CHEMISTRY

1963

SovietRxiv

Abstract

Full Text

CHEMISTRY

A. I. KONOVALOV

STERIC HINDRANCE IN THE DIENE SYNTHESIS REACTION OF CYCLOPENTADIENE WITH DIENOPHILES OF THE ISOPROPENYL TYPE

(Presented by Academician B. A. Arbuzov, January 10, 1963)

In studying the stereoselectivity of the diene synthesis reaction, a series of papers by Berson and co-workers ($^{1-3}$) showed that the behavior of methyl acrylate in the reaction with cyclopentadiene differs from that of methyl methacrylate; namely, methyl acrylate obeys Alder' s rule (^{4}) and gives predominantly the endo adduct, whereas methyl methacrylate does not obey it and gives predominantly the exo adduct. Such behavior of these compounds seemed somewhat unexpected. The authors mentioned above believe that the reason lies in weak interactions, for which it is still difficult to give an exact estimate. It seems to us that the principal reason for the different behavior of methyl acrylate and methyl methacrylate in the reaction with cyclopentadiene lies in steric hindrance, which arises in the endo orientation of methyl methacrylate as a result of interaction between the methyl group at the double bond of methyl methacrylate and the hydrogen of the methylene group of cyclopentadiene. This conclusion is made on the basis of the data given below and, we believe, is valid for the reaction of cyclopentadiene with other dienophiles of the isopropenyl type.

According to the L.F.E. principle (^{5}), one should expect a linear relationship between $\lg k$ (k is the reaction rate constant) for the reactions of one diene with a series of dienophiles and $\lg k$ for the reactions of another diene with the same dienophiles, if steric hindrance is not observed in any case, since the remaining factors affecting the reactivity of the dienophile are the same with any diene, and the difference consists only in the sensitivity of the dienes to them. Therefore we compared the logarithms of the rate constants of the reactions of cyclopentadiene with a series of dienophiles of the vinyl and isopropenyl types ($\lg k_{\mathrm{CPD}}$) with the logarithms of the rate constants of the reactions of 2,3-dimethylbutadiene-1,3 with the same dienophiles ($\lg k_{\mathrm{DMBD}}$). In the present case, however, there is the special feature that $k_{\mathrm{CPD}} = k_{\mathrm{CPD}}^{\mathrm{endo}} + k_{\mathrm{CPD}}^{\mathrm{exo}}$, where $k_{\mathrm{CPD}}^{\mathrm{endo}}$ and $k_{\mathrm{CPD}}^{\mathrm{exo}}$ are the rate constants for formation of the endo and exo adducts, respectively. Taking this fact into account shows that in this case $\lg k_{\mathrm{CPD}}$ will also depend approximately linearly on $\lg k_{\mathrm{DMBD}}$, since the resulting dependence is expressed in general

Fig. 1. Relationship between $\lg k_{\mathrm{CPD}}$ and $\lg k_{\mathrm{DMBD}}$. Dienophiles: 1–$CH_2{=}CH{-}CHO$, 2–$CH_2{=}CH{-}COOH$, 3–$CH_2{=}CH{-}COOCH_3$, 4–$CH_2{=}CH{-}CN$, 5–$CH_2{=}CH{-}SO_2C_6H_5$, 6–$CH_2{=}C(CH_3)COOH$, 7–$CH_2{=}C(CH_3)COCH_3$, 8–$CH_2{=}C(CH_3)COOCH_3$.

Figure 1: Fig. 1. Relationship between $\lg k_{\mathrm{CPD}}$ and $\lg k_{\mathrm{DMBD}}$. Dienophiles: 1–$CH_2{=}CH{-}CHO$, 2–$CH_2{=}CH{-}COOH$, 3–$CH_2{=}CH{-}COOCH_3$, 4–$CH_2{=}CH{-}CN$, 5–$CH_2{=}CH{-}SO_2C_6H_5$, 6–$CH_2{=}C(CH_3)COOH$, 7–$CH_2{=}C(CH_3)COCH_3$, 8–$CH_2{=}C(CH_3)COOCH_3$.

form by a hyperbola, and a side branch of the hyperbola (which corresponds to the conditions considered) may be regarded, to a good approximation, as linear. The rate constants of the reactions of cyclopentadiene were determined in dioxane at $t = 30^\circ$, and those of dimethylbutadiene in dioxane at $t = 150^\circ$ by a spectrophotometric method (k in $\mathrm{hour}^{-1}\cdot \mathrm{mole}^{-1}\cdot$ liter). For the reactions of cyclopentadiene with dienophiles of the isopropenyl type, the values of the reaction rate constants have not been determined; however, for the purposes of the present work it is quite sufficient that they are smaller than the rate constant for dimerization of cyclopentadiene. In Fig. 1, points have been placed for them at the value corresponding to the rate constant for dimerization of cyclopentadiene, with arrows directed downward, which means that the true positions must be somewhere lower.

It is evident from the figure that for dienophiles of the vinyl type a linear dependence is observed between $\lg k_{\mathrm{CPD}}$ and $\lg k_{\mathrm{DMBD}}$, while the points corresponding

dienophiles of the isopropenyl type do not fit this relationship. They are located below the straight line, i.e., the rate constants for the reactions of the isopropenyl-series dienophiles with cyclopentadiene proved to be smaller than would follow from the rate-constant data for these dienophiles with dimethylbutadiene. Thus, dienophiles of the isopropenyl type in the reaction with cyclopentadiene prove to be less reactive, in comparison with vinyl dienophiles, than in the reaction with dimethylbutadiene. Consequently, in the reaction of isopropenyl dienophiles with cyclopentadiene, hindrances arise that are absent with dimethylbutadiene.

Since

$$k_{\mathrm{CPD}} = k_{\mathrm{CPD}}^{\mathrm{endo}} + k_{\mathrm{CPD}}^{\mathrm{exo}},$$

the "decrease" in k_{CPD} for dienophiles of the isopropenyl type (the decrease is meant relative to the value that would correspond to the reactivity of the dienophile with dimethylbutadiene) may be a consequence of a "decrease" either in $k_{\mathrm{CPD}}^{\mathrm{endo}}$, or in $k_{\mathrm{CPD}}^{\mathrm{exo}}$, or in both. It is convenient to carry out the further discussion using two dienophiles as examples–methyl acrylate and methyl methacrylate–drawing on the data of work (^{3}).

Fig. 1. Relationship between $\lg k_{\mathrm{CPD}}$ and $\lg k_{\mathrm{DMBD}}$. Dienophiles:
1–CH_2=CH–CHO, 2–CH_2=CH–COOH,
3–CH_2=CH–$COOCH_3$,
4–CH_2=CH–CN,
5–CH_2=CH–$SO_2C_6H_5$,
6–CH_2=C(CH_3)COOH,
7–CH_2=C(CH_3)$COCH_3$,
8–CH_2=C(CH_3)$COOCH_3$.

On going from methyl acrylate to methyl methacrylate the ratio

$$\frac{k_{\mathrm{CPD}}^{\mathrm{endo}}}{k_{\mathrm{CPD}}^{\mathrm{exo}}}$$

changes sharply; this can be estimated approximately for a solution in dioxane using the relationships found in (^{3}). Since for dioxane

$$\frac{(D-1)\rho}{(2D+1)M} \simeq 0.25,$$

where D is the dielectric constant, ρ the density, and M the molecular weight, then

$$\frac{k_{\mathrm{CPD}}^{\mathrm{endo}}}{k_{\mathrm{CPD}}^{\mathrm{exo}}} \simeq 3.5$$

for methyl acrylate and ~ 0.3 for methyl methacrylate.

The data of (^{3}) show that this is partly due to the fact that the activation energy of the endo adduct of methyl methacrylate becomes greater than the activation energy of the exo adduct. The decrease in the ratio

$$\frac{k_{\mathrm{CPD}}^{\mathrm{endo}}}{k_{\mathrm{CPD}}^{\mathrm{exo}}}$$

for methyl methacrylate, compared with methyl acrylate, may be either a consequence of the fact that, in the case of methyl methacrylate, formation of the exo adduct is facilitated, i.e., $k_{\mathrm{CPD}}^{\mathrm{exo}}$ increases, or a consequence of the fact that formation of the endo adduct is hindered, i.e., $k_{\mathrm{CPD}}^{\mathrm{endo}}$ decreases. But an increase in $k_{\mathrm{CPD}}^{\mathrm{exo}}$ should have led to an "increase" in k_{CPD}, and not to a "decrease," as is actually the case. Consequently, $k_{\mathrm{CPD}}^{\mathrm{endo}}$ decreases. Thus,

one may conclude that in the formation of the *endo*-adduct of methyl methacrylate with cyclopentadiene, difficulties arise which are absent, on the one hand, in the formation of the *endo*-adduct of cyclopentadiene with methyl acrylate and, on the other hand, in the reaction of methyl methacrylate with dimethylbutadiene. Comparison of these systems (Fig. 2) leads to the conclusion that the difficulties are probably caused by steric hindrance arising from interaction of the methyl group at the double bond of methyl methacrylate with the methylene group of cyclopentadiene. This leads to a decrease in the rate constant for formation of the *endo*-adduct, hence to a decrease in the ratio $k^{\text{endo}}_{\text{CPD}}/k^{\text{exo}}_{\text{CPD}}$, and to a lowering of the rate constant for the reaction of methyl methacrylate with cyclopentadiene as a whole. The same, evidently, applies to all dienophiles of the isopropenyl type.

In conclusion I express my deep gratitude to Academician B. A. Arbuzov for his attention to the work and for discussion of the results obtained.

Kazan State University
named after V. I. Ulyanov-Lenin

Received
8 I 1963

REFERENCES

1. J. A. Berson, A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961).
2. J. A. Berson, W. A. Mueller, *Tetrahedron Letters*, No. 4, 131 (1961).
3. J. A. Berson, Z. Hamlet, W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962).
4. K. Alder, G. Stein, *Angew. Chem.*, **50**, 514 (1937).
5. V. A. Palm, *Usp. Khim.*, **30**, 1069 (1961).

Note: Figure translations are in progress. See original paper for figures.