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NEW SYNTHETIC METHODS : SODIUM ALKANECHALCOGENATES AS DEMETHYLATING AGENTS. SCOPE, LIMITATION AND NEW ONE-POT SYNTHESIS OF DIARYLDISELENIDES.

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Abstract : Sodium alkanechalcogenates (S, Se) cleave the alkylarylchalcogenides (O, S, Se). The versatility of such reagents is developed and applied to a new synthesis of diaryldiselenides.

It has been established that sodium alkanethiolates easily perform the selective monodealkylation of anisoles[1] and alkylarylsulfides[2] in dipolar aprotic solvents. We wish to report here our findings concerning the action of sodium alkaneselenolates in dimethylformamide (D.M.F.) or hexamethylphosphoric triamide (H.M.P.T.) on methylarylchalcogenides. As for its thio analog, we have observed that sodium methane selenolate (CH_3SeNa) readily cleaves methylarylethers (table 1, entries 1-17) as well as their methylthio analogs (table 1, entries 18-23). The best yields have been obtained by using 1.5 equiv. of CH_3SeNa in refluxing H.M.P.T. (8 h). The sodium methaneselenolate can be easily generated in situ through the sodium cleavage of dimethyldiselenide in H.M.P.T. It can be observed (table 1, entries 7 and 14-17) that either the aromatic bromine atom or a carbonyl function are not affected under these conditions and that (table 1, entry 9) when a dimethoxylated substrate is used, we selectively obtained the product of monodemethylation. It also appears that the O-demethylation is prefered to the S-one (table 1, entries 11-13).

In connection with this work, we have also studied the action of sodium ethanethiolate (CH_3CH_2SNa) in refluxing D.M.F. or H.M.P.T. (8 h) on various alkylarylselenides. We have been able to perfom the Se-demethylation of these substrates. This leads (table 2, entries 1-11) to a selenophenol which is readily oxidised in situ into the corresponding diselenide by treatment with iodine.

It is noteworthy that when the substrate offers a competition between a O or Se-demethylation, only the last one is observed (table 2, entries 7-11), except, when the alkyl group attached to the selenium atom becomes too bulky (table 2, entries 12-14).

Entry	Substrate	Conditions[4a]	Product[4b]	Yield (%)[4c]
1	$C_6H_5OCH_3$	A	C_6H_5OH	68
2		B		56
3		C		73
4		D		69
5	3-CH_3-$C_6H_4OCH_3$	A	3-CH_3-C_6H_4OH	63
6		C		68
7	3-Br-5-CH_3-$C_6H_3OCH_3$	A	3-Br-5-CH_3-C_6H_3OH	45
8		C		48
9	3-OCH_3-$C_6H_4OCH_3$	C	3-OCH_3-C_6H_4OH	65
10		D		59
11	4-SCH_3-$C_6H_4OCH_3$	C	4-SCH_3-C_6H_4OH	60
12		B		87
13		D		90
14	2-$COCH_3$-$C_6H_4OCH_3$	A	2-$COCH_3$-C_6H_4OH	58
15		B		56
16		C		71
17		D		80
18	$C_6H_5SCH_3$	A	C_6H_5SH	51
19		C		63
20	4-CH_3-$C_6H_4SCH_3$	A	4-CH_3-C_6H_4SH	55
21	2-CH_2OH-$C_6H_4SCH_3$	A	2-CH_2OH-C_6H_4SH	42
22		C		58
23	2-$COCH_3$-$C_6H_4SCH_3$	A	2-$COCH_3$-C_6H_4SH	60

Table 1 - Reaction of alkylarylethers and sulfides with sodium methaneselenolate.

Entry	Substrate	Conditions[4a]	Product[4b]	Yield (%)[4c]
1	$C_6H_5SeCH_3$	F	$C_6H_5Se)_2$	72
2	$4-CH_3-C_6H_4SeCH_3$	E	$4-CH_3-C_6H_4Se)_2$	83
3		F		87
4	$2-COCH_3-C_6H_4SeCH_3$	F	$2-COCH_3-C_6H_4Se)_2$	68
5	$C_{10}H_7-\beta-SeCH_3$	E	$C_{10}H_7-\beta-Se)_2$	76
6		F		82
7	$2-CH_3O-C_6H_4SeCH_3$	F	$2-CH_3O-C_6H_4Se)_2$	47
8	$3-CH_3O-C_6H_4SeCH_3$	F	$3-CH_3O-C_6H_4Se)_2$	65
9	$4-CH_3O-C_6H_4SeCH_3$	F	$4-CH_3O-C_6H_4Se)_2$	58
10	$4-CH_3CH_2O-C_6H_4SeCH_3$	F	$4-CH_3CH_2O-C_6H_4Se)_2$	67
11	$4-n-BuO-C_6H_4SeCH_3$	F	$4-n-BuO-C_6H_4Se)_2$	72
12	$3-n-BuSe-C_6H_4OCH_3$	F	$3-n-BuSe-C_6H_4OH$	64
13	$3-n-BuSe-5-OCH_3-C_6H_3OCH_3$	F	$3-n-BuSe-5-OCH_3-C_6H_3Se)_2$	52
14	$3-n-C_5H_{11}-5-OCH_3-C_6H_3SeCH_3$	F	$3-n-C_5H_{11}-5-OCH_3-C_6H_3Se)_2$	63

Table 2 - Reaction of alkylarylselenides with sodium ethanethiolate

Entry	Substrate	Conditions[4a]	Product[4b]	Yield (%)[4c]
1	$C_6H_5SeCH_3$	C	$C_6H_5Se)_2$	82
2	C_6H_5Cl	G	$C_6H_5Se)_2$	73
3	$4-Br-C_6H_4Cl$	G	$4-Br-C_6H_4Se)_2$[5]	71

Table 3 - Reaction of sodium methaneselenolate on selenoanisole and aromatic chlorides.

Therefore, these results allow a simple high yield synthesis of aromatic diselenides which can be effected in a convenient one-pot treatment of unactivated arylchlorides with CH_3SeNa in refluxing H.M.P.T. (table 3). This new synthesis of diselenides consists of a nucleophilic aromatic methylselenodechlorination followed by the Se-demethylation of the intermediate methylarylselenide formed, leading to a selenophenol which is readily oxidised in situ. Our last results are in good areement with those of TESTAFERI[3] for the synthesis of alkylarylsulfides.

These synthetic reagents, which are still under investigation, seem to be promised to further important developments.

References and Notes

1. G.I. FEUTRILL and R.N. MIRRINGTON, Tetrahedron Letters (1970) 1327
2. a. D. CHIANELLI, L. TESTAFERRI, M. TIECCO and M. TINGOLI, Synthesis (1982) 475
   b. M. TIECCO, M. TINGOLI, L. TESTAFERRI, D. CHIANELLI and M. MAIOLO, Synthesis (1982) 478
3. a. L. TESTAFERRI, M. TINGOLI and M. TIECCO, Tetrahedron Letters (1980) 3099
   b. L. TESTAFERRI, M. TINGOLI and M. TIECCO, J. Org. Chem. 45 (1980) 4376
4. a. Experimental conditions: A: CH_3SeNa (1.5 equiv) in refluxing D.M.F. (8 h) - B: $CH_3Se\rangle_2$/Na in refluxing D.M.F. (8 h) - C: A except H.M.P.T. is used instead of D.M.F. - D: B except H.M.P.T. is used instead of D.M.F. - E: 1. CH_3CH_2SNa (1.5 equiv) in refluxing D.M.F. (8 h); 2. I_2 room temperature - F: E except H.M.P.T. is used instead of D.M.F. - G: 1. CH_3SeNa (3 equiv) in refluxing H.M.P.T. (8 h); 2. I_2 room temperature.
   b. All new compounds were caracterised by ^1H - N.M.R., I.R. and t.l.c. whereas the known one are identical to authentic samples.
   c. Yields are for isolated products.
5. The preferred substitution of the bromine atom instead of the chlorine one is noteworthy. However such inversions of the reactivity of the halogen atom are not so uncommon as reported in the litterature[6].
6. L. LAITEM, L. CHRISTIAENS, M. RENSON, C.R. Acad. Sc. Paris C, 278 (1974) 275 and references cited therein.
7. The authors gratefully acknowledge Professor M. RENSON for his interest in their work.

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