

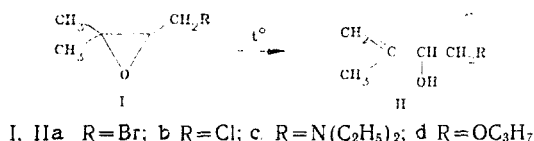
## THERMAL ISOMERIZATION OF 2-METHYL-2,3-EPOXYBUTANES TO METHALLYL ALCOHOLS

A. A. Gevorkyan, P. I. Kazaryan, S. V. Avakyan,  
and É. S. Simonyan

UDC 547.361.04'422.22-31

The isomerization of epoxides is a convenient route to certain allyl alcohols and carbonyl compounds [1]. On treatment with bases, oxiranes give allyl alcohols only [2], but with acids they afford either carbonyl compounds [1] or allyl alcohols [3]. On heating, however, epoxides give aldehydes and ketones, but not allyl alcohols [1].

We have found that epoxides on heating may also isomerize to allyl alcohols. The reaction is as regioselective as when bases are used. This is well shown in the cases of the functionally substituted 2-methyl-2,3-epoxybutanes (Ia-d). Maintaining these compounds at their boiling points results in the formation of the isomeric methallyl alcohols (IIa-d) in 70-92% yields.



For the compounds (II) obtained, the duration of the reaction (h), temperature of the reaction mixture (°C), and yield (%) are given: (IIa), 0.75, 145-168 (the temperature rose as (IIa) was formed), 92; (IIb), 11, 135-154, 90; (IIc), 14, 140-150, 72; (IIId), 8, 160-170, 70.

Compounds (IIa-c) were identical with those reported [3, 4].

2-Methyl-4-propoxy-1-buten-3-ol (IIId). bp 74-76°C (9 mm);  $n_D^{20}$  1.4360;  $d_4^{20}$  0.9187. PMR spectrum (CCl<sub>4</sub>): 0.75-1.09 (3H, m, CH<sub>3</sub>); 1.42-1.55 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 1.63 (3H, d.d, J = 1 Hz, CH<sub>3</sub>C=); 3.28 (2H, t, J = 1 Hz, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 3.23 (1H, s, OH); 3.55 (2H, d, J = 2.8 Hz, CH<sub>2</sub>O); 4.05-4.22 (1H, m, CHOH); 4.82 and 4.98 m.d (2H, m, =CH<sub>2</sub>).

The elemental analysis of (IIId) agreed with the calculated values.

## LITERATURE CITED

1. M. S. Malinovskii, *Olefine Oxides and Their Derivatives* [in Russian], Goskhimizdat, Moscow (1961).
2. J. K. Crandall and Luan-Ho-Clang, *J. Org. Chem.*, **32**, 435 (1987).
3. A. A. Gevorkyan, P. I. Kazaryan, and S. V. Avakyan, *Khim. Geterotsikl. Soedin.*, No. 1, 125 (1983).
4. A. A. Gevorkyan, P. I. Kazaryan, and S. V. Avakyan, *Khim. Geterotsikl. Soedin.*, No. 4, 450 (1985).

Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan 375094.  
Translated from *Khimiya Geterotsiklicheskich Soedinenii*, No. 2, p. 269, February, 1989.  
Original article submitted May 7, 1987; Revision submitted May 15, 1988.