Journal of Organometallic Chemistry, 94 (1975) C33—C34
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

PENTABROMOPHENYLMERCURIALS

G.B. DEACON*, G.J. FARQUHARSON
Chemistry Department, Monash University, Clayton, Victoria, 3168 (Australia)
and J.M. MILLER
Chemistry Department, Brock University, St. Catharines, Ontario (Canada)

(Received June 16th, 1975)

Summary

Bis(pentabromophenyl)mercury and pentabromophenylphenylmercury have been prepared by decarboxylation of the corresponding mercury(II) pentabromobenzoates; the former mercurial is thermally stable to at least 400 °C, but the latter and pentabromophenylmercuric chloride and bromide undergo symmetrization reactions on being heated.

The chemistry of pentabromophenylorganometallics is currently restricted to derivatives of magnesium [1, 2], lithium [1, 2], silicon [2], and copper [2]. Only the silanes have been isolated. We now report preparations and properties of some pentabromophenylmercurials.

Mercuric pentabromobenzoate and phenylmercuric pentabromobenzoate, obtained in high yield** from reaction of mercuric or phenylmercuric acetate with pentabromobenzoic acid, undergo decarboxylation in boiling pyridine to give bis(pentabromophenyl)mercury and pentabromophenylphenylmercury respectively in good yield.

$$(C_6Br_5CO_2)_2Hg \rightarrow (C_6Br_5)_2Hg + 2CO_2$$

$$PhHgO_2CC_6Br_5 \rightarrow PhHgC_6Br_5 + CO_2$$

Although a significant reduction in thermal stability might be expected from bis(pentachlorophenyl)mercury to bis(pentabromophenyl)mercury, since increased halogen size might promote halogen abstraction and benzyne elimination (see e.g. thermal decomposition of bis(*o*-iodophenyl)mercury [3]), thermogravimetric analysis indicates that $(C_6Br_5)_2Hg$ is stable to at least the melting point (406 °C), as is $(C_6Cl_5)_2Hg$ (lit. [4] m.p. 383 °C). However, the mass

---

*To whom correspondence should be addressed.

**Satisfactory analyses were obtained for all new compounds.

spectrum shows that halogen abstraction giving $C_6Br_5HgBr^+$ is a prominent breakdown path for the parent ion. Similar behaviour is not observed for $(C_6Cl_5)_2Hg$ [5].

Bis(pentabromophenyl)mercury is readily cleaved by triiodide ions in *N,N*-dimethyl formamide and by mercuric chloride and bromide in xylene/nitrobenzene giving iodopentabromobenzene and pentabromophenylmercuric chloride and bromide respectively. On heating solid pentabromophenylphenylmercury and pentabromophenylmercuric chloride and bromide, thermal symmetrization is observed prior to melting, in contrast with the behaviour of the corresponding

$$2\,PhHgC_6Br_5 \xrightarrow{>100\,^{\circ}C} Ph_2Hg + (C_6Br_5)_2Hg$$

$$2\,C_6Br_5HgX \xrightarrow{>250\,^{\circ}C} (C_6Br_5)_2Hg + HgX_2 \quad (X = Cl \text{ or } Br)$$

pentachlorophenylmercurials [4, 6].

The present decarboxylation syntheses, coupled with our recent development of permercuration and bromodemercuration as a route to several polybromobenzoic acids [7], opens the way to preparation of a wide range of polybromophenylmercurials.

Acknowledgement

We are grateful to the Australian Research Grants Committee for support.

References

1 D.J. Berry and B.J. Wakefield, J. Chem. Soc. C, (1969) 2342.
2 C.F. Smith, G.J. Moore and C. Tamborski, J. Organometal. Chem., 42 (1972) 257.
3 G. Wittig and H.F. Ebel, Ann., 650 (1961) 20.
4 F.E. Paulik, S.I.E. Green and R.E. Dessy, J. Organometal. Chem., 3 (1965) 229.
5 S.C. Cohen, J. Chem. Soc. A, (1971) 632.
6 I.P. Beletskaya, L.V. Savinykh, V.N. Gulyachkina and O.A. Reutov, J. Organometal. Chem., 26 (1971) 23.
7 G.B. Deacon and G.J. Farquharson, J. Organometal. Chem., 67 (1974) C1 and unpublished results.

Note added in proof. Since this communication was submitted, preparations of some pentabromophenylgold compounds have been reported (R. Usón and A. Laguna, Synth. React. Inorg. Met. - Org. Chem., 5 (1975) 17).