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PARTICIPATION OF THE 5-ALKOXY GROUP IN ALLYLIC CATION STABILIZATION: CONVERSION INTO *Z*-ISOMERS

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Key Words: allylic cations; alkoxy group participation; conversion into *Z*-isomers; alkoxyalkylation of 1,3-dienes.

Abstract: Stabilization of an allylic cation with *Z*-configuration by the 5-alkoxy group increases the *Z*-isomer content under the conditions of thermodynamic control.

The Lewis acid catalyzed addition of secondary and tertiary alkyl chlorides, such as Ar_2CHCl, $ArC(CH_3)_2Cl$[1], $PhC{\equiv}CCH(Ph)Cl$, $PhC{\equiv}CC(CH_3)_2Cl$[2], and $CH_3CH{=}CHCH(CH_3)Cl$[3] to 2-methyl-1,3-butadiene (**1a**) or 2,3-dimethyl-1,3-butadiene (**1b**) leads to the regioselective and stereospecific formation of (*E*)1,4-adduct with some oligomeric products. Diene **1a** with primary chlorides, such as $(CH_3)_2C{=}CHCH_2Cl$ (**2**)[4] or $(CH_3)_2C{=}C(CH_3)CH_2Cl$[5] affords, along with the major (*E*)1,4-adduct (up to 60%), some isomeric adducts, while no more than 3% of (*Z*)1,4-adduct was observed only in the reaction of **1a** with **2**[4]. But the high content of (*Z*)1,4-adducts (20-40%) was obtained upon the addition of isopropoxymethyl chloride[6] or methoxymethyl chloride (**3**)[7] to **1a**.

We investigated the product distribution at reactant conversion from low to high degrees in the reaction of **3** with **1a** or **1b** in the presence of $SnCl_4$ catalyst[8]. In both of these reactions mixtures of (*E*) and (*Z*)1,4-

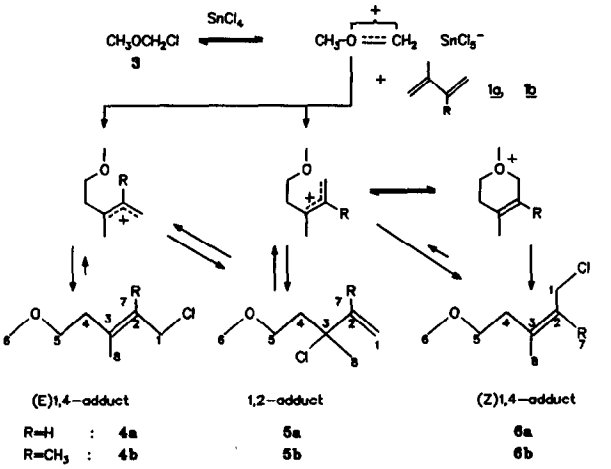
Table. Product Distribution in the Reaction of **1a** or **1b** with **3**. Catalyst $SnCl_4$, at 23°C, the initial molar ratio of RCl:diene was 1:1[8-10].

Diene	Conversion, %	Yield of adducts in product, %	Distribution of adducts, %		
			4a or **4b**	**5a** or **5b**	**6a** or **6b**
1a	7		65	25	10
	18	86	63	25	12
	40	82	65	18	17
	65	82	66	8	26
1b	8		44	26	30
	20	84	45	24	31
	46	84	46	18	36
	72	80	44	13	

adducts (**4** and **6**) and 1,2-adduct (**5**) were obtained[9], while the ratio of isomers[10] changed in the course of the reaction as shown in Table. Interpolation of the data to zero-conversion shows that the kinetic control gives approximately the following ratios of allylic isomers: **4a**:**5a**:**6a**=65:25:10 and **4b**:**5b**:**6b**=45:25:30.

Our data are in accord with the earlier results[4, 11] which demonstrate that tertiary allylic chlorides ionize

with Lewis acids more easily. Therefore, **5a** and **5b** are more prone to subsequent interactions than their primary isomers. However, conversion of **5a** and **5b** into *Z*-isomers **6a** and **6b** in the course of the reaction was unexpected, since, in general, allylic chlorides with *E*-configuration prevail as being thermodynamically more favored than *Z*-isomers. This may be accounted for the participation of the alkoxy group in the reaction as shown in the Scheme. Stabilization of the cationic intermediate with *Z*-configuration by the 5-alkoxy group is the driving force which increases the *Z*-isomer content. It has not been demonstrated previously that under conditions of thermodynamic control the conversion of allylic chlorides into *Z*-isomers may be achieved due to the participation of the 5-alkoxy group.



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8. The procedure was performed as described earlier[6] using no solvent.
9. The structures of **4a**, **5a**, and **6a** were identified earlier[7]. The structures of **4b**, **5b**, and **6b** were confirmed on the basis of their assigned ^{13}C an ^{1}H (in parentheses) chemical shifts δ_{TMS} from C-1 to C-8. Shifts for **4b**: 46.58 (3.92), 126.68, 132.56, 34.89 (2.19), 70.41 (3.23), 58.20 (3.13), 16.46 (1.62), 17.84 (1.63); **5b**: 112.24 (4.90 and 4.73), 147.09, 72.95, 41.88 (2.05), 69.16 (3.25), 58.20 (3.11), 19.08 (1.73), 29.32 (1.56); **6b**: 46.38 (3.95), 126.82, 132.48, 34.38 (2.24), 70.88 (3.24), 58.25 (3.14), 16.82 (1.60), 18.79 (1.57).
10. The isomeric composition of adducts was established by GC. The relative retention times on a glass capillary column (37mx0.3mm) with the TCEP liquid phase at 70°C were as follows: **4a** 1.79, **5a** 0.47, **6a** 1.37, **4b** 2.04, **5b** 0.81, **6b** 1.86, and the reference *o*-dichloro benzene 1.00.
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