523. *Unusual Reactions of Thallium. Part I. Alkoxides and Aryloxides of Thallium as Oxidising Agents.*

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Benzoins are quantitatively oxidised to the corresponding diketones by thallous alkoxides and aryloxides, which are thereby reduced to the metal. Aliphatic acyloins are not oxidised by similar treatment but yield normal thallium derivatives. A convenient method for the preparation of the thallous alkoxides and aryloxides is described.

Rigby (*J.*, 1951, 793) has recently described the oxidation of benzoins and aliphatic acyloins with bismuth acetate, which is reduced to the metal in the process. A similar reaction has been observed by us, in which alkoxides and aryloxides of thallium react almost quantitatively with benzoins in benzene or alcohol, thus:

$$\mathrm{Ar{\cdot}CO{\cdot}CHAr{\cdot}OH + 2TlOR = (Ar{\cdot}CO)_2 + 2Tl + 2ROH}$$

Aliphatic acyloins on the other hand are not oxidised: *e.g.*, thallous ethoxide and acetoin or butyroin in benzene yield stable thallium derivatives. Furoin and the mixed benzoyl-2-furoyl acyloin resemble the aryl compounds in being completely oxidised to furil and 2-furyl phenyl diketone respectively.

During the investigation we simplified the preparation of the thallous alkoxides (Sidgwick and Sutton, *J.*, 1930, 1461). We obtained good results by shaking a liquid thallium amalgam with the alcohol or enol in benzene at room temperature, in an atmosphere of air enriched with oxygen. The methoxide and ethoxide were prepared by treating an excess of the appropriate alcohol with the amalgam. The derivatives prepared are recorded in Table 2 (p. 2772). An attempt to prepare the thallous derivative of ethyl benzylacetoacetate by the general method gave, abnormally, a mixture of thallous acetate and the thallous derivative of ethyl phenylpyruvate, formed presumably by the oxidation of the thallous derivative of ethyl benzylacetoacetate. The pre-formed thallous derivative of ethyl benzylacetoacetate gave the same products when shaken in benzene with thallium amalgam and oxygen. 3-Benzylpentane-2 : 4-dione behaved in the same way, yielding benzyl methyl diketone and thallous acetate; the pre-formed thallous derivative in benzene reacted with oxygen to yield the same products.

The acyloins listed in Table 1 gave the stated yields of diketones by the use of thallous ethoxide as oxidising agent. The other thallous derivatives (Table 2) were examined

Table 1.

Reactant	Product	Yield, %	Reactant	Product	Yield, %
Benzoin	Benzil	86	Acetoin	Tl derivative of acetoin	High
Anisoin	Anisil	91			
Piperoin	Piperil	97	Butyroin	Tl derivative of butyroin	High
Furoin	Furil	82			
$\mathrm{Ph{\cdot}CH(OH){\cdot}CO{\cdot}C_4H_3O}$	$\mathrm{Ph{\cdot}CO{\cdot}CO{\cdot}C_4H_3O}$	92			

TABLE 2.

		Tl, %:				Tl, %:	
Thallous derivative of	M. p.	found	reqd.	Thallous derivative of	M. p.	found	reqd.
Phenol *	233°	68·4	68·7	*p*-Methoxyphenol	196°	62·2	62·4
o-Cresol	164 ‡	65·4	65·6	Thymol	164 §	57·7	57·8
m-Cresol *	199	65·6	65·6	Carvacrol	158—160 §	57·4	57·8
p-Cresol	203	65·4	65·6	Eugenol	decomp. 148—152 §	55·2	55·7
o-Methoxyphenol *	163	62·3	62·4	Ethyl acetoacetate †	88	61·1	61·3
m-Methoxyphenol *	147	62·4	62·4	Ethyl ethylacetoacetate	170 §	56·4	56·5

* Sidgwick and Sutton (*J.*, 1930, 1461).
‡ M. p. with decomp.

† Christie and Menzies (*J.*, 1925, 2369).
§ Decomp. pt.

qualitatively for action on benzoin, and in each case oxidation was made evident by precipitation of metallic thallium.

EXPERIMENTAL

M. p.s are uncorrected.

Preparation of Thallous Alkoxides and Aryloxides.—Thallium (0·02 mole) was dissolved in warm mercury to give a 3% amalgam. This was vigorously shaken in a separating funnel with the alcohol or enol (0·02 mole) in benzene (100 ml.), oxygen being passed in. Oxygen was added until absorption ceased and no further heat was evolved. The thallous compound was then either filtered off or precipitated by light petroleum (b. p. 100—120°); it was purified by solution in benzene and reprecipitation, or recrystallisation from ethanol (pyridine was found to be necessary in the case of the eugenol derivative). For *products* see Table 2.

Oxidation of Benzoins.—To a solution of the benzoin in benzene was added a weighed excess of thallous ethoxide in benzene, and the precipitated thallium was filtered off, washed with benzene and ether, and weighed. The excess of ethoxide was determined by the addition of glacial acetic acid and saturated alcoholic potassium iodide; the filtrate was evaporated to a small bulk, and the diketone recrystallised. For results see Table 1.

Thallous Derivative of Acetoin.—A solution of thallous ethoxide (8·4 g.) was added to acetoin (2·4 g.; b. p. 148°) in benzene. A colourless crystalline precipitate was formed. This was purified by dissolution in ethanol (in which it is very soluble) and precipitation with benzene. This *thallous* derivative formed plates, m. p. 126° (decomp.), decomposing in moist air (Found: Tl, 70·0. $C_4H_7O_2Tl$ requires Tl, 70·1%).

Thallous Derivative of Butyroin.—Thallous ethoxide (2·5 g.) and butyroin (1·5 g.; b. p. 84°/12 mm.) in benzene gave the colourless *thallous* derivative on addition of ether. It was purified by solution in benzene and precipitation with ether, forming plates, m. p. 129° (Found: Tl, 59·0. $C_8H_{15}O_2Tl$ requires Tl, 58·9%).

Oxidation of Ethyl Benzylacetoacetate.—Thallium amalgam (containing 8·5 g. of thallium) and ethyl benzylacetoacetate (4·5 g.) were shaken in benzene, as in the preparation of the aryloxides. Reaction proceeded in two stages, first with moderate liberation of heat and absorption of oxygen, and then with liberation of much heat and a large absorption of oxygen accompanied by the precipitation of thallous acetate (4·9 g.) (Found: Tl, 77·6. Calc. for $C_2H_3O_2Tl$: Tl, 77·6%). This salt was decomposed by means of potassium iodide and then yielded *p*-nitrobenzyl acetate, m. p. 78° (lit., 78°), and *p*-bromophenacyl acetate, m. p. 85° (lit., 85°). The filtrate from the reaction mixture, on treatment with light petroleum (b. p. 100—120°), yielded the *thallous* derivative of ethyl phenylpyruvate, a colourless solid rapidly changing to a sticky yellow mass of indefinite m. p. (Found: Tl, 51·5. $C_{11}H_{11}O_3Tl$ requires Tl, 51·7%). After decomposition with potassium iodide in alcohol, this gave a green colour with ferric chloride, and yielded a phenylhydrazone, m. p. 89° (lit., 89°), and a semicarbazone, m. p. 164°, not depressed on admixture with an authentic specimen (lit., 159—160°, 167°).

Thallous Derivative of Ethyl Benzylacetoacetate.—Addition of thallous ethoxide (2·4 g.) in benzene to a solution of the ester (2·0 g.) in benzene, and then addition of light petroleum (b. p. 100—120°), gave the *thallous* derivative of the ester as a colourless flocculent precipitate rapidly decomposing to a sticky mass of indefinite m. p. (Found: Tl, 48·1. $C_{13}H_{15}O_3Tl$ requires Tl, 48·3%).

When this derivative (from 5·2 g. of ester) in benzene was shaken with thallium amalgam (containing 4·9 g. of thallium) and oxygen, thallous acetate (5·8 g.) was precipitated; ethyl phenylpyruvate (4·0 g.) was isolated as before.

Oxidation of 3-*Benzylpentane*-2 : 4-*dione*.—Thallium amalgam (containing 4·2 g. of thallium) and the diketone (3·8 g.) were shaken in benzene in the presence of oxygen; the reaction occurred in two stages as before; thallous acetate was precipitated (4·8 g.), and the liquid containing benzyl methyl diketone (2·9 g.), after removal of the solvent, gave an osazone, m. p. 171° not depressed by the addition of an authentic sample (lit., 172—173°).

Thallous Derivative of 3-*Benzylpentane*-2 : 4-*dione*.—Addition of thallous ethoxide (2·6 g.) to the diketone (1·9 g.) in benzene and precipitation with light petroleum (b. p. 100—120°) gave a lemon-yellow powder, m. p. 78° (decomp. at 90°), which was rapidly oxidised in air (Found : Tl, 52·3. $C_{12}H_{13}O_2Tl$ requires Tl, 52·0%).

Oxidation.—A mixture of thallous ethoxide (2·6 g.) and the diketone (1·2 g.) in benzene was shaken with oxygen. It yielded thallous acetate (2·4 g.) and benzyl methyl diketone (1·4 g.).

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