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Unexpected Transformations of Alkyldiallylamines in the KOH–DMSO System

G. K. Musorin

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia

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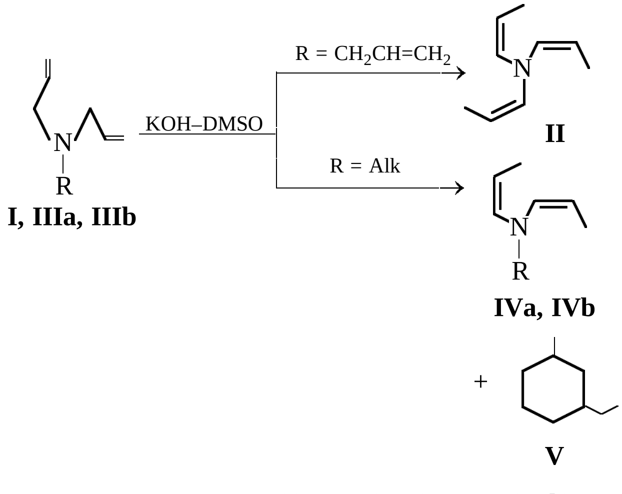
Abstract—Triallylamine in the KOH–DMSO system readily isomerizes into tri(1-propenyl)amine. Alkyldiallylamines in the same system give 1-ethyl-3-methylcyclohexane along with alkyldi(1-propenyl)amine. The effect of quantity of base and reaction temperature on product ratio was studied. A route of 1-ethyl-3-methylcyclohexane formation was proposed.

It is known that directions of transformations of allylic heteroatomic compounds in strongly basic media [alkali metal hydroxide–polar aprotic solvent (DMSO)] are determined by the nature of the heteroatom [1–3]. Thus, diallyl ether and diallyl sulfide in the KOH–DMSO system readily isomerize into the corresponding di(1-propenyl) chalcogenides [1], whereas diallyl selenide and diallyl telluride in the same system convert into 1,3,5-hexatriene [2, 3].

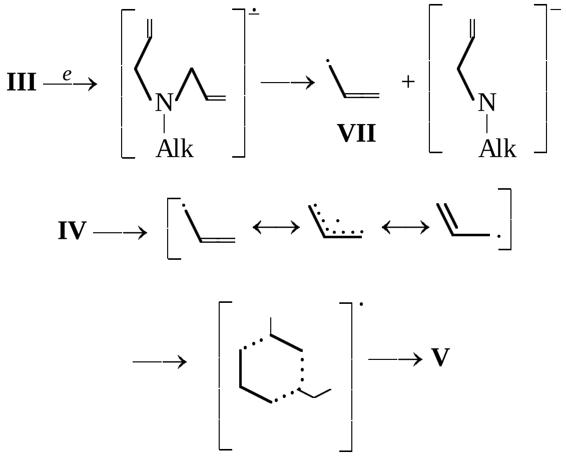
We are the first to find that directions of transformations of diallylamines in the system KOH–DMSO depend on the nature of the substrate. Whereas triallylamine (**I**) in the KOH–DMSO system (90°C, 6 h) selectively isomerizes into tri(1-propenyl)amine (**II**) in yields of up to 88%, alkyldiallylamines **IIIa** and **IIIb**, along with the isomerization into alkyl(1-propenyl)amines **IVa** and **IVb**, can also convert into 1-ethyl-3-methylcyclohexane (**V**). The **IVa** : **V** ratio in the reaction mixture [90°C, 6 h; **IIIa** : KOH = 1 : 4] is 1 : 1.5. The total yield of compounds **IV** and **V** is 66%.



R = $CH_2CH{=}CH_2$ (**I**), Et (**IIIa**), *i*-Pr (**IIIb**).

The **IV** : **V** ratio in the reaction mixture depends on the quantity of base and on the reaction temperature. Increasing quantity of potassium hydroxide in the reaction medium (**IIIa** : KOH = 1 : 10, 90°C, 6 h] increases the fraction of compound **V** (**IVa** : **V** = 1 : 2.2]. The same trend is observed as the reaction temperature is increased. In more rigid conditions (110°C, 6 h), the **IVa** : **V** ratio is 1 : 3. At 65°C, the conversion of compound **IIIa** is 84% and **IVa** : **V** = 1 : 1.

In view of the ability of the KOH–DMSO system to induce radical-anion processes [4], as well as the ability of alkali metal cations to coordinate with unsaturated compounds which subsequently convert into cyclic structures [5], we can propose the following route of formation of compound **V**.



Apparently, compound **I**, containing three acceptor allyl groups, can hold the unpaired electron in the radical anion and thus discourages the leaving group from cleaving with this electron. Substitution of one allyl group in compound **I** by an alkyl group makes the unpaired electron more mobile, produces its

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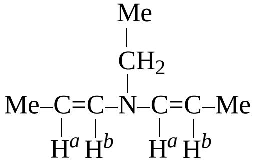
Table 1. Reactions of amines **I** and **III** with the system KOH–DMSO[a]

Initial reagents					t, °C	Fractions of the reaction products in the mixture, %			Total yield, %
$RN(CH_2CH{=}CH_2)_2$			KOH			**II**	**IV**	**V**	
R	g	mol	g	mol					
$CH_2{=}CHCH_2$	2.7	0.02	4.5	0.08	90	100	–	–	88
CH_3CH_2	6.3	0.05	11.2	0.2	90	–	38.8	58.2	66
CH_3CH_2	2.3	0.02	11.2	0.2	90	–	30	65	68
CH_3CH_2	1.6	0.01	5.6	0.1	110	–	25.9	78.3	58
CH_3CH_2	1.6	0.01	2.2	0.04	65	–	50.8	49	67
$CH_3(CH_3)CH_2$	1.7	0.01	2.2	0.04	90	–	54.3	44.8	63

[a] Reaction time 6 h, DMSO (50 ml).

Table 2. ^{1}H NMR spectrum of compound **IVa**



$$\mathrm{Me{-}\underset{H^a}{\underset{|}{C}}{=}\underset{H^b}{\underset{|}{C}}{-}\overset{\overset{\overset{Me}{|}}{CH_2}}{\overset{|}{N}}{-}\underset{H^a}{\underset{|}{C}}{=}\underset{H^b}{\underset{|}{C}}{-}Me}$$

Isomers, σ, ppm	H^a	H^b	Me	Me'	CH_2	$J_{H^aH^b}$
cis,cis	4.71	6.45	1.63	1.18	3.30	8.5
trans,trans	4.67	6.49	1.63	1.55	3.26	13.4
cis,trans				1.35	3.26	
cis	4.72	6.51	1.63			8.7
trans	4.67	6.49	1.64			13.4

shifting, and stimulates cleavage of the leaving group and favors unusual transformations of compounds **III** in the system KOH–DMSO.

We also detected traces of ethyl(1-propenyl)amine in the reaction mixture. In the presence of base, this compound probably converts into ethylamide.

EXPERIMENTAL

Gas chromatography was performed on a Chrom-5 chromatograph, column 1000ξ4 mm, packing 10% SE-30 on Chromaton N-AW-DMCS. The mass spectrum was obtained on an LKB-2091 instrument. The ^{1}H NMR spectra were measured on a Bruker DPX-400 spectrometer (400.13 MHz) internal reference HMDS, solvent $CDCl_3$.

A mixture of 6.3 g of compound **IIIa**, 11.2 g of KOH, and 50 ml of DMSO was heated at 90°C for 6 h. The reaction mixture was then diluted with water, treated with ether, the ether extracts were washed with water, dried with $CaCl_2$, and distilled to isolate 4.3 g of a mixture containing (by GLC data) 38.8% of compound **IV**, 58.2% of compound **V**, and 3% of unidentified products. The yields of compounds **IV** and **V** were 27% and 39%, respectively. The other experiments were performed in a similar way (Table 1). The ^{1}H NMR spectrum of compound **IVa** is given in Table 2.

^{1}H NMR spectrum of compound **V**: 0.76–2.06 m (10H, C_6H_{10}), 0.88–0.76 m (3H, CH_3CH), 0.91–0.89 m (3H, CH_3CH_2), 1.14–1.38 m (2H, CH_2CH_3).

By GC–MS analysis of the reaction mixture we found compounds **IV** (*m*/*e* 125), **V** (*m*/*e* 126), and ethyl(1-propenyl)amine (*m*/*e* 85).

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