The First Successful Direct Metallation of Ethene

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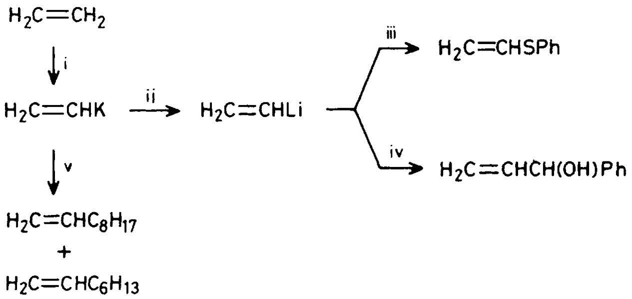
Vinyl potassium was formed directly from ethene by use of a new butyl-lithium–potassium t-butoxide–tetramethylethylenediamine metallating reagent; typical products were obtained with 1-bromo-octane and, after addition of LiBr in tetrahydrofuran, with benzaldehyde and diphenyl disulphide.

The potency of the butyl-lithium–potassium t-butoxide, BuLi·Bu^{t}OK, reagent for the deprotonation of weakly acidic compounds has been demonstrated widely.[1,2] Whereas benzene can be metallated in hexane with butyl-lithium when activated by *N,N,N′,N′*-tetramethylethylenediamine (BuLi·TMEDA),[3] all attempts at direct metallation of ethene, which has a p*K* value comparable to that of benzene,[4] have failed.† The superbase t-butyl-lithium adds to ethene,[5] while BuLi·Bu^{t}OK in hexane or a tetrahydrofuran (THF)–hexane mixture does not react at all with ethene at temperatures ranging from −90 to +20 °C.[6] Recently we developed a new reagent, butylsodium·TMEDA,[7] which is completely soluble in alkanes and which is able to deprotonate compounds such as toluene rapidly at −20 °C. Butylpotassium·TMEDA behaves similarly.

We now find that it is not necessary to prepare butylpotassium separately: simple mixing of equimolar amounts of Bu^{t}OK, BuLi, and TMEDA (the order is not essential) in hexane or pentane at temperatures below −40 °C gives an extremely efficient metallating reagent. We illustrate its exceptionally high kinetic basicity with successful metallation of ethene. When ethene is passed for 1.5—2 h through a mixture of Bu^{t}OK (0.10 mol), BuLi (0.10 mol), and TMEDA (0.10 mol) in hexane (100 ml) at −25 °C, a suspension of vinylpotassium forms gradually. Subsequent addition of THF (60 ml) and anhydrous lithium bromide (0.12 mol) dissolved in THF (40 ml) gave a white gelatinous suspension (presumably of a vinyl-lithium complex), which reacted at *ca.* −30 °C with benzaldehyde (0.095 mol) or diphenyl disulphide (0.095 mol) to give the expected alcohol and vinyl sulphide, respectively, in 90% and 75% yields. Alkylation of the vinylpotassium intermediate (before addition of lithium bromide) with bromo-octane (0.09 mol) gave dec-1-ene in *ca.* 50% yield. The formation of oct-1-ene as a by-product in *ca.* 20% yield suggested that dehydrobromination also had occurred to a considerable extent (Scheme 1).



Scheme 1. *Reagents and conditions:* i, BuLi–Bu^{t}OK–TMEDA, hexane, −25 °C; ii, LiBr, THF; iii, PhSSPh; iv, PhCHO; v, THF then $C_8H_{17}Br$.

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† Ethene can be converted into vinyl-lithium by means of 'polylithium complexes' activated by Lewis acids.[8]

Treatment of 3,3-dimethylbut-1-ene (five-fold excess) with the ternary basic system under similar conditions, followed by addition of THF and diethyl disulphide, gave impure (*E*)-$Bu^tCH{=}CHSEt$ in a low (*ca.* 20%) yield.

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