

A BAYLIS-HILLMAN ADDUCT - ETHYLCELLULOSE DERIVATIVE

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The Baylis-Hillman adduct obtained from the reaction of benzaldehyde and acrylonitrile was reacted with ethyl cellulose to form a new derivative with potential industrial applications. The structure of the derivative was established by spectroscopic and elemental analysis data. NMR spectra revealed the formation of an enantiomeric mixture. The substitution degree (DS) at the primary -OH groups of ethyl cellulose was estimated, from ¹H-NMR spectra, at a value of 1.7, which represents an about 50% substitution degree, since the total attainable substitution on ethyl cellulose is around 3.9. The formula for a glucose unit of the derivative was calculated from elemental analysis and from the value of the substitution degree.

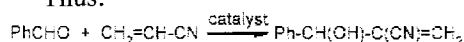
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INTRODUCTION

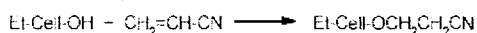
Baylis-Hillman coupling is a reaction leading to the formation of/ producing alcohols from an activated alkene and an electrophile containing a sp² hybridised carbon atom. Aldehydes have proved to be very suitable substrates, the most commonly used catalyst for the reaction being 1,4-diazobicyclo [2.2.2] octane (DABCO). The alkenes are activated by electron withdrawing groups such as esters, nitriles, acyl, amides, etc.

Particularly interesting for this study was the reaction between benzaldehyde and acrylonitrile, which leads to the formation of 3-hydroxy-2-methylene-3-phenylpropanenitrile.

Thus:



The mechanism of this reaction is explicit in the literature.^{1,2} The preparation of ethyl-cyanoethyl cellulose from ethyl cellulose and acrylonitrile, catalysed by sodium hydroxide, is expressed by the following equation:



where Et-Cell-OH stands for ethyl cellulose.

The reaction is well-known as a Michael addition reaction.³ Recently, new results⁴ on ethyl-cyanoethyl cellulose have been repor-

ted. The reaction of ethyl cellulose with maleanilic acid, a variant of the Michael addition reaction of ethyl cellulose, has been also investigated.^{5,6} In a further investigation of the Michael addition reaction of ethyl cellulose, a possible reaction of ethyl cellulose with the Baylis-Hillman adduct of benzaldehyde and acrylonitrile was proved. It seemed that the adduct should be a more suitable substrate for the preparation of an extended ethyl-cyanoethyl cellulose derivative containing asymmetric centers and chemospecific functional groups.

Thus, the two new functional groups and the newly created asymmetric centers offer several possibilities for chemo-, regio- and stereoselective transformations.



In the present report, the synthesis and structural elucidation of this new derivative is described.

EXPERIMENTAL

Ethyl cellulose, with a DS of 2.1, predominantly at the secondary hydroxy positions, was supplied by a Chinese chemical company. The NMR spectra were recorded on a BRUKER DRX 300 MHz spectrometer, using TMS as an internal standard and deuteriochloroform as a solvent.

Chemical shifts were recorded in ppm, relative to TMS. The IR spectra were recorded on a Perkin Elmer FT-IR Paragon 1000 spectrometer, and elemental analysis was performed on a Perkin Elmer 2400 CHN Elemental Analyzer. The Baylis-Hillman adduct was prepared as follows: 20.4 mL (200 mmol) benzaldehyde, 19.8 mL (300 mmol) acrylonitrile and 3.4 g (20 mmol) DABCO were mixed and allowed to react at room temperature for 40 hours. The resulting slightly brown reaction mixture was taken up in a sufficient amount of diethyl ether and washed thoroughly with a diluted HCl solution, water and sodium bicarbonate solution. The ethereal solution was dried (anhydrous magnesium sulphate), filtered and concentrated *in vacuo*. The obtained crude colourless product was practically pure enough for a subsequent Michael reaction with ethyl cellulose. A sample of the crude product distilled under reduced pressure recorded a boiling point of 121-124 °C/1.5mm, which agrees with literature data.^{7,8} The IR and NMR spectra were recorded.

Ethyl-2-hydroxymethylphenyl cyanoethyl cellulose [(E-HOMPE-CE)-C]

10 g (0.063mol) of the adduct obtained from the above reaction and 1.5 g ethyl cellulose were stirred together and, after 10 minutes, 5 mL of a 5% aqueous sodium hydroxide solution were added. The reaction mixture was heated on a water bath at 40-50 °C, for 3 hours, and a thick white paste, difficult to stir with a magnetic stirrer, was thus obtained. The reaction was quenched by the addition of 10 mL 5% aqueous acetic acid and the gummy mass was washed thoroughly with aqueous bicarbonate solution and distilled water. Still, the product was gummy and was therefore stirred in boiling water and broken into pieces with a glass by a Chinese chemical company rod. The water was drained, and the final white solid product was first air-dried and later dried under vacuum at 50 °C. The final mass of the product was of 10.75 g. NMR and IR spectra were recorded and elemental analyses conducted.

RESULTS AND DISCUSSION

The Baylis-Hillman adduct from benzaldehyde and acrylonitrile appears as a good substrate for the cyanoethylation of ethyl cellulose and other cellulose derivatives. The presence of the hydroxyl and nitrile functional groups attached, each, to a chiral carbon center, offers a good

opportunity for further chemo- and stereo-selective transformations (Fig. 1).

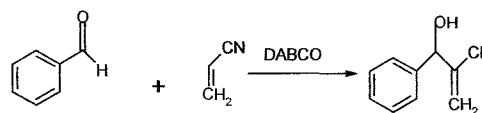


Figure 1a: Formation of the Baylis-Hillman adduct

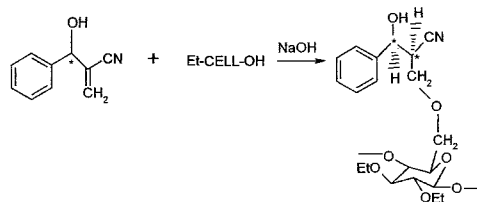


Figure 1b: Formation of the cellulose derivative

In particular, the introduction of an extra chiral center through the Michael addition reaction makes the ethyl cellulose derivative a special variant of the well known ethyl-cyanoethyl cellulose [(E-CE)-C]. Therefore, it is to be expected that this new derivative might exhibit special additional properties that might recommend it for larger applications than ethyl-cyanoethyl cellulose itself.

Determination of the Baylis-Hillman adduct structure posed no special difficulties. The IR (Fig. 2) and NMR spectra (Fig. 3) are explicit, clearly supporting the formation of a suitable product.

Of particular interest in this study is the cyano group IR stretching frequency, which showed up as a sharp signal at 2228.5 cm⁻¹, to be used in the analysis of the subsequent cyano group stretching frequency signal recorded for the final derivative.

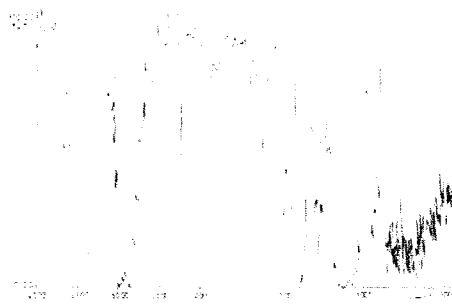


Figure 2: IR spectrum of Baylis-Hillman adduct

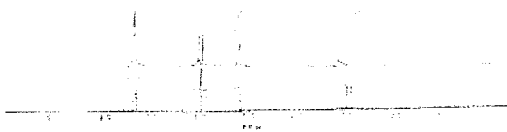


Figure 3: NMR spectrum of Baylis-Hillman adduct

The subsequent Michael addition reaction of ethyl cellulose with the Baylis-Hillman adduct proceeded smoothly. A second trial revealed that the reaction time might be actually reduced to 2 hours. The IR spectrum (Fig. 4) of the final product evidenced the cyano group stretching frequency as a sharp signal at 2305 cm^{-1} . A shift is expected, comparatively with the stretching frequency obtained for the Baylis-Hillman adduct, due to the absence of the α,β -unsaturation after the Michael addition reaction. The intensity of this signal is a significant "single operation" successful Michael addition reaction of ethyl cellulose with activated double bond substrates. In the preparation of ethyl-cyanoethyl cellulose, the IR stretching frequency of the cyano group is unimpressively negligibly weak, so that the reaction should be repeated two or three more times.

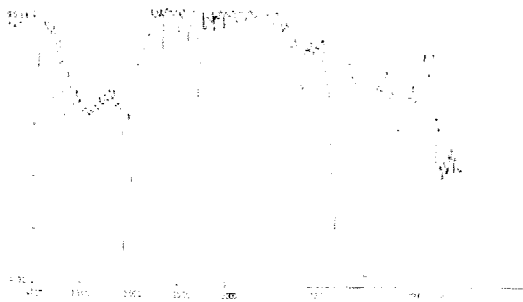


Figure 4: IR spectrum of cellulose derivative

The NMR spectrum of this derivative showed the expected signals: the $-\text{CH}_2\text{CH}_3$ signal of the cellulose backbone was

registered at the expected δ value of 0.85. The fact that two pairs of triplets were obtained is consistent with the formation of an enantiomeric mixture, the ratio of which is estimated at around 2:1. In this study, separation and determination of the exact stereochemistry of the isomers have not been considered. The $-\text{CH}_2\text{O}-$ groups of the ethyl cellulose occurred between δ 3-4 ppm, as usual. The $-\text{CH}_2-$ of the ethylene bond of the Baylis-Hillman adduct (after the Michael reaction) was registered as two doublets at δ 4.75 and 4.9 ppm, which, again, is consistent with the fact that this group is adjacent to an asymmetric (chiral) center. The broad singlet at δ 1.75 ppm proton of the hydroxyl-methylphenyl group is a doublet at δ 4.3 ppm, while the $-\text{OH}$ came up at δ 3.18 ppm.

The aromatic protons were registered as a broad singlet at δ 7.35 ppm, an assignment consistent with the structure of the expected product. From the NMR spectra, the DS was also estimated as being 1.7, as compared to a value of 0.2, normally obtained in the cyanoethylation of ethyl cellulose with acrylonitrile.



Figure 5: NMR spectrum of cellulose derivative

Elemental analysis provided the following values: C: 62.86%, H: 6.41%, N: 5.04%, O: 25.69% against the calculated values of 62.96%, 6.37%, 4.91%, 25.76%, respectively. If taking into consideration the DS value of 1.7, the formula obtained for a glucose unit of the derivative was $\text{C}_{25}\text{H}_{30.3}\text{N}_{1.7}\text{O}_{7.7}$.

CONCLUSIONS

The study opened the way for the utilization of the Baylis-Hillman adducts in the preparation of interesting cellulose

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derivatives with additional chiral centers. Efforts are now underway for a broader coverage of this type of derivatisation.

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