Addition of Li^{80m}Br to Polyhalogenoarynes

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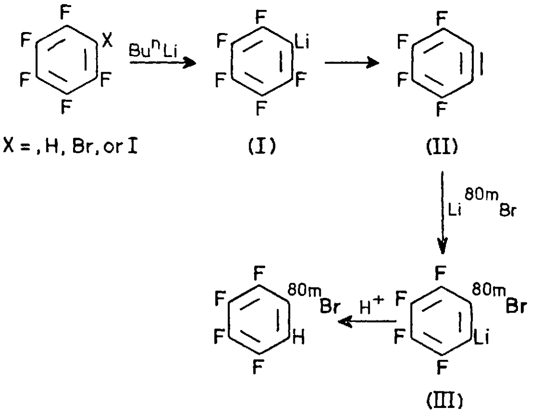
Summary Addition of radioactive lithium bromide to perhalogenoarynes generated from perhalogenophenyllithium derivatives acts as a simple and convenient gauge of aryne formation.

THE thermal decomposition of pentafluorophenyl-lithium (I) has been extensively studied in terms of reaction products[1] but little work has been done on details of the kinetics of the reaction because of the complexity of the reaction paths possible. Tatlow and his co-workers[2] have shown that below about −20 °C only slow nucleophilic reactions occur whereas above 0 °C elimination reactions predominate, and that tetrafluorobenzyne (II) adds lithium bromide and iodide. Reactions possible in the systems studied here include translithiation (between perhalogeno-aromatic species), nucleophilic attack, and benzyne addition of either lithium bromide or perhalogeno-aromatic species.

$Li^{80m}Br$, formed by 14·8 MeV neutron irradiation of dried and powdered lithium bromide has been used as a radiolabel to study incorporation of bromine into perhalophenyl-lithium derivatives. n-Butyl-lithium in hexane solution was added to an ether solution of the perhalogeno-aromatic reagent saturated with $Li^{80m}Br$, and the mixture was left for several hours before hydrolysis with 1 M sulphuric acid terminated the reaction. The products were separated into aqueous and organic species before the activity of each portion was measured.



SCHEME

The activity was originally present in the form of water-soluble species only, and blanks (in which no butyl-lithium was used) showed incorporation of ^{80m}Br into the organic phase to 3% of the available activity. In the presence of butyl-lithium, when perhalogenophenyl-lithium reagents were formed, much larger amounts of activity were found to enter the organic phase presumably *via* (II) (Scheme). Alternative reactions to form polyphenyl systems[1] are available for (II), and (III) can either lithiate other species or eliminate lithium fluoride.

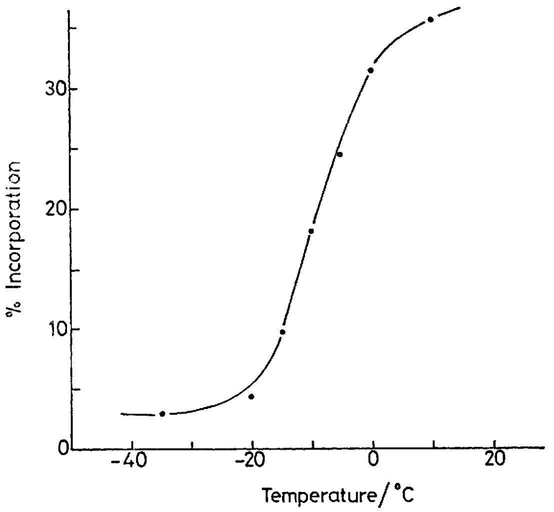


FIGURE. Effect of temperature on the thermal decomposition of C_6F_5Li in the presence of $Li^{80m}Br$; 16 h reaction time, ether–hexane as solvent.

Lithium bromide, though slightly soluble in ether, is essentially insoluble in hexane, and this allowed us to show that the addition reaction is a liquid-phase process rather that a surface reaction since (a) when hexane was used as the sole solvent <3% activity appeared in the organic phase; (b) when $Na^{80m}Br$ was used as the source of the activity only *ca.* 4% activity appeared in the organic phase even when ether was present as solvent; (c) when lithium bromide was used in ether–hexane *ca.* 20% activity appeared in the organic phase (see Table).

TABLE. Incorporation of ^{80m}Br into the organic phase at 0 °C (ether–hexane as solvent unless otherwise noted). All reactions were terminated after 6 h.

Perhalogeno-reagent	Inorganic label	Bu^nLi present	% Incorporation
C_6F_5H	LiBr	No	2·7
C_6Cl_5H	LiBr	No	2·1
C_6F_5I	LiBr	Yes	20·1
C_6Cl_5H	LiBr	Yes	20·3
C_6F_5I[a]	LiBr	Yes	1·3
C_6F_5I	NaBr	Yes	4·0
Absent	LiBr	Yes	0·9
C_6Br_6	LiBr	Yes	11·1

[a] Hexane solvent.

The effect of temperature is shown in the Figure; the results are in excellent agreement with Tatlow's temperature range quoted above for reactions thought to involve aryne intermediates.

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[1] S. C. Cohen and A. G. Massey, *Adv. Fluorine Chem.*, 1970, **6**, 83.

[2] D. D. Callander, P. L. Coe, and J. C. Tatlow, *Tetrahedron*, 1966, **22**, 419.