

**STEREOSPECIFIC SYNTHESIS OF *trans*-*t*-BUTYL β -METHYL - β -
(*p*-BROMOPHENYL)-GLYCIDATE AND ITS PYROLYSIS**

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trans-*t*-Butyl β -(*p*-bromophenyl)-glycidate has been synthesised by the stereospecific epoxidation of the unsaturated ester (V) using *m*-chloroperbenzoic acid. The *trans*-configuration was assigned on the basis of spectral analysis and comparison with the similar product obtained in the Darzens condensation. The ester on pyrolysis yields a -methyl- α -(*p*-bromophenyl) acetaldehyde.

The Darzens condensation is a base-promoted reaction between an aldehyde or ketone and a α -halo ester to yield an α , β -epoxy compound¹. This reaction often yields a mixture of isomeric *cis*- and *trans*-glycidates in varying proportions. The separation of the mixture into the individual components is sometime difficult. We needed the *trans*-glycidate for comparison with the isomers separated from a mixture of the Darzens reaction. For this purpose a scheme has been devised (Fig. 1) for the exclusive synthesis of *trans*-*t*-butyl β -methyl- β -(*p*-bromophenyl)-glycidate (VI). This ester on pyrolysis produces a higher aldehyde which was characterized by elemental and spectral analysis.

EXPERIMENTAL

All the boiling points and melting points are uncorrected. Infrared spectra were taken with a *Hilger and Watts H 800 spectrophotometer* as liquid films for liquids and *KBr* pellet for solids. NMR spectra were recorded on 60 MHz (Chemical Shifts in δ ppm) using $CDCl_3$ as solvent.

p-Bromoacetophenone (I): This compound was prepared by condensing bromobenzene (78.5 g; 0.5 mole) with acetic anhydride (48 ml) and anhydrous $AlCl_3$ (160 g; 1.23 mole) in dry CS_2 (200 ml) in 61.3% yield and had b.p. 100—103°/4.5 mm (lit.² b. p. 117°/7 mm).

Ethyl β -methyl- β -(*p*-bromophenyl)- β -hydroxy propionate^{3,4} (II) :

A mixture of *p*-bromo acetophenone (80 g; 0.402 mole) and ethyl α -bromoacetate (100g; 0.59 mole) and dry benzene (400 ml) was placed in a separatory funnel inserted in one opening of a three necked R. B. flask (11) fitted with a mechanical stirrer and a reflux condenser, containing activated zinc dust (40 g). About 50 ml of the mixture was added to the zinc dust and the contents heated on a steam bath until the reaction commenced; a vigorous reaction took place when a few crystals of iodine were added. The mixture was stirred and the remainder of the solution was added at such a rate that gentle refluxing took place. After the addition was complete, stirring and refluxing were continued for an additional period of 3 hr. After the usual workup, the product was distilled to give a colourless oil, b.p. 156—58°/2 mm. n_D^{32} 1.5265. Found : C, 49.92; H, 5.00. $C_{12}H_{15}O_3 Br$ requires : C, 50.17; H, 5.23% IR : 3560 (O-H); 1722 (C=O).

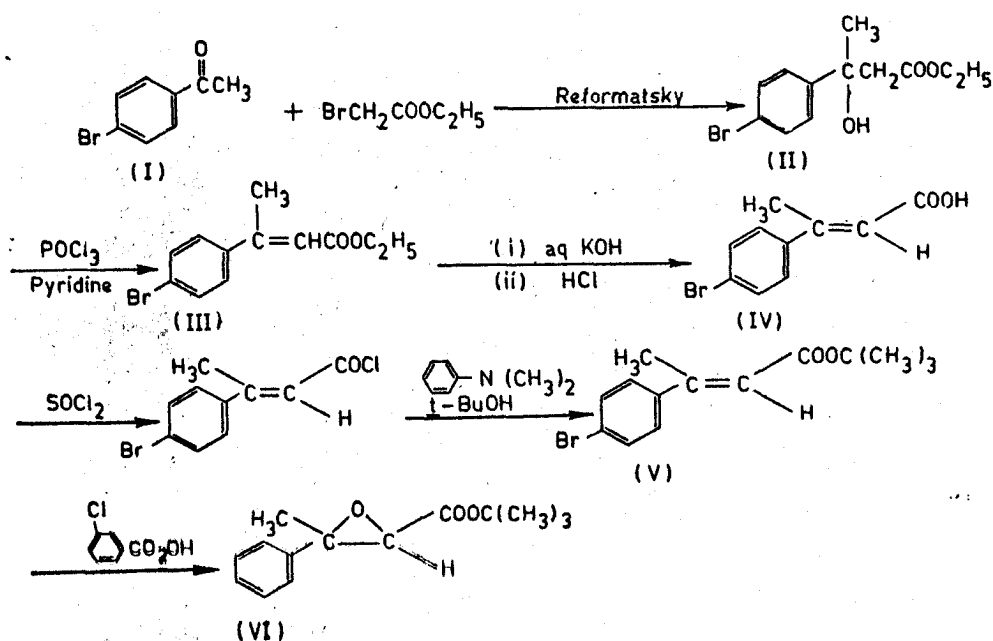


FIG. 1—A Scheme for the synthesis of *trans*-*t*-butyl- β methyl- β (*p*-bromophenyl) glycidate.

Ethyl p-bromo-β-methyl cinnamate (III) :

The hydroxy ester (II, 28.6 g; 0.1 mole) and $POCl_3$ (25 g; 0.15 mole) in 100 ml of pyridine were taken in a RB 250 ml flask fitted with a reflux condenser. The reaction mixture was then refluxed for 3 hours and left over-night at room temperature and after usual workup the solution was dried over anhydrous sodium sulphate and then concentrated. Distillation afforded 24.67 g (90%) of the product, b.p. 135-6°/1 mm (lit.³ b.p. 160-5°/3 mm). n_D^{25} 1.5995. Found : C, 53.31; H, 4.88, $C_{12}H_{13}O_2Br$ requires C, 53.12; H, 4.83%. IR : 1722 (C=O); 1635 (—C=C—).

trans-p-Bromo-β-methylcinnamic acid (IV) :

In a RB flask (250 ml) fitted with a reflux condenser, aq. KOH (150 ml, 10%) and the ester (III; 15 g; 0.62 mole) were added and the contents refluxed for 12 hr. The mixture was poured into hydrochloric acid, 15%, and the precipitated acid was filtered on a Buchner funnel and washed with water. The crude product was crystallized from ethanol to yield 12 g (89.6%) of a colourless solid, m. p. 145-46°. Found : C, 49.60; H, 3.81. $C_{10}H_9O_2Br$ requires C, 49.79; H, 3.37%.

trans-t-Butyl-p-bromo-β-methyl cinnamate (V) :

A mixture of *trans-p*-bromo-β-methylcinnamic acid (IV; 10 g; 0.42 mole) and freshly distilled thionyl chloride (30 g; 0.124 mole) was heated on a water bath until the evolution of HCl ceased. The crude acid chloride was used as such for the subsequent preparation.

trans-p-Bromo-β-methylcinnamoyl chloride (11.43 g; 0.42 mole) was taken in a flask fitted with a reflux condenser and dropping funnel; freshly distilled N,N-dimethylaniline (10 g) was added dropwise followed by dry *t*-butanol (31.08 g; 0.242 mole) with continuous stirring. The reaction mixture was stirred for 10 hr at room temperature and refluxed gently for an additional period of 14 hr. After the usual workup the residue on distillation afforded 10 g (81%) of the product, b. p. 150-55°/3mm. n_D^{25} 1.665. Found : C, 56.50; H, 5.29. $C_{14}H_{17}O_2Br$ requires C, 56.57; H, 5.72%. IR : 1715 (C=O); 1630 (—C=C—) NMR : 1.533 (s, 9H, —C(CH₃)₃ protons); 2.5 (s, 3H, CH₃ protons); 6.033 (s, 1H, CH proton); 7.408 (m, 4H, aromatic protons).

Epoxidation of trans-t-butyl-p-bromo-β-methyl cinnamate (V) :

To a solution of the ester (V; 2g; 0.0067 mole) in 50 ml of dry CH_2Cl_2 (50 ml) was added *m*-chloro perbenzoic acid (2.4 g; 0.0139 mole) in dry CH_2Cl_2 (100 ml) and the mixture refluxed for 70 hr. The contents were cooled and the solid precipitated was removed by filtration. The remaining solution was treated with aqueous sodium bicarbonate and then with saturated sodium chloride solution and dried over anhydrous sodium sulphate. The semi solid obtained on concentration was crystallized from hexane to yield the ester VI in 42.7% yield, m.p. 61-62° (lit.⁵ m. p. 60-62°). Found : C, 54.08; H, 5.54. $C_{14}H_{17}O_3Br$ requires C, 53.67; H, 5.43%. IR : 1750 (C=O) NMR : 1.51 (s, 9H, —C(CH₃)₃ protons); 1.74 (s) CH₃ protons); 3.29 (s, 1H, CH proton); 7.275 (m, 4H, aromatic protons).

Pyrolysis of ester (VI) :

The pyrolysis tube made of pyrex glass was filled completely with glass beads. The ester (VI, 1g) was dissolved in *n*-hexane (35 ml) and pyrolysed at a rate of 16 drops/min in nitrogen atmosphere, maintaining the temperature between 360—380°. The pyrolysate was collected in ether and the solution washed with aqueous sodium bicarbonate followed by water. It was dried, concentrated and distilled at 140—141.5°/18 mm to give colourless α -methyl- α -(*p*-bromophenyl) acetaldehyde (0.4 g). n_D^{30} 1.5715. Found : C, 50.61; H, 4.41. C_9H_9OBr requires C, 50.7; H, 4.23%. IR : (KBr pellet), 1740 (C=O, aldehyde).

Its 2,4-DNP derivative after purification melted at 124—126°. Found : C, 45.68; H, 3.20; N, 14.40. $C_{15}H_{13}N_4O_4Br$ requires C, 45.80; H, 3.30; N, 14.25%.

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