

TABLE I

Molar ratio of $Tl_2MoO_4 : MoO_3$ reaction mixtures	Initial solid phases formed before melting	Solid phases formed after melting (at 650°C) and cooling
1 : 1	$Tl_6Mo_7O_{24}$, Tl_2MoO_4 (at 320° C)	$Tl_2Mo_2O_7$
3 : 4	$Tl_6Mo_7O_{24}$ (at 340° C)	$Tl_2Mo_2O_7$, $Tl_2Mo_4O_{13}$
1 : 2	$Tl_6Mo_7O_{24}$, $Tl_2Mo_4O_{13}$ (at 370° C)	$Tl_2Mo_2O_7$, $Tl_2Mo_4O_{13}$
1 : 3	$Tl_2Mo_4O_{13}$ (at 430° C)	$Tl_2Mo_4O_{13}$

the reaction were characterised by chemical analysis, X-ray powder diffraction patterns and infrared data.

Different formula weight ratios of Tl_2MoO_4 (prepared by precipitation from mixing aqueous solutions of $TlNO_3$ and Na_2MoO_4) and MoO_3 [obtained by heating $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ to 450° C] were taken in an agate mortar and ground well. The mixtures were heated at specific temperatures isothermally in the range 300–430° C in a Stanton thermobalance. At an interval of 1–2 hours the mixtures were cooled to room temperature and reground and heated again. The completion of the reaction was indicated by the distinct X-ray powder diffraction patterns of the products. It required about 4–6 hours to obtain homogeneous reaction products. The products obtained at this stage, after characterisation by X-ray and infrared methods, were heated to 650° C. At this temperature all the samples were found to have melted. These samples were again characterised by X-ray and infrared measurements. Table I summarises the experimental results obtained. It could be seen that the heptamolybdate $Tl_6Mo_7O_{24}$ is one of the initial reaction products of 1:1, 3:4 and 1:2 formula weight ratios of Tl_2MoO_4 and MoO_3 and it melts incongruently to give lower molybdates. On the other hand heating of 1:3 mixture gives $Tl_2Mo_4O_{13}$ even in the initial stages.

The heptamolybdate, $Tl_6Mo_7O_{24}$ and the octamolybdate " $Tl_4Mo_8O_{26}$ " were prepared by precipitation from aqueous solutions of $TlNO_3$ and the respective ammonium molybdates. The d_{hkl} values of $Tl_6Mo_7O_{24}$ obtained by solid state reaction and precipitation agreed with one another. Both the preparations had the same thermal behaviour and melted incongruently to give mixtures of di- and tetramolybdates. However the phase obtained as $Tl_4Mo_8O_{26}$ has a different X-ray powder pattern from

the $Tl_2Mo_4O_{13}$ phase obtained from $Tl_2MoO_4 + 3 MoO_3$ interaction at higher temperatures and was transformed irreversibly to this phase on heating to 650° C. The two phases of the same composition are evidently having different Mo-O network.

The other possible isopolymolybdates of Tl(I) are being characterised and the detailed studies including the X-ray and spectral data will be published shortly.

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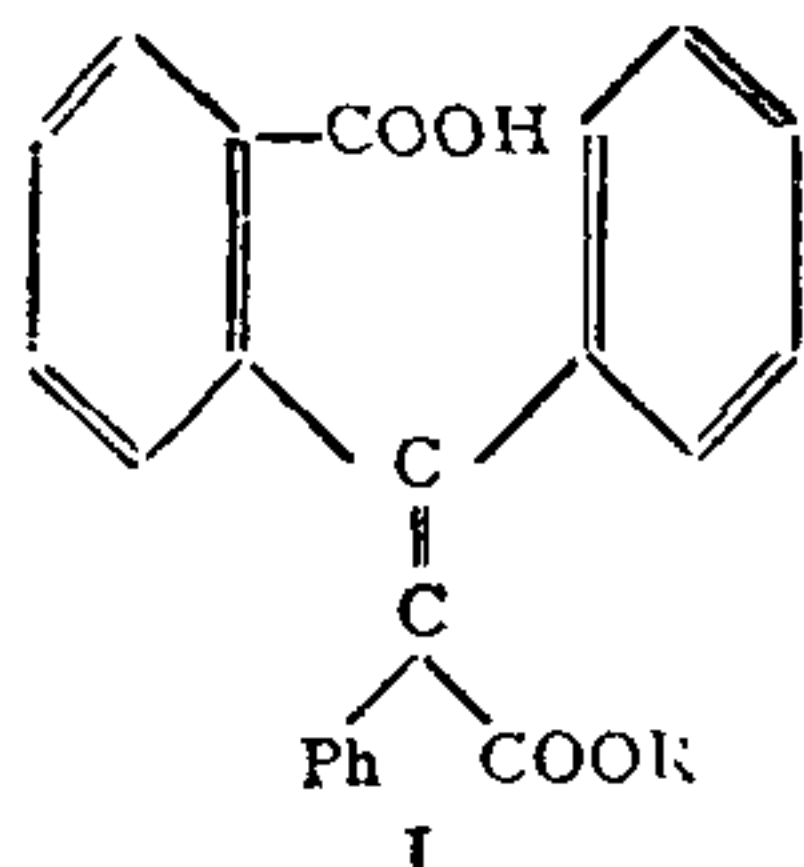
STOBBE REACTION OF PHENYLACETIC ESTERS AND *o*-BENZOYL BENZOATES

ABSTRACT

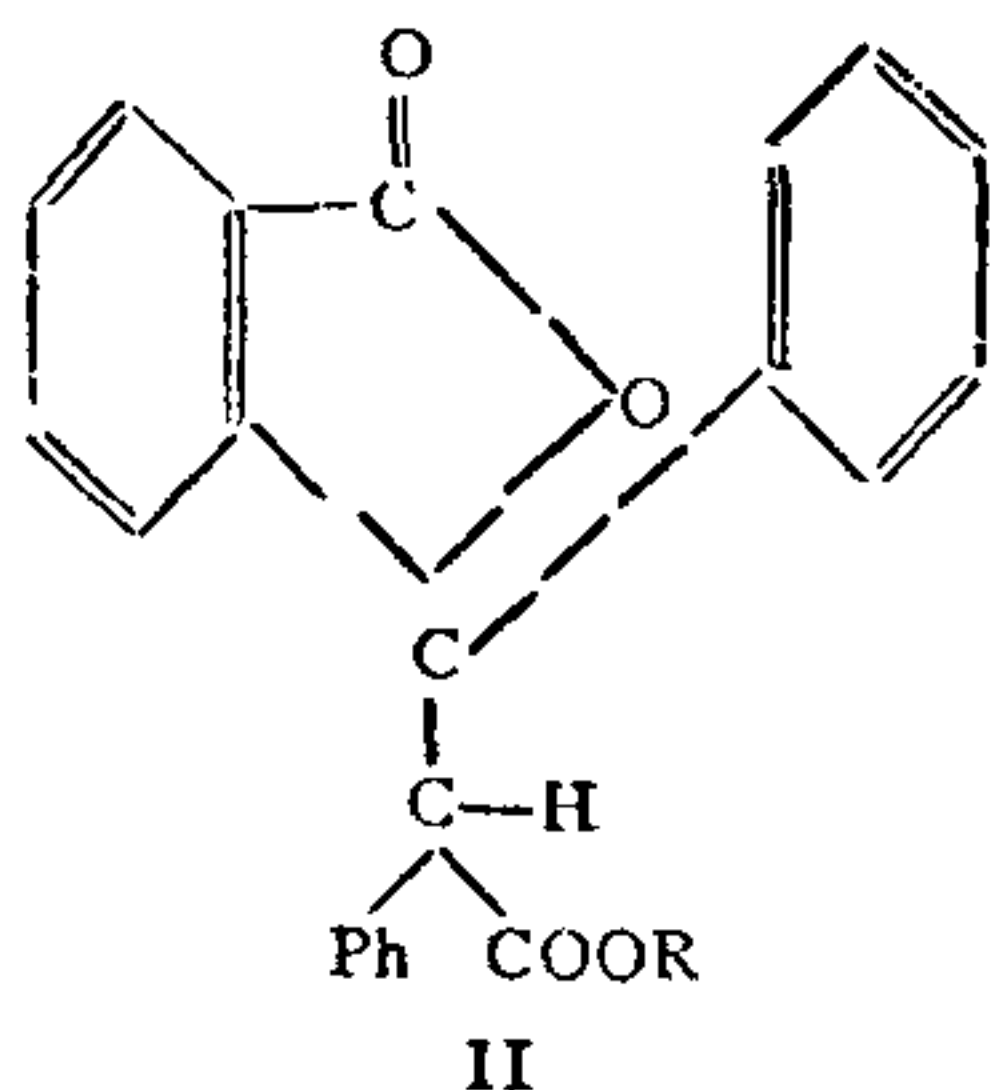
The reaction of phenylacetic esters and *o*-benzoylbenzoates leads to the corresponding acid-esters, α -carbalkoxy- β -*o*-carboxyphenylstilbenes, in excellent yields. The reaction proceeds via a γ -lactonic intermediate as in the Stobbe condensation.

PHENYLACETIC ester has been shown to react with aldehydes¹ and diketones² yielding the carboxy-stilbenes through a β -lactonic intermediate and the corresponding esters by way of a Claisen condensation.

In the reaction of phenylacetic esters and *o*-benzoylbenzoate a very high yield (95%) of an acid-ester was obtained in the acid fraction. Methyl phenyl acetate gave the same acid-ester product (m.p. 143°, eq. wt. 356) (Ia) with methyl or ethyl *o*-benzoylbenzoate; and, ethyl phenyl acetate gave the same acid-ester product (m.p. 160°, eq. wt. 372), (Ib) with methyl or ethyl *o*-benzoylbenzoate. Saponification of both these acid-esters yielded the same diacid (Ic) (m.p. 220°, eq. wt. 343). From the nature of the products it is obvious that in the intermediate, the carboalkoxy group of the benzoylbenzoate forms a γ -lactone (II) leading to the acid-esters, α -carboalkoxy- β -*o*-carboxyphenylstilbenes, (Ia, b); this corresponds to Stobbe mechanistic reaction sequence as noted by Johnson³ in the condensation of *o*-benzoylbenzoate and tert. butyl acetate leading to tert. butyl- β -*o*-carboxyphenylcinnamate.



- a. R=CH₃
b. R=C₂H₅
c. R=H



Experimental.—Ethyl-*o*-benzoylbenzoate¹ (5 g) and methyl phenyl acetate (3 g) were added to butanolic potassium tert. butoxide (from 1 g potassium in 30 ml tert. butanol) and stirred magnetically under inert anhydrous conditions for 45 minutes at room temperature. It was acidified with 6 N hydrochloric acid to Congo red, and tert. butanol was removed under reduced pressure. Residue was extracted with ether, and combined organic layers were extracted with ice-cold sodium carbonate solution. The combined alkaline layers were mixed and acidified. The precipitated solid (7.0 g) (97%),

crystallized from petroleum ether-benzene, gave α -carbomethoxy- β -*o*-carboxyphenylstilbene (Ia), m.p. 143°. Found: eq. wt. 356, C, 76.8; H, 4.7, reqd. for C₂₃H₁₈O₄: eq. wt., 358, C, 77.09; H, 5.02%. UV absorption, $\lambda_{\text{max}}^{\text{EtOH}}$ 288 nm, log $\epsilon = 3.98$. IR absorption 1727 cm⁻¹ (α - β -unsaturated ester⁵), 1692 cm⁻¹ (aryl acid⁶).

The acid-ester (1 g) was refluxed with 10% aqueous sodium hydroxide (25 ml) for 4 hours. The reaction mixture was cooled. On acidification it gave α -carboxy- β -*o*-carboxyphenylstilbene (0.9 g) (Ic), crystallized aqueous ethanol, m.p. 220°. Found: eq. wt., 343, C, 76.9, H, 4.68, reqd. for C₂₂H₁₆O₄: eq. wt., 344, C, 76.7; H, 4.65%, UV absorption $\lambda_{\text{max}}^{\text{EtOH}}$ 277 nm, log $\epsilon = 3.95$.

Similarly methyl *o*-benzoylbenzoate and methyl phenyl acetate gave α -carbomethoxy- β -*o*-carboxyphenylstilbene (95%), m.p. 143°, mixed melting point with above acid-ester was undepressed.

Ethyl-*o*-benzoylbenzoate (5 g) and ethyl phenyl acetate (3.5 g) with butanolic potassium tert. butoxide (from 1 g potassium in 30 ml tert. butanol) gave α -carboethoxy- β -*o*-carboxyphenylstilbene (Ib), (7.2 g), (96%), crystallized from aqueous ethanol, m.p. 160°. Found: eq. wt., 371, C, 77.2; H, 5.2, reqd. for C₂₄H₂₀O₄: eq. wt., 372, C, 77.4; H, 5.37%. UV absorption, $\lambda_{\text{max}}^{\text{EtOH}}$ 283 nm, log $\epsilon = 3.88$.

The acid-ester (1 g) on saponification with aqueous sodium hydroxide gave α -carboxy- β -*o*-carboxyphenylstilbene (0.85 g), m.p. 220°, mixed melting point with diacid (Ic) was undepressed.

Similarly methyl-*o*-benzoylbenzoate and ethyl phenyl acetate gave α -carboethoxy- β -*o*-carboxyphenylstilbene, m.p., 160°, (95%), mixed m.p. with above acid-ester was undepressed.

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