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Fig. 1. NMR spectrum of methyl methacrylate

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Abstract

Full Text

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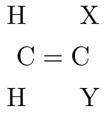
CHEMICAL SHIFT AND THE ACTIVITY OF A DIENOPHILE IN THE DIENE-SYNTHESIS REACTION

In studying the diene-synthesis reaction, it seemed of interest to us to compare the reactivity of a series of dienophiles with the magnitude of the chemical shift of the hydrogen atoms at the double bond of the dienophile. In the present work we attempted to study the activity of a series of dienophiles of the type



$$\begin{array}{ccc} H & & X \\ & C=C & \\ H & & Y \end{array}$$

as a function of the magnitude of the chemical shift of the terminal hydrogen atoms. In the case where X and Y are different substituents, the hydrogen atoms under consideration are nonequivalent owing to the diamagnetic anisotropy of the substituent groups and have different values of chemical shifts. In comparing with reactivity we took the mean values between them. The chemical shifts are given here in τ units (^{1}) with an accuracy of $\pm 0.04\,\tau$. The NMR spectra were recorded on an NMR spectrometer with an operating frequency of 24.458 MHz (^{2}). Spectra of pure liquids were recorded using tetramethylsilane as an internal standard. In Fig. 1, the spectrum of methyl methacrylate is given as an example.

Fig. 1. NMR spectrum of methyl methacrylate

As a measure of reactivity we considered the yields of the products of diene synthesis. When reactions are carried out under identical conditions, with identical concentrations of the starting substances, the yield can serve as a measure of reactivity.

We examined a series of dienophiles in reactions with isoprene and 2,3-dimethylbutadiene. The reactions were carried out by us under the following conditions: 25 ml of a benzene solution with a diene concentration equal to the dienophile concentration (2 mol/l), in the presence of 0.05 g of hydroquinone, was heated in a sealed tube at 150° for 3 hr. The amount of diene-synthesis adduct was determined from the difference between the weight of the product after distillation in vacuum of the solvent and unreacted substances and the weight of the residue after distillation. The residue usually amounted to about 5%, with the exception of reactions with styrene, where considerable amounts of polymer were formed. The error in determining the yield was of the order of ±5%.

The data obtained are presented in Table 1. From the data given it is evident that, within the range of compounds studied by us, a satisfactory linear dependence is observed of the yield on the mean value of the chemical shift of the terminal hydrogen atoms of the dienophile. Dienophiles having $\tau_{\text{av}} < 3.6$ should, under these reaction conditions with the dienes considered, give a yield of $\sim 100\%$, while dienophiles having $\tau_{\text{av}} > 4.6$ should give a yield of 0%; thus the range of dienophiles for which the observed dependence can be traced is limited by the experimental conditions, in the present case within the limits $3.6 > \tau_{\text{av}} > 4.6$. When the reactions are carried out under more severe conditions, these limits should shift toward larger values of τ. In order to cover all dienophiles at once, it is best to use the value of the reaction rate constant as a measure of reactivity. Further work is now being carried out in this direction.

Table 1

Dienophile	Chemical shifts of terminal H, τ	Mean value of chem. shift, τ_{av}	Yield, %, in reaction with isoprene	Yield, %, in reaction with 2,3-dimethylbutadiene
$CH_2{=}CH{-}CHO$	3.65	3.65	95	97
$CH_2{=}CH{-}COOH$	3.71; 3.84	3.77	81	90
$CH_2{=}CH{-}COOCH_3$	3.81; 4.01	3.91	65	79
$CH_2{=}CH{-}CN$	3.95*	3.95	63	69
$CH_2{=}C{-}COOH$	3.70; 4.29	4.00	60	74
$CH_2{=}C(CH_3){-}COOCH_3$	3.98; 4.46**	4.22	28	34
$CH_2{=}CH{-}C_6H_5$	4.29; 4.79***	4.54	0	0

* Literature data for solution in CCl_4: 3.95; 4.09 (³).
** Literature data for solution in CCl_4: 3.96; 4.51 (⁴).
*** Literature data (³).

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