Chemistry

1965

SovietRxiv

Abstract

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Chemistry

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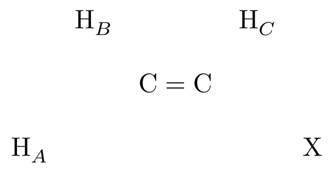
Chemical Shift and Dienophile Activity in the Diene Synthesis Reaction

(Presented by Academician B. A. Arbuzov, 30 X 1964)

In studying the diene synthesis reaction, it seemed of interest to us to compare the reactivity in a series of dienophiles of the vinyl and isopropenyl type with the magnitude of the chemical shift of the β-hydrogens of the dienophile double bond. In doing so, we proceeded from the assumption that the observed magnitude of the chemical shift is mainly a function of the electron density of the double bond. The reactivity of dienophiles is also determined by the electron density of the double bond. Therefore, between the reactivity of the dienophile and the magnitude of the chemical shift of the hydrogens at the dienophile double bond, some degree of correlation could be expected.

Correlation of chemical shifts with reactivity is known in the aromatic series from the example of the chemical shifts of fluorine nuclei ([1—5]), and also of hydrogen nuclei ([6—12]), as a function of Hammett substituent constants. There are also examples of comparison of reactivity with the magnitude of chemical shifts in a series of vinyl compounds ([13,14]). It should be noted that in works ([15,16]) a linear dependence was shown, in a series of vinyl compounds, between the chemical shift of β-hydrogen atoms (with correction for diamagnetic anisotropy) and the group dipole moment of the substituent. Recently, an approximate linear dependence has been shown between the chemical shift and reactivity in the diene synthesis reaction for a series of butadienes ([17]).

The influence of substituents on the chemical shifts of β-hydrogen atoms of vinyl compounds should be considered as the result of the action of the inductive effect and the effect of polar conjugation, as well as of the diamagnetic anisotropy of the substituting group ([13,14]). Of the two effects—inductive and polar conjugation—the latter has the greater influence on the values of chemical shifts. The influence of diamagnetic anisotropy leads to different values of the chemical shifts of the β-hydrogens (H_A and H_B)



$$\begin{array}{ccc} H_B & & H_C \\ & C=C & \\ H_A & & X \end{array}$$

Fig. 1. Change in $1/C$ with time in the diene synthesis reaction with cyclopentadiene

Figure 1: Fig. 1. Change in $1/C$ with time in the diene synthesis reaction with cyclopentadiene

Fig. 2. Change in $1/C$ with time in the diene synthesis reaction with 2,3-dimethylbutadiene-1,3

Figure 2: Fig. 2. Change in $1/C$ with time in the diene synthesis reaction with 2,3-dimethylbutadiene-1,3

The methyl group, introduced in place of the hydrogen H_C, influences the chemical shifts of the β-hydrogens mainly through its inductive effect. The influence of the diamagnetic anisotropy of methyl is small, which makes it possible, from the point of view of interest to us, to consider vinyl and isopropenyl compounds together.

The reactivity of dienophiles in the diene synthesis reaction, on the one hand, also depends on the action of the inductive effect and the effect of polar conjugation of the substituent, the latter exerting predominant influence, and, on the other hand, on the field effect exerted by the substituent on the conjugated system of double bonds of the diene.

Consideration of the factors affecting these two phenomena—chemical shifts in nuclear magnetic resonance and reactivity in the diene synthesis reaction—shows that some of them (the induction effect and the effect of polar conjugation) are the same in both cases, while others are different: diamagnetic anisotropy in NMR and the field effect in the diene synthesis reaction. Therefore, we initially assumed that the correlation would not be of a strict character and would require certain corrections. However, the fact of a satisfactory correlation of the reactivity of the dienophiles considered with the mean value of the chemical shifts of the β-hydrogen atoms of the dienophile ($\tau_{\text{av}} = (\tau_A + \tau_B)/2$; correlation with τ_A or τ_B alone is unsuccessful) gives grounds to suppose that the influence of the field effect in the diene synthesis reaction is to some extent taken into account by the influence of diamagnetic anisotropy.

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Fig. 2. Change in $1/C$ with time in the diene synthesis reaction with 2,3-dimethylbutadiene-1,3

Initially, we carried out preliminary experiments using, as a measure of the reactivity of dienophiles, the yields of products of the diene synthesis reaction ([18]). When reactions are carried out under identical conditions, with identical concentrations of the starting substances, the magnitude of the yield can serve

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

as a measure of reactivity, since within certain limits the yield is proportional to the logarithm of the reaction rate constant.

In the present work we continued the study of the dependence of the activity of dienophiles in the diene synthesis reaction on the mean value of the chemical shift of the β-hydrogen atoms of the dienophile, using as examples the reactions of 2,3-dimethylbutadiene-1,3 and cyclopentadiene with a series of dienophiles of the vinyl and isopropenyl types; the logarithm of the reaction rate constant was taken as the measure of reactivity.

The reaction rate constants were determined in dioxane with equimolar concentrations of the starting substances (0.1 mole/liter), at a temperature of 30° for cyclopentadiene and 150° for dimethylbutadiene, by the spectrophotometric method, using the absorption of cyclopentadiene with a maximum at 238.5 mμ and of 2,3-dimethylbutadiene-1,3 with a maximum at 226 mμ. The reactions were carried out in sealed ampoules in the presence of hydroquinone. The experimental data were treated by the graphical method (^{19}) in accordance with the kinetic equation of a second-order reaction

$$1/C - 1/C_0 = kt,$$

where k is the second-order reaction-rate constant, t is the time from the start of the reaction, C_0 is the initial concentration of the reactants, C is the concentration of the reactants at time t, and are presented in

Fig. 3. Dependence of $\lg k$ on τ_{av} of the dienophile in the reaction with cyclopentadiene

Fig. 4. Dependence of $\lg k$ on τ_{av} of the dienophile in the reaction with 2,3-dimethylbutadiene-1,3

Figs. 1 and 2 for cyclopentadiene and 2,3-dimethylbutadiene-1,3, respectively. The numbers of the straight lines correspond to the numbers of the dienophiles in Table 1. The constants obtained from these data are given in Table 1*. The accuracy in the experiments with cyclopentadiene is ±5%, and in the experiments with 2,3-dimethylbutadiene-1,3, ±5–10%.

Table 1

No.	Dienophile	Second-order reaction-rate constant ($h^{-1} \cdot mol^{-1} \cdot liter$) with cyclopentadiene	Second-order reaction-rate constant ($h^{-1} \cdot mol^{-1} \cdot liter$) with 2,3-dimethylbutadiene-1,3
1	$CH_2{=}CH{-}CHO$	0.367	4.5
2	$CH_2{=}CH{-}COOH$	0.174	2.8
3	$CH_2{=}CH{-}COOCH_3$	0.129	1.5
4	$CH_2{=}CH{-}CN$	0.099	1.3
5	$CH_2{=}CH{-}SO_2C_2H_5$	0.069	0.66
6	$CH_2{=}C(CH_3){-}COOH$	<0.011	0.70
7	$CH_2{=}C(CH_3){-}COOCH_3$	<0.011	0.62
8	$CH_2{=}C(CH_3){-}COOCH_3$	<0.011	0.23

The reaction-rate constants of cyclopentadiene with isopropenyl-type dienophiles proved to be smaller than the rate constant for cyclopentadiene dimerization under these conditions, and therefore their values were not obtained. In the correlation with chemical shift, for them points were placed at the value corresponding to the rate constant of cyclopentadiene dimerization, with arrows directed downward, which means that the true values are somewhere lower.

The values of the chemical shifts of compounds absent from work ([18]) are as follows:

$$CH_2{=}CH{-}SO_2{-}C_2H_5 \quad \tau(\beta H)\ 3.87;\ 4.17;\ \tau_{av} = 4.02;$$

$$CH_3{=}C(CH_3){-}COCH_3 \quad \tau(\beta H)\ 3.96;\ 4.16(268);\ \tau_{av} = 4.06.$$

The dependences of $\lg k$ on τ_{av} are given in Fig. 3 for the reaction with cyclopentadiene and in Fig. 4 for the reaction with 2,3-dimethylbutadiene-1,3. The numbers of the points correspond to the number of the dienophile in the table.

* It is well known that the diene-synthesis reaction is a second-order reaction; nevertheless, in some cases the data we obtained were treated by the Wilkinson method ([20]), which, along with the reaction-rate constant, makes it possible to determine the reaction order. The values of the reaction-rate constants obtained in this way were the same, and the reaction order was second.

From the data obtained it is seen that, for the reaction with 2,3-dimethylbutadiene-1,3, a linear dependence is observed between $\lg k$ and

τ_{cp} (correlation coefficient $r = 0.990$). In the case of cyclopentadiene, a linear dependence is observed for dienophiles of the vinyl type (correlation coefficient $r = 0.983$); for dienophiles of the isopropenyl type, the reaction-rate constant is smaller than follows from the mean value of the chemical shift of the dienophile. The reason for the reduced reactivity of these dienophiles in the reaction with cyclopentadiene, and hence for the deviations from the dependence, lies, in our opinion, in steric hindrances arising in the formation of the endo adduct as a result of the interaction of the methyl group of the dienophile and the methylene group of cyclopentadiene (21).

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

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Received
26 X 1964

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