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 δ29.1(*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): δ 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): δ 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 (33.0), 322 (28.7), 253 (29.2), 237 (100.0).

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CONDENSATION PRODUCTS OF β-PHENYLPROPIONIC ACID WITH COMMERCIAL PPA

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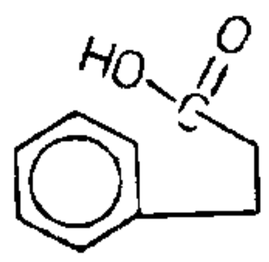
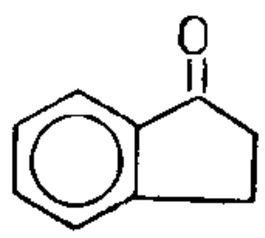
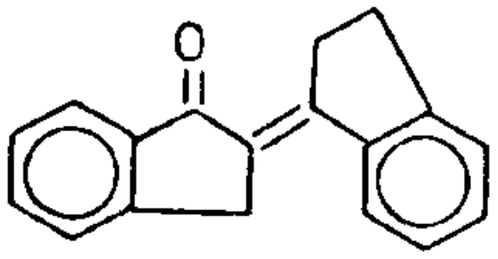
β-PHENYLPROPIONIC acid (I) is cyclized to indan–1–one(II) when the former is heated with commercial polyphosphoric acid at 70°C for 1.5 h. Indan–1–one is one of the starting materials for the synthesis of coumarins[1] and isocoumarins[2,3], two medicinally important class of compounds. During the preparation 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



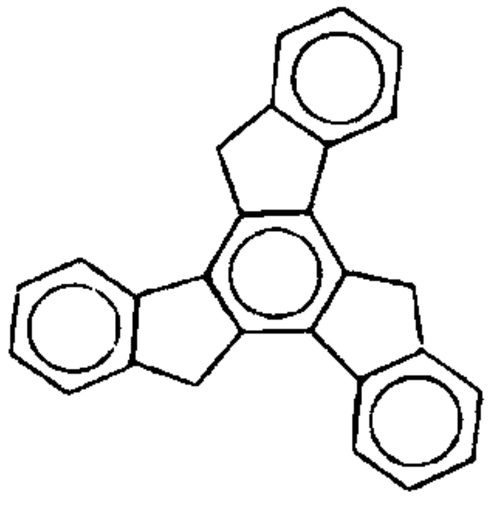
I



II



III



IV

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 intermolecular 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 $NaHCO_3$ solution, water and then dried with Na_2SO_4. 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 $C_{18}H_{14}O$ (required: C, 87.8%; H, 5.7%).

ν_{max}^{KBr} 1724, 1675, 1600, 1580, 1500, 1480 cm^{-1}

λ_{max}^{MeOH} 395, 240 nm

δ ppm ($CDCl_3$) 3.16 (*t*, Ar–CH_2, –2*H*), 3.53 (*t*, Ar–CH_2–$CH_2C{=}\dot{C}$–, –2*H*) 3.99 (*s*, Ar–CH_2–C=C, –2*H*), 7.41–7.81 (complex, 8*H*-aromatic).

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 $C_{27}H_{18}$ (required C, 94.73%; H, 5.27%).

ν_{max}^{KBr} 3050, 1600, 1450, 750, 700 cm^{-1}

λ_{max}^{MeOH} 440 nm

δ ppm ($CDCl_3$) 3.8 (*s*, Ar–CH_2–, 6*H*); 7.5–7.9 (complex, 12*H* aromatic).

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

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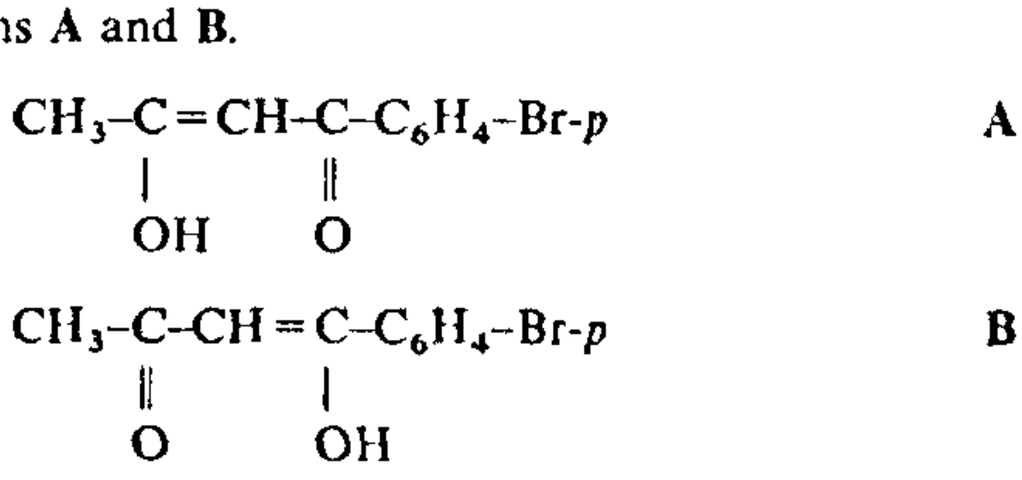
SYNTHESIS of 5- and 7-substituted 2-(*p*-bromobenzoyl)-3-methyl-4*H*-1, 4-benzothiazines by the condensation and oxidative cyclization of 3- and 5-substituted 2-aminobenzenethiols with *p*-bromobenzoylacetone in dimethyl sulphoxide is reported.

4*H*-1, 4-Benzothiazines resemble phenothiazines in having a fold along nitrogen–sulphur fold, which is the structural feature responsible for biological activity[1]. They constitute an interesting and important class of bioactive molecules. Some derivatives reported have been found to possess anti-inflammatory[2], anthelminthic[3], anti-hypertensive[4], anti-histaminic[5], tranquillizer[6], diuretic[7], lipid regulating[8], spasmolytic[9], anti-bacterial[10], CNS depressant[11] and antiulcer[12] activity.

In continuation of our programme to synthesize novel bio-active molecules[1], the title compounds have been synthesized by one-pot reaction. It involves the condensation of 2-amino-3 and 5-substituted benzenethiols and *p*-bromobenzoylacetone 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 disulphides[1,13] (Ia) under the experimental conditions. Disulphides (Ia) undergo condensation with β-diketones[13,14] yielding enaminoketones which cyclize to 1, 4-benzothiazines by scission of the sulphur–sulphur bond[1,14,15] upon attack by the nucleophilic enaminoketone systems as shown in scheme 1.

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



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.