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Abstract

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On the Influence of Temperature on the Structural Direction of Diene Synthesis

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From the general regularities of diene synthesis it is known that, in the condensation of unsymmetrical dienes and dienophiles, the formation of a mixture of structural isomers is possible (1, 2). The structural direction of this reaction has been studied in greatest detail using examples of condensations of 2-substituted dienes (I) with dienophiles of the acrylic type; it was established that the principal product in this case is the para isomer (II), whereas the amount of the meta adduct (III) formed is comparatively small (2-10).

$$\text{(III)} \quad \longleftarrow \quad \text{(I)} \quad \longrightarrow \quad \text{(II)}$$

Since such a regularity is undoubtedly connected with the mechanism of this reaction and with the nature of the transition state, attempts were made to determine the influence of temperature on the structural direction of diene synthesis.

Already in the study of the dimerization of isoprene it was noted that, with increasing temperature, the relative content of the para adduct (dipentene) increases and the amount of the meta adduct decreases markedly (11). Subsequently, in a systematic study of the influence of temperature on the structural direction of diene synthesis (4, 6), it was established that, in the condensation of isoprene, 2-isopropyl-, 2-*tert*-butyl-, and 2-phenylbutadienes with acrylic dienophiles, an increase in the reaction temperature leads to a noticeable increase in the amount of adducts of meta structure (III; R = *iso*-C_3H_7, *tert*-C_4H_9, C_6H_5). On the basis of these results, the conclusion was drawn that the activation energy for formation of the para isomer is approximately 1 kcal/mol lower than the activation energy for formation of the meta isomer (2).

However, the experimental data on which this conclusion was based were insufficiently accurate, since the relative amounts of the isomers formed were estimated only indirectly, after a series of chemical transformations. These circumstances prompted us to study anew the influence of temperature on the structural direction of diene synthesis. In order to clarify the role of steric and polar factors in these reactions, we investigated the condensation of isoprene with methyl acrylate, methyl methacrylate, and acrylic acid.

By the time our work was nearing completion, a report appeared stating that the condensation of isoprene with methyl acrylate depends very little on temperature (^{12}).

Methodologically, our work was carried out as follows. Equimolecular amounts of the reacting components, in the form of a 50% solution in benzene, were kept in sealed glass ampoules at different temperatures in an ultrathermostat preheated to the required temperature. The heating time in each case was sufficient to attain the maximum yield; moreover, by special experiments···

it was shown that it does not affect the composition of the resulting mixture of isomers. The mixture of adducts remaining after distillation of the solvent and volatile components was analyzed by gas–liquid chromatography on an apparatus described earlier (^{13}), on a column 5 m long and with an internal diameter of 5 mm, packed with refractory brick with a particle size of 0.15–0.25 mm, containing six percent by weight of a 10% solution of $AgNO_3$ in diglycerin. The column temperature was 112°, and the carrier-gas (He) flow rate was 60 ml/min. The efficiency of the column was about 2300 theoretical plates. Under these conditions the separation of the peaks of the isomeric adducts was quite sufficient for calculating the composition of the mixture by the Bartlett–Smith method (^{14}).

Analysis of the mixture of adducts formed in condensations with acrylic acid was carried out after converting them into a mixture of methyl esters by treatment with diazomethane. Chromatography of the reaction mixtures before and after distillation of the volatile components showed that during this operation the composition of the adduct mixture does not change. Preliminary chromatography of a known para-adduct and of the mixture remaining after its isolation showed the absence of processes of destruction or isomerization of the products being analyzed in the chromatographic column. Special experiments established that heating at 180 or 260° of the pure para-adduct and of the reaction mixture formed at 100° likewise does not lead to any appreciable change in composition. In each of the examples studied, no fewer than two experiments were carried out, for which 2–3 chromatograms were recorded. The discrepancies in parallel experiments and chromatograms did not exceed 0.2–0.3%.

The mean values, obtained by the method described above, of the isomeric composition of the adducts at various temperatures, as well as the values of the isomer ratios, are given in Table 1.

Table 1

Composition of the adducts of isoprene with dienophiles of the acrylic type

Dienophile	20° (1 mo): amount of para- and meta-adducts, %	20° (1 mo): para:meta ratio	100° (6 h): amount of para- and meta-adducts, %	100° (6 h): para:meta ratio	180° (2 h): amount of para- and meta-adducts, %	180° (2 h): para:meta ratio	260° (1 h): amount of para- and meta-adducts, %	260° (1 h): para:meta ratio
Methyl acrylate	70.429.6	2.38	68.831.2	2.24	67.232.8	2.05	66.933.1	2.02
Methyl methacrylate	68.131.9	2.14	66.533.5	1.98	65.934.1	1.92	65.035.0	1.85
Acrylic acid	75.224.8	3.03	72.227.8	2.60	69.530.5	2.27	67.432.6	2.07

As can be seen from the data in Table 1, the structural orientation of the diene condensation of isoprene with methyl acrylate and methyl methacrylate, contrary to earlier conclusions, depends only slightly on temperature. This makes it possible to assume that in such condensations the activation energies of the reactions forming the para- and meta-adducts are close to one another, and that the difference in the rates of their formation is apparently due to a difference in the pre-exponential factors, i.e., to the different entropy of these two parallel processes. Such a difference in the entropies of formation of the structural isomers, in turn, can be attributed to the greater steric difficulty of the transition state for the meta-adduct.

In contrast, the structural orientation of the diene condensation of isoprene with acrylic acid depends appreciably on temperature, although not to the extent noted earlier (^{4}). Apparently, in this case

the influence of the polar effect of the free carboxyl group in the cyclic transition complex responsible for the formation of the para isomer decreases with temperature, which leads to a relative increase in the yield of the meta adduct.

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