is known that compounds of type 2 fragment extensively\(^2\) at 70 eV and the molecular ions may not be observed. In view of the above, the reaction was repeated under typical conditions reported\(^1\), using piperidine as the base. A product with the same m.p. and other data reported for 1 was obtained. However, the \(^{13}\)C NMR spectrum of the product showed two upfield signals at \(\delta\) 29.1(t) and 54.2(d) only, suggesting that the structure of the product is 2 and not 1. In fact, the mass spectrum recorded in CI mode using methane as ionizing gas gave the ion at m/z 461, corresponding to \((M + H)^+\) of 2.

From the foregoing, it is necessary to revise the structure of the product in the title reaction to 2. It is interesting to note that the reaction of dibenzoylmethane and formaldehyde in ether in presence of diethylamine was reported to give 1,1-dibenzoylethylene\(^5\), but revised latter to 2\(^3\). \(^4\). Formation of 2 was also favoured by Lieberman and Wagner\(^6\) in both acid- and base-catalysed reactions, but without any spectroscopic evidence.

**Experimental**

A mixture of 1,3-diphenyl-1,3-propanedione (1.12 g, 0.005 mol), formaldehyde (35% aq. solution, 1 ml, 0.01 mol), piperidine (0.5 ml) and ethanol (20 ml) was heated on a steam bath for 20 min and the reaction mixture was then kept overnight at room temperature. The precipitated solid was recrystallized from ethanol.

Yield: 0.69 g (60%), m.p. 178–180°C. IR (KBr): 1688 and 1668 cm\(^{-1}\). PMR (CDCl\(_3\), 90 MHz): \(\delta\) 2.78 (t, \(J = 7.5\) Hz, 2 H), 5.75 (t, \(J = 7.5\) Hz, 2 H), 7.40–7.60 (m, 12 H), 8.05–8.20 (m, 4 H). CMR (CDCl\(_3\), 22.5 MHz): \(\delta\) 196.7 (s), 135.7 (s), 134.0 (d), 129.1 (d), 128.9 (d), 54.2 (d), 29.1 (t). Mass (CI/CH\(_4\)): m/z (%)—461 (22.2), 369 (22.2), 329 (33), 322 (28.7), 253 (29.2), 237 (100).

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**CONDENSATION PRODUCTS OF \(\beta\)-PHENYLPROPIONIC ACID WITH COMMERCIAL PPA**

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\(\beta\)-PHENYLPROPIONIC acid (I) is cyclized to indan-1-one(II) when the former is heated with commercial polyphosphoric acid at 70°C for 1.5 h. Indan-1-one is one of the starting materials for the synthesis of coumarins\(^1\) and isocoumarins\(^2\),\(^3\), two medicinally important class of compounds. During the preparation of indan-1-one by the literature method\(^1\) it was found that when the temperature is raised to 140°C keeping the reaction mixture well stirred for 3.5 h, a product characterized as anhydrobis-indan-1-one(III), is obtained. However, carrying out the
reaction at 165°C for 4.5 h, a different product characterized as anhydrotris-indene(IV), was obtained. Both III and IV are formed due to intramolecular cyclodehydration of two and three molecules of indan-1-one (II) respectively.

Anhydrobis-indan-1-one (III): β-Phenylpropionic acid (6 g) and PPA (90 g) were kept at 140°C for 3.5 h with constant stirring. The whole mass was then poured into ice-cold water. The organic portion was extracted with ether (3 × 50 ml), washed with 5% aqueous NaHCO₃ solution, water and then dried with Na₂SO₄. Removal of the solvent afforded a solid mass which upon recrystallization with ethyl acetate gave shining yellow crystals (1.97 g, 40%), m.p. 141–42°C; M⁺ 245; Found C, 87.78%; H, 5.68%; Calcd. for C₁₉H₁₄O (required: C, 87.8%; H, 5.7%).

ν_KBr max 1724, 1675, 1600, 1580, 1500, 1480 cm⁻¹
λ_MeOH max 395, 240 nm
δ ppm (CDCl₃) 3.16 (t, Ar–CH₂, –2H), 3.53

Anhydrotris-indene (IV): β-Phenylpropionic acid (4.5 g) and PPA (100 g) were kept at 165°C for 4.5 h with constant stirring followed by similar treatments as for (III) afforded deep yellow crystals, which did not melt up to 295°C, M⁺ 341; C, 94.72%; H, 5.26%; Calcd. for C₂₇H₁₈ (required C, 94.73%; H, 5.27%).

ν_KBr max 3050, 1600, 1450, 750, 700 cm⁻¹
λ_MeOH max 440 nm
δ ppm (CDCl₃) 3.8 (s, Ar–CH₂, 6H); 7.5–7.9 (complex, 12H aromatic).

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A SINGLE-STEP SYNTHESIS OF 5- AND 7-SUBSTITUTED 2-(p-BROMOBENZOYL)-3-METHYL-4H-1, 4-BENZOTHIAZINES

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SYNTHESIS of 5- and 7-substituted 2-(p-bromobenzoyl)-3-methyl-4H-1, 4-benzothiazines by the condensation and oxidative cyclization of 3- and 5-substituted 2-aminobenzenethiols with p-bromobenzoylaceton in dimethyl sulphoxide is reported.

4H-1, 4-Benzothiazines resemble phenothiazines in having a fold along nitrogen–sulphur fold, which is the structural feature responsible for biological activity¹. They constitute an interesting and important class of bioactive molecules. Some derivatives reported have been found to possess anti-inflammatory¹, antimicrobial³, anti-hypertensive⁴, anti-histaminic⁵, tranquillizer⁶, diuretic⁷, lipid regulating⁸, spasmolytic⁹, anti-bacterial¹⁰, CNS depressant¹¹ and antilucre¹² activity.

In continuation of our programme to synthesize novel bio-active molecules¹, the title compounds have been synthesized by one-pot reaction. It involves the condensation of 2-amino-3 and 5-substituted benzenethiols and p-bromobenzoylaceton in DMSO which causes oxidative cyclization. The reaction is believed to proceed via the formation of an enaminoketone. 2-Aminobenzenethiols (I) are readily oxidized to disulphides¹²,¹³ (Ia) under the experimental conditions. Disulphides (Ia) undergo condensation with β-diketones¹³,¹⁴ yielding enaminoketones which cyclize to 1,4-benzothiazines by scission of the sulphur–sulphur bond¹⁴,¹⁵ upon attack by the nucleophilic enaminoketone systems as shown in scheme 1.

p-Bromobenzoylaceton can exist in two enolic forms A and B.

CH₃-C=CH-C-C₆H₄Br-p
\|\| \|\| \|\| \|\| \|\|
OH O

CH₃-C=CH-C-C₆H₄Br-p
\|\| \|\| \|\| \|\|
O OH

From A is likely to predominate due to the electron-pushing nature of the methyl group and electron-withdrawing nature of benzene molecule, hence this form participates in the reaction.