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STUDIES ON OXYGEN HETEROCYCLES
Part 2[1]: SYNTHESIS OF 2-ARYLCOUMARANONES AND 2-PHENYLBENZOFURAN#

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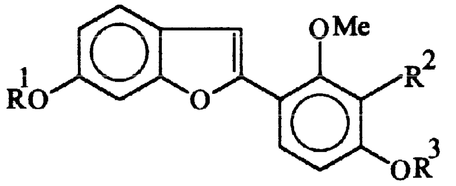
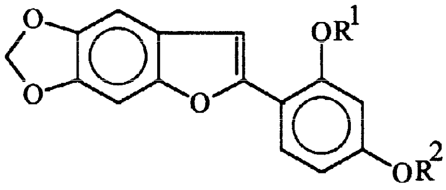
ABSTRACT: **The synthesis of 2-arylcoumaranones and 2-phenyllbenzofuran has been achieved in good yields under acid catalysed conditions from readily accessible and suitably substituted aryl α-diazo-arylmethyl ketones.** © 1999 Published by Elsevier Science Ltd. All rights reserved.

2-Arylbenzofurans constitute an important class of naturally occurring heterocycles known for their various biological activities. For example, pterofuran[2] (**1**), isopterofuran[3] (**2**), vignafuran[4] (**3**), 6-demethylvignafuran[5] (**4**), 2-(2,4-dihydroxyphenyl)-5,6-dimethoxybenzofuran[6] and moracins A-H[7-9] are of interest, since several of them have been recognised as antifungal phytoalexins. In addition to the above, the two compounds (**5, 6**) isolated from the aerial parts of *Sophora tomentosa* L., on methylation gave the dimethoxyphenylbenzofuran[10] (**7**), previously known as a degradation product of medicagol and flemichapparin-C.



1 $R^1 = H, R^2 = OH, R^3 = Me$
2 $R^1 = H, R^2 = OMe, R^3 = H$
3 $R^1 = Me, R^2 = R^3 = H$
4 $R^1 = R^2 = R^3 = H$



5 $R^1 = R^2 = H$
6 $R^1 = H, R^2 = Me$
7 $R^1 = R^2 = Me$

In connection with our interest in the synthesis of naturally occurring heterocycles,[11-13] we have reported[1] some time ago a very convenient procedure for the synthesis of 5-, 6- and 7-membered cyclic oxaketones and benzofuran by acid catalysed and photochemical reactions of some easily accessible α-diazocarbonyl compounds. We now wish to report our further studies in this area leading to some efficient synthesis of a few 2-arylcoumaranones and 2-phenylbenzofuran, although some other methodologies have been described in the literature[14-20] for the synthesis of the above compounds. The synthesis of the title compounds in the present case is based on the following retrosynthetic analysis involving the key intermediate **aryl α-diazo-arylmethyl ketones (10)** readily available from inexpensive starting materials as shown below.

Thus, in order to synthesise the desired 2-phenylcoumaranone following the above retrosynthetic pathway, we

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 # Dedicated to Professor (Mrs.) Asima Chatterjee on the occasion of her 80th Birth Anniversary.

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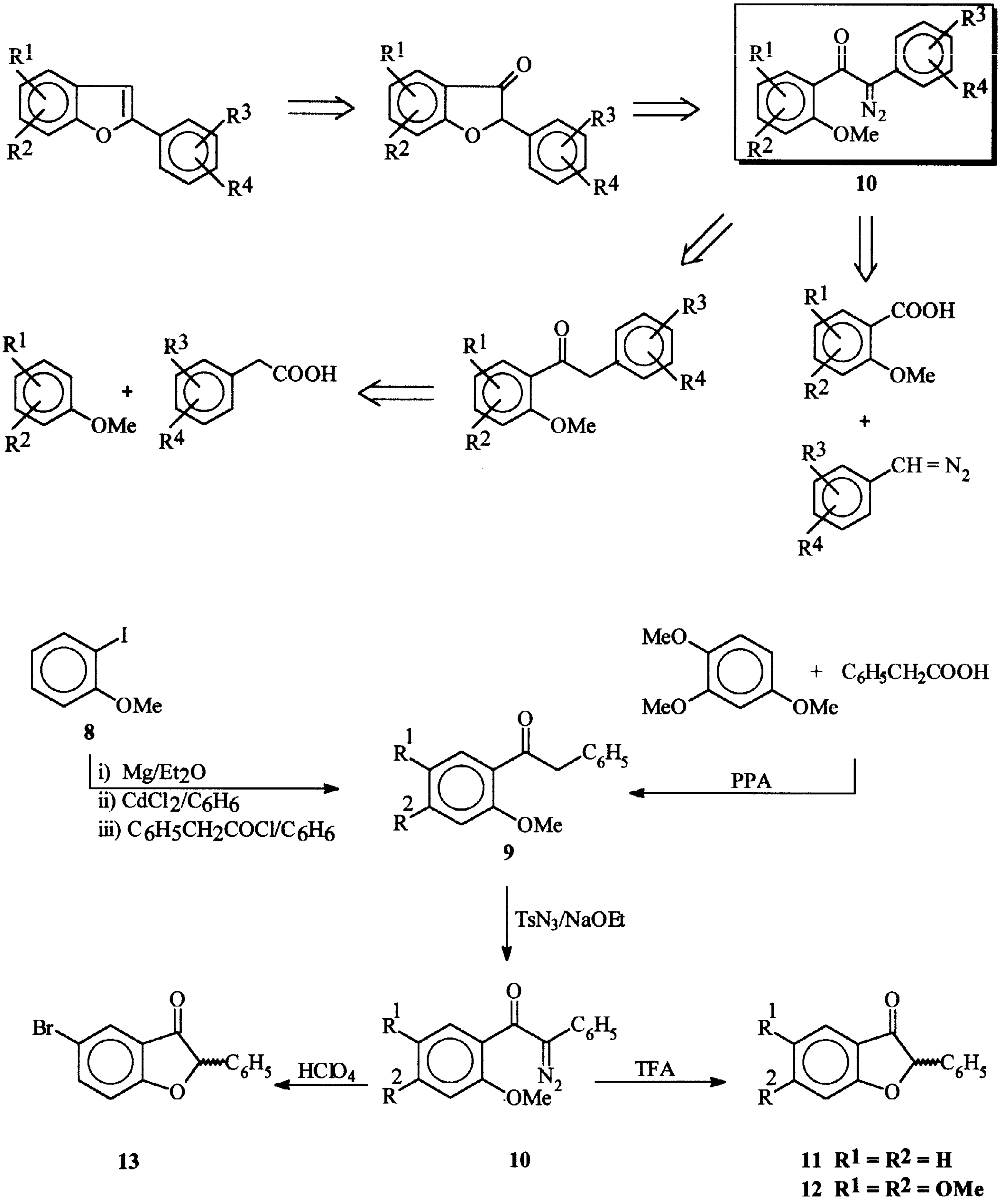
converted 2-iodoanisole (**8**) in four steps (Scheme 1) to α-diazo-α-phenyl-2-methoxyacetophenone (**10a**) and its

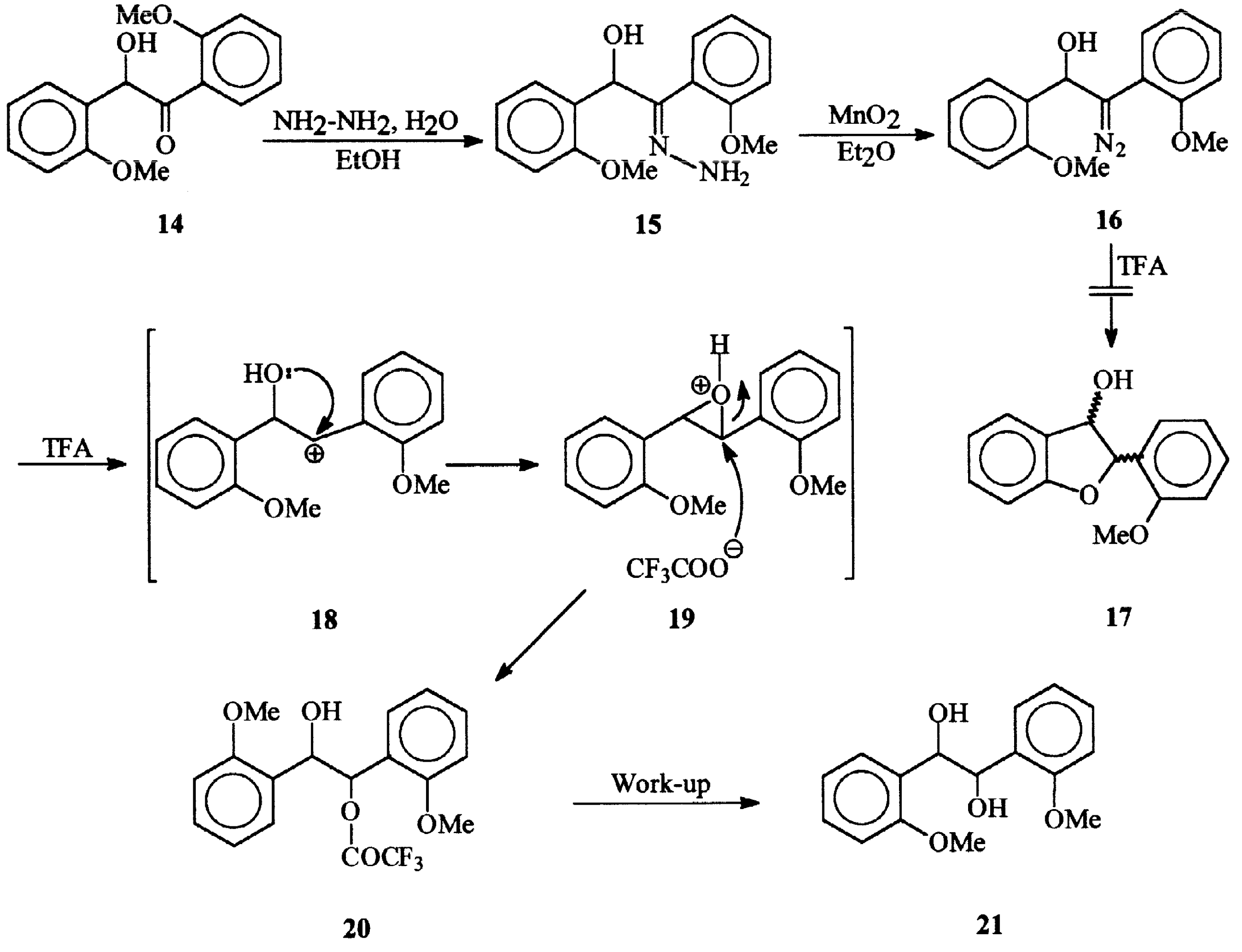


a; $R^1 = R^2 = H$ b; $R^1 = R^2 = OMe$ c; $R^1 = Br, R^2 = H$

Scheme 1

subsequent cyclisation by trifluoroacetic acid (TFA), involving the participation of the neighbouring methoxyl group onto the protonated diazocarbonyl functionality, led to a clean synthesis of 2-phenylcoumaranone **(11)**, mp. 215°C (lit.[21] mp. 220°C), ν_{max} 1725 cm^{-1}. Extension of this procedure led us to synthesise some other coumaranones **(12, 13)** in good yields. It may be pointed out that all these reactions involve the utilisation of the readily available cheap starting materials.

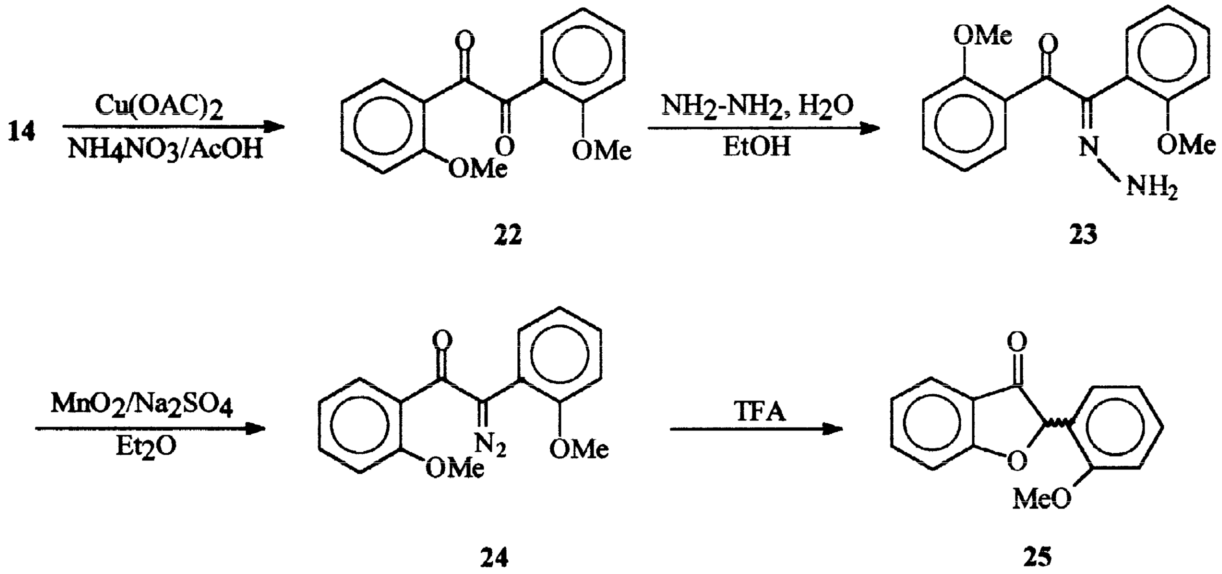
While working on this scheme, we also attempted to synthesise the diazo compound by the oxidative transformation of a hydrazone (Scheme 2), for which, we had chosen 2,2′-dimethoxybenzoin hydrazone **(15)**. The oxidation of **15** by manganese dioxide in anhydrous ether at ice-bath temperature for *ca.* 30 min afforded the unstable diazo compound **(16)**, IR (neat) ν_{max} 3300-3500, 2060 cm^{-1}, and this was immediately treated with TFA



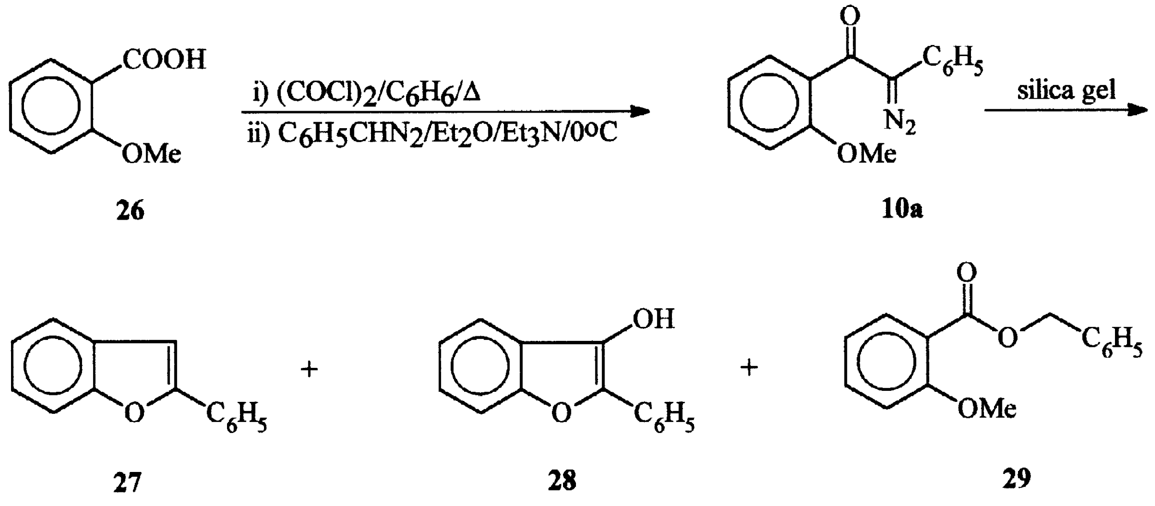
Scheme 2

at -15°C. However, it failed to give the desired 3-hydroxy-2-(2-methoxyphenyl)-2,3-dihydroxybenzofuran **(17)**. Instead, we could isolate only the dihydroxy compound **(21)** in 42% yield, probably due to the preferential attack of the adjacent hydroxyl group on the carbocation **(18)** to produce the protonated oxirane **(19)**. This was subsequently opened by the trifluoroacetate anion to **20** [IR (neat) ν_{max} 3320-3540, 1780 cm^{-1}] which on work-up afforded **21**.

We, therefore, converted the benzoin (**14**) to the corresponding benzil (**22**) and repeating the reaction under the afore-mentioned conditions, we could cleanly synthesise 2-(2-methoxyphenyl)coumaranone (**25**) in 70% yield (Scheme 3).



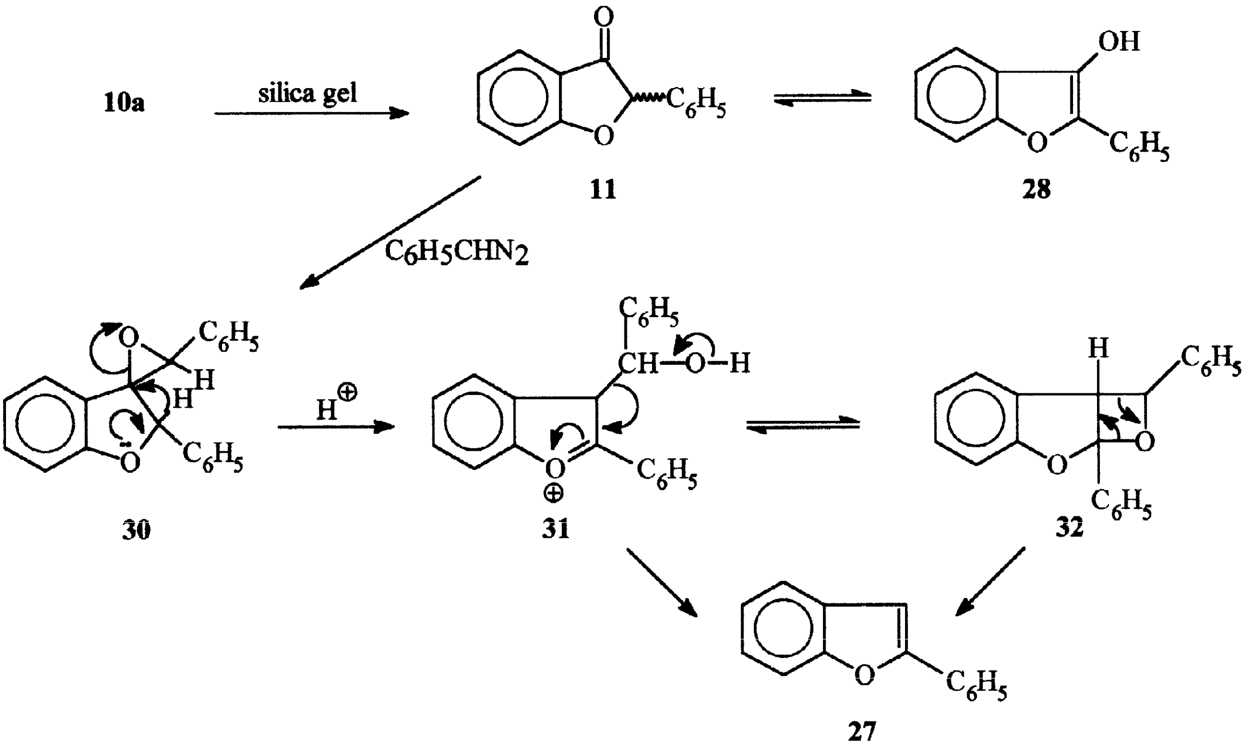
Scheme 3



Scheme 4

We also looked forward for yet another approach for the synthesis of the potential intermediate (**10a**) involving for the first time, the reaction of 2-methoxybenzoyl chloride and phenyl diazomethane (Scheme 4). Thus, the reaction of the acid chloride with excess phenyl diazomethane gave **10a**, but during its subsequent purification over silica gel afforded, to our surprise, 2-phenylbenzofuran (**27**) in 24% yield along with 3-hydroxy-2-phenylbenzofuran (**28**) (8%) and the ester, benzyl-2-methoxybenzoate (**29**) (24%).

The genesis of the product (**28**) may be explained by an acid catalysed tautomerisation of the expected coumaranone (**11**), formed *in situ* by the anchimeric assistance of the neighbouring methoxyl group upon the protanated diazoketone (**10a**) in the presence of silica gel. It is also important to note that the aromatisation of **11** to **28** is a strong guiding factor for this process (Scheme 5). However, the unexpected formation of 2-phenylbenzofuran (**27**) in this reaction possibly stemmed from the reaction of the residual phenyl diazomethane with the carbonyl group of **11** to produce an intermediate epoxide (**30**). The oxirane (**30**) then can undergo an acid induced pinacolic rearrangement involving a 1,2-hydrogen shift in **30** to generate the highly resonance stabilised oxonium ion (**31**) that either could follow a retro-aldol pathway to furnish 2-phenylbenzofuran (**27**) or could give rise to the betaine **32**, which on [2 + 2]-cycloreversion led to the formation of **27** as depicted in Scheme 5.



Scheme 5

Incidentally, we could isolate and detect spectroscopically (IR) the by-product of this reaction, i.e., benzaldehyde and checked the melting point of its DNP derivative with that of an authentic sample. The ester

(29) is, however, formed by the reaction of the acid **(26)** produced, by the partial hydrolysis of the acid chloride *in situ*, with phenyldiazomethane.

To the best of our knowledge, such type of formation of 2-phenylbenzofuran is unknown till date and we are presently pursuing this reaction in more detail for the direct synthesis of naturally occurring benzofurans.

In conclusion, we have made several approaches for some practical and efficient synthesis of 2-arylcoumaranones by the acid catalysed cyclisation of readily accessible and suitably substituted α-diazocarbonyl compounds and have observed a new reaction for the synthesis of 2-phenylbenzofuran.

EXPERIMENTAL

The melting points, recorded in a Köfler block apparatus, or boiling points are uncorrected. The IR spectra were obtained in a Perkin-Elmer 297 Infrared spectrophotometer, the ^{1}H NMR spectra were recorded in $CDCl_3$ with TMS as internal standard and elemental analyses were performed in a Perkin-Elmer 240C Elemental analyser. The solvent abbreviations are: A - Acetone, E - Diethyl ether, P - Light Petroleum (60-80°C) and P$^{/}$ - Light petroleum (40-60°C) and the yield denotes the combined amounts of crystallised or sublimed material isolated after chromatography.

2-Methoxyphenyl benzyl ketone (9a): To a suspension of purified magnesium (1.3 g, 53 g atom) in dry ether (10 ml) at 0°C, 2-iodoanisole **(8)** (13 g, 56 mmol) in dry ether (19 ml) was slowly added in a dropwise fashion. After the addition, it was stirred for 1 h at room temperature followed by the addition of anhydrous cadmium chloride (5.5 g, 30 mmol) and further stirred for 1 h more, after which ether was distilled off and azeotroped with dry benzene (2 x 20 ml).

To the organo-cadmium complex so prepared, a solution of phenylacetyl chloride, obtained from phenylacetic acid (7.6 g, 56 mmol), in dry benzene (20 ml) was added at 0°C and kept overnight. The mixture was refluxed for 4 h and the reaction mixture was worked up in the usual way. Evaporation of the solvent gave the ketone **(9a)** (9 g, 71%), mp. 64-65°C (E-P$^{/}$) as light yellow coloured crystals, IR (KBr): ν_{max} 1650, 1250, 1020, 815, 725 and 690 cm^{-1} . Analysis: Calc.for $C_{15}H_{14}O_2$ (226.27) C, 79.62%, H, 6.24%; Found: C, 79.25%, H, 6.18%.

2,4,5-Trimethoxyphenyl benzyl ketone (9b): The Friedel-Crafts acylation reaction of 1,2,4-trimethoxybenzene (5 g, 30 mmol) and phenylacetic acid (4 g, 29 mmol) using PPA at 60°C afforded, after usual work-up, 8.2 g (96%) of the ketone **(9b)**, mp. 79°C (E-P$^{/}$) (lit.[22] mp. 76-77°C) as cream coloured crystals. IR (KBr): ν_{max} 1655, 1270, 1045, 826, 730 and 700 cm^{-1}, ^{1}H NMR (100 MHz): δ 3.84 (3H, s), 3.89 (3H, s), 3.93 (3H, s), 4.30(2H, s), 6.49 (1H, s), 7.25 (5H, s), 7.42 (1H, s).

4-Bromo-2-methoxyphenyl benzyl ketone (9c): The ketone **(9c)** was prepared following the above procedure using 4-bromoanisole (5.9 g, 32 mmol) and phenylacetic acid (4.7 g, 35 mmol) in the presence of PPA at 60° C, yield 4.2 g (44%), b.p. 190-92°C/0.2 mm Hg, IR (neat): ν_{max} 1680, 1250, 1020, 810, 735, 700 cm^{-1}; ^{1}H NMR (60 MHz): δ 3.81 (3H, s), 4.15 (2H, s), 6.70 (1H, d, J = 8.0 Hz), 7.21 (5H, s), 7.45 (1H, dd, J = 8.0, 2.0 Hz), 7.69 (1H, d, J = 2.0 Hz). Analysis: Calc. for $C_{15}H_{13}O_2Br$ (305.17) C, 59.04%, H, 4.29%; Found: C, 59.15%, H, 4.41%.

2-Methoxy-α-phenyl-α-diazoacetophenone (10a): To a solution of sodium ethoxide (4.8 g, 71 mmol) in dry ethanol (20 ml) was added an ethanolic solution (10 ml) of the ketone **(9a)** (2 g, 9 mmol) at 0°C. After stirring for 30 min, tosyl azide (2.1 g, 11 mmol) was added and stirring continued for 30 min. The reaction mixture was decomposed with ice-cold water and worked up in the usual way. Removal of the solvent in *vacuo* afforded 2 g (91%) of **10a**, mp. 76-78°C (E-P$^{/}$) as deep orange hexagonal plates. IR (KBr): ν_{max} 2080, 1620, 1600, 1255, 1030, 835, 735, 690 cm^{-1}.

2,4,5-Trimethoxy-α-phenyl-α-diazoacetophenone (10b): Following the above procedure, the ketone **(9b)** (2 g, 7 mmol), tosyl azide (1.7 g, 9 mmol) and sodium ethoxide (1.7 g, 25 mmol) in dry ethanol (40 ml) was allowed to react, whence 1.5 g (68%) of the diazo compound **(10b)** was obtained, mp. 108-109°C (E-P$^{/}$) as orange needle-shaped crystals. IR (KBr): ν_{max} 2080, 1600, 1270, 1200, 1020, 755 cm^{-1}.

4-Bromo-2-methoxy-α-phenyl-α-diazoacetophenone (10c): The ketone **(9c)** (2 g, 7 mmol) was reacted with sodium ethoxide (2.5 g, 37 mmol) and tosyl azide (1.6 g, 8 mmol) in dry ethanol (30 ml) and the diazo compound **(10c)**, after usual work-up, was obtained as a thick orange oil, yield 1.2 g (55%). IR (neat): ν_{max} 2090, 1615, 1250, 1020, 810, 765 cm^{-1}.

2-Phenylcoumaranone (11): A solution of the diazoketone **(10a)** (0.7 g, 2.8 mmol) in dry dichloromethane (5 ml) was added slowly to TFA (2 ml) at -15°C and stirred for 30 min. The reaction mixture was decomposed with ice-cold water and extracted with ether (3 x 10 ml). The combined ethereal extracts were washed, dried (Na_2SO_4) and evaporated. The residue on chromatography (silica gel) gave 0.55 g (95%) of coumaranone **(11)**, mp. 215°C (A-P) (lit.[21] mp. 220°C), IR (KBr): ν_{max} 1725, 1600, 1250, 1020, 755, 700 cm^{-1}.

5,6-Dimethoxy-2-phenylcoumaranone (12): Following the above procedure and using 1.2 g (4 mmol) of **10b** and TFA (5 ml), the coumaranone **(12)** was obtained, yield 1 g (96%), mp. 168-70°C.

5-Bromo-2-phenylcoumaranone (13): The reaction of bromodiazoketone **(10c)** (0.9 g, 2.7 mmol) in dry dichloromethane (5 ml) with perchloric acid (70%, 1.5 ml) at -10°C for 15 min afforded, after usual work-up and chromatography, the coumaranone **(13)**, yield 0.5 g (66%) as a thick yellow oil, homogeneous by tlc; IR (KBr): ν_{max} 1730, 1245, 1005, 810, 775, 660 cm^{-1}. Analysis: Calc. for $C_{14}H_9O_2Br$ (289.13) C, 58.16%, H, 3.14%; Found: C, 57.91%, H, 3.27%.

2,2$^{/}$-Dimethoxybenzoin (14): To a solution of 2-methoxybenzaldehyde (16 g, 117 mmol) in 95% ethanol (17 ml) was added a solution of NaCN (2.45 g , 1.2 mmol) in water (13 ml) and the mixture was heated at 110°C with stirring for 45 min followed by heating on a steam-bath for 30 min. The reaction mixture was decomposed by crushed ice and allowed to stand overnight, whence 12 g (75%) of **14** was obtained, crystallised further from dichloromethane-petroleum ether, 60-80°C mixture to yield pure **14** as shining colourless crystals, mp. 98°C (lit.[23] mp. 101.5°C), IR (KBr): ν_{max} 3440, 1665, 1290, 1250, 1045, 1025, 970, 750 cm^{-1}, ^{1}H NMR (60 MHz): δ 3.67 (3H, s), 3.70 (3H, s), 4.03 (1H, d, J = 6.0 Hz), 5.91 (1H, d, J = 6.0 Hz), 6.60-7.70 (8H, m).

2,2′-Dimethoxybenzoin hydrazone (15): 2,2′-Dimethoxybenzoin **(14)** (6 g, 21 mmol) was refluxed with hydrazine hydrate (4 g, 80% v/v) in ethanol (25 ml) for 4 h. The reaction mixture was cooled and the precipitated crystalline colourless hydrazone **(15)** was filtered off, yield 5 g (79%), mp. 60-62°C (ethanol), IR (KBr): ν_{max} 3360, 3210, 1645, 1240, 1020, 920, 830, 765 cm^{-1}. Analysis: Calc. for $C_{16}H_{18}O_3N_2$ (286.33) C, 67.12%, H, 6.34%, N, 9.78%; Found: C, 67.23%, H, 6.23%, N, 9.69%.

2-Methoxyphenyl-α-(2-methoxyphenyl)-α-diazo-methyl carbinol (16): An ethereal solution (30 ml) of the hydrazone **(15)** (2 g, 7 mmol) was oxidised by freshly prepared manganese dioxide (12 g, 140 mmol) at 0°C for 30 min. Filtration of the reaction mixture over neutral alumina and subsequent removal of the solvent in *vacuo* afforded the diazo compound as a thick orange oil, yield 1.8 g (95%), IR (neat): ν_{max} 3300-3500, 2060, 1600, 1245, 1025, 750 cm^{-1}.

1,2-Di-(2-methoxyphenyl)-ethylene glycol (21): To TFA (5 ml) at -15°C, the diazo compound **(16)** (2 g, 7 mmol) was added cautiously and allowed to stir for 30 min. Removal of TFA in *vacuo* gave a thick residue, IR (neat): ν_{max} 3320-3540, 1780 cm^{-1} as diagnostic absorptions accounting for the formation of **20**. This on subsequent work-up and chromatography over silica gel furnished **21** (0.8 g, 42%), mp. 147°C (lit.[24] mp. 153-54°C), IR (KBr): ν_{max} 3520, 1610, 1600, 1250, 1020, 830, 760 cm^{-1}; ^{1}H NMR (60 MHz): δ 3.08 (2H, bs, D_2O-exchangeable), 3.73 (6H, s), 5.33 (2H, s), 6.80-7.47 (8H, m).

2,2′-Dimethoxybenzil (22): 2,2′-Dimethoxybenzoin **(14)** (9 g, 33 mmol) was oxidised by copper (II) acetate (0.15 g, 0.83 mmol) and ammonium nitrate (7 g, 90 mmol) in aqueous acetic acid (30 ml, 80% v/v) solution, and **22** was obtained as colourless crystals (6.2 g, 67%), mp. 130°C (ethanol) (lit.[25] mp. 127°C), IR (KBr): ν_{max} 1650, 1250, 1010, 755 cm^{-1}, ^{1}H NMR (60 MHz): δ 3.58 (6H, s), 6.87-7.77 (6H, m), 8.10 (2H, dd, J = 7.0, 2.0 Hz).

2,2′-Dimethoxybenzil hydrazone (23): An alcoholic solution (20 ml) of **22** (6 g, 22 mmol) and hydrazine hydrate (1 g, 80% v/v) was refluxed for 4 h whence 4.5 g (80%) of **23** was obtained as a white crystalline compound, crystallised further from acetone-petroleum ether, 60-80°C, mp. 140°C, IR (KBr): ν_{max} 3420, 3280, 1650, 1250, 1020, 750 cm^{-1}. Analysis: Calc. for $C_{16}H_{16}N_2O_3$ (284.31) C, 67.52%, H, 5.67%, N, 9.85%; Found: C, 67.55%, H, 5.57%, N, 9.77%.

2-Methoxy-α-(2-methoxyphenyl)-α-diazoacetophenone (24): The hydrazone **(23)** (3.5 g, 12 mmol) was dissolved in dry ether (40 ml) and to it freshly prepared manganese dioxide (5.6 g, 64 mmol) and anhydrous sodium sulphate (3.5 g, 25 mmol) were added. The solution was stirred for 30 min in an ice-bath and filtered over neutral alumina (BDH) bed. Evaporation of the solvent gave **24** as a yellow semi-solid material (2.5 g, 72%), homogeneous by tlc, IR (neat): ν_{max} 2095, 1670, 1600, 1250, 1020, 750 cm^{-1}.

2-(2-Methoxyphenyl)coumaranone (25): A solution of **24** (2.5 g, 9 mmol) in dry ether (3 ml) was added dropwise to TFA (-15°C) under nitrogen. The solution was stirred for 30 min after which it was worked up in the usual way. Chromatography of the crude product over silica gel afforded **25** with petroleum ether (60-80°C)-ethyl acetate (9:1 v/v) mixture as eluent, yield 1.5 g (70%), mp. 191-93°C (E-P), IR (KBr): ν_{max} 1760, 1250, 1020 ,750 cm^{-1}; ^{1}H NMR (60MHz): δ 3.95 (3H, s), 7.03 (1H, s), 7.09-7.69 (7H, m), 8.05 (1H, dd, J = 7.0, 2.0 Hz). Analysis: Calc. for $C_{15}H_{12}O_3$ (240.26) C, 74.99%, H, 5.03%; Found: C, 74.82%, H, 4.87%.

2-Methoxy-α-phenyl-α-diazo-acetophenone (10a): A solution of 2-methoxybenzoyl chloride in dry ether (30 ml), prepared from 2-methoxybenzoic acid **(26)** (9 g, 59 mmol), was added to an ethereal solution (30 ml) of phenyl diazomethane previously prepared[26] from *N*-benzyl-*N*-nitroso-*p*-toluene sulphonamide (29 g, 100 mmol), containing triethyl amine (8.4 ml) at 0°C and stirring was continued overnight. The reaction mixture was refluxed on the next day for 45 min, cooled and filtered to remove the precipitated triethylamine hydrochloride. Removal of the solvent in *vacuo* gave a red oil (10 g, 66%) which on fractionation over silica gel afforded:

* **2-Phenyl benzofuran (27)** as a colourless solid (1.7 g, 24%), mp. 123°C (lit.[27] mp. 124°C) with petroleum ether (b.p. 60-80°C) as eluent, IR (KBr): ν_{max} 3010-3060, 1600, 1070, 960, 760 cm^{-1}, ^{1}H NMR (200 MHz): δ 7.24 (1H, s), 7.28 (1H, dd, J = 6.7, 2.0 Hz), 7.36 (2H, dd, J = 6.7, 1.7 Hz), 7.38 (2H, dd, J = 8.0, 1.7 Hz), 7.51 (4H, dd, J = 8.0, 2.0 Hz);

* **3-Hydroxy-2-phenylbenzofuran (28)** as a colourless compound (0.6 g, 8%), mp. 185-87°C with benzene as eluent, IR (KBr): ν_{max} 3360, 1620, 1235, 1020, 840, 780, 760 cm^{-1}, ^{1}H NMR (200 MHz): δ 7.10 (5H, m), 7.54 (2H, dd, J = 8.0, 2.0 Hz), 8.26 (2H, dd, J = 8.0, 2.0 Hz), 11.29 (1H, s, D_2O-exchangeable); Analysis: Calc. for $C_{14}H_{10}O_2$ (210.23) C, 79.99%, H, 4.79%; Found: C, 80.25%, H, 4.62%.

* **Benzyl 2-methoxybenzoate (29)** as thick yellowish oil (3.4 g, 24%), b.p. 200°C/0.4 mm Hg (lit.[28] mp. 59°C, b.p. 206°C/12 mm Hg) with petroleum ether (b.p. 60-80°C) as eluent, IR (neat): ν_{max} 1725, 1600, 1250, 1025, 760 cm^{-1}, ^{1}H NMR (200 MHz): δ 3.90 (3H, s), 5.38 (2H, s), 7.02 (2H, dd, J = 8.0, 2.0 Hz), 7.42 (3H, m), 7.49 (3H, m), 7.89 (1H, dd, J = 8.0, 2.0 Hz).

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