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Stereochemistry of Dehydration of Oxolanes to Dienes on γ -Alumina

Mihály Bartók and Árpád Molnár

Department of Organic Chemistry, József Attila University, Szeged, Hungary

On γ -alumina gaseous (±)-2,2,3,4,5,5-hexamethyloxolane (1) is converted mainly into 2,3,4,5-tetramethylhexa-1,5diene, while its *meso*-isomer (2) reacts at a higher rate than (1) to give 2,3,4,5-tetramethylhexa-2,4-diene with high selectivity; this is the first reported experimental observation of the stereochemistry of this dehydration reaction.

The dehydration of oxolanes to dienes, in the liquid phase on acids, and in the vapour phase on oxides, phosphate catalysts, zeolites, and other heterogeneous catalysts, is an interesting reaction.¹⁻⁴ However, experimental data on the stereochemistry and mechanism of the reaction are lacking. Our observations on the dehydration of (\pm) -(1) and *meso*-(2) 2,2,3,4,5,5-hexamethyloxolane on γ -alumina provide a basis for understanding the stereochemistry of the process. Grignard reaction with MeMgI of a mixture of (\pm) and *meso*-3,4-dimethylhexane-2,5-dione gave 2,3,4,5-tetramethylhexane-2,5-diol, which was then dehydrated in the presence of PdCl₂ + CuCl₂.⁵ Resolution of the product (Fischer concentric tube column with a theoretical plate number of 90) yielded (1) and (2) (b.p. 64 °C and 69 °C at 34 mmHg, respectively, isomer purity 98%).

The data in Table 1 reveal that the racemic compound (1) is



Table 1. Product compositions in transformations of (1) and (2).^a

Т /°С	% Conversion	Selectivity, mole %			
		(3)	(4)	(5)	Other products ^b
Compou	nd (1):	. ,	~ /	~ /	•
250	2	25	50	0	25
275	2	25	50	0	25
300	18	8	50	0	42
325	33	9	46	0	45
350	78	5	55	13	27
375	93	7	43	10	40
Compou	nd (2):				
250	21	85	0	15	0
275	42	76	0	12	12
300	64	80	0	12	8
325	77	77	0	14	9
350	89	70	0	15	15
375	97	59	0	13	28

^a Method: pulse microreactor technique, 1µl pulses. G.I.c.: Carlo Erba Model G: 1.2 m 15% Apiezon M on Kieselguhr column: 130 °C; 40 ml H₂ min⁻¹. Catalyst: 50 mg of γ -alumina (Strem 13—255); particle size: 0.25—0.4 mm; surface area: 100 m²g⁻¹; acidic centres: 0.20 mequiv. g⁻¹; basic centres: 0.46 mequiv. g⁻¹. Catalyst pretreatment: 40 ml air min⁻¹ for 60 min at 300 °C, then 40 ml H₂ min⁻¹ for 30 min. Product identification via n.m.r. and mass spectroscopy. ^b Unidentified, primarily fragmentation, products. On the basis of n.m.r. spectra and conclusion (iv) below, the presence of (*E*, *E*)-3,6-dimethylocta-2,6-diene, formed from (4) via Cope rearrangement, can be excluded.

dehydrated primarily to give 2,3,4,5-tetramethylhexa-1,5diene (4), and the *meso*-compound (2) with high selectivity to give 2,3,4,5-tetramethylhexa-2,4-diene (3) (Scheme 1).

On the basis of the experimental results the following main conclusions can be drawn. (i) The rate of formation of the conjugated diene (3) is considerably higher than that of the isolated diene (4) [in other words, the rate of dehydration of (2) is much higher than that of (1)]. (ii) The selectivity of the dehydration is higher for (2) than for (1). (iii) Formation of the conjugated diene (3) is promoted by *cis* C(3) and C(4) hydrogen atoms, the stereochemical condition for this transformation to take place. (iv) Under the experimental conditions employed, the mutual isomerization of the dienes (3), (4), and (5) is not observed.

Detailed investigations are needed to establish and interpret the mechanism of this unusual transformation.

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