Tetrahedron Letters No. 2, pp. 69-73, 1962. Pergamon Press Ltd. Printed in Great Britain.

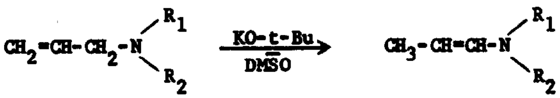
THE BASE-CATALYZED ISOMERIZATION OF ALLYL TO PROPENYL AMINES

Charles C. Price and William H. Snyder

Department of Chemistry, University of Pennsylvania, Philadelphia 4, Pa.

(Received 27 December 1961)

Recently, the base-catalyzed isomerizations of allyl to propenyl ethers[1,2] and 1- to 2-olefins[3] have been reported to be highly selective in yielding the cis-isomers. We wish to report on a similar isomerization of tertiary allyl amines which appears to be very much less selective under conditions essentially equivalent to those reported previously[1,3].



$$\mathrm{CH_2{=}CH{-}CH_2{-}N}\begin{matrix}\diagup R_1\\ \diagdown R_2\end{matrix} \xrightarrow[\text{DMSO}]{\text{KO-t-Bu}} \mathrm{CH_3{-}CH{=}CH{-}N}\begin{matrix}\diagup R_1\\ \diagdown R_2\end{matrix}$$

I, $R_1 = R_2 = CH_3$
II, R_1 = allyl, $R_2 = CH_3$
III, R_1 = allyl, $R_2 = C_6H_5$

Allyl dimethyl amine (17.0 g , 0.2 mole), potassium t-butoxide (0.02 mole) and 10 ml of dimethyl sulfoxide were allowed to stand at room temperature for 3 days, yielding 13.4 g of material, b.p. 70-77°. On examination

---

[1] **C. C. Price and W. H. Snyder, J. Am. Chem. Soc. 83, 1773 (1961).**

[2] **T. J. Prosser, J. Am. Chem. Soc. 83, 1701 (1961).**

[3] **A. Schriesheim, J. H. Hofmann and C. A. Rowe, Jr., J. Am. Chem. Soc. 83, 3731 (1961).**

by gas chromatography (12.5% THEED on anhydrous lithium hydroxide, column temperature = 25°), two major components were found. The first (in order of increasing retention time) was 34.6% of unrearranged amine and the second was 64.4% of trans-propenyl dimethylamine. A minor component (< 1%) was also present (not examined) which may have been the cis-isomer. Infrared examination of the product showed no absorption at 13.8μ characteristic of the cis C-H out-of-plane bending vibrations.

Diallyl methyl amine (22.2 g , 0.2 mole) was treated at room temperature with 0.02 moles of alcohol-free potassium t-butoxide in the presence of 10 ml of dimethylsulfoxide for 3 days to yield two main fractions; 5.7 g , b.p. 120-128° and 9.5 g , b.p. 128-132°. The higher boiling fraction was examined by gas chromatography (12.5% THEED on anhydrous lithium hydroxide, column temperature = 60°) and was found to contain unrearranged amine (4.0%), cis-trans-dipropenyl methyl amine (80.3%, infrared C-H out-of-plane bending vibrations at 10.58, 10.78μ (trans) and 13.63, 13.95μ shoulder (cis)), and trans, trans-dipropenyl methyl amine (15.7%, infrared absorption at 10.62 and 10.77μ (trans)).

Diallylaniline (10 g , 0.058 mole), potassium t-butoxide (0.032 mole) and dimethyl sulfoxide reacted exothermically. After standing a day at room temperature, 6.7 g of product, b.p. 110-113° (11 mm), was obtained. Gas chromatography (25% THEED on Chromosorb, column temperature = 200°) showed two components in 74.5 and 25.5% amounts, respectively, in order of increasing retention time. These components were judged to be the cis-trans- and trans-trans-dipropenylanilines, respectively, based on the relative intensities of the cis and trans C-H out-of-plane bending vibrations in the infrared at 13.68 and 10.68μ, respectively.

All of the preceding propenyl amines showed strong absorption at about 6.05μ (characteristic of the C=C stretching vibration) in contrast to the weak absorption shown by the unrearranged allyl derivatives in this region.

Isolation of all products was accomplished by carefully adding a three-fold excess of water, extracting the organic layer with three 40-ml. portions of ether, drying the ether layer over anhydrous potassium carbonate and distilling the ether at atmospheric pressure. The product was then distilled in a semi-micro distilling apparatus through a six-inch Vigreux column.

Diallyl ether (19.6 g , 0.2 mole), potassium t-butoxide (0.02 mole) and 10 ml of DMSO were allowed to stand for 2 months at room temperature. Distillation of the product afforded 11.2 g of material, b.p. 90-94° at atmospheric pressure. Infrared and gas chromatography showed that more than 95% of the material was the cis,cis-dipropenyl ether.

The preceding results with diallyl ether would preclude an initial isomerization to cis-product followed by conversion to trans-isomer. These results are in accord with those of Prosser[2] who showed that trans-propenyl n-propyl ether was no converted into the cis-isomer by heating with potassium t-butoxide at 150° and our observation[4] that cis-propenyl n-hexyl ether was not converted into the trans-isomer by prolonged heating with potassium t-butoxide (1 equivalent) in dimethoxyethane solvent. Since the acidity of C-H bonds in both the allyl and propenyl amines should be considerably lower than with the analogous ethers due to the relatively lower electronegativity of nitrogen it seems likely that the allyl amines isomerize irreversibly directly to either the cis or trans propenyl amines. In this connection, there is essentially no difference in the cis-trans ratio produced by the isomerization of diallyl methyl amine after 3 days

---

[4] W. H. Snyder, Doctoral Thesis, University of Pennsylvania, 1961.

and after 2 months under the conditions reported above.

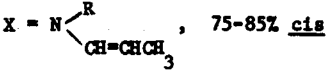
Results of the steric course for the various isomerization reactions may be summarized as follows.

$CH_2{=}CHCH_2X \xrightarrow{base} CH_3CH{=}CHX$

X = CH_3 or CH_2R, > 96% cis[5]

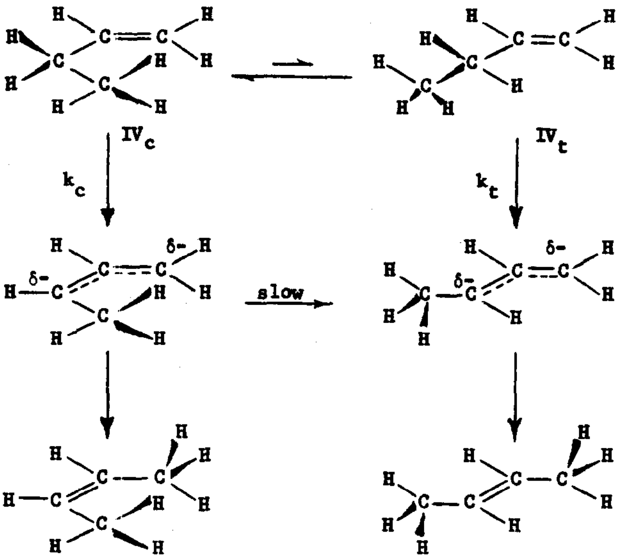
X = OR, > 98% cis

X = NR_2, mainly (> 95%) trans



$X = N\begin{matrix} R \\ CH{=}CHCH_3 \end{matrix}$, 75-85% cis

We wish to suggest the following general explanation for the widely different steric course of the various rearrangements.



(1)

If one assumes that conformation IV$_c$ is favored over IV$_t$ by a factor as

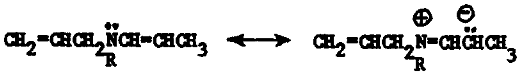
---

[5] For the olefins, the cis-isomer inititially formed is gradually transformed largely into the more stable trans-isomer.[3]

small as 2 kcal/mole, due perhaps in part to favorable interaction between two of the methyl group hydrogens and the π-electrons of the double bond, then rate constants k_c and k_t can be nearly equal and yet there will be a great preference for cis-2-butene in the initial isomerate. The cis-to-trans interconversion of carbanions would presumably be slow due to double bond character at the 2,3-bond, which would restrict rotation there.

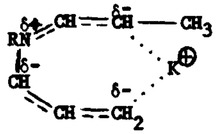
If the methyl group in IV_c and IV_t were replaced by the dimethylamino group (I_c and I_t), the repulsion between the double bond π and nitrogen 2p electrons would shift the equilibrium (1) to strongly favor the trans form. Again there would need to be no great difference in k_c and k_t to explain the great preponderance of trans-propenyl amine.

The presence of a propenyl group on the amine nitrogen could by resonance substantially diminish the 2p-electron availability on nitrogen.



$$CH_2{=}CHCH_2\underset{R}{\ddot{N}}CH{=}CHCH_3 \longleftrightarrow CH_2{=}CHCH_2\underset{R}{\overset{\oplus}{N}}{=}CH\overset{\ominus}{\ddot{C}H}CH_3$$

This would not only decrease the repulsion favoring the trans-conformation for a non-resonating amine (I or II), but would also provide opportunity for the formation of a cyclic "chelated" transition state similar to that proposed earlier[1,2] to account for cis-stereospecificity in the ether rearrangements. Such cyclic contributions to the transition state would so enhance the value of k_c compared to k_t as to overcome unfavorable conformational factors in the reactant molecule.



We wish to acknowledge valuable discussions with Drs. F. V. Brutcher, Jr. and E. R. Thornton.