Tetrahedron Letters,Vol.27,No.13,pp 1429-1432,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain

ON THE CHEMISTRY OF LITHIUM DIALLYL CUPRATE[1]

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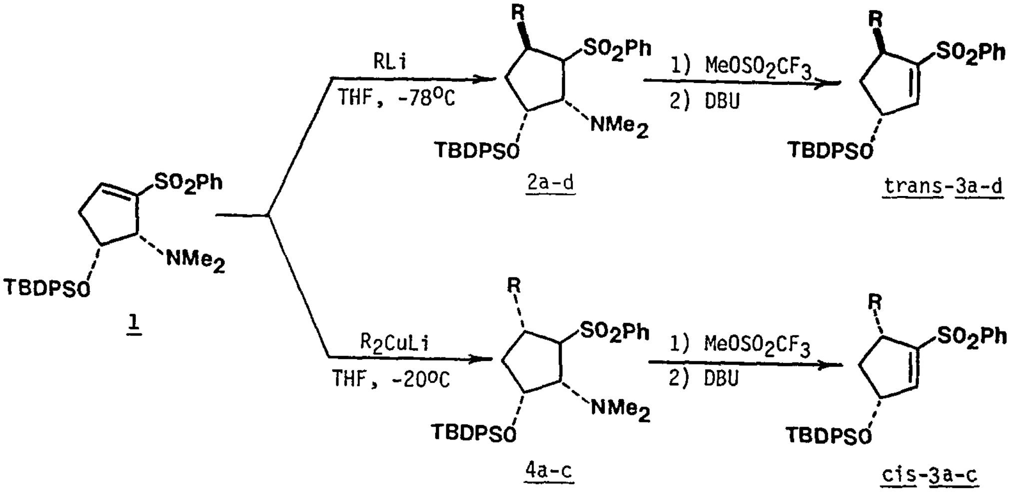
Abstract: The anomalous addition reactions of lithium diallyl cuprate with enones and an amino vinyl sulfone are shown to not result from allyl lithium in equilibrium with allyl cuprate. A mechanism involving an $^3\eta$, 18-electron cuprate is proposed.

In the course of our research on the functionalization of vinyl sulfone 1 we have observed that organolithium reagents undergo conjugate-addition at -78°C to afford trans-adducts 2a-d in high yield,[2] while organocuprate reagents undergo an amine-directed conjugate-addition[1] at approximately -20°C to afford cis adducts 4a-c.[1] Both reactions occur with excellent stereocontrol as assayed by quaternization and elimination of the amine moiety to produce trans- and cis vinyl sulfones trans-3a-d and cis-3a-c, respectively.[1,2]

Thus, we were initially quite surprised to discover that reaction of "lithium diallyl cuprate[3]" with amino vinyl sulfone 1 yielded the same adduct (2d) as was obtained with allyl lithium.[3,4]

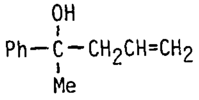


a R= Me; b R= Ph; c R= $CH=CH_2$; d R= $CH_2CH=CH_2$

Lithium diallyl cuprate has been reported to be a less well-behaved cuprate than other members of this important family of reagents.[5] For example, in reactions with enones it has been found that increased substitution at the ß-position results in a shift away from the expected 1,4-addition mode in favor of the 1,2-adduct.[6-9]

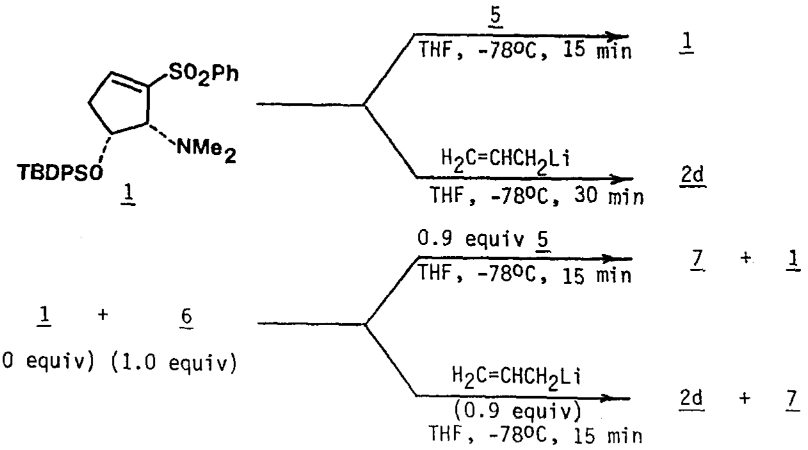
In his seminal paper on this subject, House has raised the question of whether an equilibrium exists between diallyl cuprate and allyl copper plus allyl lithium.[7] Clearly, the finding of 1,2-addition products from those substrates whose 1,4-addition pathway is more sterically encumbered is well in accord with such a postulate. Additionally, the isolation of 2d in the above vinyl sulfone reaction is formally consistent with an allyl lithium hypothesis. Finally, we have found that lithium diallyl cuprate 5 gives a strongly positive Gilman test[10] and also rapidly adds to acetophenone 6 at -78°C to afford homoallyl alcohol 7 in 82% isolated yield.[11,12]

$$\underset{\underline{5}}{(H_2C{=}CHCH_2)_2CuLi} \overset{?}{\rightleftharpoons} H_2C{=}CHCH_2Cu + H_2C{=}CHCH_2Li$$



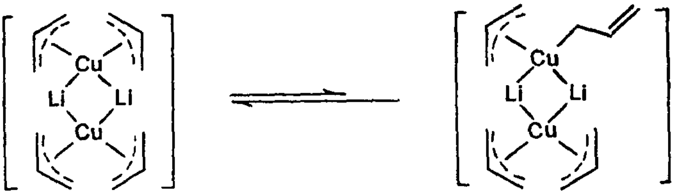
$$\underline{5} + \underset{\underline{6}}{PhCOMe} \xrightarrow[\text{10-15 min}]{\text{THF, -78}^\circ\text{C}} \underset{\underline{7}}{Ph{-}\overset{OH}{\underset{Me}{C}}{-}CH_2CH{=}CH_2}$$

However, several additional experiments are totally inconsistent with invoking allyl lithium as the nucleophilic species responsible for the aformentioned allylation reactions: 1) The reaction of allyl lithium with vinyl sulfone 1 is complete within 15 minutes at -78°C but 1 is recovered in >95% yield after reaction with lithium diallyl cuprate for 30 minutes at -78°C; and 2) Allyl lithium (0.9 eq) reacts with 1.0 eq each of vinyl sulfone 1 and acetophenone 6 to afford a 1:1 mixture of adducts 2d and 7, but lithium diallyl cuprate (0.9 eq) reacts with 1.0 eq each of vinyl sulfone 1 and acetophenone 6 to only afford adduct 7, the vinyl sulfone being completely recovered.[13]



Faced with the unsuitability of the above equilibrium hypothesis one must apparently find the source of the unusual reactivity of allyl cuprate in the structure of the reagent itself. The Pearson dimeric D_{2h} cuprate model[14] is supported by NMR[15] and X-ray[16] studies, although calculations by Whangbo[17] favor non-bridging ligands. The situation has been shown to be even more complex by Lipshutz,[12] who has recently demonstrated that the structure of the parent dimethyl cuprate reagent is profoundly dependent upon its mode of generation.

Thus it is proposed that the 'abnormal' reactivity of lithium diallyl cuprate is a specific manifestation of the four-electron allyl ligands. By utilizing the olefin π-orbitals lithium diallyl cuprate can exist in the $^{3}\eta$ 18-electron configuration 6a. This species is coordinatively saturated and would not be expected to undergo the oxidative insertion reactions associated with normal 14-electron cuprate reagents whose coordination sphere is completed by solvent molecules. Such a species could, however, undergo direct allylation reactions with ketones, enones, and vinyl sulfones.[18] Equilibration of 6a with 6b, a 16-electron $^{1}\eta$ species capable of undergoing oxidative insertion would provide a pathway for the 1,4-addition reactions observed with non-hindered enones.[19]



6a 6b

ACKNOWLEDGEMENT: We wish to thank the NIH (GM 32693) for their generous support of this research. We thank the Purdue University Biological Magnetic Resonance Laboratory (NIH RR01077) for access to the 470-MHz ^{1}H NMR spectrometer and Tamim Braish for spectral assistance.

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3. Allyl lithium was prepared by the method of Seyferth and Weiner (J. Org. Chem. 1961, 26, 4797) using 3.9 eq. of phenyl lithium and 1.0 eq of tetraallyl tin. The diallyl cuprate was formed from this solution by reaction with 2.0 eq of copperbromide-dimethylsulfide complex.

4. Verification of the stereochemical assignment of this adduct was secured by quaternization and elimination to afford the known vinyl sulfone trans-3d. A direct HPLC comparison with authentic cis-3d[2] indicated the "diallyl cuprate" adduct to be of greater than 95% trans stereochemistry.

5. (a) Posner, G.H., Organic Reactions 1972, Vol. 19, 1; (b) Normant, J.F., Synthesis 1972, 63; (c) House, H.O., Accounts of Chemical Research 1976, 9, 61; (d) Lipschutz, B.H.; Wilhelm, R.S.; Kozlowski, J.A., Tetrahedron 1984, 24, 5005.

6. House, H. O.; Fischer, Jr., W. F.; J. Org. Chem. 1969, 34, 3615.

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9. Majetich, G.; Casares, A.M.; Chapman, D.; Behnke, M; Tet. Lett., 1983, 24, 1909.

10. This color test involves the addition of organolithium and Grignard reagents to bis p-dimethylamino benzophenone followed by treatment of the resulting tertiary carbinol with iodine in acetic acid. A green to blue color results from solvolysis or dehydration/iodination of the carbinol. (Gilman, H.; Schultz, F., J. Amer. Chem. Soc. 1925, 47, 2002).

11. Lipschutz and coworkers[12] have used the Gilman test[10] and the acetophenone addition reaction to demonstrate the presence of free methyl lithium in solutions of various methyl cuprate reagents.

12. Lipshutz, B.; Kozlowski, J. A.; Breneman, C. M., J. Amer. Chem. Soc. 1985, 107, 3197.

13. Control experiments show that allyl copper does not add to either vinyl sulfone 1 or acetophenone 6 under the above conditions.

14. Pearson, R. G.; Gregory, C.D., J. Amer. Chem. Soc. 1976, 98, 4098.

15. Van Koten, G.; Noltes, J. G., J. Amer. Chem. Soc. 1979, 101, 6593.

16. Hope, H.; Oram, D.; Power, P. P., J. Amer. Chem. Soc. 1984, 106, 1149.

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18. Presumably the higher temperature of the reaction of vinyl sulfone 1 with cuprate reagents does not allow effective intervention of an amine-directed[1] substrate-6b complex, therefore only affording adduct 2d via allylation from the less sterically encumbered face.

19. Numerous variants of this scheme can be imagined, including monomeric species, versions of 6b with additional $^1\eta$ ligands, and substrate-induced promotion of the 6a to 6b transformation.

(Received in USA 12 November 1985)