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In studying the action of hydrogen peroxide in methanolic KOH solution on 3-acetyl-3-carene we found that, together with  $3\beta$ -acetyl- $\alpha$ -3,4-epoxycarane (I), the reaction products contain its isomeric unsaturated ketol [1]. These data indicated the ability of epoxide (I) to rearrange under the influence of base to the  $\alpha$ , $\beta$ unsaturated alcohol. In the present paper were studied the transformations of epoxide (I) in the reactions with LiN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, HBr, and ZnBr<sub>2</sub>. The reaction of epoxide (I) with LiN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> gives the above-mentioned ketol as the sole isomerization product. The isomerization of the tetra-substituted oxides to the  $\alpha$ , $\beta$ -unsaturated alcohols under the influence of base proceeds by the  $\beta$ -elimination mechanism E<sub>2</sub> [2-4]. In such a case, structures (II), (III), and (IV) are possible for the  $\alpha$ , $\beta$ -unsaturated alcohol from epoxide (I), in harmony with the involvement of the bonds at C<sub>4</sub>-C<sub>7</sub>, C<sub>4</sub>-C<sub>5</sub>, and C<sub>2</sub>-C<sub>3</sub> in the  $\beta$ -elimination reaction



The IR and NMR spectra of the ketol are in agreement with the structure of  $3\beta$ -acetyl-4-caren-3-ol (III). In the IR spectrum ( $\nu_{\rm C} = 0.1705$ ,  $\nu_{\rm C} = c.1660$ ,  $\nu_{\rm CH} 3005$ , 3015,  $\nu_{\rm OH} 3400$ ,  $\delta_{\rm OH} 1090$ ,  $\delta_{\rm CH} 830$  cm<sup>-1</sup>) the ketol fails to show the bands of a semicyclic double bond, which is present in (II), and bands that are characteristic for structure (IV), i.e., the bands of the conjugated system C = C - C = O. The structure of (III) for the ketol is corroborated by the data of the NMR spectrum, and specifically the presence in the spectrum of the signals of the protons of a CH<sub>3</sub> group attached to a double bond ( $\delta$  1.57 ppm, 3 H).

The isomerization of epoxide (I) to the  $\alpha$ , $\beta$ -unsaturated alcohol (III) is also observed to a slight degree in the reaction with HBr in acetic acid solution. The mechanism of this transformation can be depicted by the scheme



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Consequently, the progress of the rearrangement (I)  $\rightarrow$  (III) under the influence of an electrophilic agent [5-7] could be expected. Ketol (III) was detected in the products of the isomerization of epoxide (I) with ZnBr<sub>2</sub>, but also in small amounts. The main reaction product proved to be 2-acetyl-p-cymene [8]. Not excluded is the fact that it is obtained as the result of the dehydration of the initially formed ketol (III) by ZnBr<sub>2</sub>.

## EXPERIMENTAL METHOD

<u>Reaction of LiN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> with  $3\beta$ -Acetyl- $\alpha$ -3,4-epoxycarane (I). To a solution of LiN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, prepared from 8.6 g of Li, 68.5 g of C<sub>4</sub>H<sub>9</sub>Br, 23.9 g of (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH and 450 ml of absolute ether [9], was added 21.1 g of epoxide (I) at -13° in 2 h. After standing at room temperature for 24 h the reaction mixture was refluxed for 5 h, and the next day it was poured into water, extracted with ether, and the ether extract was washed in succession with saturated NH<sub>4</sub>Cl solution and water, and then dried over Na<sub>2</sub>SO<sub>4</sub>. Most of the product crystallized after removal of the ether. The product was filtered to give 14 g (66.3%) of the ketol with mp 88-90° (from n-hexane);  $[\alpha]_D$  +177.4° (C 3.1; CCl<sub>4</sub>); semicarbazone, mp 179-180.5 [1].</u>

<u>Reaction of HBr with  $3\beta$ -Acetyl- $\alpha$ -3,4-epoxycarane (I) in Acetic Acid.</u> To a solution of 3.2 g of epoxide (I) in 15 ml of glacial acetic acid, with cooling by tap water, was added a solution of 1.3 g of HBr in 80 ml of glacial acetic acid. After 25 min the reaction mixture was poured on ice. The obtained solid product (bromohydrin) was filtered and washed with hexane; weight 2.8 g (yield 61.6%). After recrystallization from n-hexane, mp 119-120°,  $\alpha_D 0$  [1]. The aqueous layer from the removal of the bromohydrin was extracted with ether; the ether extract was neutralized with saturated NaHCO<sub>3</sub> solution and then dried over Na<sub>2</sub>SO<sub>4</sub>. The residue from the removal of the ether (thick mass) on distillation gave 0.6 g of a product with bp 99-112° (6 mm),  $n_D^{20}$  1.4979, which partially crystallized. Recrystallization from n-hexane gave 0.2 g (6.3% yield) of a product with mp 88-88.5°, which failed to depress the mixed melting point with  $3\beta$ -acetyl-4caren-3-ol.

<u>Reaction of ZnBr<sub>2</sub> with 3β-Acetyl- $\alpha$ -3,4-epoxycarane (I).</u> The reaction was run by the production given in [10]: a solution of 13 g of epoxide (I) in 75 ml of absolute benzene was refluxed for 1 h in a system protected by a moisture trap, after which 0.2 g of freshly prepared fused ZnBr<sub>2</sub> was added to the solution. The reaction mixture was refluxed for 5 h. The next day the reaction mixture was washed with water and then dried over Na<sub>2</sub>SO<sub>4</sub>. The products (11 g) were distilled from an Arbuzov flask: bp 98° (8 mm). 104° (6 mm). Based on the GLC data, the products contain 26.6% of the starting oxide, 1.8% of the isomeric oxide of the ketol (mp 89-90°), and 51.9% of 2-acetyl-p-cymene. The isomerization products (9 g) were chromatographed on SiO<sub>2</sub> (270 g). The 2-acetyl-p-cymene was eluted with petroleum ether (bp 70-100), (I) was eluted with a 3:2 petroleum ether -benzene mixture, and (III) was eluted with benzene. The fractions containing 2-acetyl-p-cymene (2.1 g), when treated with semicarbazide hydrochloride (1.75 g), gave 1.3 g of the semicarbazone with mp 145-146° [8]. Hydrolysis of the latter by heating with saturated oxalic acid solution, with the simultaneous removal of the ketone by distillation, gave 0.45 g of 2-acetyl-pcymene with bp 94.5-95° (7 mm);  $n_{D}^{20}$  1.5184;  $d_{4}^{20}$  0.9621. The 2,4-dinitrophenylhydrazone was obtained as yellow needles with mp 154-155°,  $\lambda$  (methanol) 360 nm ( $\epsilon$  22,460),  $\lambda$  (isooctane) 350 p. ( $\epsilon$  27,000). Found: C 61.04; H 5.63%. C<sub>18</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub>. Calculated: C 60.66; H 5.65%.

## CONCLUSIONS

 $3\beta$ -Acetyl- $\alpha$ -3,4-epoxycarane under the influence of bases is easily rearranged to the  $\alpha$ , $\beta$ -unsaturated ketol, namely  $3\beta$ -acetyl-4-caren-3-ol, by the E<sub>2</sub> mechanism of the  $\beta$ -elimination reaction.

## LITERATURE CITED

- 1. B. A. Arbuzov, Z. G. Isaeva, and N. D. Ibragimova, Dokl. Akad. Nauk SSSR, 195, 91 (1970).
- 2. Z. G. Isaeva, Dissertation [in Russian], Kazan (1967).
- 3. J. K. Crandall and Luan-Ho Chang, J. Org. Chem., 32, 435 (1967).
- 4. J. K. Crandall and Luan-Ho Chang, J. Org. Chem., 33, 2375 (1968).
- 5. W. Kirchof, Ber., 93, 2712 (1960).
- 6. L. I. Zakharkin and I. M. Khorlina, Izv. Akad. Nauk SSSR, Ser. Khim., 862 (1965).
- 7. L. H. Briggs, R. C. Cambie, and P. S. Rutledge, J. Chem. Soc., 5374 (1963).
- 8. Beilstein, Vol. VII, Berlin (1928), p. 262.
- 9. H. Gilman and R. G. Jones, in: Organic Reactions, Vol. 6, New York (1951), p. 339.
- 10. J. B. Lewis and G. W. Hedrick, J. Org. Chem., 30, 4271 (1965).