Oxidative Aminomercuriation of Prop-2-ynol. Syntheses of Substituted Propane-1,2-di-imines and 2-Aminopropionamidines

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Summary *NN′*-Diarylpropane-1,2-di-imines and 2-amino-*NN′N″*-triarylpropionamidines have been obtained by oxidative addition of primary aromatic amines to prop-2-ynol in the presence of mercury(II) acetate.

Although aminomercuriation of olefins is well established in synthesis,[1] aminomercuriation of acetylenes has been little studied.[2] In the latter case, mercury(II) acetate and chloride have been mainly used as the mercuriation agents,[3–5] and Schiff's bases, enamines, and 1,2,3,4-tetrahydroquinoline derivatives have been obtained. Whereas mercury(II) chloride shows remarkable catalytic activity in this kind of reaction, mercury(II) acetate shows little activity, probably because of its greater oxidative power. Indeed, mercury(II) acetate produces allylic oxidations;[6] likewise, it gives rise to oxidative aminomercuriation of acetylene itself in the presence of aromatic amines.[5] These antecedents have prompted us to study the behaviour of some suitably propyn-2-yl-functionalized alkynes in aminomercuriation reactions using mercury(II) acetate.†

We now report the syntheses of the non-readily available *NN′*-diarylpropane-1,2-di-imines (**1**) and 2-amino-*NN′N″*-triarylpropionamidines (**2**), using prop-2-ynol, primary aromatic amines, and mercury(II) acetate at room temperature. We have shown that the di-imines (**1**) are almost quantitatively transformed into the amino-amidines (**2**) *via* addition of the corresponding arylamine in acetic acid medium. Consequently, when carrying out the reaction in the presence of potassium carbonate the process stops in the di-imine step. Without the use of this salt, amino-amidines are obtained directly (Scheme 1).

The formation of these compounds can easily be understood in terms of an initial amine addition catalysed by the mercury(II) salt,[5] to give the substituted allyl alcohol (**3**).

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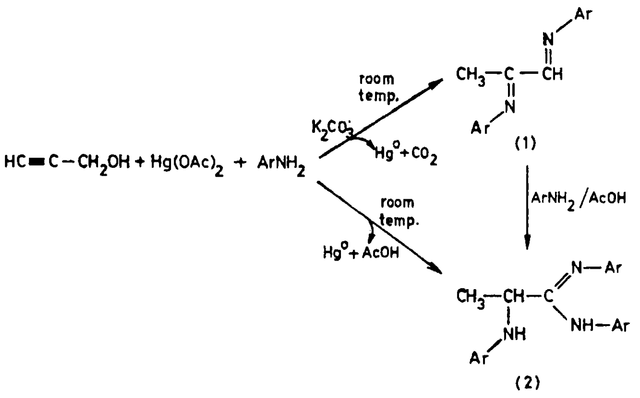
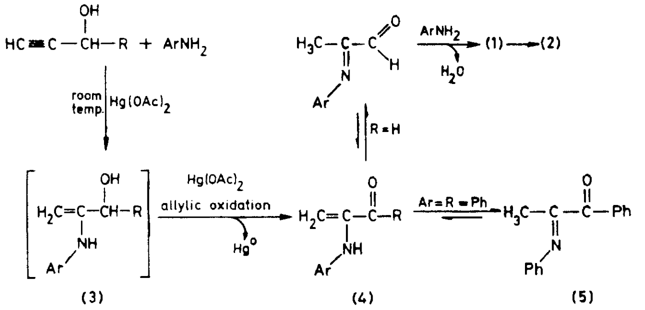
† Non-functionalized monoalkylacetylenes are not noticeably oxidized in this type of reaction.



SCHEME 1

Until now, we have failed to isolate (**3**), but, during the allylic oxidation of olefins, allyl alcohols have been isolated as intermediate products.[7] This allylic oxidation explains the formation of the intermediate (**4**), the precursor of the reaction products, the participation of which has been proved by carrying out the reaction of 1-phenylprop-2-yn-1-ol with aniline, and mercury(II) acetate which brings about, almost quantitatively, the 1-phenyl-2-phenyliminopropan-1-one (**5**). Such a process represents a convenient one-pot regioselective mono-imination of α-diketones[8] (Scheme 2).



SCHEME 2

In a typical procedure, mercury(II) acetate (20 mmol) was added during 15 min, at room temperature, to a stirred solution of prop-2-ynol (20 mmol) in a primary aromatic amine (400 mmol). Mercury (> 90%) was filtered off after 5—7 h. The organic phase was treated with 3M aqueous potassium hydroxide (15 ml) and then extracted with ether.

TABLE

Product[a]	Ar	Yield/%	M.p./°C[b]
(**1a**)	2-MeC$_6$H$_4$	56	56—58
(**1b**)	4-MeC$_6$H$_4$	32	77—79
(**1c**)	4-MeOC$_6$H$_4$	45	106—108
(**1d**)	2,6-Me$_2$C$_6$H$_4$	30	78—80
(**2a**)	Ph	50	134—135
(**2b**)	2-MeC$_6$H$_4$	71	149—150
(**2c**)	4-MeC$_6$H$_4$	38	187—189
(**2d**)	4-MeOC$_6$H$_4$	36	159—161

[a] All the products gave satisfactory spectral and elemental analysis data. [b] Uncorrected.

Elimination of the volatile components *in vacuo* and recrystallization in hexane–toluene (3 : 1) yielded the 2-aminoamidines (**2**) {*e.g.*, (**2b**), i.r. (Nujol), $\nu_{C=N}$ 1645, ν_{N-H} 3360, and 3380 cm^{-1}; ^{1}H n.m.r. δ (CDCl$_3$) 1·4 (d, 3 H), 2·05, 2·2, and 2·3 (3 s, 9 H), 4·3 (q, 1 H), and 6·3—7·3 (m, 12 H_{Ar}); ^{13}C n.m.r. δ (CDCl$_3$) 17·2 (q), 17·5 (q), 20·5 (q), and 49·8 (d) p.p.m.; *m/e* 357 (M^+), 120 ([M − MeC$_6$H$_4$NCNHC$_6$H$_4$Me], 95%)}. For the syntheses of di-imines (**1**), only 100 mmol of amine in tetrahydrofuran (50 ml) were employed in the presence of potassium carbonate (40 mmol). The crude residue was recrystallized from cold hexane {*e.g.*, (**1c**), i.r. (Nujol), $\nu_{C=N}$ 1610 and 1625 cm^{-1}; ^{1}H n.m.r. δ (CCl$_4$) 2·2 (s, 3 H), 3·75 and 3·8 (2 s, 6 H), 6·55—7·35 (m, 8 H_{Ar}), and 8·15 (s, 1 H); ^{13}C n.m.r. δ (CDCl$_3$) 14·7 (q), 55·4 (q), 160·1 (d), and 167·3 (s) p.p.m.; *m/e* 282 (M^+), 148 ([M − CHNC$_6$H$_4$OMe], 100%)}.

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[1] M. B. Gasc, J. Périé, and A. Lattes, *Tetrahedron*, 1978, **34**, 1943; R. C. Griffith, R. J. Gentile, T. A. Davidson, and F. L. Scott, *J. Org. Chem.*, 1979, **44**, 3580; J. Barluenga, C. Jiménez, C. Nájera, and M. Yus, *Synthesis*, 1981, 201.
[2] R. C. Larock, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 27.
[3] P. F. Hudrlik and A. M. Hudrlik, *J. Org. Chem.*, 1973, **38**, 4254.
[4] J. Barluenga and F. Aznar, *Synthesis*, 1975, 704.
[5] J. Barluenga, F. Aznar, R. Liz, and R. Rodes, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2732.
[6] W. Treibs and M. Weissenfels, *Chem. Ber.*, 1960, **93**, 1974; T. R. Hoye and M. J. Rother, *J. Org. Chem.*, 1979, **44**, 458.
[7] H. B. Tinker, *J. Organomet. Chem.*, 1971, **32**, C25.
[8] K. Oka and S. Hara, *Tetrahedron Lett.*, 1977, 2939.