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LETTERS TO THE EDITOR

Anomalous Steric Effect of a Remote Substituent in a High-Pressure Reaction

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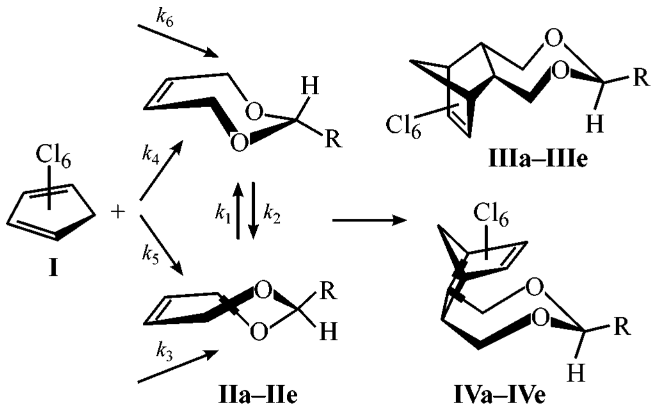
Data on the reactivity of a series of conformationally nonuniform substrates significantly differing in the position of the equilibrium can furnish very useful information on the role of conformers in a chemical process [1]. Previous NMR and X-ray diffraction studies showed that reaction of hexachlorocyclopentadiene **I** with 2-R-1,3-dioxacyclohept-5-enes **II** under elevated external pressure yields a mixture of isomeric 1,9,10,11,12,12-hexachloro-5-R-4,6-dioxatricyclo-$[7.2.1.0^{2,8}]$dodec-10-enes in a practically quantitative yield [2].

We have studied the diastereoselectivity of this reaction under conditions of kinetic control (5300 atm, 80°C, 3 h, solvent toluene).



R = Me (**a**), Et (**b**), Pr (**c**), *i*-Pr (**d**), *t*-Bu (**e**).

The ratio of the adducts **IV**/**III** in the reaction mixtures, determined by ^{1}H NMR spectroscopy, was as follows: 65/35 (**a**), 70/30 (**b**), 73/27 (**c**), 82/18 (**d**), and 94/6 (**e**). Contrary to our expectations, attack from the side of the substituent at the acetal carbon atom prevails in all cases. Moreover, the reaction stereoselectivity increases with increasing volume of the substituent. Correlation analysis using the single-parameter Taft equation revealed a high-quality correlation between the logarithm of the diastereomer ratio and the steric constant E_S^0 of the substituent at C^2:

$$\ln(endo/exo) = (0.57 \pm 0.06) - (1.02 \pm 0.02)E_S^0;$$
$$r\ 0.995,\ S\ 0.09,\ n\ 5.$$

Formally, there are two alternatives for realization of this ratio. The first alternative is related to conformationally rigid compounds and the second, to a series of conformationally nonuniform compounds, with certain ratios of the partial rate constants of the reagent attack from the diastereotopic sides of the double bond differing in the steric features.

As for the first alternative, it should be noted that in the chosen reaction series the position of the conformational equilibrium varies in a wide range along the series. It is significant that the free energy of the conformational equilibrium *chair* ⇄ *twist* is not a linear function of the size of the substiutuent R at the acetal carbon atom. For example, the first four members of the series, **IIa**–**IId**, are isoconformational (the relative content of the *chair* form is 0.15), whereas in **IIe** the *chair* form prevails (0.75) [3, 4]. The effect of pressure on the position of the conformational equilibrium is insignificant, since the difference between the molar volumes of the conformers does not exceed 5 cm^3 mol^{-1} [5, 6]. For example, under applied pressure of 5300 atm, the relative content of the *chair* form can increase, at most, to 0.3 for **IIa** and to 0.9 for **IIe**.

Thus, it is evident that the preferential attack of the diene at the dienophile from the side of the substituent, observed in all cases, cannot be interpreted in terms of secondary orbital interactions involving the lowest unoccupied molecular orbital of the diene and the occupied molecular orbital of the lone electron pairs of the oxygen atoms.

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Thus, the series in question should be interpreted on the basis of the second alternative. As follows from the formal kinetic equations for cross reactions [7], the diastereomer ratio can be independent of the constant of the conformational equilibrium if $k_5/k_3 = k_4/k_6$, provided that all the four reaction series corresponding to the reagent attack at two diastereotopic sides of two conformers with variable substituents follow the linear free energy relationship. It should be particularly emphasized that the conclusion about equal ratios of the partial rate constants for reagent attack at the diastereotopic sides of the alternative structures significantly differs from the stereochemical result of the related reaction of the same seven-membered acetals with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate [8] in which addition from the *exo* side of the double bond prevails.

In total with data of [1, 9–12], the results of this work additionally demonstrate the rich chemical behavior of conformers.

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