yellow needles (0.2 g) m.p. 278-80°. It was found to be identical with an authentic sample of 1, 3-dimethoxy-6, 7-dihydroxyxanthone (ehryiol 1-methyl ether).

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CYCLOLIGNANS THROUGH STOBBE CONDENSATION

II. Synthesis of Thomasioic Acid Dimethyl Ester Dimethyl Ether

The Stobbe condensation presents the most fascinating and prolific entry to syntheses of lignans. Fulgenic acids, the decondensation product in the Stobbe reaction obtained in one-step or two-step sequence has been used for several approaches to the open-chain lignan systems. Photochemical cyclization of the fulgides, anhydride of fulgenic acids, leads to the 1-arylphenanthrene systems of cycloglignans. Benzyllsuicinic 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-dihydrolignans. Benzhydrylidenesuccinates, from the Stobbe condensation of substituted benzophenones and o-carbethoxybenzophenones, are the starting materials for several of the cycloglignan syntheses.

On a different route to 1-aryl-1, 2-dihydrophenanthrenes, dehydrofuralic acid diacete (2a), obtained by oxidative coupling of furalic acid (1a), was cleaved and recycizld with methanolic hydrogen chloride to 1-aryl-1, 2-dihydrophenanthrene (3a)x.

A similar diacete (5) has been considered as an intermediate in the formation of fulgenic acid in the Stobbe condensation. 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-dihydrophenanthrene, and consequently be a proof of the formation of such intermediate in the Stobbe reaction.

\[ R^1 = \text{OCH}_3, \quad R^2 = \text{OH}, \quad R^3 = \text{H} \]
\[ R^1 = \text{OCH}_3, \quad R^2 = \text{OH} \]
\[ R^1 = R^2 = R^3 = \text{OCH}_3 \]

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 diacete 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-dicarboxymethoxy-6, 7, 8-trimethoxy-1, 2-dihydrophenanthrene (thomasioic acid dimethyl ester dimethyl ether) (3c) as a white crystalline material, m.p. 121-122°. Its NMR spectrum showed four singlets at 3.70, 3.77, 3.80 and 3.93 7 for methoxy and carboxymethyl groups. The proton at C5 appeared as a doublet (J = 1.5 Hz) at 4.13 7 and that at C6 appeared as a broad singlet at 5.07 7. The olefinic proton showed a singlet at 7.77 7. The aromatic protons at C5 and C6 showed a singlet at 6.37 7 and that of C6 showed a singlet at 6.80 7.

This data is in agreement with that reported by Stevenson et al.10 for (3c), obtained through the diacete (2b)9 [prepared by oxidative coupling of senech 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 steam of dry hydrogen chloride. The reaction mixture was cooled, diluted with water (150 ml) and extracted with benzene (3 x 50 ml). The combined organic layer...
was successively washed with water, aq. sodium bicarbonate and water, dried (MgSO₄) 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 thomasamino acid dimethyl ester dimethyl ether (3c); crystallized from ether-petroleum ether (40–60°), m.p. 115–117°. Recrystallization from aq. acetone afforded white crystalline solid, m.p. 121–122° (Lit.° 117–118°, 121–122°). UV: λ_{max} 244 (log ε 4.38) and 307 nm (log ε 4.17); NMR (CDCl₃) δ 3.70, 3.77, 3.80, 3.93 (singlets, 24 H, 6 methoxyls and 2 carboxomethoxyls), 4.13 (d, J = 1.5 Hz, 1H, C₃=H), 5.07 (br.s., 1H, C=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 metals. But the studies on the dielectric properties of such capacitors have shown little attention. The present communication reports the investigation on the dependence of capacitance of thermally grown Bi₂O₃ 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 system. 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 capacitor. 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 and the conductance Gp for parallel representation were measured with Marconi Universal Bridge type 11F 2700 in open air. The thickness was calculated from the relation

\[ C = \frac{8.85 \times 10^{-14}}{N} \text{ Kfads} \]