

NOTE

ON THE REPORTED SELECTIVITY OF THE BROMINATION OF MIXED TETRAALKYLTINS IN CARBON TETRACHLORIDE

S. BOUË, M. GIELEN, J. NASIELSKI, J. AUTIN AND M. LIMBOURG

Service de Chimie Organique, Faculté des Sciences, Université Libre de Bruxelles, 50, avenue F. D. Roosevelt, Bruxelles 5 (Belgium)

(Received July 24th, 1968)

Faleschini and Tagliavini recently published kinetic results on the cleavage of mixed tetraalkyltins R_3SnR' in carbon tetrachloride¹. They claim to have shown that bromine reacts with Bu_3SnEt and Bu_3SnPr in such a way that the organic bromide with the smallest molecular weight is the only alkyl bromide formed, and that this has been checked by VPC analysis ("... accertando, per via gas-cromatografica, per le altre alogenazioni, la sola presenza dell'alogenuro di alchile a minor peso molecolare.").

This result is surprising because it is difficult to imagine what sort of effect could come into play to make such a sharp distinction between Et and n-Bu, let alone between n-Pr and n-Bu. Moreover, evidence has accumulated² that in the poorly nucleophilic solvent chlorobenzene, the selectivity among alkyl groups is poor³, and there is no obvious reason why carbon tetrachloride should lead to an important differentiation.

We have synthesized Bu_3SnEt and Bu_3SnPr , and have brominated both

TABLE I

SELECTIVITY OF THE BROMOMETALLATION OF ALKYLTRIBUTYLTINS

Bu_3SnR'	Solvent (temp. °C)	$[R'Br]/[n-BuBr]$
R' = Et	PhCl (20)	1.30
		1.15
		1.10
		1.20
		1.15
		0.50
	CCl ₄ (35)	0.37
		0.40
R' = n-Pr	PhCl (20)	0.44
		0.42
		0.33
		0.38
	CCl ₄ (35)	1.4
		1.2

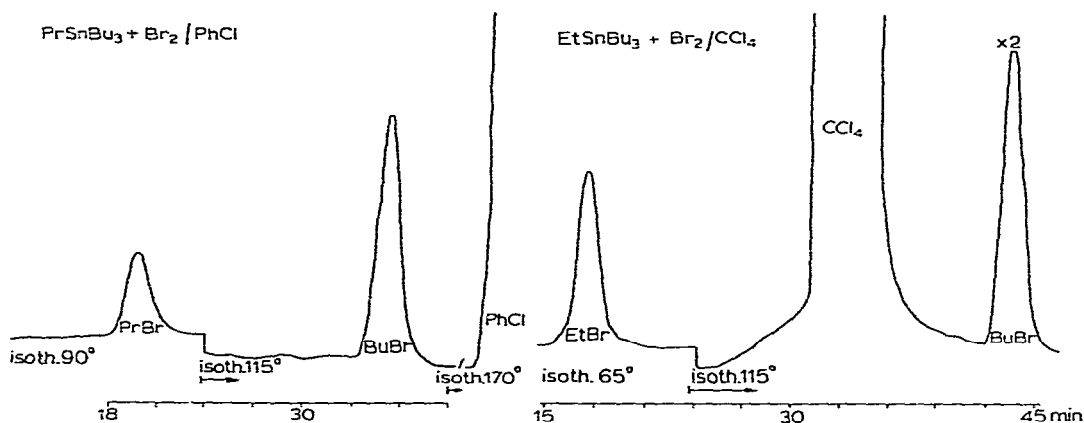


Fig. 1. Typical chromatograms obtained for the bromodemetalation of alkyltributyltins. (F & M 500 gas chromatograph; column, copper 3 m, \varnothing 6 mm); liquid phase, diisodecyl phthalate 33% on Chromosorb; gas, hydrogen (30 ml/min); inlet pressure, 2 kg/cm²; detector temperature, 230°; injection temperature, 190°; column temperature, isothermal at 65, 90, 115 and/or 170°.)

compounds in chlorobenzene and carbon tetrachloride, in the dark and at a constant temperature. The results are summarized in Table 1, and two typical chromatograms are shown in Fig. 1. It is clear from our results that the bromodemetalation of mixed tetraalkyltins is far from showing the selectivity claimed by Faleschini and Tagliavini. Since the rate constants have thus to be dissected into the contributions for both cleavages, and since their discussion is based on the assumption of a very high selectivity, we think that their rate constants and discussion should be reexamined in the light of these new, but not unexpected, results.

REFERENCES

- 1 S. FALESCHINI AND G. TAGLIAVINI, *Gazz. Chim. Ital.*, 97 (1967) 1401.
- 2 S. BOUÉ, M. GIELEN AND J. NASIELSKI, *Tetrahedron Lett.*, (1968) 1047.
- 3 S. BOUÉ, M. GIELEN AND J. NASIELSKI, *J. Organometal. Chem.*, 9 (1967) 443.

J. Organometal. Chem., 15 (1968) 267-268