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Modified Synthesis and ^{1}H NMR Structure Elucidation of tert-Butyl-4,5-epoxypentanoate

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Abstract

Tert-butyl 4,5-epoxypentanoate is a key epoxide-functionalized ester that could be useful in materials development, polymer chemistry, and organic synthesis. The organic synthesis involved two main steps that is esterification of 4-pentenoic acid and selective epoxidation of the allylic double bond using a mild oxidizing agent. Ideally, this pathway produced the target epoxide in good yield. Structural confirmation and purity assessment were carried out using ^{1}H NMR spectroscopy. The ^{1}H NMR spectra displayed characteristic resonances consistent with the butyl ester group, allylic signals, and epoxide protons, aligning with the expected chemical structure. Additionally, successful ring formation and the absence of significant byproducts were confirmed through integration patterns and coupling constants. Overall, the study offers an effective synthesis route and detailed ^{1}H NMR data for tert-butyl-4,5-epoxypentanoate, serving as valuable reference information for future research and applications involving epoxide-containing esters. Furthermore, the findings of this study showed that the modified synthesis resulted in the formation of tert-butyl-4,5-epoxypentanoate in higher yield compared to previously reported literature values.

Keywords: Epoxide functionalized ester, Esterification, Epoxidation, ^{1}H NMR.

Introduction

Carboxylic acids are commonly present in structures during chemical synthesis and pharmaceutical development. They are often protected and deprotected in multiple steps of synthetic procedures. Esters, which derive from carboxylic acids, are frequently used as protecting groups for the carboxyl functional group. Due to their stability against nucleophilic attack and their straightforward cleavage, converting a carboxylic acid into a tert-butyl ester is a particularly useful method in synthesis (1).

Various methods are commonly used to prepare tert-butyl esters. These include reacting a carboxylic acid chloride with t-butanol in pyridine or with an alkali metal t-butoxide. Other techniques involve combining a carboxylic acid

with a t-butyl halide or tert-butoxy carbonyl (BOC) anhydride, or converting a carboxylic acid *S*-2-pyridinyl ester with t-butanol. Additional approaches consist of oxidizing an aldehyde in t-butanol, reacting a carboxylic acid with DMF di-t-butyl acetal or t-butyl isourea, and directly forming the ester from a carboxylic acid with t-butanol using 1,1'-carbonyldiimidazole, a carbodiimide [2].

Traditional methods for synthesizing tert-butyl esters usually involve reacting the corresponding carboxylic acids with isobutene in the presence of a strong acid, such as concentrated sulfuric acid. Alternatively, they can be prepared by converting acids to acid chlorides using thionyl chloride, then treating these chlorides with excess tert-butanol and triethylamine. More recent techniques employ 1-(3-dimethylaminopropyl)-3 ethyl carbodiimide and 4-dimethylaminopyridine to facilitate the esterification of carboxylic acids with tert-butanol [3]. Esters play an important role in producing useful chemicals, such as polymers, perfumes, and fatty acids, making them vital to the chemical and pharmaceutical industries. Approximately 25% of all chemical processes are dedicated to pharmaceutical manufacturing. Given these applications, esterification of carboxylic acids is a key and widespread step in organic synthesis. Consequently, numerous chemical methods have been developed to perform this essential transformation [4].

Significant progress has been achieved in developing various mild esterification techniques. Esterification of carboxylic acids is a well-established reaction commonly used in the synthesis and modification of many natural compounds [5]. Although the epoxidation of double bonds is well documented, the ester of unsaturated carboxylic acids has not been reported. Depending on the reaction conditions and the peracids employed, the process may yield either an epoxide or a glycol [6].

This report details the synthesis of tert-butyl-4-pentenoate from 4-pentenoic acid, utilizing 4-Dimethylaminopyridine (DMAP), dry tetrahydrofuran (THF) and BOC anhydride. It then describes the formation of tert-butyl-4,5-epoxypentanoate in higher yield compared to previously reported values [7] through the epoxidation of tert-butyl pent-4-enoate using meta-chloroperoxybenzoic acid (m-CPBA), followed by characterization using a ^{1}H NMR spectrometer at 400 MHz to verify its structure and purity.

Materials and Methods

Reagents

The list includes 4-Pentenoic acid, 4-Dimethylaminopyridine (DMAP), dry tetrahydrofuran (THF), tert-butoxy carbonyl (BOC) anhydride, dichloromethane (DCM), hydrochloric acid (HCl), distilled water, meta-chloroperoxybenzoic acid (m-CPBA), sodium hydrogen thiocarbonate ($NaHCO_3$), magnesium sulphate ($MgSO_4$), sodium thiosulfate ($Na_2S_2O_3$), and tetrahydrofuran (THF).

Experimental

Synthesis of tert-butyl pent-4-enoate (Esterification)

The method was adopted from a patent published by WIPO, the World Intellectual Property Organization [8] with slight modifications. The modifications include using dry THF as a solvent, using ^{1}HNMR to confirm chemical shift in the structure of the compound after 4 hours of the reaction before addition of tert-butanol, carrying out the reaction under Nitrogen atmosphere and all the work up procedure.

In a dry, clean round-bottom flask, 1.00 g of 4-pentenoic acid (1 equivalent, 0.00999 moles) was added. Next, 1.71 g of DMAP (1.40 equivalents, 0.014 moles) was incorporated, followed by 3 mL of dry THF. The mixture was stirred for 30 minutes before being transferred to the system, where 4.67 g of BOC anhydride (2.14 equivalents, 0.021 moles) was added dropwise under a Nitrogen atmosphere. The reaction was stirred for 4 hours, after which a ^{1}H NMR was performed to check for any chemical shift changes. Then, 5.0 mL of tert-butanol was added, and the mixture was stirred for 16 hours. The product was formed as brown oily liquid. Finally, ^{1}H NMR was used again to confirm the formation of the desired chemical structure. The reaction was carried out at room temperature.

Work Up

The product from the above procedure was dissolved in 200 mL of DCM, transferred to a separating funnel, and washed five times with 100 mL of 2.00 M HCl solution. TLC was employed to assess the purification level. Subsequently, it was distilled using a rotary evaporator. ^{1}H NMR confirmed the product's purity and structure. The actual yield obtained was 1.53 g, the theoretical yield was 1.56 g (% yield is 98%).

Synthesis of tert-butyl-4,5-epoxypentanoate (Epoxidation)

The method was adapted from the one described by [7].

In a clean, dry round-bottomed flask, 1.53 g of tert-butyl pent-4-enoate from the previous step was dissolved in 5 mL of DCM. The mixture was cooled to 20 °C. Meanwhile, 3.5 g of m-CPBA was dissolved in 20 mL of DCM and added dropwise to the cooled mixture with vigorous stirring. The reaction was heated for 48 hours, then cooled to 0.0 °C, and aqueous $NaHCO_3$ was added with stirring. The organic layer was separated and washed three times with 100 mL of aqueous $Na_2S_2O_3$ solution. It was then extracted with 100.0 mL of aqueous $NaHCO_3$ and dried over $MgSO_4$. The product was distilled at room temperature and purified by column chromatography. Its structure and purity were verified using ^{1}H NMR. The product obtained was colorless oily liquid. The actual yield

obtained was 1.40 g, the theoretical yield was 1.81 g (% yield of 77%).

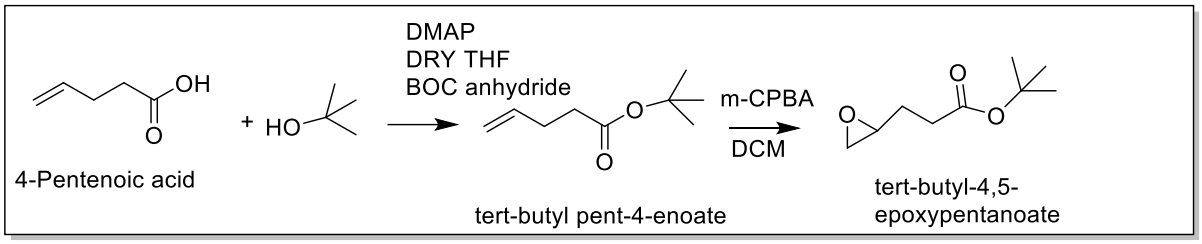


Figure1.Chemical reaction equation of the formation of tert-butyl-4,5-epoxypentanoate

Result and Discussion

Result

^{1}H NMR result of synthesis of tert-butyl pent-4-enoate

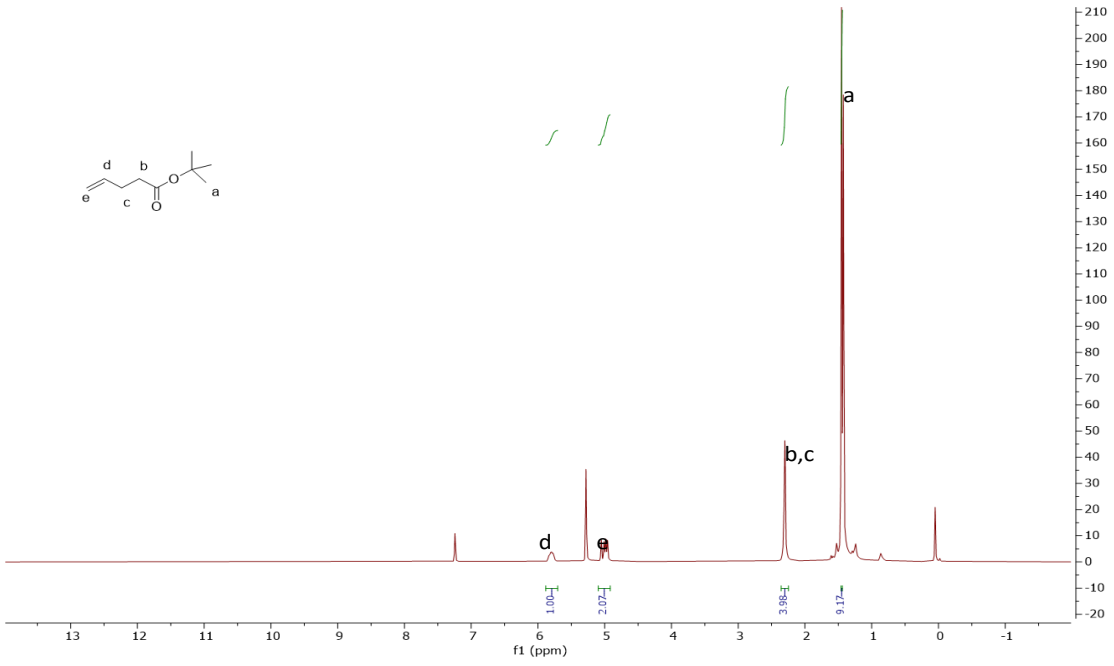


Figure 2: ^{1}H NMR spectra of tert-butyl pent-4-enoate

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78 (m, 1 H), 4.97 (m, 2 H), 2.28 (m, 4 H), 1.45 (s, 9 H, $C(CH_3)_3$).

3.1.2 ^{1}H NMR result of synthesis tert-butyl-4,5-epoxypentanoate

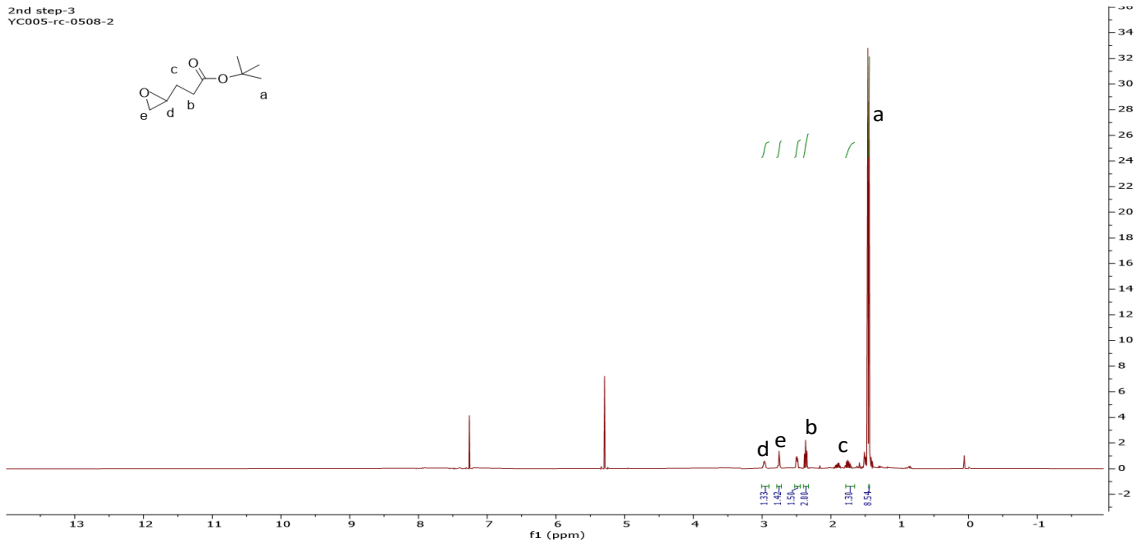


Figure 3: ^{1}H NMR spectra of butyl-4,5-epoxypentanoate

^{1}H NMR (400 MHz, $CDCl_3$) : δ 2.97 (m, 1H, CH epoxide), 2.74 (m, 1H, CH_2 epoxide), 2.45 (dd, J=5.1, 2.7 Hz, 1H, CH_2 epoxide), 2.34 (t, J=7.4 Hz, 2H, CH_2-CH_2-C=O), 1.72 (dtd, J=11.0, 7.3, 5.5 Hz, 2H, CH_2-CH_2-C=O), 1.44 (s, 9H, O-C-$(CH_3)_3$).

Discussion

3.2.1 Discussion of ^{1}H NMR result of synthesis of tert-butyl pent-4-enoate

The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) exhibits resonances consistent with the proposed molecular structure, enabling clear assignment of the major proton environments. A multiplet observed at δ 5.78 ppm, representing a single proton, probably originates from a vinylic methine (–CH=) proton. This downfield resonance suggests deshielding due to the nearby π-electron system and possibly an adjacent electron-withdrawing group. Its multiplicity indicates coupling with neighbouring vinylic or allylic protons.

The resonance at δ 4.97 ppm is a multiplet integrating for two protons and is attributed to vinylic methylene (=CH_2) protons. This chemical shift is typical for terminal alkene protons, and the multiplet pattern suggests coupling with the neighbouring vinylic methine proton. A multiplet at δ 2.28 ppm, integrating for four protons,

indicates two equivalent methylene groups (–CH_2–). These protons are likely located at an allylic position or adjacent to a carbonyl or epoxide group, which accounts for their slight deshielding relative to standard aliphatic methylene protons.

The intense singlet at δ 1.45 ppm, representing nine protons, indicates a tert-butyl group [$C(CH_3)_3$]. Its singlet form confirms that the three methyl groups are equivalent and that there is no vicinal proton coupling. Additionally, the chemical shift aligns with a tert-butyl group linked to a heteroatom or an electron-withdrawing group.

Overall, the observed chemical shifts, integrations, and multiplicities in the ^1H NMR spectrum align well with the expected proton environments of the target compound, confirming the successful formation of the proposed structure. The ^1H NMR spectrum (400 MHz, $CDCl_3$) provides clear evidence for distinct structural fragments that can be individually assigned and then assembled to support the proposed molecular framework.

Vinylic fragment (–$CH=CH_2$)

The signal at δ 5.78 ppm (multiplet, ^1H) is attributed to a vinylic methine proton (–CH=). Its downfield position is typical of a proton attached to an sp^2 carbon within a C=C bond and affected by conjugation with an adjacent functional group. The multiplet pattern suggests scalar coupling with neighbouring vinylic protons. In addition, the multiplet at δ 4.97 ppm, integrating for 2 protons, corresponds to a vinylic methylene (=CH_2). The chemical shift range and integration are consistent with those of terminal alkene protons. Coupling between the methine (δ 5.78 ppm) and methylene (δ 4.97 ppm) protons indicates a –$CH=CH_2$ unit, confirming a terminal olefin fragment molecule.

Allylic methylene fragment (–CH_2–CH_2–)

The peak at δ 2.28 ppm, corresponding to four protons, is assigned to two methylene groups. Its downfield shift relative to typical saturated aliphatic methylene signals (δ around 1.2–1.6 ppm) indicates deshielding due to proximity to unsaturated carbons or heteroatoms. The total integration of 4H and the multiplet pattern suggest a –CH_2–CH_2– fragment, most likely situated next to a vinylic system (allylic position), and involved in coupling with nearby alkene protons.

tert-butyl fragment [$C(CH_3)_3$

The sharp singlet at δ 1.45 ppm integrating for nine protons clearly indicates a tert-butyl group. The singlet and integration reflect the equivalence of the three methyl groups. Additionally, the chemical shift suggests that the tert-butyl group is attached to an electron-withdrawing substituent, such as an ester oxygen or a heteroatom, rather than to an elemental alkyl carbon.

Assembly of fragments into the proposed stru cture

Overall, the spectral data reveal three main fragments: a terminal alkene (–CH=CH_2), an allylic –CH_2–CH_2– linker, and a tert-butyl group. The coupling between the vinylic methine and methylene protons confirms their direct connection. Meanwhile, the deshielded methylene protons at δ 2.28 ppm suggest that this saturated chain is attached to the unsaturated portion. The singlet for the tert-butyl group, which shows no coupling, indicates that it is connected via a quaternary carbon or a heteroatom, consistent with a protecting or ester group in the proposed structure. The logical arrangement of these fragments connecting the terminal alkene through an allylic chain to a tert-butyl substituted functional group provides strong spectroscopic evidence supporting the molecular structure and confirms the formation of the intended compound. These findings closely match the results obtained in reference [7].

Discussion of ^{1}H NMR result of synthesis of tert-butyl-4,5-epoxypentanoate

The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) offers detailed information on the proton environments in a chain containing an epoxide and connected to a tert-butyl–substituted carbonyl fragment. Each signal can be logically assigned, collectively confirming the proposed structure. The signals between δ 2.97 and 2.45 ppm indicate the presence of an epoxide group. The multiplet at δ 2.97 ppm, which corresponds to one proton, is attributed to the epoxide methine (CH) proton. Its relatively downfield position is due to the strong deshielding effect of the neighbouring epoxide oxygen atoms and the ring strain of the three-membered ring. The complex pattern of this signal results from vicinal coupling with the two non-equivalent methylene protons on the epoxide ring.

The resonances at δ 2.74 ppm (multiplet, 1H) and δ 2.45 ppm (doublet of doublets, J = 5.1, 2.7 Hz, 1H) correspond to the diastrophic methylene (CH_2) protons of the epoxide. Their non-equivalence arises from the asymmetric environment caused by substitution on the epoxide ring. The doublet of doublets observed for one of these protons indicates coupling with both the epoxide methine proton and its geminal partner, which aligns with typical coupling patterns in substituted oxirane systems. Collectively, these signals confirm the presence of an intact epoxide ring.

The signal at δ 2.34 ppm (J = 7.4 Hz), integrating for two protons, is assigned to a methylene group next to another methylene in a saturated chain (–CH_2–CH_2–C=O). The more downfield chemical shift indicates deshielding from the nearby carbonyl, and the clear triplet pattern reflects coupling to the adjacent methylene. The resonance at δ 1.72 ppm appears as a dtd (J = 11.0, 7.3, 5.5 Hz), accounting for two protons, and is attributed to the methylene group next to the chain, further from the carbonyl (–CH_2–CH_2–

C=O). Its more upfield position compared to the δ 2.34 ppm signal indicates a weaker influence from the carbonyl. Additionally, the complex splitting pattern arises from coupling to neighbouring methylene protons and from long-range interactions within the chain.

Finally, the distinct singlet at δ 1.44 ppm, integrating for nine protons, indicates a tert-butyl group [O–C(CH_3)$_3$]. This singlet confirms that the three methyl groups are equivalent and that there is no vicinal proton coupling. Its chemical shift is consistent with a tert-butyl group linked via an oxygen atom, a feature typical of tert-butyl esters or protecting groups.

In summary, the resonances specific to the epoxide (δ 2.97–2.45 ppm), the methylene signals linked to a carbonyl-bearing alkyl chain (δ 2.34 and 1.72 ppm), and the characteristic tert-butyl singlet at δ 1.44 ppm together strongly support the proposed molecular structure. The observed chemical shifts, integrations, and coupling constants are consistent with a carbon chain bearing an epoxide substituent and a tert–butyl protected carbonyl group. The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) enables decomposition of the molecule into clear structural fragments, which can then be connected logically to support the proposed overall structure.

Epoxide fragment

The resonance signals between δ 2.97 and 2.45 ppm indicate the presence of a substituted epoxide (oxirane) ring. The multiplet at δ 2.97 ppm (1H) is assigned to the epoxide methine (CH) proton. Protons attached to epoxide carbons usually appear in the δ 2.5–3.5 ppm range because of the strong deshielding from the electronegative oxygen atoms and the ring strain in this three-membered structure. The multiplet pattern results from vicinal coupling with the two methylene protons on the epoxide ring.

The signals at δ 2.74 ppm (multiplet, 1H) and δ 2.45 ppm (doublet of doublets, J = 5.1, 2.7 Hz, 1H) represent the two diastereotopic protons of the epoxide methylene (CH_2) group. Their chemical non-equivalence results from asymmetric substitution on the epoxide ring. The doublet of doublets observed aligns with geminal coupling and vicinal coupling to the epoxide methine proton. Collectively, these three resonances (one CH and two CH_2 protons) clearly indicate an intact epoxide fragment.

Alkyl–carbonyl chain fragment

Two further signals identify a –CH_2–CH_2–C=O segment linking the epoxide to a carbonyl group. The triplet at δ 2.34 ppm (J = 7.4 Hz, 2H) is ascribed to the methylene adjacent to the carbonyl (–CH_2–C=O). Its downfield position results from deshielding by the nearby carbonyl group, and the triplet pattern indicates that it couples to an adjacent methylene group. The signal at δ 1.72 ppm (dtd, J = 11.0, 7.3, 5.5 Hz, 2H) corresponds to the β-methylene group (–CH_2–CH_2–C=O). Its more shielded position compared to the α-methylene reflects its greater distance from the

carbonyl. The complex splitting pattern results from coupling with both the α-methylene protons and neighbouring protons on the epoxide-bearing chain. Together, these signals confirm the presence of a contiguous $–CH_2–CH_2–$ segment ending at a carbonyl group.

Tert-butyl fragment

The intense singlet at δ 1.44 ppm, accounting for nine protons, indicates a tert-butyl group bond to an oxygen atom [$O–C(CH_3)_3$]. This singlet verifies that the three methyl groups are equivalent and that there is no vicinal proton coupling. The chemical shift is consistent with a tert-butyl group linked via an oxygen atom, typical of a tert-butyl ester.

Assembly of fragments into the proposed structure

When these fragments are connected, a consistent molecular structure appears. The epoxide fragment is attached to an alkyl chain, as shown by the coupling patterns and the chemical shifts of the epoxide and β-methylene protons. This chain continues to a carbonyl group, confirmed by an α-methylene signal at δ 2.34 ppm. The carbonyl group is further substituted with a tert-butyl group via an oxygen atom, indicated by the distinctive tert-butyl singlet.

The spectrum indicates a structure with an epoxide-substituted alkyl chain ending in a tert-butyl ester. Consistent chemical shifts, integrations, and coupling constants across all proton environments strongly support the proposed molecular structure. These results closely align with those reported by [7].

Conclusion

This study successfully synthesized tert-butyl-4,5-epoxypentanoate in high yield by esterifying 4-pentenoic acid, followed by selective epoxidation of the resulting tert-butyl pent-4-enoate. Although m-CPBA effectively facilitated clean epoxidation of the allylic double bond under mild conditions, the modified esterification method using DMAP, dry THF, and BOC anhydride proved to be an efficient route to produce the ester intermediate. ^1H NMR spectroscopy suggest the structure through distinctive resonances indicative of the epoxide ring and butyl ester framework, with integration and coupling constants aligning with the expected molecular structure. The pathway's success was further supported by the absence of significant contaminants. Overall, this work demonstrates a reliable, high-yield process for preparing tert-butyl-4,5-epoxypentanoate and provides detailed spectroscopic data, serving as a valuable resource for future research involving epoxide-functionalized esters in synthetic, materials, and application-driven studies.

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