832. *Reactions of Thallium. Part II.* Thallous Ethoxide as a Catalyst in the Oxidation of the Aromatic Acyloins by Nitrobenzene.*

By L. P. McHatton and M. J. Soulal.

In the presence of a small quantity of thallous ethoxide nitrobenzene oxidises aromatic acyloins to the corresponding α-diketones. Nitroalkanes do not react in this way.

Metallic thallium reduces aromatic nitro-compounds in alcoholic solution to the corresponding azoxy-compound in high yield, the thallium being oxidised to thallous ethoxide :

$$2Ar{\cdot}NO_2 + 6Tl + 6EtOH = Ar{\cdot}N{:}NO{\cdot}Ar + 6TlOEt + 3H_2O \quad . \quad . \quad (1)$$

The reaction takes place at room temperature and requires about 28 days; if finely divided thallium is used, about 14 days are required for reduction; from *m*-dinitrobenzene, 3 : 3′-dinitroazoxybenzene was obtained by using thallium amalgam. Refluxing the reaction mixtures caused considerable tar formation.

In the presence of a small quantity of thallous ethoxide, an alcoholic solution of nitrobenzene oxidises aromatic acyloins to α-diketones in yields of 80—90%. Probably the thallous ethoxide is reduced to thallium by the acyloin (McHatton and Soulal, *J.*, 1952, 2771) which yields the diketone :

$$Ar{\cdot}CO{\cdot}CHAr{\cdot}OH + 2TlOEt = (Ar{\cdot}CO)_2 + 2Tl + 2EtOH$$

and this is followed by reaction (1). The ultimate fate of the thallium is indicated by the isolation of the thallous salt of the aryl-carboxylic acid corresponding to the diketone formed : the formation of this salt is possibly due to the formation of an unstable adduct between the diketone and thallous ethoxide, which in its decomposition yields the salt and other products (cf. the reaction between benzil and sodium ethoxide; Lachman, *J. Amer. Chem. Soc.*, 1923, **45**, 1509) :

$$(Ar{\cdot}CO)_2 + TlOEt = Ar{\cdot}CO{\cdot}CAr(OTl)(OEt) \longrightarrow Ar{\cdot}CO_2Tl$$

Reaction between thallous ethoxide and benzil yielded an unstable adduct which could not be analysed; the products of its decomposition contained thallous benzoate. With anisil and furil the adducts were very much more unstable and could not be isolated, thallous anisate or furoate being formed instantly.

Nitroalkanes are not reduced to azoxy-compounds by thallium, but after one month's contact with thallium foil an alcoholic solution of nitroethane gave a precipitate of thallous nitrite, the solution yielding acetaldehyde on distillation, and the residue from this distillation on hydrolysis gave a further quantity of acetaldehyde. That the same products can be obtained more rapidly by reaction between an alcoholic solution of nitroethane and thallous ethylnitronate, suggests that the initial stage of the thallium–nitroethane reaction is the formation of thallous ethoxide by extraneous air, this then reacting with the nitroethane to give thallous ethylnitronate, which eliminates thallous nitrite with a further molecule of nitroethane to yield ethyl ethylnitronate :

$$Me{\cdot}CH{:}NO{\cdot}OTl + EtNO_2 = Me{\cdot}CH{:}NO{\cdot}OEt + TlNO_2$$

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* Part I, *J.*, 1952, 2771.

This nitronic ester on distillation yields acetaldehyde and acetaldoxime, in an analogous way to that in which methylnitronates yield formaldehyde on heating (Arndt and Rose, *J.*, 1935, 1). Nitromethane and 1-nitropropane reacted similarly.

EXPERIMENTAL

Reduction of Aromatic Nitro-compounds.—A mixture of thallium foil (0·6 g.-atom), the nitro-compound (0·2 mole), and absolute ethanol (100 ml.) was left in a warm place for 28 days. The thallium in solution was then precipitated by ethanolic potassium iodide. The azoxy-compound crystallised.

Finely divided thallium was prepared by the reduction of thallous ethoxide with benzoin in ethereal solution. As it is pyrophoric it must be stored and handled under an inert solvent. When this was used as a reducing agent the reaction was allowed to proceed for 14 days.

For the reduction of *m*-dinitrobenzene, a 10% thallium amalgam (100 g.) was added to a solution of the nitro-compound (2·0 g.) in ethanol (75 ml.). The surface of the amalgam instantly became red, and solid commenced to separate; after 4 days the crude azoxy-compound was filtered off and recrystallised from formic acid. The yield of pure 3 : 3′-dinitroazoxybenzene, m. p. 143° (lit., 143°), was 0·8 g. Results are tabulated.

Nitro-compound	Azoxy-compound (%)	Nitro-compound	Azoxy-compound (%)	Nitro-compound	Azoxy-compound (%)
Nitrobenzene	84	*o*-Nitroanisole	41	4-Nitro-*o*-xylene [a] ...	45
o-Nitrotoluene......	62	*p*-Nitroanisole	50	*m*-Dinitrobenzene ...	12
m-Nitrotoluene ...	57	2-Nitrodiphenyl ...	81	*m*-Dinitrobenzene [b]	52
p-Nitrotoluene ...	80	Nitro-*p*-xylene [a]	47		

[a] In contact with finely divided thallium for 14 days.
[b] In contact with thallium amalgam for 4 days.

Catalysed Oxidation of the Benzoins.—To a mixture of the benzoin (0·03 mole) and nitrobenzene (0·02 mole) in absolute ethanol (100 ml.) was added a saturated solution of thallous ethoxide in ethanol (1 ml., containing approx. 0·1 g. of ethoxide). After 24 hr. the precipitated thallous salt was filtered off (only obtained from benzoin, anisoin, and furoin), and any thallium in solution was precipitated by ethanolic potassium iodide; the α-diketone then crystallised. Results were :

Benzoin	α-Diketone (%)	Benzoin	α-Diketone (%)
Benzoin	90	Furoin	83
Anisoin	90	$Ph{\cdot}CH(OH){\cdot}CO{\cdot}C_4H_3O$	89
Piperoin	95	p-$MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CHPh{\cdot}OH$	69
6 : 6′-Dinitropiperoin	75	p-$MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CH(OH){\cdot}C_6H_4Cl$-$p$	88
2 : 2′-Dichlorobenzoin	50		

Reaction of Thallous Ethoxide with α-Diketones.—Addition of a solution of thallous ethoxide (2·5 g.) in benzene to benzil (2·1 g.) in ether gave a pale yellow precipitate which within 30 sec. decomposed to a grey solid, composed of thallous benzoate with some benzil; the solution contained ethyl benzoate.

With anisoin or furoin in ether, addition of thallous ethoxide in benzene gave a precipitate of thallous anisate or furoate, with no preliminary separation of the adduct.

Reaction of Thallium with Nitro-paraffins.—*Nitroethane.* After a mixture of thallium foil (11 g.), nitroethane (15 g.), and absolute ethanol (30 ml.) had been kept in a warm place for 2 months, all the thallium had gone into solution and thallous nitrite (13·3 g.) had separated. The supernatant liquid gave a negative test for free acetaldehyde (2 : 4-dinitrophenylhydrazine), but on distillation its presence in the distillate was proved by the preparation of its 2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p. 168°). The residue from the distillation on hydrolysis with dilute sulphuric acid gave a further quantity of acetaldehyde.

Thallous ethylnitronate was prepared by the addition of nitroethane to thallous ethoxide in benzene, recrystallisation of the precipitated derivative from ethanol, giving lemon-yellow plates, m. p. 83° (lit., 82°; Gilman and Abbott, *J. Amer. Chem. Soc.*, 1949, **71**, 659). The pre-formed thallous ethylnitronate (1·72 g.) reacted with nitroethane (0·84 g.) in ethanol (20 ml.), within one month to give thallous nitrite (1·50 g.), the mother-liquor behaving as in the previous experiment.

1-*Nitropropane.* Thallium foil (3·0 g.), 1-nitropropane (4·0 g.), and ethanol (25 ml.) yielded, after 12 months, thallous nitrite (0·9 g.).

Thallous n-*propylnitronate* was prepared, by the addition of 1-nitropropane to thallous ethoxide in benzene, and recrystallisation of the precipitated derivative from ethanol, as yellow plates, m. p. 110° (Found: Tl, 69·8. $C_3H_6O_2NTl$ requires Tl, 69·9%). A mixture of this derivative (1·095 g.) and 1-nitropropane (0·574 g.) in ethanol (50 ml.), after 1 month yielded thallous nitrite (0·056 g.). The mother-liquor reacted analogously to that from nitroethane, to give propaldehyde.

Nitromethane. Reaction of thallium foil (10 g.) with nitromethane (5 g.) in ethanol (10 ml.) was so slow that after 4 months only 0·11 g. of thallous nitrite had been produced. Distillation of the mother-liquor into 2 : 4-dinitrophenylhydrazine reagent gave a trace of precipitate, too small for characterisation. On hydrolysis and distillation, a trace of formaldehyde was obtained and characterised as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 166°.

Thallous Nitrite.—This was produced in the above reactions as salmon-pink to orange needles. It was purified by dissolution in water and precipitation with ethanol, to give pale pink needles m. p. 183—184° (Found: Tl, 81·6; N, 5·9. Calc. for TlO_2N: Tl, 81·7; N, 5·6%).

In aqueous solution it reacts with thiourea to give a complex $Tl[CS(NH_2)_2]_4NO_2$ (cf. Rosenheim and Löwenstamm, *Z. anorg. Chem.*, 1903, **34**, 72) as colourless needles (from hot water) which darken at 150° and decompose at 180° (Found: S, 22·9; Tl, 36·8. $C_4H_{16}O_2N_9S_4Tl$ requires S, 23·1; Tl, 36·8%).

We thank the Chemical Society for a grant from the Research Fund, and the D.S.I.R. for a maintenance grant to one of us (M. J. S.).

ACTON TECHNICAL COLLEGE, ACTON, LONDON, W.3.

[*Received, June* 11*th*, 1953.]