Hydrazinomercuriation of Terminal Alkynes and 3-Alken-1-ynes. Syntheses of Hydrazones and 1-Amino-1-aza-1,3-dienes

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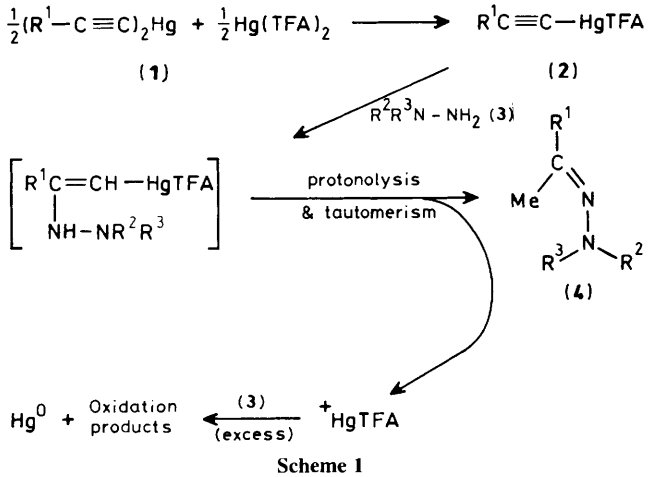
Although hydrazines cannot be directly added to non-activated, terminal acetylenes in the presence of mercury(II) salts, this difficulty was circumvented by treating hydrazines with 1-alkynylmercury trifluoroacetates (**2**); in this way, several hydrazones (**4a—h**) and 1-amino-1-aza-1,3-dienes (**4i—m**) were easily prepared.

In contrast with the well established solvomercuriation–demercuriation of alkenes,[1] that of the alkynes has been much less exploited for synthetic purposes. However, considerable efforts have been made recently to extend the classical scope of this latter reaction (hydroxy-, alkoxy-, and acyloxymercuriation)[2] to a larger range of nucleophiles (amines,[3] phenols,[4] thiocyanic acid,[5] ethers and thioethers,[6] and even carbanions[7]). We report here the solvomercuriation–demercuriation of terminal alkynes with a new class of nucleophiles, namely, mono-, 1,1-disubstituted hydrazines, or hydrazine itself.

The fact that hydrazines have been never employed in this type of reaction can be attributed to their susceptibility to oxidation by mercury(II) species.[8] In fact, when the reaction of a terminal alkyne, mercury(II) trifluoroacetate, and a four-fold excess of an hydrazine was carried out, only the quantitative precipitation of metallic mercury and the formation of the corresponding products of hydrazine oxidation were observed; no trace of the desired addition product was detected. However, we have previously shown[9] that 1-alkynylmercury(II) salts are intermediates in the catalytic aminomercuriation of terminal acetylenes. Accordingly, we decided to prepare *in situ* [from the appropriate di-(1-alkynyl)mercury (**1**) and mercury(II) trifluoroacetate] several 1-alkynylmercury trifluoroacetates (**2**), and to then allow them to react with an excess of hydrazine, (**3**). This strategy would prevent interaction between the hydrazines (**3**) and free mercury(II) trifluoroacetate, and so, if the process is able to proceed by a mechanism similar to that of aminomercuriation,[9] the formation of the corresponding hydrazone (**4**) could be expected. This was, in fact, the observed result, together with the precipitation of metallic mercury, which can be explained as a side-reaction between the excess of hydrazine and free mercury(II) species arising from the protonolysis step[9] (Scheme 1, Table 1).†



Scheme 1

† In a typical run, mercury(II) trifluoroacetate (5 mmol) was added under argon to a solution of the corresponding di-(1-alkynyl)mercury (**1**) (5 mmol), in anhydrous tetrahydrofuran (25 ml). [Anhydrous ethanol (25 ml) was used as solvent for compounds (**4a**) and (**4e**). In the case of (**4i—m**), anhydrous potassium carbonate (5 mmol) was previously added.] The mixture was stirred for 30 min and then cooled (to 0 °C). The corresponding hydrazine (**3**) (40 mmol) was then added under argon, and the stirred mixture allowed to warm to room temperature over 4 h. The precipitated metallic mercury (>85%) was filtered off and [for (**4a—h**)] aqueous 3 M-KOH (10 ml) added. After extraction with ether (3 × 20 ml), the elimination of the volatile components (15 and 0.05 torr, successively) gave the corresponding product (**4a—h**) as essentially pure, yellow oil [*e.g.*, (**4b**): ^{1}H n.m.r. (CCl_4): δ 1.9 (s, 3H), 3.0 (s, 3H), 4.9 (br. s, 1H), 7.15—7.8 (m, $5H_{Ar}$); ^{13}C n.m.r. (neat): δ 12.8 (q), 38.8 (q), 126.0 (d), 127.9 (d), 128.8 (d), 140.4 (s), 142.9 (s)]. For compounds (**4i—m**), metallic mercury was filtered off under argon, and the liquid phase evaporated (0.05 torr). The resulting residue was treated with dry n-hexane (3 × 15 ml), filtered under argon, and the liquid phase concentrated *in vacuo* (0.05 torr). (**4i**) and (**4k**) were subsequently purified by flash chromatography on neutral aluminium oxide, using ether as eluant. [*E.g.*, (**4l**): ^{1}H n.m.r. ($CDCl_3$): δ 1.9 (s, 3H), 2.1 (s, 3H), 2.5 (s, 6H), 3.4 (s, 3H), 4.15 (d, 2H), 6.05 (t, 1H); ^{13}C n.m.r. ($CDCl_3$): δ 13.1 (q), 13.7 (q), 47.5 (q), 58.3 (q), 70.2 (t), 129.4 (d), 138.5 (s), 162.8 (s)].

Table 1. Hydrazones (**4a—h**) and 1-amino-1-aza-1,3-dienes (**4i—m**).

Compound	R^1	R^2	R^3	Yield/%
(4a)[a]	Ph	H	H	85
(4b)	Ph	Me	H	87
(4c)	Ph	Ph	H	93
(4d)	Ph	Ph	Me	66
(4e)[a]	n-C_6H_{13}	H	H	84
(4f)	n-C_6H_{13}	Me	H	90
(4g)	n-C_6H_{13}	Me	Me	94
(4h)	n-C_6H_{13}	Ph	H	65
(4i)	CH_2=CMe	Me	H	51
(4j)	CH_2=CMe	Me	Me	67
(4k)	(*E*)-$MeOCH_2CH$=CMe	Me	H	55
(4l)	(*E*)-$MeOCH_2CH$=CMe	Me	Me	62
(4m)	(*E*)-$MeOCH_2CH$=CMe	Ph	Me	40

[a] On standing, converts into the azine R^1CMe=N–N=$CMeR^1$.

It should be pointed out that 1-amino-1-aza-1,3-dienes (**4i—m**), a group of compounds potentially useful as dienes in cycloaddition reactions,[10] are easily obtained from bis-(3-alken-1-ynyl)mercury derivatives. In these cases, anhydrous potassium carbonate should be incorporated into the reaction mixture in order to avoid the undesired Michael-type addition of the hydrazine (**3**) to the C=C double bond present in (**4i—m**).

From ^1H and ^{13}C n.m.r. spectroscopic data (80 and 20 MHz, respectively) for the crude reaction products, one can deduce the almost exclusive existence of a single stereoisomer (probably *E*,[11] for steric reasons) in compounds (**4a—m**). However, in some instances, the duplication of some signals suggests the presence of up to 10% of the *Z* stereoisomer in the hydrazone moiety.

In conclusion, the processes described here represent the first addition of hydrazine derivatives to non-activated alkynes, the reactions taking place under very mild reaction conditions.

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