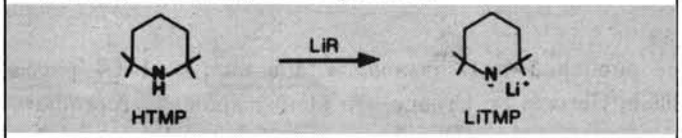
GOT A  OF A PROBLEM?

LET ALDRICH H+ARPOON IT!

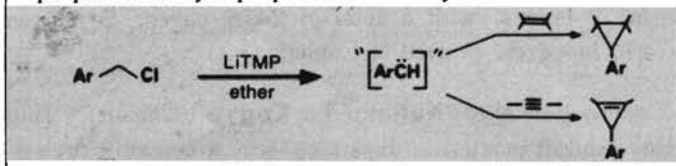
PROTON-SELECTIVE BASE

As the goals of synthetic and mechanistic chemistry become increasingly complex, the need for highly selective reagents becomes more critical. The quest for **non-nucleophilic strong bases**, for example, has sparked the research of many workers.

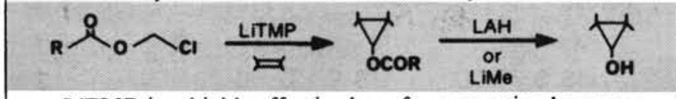
One of the most effective new proton-selective reagents is lithium 2,2,6,6-tetramethylpiperidide **(LiTMP)**, a member of the class of strong bases which Olofson[1] has termed **"H+arpoons." LiTMP** is conveniently prepared by treating an ethereal solution of **2,2,6,6-tetramethylpiperidine (HTMP)** with methyl- or butyllithium.[2]



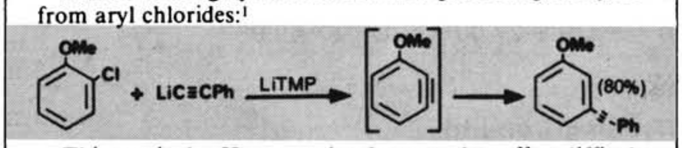
LiTMP has been found to be superior to NaOEt, KO-*t*-Bu, NaH, $NaNH_2$, LiAr, LiR, $NaCPh_3$, $LiN(SiMe_3)_2$, $LiN(i\text{-}Pr)_2$, and $BrMgN(i\text{-}Pr)_2$ for the practical synthesis of arylcyclopropanes and cyclopropenes from benzyl chlorides.[1,2]



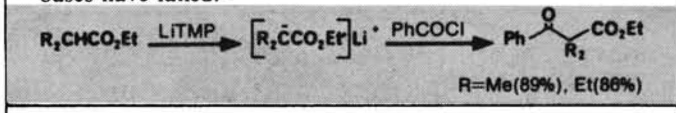
Very recently, Olofson reported a useful synthesis of cyclopropyl esters (and ultimately cyclopropanols) from chloromethyl esters, **LiTMP**, and a variety of olefins.[3]



LiTMP is a highly effective base for generating benzynes from aryl chlorides:[1]



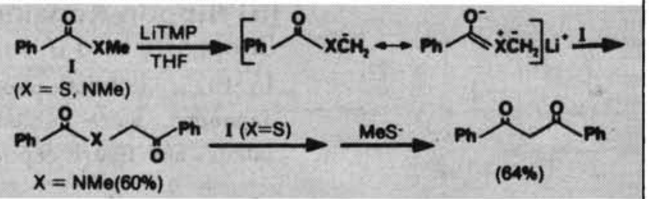
This particular **H+arpoon** has been used to effect difficult carbonyl condensations in cases where more conventional bases have failed.[1]



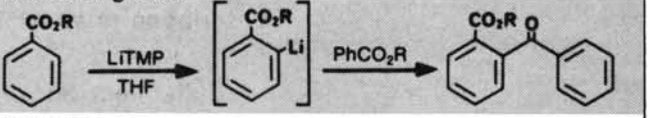
Early work by Rathke and Kow[4] provided the "first example of base-promoted α proton removal from an organoborane."

In subsequent findings,[5] the authors demonstrated the superiority of **LiTMP** over bases such as $LiN(i\text{-}Pr)_2$ and $LiN(i\text{-}Pr)(c\text{-}Hex)$ for producing boron-stabilized carbanions from vinylboranes, effective precursors for 3-silylated aldehydes and ketones.

LiTMP has been used by Beak to generate transient dipole-stabilized carbanions *via* deprotonation of aromatic thioesters[6] and amides.[6,7]



Unless additional stabilization of the incipient carbanion is provided (*e.g.*, by unsaturation), the analogous reaction for *esters* does not occur. Thus, alkyl benzoates afford *o*-benzoylbenzoates, apparently the result of ortho lithiation of the starting ester.[8]



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2) R.A. Olofson and C.M. Dougherty, *ibid.*, **95**, 581 (1973).
3) R.A. Olofson, K.D. Lotts, and G.N. Barber, *Tetrahedron Lett.*, 3381 (1976).
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5) R. Kow and M.W. Rathke, *ibid.*, **95**, 2715 (1973).
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7) P. Beak, G.R. Brubaker, and R.F. Farney, *ibid.*, **98**, 3621 (1976).
8) C.J. Upton and P. Beak, *J. Org. Chem.*, **40**, 1094 (1975).

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