

Identification of *cis*-4,5-Epoxy-2-Pentalenol from Pyrolysis of H_3PO_4 -Treated Cellulose*

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Synopsis

An important product, $\text{C}_6\text{H}_6\text{O}_2$, from the pyrolytic decomposition of phosphoric acid, treated cellulose was isolated and identified as *cis*-4,5-epoxy-2-pentalenol. NMR, IR, UV, and mass-spectral data of this product were analyzed and discussed. A method for the preparation of *cis*-4,5-epoxy-2-pentalenol is presented, and a mechanism for its formation is proposed.

INTRODUCTION

The thermal decomposition of cellulose has been extensively studied, and work in this area has been reviewed by Browne¹ and by MacKay.² Recently, studies on the pyrolysis of cellulose treated with various fire retardants were reported.³⁻¹⁰ Most of these investigations were directed toward the understanding of the mechanism of fire retardance in the search for more effective fire retardant treatments of wood and cellulose.

Several theories have been advanced to account for the mechanism of fire retardants on cellulose, among them the "levoglucosan theory."

This theory was proposed by Parks et al.¹⁰ who suggested that the first and rate-determining step during the pyrolysis of cellulose was the depolymerization step to form flammable tar, or levoglucosan (1,6-anhydro- β -D-glucopyranose). This study implied that the prevention of levoglucosan formation by chemical means would decrease the flammability of the resultant cellulose derivative. Good fire retardants are expected to reduce the amount of levoglucosan formation more than poor fire retardants can. This theory was later supported by Schwenker and Pacsu¹¹ who chemically modified cellulose fabrics to impart flame retardance and glow resistance.

Recently, we quantitatively analyzed the pyrolysis products of untreated cellulose and investigated the effect of eleven inorganic fire retardants (acidic, alkaline, and neutral) on the formation of these products

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from cellulose.⁴ The relationship between flammability (as measured by the oxygen index test)¹² of the treated cellulose samples and the yield of levoglucosan from the pyrolysis of these samples was studied.⁵ It was found that all fire retardants investigated in this study lowered the amount of levoglucosan formation. There was no direct correlation between the effectiveness of a fire retardant and the amount of levoglucosan formation, however. Hence, the validity of the "levoglucosan theory" was questioned, and alternative mechanisms were sought to explain the action of fire retardants on cellulose.

Tsuchiya and Sumi⁴ reported the finding of a new pyrolysis product of cellulose (designated compound I in the present paper) and noticed that the yield of this compound was increased substantially when cellulose was treated with either phosphoric acid or ammonium dihydrogen orthophosphate prior to pyrolysis. Potassium carbonate suppressed the formation of compound I completely. These results suggest that pyrolytic mechanism of cellulose depends on the nature of the added fire retardant. The course of the reaction may be dependent on the chemical or physical association of the fire retardant molecules with the cellulose. It appears that compound I plays an important role in the pyrolysis of cellulose in the presence of acidic additives, and its identification may shed some light on the mechanism of decomposition of cellulose.

This paper describes the preparation and the identification of compound I and a proposed mechanism for its formation from the pyrolysis of cellulose treated with phosphoric acid.

EXPERIMENTAL

Treatment of Cellulose with H_3PO_4

Whatman No. 1 filter paper (50.2 g) was cut into strips of 1 $\frac{1}{2}$ in. by 2 $\frac{1}{2}$ in. and dipped into 1% (v/v) solution of 85% H_3PO_4 (500 ml) for about 2 min. The treated sample was blotted with paper towels, dried at 60°C (3.5 mm) for 24 hr, and air dried overnight. The final weight of the treated sample was 50.8 g.

Pyrolysis Procedure

Pyrolysis was carried out in a Pyrex tube (3 in. by 16 in.) with a side arm for evacuation. This side arm was connected to a cold trap (-78°C) in such a manner that the system could be evacuated by a mechanical pump. The H_3PO_4 -treated sample (50.8 g) was introduced into the tube which was preheated to the desired temperature (320°C). The pressure of the system ranged from 2 to 3 mm during the period of pyrolysis (100 min).

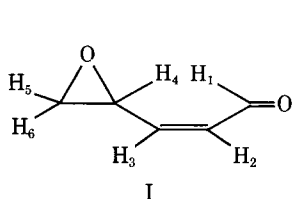
The liquid pyrolyzate, solution II (approx. 15 ml), separated into two layers in the cold trap. The top layer was colorless and the bottom layer was brownish in color. After II was transferred into a 250-ml Erlenmeyer flask, water (5 × 5 ml) was used to rinse the trap, and the washings were added to solution II in the flask. After II was neutralized with 5%

NaHCO₃ solution (105 ml), it was filtered and the filtrate was extracted with ether (8 × 25 ml). The ethereal extract was dried over anhydrous Na₂SO₄, and the ether was evaporated. A brown liquid (5 g; yield, 10%) was obtained. It contained approximately 90% of I. Compound I had a high boiling point, and attempts to distil it *in vacuo* were not successful, probably because of its decomposition and rearrangement to other products. However, compound I could be easily purified by preparative gas chromatography.

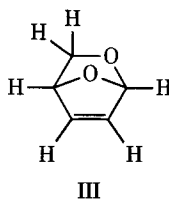
A Perkin-Elmer F-21 preparative chromatograph equipped with a 1/2-in. by 6-ft 5% Carbowax 20M on acid-washed chromosorb stainless steel column, and with temperature programming in the range of 50°–180°C, was used to purify compound I. The infrared spectra were recorded on a Beckman IR-12 spectrophotometer, and NMR spectra were recorded on a Jeolco JNM-c60HL instrument in CDCl₃. Mass spectra were obtained on the LKB 9000 combined gas chromatography mass spectrometer, and ultraviolet spectra were obtained on a Perkin-Elmer 350 UV spectrophotometer.

RESULTS AND DISCUSSION

Wodley⁷ investigated the pyrolysis products of cellulose and reported the finding of an unknown compound III having an empirical formula of C₆H₆O₂. This compound gave similar mass-spectral and gas-chromatographic data as compound I. Compound III was further examined by Lipska and McCasland,⁸ who tentatively assigned a structure of 1,5-anhydro-2,3-dideoxy-β-D-pent-2-ene-furanose for III based on their interpretation of IR, NMR, and mass-spectral data. Both Wodley and Lipska pointed out the importance of III and suggested that its identification might assist in the understanding of the mechanism of fire retardance on cellulose:



cis-4, 5-epoxy-2-pentenal



1, 5-anhydro-2, 3-dideoxy-β-D-pent-2-ene-furanose

Although both compounds I and III were obtained from the same source and have very similar features in their mass-spectral and gas-chromatographic analyses, the structure of III proposed by Lipska does not agree with the IR and NMR data we obtained for I. If I and III were the same compound, we prefer the structure of I.

Structure of Compound I

Compound I is a colorless liquid, and its molecular weight is 98 as determined by the mass spectrometer (Table I). It has a molecular formula of

TABLE I
Mass Spectrum of Compound I

<i>m/e</i>	I, %
98	58
97	26
96	40
70	25
68	86
53	62
52	26
43	20
42	36
41	36
40	24
39	100

$C_6H_6O_2$ and can be prepared readily from the pyrolysis of cellulose treated with 1% phosphoric acid at 320°C. The yield of I ranged from 10% to 15% by this method. The crude product from the reaction was extracted with ether and then purified by preparative gas chromatography.

The NMR spectrum of I is shown in Figure 1. Two quartets at the low-field region are signals of the vinyl protons. The quartet at 7.15 δ is lower than ordinary olefinic proton signals and is indicative of the β -proton signal of an α,β -unsaturated carbonyl compound. The coupling constant between the vinyl protons being 10.1 Hz indicates that they are *cis* to each other. The two multiplets centred at 4.90 δ and 3.75 δ are the protons of the epoxy ring. Insets in Figure 1 show the expanded scale of these multiplets. It is clear from these spectra and from the results of double-irradiation work that these protons are coupled to each other and have the multiplicities and coupling constant expected of an epoxy ring. Table II shows the chemical shifts and coupling constants for all six nonequivalent protons in Compound I. The doublet at 5.18 δ is assigned to the aldehydic proton. While this value deviates considerably from the normal chemical shifts of aldehydic protons, we believe that making such an assignment is justified for the following reasons. First, from the chemical as well as spectral data we believe that compound I is an α,β -unsaturated carbonyl

TABLE II
Observed NMR Values of Compound I

Proton	δ , ppm	Coupling constants, Hz
1	5.18	$J_{1,2} = 1.7$
2	6.00	$J_{2,3} = 10.1$
3	7.15	$J_{3,4} = 4.8$
4	4.90	$J_{4,6} = 1.3$
5	3.82	$J_{5,4} = 4.2$
6	3.68	$J_{6,5} = 6.6$

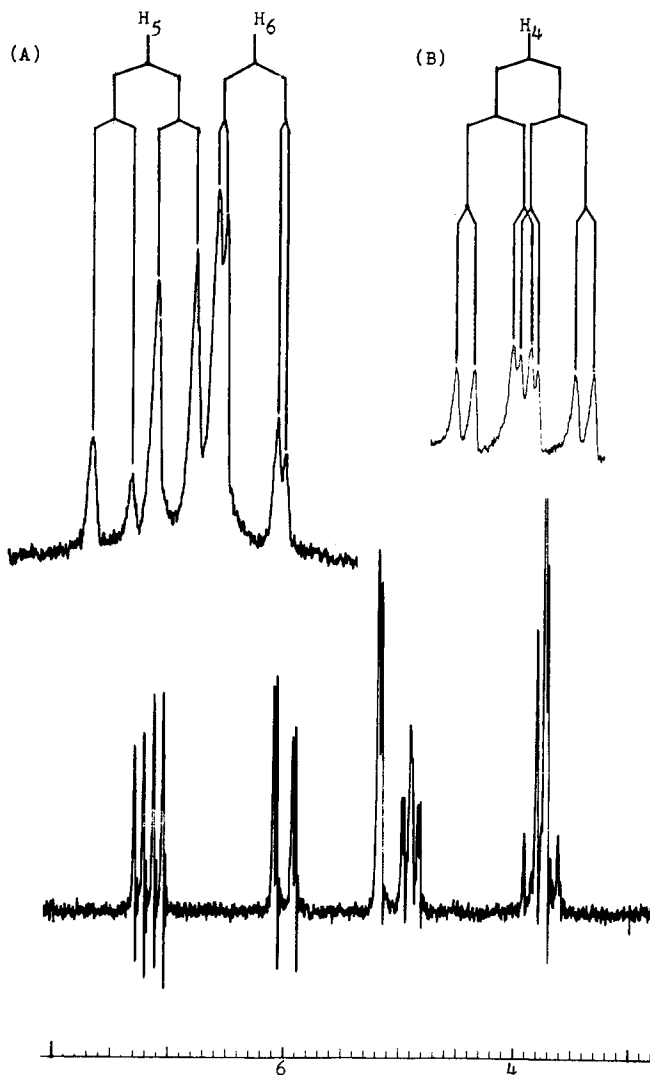


Fig. 1. 60-MHz NMR spectrum of compound I in CDCl₃, SW500: (A) 60-MHz spectrum of H₅ and H₆, SW100; (B) 100-MHz spectrum of H₄, SW50.

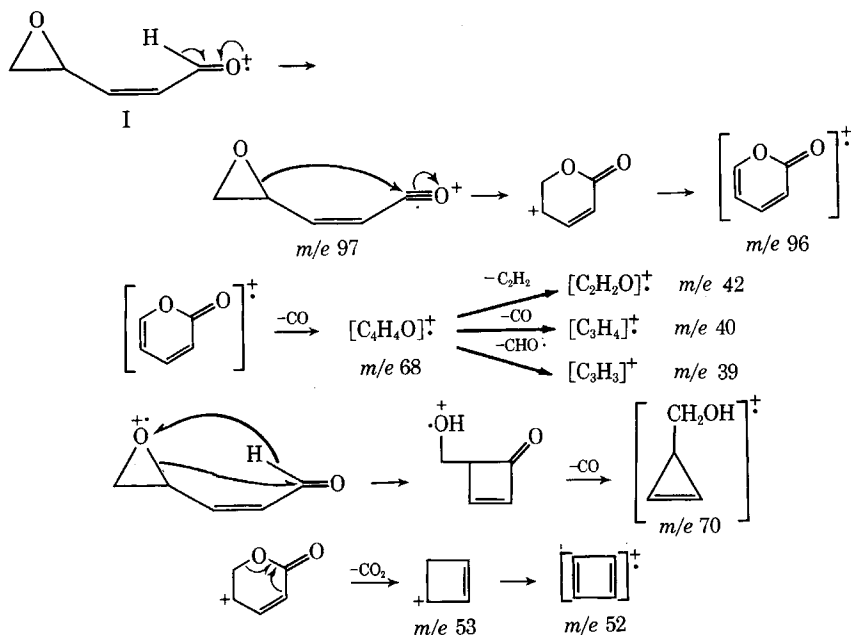
compound. Taking the resonance signals of other protons of the molecules into account, together with the IR data and the molecular formula, it is reasonable that the doublet at 5.18 δ be assigned to the aldehydic proton. Secondly, construction of a molecular model of I showed that the most preferred conformation of the compound has the carbonyl group trans to the double bond and the plane of the epoxy ring perpendicular to the plane containing the two unsaturated bonds. This places the aldehydic proton directly above the plane of the epoxy ring. Thus, the aldehydic proton can be expected to be strongly shielded by the epoxy ring. Consideration

of the NMR spectrum of I in this manner not only can derive the structure of I but also can gain some insight into the conformation of the molecule. As far as we know, this is the first reported instance in which an aldehydic proton signal is considerably shifted upfield.

The C-13 spectra of compound I confirm the presence of a carbonyl carbon, a carbon-carbon double bond conjugated with the carbonyl carbon and an allylic carbon atom. The α,β -unsaturated carbonyl system in I was also confirmed by its UV absorption at λ_{\max} 234 $m\mu$ in ethanol.

Figure 2 shows the infrared spectrum of I. The absorption band at 680 cm^{-1} is the bending frequency of C—H of the olefin, and the band 1610 cm^{-1} is the C=C stretching frequency of the olefin. The absorption bands at 830 cm^{-1} and 1260 cm^{-1} are due to the C—O—C stretching frequencies of the epoxy ring. The twin bands at 1705 cm^{-1} and 1725 cm^{-1} are characteristic of α,β -unsaturated carbonyl compounds. The band at 2900 cm^{-1} is assigned to the C—H stretching frequency of the aldehydic hydrogen. The band at 2250 cm^{-1} is due to CDCl_3 solvent.

The P-1 peak m/e 97 of the mass spectrum in Table I gives further support to the presence of an aldehydic function in compound I. The other prominent peaks at m/e 96, 70, 68, 53, 42, 40, and 39 from I can be rationalized as follows. Pirkle and Dines have found similar mass-spectral results for 2-pyrone¹³:



On the basis of our interpretation of the data obtained by UV, NMR, IR, and MS, we have assigned the structure of *cis*-4,5-epoxy-2-pentenal to compound I.

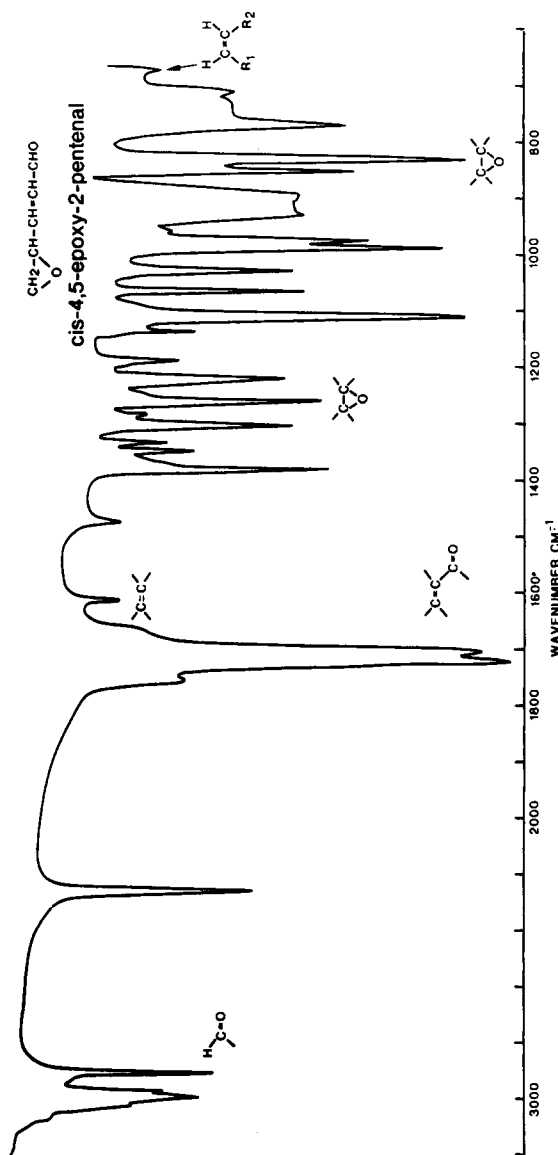


Fig. 2. The IR spectrum of compound I (in CDCl_3).

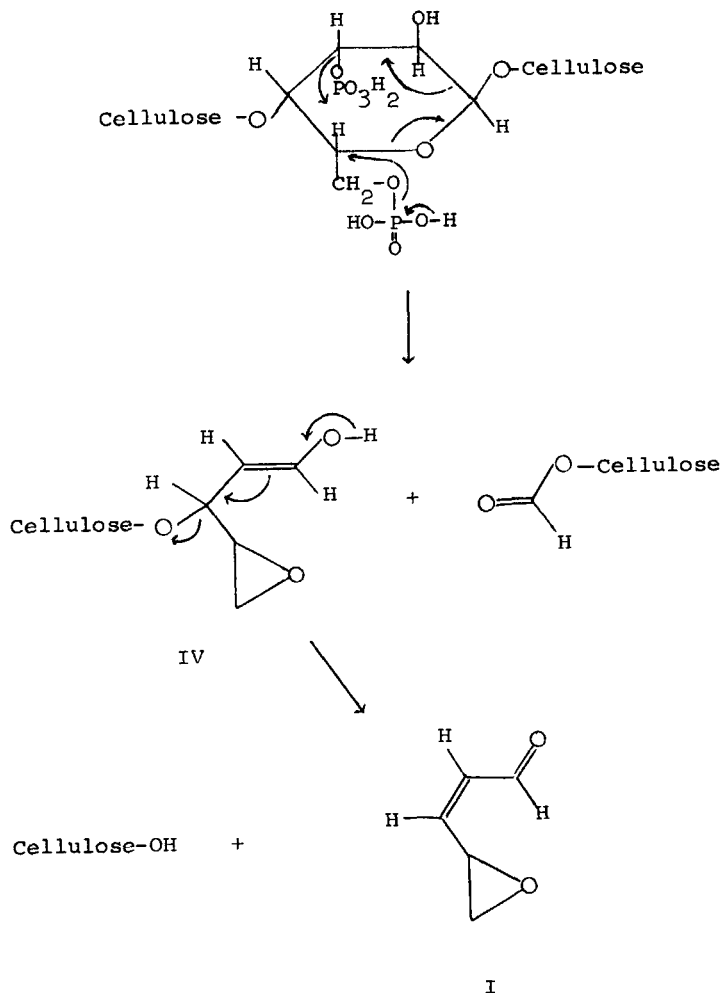


Fig. 3. Proposed mechanism for the formation of *cis*-4,5-epoxy-2-pental.

Mechanism for the Formation of Compound I

A mechanism for the formation of I from the pyrolysis of phosphoric acid-treated cellulose can be postulated as shown in Figure 3. It is assumed that cellulose phosphate is formed after the treatment of cellulose with phosphoric acid^{6,14} and that the extent of phosphorylation depends on the treating conditions. At temperatures below 320°C, cellulose phosphate decomposes to form intermediate compound IV by bond-breaking and bond-forming processes. Rearrangement of IV yields I. It is to be noted that the untreated cellulose could also undergo similar processes to give I, but its yield would be lower than that from the treated material.⁴

Another possibility is that phosphoric acid-treated cellulose may degrade to compound I via the formation of levoglucosan which disappears as

a result of secondary pyrolysis. If this is the case, one would expect to find a large amount of I from the pyrolysis of both levoglucosan and phosphoric acid treated levoglucosan. This, however, was not observed in our previous investigation.⁴ Since phosphoric acid-treated cellulose degrades to yield much larger amounts of *cis*-4,5-epoxy-2-pentenal than the untreated material, it appears that I plays an important role in the flame retardance of cellulose treated with phosphoric acid.

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