Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

---

cis, *trans*-Isomerism in *O*-silylated monocarbonyl compounds

G.S. BURLACHENKO, T.A. MANUKINA and Yu.I. BAUKOV
Chemistry Department, M.V. Lomonosov State University, Moscow (U.S.S.R.)

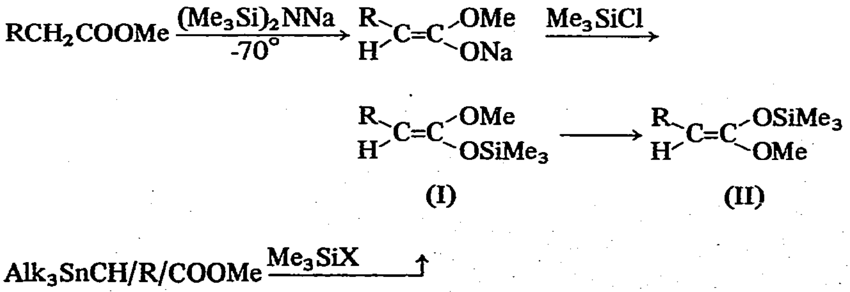
(Received September 29th, 1971)

In a study of the reaction[1] of halosilanes with metallated acetic esters we have found that metal (Na, Sn) derivatives of silyl or phenyl acetates give, depending on the conditions, either the *cis* or the *trans* *O*-silylated keteneacetal isomers, the formation of the one being kinetically controlled whilst that of the other is thermodynamically controlled.

For example, one isomer Ia (yield 64%, b.p. 68–70° at 1.5 mm, n_D^{20} 1.4433, ν(C=C) 1600–1620 cm^{-1}, δ (CH=) 2.92 ppm) was isolated when the mixture formed after the addition of trimethylchlorosilane to the sodium derivative of methyltriethylsilyl acetate was fractionated immediately. The second isomer IIa (yield 51%, b.p. 63–64° at 1 mm, n_D^{20} 1.4476, ν (C=C) 1600–1620 cm^{-1}, δ (CH=) 2.77 ppm) was isolated when fractionation was delayed for 15–20 hours after the addition, the reaction mixture meanwhile having been kept at room temperature.

Sodium derivatives of trimethylsilyl- or phenylacetic esters react with trimethylchlorosilane in a similar manner. With stannylated silylacetates, the products of the kinetically controlled reaction could not be isolated but their formation as intermediates has been demonstrated by means of PMR spectroscopy.

On the basis of the reported data for the chemical shifts in the isomeric *cis,trans*-*O*-silyl-substituted enols[2], we have assumed that *cis* isomers (I) are those which exhibit a low-field signal for the vinylic proton, the hydrogen atom in these isomers being *cis* relative to the trialkylsiloxy group. The results are summarised in Scheme 1 and in Table 1.

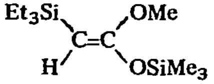
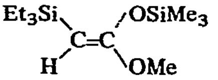
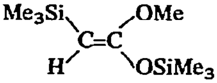
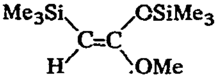
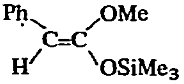
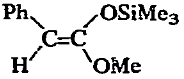
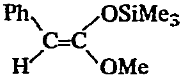


(a, R = Et$_3$Si; b, R = Me$_3$Si; c, R = Ph)

Scheme 1

TABLE 1

Methods:
A, reaction of Me_3SiCl with Na(RCHCOOMe); B, rearrangement in the presence of $HgBr_2$ + Me_3SiBr; C, reaction of Me_3SiX with $Bu_3Sn(Alk_3Si)CHCOOMe$.

Compound[a]		Method	Yield (%)	B.p. (°C/mm)	n_D^{20}	δ (CH=) (ppm)[d]	ν(C=C) (cm^{-1})
	(Ia)	A[b]	64	68–70/1.5	1.4433	2.92	
	(IIa)	A[c] B C	51 84 52	63–64/1 76–77/2 72–76/1.5	1.4476 1.4472 1.4472	2.77	1600–1620
	(Ib)	A[b]	44	75–76/15	1.4270	2.98	
	(IIb)	B C	75 53	76–77/17 81–82/25	1.4282 1.4272	2.88	1600–1620
	(Ic) 36%	A[b]	30	98–99/2.5	1.5184	4.52	
	(IIc) 64%					4.45	
	(IIc)	A[c] B	64 85	88–89/1.5 102–103/3.5	1.5212 1.5180	4.45 4.45	1640–1660

[a] All compounds had correct elemental analyses. [b] Distilled immediately after adding Me_3SiCl. [c] Distilled 15–20 hours after adding Me_3SiCl. [d] Using benzene as an internal reference.

The pure *cis* isomers (I) isomerise to give the *trans* derivatives (II) in the presence of catalytical amounts of $HgBr_2$ and Me_3SiBr*, after several hours at room temperature.

REFERENCES

1 I.F. Lutsenko, Yu.I. Baukov, G.S. Burlachenko and B.N. Khasapov, *J. Organometal. Chem.*, 5 (1966) 20.

2 H.O. House, L.J. Czuba, M. Gall and H.D. Olmstead, *J. Org. Chem.*, 34 (1969) 2324.

3 Yu.I. Baukov and I.F. Lutsenko, *Organometal. Chem. Revs.*, *A*, 6 (1970) 355; G. Berth, K. Fechner, K.-D. Kaufmann, G. Michael and G. Tomaschewski, *Z. Chem.*, 11 (1971) 102.

---

*These are the usual catalysts employed for silylated ketoenol transformations[3].