Tetrahedron Letters No. 23, pp 2015 - 2016, 1978. 0040-4039/78/0601-2015$02.00/0
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TRANSMETALLATION REACTIONS OF ORGANOMERCURY(II) COMPOUNDS VII.(1)

SYNTHESIS AND CHEMICAL CHARACTERIZATION OF β-HYDROXY- AND β-AMINOLITHIUM DERIVATIVES

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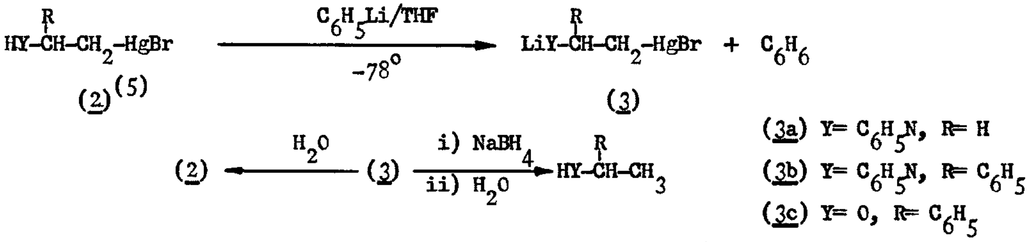
(Received in UK 27 March 1978; accepted for publication 13 April 1978)

Attempts to synthesize β-substituted organometallic compounds (1) derived from metals of Groups IA and IIA have been unsuccessful until now unless the metal was linked to a sp^2 hybridized carbon$^{(2)}$, since they undergo a β-elimination process. However, compounds type (1) have been proposed as intermediates in the reduction of organomercurials by mercury/metal exchange$^{(3)}$ in the presence of a proton source.

(1)

Y= O, RN; M= Li, Na, K, MgX

We wish to report now the chemical stabilization and characterization at low temperature of β-hydroxy- and β-aminolithium derivatives generated from the corresponding organomercurials. When β-hydroxy- and β-aminomercury(II) compounds (2) were allowed to react with phenillithium in molar ratio 1:1 in THF solution at -78°, led to the corresponding mercurated lithium alkoxide or amide (3) and benzene$^{(4)}$ in equimolecular amount. At higher temperature, side reactions were observed to take place at the Hg-Br bond. Structure of (3) was substantiated in each instance by hydrolysis and sodium borohydride reduction as shown below.

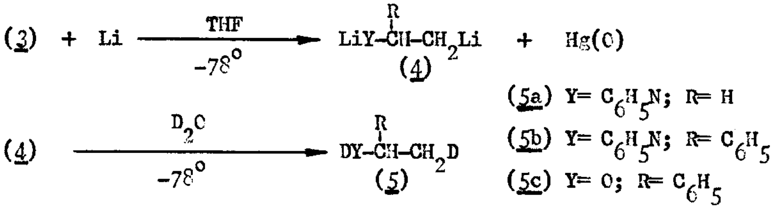


$$\underset{(2)^{(5)}}{\mathrm{HY\text{-}\overset{R}{C}H\text{-}CH_2\text{-}HgBr}} \xrightarrow[-78^\circ]{C_6H_5Li/THF} \underset{(3)}{\mathrm{LiY\text{-}\overset{R}{C}H\text{-}CH_2\text{-}HgBr}} + C_6H_6$$

$$(2) \xleftarrow{H_2O} (3) \xrightarrow[\text{ii) } H_2O]{\text{i) } NaBH_4} \mathrm{HY\text{-}\overset{R}{C}H\text{-}CH_3}$$

(3a) Y= C_6H_5N, R= H
(3b) Y= C_6H_5N, R= C_6H_5
(3c) Y= O, R= C_6H_5

Mercury/lithium exchange in (3) led to β-substituted organolithium derivatives (4) which are substantially stabilized relative to (1) since the electronegative group Y in (1) has been substituted for Y^-, with a partial negative charge, in (4). Compounds type (4) were transformed into their deuterated derivatives (5) by treatment with D_2O in THF solution at -78° in order to be characterized. Solutions of the organolithium compounds (4) could be stored at -78° for several hours without noticeable decomposition. When the temperature of these solutions was raised to



$$(\underline{3}) + \mathrm{Li} \xrightarrow[-78^{\circ}]{\mathrm{THF}} \underset{(\underline{4})}{\mathrm{LiY\text{-}\overset{R}{C}H\text{-}CH_2Li}} + \mathrm{Hg(0)}$$

$$(\underline{4}) \xrightarrow[-78^{\circ}]{\mathrm{D_2O}} \underset{(\underline{5})}{\mathrm{DY\text{-}\overset{R}{C}H\text{-}CH_2D}}$$

($\underline{5a}$) Y= C_6H_5N; R= H

($\underline{5b}$) Y= C_6H_5N; R= C_6H_5

($\underline{5c}$) Y= O; R= C_6H_5

-60° prior to deuteration , metallation of the THF took place and no deuterium incorporation in ($\underline{5}$) could be detected.

Reaction conditions and ^1H NMR spectroscopic data of the products are summarized in Table I.

Our detailed work on the synthetic utility of these new reagents will be published in a forthcoming paper

Table I

Product	($\underline{3}$):Li ratio	transmetallation time	Hg(0) yield (%)[a]	($\underline{5}$) yield (%)[b]	$\delta_{C\text{-}H}$ and multiplicity[c]
($\underline{5a}$)(6)	1:5	8 h	80	90	3.0 (t)
($\underline{5b}$)(7)	1:6	8 h	78	87	4.3 (t)
($\underline{5c}$)(8)	1:6	8 h	75	75	4.6 (t)

a)Relative to starting organomercurial ($\underline{2}$). b)Relative to Hg(0) precipitated. c)Proton chemical shifts are relative to internal Me_4Si. Spectra were recorded in CCl_4 solution in a Varian EMR-390 NMR spectrometer.

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