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Behavior of Allylamines in the System KOH–DMSO

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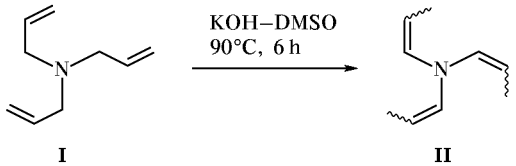
Abstract—Isomerization of triallylamine in the system KOH–DMSO at 90–100°C leads to formation of tris-(1-propenyl)amine in quantitative yield. Under similar conditions, diallyl(ethyl)amine is converted into ethyl-bis(1-propenyl)amine and 1-ethyl-3-methylcyclohexane. Diallylamine in KOH–DMSO gives rise to a complex mixture of products consisting of bis(1-propenyl)amine, methylbis(1-propenyl)amine, 1-ethyl-3-methylcyclohexane, and 2-ethyl-3,5-dimethylpiperidine. Ways of formation of these products are discussed.

Strongly basic systems consisting of an alkali metal hydroxide and a dipolar aprotic solvent are known to be effective media for prototropic isomerization of an allyl group into 1-propenyl [1–4]. Transformations of heteroelement-containing allyl derivatives in the system KOH–DMSO are determined by both the reaction conditions and the nature of heteroelement. Diallyl ether (80°C, 15 h) and diallyl sulfide (50°C, 3 h) in KOH–DMSO undergo isomerization into bis-(1-propenyl) ether and bis(1-propenyl) sulfide, respectively, in up to 90% yield, while diallyl selenide and telluride in the same system are converted into 1,3,5-hexatriene [1, 2]. Unsymmetrical alkyl allyl selenides and tellurides in KOH–DMSO are readily transformed into the corresponding alkyl 1-propenyl selenides and tellurides [3–5].

It was found that triallylamine (**I**) in the system KOH–DMSO at 90°C (6 h) readily undergoes isomerization into tris(1-propenyl)amine (**II**) in up to 88% yield (Scheme 1).

Scheme 1.



I **II**

Prior to these studies, the isomerization of **I** was carried out in KNH_2–Al–C_5H_{12}–N_2 [6] and K(Na)–Al_2O_3–Ar [7, 8]. In these cases, the reaction was often accompanied by cyclization of **I** to 3-methyl-*N*-(*trans*-1-propenyl)-1,2,3,4-tetrahydropyridine; moreover, Balu *et al.* [9] found conditions for selective formation of the latter product. The isomerization of **I** in the system KOH–DMSO in the presence of hydroquinone is characterized by considerably lower efficiency. Taking into account that small amounts of dimsylsodium in DMSO are known to initiate radical ion reaction [10, 11] and that dimethyl sulfoxide anions can be generated in the KOH–DMSO system [12], the transformation of compound **I** into **II** may be represented by Scheme 2. Insofar as the process cannot be suppressed completely by addition of a radical inhibitor, both radical anion and ionic paths are possible.

Compound **II** is formed as a mixture of *cis,cis,cis*, *cis,cis,trans*, *cis,trans,trans*, and *trans,trans,trans* isomers. The isomer ratio strongly depends on the reaction temperature and the amount of potassium hydroxide. Elevated temperature, as well as increased concentration of KOH, favors formation of the *trans* isomers of **II**. According to the data of [10], radical ions with alkali metal cations in dissociating solvents give rise to coordination compounds which favor formation of the *cis* isomers. Therefore, we presume that raising the temperature or KOH concentration leads to decomposition of such complexes. As a result, the predominant radical ion isomer is *trans* rather than *cis*. The *cis–trans* isomerization is likely to occur in the radical anions, for a definite isomer of **II** almost does not change in the system KOH–DMSO at 90°C. No transformation of **I** into **II** was observed when KOH was replaced by LiOH; in the presence of sodium hydroxide, the conversion of **I** was as low as 15%. The efficiency of the isomerization in KOH–DMSO decreases on addition of water.

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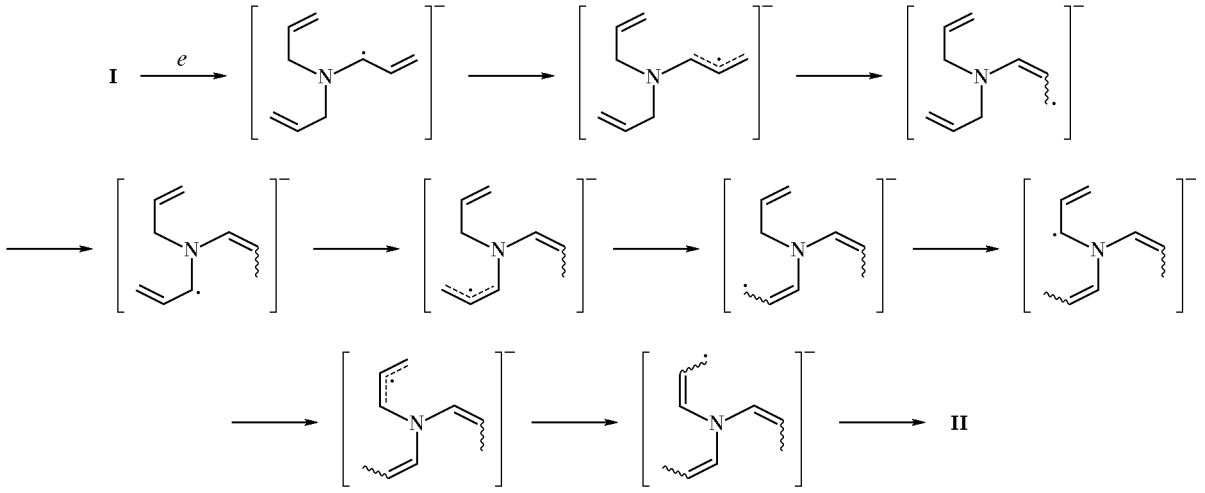
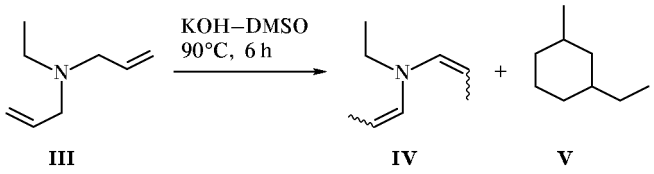
Scheme 2.



This fact can readily be understood, taking into account that the presence of even small amounts of water in DMSO sharply reduces the acidity function H_- [13, 14].

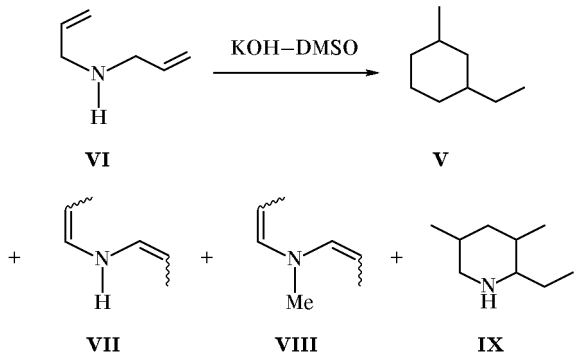
It seemed obvious that the behavior of ethyldiallylamine (**III**) in the system KOH–DMSO should be analogous to the behavior of **I** in the same system. However, the isomerization of **III** into ethylbis(1-propenyl)amine (**IV**) was accompanied by formation of 1-ethyl-3-methylcyclohexane (**V**) (Scheme 3). The ratio of products **IV** and **V** in the reaction mixture was 1:1.5 (90°C, 6 h).

Scheme 3.

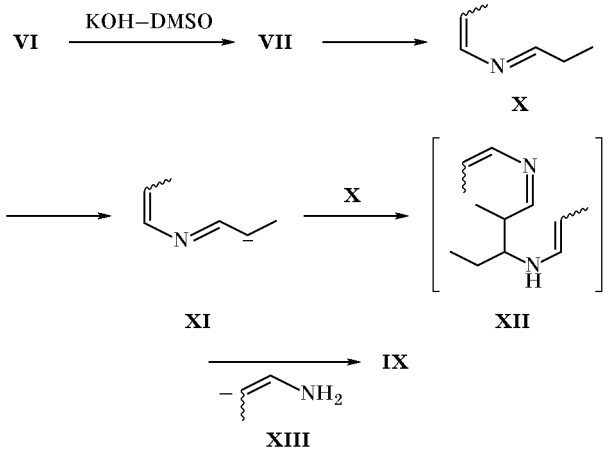


Even more complex mixture was obtained from diallylamine (**VI**) in KOH–DMSO; according to the GLC data, more than 8 compounds were present in the reaction mixture. By gas chromatography–mass spectrometry we succeeded in identifying the following compounds: 1-ethyl-3-methylcyclohexane (**V**), bis(1-propenyl)amine (**VII**), methylbis(1-propenyl)amine (**VIII**), and 2-ethyl-3,5-dimethylpiperidine (**IX**) (Scheme 4). The fraction of enamine **VII** did not exceed 5%. Compound **VIII** is formed by methylation of **VII** with the system KOH–DMSO [15, 16]. The formation of product **IX** may be explained as follows. Prototropic isomerization of **VI** yields compound **VII** which is then converted into *N*-propylidene-1-propenylamine (**X**). Schiff bases like **X** are known [17] to be formed from enamines in the presence of bases. Compound **X** in KOH–DMSO gives rise to carbanion **XI** which attacks the carbon atom at the

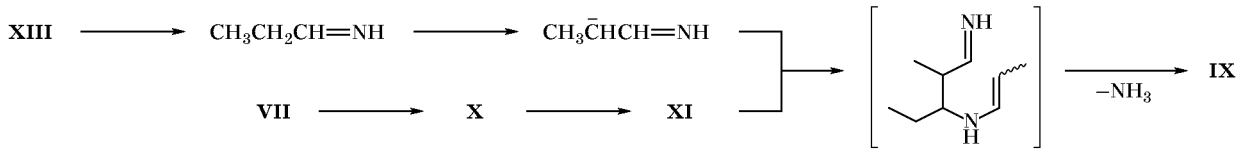
Scheme 4.



Scheme 5.



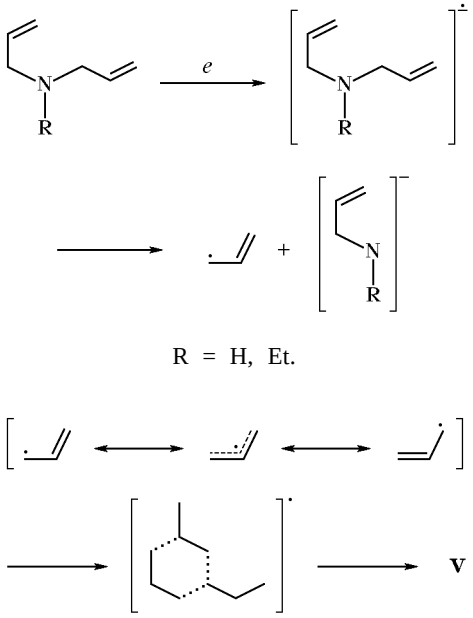
Scheme 6.



double C=N bond in **X** to give intermediate **XII**. At 90–100°C, the latter undergoes cyclization with elimination of 1-propenylamine molecule (**XIII**), yielding product **IX** (Scheme 5). It is also possible that liberated 1-propenylamine (**XIII**) reacts with compound **VII** according to Scheme 6.

Presumably, both ionic and radical ion processes are responsible for the variety of products obtained from compound **VI** in the system KOH–DMSO. The presence of three acceptor groups in molecule **I** stabilizes radical anion derived therefrom, so that elimination of some moiety with unpaired electron is unfavorable. In going to structures **III** and **VI**, the mobility of unpaired electron increases, and it readily leaves the parent molecule together with appropriate departing group (Scheme 7), giving rise to unusual transformations in the system KOH–DMSO.

Scheme 7.



R = H, Et.

EXPERIMENTAL

The reaction mixtures were analyzed by GLC on a Khrom-5 chromatograph equipped with a 2000 × 4-mm column; stationary phase 10% of SE-30 on Chromaton N-AW-DMCS. The mass spectrum was obtained on an LKB-2091 GC–MS system. The ^{1}H NMR spectra were recorded on a Bruker DPX-400 instrument operating at 400.13 MHz; chloroform-*d* was used as solvent, and hexamethyldisiloxane, as internal reference.

Isomerization of triallylamine (I). *a*. A mixture of 2.7 g (0.02 mol) of compound **I**, 4.5 g (0.008 mol) of KOH (**I**-to-KOH ratio 1:4), and 50 ml of DMSO was heated for 6 h at 90°C. The mixture was diluted with water and extracted with ether, the ether extracts were washed with water, dried over $CaCl_2$, and subjected to fractional distillation to isolate 4.2 g (88%) of compound **II** (the still residue was a tarry material). The *cis,cis,cis*–*cis,cis,trans*–*cis,trans,trans*–*trans,-trans,trans* ratio was 5:3:1:1.

b. A mixture of 1.2 g (0.009 mol) of compound **I**, 4.4 g (0.08 mol) of KOH (**I**-to-KOH ratio 1:9), and 50 ml of DMSO was heated for 6 h at 90°C. After appropriate treatment, 0.9 g (75%) of compound **II** was isolated; *cis,cis,cis*–*cis,cis,trans*–*cis,trans,trans*–*trans,trans,trans* ratio 3:2:2:1.

c. A mixture of 1 g (0.007 mol) of compound **I**, 9.2 g (0.16 mol) of KOH (**I**-to-KOH ratio 1:23), and 50 ml of DMSO was heated for 6 h at 90°C. After appropriate treatment, 0.6 g (60%) of compound **II** was isolated; *cis,cis,cis*–*cis,cis,trans*–*cis,trans,trans*–*trans,trans,trans* ratio 1:2:4:6.

d. A mixture of 3.1 g (0.02 mol) of compound **I**, 6.6 g (0.12 mol) of KOH (**I**-to-KOH ratio 1:6), and 50 ml of DMSO was heated for 5 h at 110°C. After appropriate treatment, 1.5 g (48%) of compound **II** was isolated; *cis,cis,cis*–*cis,cis,trans*–*cis,trans,trans*–*trans,trans,trans* ratio 2:2:3:5.

e. A mixture of 1.2 g (0.009 mol) of compound **I**, 4.4 g (0.08 mol) of KOH (**I**-to-KOH ratio 1:9), 0.12 g of hydroquinone (10 wt % with respect to **I**), and 50 ml of DMSO was heated for 6 h at 90°C. After appropriate treatment, 0.4 g (35%) of compound **II** was isolated; *cis,cis,cis*–*cis,cis,trans*–*cis,trans,trans*–*trans,trans,trans* ratio 4:2:2:1.

It was difficult to assign the ^{1}H NMR signals to particular isomers; therefore, their quantitative determination was performed by GLC, taking into account

that the *cis* isomer leaves the column before the *trans* isomer [18].

Isomerization of diallyl(ethyl)amine (III). A mixture of 6.3 g (0.05 mol) of compound **III**, 11.2 g (0.2 mol) of KOH, and 50 ml of DMSO was heated for 6 h at 90°C. Appropriate treatment gave 4.3 g of a mixture containing (GLC) 39% of **IV**, 58% of **V**, and 3% of unidentified products. Yield of **IV** 27%; yield of **V** 39%. ^{1}H NMR spectrum of **IV**, δ, ppm: *cis,cis* isomer: 4.71 d.q (2H, $CH_3C\mathbf{H}$), 6.45 d.q (2H, NCH), 1.63 d.d (6H, $C\mathbf{H}_3CH$), 1.18 t (3H, $C\mathbf{H}_3CH_2$), 3.30 q (2H, CH_2); ^3J(CHCH) = 8.5 Hz, $^3J(CH_3CH)$ = 7.0 Hz; *cis,trans* isomer: 4.72 d.q (1H, $CH_3C\mathbf{H}$), 6.51 d.q (1H, NCH), 1.66 d.d (3H, $C\mathbf{H}_3CH$), 4.65. ^{1}H NMR spectrum of **V**, δ, ppm: 0.76–2.06 m (10H, CH_2), 0.88–0.76 m (3H, $C\mathbf{H}_3CH$), 0.91–0.89 m (3H, $C\mathbf{H}_3CH_2$), 1.14–1.38 m (2H, $CH_3C\mathbf{H}_2$). GC–MS analysis of the reaction mixture showed the presence of compounds **IV** (*m*/*z* 125) and **V** (*m*/*z* 126) and ethyl(1-propenyl)amine (*m*/*z* 85).

Isomerization of diallylamine (VI). A mixture of 6.3 g (0.05 mol) of compound **VI**, 11.2 g (0.2 mol) of KOH, and 50 ml of DMSO was heated for 6 h at 90°C. Appropriate treatment gave 4.3 g of a mixture containing (GLC) 8 compounds. The following products were identified by GC–MS: **V** (*m*/*z* 126), **VII** (*m*/*z* 97), **VIII** (*m*/*z* 111), **IX** (*m*/*z* 141), **X** (*m*/*z* 181). Also, compounds giving rise to ion peaks with *m*/*z* 133, 160, and 195 were present.

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