Der Einfluss der Substitution auf die Dynamik des Homotropilidensystems
eine synthetische und 1-H-NMR spektroskopische Untersuchung

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Der Einfluss der Substitution auf die Dynamik des Homotropilidensystems

Eine synthetische und $^1$H-NMR spektroskopische Untersuchung

ABHANDLUNG

zur Erlangung

des Titels eines Doktors der Naturwissenschaften
der
EIDGENÖSSISCHEN TECHNISCHEN HOCHSCHULE
ZÜRICH

vorgelegt von

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9. SUMMARY

The syntheses of 1,3,5,7-tetramethyl-anti-tricyclo[5.1.0.0^3,5]octane-2,6-cis- and trans-diols as well as those of their 4,8-di- and 4,4,8,8-tetrachloro-derivatives are reported. These diols were used as educts in P2I4-reactions in order to synthesize the corresponding substituted bicyclo[5.1.0]octa-2,5-dienes (homotropilidenes). A range of interesting products (two bishomobenzene-derivatives, two styrene-derivatives, one oxabicyclo[4.2.1]nona-2,4,7-triene-derivative, one COT-derivative but only one homotropilidene-derivative) were isolated in yields of 1 to 10%. Their formation can be explained on the assumption of primary conversion of the hydroxyl-functions into leaving groups which can depart either as cations or as anions.

Different pathways were used for the attempted synthesis of a conformationally fixed transoid homotropilidene. These involved the synthesis of octahydroanthraquinone as well as s-hydrindaquinone, which were both subjected to various carbene type reactions in order to generate the tricyclo[5.1.0.0^3,5]octane-2,6-dione system. Only in the case of s-hydrindaquinone could the desired precursors, anti-pentacyclo[7.3.1.1^3,7.0^3,7.0^1,9]tetradecane-2,8-cis- and trans-diols, be synthesized. Their P2I4-reaction was studied and the presence of several C14H18 isomers in the reaction mixture could be shown by GC/MS; one of these may have been the desired bridged transoid homotropilidene.

^1H-NMR line shape analyses were carried out with six differently substituted (CH3, COOCH3, CN) homotropilidenes. The kinetic parameters for five isodynamic cases and one nonisodynamic case were obtained. An isokinetic relationship was found to be valid for the ΔH^‡obs and ΔS^‡obs of the rearrangement of the above and some other homotropilidenes. The influence of substitution on the energy profile of homotropilidene is discussed in terms of ΔH^‡obs and ΔS^‡obs.
A correlation between the value of $\Delta S^\pm_{\text{obs}}$ and the geometry of the transition state during ring inversion could be established.