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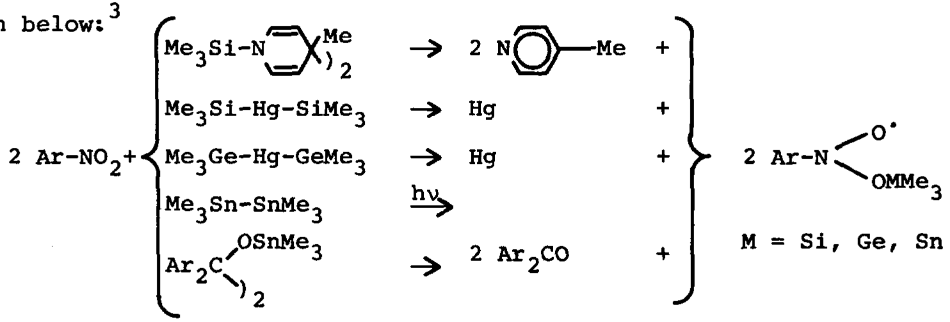
NEW NITROGEN CONTAINING RADICALS FROM NITRO AND ORGANOMETALLIC COMPOUNDS: $R'\text{-}NO^{\bullet}\text{-}OMR_3$ (R'=ARYL, ALKYL), $Ar\text{-}N^{\bullet}\text{-}OMR_3$, AND $Ar\text{-}N(OMR_3)\text{-}N^{\bullet}Ar$ (M=Si,Ge,Sn)

Knud Reuter[1] and Wilhelm P. Neumann[2]*
Lehrstuhl für Organische Chemie I der Universität Dortmund
Otto-Hahn-Str., D 4600 Dortmund 50

High concentrations of trialkylmetaloxy nitroxide radicals are obtained, when aromatic nitro compounds are mixed with the silyl, germyl, or stannyl compounds shown below:[3]



Only with the distannane, u.v. irradiation is essential. In all other cases, warming to 40°C or even room temperature is sufficient. But, the reaction is enhanced by irradiation. Thus, a free radical mechanism might be in operation, as shown for some heterocyclic and the phenyl nitro derivatives with $Et_3SiH/tBu_2O_2/h\nu$,[4] as well as a molecular or cryptoradical one,[1] or a photoexcited state of the organometallic molecule.[5] The e.s.r. parameters are reported in table 1.

There is little influence of M on a_N, when passing the sequence C, Si, Ge to Sn. a_M is very small, mostly not detectable, possibly because of fixation of M into the O-N-O-plane by coordination with the second O. Evalution of a_N versus the σ-values of the substituents indicates an O-type [6] of these radicals, as in the case of nitro anion radicals.[7] Bulky ortho groups cause higher a_N values (and lower a_2 and a_4) by twisting the aryl residue out of the C-N-O-plane, resulting additionally in a more pyramidal structure at the N, which is equivalent to higher s character of the odd electron. This suggestion is nicely supported by the 2,4,6-tBu_3Ph-derivatives. Though obviously more hindered than the other 2,4,6-trialkylphenyl- and the 2-tert.butylphenyl-derivatives and surely twisted by about 90°, these radicals exhibit remarkably lower a_N values. Very likely the bulky o-tBu-groups flatten the pyramidal N enviroment, so decreasing the s character of the odd electron and consequently a_N.

Table 1.

Aryl trialkylmetaloxy nitroxyls Ar-NO$^\bullet$-OMR$_3$, 22-60°C in toluene, a values in G.

Ar	MR$_3$	a_N	$a_{2,6}$	$a_{3,5}$	a_4
Ph	CMe$_3$	14.70	3.03	0.94	3.07
	SiMe$_3$	15.22	3.18	1.07	3.18
	SiEt$_3$	14.76	3.20	1.04	3.10
	GeMe$_3$	14.90	3.41	1.16	3.41
	SnMe$_3$	14.10	3.36	1.14	3.72
4-Me-Ph	SiMe$_3$	15.71	3.12	1.07	3.44
	SnMe$_3$	14.52	3.41	1.19	3.78
4-OH-Ph	SnMe$_3$	16.15	3.53	1.03	-
3-OH-Ph	SnMe$_3$	15.20	3.56	1.19	3.56
4-Cl-Ph	SnMe$_3$	14.42	3.59	-	-
3-Cl-Ph	SnMe$_3$	14.24	3.63	1.20	3.63
4-CN-Ph	SnMe$_3$	12.80	3.56	1.20	0.57
4-COOCH$_2$-Ph-Ph	SnMe$_3$	12.78	3.45	1.16	0.2
2-Me-Ph	SiMe$_3$	17.37	2.79	1.06	2.79
	SnMe$_3$	15.87	3.24	1.18	3.24
2,4,6-Me$_3$-Ph	SiMe$_3$	24.81	0.71	0.71	0.71
	SnMe$_3$	21.90	0.87	0.87	1.15
2,4,6-Et$_3$Ph	SiMe$_3$	25.15	0.36	0.72	0.36
	SnMe$_3$	22.65	0.50	1.00	0.50
2,4,6-iPr$_3$-Ph	SiMe$_3$	25.75	not resolved		
	SnMe$_3$	23.91	n.r.	1.01	n.r.
2-tBu-Ph	SiEt$_3$	26.65	n.r.	1.10	n.r.
	SnMe$_3$	24	n.r.	1.10	1.10
2,5-tBu$_2$-Ph	SiMe$_3$	27.50	not resolved		
	SnMe$_3$	24.05	n.r.	1.10	1.10
2,4,6-tBu$_3$-Ph	SiMe$_3$	23.1	-	0.87	-
	GeMe$_3$	22.45	-	0.89	-
	SnMe$_3$	21.30	-	0.97	-[a)]

a) a(^{117,119}Sn) = 4.17 G

With aliphatic nitro compounds, the corresponding radicals arise by means of the methods described above, see table 2. The methyl, ethyl, and benzyl derivatives are persistent, the others decay. They can be considered as pyramidal. When R = tBu, simultaneously the nitroxyl tBu$_2$NO$^\bullet$ appears in the e.s.r.

Table 2.

Alkyl trimethylmetaloxy nitroxyls R'-NO$^\bullet$-OMMe$_3$, 22-60°C in toluene, a values in G

R'	M	a_N	a_H	a_M	R'	M	a_N	a_H	a_M
Me	Si	29.5	9.43	-	iPr	Si	30.0	4.82	-
Me	Ge	29.6	9.48	-	tBu	Si	30.2	-	-
Et	Si	29.7	8.33	-	tBu	Ge	30.3	-	-
PhCH$_2$	Si	30.0	6.43	-	tBu	Sn	30.1	-	4.78

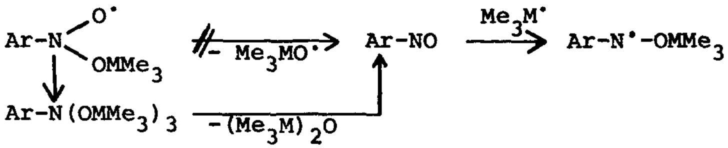
If an excess of the metalating agent is used (best investigated with (Me$_3$Si)$_2$Hg and Me$_6$Sn$_2$) the aryl nitroxide radicals, see table 1, desappear, and metaloxy aminyls Ar-N$^\bullet$-OMMe$_3$ (M = Si, Sn), appear, see table 3. They are well observable with bulky groups in ortho position, especially tBu, retarding the dimerization forming hydrazines which is well known from other aminyls,[8] and they do not rearrange to nitroxyls.

Table 3.

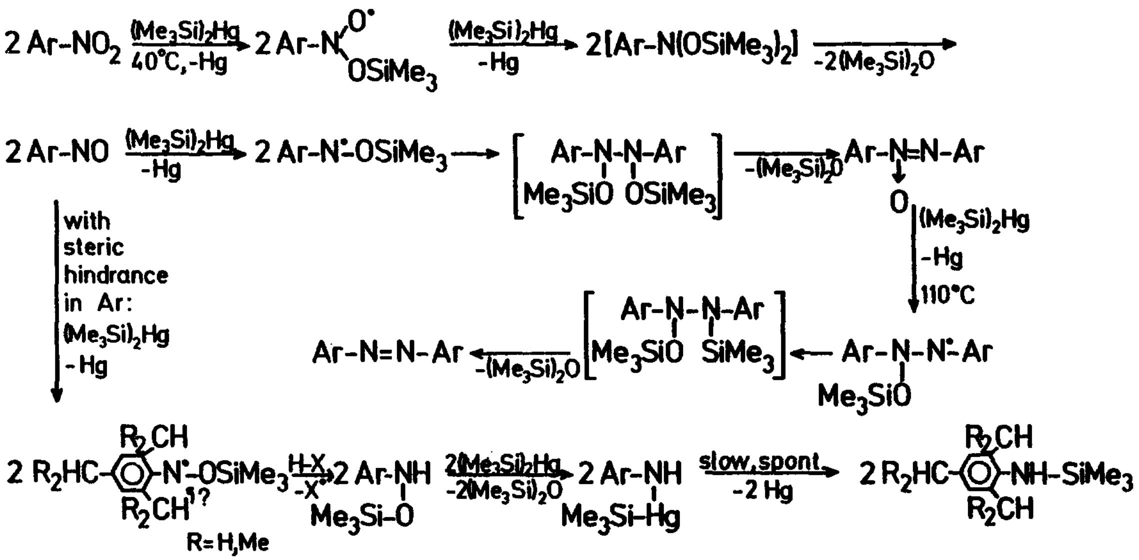
Aryl trialkylmetaloxy aminyls Ar-N$^{\bullet}$-OMR$_3$, 40-60°C in toluene, a values in G.

Ar	MR$_3$	a_N	$a_{2,6}$	$a_{3,5}$	a_4	Ar	MR$_3$	a_N	$a_{2,6}$	$a_{3,5}$	a_4
2,4,6-	SiEt$_3$	10.70	-	1.51	1.51	2,4,6-	SiMe$_3$	10.93	-	2.01	-
iPr-Ph	SnMe$_3$	10.85	-	2	2	tBu$_3$Ph	SiEt$_3$	10.71	-	1.99	-
2-							SiEt$_3$	10.33	-	1.96	-[11]
tBu-Ph	SnMe$_3$	11.20	5.04	1.57	5.42		SnEt$_3$	9.98	-	1.95	-[11]
2,5	SiMe$_3$	11.11	5.38	1.71	6.14						
TBu$_2$-Ph	SnMe$_3$	11.10	5.04	1.51	5.48						

Since a spontaneous splitting is not likely,[9] we assume a stepwise formation of the new radicals:



These aminyls, too, are transient. Lastly, with sterically less hindered aryl residues, azobenzenes[10] are the final products, and metalated anilines with more hindered aryl residues. (Yields for thermal reactions are given in table 4):



No direct evidence is available for the compounds in brackets, but the corresponding siloxane is found in correct amounts. The silyloxy hydrazyl, part of the reaction scheme above, could be observed in the case of the 2,5-tBu$_2$ derivative: a_N = 9.9, a_N = 5.0, $a_{2,4}$ = 4.9, a_3 = 1.4 G. in toluene at 22°C.

Several steps could be carried out by separate experiments and support the general reaction scheme given above:

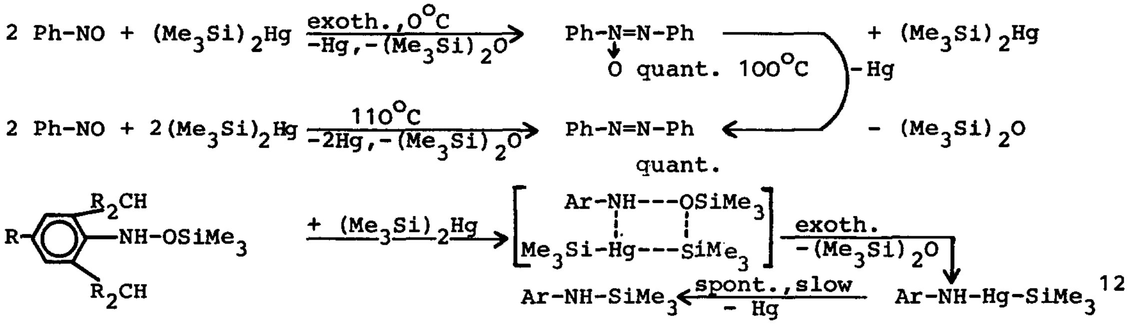


Table 4.

Yields (%) of products from Ar-NO_2 with $(Me_3Si)_2Hg$ in toluene, 110°C

Ar	Ar-N=N-Ar	Ar-NH-$SiMe_3$	Ar	Ar-N=N-Ar	Ar-NH-$SiMe_3$
Ph	96	0	2,4,6-Et_3-Ph	trace	62
2-Me-Ph	77	3	2,4,6-iPr_3-Ph	0	37[12]
2,4,6-Me_3-Ph	5	53	2,4,6-tBu_3-Ph	0	0[b)]
2,5-tBu_2-Ph	0	74[a)]			

a) from the nitroso compound; b) at least 3 other products, all not containing Si.

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