Synthesis of 1-Aza-1,3-dienes and 2-Morpholino-1,3-dienes *via* Catalytic Aminomercuriation of Alk-3-en-1-ynes

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Under specific reaction conditions, only the terminal C≡triple bond of several alk-3-en-1-ynes adds amines, *via* catalytic aminomercuriation, to afford 1-aza- and 2-morpholino-1,3-dienes.

1-Aza-1,3-dienes and 2-amino-1,3-dienes are valuable synthetic targets because of their potential usefulness as versatile building blocks for cycloaddition reactions.[1,2] However, both systems remain underexploited,[1d,3] markedly if compared with related oxygen-analogues,[4,5] owing to their difficult availability. In fact, their preparation *via* condensation reactions between amines and α,β-unsaturated carbonyl compounds, especially in the case of the ketones, only works in some specific instances,[6] since Michael-type addition of the amine usually occurs.[6c,7,8] On the other hand, imines and enamines are easily obtained by catalytic aminomercuriation of terminal alkynes.[9] Since the catalytic aminomercuriation of a terminal C≡C triple bond is preferred over the stoicheiometric aminomercuriation of a non-conjugated C=C double bond,[9b,10] we have studied the behaviour of alk-3-en-1-ynes (**1**) as α,β-unsaturated ketone synthons in these aminomercuriation reactions. We report here the use of this reaction for the synthesis of 1-aza- and 2-morpholino-1,3-dienes.

The reaction between alk-3-en-1-ynes (**1**)† and primary aromatic amines, in the presence of potassium carbonate and catalytic amounts of mercury(II) chloride [solvent, tetrahydrofuran (THF)–water; 70 °C, 3 h], afforded the corresponding 1-aza-1,3-dienes (**2**) in 45—80% isolated yields (Scheme 1).

The stability of compounds (**2**) in aqueous alkaline media allows a further sodium borohydride reductive step, which facilitates the reaction work-up and improves yields. However, it should be pointed out that reaction and reduction conditions decisively affect the reaction path. Thus, azadienes were not isolated in some previously described aminomercuriation reactions of enynes[13] and, in the reactions reported

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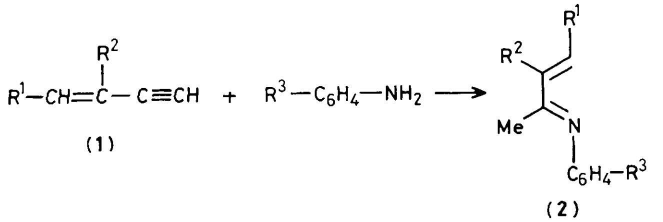
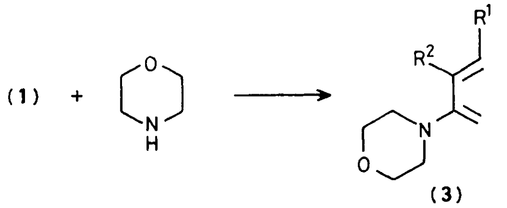
† Prepared as described,[11] except the previously unknown 3-methoxy-5-phenylpent-3-en-1-yne (**1**; R^1 = $PhCH_2$, R^2 = MeO), which is obtained from 1-phenylpent-1-en-4-yn-3-ol[12] and ethereal butyl-lithium (−60 °C, 3 h; room temp., 24 h), followed by reaction with methyl iodide (THF reflux, 4 days).



	R^1	R^2	R^3
a;	H	Me	H
b;	H	Me	2-Me
c;	H	Me	3-Me
d;	$-[CH_2]_3-$		H
e;	$-[CH_2]_4-$		H
f;	$-[CH_2]_4-$		2-Me
g;	$PhCH_2$	MeO	H

Scheme 1. *Reagents and conditions:* $HgCl_2$–K_2CO_3, THF–H_2O, 70 °C, 3 (or 6) h.



	R^1	R^2
a;	H	Me
b;	$-[CH_2]_3-$	
c;	$-[CH_2]_4-$	
d;	$PhCH_2$	MeO

Scheme 2. *Reagents and conditions:* $Hg(OAc)_2$, THF, room temp., 6 h, Ar atmosphere.

here, the absence of potassium carbonate and water led to the corresponding 3-iminoamines, presumably coming from the Michael-type addition of a second molecule of amine on the C=C double bond of azadienes (**2**).‡ Apparently, water improves the system's homogeneity, but it does not participate in the actual course of the reaction, since reaction-tests carried out in the absence of amine did not afford the corresponding alkenyl methyl ketone, but the corresponding bis(3-alken-1-ynyl)mercury. Thus catalytic aminomercuriation of C≡C triple bond of enynes (**1**) was shown to be the true reaction path.

In a typical run, a stirred mixture of potassium carbonate (10 mmol), mercury(II) chloride (5 mmol), alk-3-en-1-yne (**1**) (10 mmol),§ amine (40 mmol), THF (40 ml), and water (10 ml) was heated at 70 °C for 3 h [(**2e**) and (**2g**) required 6 h]. After cooling and reducing mercury(II) species with sodium borohydride (5 mmol) in 2 M aqueous potassium hydroxide (10 ml), standard work-up afforded the corresponding (**2**) as a nearly pure brown oil, which was then trap-to-trap condensed (preheated oil bath temperature, 80—130 °C, 0.001 Torr) [*e.g.* (**2b**), i.r. (film) ν(C=N) 1625 cm^{-1}; ^{1}H n.m.r. δ (CCl_4) 1.9 (s, 3H), 2.05 (s, 3H), 2.1 (s, 3H), 5.5 and 5.6 (2s, 2H), 6.3—6.55 (m, 1H), and 6.7—7.25 (m, 3H); ^{13}C n.m.r. δ (neat) 15.8 (q), 17.9 (q), 19.7 (q), 119.6 (t), 126.8 (s), 146.2 (s), 151.0 (s), and 165.5 (s); *m/z* 173 (M^+)].

2-Morpholino-1,3-dienes (**3**) were obtained¶ in 45—65% isolated yields when alk-3-en-1-ynes (**1**) were treated under argon with morpholine, in the presence of catalytic amounts of mercury(II) acetate (dry THF, room temp., 6 h) (Scheme 2). The crude reaction product is a nearly pure yellow oil which was then trap-to-trap condensed (preheated oil bath temperature, 75—120 °C, 0.001 Torr) [*e.g.* (**3a**), ^{1}H n.m.r. δ (CCl_4) 1.8 (s, 3H), 2.55—2.8 (m, 4H), 3.85 and 4.05 (2s, 2H), 4.85 and 5.05 (2s, 2H); ^{13}C n.m.r. δ (neat) 21.9 (q), 50.6 (t), 67.2 (t), 90.2 (t), 115.1 (t), 143.4 (s), and 159.0 (s); *m/z* 153 (M^+)].

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‡ Seemingly, this may account for the different products reported by Badanyan and coworkers.[13]

§ A 1 : 2 molar ratio of $HgCl_2$: (**1**) was necessary in order to avoid the formation of bis(alk-3-en-1-ynyl)mercury, which is observed in increasing amounts as the relative amount of $HgCl_2$ is lowered. However, the catalytic role of the mercury(II) salt was shown by evaporation of the volatile components from the final reaction mixture followed by addition of fresh reactants to the gummy residue; this process was repeated three times without apparent loss of catalytic activity.

¶ A typical procedure for compounds (**3**) is an adaptation of method E/X described in ref. 9(b), except that THF and trap-to-trap condensation are substituted for dichloromethane and *in vacuo* distillation, respectively. It should be pointed out that a work-up involving $NaBH_4$ reduction does not afford 2-aminobutadienes.[13,14]

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