

## Trianions derived from Secondary Amines

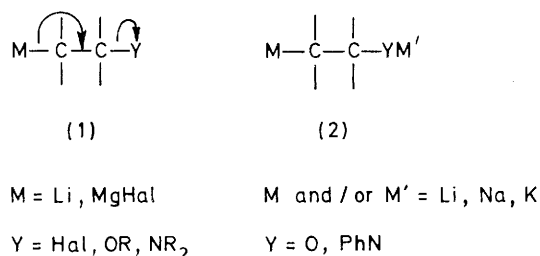
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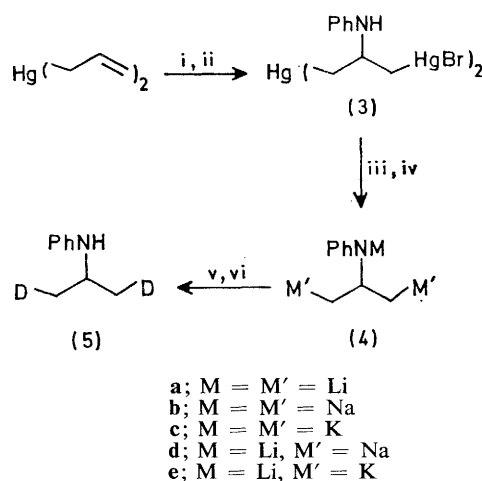
New  $\beta$ -substituted homo- and hetero-metallic trianions of the type  $\bar{C}C(\bar{N}Ph)\bar{C}$  with alkali metal cations (Li, Na, and K) are obtained from  $\beta$ -substituted organomercury compounds *via* low temperature mercury-alkali metal transmetallation; the lithiated trianion reacts regioselectively at both carbanionic carbon atoms with electrophilic agents such as  $D_2O$ , EtBr,  $Me_2S_2$ , and  $Me_3SiCl$ .

$\beta$ -Substituted organometallic compounds of type (1) are prone to  $\beta$ -elimination leading to the formation of olefins.<sup>1</sup> However, the organometallic compounds (2), prepared from  $\beta$ -functionalized organomercurials by mercury-alkali metal transmetallation,<sup>2,3</sup> are more stable at low temperatures owing to the loss of electronegativity on the heteroatom Y, thus hindering the  $\beta$ -elimination, and may be useful in synthesis.<sup>3,4</sup>

We report a new type of trianion derivative (4) made by mercury-alkali metal transmetallation from  $\beta$ -substituted organomercury(II) compounds (Scheme 1).<sup>5</sup> Successive treatment of the compound (3)<sup>†</sup> [obtained by the *in situ* aminomercuriation of diallylmercury<sup>6</sup> with aniline-mercury(II) acetate and further double decomposition with potassium bromide] with phenyl-lithium<sup>7</sup> and lithium powder yielded the corresponding trianion derivative (4a). This compound was characterized by transformation into its dideuterio-derivative



(5) with deuterium oxide at low temperature. Use of phenyl-sodium<sup>8</sup>-sodium<sup>‡</sup> or phenylpotassium<sup>9</sup>-potassium<sup>‡</sup> to give the corresponding trianion derivatives (4b) and (4c) required a reaction temperature of  $-100^\circ C$  to avoid  $\beta$ -elimination. The heterometallic trianion derivatives [(4d) and (4e)], which are more stable than the homosodium and homopotassium derivatives, were obtained using phenyl-lithium-sodium or



**Scheme 1.** i,  $PhNH_2-Hg(OAc)_2$ ; ii, KBr; iii, PhM; iv, M'; v,  $D_2O$ ; vi,  $HCl-H_2O$ .

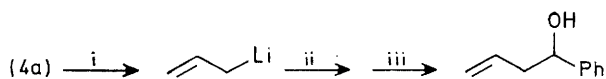
<sup>†</sup> In the case of the oxygenated derivative  $M'CH_2CH(OM)-CH_2M'$  (M and/or M' = Li, Na, or K) the isolation of the corresponding trianion derivatives, even at  $-100^\circ C$ , was not possible owing to their fast decomposition by  $\beta$ -elimination.

<sup>‡</sup> Sodium and potassium were used as metal plates prepared by dissolution of the corresponding metal in liquid ammonia at  $-50^\circ C$  followed by evaporation at 0.1 Torr.

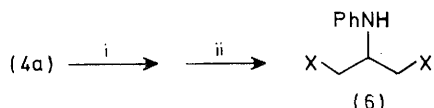
**Table 1.** Synthesis of the trianion derivatives (4).

Trianion	Reaction conditions		% Yield	
	$T/^\circ\text{C}^a$	Time PhM; M'	Hg <sup>0</sup> <sup>b</sup>	(5) <sup>c</sup>
(4a)	-78	10 min; 8 h	90	55
(4b)	-100	2 h; 6 h	94	60
(4c)	-100	2 h; 6 h	78	63
(4d)	-78	10 min; 8 h	92	59
(4e)	-78	10 min; 8 h	92	54

<sup>a</sup> Bath temperature. <sup>b</sup> Based on amount of (3) used. <sup>c</sup> Yield of isolated product, based on Hg<sup>0</sup> precipitated.



**Scheme 2.** Reagents and conditions: i, -78 to -50 °C; ii, PhCHO; iii, HCl-H<sub>2</sub>O.



**Scheme 3.** Reagents and conditions: i, E<sup>+</sup> = EtBr, Me<sub>2</sub>S<sub>2</sub>, or Me<sub>3</sub>SiCl; ii, HCl-H<sub>2</sub>O.

phenyl-lithium-potassium at -78 °C. Compounds (4b-e) were again characterized by deuteriolysis and spectroscopic analysis of compounds (5) (Table 1).

Increasing the temperature to -50 °C after preparation of (4a) caused decomposition of the trianion to give allyl-lithium. The latter was isolated by reaction with benzaldehyde and hydrolysis (yield 75%, with no trace of isopropylaniline as reaction product, Scheme 2).

The reactivity of the lithium anion (4a) with different electrophiles has been studied. Compound (4a) was allowed to react at -78 °C with an excess (3:1, 3 h) of ethyl bromide,

**Table 2.** Synthesis of compounds (6) by reaction of the trianion derivative (4a) with electrophiles E<sup>+</sup> (Scheme 3).

Product	E <sup>+</sup>	X	% Yield		B.p., $T/^\circ\text{C}$ (p/mmHg) of (6)
			Hg <sup>0</sup> <sup>a</sup>	(6) <sup>b</sup>	
(6a)	EtBr	Et	70	65	96-99 (0.1)
(6b)	Me <sub>2</sub> S <sub>2</sub>	MeS	75	76	172-176 (0.001)
(6c)	Me <sub>3</sub> SiCl	Me <sub>3</sub> Si	80	62	105-108 (0.001)

<sup>a</sup> Based on amount of (3) used. <sup>b</sup> Based on (4a).

dimethyl disulphide, or trimethylchlorosilane, followed by hydrolysis at the same temperature with aqueous hydrochloric acid, and the corresponding products (6) were obtained (Scheme 3). The reaction takes place regioselectively at both carbanionic carbon atoms.

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