DIENE CONDENSATION OF 1,3-DIMETHYLBUTADIENE WITH UNSYMMETRIC DIENOPHILES

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In condensations of 1-substituted dienes with unsymmetric dienophiles, the orienting influence of the substituent in the diene molecule leads to the predominant formation of ortho adducts, while in condensations of 2-substituted dienes it leads to the predominant formation of the para adducts. The orienting influence of the methyl groups in 1,2-dimethylbutadiene is in opposite directions, thus aiding the formation of a mixture of structural isomers. In reality we succeeded in showing [1] the existence of such a mixture in condensations of 1,2-dimethylbutadiene with acrylic and methacrylic acid derivatives. For the 1,3-dimethylbutadiene, however, the orienting influence of both substituents is coincident, being directed toward the formation of the "unsymmetric" adducts (I). It appeared interesting to verify whether or not the diene condensations of 1,3-dimethylbutadiene lead to formation of homogeneous products and whether or not a mixture of structural isomers (I) and (II) is formed in this case as well.

\[
\begin{align*}
& \text{H}_3\text{C} \quad \text{CH}_2 \quad \text{X} \quad \text{CH}_2 \quad \text{X} \\
& \text{H}_3\text{C} \quad \text{H}_3\text{C} \\
& \text{H}_3\text{C} \quad \text{H}_3\text{C}
\end{align*}
\]

The diene condensations of 1,3-dimethylbutadiene with various unsymmetric dienophiles have been run many times, but in only two papers [2, 3] was the structural proof of the resulting products provided. It was possible to isolate only the corresponding "unsymmetric" adduct (III), whose structure was proved through the scheme shown below, in the condensation of 1,3-dimethylbutadiene with acrolein [2]:

\[
\begin{align*}
& \text{H}_3\text{C} \quad \text{CH}_2 \quad \text{CHO} \quad \text{CHO} \quad \text{CH}_3 \quad \text{CO}_2\text{H} \\
& \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C}
\end{align*}
\]

Only the "unsymmetric" adduct was isolated in the reaction of 1,3-dimethylbutadiene with crotonaldehyde [2].

Only the "unsymmetric" adduct (IV) was isolated in the condensation of 1,3-dimethylbutadiene with acrylic acid [4] and its structure was proven by dehydrogenation to 2,4-dimethylbenzoic acid:
Finally, it was possible to prove the existence of only the "unsymmetric" adducts [4] in the diene syntheses with acrylic acid and other 1,3-disubstituted dienes (1-methyl-3-phenyl- and 1-phenyl-3-methylbutadienes).

Thus, the "symmetric" adducts (II) have not been detected, until the present study, in the adduct mixture formed in the condensation of 1,3-disubstituted dienes with unsymmetric dienophiles.

We studied the condensations of 1,3-dimethylbutadiene with methyl acrylate and methacrylate, as well as with acrylonitrile.

A mixture of adduct (V) and (VI) with the great predominance of the "unsymmetric" isomer (V) was obtained in 60% yield after heating 1,3-dimethylbutadiene with methyl acrylate for two hours at 220°.

The adducts were dehydrogenated over palladium precipitated on carbon at 350°. Saponification of the dehydrogenation products gave a mixture of known 2,4- and 3,5-dimethylbenzoic acids in 26:1 proportion.

A condensation of 1,3-dimethylbutadiene with methyl methacrylate at 220° for one and a half hours led to the formation of a 76% yield of a mixture of adducts (VII) and (VIII) in which the "unsymmetric" isomer (VII) was again greatly predominant.