THERMAL-CATALYTIC ISOMERIZATION OF SUBSTITUTED VINYLCYLOPROPANES

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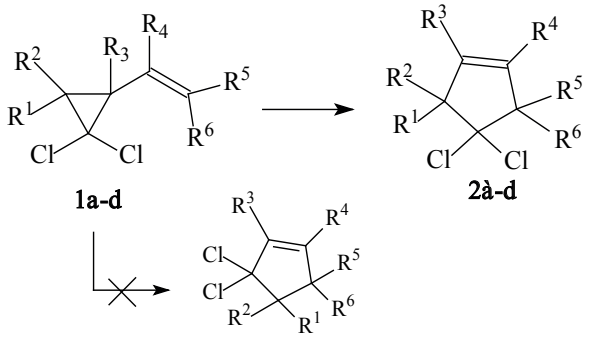
It is known that dichlorocarbenesses of industrial dienes form vinyl-gem-dichlorocyclopropanes, which are widely used in the synthesis of reagents, oligo- and polymers [1].

We have carried out thermocatalytic isomerization of mono-dichlorocarbene olefins 1a-d to the corresponding gem-dichlorocyclopentenes 2a-d.



R^1, R^2, R^3, R^4, R^5, R^6 = H (**1à, 2à**), R^1, R^2, R^3, R^5, R^6 = H, R_3 = CH_3 (**1á, 2á**),
R^1, R^2, R^4, R^5 = H, R^3, R^4 = CH_3 (**1â, 2â**), R^3, R^4 = H, R^1, R^2, R^5, R^6 = CH_3 (**1ã, 2ã**),
R^1, R^2, R^4, R^5, R^6 = H, R^3 = Ph (**1ã, 2ã**)

From literature [2] it follows that during thermal isomerization (450-550°C) vinyl-gem-dichlorocyclopropane undergo partial or complete dehydrochlorination. In our case (zeolites: SAPO-34, HY, ceocar-600; 280°C) 5-dichloro-isomeric isomeric cyclopentenes 2a-5 were not detected in the reaction products, which is explained by lower bond strength $R_3C\text{-}CCl_2$ (42-43 kcal / mol) than $R_3C\text{-}CR_1R_2$ (49-50 kcal / mol) in cyclopropane fragment [3].

References
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