Multiple pathways in the cleavage of benzyl groups from phosphonium salts by lithium aluminium hydride

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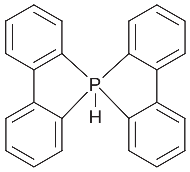
Reduction of benzylphosphonium salts by $LiAlD_4$ affords a phosphine and $PhCH_2D$, $2\text{-}DC_6H_4CH_3$ and $PhCH_3$; pathways involving P^V and P^{VI} intermediates are proposed to account for these products.

Benzyl groups are readily removed from benzylphosphonium salts by $LiAlH_4$ in THF to give a phosphine and toluene in good yields.[1,2] The reaction forms the basis of a general method for the preparation of unsymmetrical phosphines[1b] and has found use in the synthesis of cyclic phosphines,[3] but attempts to extend the utility of the reaction to the cleavage of phenyl groups from the more readily accessible arylphosphonium salts have met with limited success,[4] loss of either alkyl or aryl groups or both occurring in an apparently inconsistent way. Reduction of ylides from alkyltriphenylphosphonium salts proceeds exclusively with loss of phenyl[4,5] even when the ylidic carbon is benzylic, establishing that reduction of salts does not proceed *via* ylide formation. Reduction of resolved chiral benzylic salts occurs with partial or complete racemisation at phosphorus,[6] implying that the reaction proceeds *via* a configurationally mobile phosphorane of the type R_4PH. Such compounds have only been observed to form from phosphonium salts in the specialised case of the spirobisbiphenylyl system **1**.[7]



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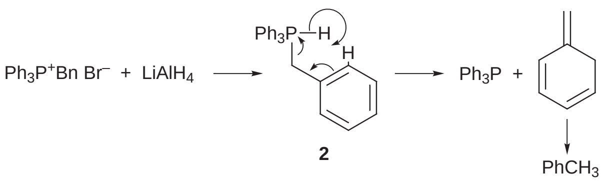
Theoretical considerations[8] suggest that the decomposition, shown in eqn. (1), is an allowed concerted process for two

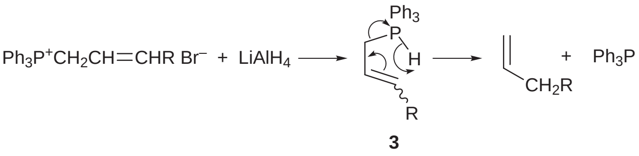
$$R_5P \rightarrow R_3P + RR \qquad (1)$$

substituents in the equatorial plane of a trigonal bipyramid, suggesting a reasonable pathway for the overall reduction, but it is not obvious why benzyl groups are a favoured leaving group if ionic stability of the leaving group were not an important factor, as had been generally supposed.[2] A possible reason could be a cheleotropic rearrangement of an intermediate phosphorane **2** with transfer of hydrogen from phosphorus to the *ortho* carbon of the benzyl group, followed by aromatisation of the methylenecyclohexa-2,4-diene thus expelled (Scheme 1).



Scheme 1

A similar pathway (Scheme 2) can be visualised for allylphosphonium salts and reported reductions of these by $LiAlH_4$ appear to proceed exclusively with allylic inversion ('S_N2' substitution').[2b] Thus, reduction of (*E*)-cinnamyltriphenylphosphonium bromide with $LiAlD_4$ yields triphenylphosphine and 1-phenyl[1-^{2}H]but-2-ene. Further, these allylic cleavages proceed more rapidly with phosphonium salts than they do with the analogous ammonium salts, which are similarly cleaved but largely without allylic inversion.[9]



Scheme 2

We now report that reduction of benzyltriphenylphosphonium bromide with $LiAlD_4$ in refluxing THF (5 h) affords toluene, [α-^{2}H]toluene and [*o*-^{2}H]toluene in a ratio of approximately 1:1:1 as determined by ^{1}H, ^{2}H and ^{13}C NMR spectroscopy; the other product, Ph_3P, showed no deuterium incorporation. The identity of the *o*-deuterated toluene was further confirmed by HSQC 2D ^{1}H/^{13}C{^{1}H} NMR and by comparison with authentic material obtained by quenching $2\text{-}CH_3C_6H_4MgBr$ with D_2O. Analogous comparisons confirmed the absence of detectable amounts of *m*- or *p*-deuterated toluene in the salt reduction. No exchange is observed when toluene is refluxed with $LiAlD_4$ in THF or when the product mixture of toluenes is treated with $LiAlH_4$, indicating that the three hydrocarbons all arise in the reduction process.

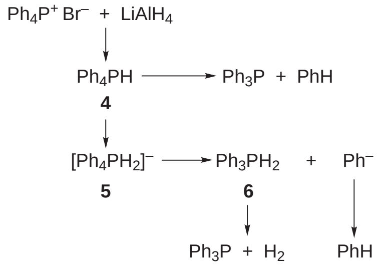
We extended the examination to the products from the $LiAlD_4$ reduction of all the phosphonium salts, $Bn_nP^+Ph_{4-n}$ Br^- (n = 0–4) and the results are summarised in Table 1. Ph_4P^+ Br^- cannot, of course, give toluene but under the same conditions it affords a mixture of PhH (21%) and PhD (79%) measured by mass spectrometry.

We have elsewhere presented evidence that the reduction of phosphonium salts with metal hydrides proceeds *via* a number of intermediates,[10] **4–6** (Scheme 3). Clearly, formation of R^-, which subsequently abstracts a proton from THF, could account for the formation of undeuterated hydrocarbon and decomposition of **2** by concerted processes could lead to either α- or *o*-deuterated toluene. Part of the [α-^{2}H]toluene will arise during the conversion of the 6-[^{2}H]methylenecyclohexa-1,3-diene to

Table 1 Yields of toluenes formed by reduction of $Bn_nP^+Ph_{4-n}$ Br^- with $LiAlD_4$

	Yield (%)		
n	$PhCH_3$	$PhCH_2D$	$2\text{-}DC_6H_4CH_3$
4	9	86	5
3	7	84	9
2	11	62	27
1	31	31	38
0	21[a]		79[b]

[a] C_6H_6. [b] C_6H_5D.



Scheme 3

toluene but there is too much deuterium on the benzylic carbon to be all accounted for in this way, since the ^1H–^2H isotope effect should ensure that the bulk of the deuterium originally in the *ortho* position, remains there. Therefore, most of the deuterium in $PhCH_2D$ arises by other processes of which there seem to be two, either a concerted loss of deuterium and $PhCH_2$ from **4**, or S_N2 type displacement at the benzylic carbon by hydride ion equivalent. We are unable to determine the relative contributions of these two pathways but we have observed that benzyldimethylphenylammonium bromide exclusively loses $PhCH_2D$ when refluxed in THF with $LiAlD_4$ [eqn. (2)], and,

$$Ph(CH_3)_2N^+CH_2Ph\ Br^- + LiAlD_4 \rightarrow PhNMe_2 + PhCH_2D \quad (2)$$

since an N^V intermediate is very improbable, this presumably goes *via* an S_N2 related process. Also, thermal decomposition of R_5P has resulted in products understandable in terms of concerted loss of two groups [eqn. (1)], *e.g.* the dissociation of PCl_5 to PCl_3 and Cl_2.[11] The exclusive *ortho* selectivity is, we believe, best explained by a concerted intramolecular hydride transfer since an S_N2' attack on the ring might reasonably be expected to give some of the [4-^{2}H]toluene. An alternative process involving radicals, formed by homolysis of P–C (or P–H) bonds, has not been excluded but the exclusive *ortho* deuterium transfer and the absence of the coupling product, 1,2-diphenylethane, lead us to favour a concerted pathway.

We thank the Australian Research Council for support.

Notes and References

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Received in Cambridge, UK, 6th July 1998; 8/05179H