, **83**, 1701.

[6] A. Schrieshein, J. E. Hofmann, and C. A. Rowe, *J. Amer. Chem. Soc.*, 1961, **83**, 3731.

[7] J. Sauer and H. Prahl, *Tetrahedron Letters*, 1966, **2863**; G. Opitz, H. Hellmann, and H. W. Schubert, *Annalen*, 1959, **623**, 114.

enamine was obtained in low yield (20%) but the starting material contained some *N*-prop-1-enylcyclohexylamine as impurity, b.p. 72°/1 mm. (Found: C, 80·0; H, 11·9; N, 7·85. $C_{12}H_{21}N$ requires C, 80·4; H, 11·8; N, 7·8%).

Preparation of Tri(prop-1-enyl)amine † (II; $x = 3$).—The isomerization was made under the standard conditions (see above) (Found: C, 78·8; H, 11·2; N, 10·45. $C_9H_{15}N$ requires C, 78·8; H, 11·0; N, 10·2%). The i.r. spectrum was slightly different from the others: the band which was observed at 10·7 μ in the case of diethylpropenylamine was shifted to 10·8 μ. A band was also observed at 13·6 μ.

Preparation of N-*prop-1-enylcarbazole*.—The isomerization was performed as above. This *enamine* was much more stable than those described above (Found: C, 86·8; H, 6·2; N, 6·7. $C_{15}H_{13}N$ requires C, 86·9; H, 6·3: N, 6·75%). The isomerized material was a mixture of two isomers (67% *cis* and 33% *trans*) which were separated by g.l.c. The *trans*-isomer had m.p. 35°. The *cis*-isomer was a liquid. The i.r. spectra of the two isomers were very different. The *cis*-isomer absorbed at 3·28, 3·43, 6·0, 6·16, 6·26, 6·70, 6·75, 6·88, 7·31, 7·42, 8·07, 8·17, 8·65, 10·56, 10·78, 13·36, and 13·88 μ, and the *trans*-isomer at 3·28, 3·38, 6·05, 6·13, 6·25, 6·68, 6·75, 6·86, 7·13, 7·32, 7·48, 7·58, 8·02, 8·12, 8·68, 10·76, 13·25, 13·47, and 13·80 μ.

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† W. E. Billups prepared this compound by another method (personal communication).