Thallium(III) Acetate as Catalyst in the Addition of Aromatic Amines to Phenylacetylene

J. BARLUENGA*, F. AZNAR.

Dpto. de Química Orgánica, Facultad de Ciencias de la Universidad de Oviedo, Oviedo, Spain

Thallium(III) salts have found a great number of applications in organic synthesis, mainly when they act on aromatic systems[1a]. In the olefinic series, only few reactions of special interest from the point of view of synthesis are known[1b].

The major problem in the oxidation of olefins by thallium(III) salts is that a mixture of products is obtained. However, the reaction of olefins with thallium(III) acetate in presence of aromatic amines leads essentially to the formation of 1,2-diamines[2].

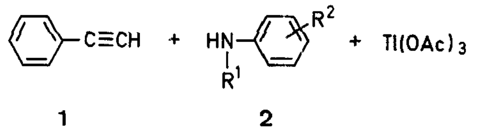
The reaction of thallium(III) nitrate with various acetylenes leads to single products in high yields[3]; this can be considered as an important extension of the usefulness of acetylenes as intermediates in organic synthesis.

Thallium(III) ions undergo a reduction process to thallium(I) ions, the reaction being stoichiometric with respect to the metal.

In a previous publication[4], the addition of aromatic amines to acetylenes in presence of thallium(III) acetate has been reported. In that work it was shown that thallium(III) is recovered at the end of the reaction; this suggests that the process may be catalytic when the appropriate reaction conditions are chosen.

The reaction of phenylacetylene (**1**) with an excess of a primary aromatic amine (**2**) in presence of thallium(III) acetate, leads to the catalytic formation of the Schiff base (**3**); the yield varies from 6 to 45 mol per mol of thallium(III) acetate used. The catalytic formation of enamines (**4**) can be achieved by the same process as for the Schiff bases, when secondary aromatic amines (**2**, $R^1 \neq H$) are used instead of primary aromatic amines (**2**, $R^1 = H$).

The reaction probably proceeds via an unstable organothallium(III) derivative as intermediate, followed by a hydrothallation process, in accord with the results obtained by Uemura[5] in the case of the acetoxythallation of internal alkynes.



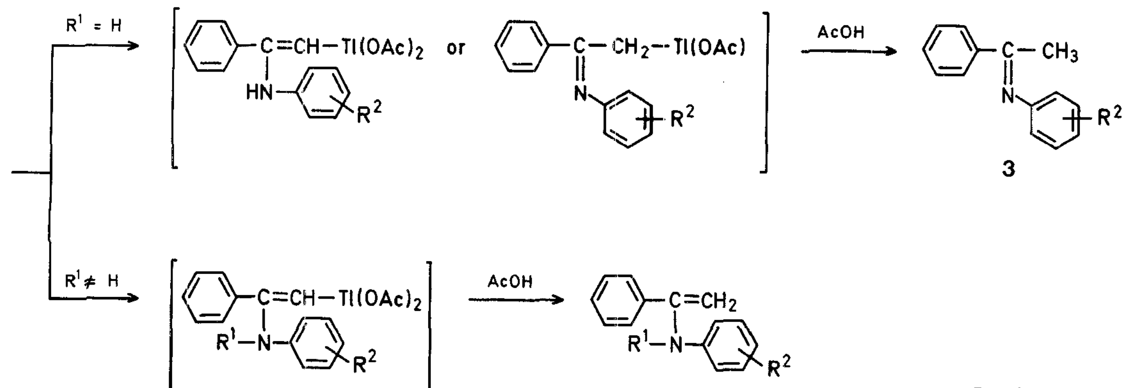


Table. Preparation[a] of Imines **3** and Enamines **4**

Product[b]	R^1	R^2	mol of product / mol of $Tl(OAc)_3$	b.p./torr or m.p.
3a	H	H	31	m.p. 41°
3b	H	4-H_3C	8.2	82–85°/0.001
3c	H	2-H_3C	44.5	m.p. 45–47°
3d	H	4-H_3CO	6.1	m.p. 84–85°
3e[c]	H	2-H_3CO	15.2	110–116°/0.1
3f	H	4-Cl	21.5	80–85°/0.001
4a	CH_3	H	16.3	90°/0.001
4b	C_2H_5	H	32.3	95–97°/0.001
4c	$C_6H_5CH_2$	H	4.2	m.p. 126–128°

[a] In all reactions **1** (0.125 mol), **2** (0.375 mol) and $Tl(OAc)_3$ (2.5 mmol) were used.

[b] See Ref.[4] for alternative preparations of all products except **3e**.

[c] $C_{15}H_{15}NO$ (225.3) calc. C 79.89 H 6.65 N 6.21; found 79.63 6.74 6.35

The termination of this catalytic reaction results essentially from the reaction of thallium(III) acetate with the Schiff bases as well as with the enamines produced. Thallium(III) ions employed are recovered quantitatively as thallium(I) salts.

Preparation of *N*,1-Diphenylethanimine (Acetophenone *N*-Phenylimine; 3a, R^2 = H):

Thallium(III) acetate (0.95 g, 2.5 mmol) is added to a stirred solution of phenylacetylene (13.7 ml, 0.125 mol) and aniline (38.5 ml, 0.375 mol). The mixture is refluxed at 60° for 7 h and then cooled. Ether is added and the thallium(I) salt precipitates. After filtration, the filtrate is evaporated under reduced pressure and the crude product is distilled under vacuum; yield 14 g; b.p. 82°/0.001 torr; m.p. 40–41°.

I.R. (nujol): ν_{max} = 3040, 1600, 1500, 745, 700 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$): δ = 2.15 (s), 6.8 ppm (m).

Preparation of 1-(*N*-Methylanilino)-1-phenylethene (4a; R^1 = CH_3):
Thallium(III) acetate (0.95 g, 2.5 mmol) is added to a stirred solution of phenylacetylene (13.7 ml, 0.125 mol) and *N*-methylaniline (41 ml, 0.375 mol). The mixture is refluxed at 60° for 7 h and cooled. Ether is added and the thallium(I) salt precipitates. After filtration, the filtrate is evaporated under reduced pressure and the crude product is distilled under vacuum; yield 8 g; b.p. 90°/0.001 torr.

I.R. (nujol): ν_{max} = 3050, 1600, 1500, 750, 700 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$): δ = 3.0 (s), 4.6 (s), 4.8 (s), 7.0 ppm (m).

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* To whom all correspondence should be addressed.

[1a] A. McKillop, E. C. Taylor, *Recent Advances in Organothallium Chemistry* **11**, p. 169, Academic Press (1973).

[1b] Ref. 1a, p. 179.

[2] V. Gómez Aranda, J. Barluenga, F. Aznar, *Synthesis* **1974**, 504.

[3] A. McKillop, O. H. Oldenziel, B. P. Swann, E. C. Taylor, R. L. Robey, *J. Am. Chem. Soc.* **93**, 7331 (1971).

[4] J. Barluenga, F. Aznar, *Synthesis* **1975**, 704.

[5] S. Uemura, H. Tara, M. Okano, K. Ichikawa, *Bull. Chem. Soc. Jpn.* **47**, 2663 (1974).