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Abstract

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INFRARED ABSORPTION SPECTRA OF THE STEREOISOMERS OF PROPENYLLITHIUM

Earlier we reported data on an investigation of the IR absorption spectra of the cis- and trans-stereoisomers of propenyllithium (the spectra of these substances were recorded in a 20% ether solution) ([1]). In connection with the paper by Allinger and Hermann ([2]), the present work gives the results of a repeated measurement of the IR spectra, carried out both for solutions in ether and for pastes of the above-mentioned substances in Vaseline oil. Our aim was to obtain more reliable information on the frequencies of the cis- and trans-isomers, since in the first version ([1]) a number of frequencies, naturally, belonged to the ether itself, which misled Allinger and Hermann. The following results were obtained: for cis-propenyllithium, three frequencies in the spectrum of the Vaseline paste coincide with frequencies in the ether solution (1625 cm^{-1}, 1540 cm^{-1}, 1300 cm^{-1}), while three frequencies in the ether solution are not observed (2755 cm^{-1}, 1148 cm^{-1}, 1122 cm^{-1}). In the case of the trans-isomer of propenyllithium, the frequencies 1635 cm^{-1} and 1550 cm^{-1} coincide for the spectra of the ether solution and the oil paste. The remaining frequencies of the spectrum in the paste of the trans-isomer (2730 cm^{-1}, 1220 cm^{-1}, 1030 cm^{-1}) were not observed by us in the spectrum of the ether solution.

The higher frequencies (1635 cm^{-1}, 1545 cm^{-1}) of the C=C vibrations in the IR spectrum of propenyllithium, recorded in Vaseline paste and in ether solution, characterize the trans-isomer, while the lower frequencies of the C=C vibrations (1625 cm^{-1} and 1535 cm^{-1}) characterize the cis-isomer.

Consequently, in studying the cis- and trans-isomers of propenyllithium obtained by the previously described method ([1]) by means of IR absorption spectra, we arrived at the very same results as those reported by Allinger and Hermann ([2]). Our data indicate the absence of any impurities in our products, as stated in ([2]), and also a substantial difference in the spectra depending on the recording conditions. It should be noted that the bands with frequencies 2050 cm^{-1} in the cis-isomer and 2070 cm^{-1} in the trans-isomer, which are discussed in ([2]), were not found by us; moreover, from our point of view the use of bands with frequencies 1035 cm^{-1} (cis) and 1045 cm^{-1} (trans) is hardly correct.* Thus, the conclusions we made earlier regarding the configuration of cis- and trans-propenyllithium, which we reached on the basis of optical and chemical data (the method of even and odd cycles ([1])), remain valid.

Experimental Part

Synthesis of cis- and trans-propenyllithium. To 0.5 g (0.073 mole) of finely cut metallic lithium in 30 ml of dry ether was added a solution of 4 g (0.0033 mole) of cis-propenyl bromide at 5-7°. After 30 minutes of stirring, the solution was filtered through a funnel with a porous glass plate to remove excess metallic lithium. Ether was evaporated from the solution to 40% of the initial volume. The ether solution of cis-propenyllithium was subjected to investigation of the IR absorption spectrum. From a second portion the ether was completely removed; the remaining dry, easily crumbling white

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* In this region ether itself absorbs, and its residues may give bands.

The powder was mixed with vaseline oil and likewise subjected to spectroscopic investigation.

Trans-propenyllithium was obtained analogously. All operations in obtaining cis- and trans-propenyllithium, evaporating the ether, and filling the cuvettes were carried out in pure argon.

Investigation of the IR absorption spectra of the stereoisomers of propenyllithium in ether solution and in vaseline oil confirmed the configurations of the cis-trans isomers established earlier ([1]).

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CITED LITERATURE

[1] A. N. Nesmeyanov, A. E. Borisov, N. V. Novikova, DAN, **119**, 712 (1958); A. N. Nesmeyanov, A. E. Borisov, N. V. Novikova, Izv. AN SSSR, OKhN, **1959**, 1216. [2] N. L. Allinger, R. B. Hermann, J. Org. Chem., **26**, 1040 (1961).

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

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