

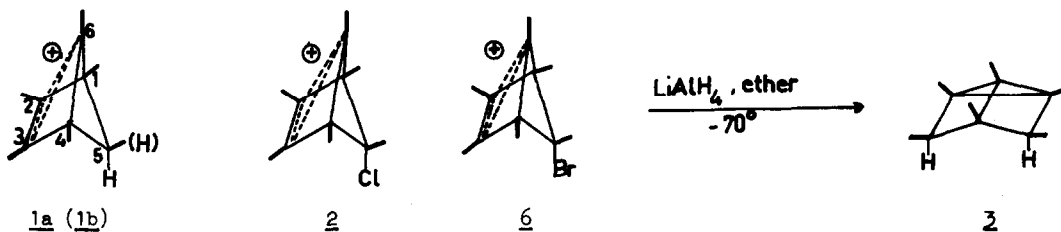
KINETICALLY CONTROLLED REACTIONS OF 5-SUBSTITUTED 1,2,3,4,5,6-HEXAMETHYLBICYCLO [2.1.1] HEXENYL CATIONS WITH NUCLEOPHILES.

H. Hogeveen and P.W. Kwant

Department of Organic Chemistry, The University,
Zernikelaan, Groningen, The Netherlands.

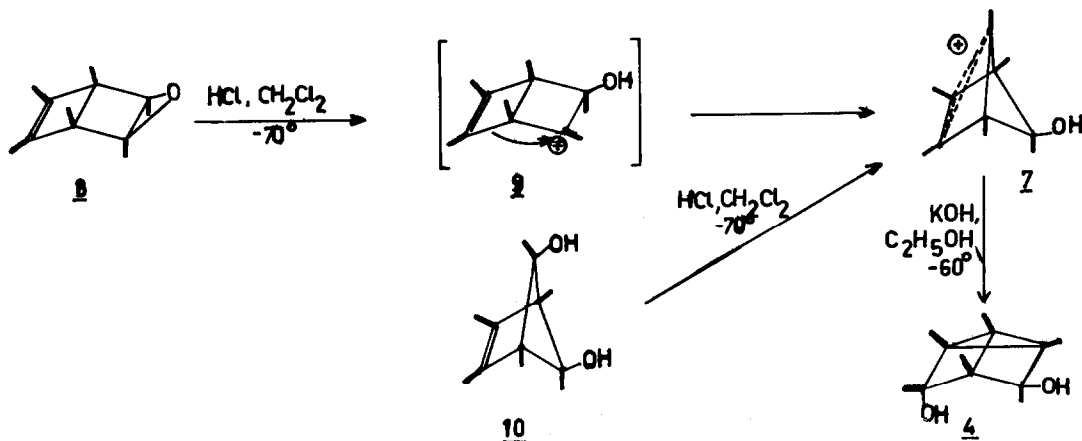
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The non-classical 1,2,3,4,5,6-hexamethylbicyclo [2.1.1] hexenyl cations (1a), (1b) were shown to react with nucleophiles at carbon atoms 2 and 3 as well as at carbon atom 6. The former reactions lead to tricyclic products and the latter to bicyclic products^{1,2}. Very recently it was reported³ that the reaction of 2 (AuCl_4^- as anion) with LiAlH_4 yields exo-CH}_3-1,2,3,4,5,6-hexamethyltricyclo[2.2.0.0^{2,6}] hexane (3). We wish to report here the formation of the tricyclic compounds 3 and 4 from 5-substituted 1,2,3,4,5,6-hexamethylbicyclo [2.1.1] hexenyl cations, by a method closely related to that used for the parent tricyclo [2.2.0.0^{2,6}] hexane observed recently.⁴



Compound 3 was obtained in a one-pot reaction by treating a solution of hexamethylDewarbenzene, 5 (1.62 g, 10 mmole) in methylene chloride with bromine (1.75 g, 11 mmole) at -70° ^{2,5} and subsequently with a suspension of LiAlH_4 (1.0 g, 26 mmole) in ether at -70° during 2 hrs. The FMR spectrum of the oil obtained after workup showed the presence of 3 (85 %) and 5 (10 %); preparative glc yielded 1.2 g (7.5 mmole, 75 %) of 3.

The exo-5-hydroxy ion 7 was proposed as an intermediate in some reactions.⁶ It was possible to generate this ion in a methylene chloride - liquid HCl mixture (2:1 v/v) of -70° from the epoxide 8⁷ and from the diol 10^{6,7}. The FMR spectrum of ion 7 under these conditions showed methyl singlets at $\delta=2.15$ (2 CH_3), 1.62 (3 CH_3) and 1.39 (1 CH_3). On pouring a solution of ion 7 in excess $\text{KOH}/\text{C}_2\text{H}_5\text{OH}$ at -60° a reaction mixture was obtained which consisted of 80 % of the unsymmetrical diol 4². This product permits the conclusion that the hydroxy group in ion 7 is in the exo position, which is consistent with the FMR chemical shift of the methyl group at carbon atom 5.²



The observed reactions with nucleophiles, occurring at carbon atoms 2 and 3 rather than at carbon atom 7, are best explained as kinetically controlled reactions at the site of the lowest electron density. Preliminary results suggest that this conclusion on charge distribution in the carbonium ions 1,2,6, and 7 is substantiated from FMR and CMR spectral data.⁸

References:

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