Birch Reduction of Arylphosphines

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In contrast to unsubstituted tri(aryl)phosphines, bis(*p*-dimethylaminophenyl)phenylphosphine is not cleaved by sodium in liquid ammonia; instead, the hitherto unknown Birch product is formed *via* an intermediary phosphinocyclohexadienyl anion.

Triphenylphosphine is readily cleaved by sodium in liquid ammonia at −78 °C.[1,2] The resulting orange-red diphenylphosphide ion is a key intermediate in the synthesis of many phosphine ligands used in homogeneous catalysis.[3] An attractive extension of this route would be the cleavage of substituted arylphosphines as this may lead to electronic and/or steric modifications of the ligand.

We have attempted to prepare sodium bis(*p*-dimethylaminophenyl)phosphide from tris(*p*-dimethylaminophenyl)phosphine using similar conditions to those for triphenylphosphine. However, the solution remained blue and so apparently no electrons had been transferred to the phosphine. The starting compound was recovered unchanged after hydrolytic work-up.

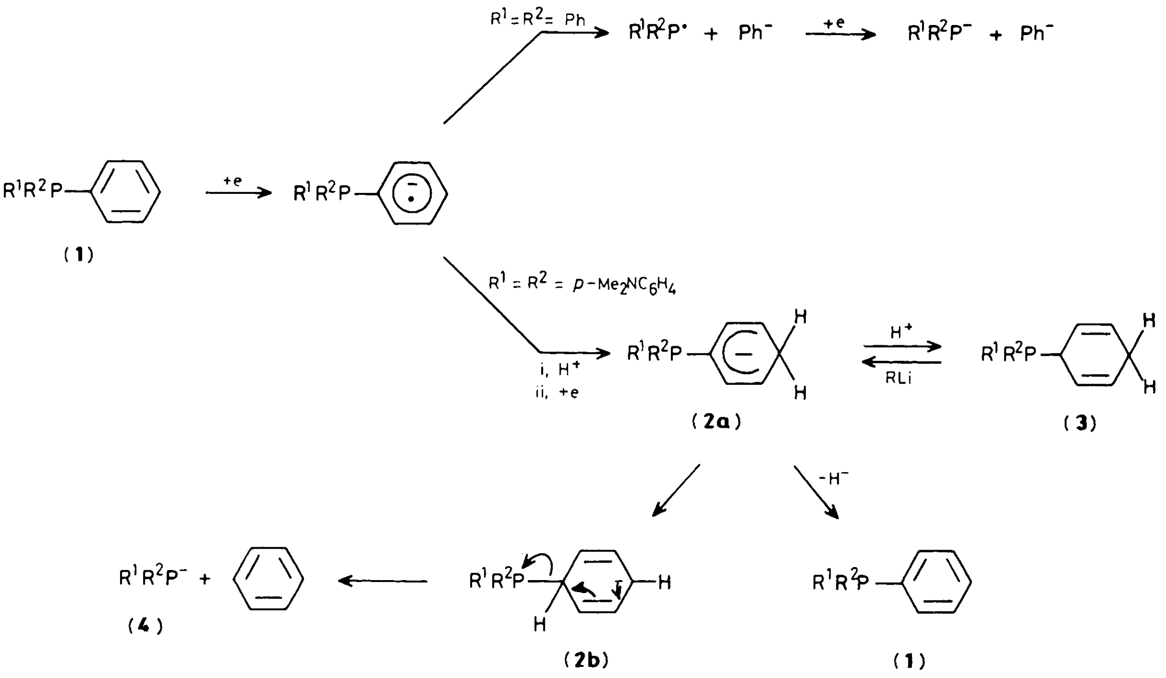
We expected that an electron could be transferred to the phenyl group of bis(*p*-dimethylaminophenyl)phenylphosphine (**1**; $R^1 = R^2 = p\text{-}Me_2NC_6H_4$) (Scheme 1) and that by cleavage of this phenyl group the desired phosphide would be formed. Indeed, compound (**1**) readily consumed two equivalents of sodium and the solution turned orange-red. However, to our surprise, upon hydrolytic work-up it appeared that after 4 h at −78 °C only 5% of the compound had been cleaved to bis(*p*-dimethylaminophenyl)phosphide. In addition to recovered starting material (52%), a new tertiary phosphine was found in 43% yield. The use of a cosolvent, tetrahydrofuran (THF), led to an increase of the yield of this product and in a preparative run we were able to isolate the pure compound in 75% yield.

The n.m.r. data (^1H, ^{31}P, and ^{13}C) and the elemental analysis of this compound are fully consistent with structure (**3**; $R^1 = R^2 = p\text{-}Me_2NC_6H_4$), *i.e.* the hitherto unknown Birch product. This Birch product is formed in a stepwise process. In

Table 1. Yield of Birch reduction of arylphosphines R^1R^2PPh.[a]

R^1	R^2	% Birch reduction	$\delta(^{31}P)$/p.p.m.	% Cleavage to R^1R^2P	% Starting phosphine
$p\text{-}Me_2NC_6H_4$	$p\text{-}Me_2NC_6H_4$	43	−6.1	5	52
$p\text{-}Me_2NC_6H_4$	$p\text{-}Me_2NC_6H_4$[b]	*ca.* 92[c]		*ca.* 4	
Ph	Bu^n	21	−12.1	57	22
Ph	Pr^i	73	6.1	12	15
Pr^i	Pr^i	13	23.0	5	81
$(o\text{-}MeC_6H_4)_3P$		*ca.* 40	−16.9	55	5

[a] 4 mmol of phosphine, 8 mmol of sodium in 100 ml of NH_3; 4 h at −78 °C. [b] 2 h at −78 °C, 50 ml of THF added. [c] 75% after recrystallisation.



Scheme 1

the ammoniacal solution a red carbanion (**2a**; $R^1 = R^2 = p\text{-}Me_2NC_6H_4$) is formed, which was identified by ^{13}C n.m.r. spectroscopy in $[^2H_8]$THF solution.

This anion is formed by the addition of two electrons and the abstraction of a proton from ammonia, probably in the order depicted in Scheme 1. The same anion can be obtained from (**3**; $R^1 = R^2 = p\text{-}Me_2NC_6H_4$) deprotonation with neopentyl lithium. Anion (**2a**) is much more stable than the parent ion, the cyclohexadienyl anion, which decomposes at −20 °C to give benzene,[4] because of the stabilisation of the negative charge by the phosphino group. Only minor decomposition occurs in 1 h at 20 °C in THF solution. At 60 °C the decomposition is nearly complete in *ca.* 2 h. Benzene and the target molecule bis-(*p*-dimethylaminophenyl)phosphide (**4**; $R^1 = R^2 = p\text{-}Me_2NC_6H_4$) are products which are probably formed by cleavage of an isomeric ion (**2b**). However, this reaction is not of preparative value because the major product is (**1**; $R^1 = R^2 = p\text{-}Me_2NC_6H_4$) formed by a similar aromatisation process to that found for the parent cyclohexadienyl ion.

We have also observed the Birch reduction with other relatively basic arylphosphines. Table 1 gives the results.

Received, 27th May 1987; Com. 714

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