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Synthesis of 2-Amino-5-Aryl-4-Oxo-4,5-Dihydrothiazole

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When α,β-dibromocinnamates were subjected to condensation with thiourea substituted dihydrothiazole compounds were found to be formed.

INTRODUCTION

2-Aminothiazoles and 2-amionobenzothiazoles constitute the largest and the best known class of thiazoles. They are particularly important because of the ease of synthesis and the facility with which they can be transformed into other derivatives.

Earlier workers[1] synthesised various cinnamates through tedious procedures. Those procedures were time consuming and laborious also. This work involves the synthesis of various cinnamates in a simple method, followed by bromination and condensation.

EXPERIMENTAL

To 0.025 mole of phosphorous pentachloride was added 0.035 mole of cinnamic acid. The contents on thoroughly mixing gave a clear solution of cinnamoyl chloride. To this cinnamoyl chloride, phenol (0.04 mol) was added with constant stirring. The reaction mixture was dissolved in alcohol, cooled and poured into water. The precipitated crude product was recrystallised from alcohol. Cinnamates thus prepared are presented in Table 1.

TABLE 1
ARYL CINNAMATES

No.	Compound	m.p. (°C)	Yield (%)
1.	Phenylcinnamate	70	70
2.	*m*-Cresylcinnamate	59–60	65
3.	*p*-Cresylcinnamate	90	67

The cinnamates prepared by the above method were subjected to bromine addition with equimolar amount of bromine in acetic acid. The resulting products were found to be the corresponding α,β-dibromocinnamates. These dibromocinnamates are presented in Table 2.

TABLE 2
α,β-DIBROMOARYLCINNAMATE

No.	Compound	m.p. (°C)	Yield (%)
1.	α,β-Dibromophenylcinnamate	123	62
2.	α,β-Dibromo-*m*-cresylcinnamate	72	54
3.	α,β-Dibromo-*p*-cresylcinnamate	111	56.6

The above dibromocinnamates (0.0025 mol) in absolute ethanol (20 mL) were refluxed with thiourea (0.005 mol) for 3 h over water bath[2]. The residue obtained after the evaporation of the solvent was stirred with saturated potassiumcarbonate (120 mL) for 1 h. The solid thus obtained was filtered, washed well with water, dried and recrystallised from ethanol to give a single product which was confirmed with TLC.

RESULTS AND DISCUSSION

Though different cinnamates were employed, the product obtained was found to be the same. This was confirmed with mixed melting point, TLC, IR and NMR spectral data.

The IR and NMR spectral data confirm the compound to be 2-amino-5-(ω-bromobenzyl)-4-oxo-4,5-dihydrothiazole (Fig. 1). The plausible mechanism, may be formulated as shown in Fig. 2. The driving force for the isomerisation in the last step may be conjugation of the double bond with C^{4-} carbonyl group.

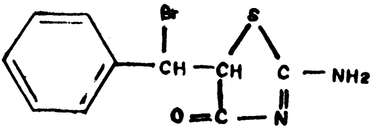

Fig. 1

The IR spectrum of the compound shows an absorption band near 1710 cm^{-1} due to the >C=O stretching frequency and another band at 3000 cm^{-1} due to —NH stretching frequency. NMR spectrum shows four signals at 2.2δ (s, 2H), 6.3δ (d, 1H, J = 15 Hz), 7.0δ (m, 5H) and 7.5δ (d, 1H, J = 15 Hz).

The signal at 2.0δ accounts for the amino protons. The signal at 6.3δ accounts for the C_5-proton and 7.5δ accounts for benzyl proton. This is confirmed by the same coupling constant *viz.* 15 Hz. The multiplet centering at 7.0δ accounts for the five aromatic protons.

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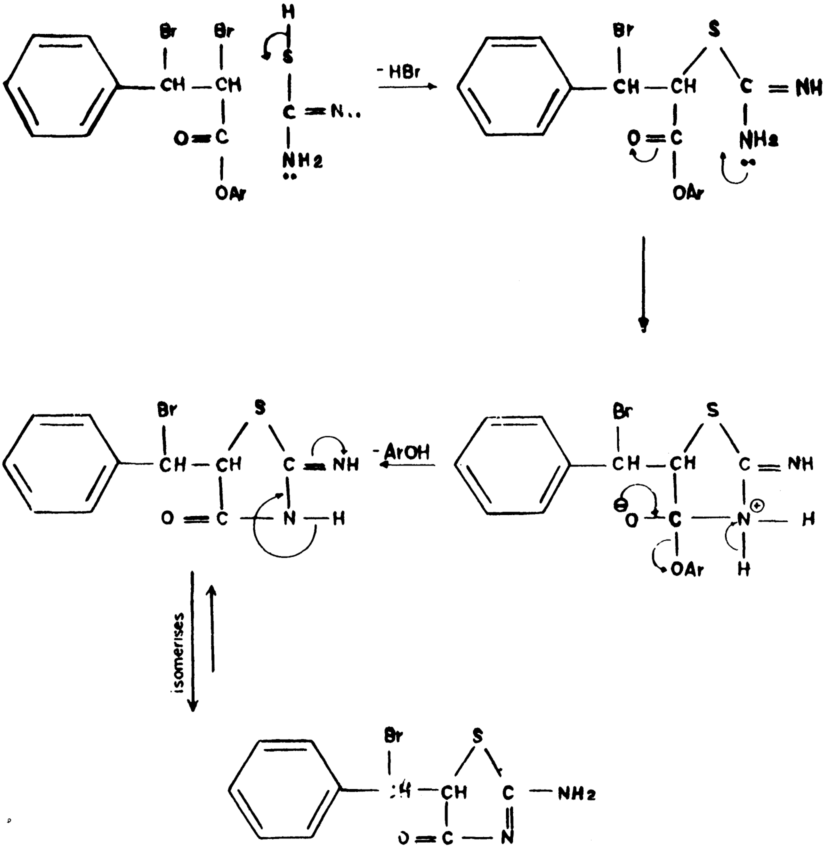

Fig. 2

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