

yellow needles (0.2 g) mp. 278–80°. It was found to be identical with an authentic sample of 1, 3-dimethoxy-6, 7-dihydroxyxanthone (athyriol 1-methyl ether⁵).

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CYCLOLIGNANS THROUGH STOBBE CONDENSATION

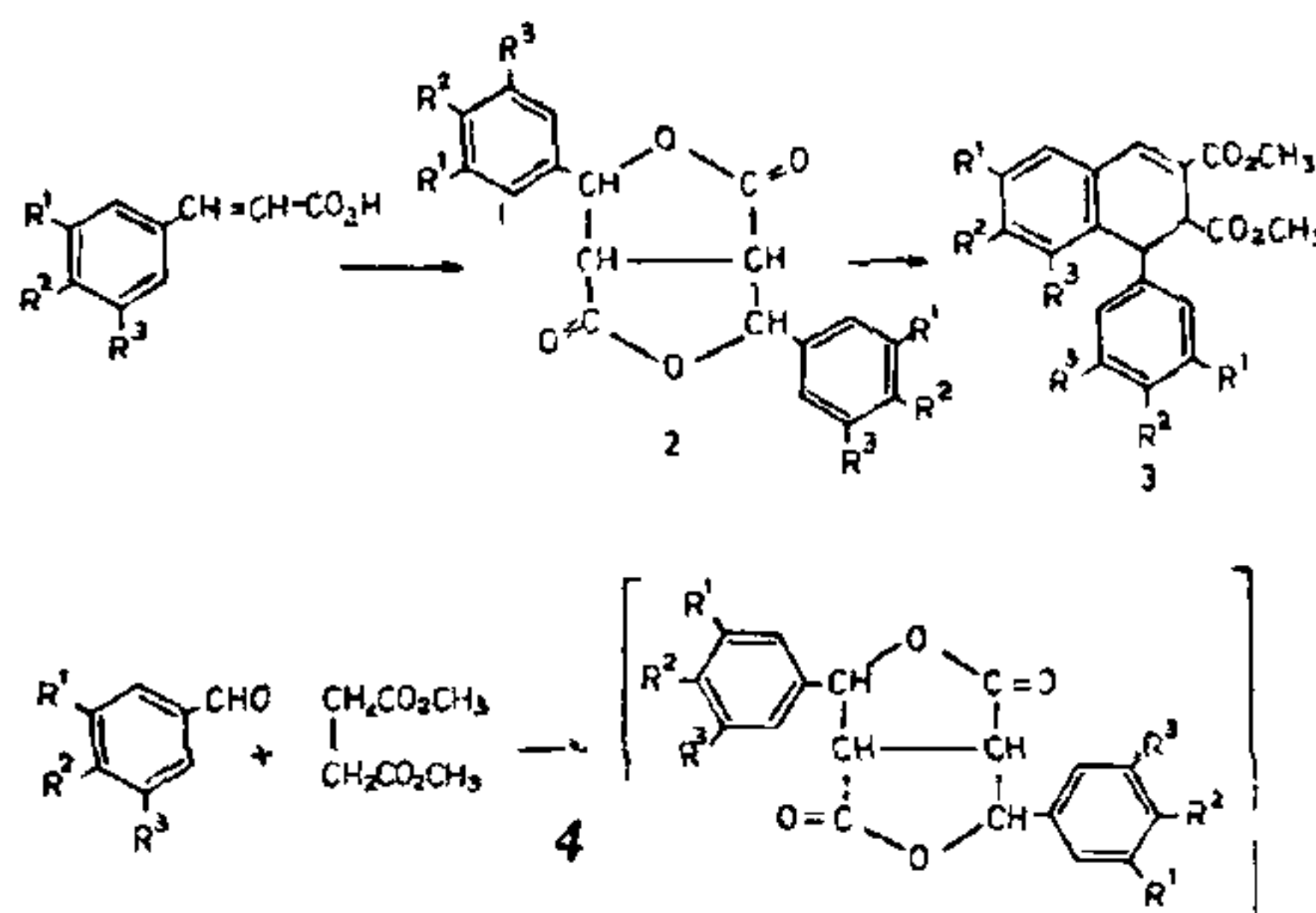
II.* Synthesis of Thomasidic Acid Dimethyl Ester Dimethyl Ether

THE Stobbe condensation presents the most fascinating and prolific entry to syntheses of lignans. Fulgenic acids, the dicondensation product in the Stobbe reaction obtained in one-step or two-step sequence has been used for several approaches to the open-chain lignan systems¹. Photochemical cyclization of the fulgides, anhydride of fulgenic acids, leads to the 1-arylnaphthalene systems of cyclolignans². Benzylsuccinic compounds, from reduction of the mono-condensation products (itaconic acids) of the Stobbe reaction, after a second Stobbe condensation have been used for the syntheses of the 7, 8-dihydrolignans³. Benzhydrylidenesuccinates, from the Stobbe condensation of substituted benzophenones and *o*-carbomethoxybenzophenones, are the starting materials for several of the cyclolignan syntheses⁴.

On a different route⁵ to 1-aryl-1, 2-dihydronaphthalenes, dehydroferulic acid dilactone (2a), obtained by oxidative coupling of ferulic acid (1a), was cleaved and recycled with methanolic hydrogen chloride to 1-aryl-1, 2-dihydronaphthalene (3a)^{5a}.

A similar dilactone (5) has been considered as an intermediate in the formation of fulgenic acid in the Stobbe condensation⁶. Hence a practical *in situ* treatment of an interrupted Stobbe reaction mixture with methanolic hydrogen chloride was expected to result in the formation of 1, 2-dihydronaphthalene,

and consequently be a proof of the formation of such intermediate in the Stobbe reaction.



- a, $R^1 = \text{OCH}_3$, $R^2 = \text{OH}$, $R^3 = \text{H}$
 b, $R^1 = \text{OCH}_3$, $R^2 = \text{OH}$
 c, $R^1 = R^2 = R^3 = \text{OCH}_3$

3, 4, 5-Trimethoxybenzaldehyde (4) and dimethyl succinate were reacted in the presence of dry sodium methoxide in ether at -10° for 24 hr and the reaction mixture which would contain the dilactone was treated with methanolic hydrogen chloride. After working up, it afforded a neutral fraction (94%) which on chromatographic separation and crystallization yielded 1-(3, 4, 5-trimethoxyphenyl)-2, 3-dicarbomethoxy-6, 7, 8-trimethoxy-1, 2-dihydronaphthalene (thomasidic acid dimethyl ester dimethyl ether) (3c) as a white crystalline material, mp 121–122°. Its NMR spectrum showed four singlets at 3.70, 3.77, 3.80 and 3.93 δ for methoxyl and carbomethoxyl groups. The proton at C_2 appeared as a doublet ($J = 1.5 \text{ Hz}$) at 4.13 δ and that at C_1 appeared as a broad singlet at 5.07 δ . The olefinic proton showed a singlet at 7.77 δ . The aromatic protons at C_2' and C_6' showed a singlet at 6.37 δ and that of C_5 showed a singlet at 6.80 δ .

This data is in agreement with that reported by Stevenson *et al.*^{5a} for (3c), obtained through the dilactone (2b)⁵ [prepared by oxidative coupling of sinapic acid (1b)] by treatment with methanolic hydrogen chloride.

Experimental

A solution of 3, 4, 5-trimethoxybenzaldehyde 1.37 g (7 mm) and dimethyl succinate, 0.51 g (3.5 mm) in dry ether (20 ml) was added to a suspension of dry sodium methoxide (7 mm) in ether (20 ml) at -5 to -10° and the mixture was kept at -10° for 24 hr with occasional stirring. Then it was poured into methanol (40 ml) saturated with dry hydrogen chloride at 0° and refluxed for 4 hr under a slow stream of dry hydrogen chloride. The reaction mixture was cooled, diluted with water (150 ml) and extracted with benzene ($3 \times 50 \text{ ml}$). The combined organic layer

* Part I: Ganeshpure, P. A., *Curr. Sci.*, 1976 45, 494.

was successively washed with water, aq. sodium bicarbonate and water, dried ($MgSO_4$) and evaporated to give a brown gum, 1.76 g (94%). On chromatography over silica gel and elution with benzene-ethyl acetate (99:1) it gave thomasidioic acid dimethyl ester dimethyl ether (3c); crystallized from ether-petroleum ether (40–60°), m.p. 116–117°. Recrystallization from aq. acetone afforded white crystalline solid, m.p. 121–122° (Lit^{5a} 117–118°, 121–122°); UV: λ_{max}^{EtOH} 244 (log ϵ 4.38) and 307 nm (log ϵ 4.17); NMR ($CDCl_3$) δ 3.70, 3.77, 3.80, 3.93 (singlets, 24 H, 6 methoxyls and 2 carbomethoxyls), 4.13 (d, J = 1.5 Hz, 1H, C₂-H), 5.07 (br.s., 1H, C₁-H), 6.37 (s, 2H, aromatic), 6.80 (s, 1H, aromatic) and 7.77 (s, 1H, olefinic).

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COMMENT ON THICKNESS MEASUREMENT OF THERMALLY GROWN OXIDE LAYER ON BISMUTH FILM

Introduction

THE capacity measurement method has become an important tool for the determination of thickness of thin insulating layer sandwiched between two metals¹⁻³. But the studies on the dielectric properties of such capacitors has drawn very little attention. The present communication reports the investigation on the dependence of capacitance of thermally grown Bi_2O_3 on various factors.

Experimental

A bismuth film of about 4000 Å thick was obtained on a clean glass substrate by vacuum evaporation at a pressure of less than 1×10^{-4} Torr using a conventional vacuum system⁴. The substrate was subjected to chemical and electrical discharge cleaning. The bismuth film was then oxidised in atmosphere at room temperature (303°K) for different times of exposure, to obtain different oxide thickness. As upper electrode, another bismuth film (~ 4000 Å) was then deposited cross-wise above the oxide layer to fabricate the capacitor⁵. In order to make electrical connections, thin copper-wires were connected at the appropriate positions by Indium solders prior to the deposition of the films and then silver paint was used at the contact plane to ensure good conduction.

The capacitance C_p and the conductance G_p for parallel representation were measured with Marconi Universal Bridge type IP 2700 in open air. The thickness was calculated from the relation⁶,

$$C = 8.85 \times 10^{-14} KA/t \text{ farads} \quad (1)$$