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Preliminary communication

Cleavage of hexamethylphosphoramide by means of n-butyllithium

EDWIN M. KAISER, JIMMIE D. PETTY and LANCE E. SOLTER
Department of Chemistry, University of Missouri, Columbia, Columbia, Missouri 65201 (U.S.A.)

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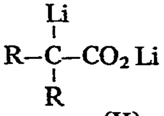
Hexamethylphosphoramide (HMPA) has been recognized as an outstanding solvent for a wide variety of chemical transformations including but not limited to nucleophilic substitutions, β-eliminations, metalations, Birch-type reductions, and certain oxidations. It has generally been accepted that HMPA is stable to most basic reagents; for example, it is resistant to reaction with potassium hydroxide at temperatures as high as 80° though it will react with this base at 110–120° [1]. In fact, stronger basic reagents like alkali amides[2], Grignards[3], and organozinc compounds[4] have been routinely employed as metalating agents in this solvent, apparently without decomposition, to afford a wide variety of new organometallic reagents[1]. When these latter reagents have been organoalkali compounds, the negative charge of the carbanion portion has usually been resonance delocalized as illustrated by the highly stabilized lithiotriphenylmethane (I) [5] and by the less highly stabilized dilithiodialkylacetates (II) [6].

$(C_6H_5)_3CLi$

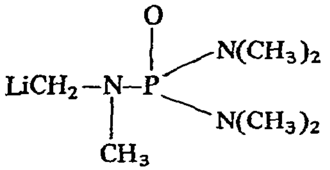
(I)



$$R{-}\overset{\displaystyle Li}{\underset{\displaystyle R}{C}}{-}CO_2Li$$

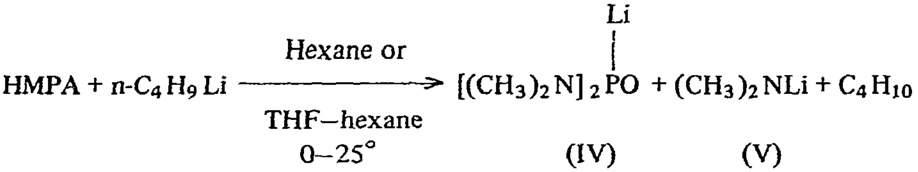
(II)

In contrast, there have been only a few reports dealing with the decomposition of HMPA by certain organometallic reagents; such reactions appear to generally occur by one of two routes: (1) alkylation at phosphorus (or phosphorylation), and (2) metalation of an *N*-methyl group. For example, various solid complexes of Grignard and organolithium reagents decompose upon standing to presumably give phosphorylated derivatives of the metallic compounds[7]. Also, various lithiotrialkylgermanes and -silanes cleave HMPA in a similar fashion[8]. Second, bases like lithium cyclohexylamide at 60° [9] and methyllithium at 0° [10] seem to ionize HMPA to give metalated derivative III; evidence for such formation of III consisted of deuteration in the former case and the formation of methane in the latter one.



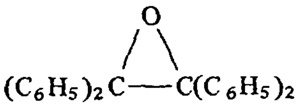
(III)

It is the purpose of this Communication to report that a third mode of decomposition of HMPA effected by organometallic reagents has now been realized. Specifically, addition of n-butyllithium in hexane to either neat HMPA or to HMPA–THF at 0–25° (but not at lower temperatures) instantaneously affords red-colored solutions which contain large amounts of lithium bis(dimethylamino)phosphite (IV) and apparently lithium dimethylamide (V) (eqn. 1). Butane, identified by mass spectroscopy, is a by-product in these reactions.

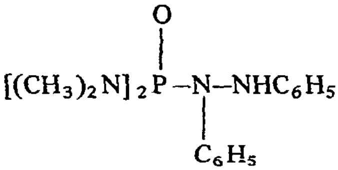


$$\text{HMPA} + n\text{-}C_4H_9Li \xrightarrow[\substack{\text{THF–hexane}\\ 0\text{–}25°}]{\text{Hexane or}} \underset{\text{(IV)}}{[(CH_3)_2N]_2\overset{\overset{\displaystyle Li}{|}}{P}O} + \underset{\text{(V)}}{(CH_3)_2NLi} + C_4H_{10} \qquad (1)$$

That IV is formed was demonstrated by subjecting the above reaction mixture to previously described chemical transformations[1]. For example, one hour after the above reagents are mixed (THF co-solvent) treatment of the red solution with benzophenone and azobenzene gives 1,1,2,2-tetraphenylethylene oxide (VI) [11] and hydrazobenzene derivative (VII) [1] in yields of about 70%, respectively. Also, treatment of the red solution obtained from neat HMPA and n-butyllithium in hexane after 15 minutes with chalcone gives the conjugate addition product VIII [11] in nearly quantitative yield. That V is also apparently present was demonstrated by adding diphenylmethane to the reaction mixture (eqn. 1) and subsequently trapping dimethylamine gas which was evolved. The amine probably arises from metalation of the hydrocarbon by V since no such gas is evolved in the absence of diphenylmethane or other active hydrogen compounds.

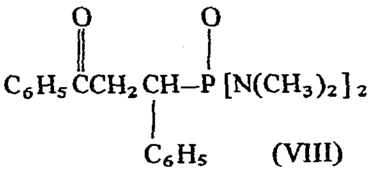


(VI)



$$[(CH_3)_2N]_2\overset{\overset{\displaystyle O}{|}}{P}-\underset{\underset{\displaystyle C_6H_5}{|}}{N}-NHC_6H_5$$

(VII)



$$C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}CH_2\underset{\underset{\displaystyle C_6H_5}{|}}{C}H-\overset{\overset{\displaystyle O}{|}}{P}[N(CH_3)_2]_2$$

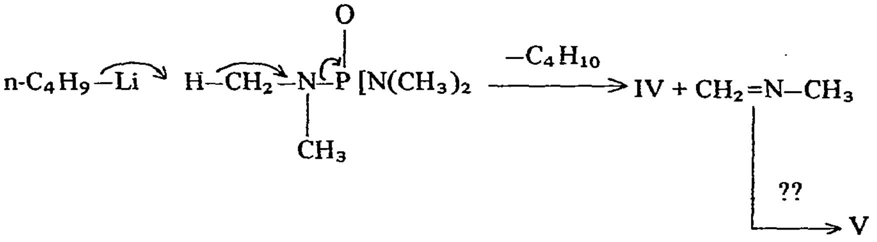
(VIII)

In contrast to the above but supportive of earlier workers[1,5], solutions of the resonance stabilized lithiodiphenylmethane in HMPA were found to be stable. Thus, this compound was alkylated by methyl iodide and n-butyl bromide to give IX and X in yields of 75 and 79%, respectively. Moreover, this organometallic was deuterated by D_2O to give diphenylmethane-α-d_1 in nearly quantitative yield.

$(C_6H_5)_2CHCH_3$ (IX)

$(C_6H_5)_2CH(CH_2)_3CH_4$ (X)

The above cleavage of HMPA by n-butyllithium is rather remarkable if it is recalled that anions IV and V have previously been formed from this compound only upon its reduction by alkali metals. Two mechanisms suggest themselves: (1) the n-butyllithium may be acting as an electron transfer reagent towards the HMPA, or (2) the base may be abstracting a proton from a methyl group of HMPA resulting in the direct formation of IV (eqn. 2). The actual situation is probably more complicated, though, since neither 1-butene nor octane are present as they should be if mechanism 1 were operating; also, the formation of V is rather difficult to envision from mechanism II.



$$\text{n-}C_4H_9\text{—Li} \quad H\text{—}CH_2\text{—}\underset{CH_3}{\underset{|}{N}}\text{—}\overset{O}{\overset{|}{P}}[N(CH_3)_2 \xrightarrow{-C_4H_{10}} \text{IV} + CH_2{=}N\text{—}CH_3 \quad (2)$$

$$\xrightarrow{??} \text{V}$$

Whatever the mechanism of eqn. 1, it is obvious that the area of the stability of organolithium and related reagents in HMPA should be considered carefully. Of particular interest is the question concerning the identity of the metalating agent or agents in metalations carried out in this solvent.

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