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Deuterated Epoxides and Their Polymers. I. Synthesis of cis- and trans-Propylene Oxide-1-d and Their NMR Spectra

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SUMMARY

cis- and trans-Propylene oxide-1-d were synthesized from the corresponding propenyl halides via propenyllithium and propylene bromohydrin. Their NMR spectra (about 3% in benzene) were analyzed in terms of ABX_3 spin system and the assignment was carried out. The chemical shift of the methylene proton in cis position to the methyl group was found to be $\delta = 1.86$ ppm and that of the methylene proton in trans position $\delta = 2.18$ ppm (downfield from HMDS). The H-D couplings were observed in the methine-methylene part spectra decoupled from methyl protons. The observed J_{HD}'s agree with the theoretical relation: $J_{HH} = 6.514 \times J_{HD}$.

INTRODUCTION

During the study of the optical rotation behavior of poly(R-(+)-propylene oxide) in different solutions [1], it was expected that the coupling constant between methine-methylene protons attached to the central C–C bond of the monomeric unit in the polymer would help us understand the conformation around this bond and the nature of the optical rotatory phenomena. This has led us, in the first stage, to the syntheses of cis- and trans-propylene oxide-1-d.

In this paper we wish to report the synthesis and the results of measuring the NMR spectra of these monomers.

EXPERIMENTAL

Synthesis of cis-Propenyl Bromide

cis-Propenyl bromide was synthesized from crotonic acid according to the method of Braude and Coles [2]. Results are in agreement with the reference (bp 58°C).

Synthesis of trans-Propenyl Chloride

1,2-Dichloropropane (2 moles) was reacted with sodium phenolate [3] (2 moles) in ethanol at reflux temperature. trans-Propenyl chloride (25% yield), bp 36.7°C, was isolated from cis-propenyl chloride (bp 32°C) and 2-chloro-1-propene (bp 23°C) by fractional distillation.

Synthesis of cis- and trans-Propenyllithium

Propenyllithium was synthesized according to the method of Braude and Coles [2].

Synthesis of cis- and trans-Propylene-1-d

Glass adaptors and rubber tubings were used to connect the reflux condenser of the propenyllithium reaction system to 4 successive traps, the first of which, relatively large, was cooled in a Dry Ice-methanol mixture while the others were cooled in liquid nitrogen. Heavy water (in excess, 1 mole) was placed in the dropping funnel. Gentle stirring was started before heavy water was carefully added dropwise to the propenyllithium solution. Ether and deuterated propylene were collected in the first trap. The desired olefin was then purified by successive trap-to-trap distillation. The end product was introduced as a gas into a 2-liter rubber balloon attached to the last trap outlet.

Synthesis of Deuterated Propylene Bromohydrin

In order to assure good contact between the gaseous propylene and the hypobromous acid solution, the latter was introduced dropwise to the top of a 80-cm glass column packed with glass beads while deuterated propylene was admitted at the column base. The reaction was followed by observing the discoloration of the hypobromous acid solution.

The reaction product was neutralized by a solution of sodium carbonate, saturated with potassium iodide, and extracted with ether. The ether extract was dried over sodium sulfate, then submitted to vacuum evaporation.

The remaining product, expected to be deuterated propylene bromohydrin (about 1.9 ml), was collected into a bent tube with a ground-glass joint.

Synthesis of cis- and trans-Propylene Oxide-1-d

The bent tube mentioned above was attached to a microdistillation apparatus on a 20-ml flask containing saturated potassium hydroxide aqueous solution heated to 40°C. The bent tube was shaken to let its content drop into the potassium hydroxide solution where vigorous reaction occurred. The gaseous propylene oxide-1-d was distilled through a column packed with potassium hydroxide for drying and purification, and was collected in a trap cooled to -78°C. The yield (0.6 ml) was 4% of the theoretical amount based on the original quantity of propenyl halide.

Spectroscopy

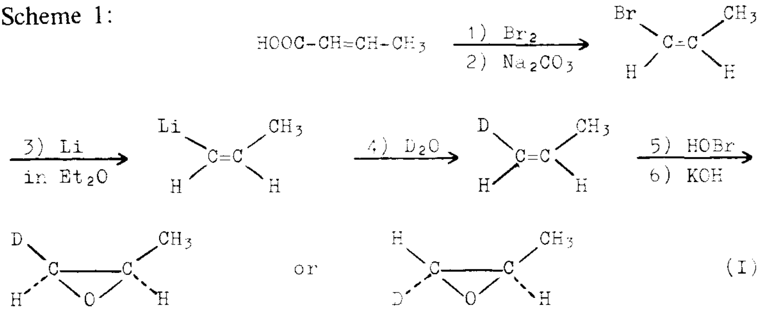
IR spectra were recorded on a Hitachi Model EPI-G3 grating infrared spectrometer.

The NMR spectra of 3.0-3.2 w/v% benzene solutions of deuterated propylene oxide were recorded on a 100 MHz Varian spectrometer at 28°C with hexamethyldisiloxane (HMDS) as internal standard.

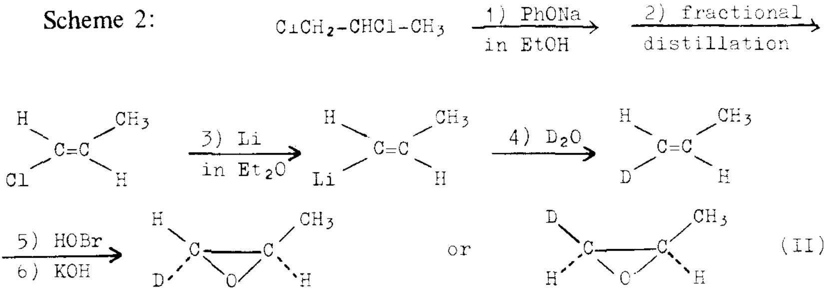
RESULTS AND DISCUSSION

The methylene-methine parts of NMR spectra of the products I and II obtained from cis- and trans-propenyl halides according to Schemes 1 and 2 are shown in Figs. 1 and 2 respectively.

Scheme 1:



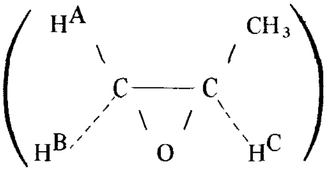
Scheme 2:



Analysis of these spectra as the AB parts of ABX$_3$ system by the LAOCN3 computer program [4] (modified to include a curve plotting subroutine) using the observed chemical shift and coupling constant values gave the calculated spectra shown in Figs. 1 and 2. In both cases, agreement between the calculated and experimental spectra is observed.

By combining the data of the spectra of I and II, a computation by the same LAOCN3 program gave a spectrum which is identical to that of the ordinary propylene oxide in benzene solution (Fig. 3). Furthermore, the products of the syntheses were transformed by the diethylzinc-methanol (1:1.7) catalyst system into polymers which were shown by IR and NMR spectroscopy to be poly(cis-propylene oxide-1-d) and poly(trans-propylene oxide-1-d). Thus the successive reactions of Schemes 1 and 2 were concluded to have led to deuterated propylene oxides.

The lines around $\delta = 2.44$ ppm existing in the spectra of both I and II can be assigned to the methine H^C because they are characterized by a coupling constant of 5.2 Hz with the methyl protons.



As for H^A and H^B, it is expected by virtue of Karplus relation [5] that the proton in the cis position to H^C, subtending a dihedral angle of 0°, is characterized by a larger coupling constant than that of the proton in the trans position [6] to H^C, subtending a dihedral angle of 151°22′ [7]. Owing to the existence of only one methylene proton in each of our samples, the chemical shifts of each of the two methylene protons can be assigned without any ambiguity and it was possible to measure accurately the methine-methylene coupling constants from the corresponding spectra. A coupling

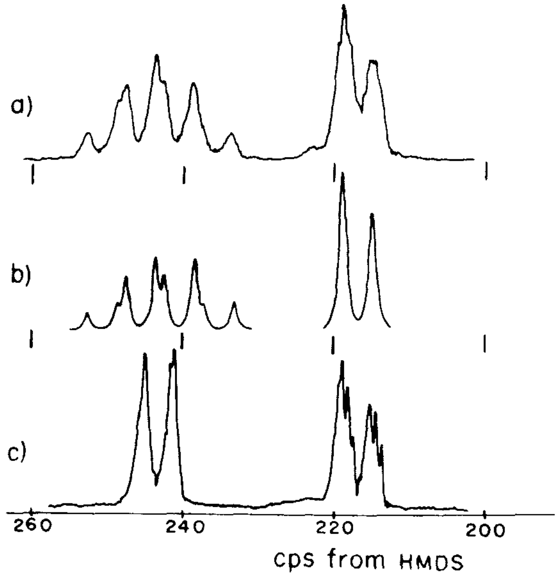


Fig. 1. Methylene-methine NMR spectra of cis-propylene oxide-1-d. (a) Observed spectrum. (b) Calculated spectra obtained by using the LAOCN3 program. The line shapes were assumed as Lorentzian with half-widths of 0.8 Hz. (c) Observed spectrum, decoupled from the methyl protons.

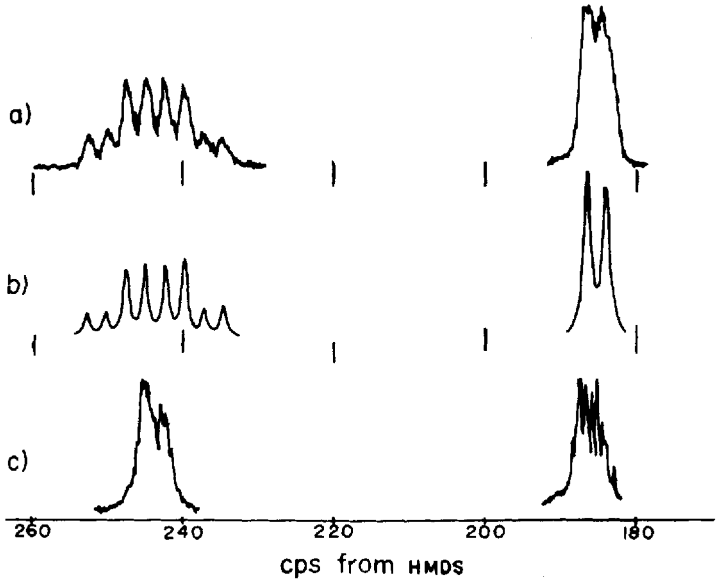


Fig. 2. Methylene-methine NMR spectra of trans-propylene oxide-1-d. (a) Observed spectra. (b) Calculated spectra obtained by using the LAOCN3 program. The line shapes were assumed as Lorentzian with half-widths of 0.8 Hz. (c) Observed spectra, decoupled from the methyl protons.

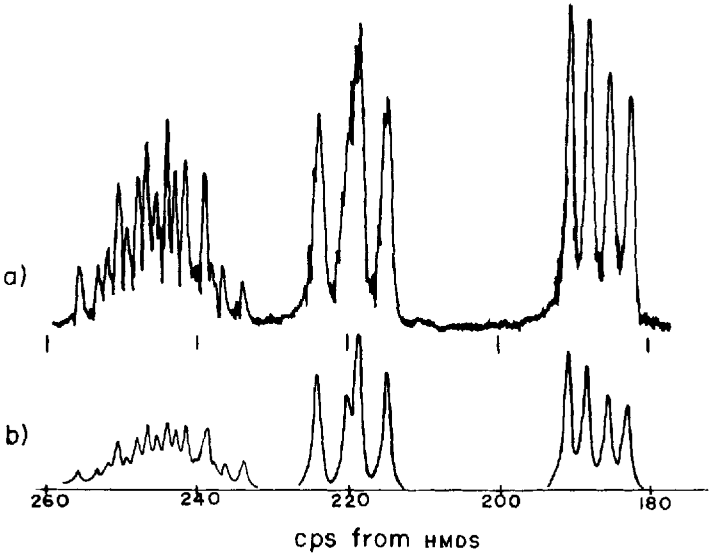


Fig. 3. Methylene-methine NMR spectra of propylene oxide (3 w/v% in benzene at 28°C with HMDS as internal standard). (a) Observed spectrum. (b) Calculated spectra obtained using the LAOCN3 program. The line shapes were assumed as Lorentzian with half-widths of 0.8 Hz.

Table 1. Chemical Shifts[a] and Coupling Constants[b] of Different Protons in cis-Propylene Oxide-1-d (cis-PO) and trans-Propylene Oxide-1-d (trans-PO)

	cis-PO	trans-PO	Reference values
δ_X	0.86	0.86	1.32[c]
δ_A		1.86	2.42[c]
δ_B	2.18		2.72[c]
δ_C	2.44	2.45	~2.98[c]
$\lvert J_{XC} \rvert$	5.2	5.2	5.0[e]
$\lvert J_{AB} \rvert$			5.5 ± 0.3[d,e]
$\lvert J_{AC} \rvert$		2.5	~2.5[d,e]
$\lvert J_{BC} \rvert$	3.9		~4.5[d,e]

[a] The chemical shifts are given in ppm from HMDS, internal standard. Positive value of δ means that the line appears at lower field than that of HMDS.

[b] The coupling constants are given in Hz.

[c] Values given by Bhacca et al. [8] for propylene oxide, 5 w/v % in $CDCl_3$ with TMS as internal standard, at 60 MHz.

[d] Values given by Gutowsky et al. [9] for propylene oxide, neat, at 40 MHz.

[e] Values given by Musher et al. [10] for propylene oxide, at 60 MHz with hexamethyldisiloxane as internal standard. (Other experimental conditions not reported).

Table 2. H-D Coupling Constant, J_{HD}, in Deuterated Epoxides[a]

Epoxide	$\lvert {}^2J_{HD} \rvert$	$\lvert {}^3J_{HD}^{trans} \rvert$	$\lvert {}^3J_{HD}^{cis} \rvert$
trans-Propylene oxide-1-d	~0.9	-	~0.6
cis-Propylene oxide-1-d	~0.9	~0.4	-
trans-Ethylene oxide-1,2-d_2[b]	~0.9	-	~0.6

[a] In Hz.

[b] About 5 w/v % in benzene (synthesized according to the method of Price et al. [13]).

constant of 3.9 Hz was observed for I in benzene and a value of 2.5 Hz for II, showing that I can be identified as cis- and II as trans-propylene oxide-1-d. The lines around δ = 1.86 ppm are therefore assigned to H^A and those around δ = 2.18 ppm to H^B. These chemical shifts and coupling constants, thus determined, are listed in Table 1 together with values given by Bhacca et al. [8] for propylene oxide in chloroform. Coupling constant values given by Gutowsky [9] and Musher et al. [10] are also given in the same table for comparison.

Our unambiguous assignment of the chemical shifts of the methylene protons (Table 1) confirms the empirical assignment [6] of the higher field lines to that methylene proton which is in the cis position to the methyl substituent in an epoxide compound.

In the methylene-methine resonance spectra decoupled from the methyl group, H-D coupling was clearly observed. The H-D coupling constants obtained from these spectra (Figs. 1 and 2) are listed in Table 2. They are found to fit well the theoretical relation [14]:

$$J_{HH} = 6.514 \times J_{HD}$$

This is additional support for our spectral assignment. The H-D coupling constants for trans-ethylene oxide-1,2-d_2 are also given in Table 2.

The identification mentioned above has shown that cis- and trans-propylene oxide-1-d can be synthesized from the corresponding cis- and trans-propenyl halides. As for Steps 3) and 4) of Schemes 1 and 2, the over-all retention of the configuration was reported by G. Natta et al. [11].

Therefore, over-all retention of the configuration in Steps 5) and 6) was concluded from our results. This over-all retention was also observed for higher analogs, cis- and trans-2-butene oxides [12], and for lower ones, cis- and trans-ethylene oxide-1-2-d_2 [13].

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