β-Substituted Organosodium and Organopotassium Compounds. Preparation and Characterization

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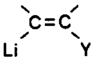
β-Functionalized organosodium and organopotassium compounds are prepared for the first time through a mercury–alkali metal transmetalation process. These new organometallics are characterized by in situ D_2O hydrolysis. Dianions containing two different alkali metals as the counterions are also synthesized and their stability is compared with that of the corresponding β-substituted organolithium, organosodium, and organopotassium analogues.

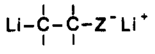
The preparation of organometallic derivatives of the main groups elements substituted at the β carbon by heteroatoms (1) is greatly hindered by the tendency of these systems to undergo β-elimination reactions which lead to the formation of olefins[1-3] (Scheme I). For this reason, earlier attempts to synthesize β-substituted organometallic derivatives from magnesium[1,4] or lithium[5] afforded the expected products in only very low yields even at temperatures as low as −100 °C.[4,5] On the other hand, these species were postulated to be highly reactive not isolated intermediates which decompose very readily.[6-9]

The stability of β-substituted organometallics is enhanced when the metal is linked to an sp^2 hybridized carbon[1] and also if the metal and the heteroatom are cis to one another in an olefinic backbone (2).[10-12]



2 (Y=OR, NR_2)

Recently,[13] we reported the stabilization of β-hydroxy and β-amino organolithium compounds by transforming these functions into the corresponding lithium alkoxides or amides (3). In this way, the starting electronegative

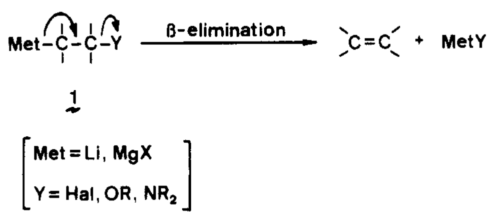


$$\mathrm{Li{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}Z^{-}Li^{+}}$$

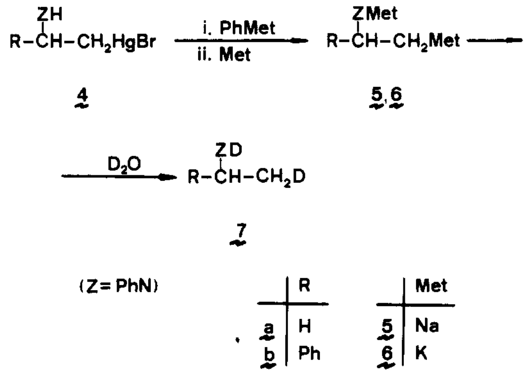
3 (Z = O, PhN)

heteroatom is converted into a new type of substituent which bears a partial negative charge and the resultant products are stable species which do not undergo β-elimination below −78 °C. Compounds 3 are suitable synthons for the regioselective preparation of bifunctional compounds.[14]

Scheme I



Scheme II



In general, very little is known about organosodium and organopotassium derivatives compared to their lithium homologues due to their great reactivity and the difficulties inherent in their preparation.[15] In the present paper we report the preparation of β-substituted organosodium and organopotassium compounds as well as their characterization and stabilization.

Results and Discussion

When aminomercurials[16,17] (4, Z = PhN)[18] are allowed to react with phenylsodium[19] at −78 °C in THF solution for 2 h and then with an excess (1:6) of sodium[20] at −100

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[14] Barluenga, J.; Fañanás, F. J.; Yus, M. *J. Org. Chem.* **1979**, *44*, 4798.

[15] For a review see: *Methoden Org. Chem. (Houben-Weyl), 4th Ed.* **1970**, *13/1*, 87–731.

[16] β-Substituted organomercurials were prepared by addition of mercuric salts to alkenes in the presence of the apropiate protic media. For a review see: *Methoden Org. Chem. (Houben-Weyl), 4th Ed.* **1974**, *13/2b*, 130–152.

[17] For a general scope of the mercury/sodium and potassium exchange process in organomercurials see ref 15.

[18] Only decomposition products were detected in the reaction of oxymercurials 4 (Z = O) with sodium or potassium even at −100 °C.

[19] Nobis, J. F.; Moormeier, L. F. *Ind. Eng. Chem.* **1954**, *46*, 539.

[20] Sodium and potassium were used as metal plates prepared by dissolution of the corresponding metal in liquid ammonia at −50 °C followed by evaporation under vacuum (0.1 mmHg).

0022-3263/81/1946-1281$01.25/0

Table I. Preparation and Deuterolysis of β-Substituted Organosodium and Organopotassium Compounds

			^{1}H NMR[d]		^{13}C NMR[e]		
compd[a]	Hg^0, yield, %[b]	7, yield, %[c]	δ_{CH} (multiplicity)	J, Hz	δ_{CH_2D} (multiplicity)	J_{CD}, Hz	bp, °C (mmHg)[f]
5a	85	76	3.0 (t)	6.0	13.49 (t)	19.75	93-96 (15)[g]
6a	80	77					
8a (10a)	79	80					
9a (11a)	82	83					
5b	75	81	4.3 (t)	6.0	23.56 (t)	19.45	71-74 (0.001)[h]
6b	77	83					
8b (10b)	76	86					
9b (11b)	87	89					
8c (10c)	75	70	4.6 (t)	6.0	23.67 (t)	19.40	95-98 (15)[i]
9c (11c)	81	72					

[a] See ref 13. [b] Relative to starting organomercurial 4. [c] Relative to Hg precipitated. [d] Proton chemical shifts are relative to internal Me_4Si. Spectra were recorded in CCl_4 solution in a Varian EMR-390 NMR spectrometer. [e] Carbon chemical shifts are relative to internal $CDCl_3$. Spectra were recorded in $CDCl_3$ in a Varian CFT-80 NMR spectrometer. [f] Literature values correspond to nondeuterated compounds. [g] Lit.[23] bp 97.5-98 °C (18 mmHg). [h] Lit.[24] bp 70-72 °C (0.001 mmHg). [i] Lit.[25] bp 100 °C (18 mmHg).

Table II. Reaction of Dianions 5, 6, 8 (10), and 9 (11) with Electrophiles

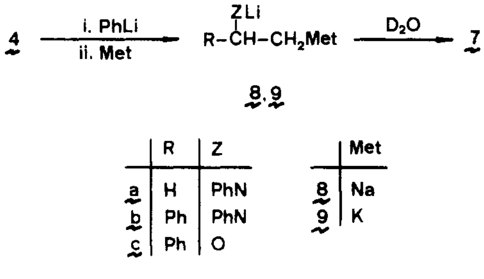
starting mercurial	dianion	E$^+$	F	Hg^0, yield, %[a]	12,[b] yield, %[c]	bp, °C (mmHg), or mp, °C (solvent)
4a	5a	O_2	OH	76	47	71-76 (0.001)[d]
4a	6a	O_2	OH	81	43	72-76 (0.001)[d]
4a	8a (10a)	O_2	OH	87	51	70-75 (0.001)[d]
4a	8a (10a)	CO_2	CO_2Et[e]	97	62	72-77 (0.001)[f]
4a	9a (11a)	O_2	OH	89	50	70-74 (0.001)[d]
4a	9a (11a)	CO_2	CO_2Et[e]	90	54	73-78 (0.001)[f]
4b	8b (10b)	O_2	OH	76	58	[g]
4b	8b (10b)	CO_2	CO_2Et[e]	79	60	72-74 (hexane/$CHCl_3$)[h]

[a] Relative to starting organomercurial 4. [b] GLC and spectral data for compounds 12 were identical with those previously reported.[14] [c] Relative to Hg precipitated. [d] Lit.[14] bp 70-75 °C (0.001 mmHg). [e] After esterification with HCl/ethanol (anhydrous).[14] [f] Lit.[14] bp 73-77 °C (0.001 mmHg). [g] Oil.[14] [h] Lit.[14] mp 72-73 °C.

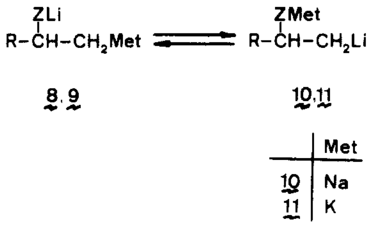
°C (bath temperature) for 0.5 h, a solution of the corresponding β-aminoorganosodium compound (**5**) and elemental mercury are obtained. If phenylpotassium[21] and potassium[20] are used instead, the corresponding β-substituted organopotassium derivatives (**6**) are obtained. The existence of compounds **5** and **6** was ascertained by treatment of the above solutions with D_2O at low temperature which led to the corresponding products of deuterolysis **7** (Scheme II and Table I).

The stability of compounds **5** and **6** strongly depends on the temperature. For instance, when the transmetalation is carried out at -78 °C the total decomposition of the organometallic by abstraction of a proton from the reaction medium is observed.[4] Since no deuterium incorporation in **7** can be detected at this temperature total proton abstraction must take place prior to the deuterolysis, that is, in less than 30 min. Even at -100 °C a slight decomposition occurs when reaction times longer than 1 h are used. Organosodium derivatives **5** were found to possess greater stability than their organopotassium analogues **6**. This is in good agreement with previously reported data for unsubstituted organosodium and organopotassium compounds.[15]

Scheme III



Scheme IV



The incorporation of two different metals, one of them being lithium, to these dianions results in a great enhancement of their stability. When oxy- and aminomercurials **4** were allowed to react with phenyllithium at -78 °C in THF solution and then with an excess of sodium or potassium (molar ratio 1:6) at the same temperature for 2 h,[22] elemental mercury and a solution of the organometallics **8** or **9** (**10** or **11**; see Scheme IV) are obtained (Scheme III). Their presence as stable species in the THF solution was ascertained by the generation of **7** after D_2O hydrolysis.

The following alternative explanations would account for the enhanced stability of **8** and **9** relative to **5** and **6**. (a) Once **8** and **9** have been generated they undergo a fast

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(21) Maercker, A.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 1742.

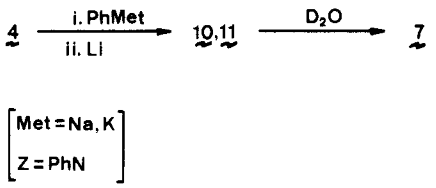
(22) This modification is interesting from a synthetic point of view since reaction times are reduced from 8 (ref 13) to 2 h.

(23) "Handbook of Chemistry and Physics", 57th ed.; The Chemical Rubber Co.: Cleveland, OH, 1976-77; p C-116.

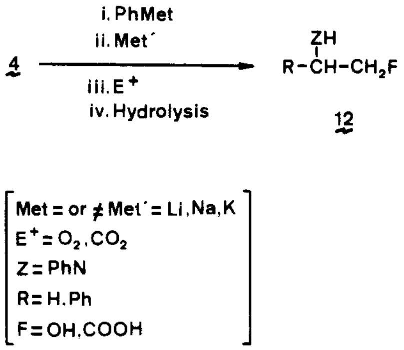
(24) Barluenga, J.; Ara, A.; Asensio, G. *Synthesis* **1975**, 116.

(25) Reference 23, C-297.

Scheme V



Scheme VI



metal-exchange process to give the more stable β-substituted organolithium compounds[13] **10** and **11** (Scheme IV). (b) The polarity of the Z–Met bond in the β-substituted organoalkali compound is expected to modify the reactivity of the anionic carbon, this being enhanced as the bond becomes more ionic.

In fact, the stability of **10** and **11** decreases in the series Li > Na > K (Scheme V) when **4** (Z = PhN) is treated succesively with a solution of a phenylalkali compound and then with lithium powder at −78 °C. At this temperature, when Met = K, a decomposition of **11** of above a 40% is observed to take place in a period of 8 h. No decomposition of **10** (Met = Na) or of the dilithio dianions[13] is detected under similar conditions.

Dianions **5**, **6**, **8** (**10**), and **9** (**11**) were further characterized upon preparation of a few condensation derivatives **12** by reaction with oxygen and carbon dioxide at low temperature followed by dilute hydrochloric acid hydrolysis (Scheme VI and Table II).

Experimental Section

Preparation and Deuterolysis of 5a. Typical Procedure. To a 250-mL two-necked flask equipped with an argon inlet and a mechanical stirrer were added dry THF (75 mL) and 2-(phenylamino)ethylmercury(II) bromide **4a** (6.0 g, 15 mmol). The resulting solution was cooled to −78 °C, phenylsodium (1.5 g, 15 mmol) was added, and the suspension was stirred for 2 h. The reaction mixture was cooled to −100 °C, then sodium plates (2.07 g, 90 mmol) were added, and the mixture was vigorously stirred. After 30 min deuterium oxide (3 mL) was added and the elemental mercury precipitated was filtered out and weighed (yield 2.55 g, 85%). The resulting solution was neutralized with aqueous hydrochloric acid and extracted with ether and the ether layer washed with water and dried over anhydrous sodium sulfate. Solvents were removed and the residue was distilled under vacuum (15 mmHg) to give the product, yield 1.18 g, 76% relative to Hg precipitated.

Preparation and Deuterolysis of 8a. Typical Procedure. To a 250-mL two-necked flask equipped with an argon inlet and a mechanical stirrer were added dry THF (75 mL) and 2-(phenylamino)ethylmercury(II) bromide **4a** (6.0 g, 15 mmol). The resulting solution was cooled to −78 °C, and a 0.83 N ether solution of phenyllithium (18 mL, 15 mmol) was added in 5 min. Sodium plates (2.07 g, 90 mmol) were added and the mixture was stirred for 2 h. Deuterium oxide (3 mL) was added and the elemental mercury precipitated was filtered out and weighed (yield 2.37 g, 76%). The resulting solution was neutralized with aqueous hydrochloric acid and extracted with ether and the ether layer washed with water and dried over anhydrous sodium sulfate. Solvents were removed and the residue was distilled under vacuum (15 mmHg) to give the product, yield 1.16 g, 80% relative to Hg precipitated.

Reaction of Dianions 5, 6, 8 (10), and 9 (11) with Oxygen and Carbon Dioxide. Obtention of Compounds 12. Dianions **5**, **6**, **8** (**10**), and **9** (**11**) obtained as above described were reacted with a precooled stream of oxygen or solid carbon dioxide, following the procedure previously reported.[14]

Registry No. 4a, 52969-23-0; **4b**, 55552-57-3; **5a**, 76269-88-0; **5b**, 76269-89-1; **6a**, 76269-90-4; **6b**, 76269-91-5; **7a**, 68090-84-6; **7b**, 68090-85-7; **7c**, 68090-86-8; **8a**, 76269-92-6; **8b**, 76269-93-7; **8c**, 76269-94-8; **9a**, 76269-95-9; **9b**, 76269-96-0; **9c**, 76269-97-1; **10a**, 76269-98-2; **10b**, 76269-99-3; **10c**, 76270-00-3; **11a**, 76270-01-4; **11b**, 76270-02-5; **11c**, 76281-99-7; **12a** (F = OH), 122-98-5; **12a** (F = CO_2Et), 62750-11-2; **12b** (F = OH), 13891-02-6; **12b** (F = CO_2Et), 6846-55-5.

Silyl Halides from (Phenylseleno)silanes. Reaction with Oxiranes and Alcohols To Give Hydrolytically Stable Silyl Ethers

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The preparation of (phenylseleno)silanes and their reactions with halogens (Cl_2, Br_2, I_2) to give silyl halides and diphenyl diselenide are described. Highly hindered *tert*-butyldimethyl and *tert*-butyldiphenylsilyl halides were easily prepared. The reaction of silyl bromides and iodides with oxiranes followed by diazabicyclononane treatment gave allylic alcohol silyl ethers. Tertiary alcohols reacted rapidly with silyl iodides to give hydrolytically stable silyl ethers. Treatment of the silyl ethers with tetra-*n*-butylammonium fluoride gave the free alcohols without rearrangement or isomerization.

(Phenylseleno)trimethylsilane (**1**) has emerged as a very useful synthetic reagent for (a) the generation of potassium phenylselenide,[1] (b) the preparation of γ-phenylseleno trimethylsilyl enol ethers,[2,3] *O*-(trimethylsilyl)phenylseleno acetals,[2-4] diseleno acetals,[4] and phenylseleno esters from acid chlorides,[5] (c) the deoxygenation of sulfoxides, selenoxides, and telluroxides,[6] and (d) the in situ preparation of trimethylsilyl iodide.[2] The chemistry and preparation

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