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DO THE COMPOUNDS $PhCH_2Y$ GIVE GEMINAL DIANIONS ON ADDITION OF TWO EQUIVALENTS OF STRONG BASE?

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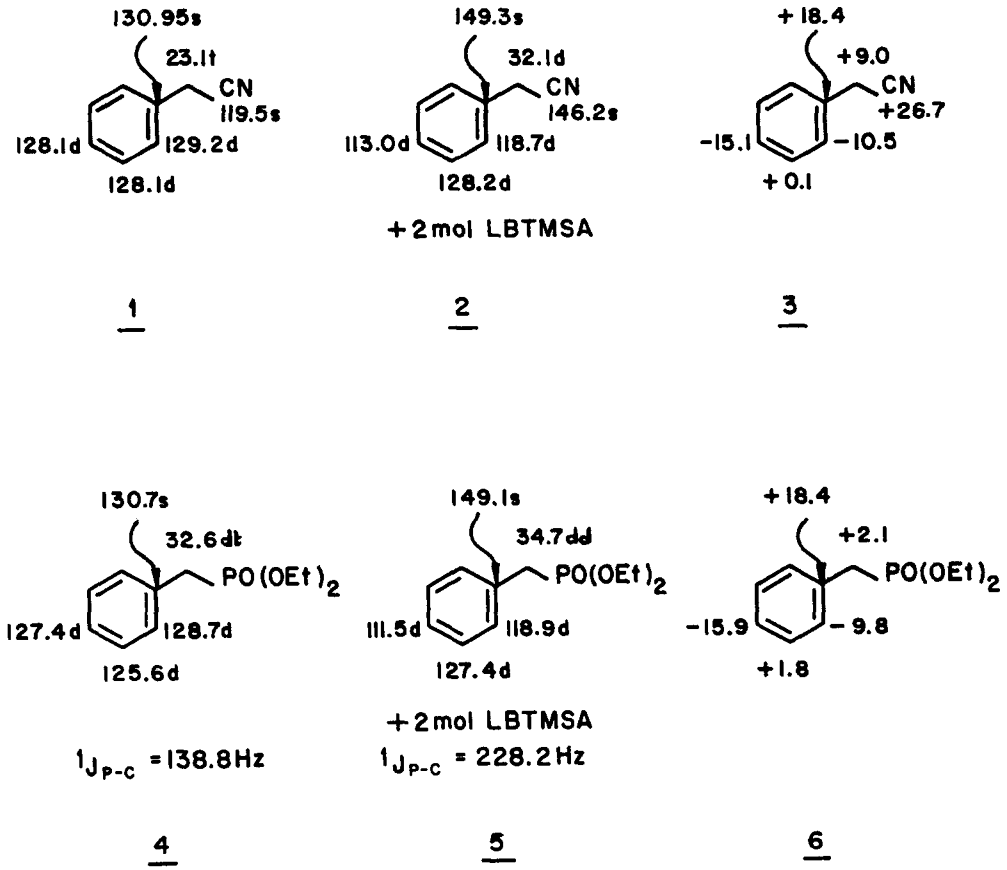
Abstract: Examples of the title reaction are shown not to yield geminal dianions as believed but rather monoanions complexed with a second molecule of the base.

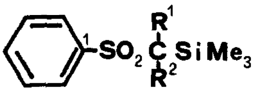
A number of true examples of geminal dilithio- compounds have been demonstrated to exist by NMR or X-ray data.[1] In the family of compounds of the type $PhCH_2Y$ it has been assumed that similar dilithio- species, $PhCLi_2Y$, (Y = CN,[2] SOPh,[2] SO_2Ph,[2-4] SO_2NMe[2] and NO_2[5]) are formed and extensive chemical, infrared and isotopic data has been marshalled to prove their involvement.[2] Similar dilithio species have been proposed in the ferrocene (Fc) series $FcCH_2Y$ (Y = CN,[6] $POPh_2$,[7-8] $PO(OEt)_2$[8] and SO_2Ph[9]) and the whole matter has been reviewed.[10] During work on reactions of such geminal dianions we have investigated the ^{13}C nmr spectra of two typical examples of such systems derived from $PhCH_2CN$ and $PhCH_2PO(OEt)_2$ which demonstrate unequivocally that although the apparent geminal dianions react appropriately they are in fact mono-anions complexed with a second molecule of base. The geminal dianion structure of all such systems in solution should therefore be viewed with caution in the absence of ^{13}C nmr data. We term such systems QUADAC's (Quasi Dianion Complexes).[11]

The ^{13}C nmr data of $PhCH_2CN$ and $PhCH_2PO(OEt)_2$ in tetrahydrofuran and their derived QUADAC's are shown in Scheme 1 together with the difference in chemical shifts on addition of two equivalents of the base (lithium bis(trimethylsilyl) amide (LBTMSA)). The methylene triplet in $PhCH_2CN$ is converted into a doublet not a singlet on base treatment. Interestingly when one equivalent of base is added the chemical shifts are almost identical to



Scheme 1

those of the QUADAC. Addition of a second equivalent to this solution has only one significant effect - the appearance of an absorption at 6.04 ppm characteristic of LBTMSA, accompanied by a colour change in the solution.



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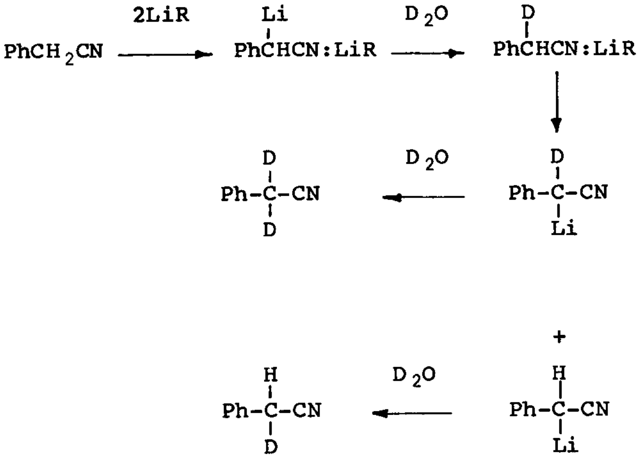
R^1	H	H	Li
R^2	H	Li	Li
δC_α	48.5 t	33.8 d	50.5 bs
δC_1	145.4 s	156.5 s	157.5 s

Similar effects with added phosphorus coupling are observed with the phosphonate (4). These data are in contrast to those reported by Gais et al.[1a] recently for the sulphone (7) which clearly shows mono- and dianion formation. The C-P coupling of the phosphonate increases from 138.8 to 228.2 Hz on lithiation (Scheme 1), clearly indicative of an sp^3 to sp^2 transformation at carbon as noted by Bottin-Strzalko et al.[12]

The chemical data suggestive of a geminal dianion (e.g. ready and high yielding dialkylation on addition of an alkyl halide[10]) is accounted for by a sequential metallation and reaction. Deuteriation studies in which Kaiser and Hauser[2] observed incorporation of 1.60-1.78 deuteriums per molecule when $PhCH_2CN$ was treated with 2.3 equivalents of butyl-lithium in tetrahydrofuran followed by a D_2O quench also support a sequential process as shown in Scheme 2, involving a rapid intra-aggregate lithiation. Such lithiations in the presence of water are known.[13] These results are in contrast to the almost quantitative deuteriation of the dilithio- species (7, $R^1 = R^2 =$ Li).[1a]



$$PhCH_2CN \xrightarrow{2LiR} Ph\overset{Li}{C}HCN{:}LiR \xrightarrow{D_2O} Ph\overset{D}{C}HCN{:}LiR$$

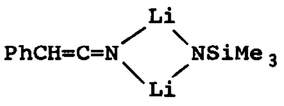
$$Ph\text{-}\underset{D}{\overset{D}{C}}\text{-}CN \xleftarrow{D_2O} Ph\text{-}\underset{Li}{\overset{D}{C}}\text{-}CN$$

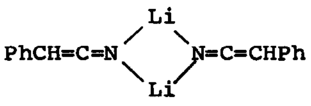
$$+$$

$$Ph\text{-}\underset{D}{\overset{H}{C}}\text{-}CN \xleftarrow{D_2O} Ph\text{-}\underset{Li}{\overset{H}{C}}\text{-}CN$$

Scheme 2

We suggest that the structure of the QUADAC's could be reasonably viewed as, for example, (8). This structure would satisfy (a) the downfield shift of C_α due to ketenimine character on lithiation of $PhCH_2CN$ but otherwise little change in the ^{13}C nmr on addition of a second equivalent of base. (b) The change in colour on addition of the second equivalent of base and infrared (1 equiv. base - ν_{max} 2160 and 2130 cm^{-1}; 2 equivs. base - ν_{max} 1905 cm^{-1}) on treatment of $PhCH_2CN$ with base.[2] The mono-anion could also be


(8)


(9)

a related bridged dimer (e.g. 9), a common structural type in the organolithium field.[1e]

The considerable current interest in both the structure and synthetic application[1c, 5, 14] of apparent geminal dilithiated compounds demands a careful reappraisal of much of the existing data.

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