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THE REACTION OF n-BUTYLLITHIUM/SODIUM(POTASSIUM) TERT.-BUTOXIDE (LOCHMANN-SCHLOSSER BASE) WITH A CH-ACID LEADS TO ORGANO-SODIUM(POTASSIUM) COMPOUNDS. AN NMR SPECTROSCOPICAL STUDY OF SEVERAL ORGANO-LITHIUM, -SODIUM AND -POTASSIUM COMPOUNDS IN TETRAHYDROFURAN-D_8

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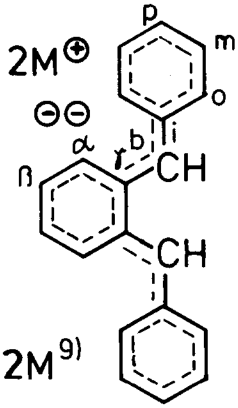
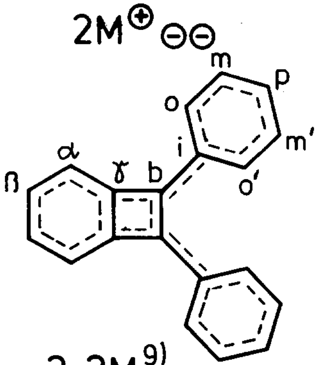
Abstract: Deprotonation of the corresponding hydrocarbons with the LOCHMANN-SCHLOSSER base n-BuLi/Na(K)O-t-Bu leads only to the sodium (1-2Na, 2-2Na) and potassium compounds (1-2K, 2-2K, 3-2K), respectively, and not to the lithium compounds. This seems to be generally the case.

The powerful base system n-butyllithium/potassium tert.-butoxide (n-BuLi/KO-t-Bu), normally used in pentane, hexane or heptane, can in principle transform a carbon acid R-H into the organolithium R-Li and/or organopotassium compound R-K. A similar dichotomy exists for n-BuLi/NaO-t-Bu. According to Lochmann[1], triphenylmethane and n-BuLi/NaO-t-Bu lead to triphenylmethylsodium, and n-BuLi/KO-t-Bu react with toluene to give benzylpotassium. The latter reaction has been confirmed by Schlosser[2,3] who also prepared allyl[4] and pentadienyl[5] potassium compounds via this route[6].

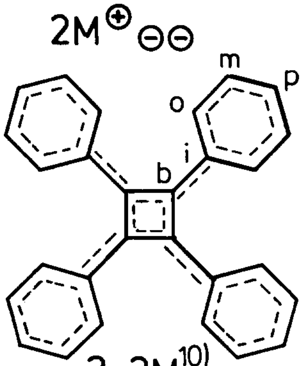
The formation of pentadienyl potassium compounds and thus the formation of "organopotassiums" by means of n-BuLi/KO-t-Bu, however, has been questioned recently. Smith and coworkers[7] observed a similar reactivity of authentic pentadienyllithium (C_5H_7Li) prepared from pentadiene with n-BuLi in tetrahydrofuran (THF), and the species prepared from pentadiene with n-BuLi/KO-t-Bu in pentane followed by replacement of the solvent by THF. Therefore, these authors suggested that the reactive organometallic is the same in both cases, namely C_5H_7Li. Their supposition seems to be supported by the different reactivity of authentic pentadienylpotassium[8].



1-2M[9)]



2-2M[9)]



3-2M[10)]

M= Li,Na,K

We provide NMR-spectroscopical evidence that deprotonation of the corresponding hydrocarbons with the LOCHMANN-SCHLOSSER base n-BuLi/Na(K)O-t-Bu leads only to the sodium (1-2Na, 2-2Na) and potassium compounds (1-2K, 2-2K, 3-2K), respectively.

The ^1H- and ^{13}C nmr spectra of 1-2Li, 1-2Na and 1-2K are gathered in Tab. 1a and b.

Tab. 1a. ^1H nmr chemical shifts (δ[ppm]) of 1-2Li, 1-2Na and 1-2K in THF[D_8] at room temp.

compound	conditions	protons					
		α	ß	b	o	m	p
1-2Li	1: n-BuLi	7.23	6.04	3.69	6.61	6.46	5.56
1-2Li	2: n-BuLi, TMEDA	7.25	6.04	3.75	6.68	6.47	5.57
1-2Na	3: n-BuLi/NaO-t-Bu	7.22	5.98	3.98	6.73	6.52	5.62
1-2Na	4: n-C_5H_{11}Na/TMEDA	7.24	6.01	3.95	6.75	6.60	5.68
1-2K	5: n-BuLi/KO-t-Bu	7.06	6.00	4.00	6.58	6.46	5.49
1-2K	6: $(CH_3)_3SiCH_2K$	7.03	5.99	4.00	6.59	6.48	5.52

Tab. 1b. ^{13}C nmr chemical shifts (δ[ppm]) of 1-2Li, 1-2Na and 1-2K in THF[D_8] at room temp.

compound	conditions	carbon atoms							
		α	ß	γ	b	i	o	m	p
1-2Li	1	116.3	113.9	134.7	65.0	148.5	116.3	128.0	106.3
1-2Li	2	116.0	114.0	134.0	65.8	148.9	117.3	128.3	106.9
1-2Na	4	112.3	111.8	132.2	68.1	147.4	117.5	128.5	107.4
1-2K	5	113.6	112.9	134.3	74.0	146.3	116.1	129.0	105.5

As shown in Tab. 1a the hydrogens H^b of 1-2Li and 1-2Na are significantly different to characterize the compounds in solution. Moreover, 1-2Na prepared via n-BuLi/NaO-t-Bu (conditions 3) has almost the same signals as authentic 1-2Na prepared with n-pentylsodium/TMEDA (4). Similarly, authentic 1-2K prepared by means of trimethylsilylmethylpotassium[11] (6) is ^1H nmr-spectroscopically identical to 1-2K prepared with n-BuLi/KO-t-Bu (5); in the case of 1-2K especially the hydrogens H^α and H^o are characteristically different from those of 1-2Li (and 1-2Na).

In the ^{13}C spectra, different absorptions of 1-2Li, 1-2Na and 1-2K are found especially at the benzylic positions C^b, s. Tab. 1b.

Tab. 2a and b give a comparison between 2-2Li, 2-2Na and 2-2K; 2-2Na has been prepared via different routes (8 and 9).

Looking at Tab. 2a and b it is immediately obvious that **2**-2Li, **2**-2Na and **2**-2K are significantly different in, and accordingly easily characterized by means of their ^{1}H- and ^{13}C-nmr spectra, (see e.g. H^{α}, H^{o}, H^{p}; C^{α}, C^{b}, C^{p}). It is also quite clear, that n-BuLi/NaO-t-Bu (8) leads to the same compound - **2**-2Na - as this is the case with n-C_5H_{11}Na/TMEDA (9).

Tab. 2a. ^{1}H nmr chemical shifts (δ[ppm]) of **2**-2Li, **2**-2Na and **2**-2K in THF[D_8] at room temp.

compound	conditions	protons				
		α	ß	o'	o,m,m'	p
2-2Li	7: n-BuLi, TMEDA	6.42	6.04	6.54	—— 6.71	5.67
2-2Na	8: n-BuLi/NaO-t-Bu	6.17	5.87	6.12	6.41 - 6.53	5.36
2-2Na	9: n-C_5H_{11}Na/TMEDA	6.16	5.96	6.16	6.41 - 6.69	5.43
2-2K	10: n-BuLi/KO-t-Bu	6.10	5.85	6.01	6.37 - 6.52	5.34

Tab. 2b. ^{13}C nmr chemical shifts (δ[ppm]) of **2**-2Li, **2**-2Na and **2**-2K in THF[D_8] at room temp.

compound	conditions	carbon atoms							
		α	ß	γ	b	i	o,o'	m,m'	p
2-2Li	7	109.7	113.1	132.4	83.2	144.3	116.9	128.7	108.4
2-2Na	8	106.0	111.9	136.5	88.8	142.0	117.7 114.4	129.4 128.0	104.2
2-2Na	9	106.3	112.1	137.1	88.4	142.0	117.9 114.4	129.5 128.0	104.5
2-2K	10	105.9	111.6	137.3	94.7	141.4	117.5 114.6	129.9 128.5	104.5

Although it is only possible to prepare the potassium salt **3**-2K which excludes comparisons with the lithium and sodium species, it is clear that $(CH_3)_3SiCH_2K$ (12) as well as n-BuLi/KO-t-Bu (11) lead to the identical species - **3**-2K -, s. Tab. 3.

Tab. 3. ^{1}H- and ^{13}C nmr chemical shifts of **3**-2K in THF[D_8] at room temp.

compound	conditions	protons			carbon atoms				
		o	m	p	b	i	o	m	p
3-2K	11: n-BuLi/KO-t-Bu	6.95	6.63	5.98	108.7	141.8	122.8	127.6	112.7
3-2K	12: $(CH_3)_3SiCH_2K$	6.93	6.61	5.96	108.8	141.9	122.9	127.7	112.8

It would be rather accidentical if the lithium compound 3-2Li formed possibly via route 11 would have (almost) exactly the same ^{1}H- and ^{13}C nmr spectrum as 3-2K formed via route 12!

In summary, reaction of the corresponding hydrocarbons with the LOCHMANN-SCHLOSSER base n-BuLi/Na(K)O-t-Bu leads to the sodium (potassium) compounds 1-2Na, 2-2Na, 1-2K, 2-2K and 3-2K, and not to the lithium species 1-2Li, 2-2Li and 3-2Li, as shown by a comparison of the ^{1}H- and ^{13}C-chemical shifts of these compounds prepared via unequivocal reactions as well as n-BuLi/Na(K)O-t-Bu. This result seems to be generally valid[1-6]. Additional evidence, e.g., for the formation of 2-2Na and 2-2K with the LOCHMANN-SCHLOSSER base is provided by the splitting of the ortho and meta protons and carbon atoms at room temperature into the signals of the o(m)- and o'(m')-positions, which is not so in the case of 2-2Li (see 7, 8, 10 in Tab. 2a and 2b).

Finally, it is noteworthy that the nmr spectra of the "authentic" compounds 1-2Na, 1-2K, 2-2Na and 3-2K are not significantly different from the same species prepared by the LOCHMANN-SCHLOSSER base (comp. 3/4, 5/6, 8/9 and 11/12) although in the latter case they are "coordinated" with LiO-t-Bu. The influence of LiO-t-Bu, however, seems to be generally unimportant: if 2-2Li is prepared with n-BuLi/TMEDA in the presence of or without LiO-t-Bu only marginal differences are observed in the ^{1}H- and ^{13}C-spectra.

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