Mechanism of Reactions of Sulphonium Salts with Organolithium Reagents

By D. Harrington, J. Weston, and J. Jacobus*
(*Department of Chemistry, Clemson University, Clemson, South Carolina* 29631)
and Kurt Mislow
(*Department of Chemistry, Princeton University, Princeton, New Jersey* 08540)

Summary Labelling experiments have established that tetraphenylsulphurane is the principal intermediate in the reaction of phenyl-lithium with triphenylsulphonium tetrafluoroborate to give biphenyl and diphenyl sulphide.

SULPHURANES (R_4S; R = alkyl or aryl) have been postulated as unstable intermediates in reactions of organolithium reagents with sulphonium salts.[1,2] The present work describes labelling data which implicate sulphuranes as the *principal* intermediates in these reactions where R = aryl, and which eliminate to a significant extent other plausible intermediates arising from alternate mechanistic pathways.

Non-specifically ^{14}C-labelled phenyl-lithium (1·0M in 3:1 benzene–ether) was added to an ethereal slurry of triphenylsulphonium tetrafluoroborate at −78° to yield homogeneous solutions, which were subsequently warmed rapidly to room temperature. The products were isolated by removal of solvent, oxidation of the residue with sodium metaperiodate in ethanol (sulphide to sulphoxide), and column chromatography of the products over alumina with subsequent recrystallization of the isolated biphenyl and phenyl sulphoxide. Homogeneity was established by t.l.c. analysis and m.p. The results of the radio-assay are in the Table.

If reaction of R_3S^+ with R*Li (label depicted by asterisk) were to give R_3R^*S, disproportionation of the sulphurane, in the absence of label exchange and discounting any isotope effect, should yield either singly labelled biphenyl and unlabelled diphenyl sulphide, or unlabelled biphenyl and singly labelled diphenyl sulphide, with equal probability. Thus, half of the original label should appear in each of the products (RR and RSR), granted disproportionation to products solely from R_3R^*S. For reactant ratios (R*Li: R_3S^+) of 0·5: 1·0 and 1·0: 1·0, this expectation

^{14}C *Counting data*

Mole ratio of reactants		Specific activity[a] of products	
PhLi	$Ph_3S^+BF_4^-$	Ph_2	Ph_2S[b]
0·5	1·0[c]	57·9	52·5
1·0	1·0	56·9	52·7
2·0	1·0	87·7	80·7
3·0	1·0	95·8	85·3

[a] Scaled to 100 dis. min^{-1} μmol^{-1} relative to starting PhLi (assayed as $PhCO_2H$.) [b] Analysed as Ph_2SO. [c] Recovered $Ph_3S^+BF_4^-$ displayed an activity of 1·5 dis. min^{-1} μmol^{-1} scaled as in a above.

is qualitatively borne out.† Label exchange (at a ratio of 0·5 : 1·0 for $R^*Li : R_3S^+$) would result in label dilution in the products, *i.e.*, if R_3R^*S reverts to organolithium reagent and sulphonium salt the probability of forming unlabelled organolithium reagent is three times that of forming labelled organolithium reagent, and subsequent reaction of produced RLi (unlabelled) with excess of R_3S^+ to yield R_4S would result in an increase in the concentration of unlabelled product molecules. Conversely, with an excess of R^*Li (labelled), exchange would ultimately lead to an increase in concentration of multiply labelled product molecules. Indeed, as is seen from the data in the Table, exchange is not significant at $R^*Li : R_3S^+$ ratios of less than unity, but becomes appreciable at higher ratios.‡

Since label exchange is not operative at low organolithium–sulphonium salt ratios, prediction of labelling patterns for mechanistic alternatives§ is considerably simplified. These alternatives must be able to account for the two major observed products, *i.e.*, coupling product (RR) and organosulphide (RSR). In the absence of label exchange, reactions proceeding *via* benzyne or radical intermediates cannot produce labelled diphenyl sulphide, nor can direct aromatic substitution. The present labelling experiments thus provide unambiguous evidence for the formation and subsequent disproportionation of an intermediate sulphurane into the observed products.

Support by the National Science Foundation is gratefully acknowledged.

(*Received*, 31*st July* 1972; *Com.* 1339.)

---

† The slightly greater activity of biphenyl relative to diphenyl sulphide can be attributed to the operation of minor reaction pathways or to biphenyl formation in the preparation of PhLi (from bromobenzene and lithium metal in benzene–ether).

‡ Label dilution of unchanged PhLi at a 1·5 : 1·0 ($R^*Li–R_3S^+$) ratio under unspecified conditions has been reported.[3]

§ These alternatives have been discussed by a variety of authors; see ref. 1 and references cited therein.

[1] R. W. LaRochelle and B. M. Trost, *J. Amer. Chem. Soc.*, 1971, **93**, 6077.
[2] W. A. Sheppard, *J. Amer. Chem. Soc.*, 1971, **93**, 5597.
[3] V. Franzen and C. Mertz, *Annalen*, 1961, **643**, 24.