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STRUCTURE OF THE ADDUCTS OF LITHIUM DIMETHYLCUPRATE TO ACETYLENIC ESTERS: SPECTROSCOPICAL PROOF FOR THE PRESENCE OF COPPER ALLENOLATES+)

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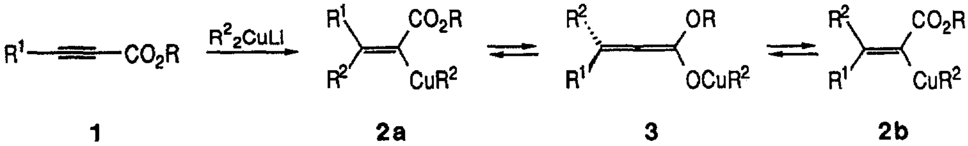
Abstract: The ^{13}C NMR spectra of the adducts of Me_2CuLi to acetylenic esters $RC{\equiv}CCO_2Me$ (R = H, Me, Et) were obtained in diethyl ether and THF between -100° and -60°C. Comparison with model compounds shows that these adducts possess copper allenolate structures.

The Michael addition of cuprates to acetylenic esters[2] provides a convenient access to substituted acrylic esters. This reaction has found wide application[3]; yet, as in the case of other reactions of cuprates[4], there has been no thorough investigation of its mechanism[5]. The observed cis stereoselectivity of the addition at low temperature was explained in terms of a cis-vinylcuprate intermediate **2a**[2], while the loss of stereoselectivity at higher temperature was attributed to the formation of the trans-vinylcuprate **2b**, possibly via copper allenolate **3**[2]. The formation of the adduct is irreversible, since no mixing of different groups R^1 and R^2 is taking place[2-4].



Trapping reactions of the intermediates at 0°C with chlorotrimethylsilane yield silyl allenolates[3a,6], whereas the infrared spectrum of the Me_2CuLi adduct to methyl phenylpropiolate at room temperature has been interpreted in terms of a vinylcuprate intermediate[7]. In order to gain more information on the nature of the intermediates at low temperature, the ^1H and ^{13}C NMR spectra of the adducts of Me_2CuLi to methyl propiolate (**1a**), methyl tetrolate (**1b**), and methyl 2-pentynoate (**1c**) in diethyl ether and THF, respectively, were obtained between -100° and -60°C; the ^{13}C NMR data for -100°C are collected in the following Table . Since the concentration of the cuprate, prepared from 2 eq. of MeLi and 1 eq. of CuI at 0°C, was rather high (0.2 - 0.5 M), a white precipitation of Me_2CuLi was formed upon cooling to -80°C[8]. After addition of 1 eq. of the acetylenic ester, it is necessary to warm the mixture to -50°C to get a clear solution; the precipitation dissolves irreversibly, i.e. it does not reappear upon cooling back to -100°C.

The ^{13}C NMR spectra of the Me_2CuLi adducts to all three esters in diethyl ether show two signal groups for the methyl group attached to the copper atom and for the olefinic/allenic carbons; likewise, in the ^1H NMR spectra two signals are found for the MeCu groups. The intensities of the signals are temperature dependent: e.g. for the adduct to **1b** the ratio varies between ca. 2:1 at -100°C and ca. 1:1 at -60°C; upon recooling to -100°C the original ratio of 2:1 is observed. Therefore, it is concluded that two different intermediates are present in this solvent which are interconverting rapidly. Above -60°C, line broadening due to fast exchange processes is taking place. In THF, however, only one intermediate is observed for esters **1b** and **1c**; in the case of **1a**, the adduct formed during the addition of the ester to the cuprate solution is protonated by **1a**, giving rise to the formation of methyl crotonate[9].

+) Dedicated to the memory of Prof. Dr. Hans Musso.

Table: ^{13}C NMR data of the adducts of Me$_2$CuLi to the acetylenic esters **1a-c**[a]

Ester	Solvent	Species	C-1	C-2	C-3	MeO	MeCu	R^1, R^2
HC≡CCO$_2$Me	Et$_2$O[b]	A	162.2	188.5	125.8[c]	56.4	-11.6	23.4
1a		B	161.7	188.3	125.8[c]	50.8	-10.3	21.6
	THF					-[d]		
MeC≡CCO$_2$Me	Et$_2$O[b]	A	155.3	187.1	131.4	55.5	-11.8	28.3, 24.3
1b		B	155.9	186.9	132.2	52.5	-9.9	25.2
	THF		159.9	185.3	132.1	51.4	-11.0	30.2, 23.7
EtC≡CCO$_2$Me	Et$_2$O[b]	A	155.2	187.0	136.7	55.2	-11.8	35.2, 21.5, 13.6
1c		B	154.7	187.0	137.5	55.2	-10.4	32.0, 24.8, 12.3
	THF		158.5	185.0	137.7	51.4	-10.9	32.1, 14.8

[a] Spectra obtained with a Bruker WM 250 spectrometer; temperature: -100°C; chemical shifts with diethyl ether (δ=14.6) or THF (δ=26.5) as internal standards.

[b] Only species A is observed in the absence of lithium iodide.

[c] Assigned with the DEPT method.

[d] Formation of methyl crotonate by protonation of the adduct by **1a**; see text.

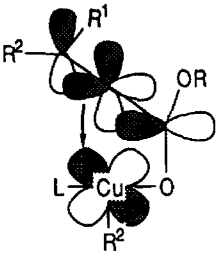
In order to assign the observed signals for the olefinic/allenic carbon atoms, one has to consider the effect of different substitution on the chemical shift of C-3. For numerous olefinic as well as allenic systems a low-field shift has been observed in the order H - methyl - ethyl for the carbon atom attached to these groups[10]. In the case of the adduct of Me$_2$CuLi to methyl propiolate in diethyl ether, the signals for C-3 can be identified with the DEPT method[10]; they are found at δ=125.8 for both species. If R^1=H is replaced by methyl, the expected low-field shift of the resonances to δ=131.4/132.2 allows the identification of the signals for C-3; virtually the same chemical shift is observed in THF (δ=132.1). Again, a low-field shift of the resonances for C-3 is found if R^1=Me is replaced by ethyl (to δ=136.7/137.5 in Et$_2$O, δ=137.7 in THF). Thus, as can be seen from the Table, for all three esters and both solvents examined in this work the resonances of C-3 are shifted to high field, relative to those of C-1 and C-2.

The use of the observed chemical shifts of C-3 for distinguishing a vinylcuprate from a copper allenolate structure requires the knowledge of the chemical shifts of model compounds that are as closely related to the proposed intermediates as possible. Compounds with an allenolate structure are well-known, e.g. 1-methoxy-1-trimethylsilyloxy-1,2-butadiene[3a] (δ=145.8 (C-1), 172.0 (C-2), 115.0 (C-3)[11]), and the lithium allenolate obtained from the adduct of Me$_2$CuLi to **1b** by adition of 2-3 eq. of MeLi[7] (R^1=R^2=Me, Li instead of CuR^2 in formula **3**; δ=148.7 (C-1), 181.1 (C-2), 111.0 (C-3)[12]). In both cases the resonances for C-3 are shifted to high field, compared to those for C-1 and C-2; the same result is obtained by calculation of the chemical shifts of several allenolates using an increment method[10]. In contrast to this, the only compounds known that are closely related to a vinylcuprate are the adducts of DIBAH to methyl propiolate[13] and methyl tetrolate, both existing as vinylaluminum species; for the latter, the following chemical shifts are observed: δ= 176.7 (C-1), 138.0 (C-2), 143.0 (C-3)[14]. The same order of the signals is found for methyl 3,3-dimethylacrylate (δ=167.1 (C-1), 115.7 (C-2), 156.6 (C-3)[11]). However, it is likely that the nature of the substitutent at C-2 as well as the ligands attached to it have a strong influence on the chemical shifts of the olefinic carbons. Calculations using an increment system10) with various electropositive substituents (SiR_3, SnR_3, PbR_3, BR_3) show that in all cases the resonance for C-3 is shifted to low field, compared to that of C-2; the chemical shift difference varies between 9 and 20 ppm. Since for all intermediates observed in this work the signals for C-3 are shifted to high field, relative to those of C-1 and C-2, with chemical shift differences of 18-36 ppm, it is concluded that the intermediates are far better represented by a copper allenolate structure **3** than by a vinylcuprate structure **2**.

However, it is important to consider not only the carbon framework but the entire structure of the adducts examined. In the case of homocuprates, different techniques like X-ray structure determination15) and ebullioscopic and vapor pressure depression measurements16) have shown that these compounds exist in oligomeric as well as in monomeric forms; in etheral solution, the majority of homocuprates examined are dimeric aggregates16). The lithium iodide formed during the preparation of the cuprate can play an important role in the formation of different homocuprates by equilibration. Thus, the equilibrium between Me_2CuLi and Me_3Cu_2Li + MeLi in Et_2O/THF exists only in the absence of LiI17); in contrast to this, Ph_2CuLi in dimethyl sulfide was found to exist in two forms in the presence of LiI and only in one form in the absence of LiI18). In order to examine the effect of lithium iodide on the adducts of Me_2CuLi to the esters **1a-c** in diethyl ether, the LiI-free cuprate was used17); under these conditions the equilibrium between Me_2CuLi and Me_3Cu_2Li + MeLi is known to exist17), and no precipitation was formed upon cooling of the cuprate solution to -80°C. Strikingly, the ^1H and ^{13}C NMR spectra obtained after addition of the acetylenic ester showed only the presence of species A! This could mean that the lithium iodide is essential for the existence of the equilibrium between species A and B; an alternative explanation could be that LiI is actually a part of species B, which therefore cannot be formed in the absence of this salt. Interestingly, the stereoselectivity of the protonation of the Me_2CuLi adduct to methyl propiolate in diethyl ether was also found to depend strongly on the presence of LiI; the selectivity in the presence of 1 eq. of LiI is E:Z = 92:8, in the absence of LiI E:Z = 77:23 (protonation with methanol).

From these findings, the following questions are arising: (i) What is the structural difference between the two copper allenolates present in diethyl ether as solvent? (ii) Why are there two resonances for the methyl groups attached to C-3 in the case of the adduct to methyl tetrolate in diethyl ether (species A) and in THF? (iii) Why does the protonation of copper allenolates produce exclusively (THF) or preferably (Et_2O) cis-addition products? Possible explanations for the first question base on the steric properties of the adducts examined. If they were dimeric aggregates, they could exist as cis and trans isomers, as has been observed for other mixed cuprates19). The number of possible stereoisomers rises further if one takes into account the possible stereoisomerism of the allenic system (for $R^1 \neq R^2$) and of the copper atom(s). Thus, the two species found in Et_2O could be cis and trans isomers, whereas in THF the equilibrium could be shifted to one side, or the equilibration could be too fast to be observable by NMR spectroscopy. The determination of the aggregation number of the adducts is mandatory in order to draw further conclusions on this point. An alternative explanation could be that in Et_2O one species is containing LiI whereas the other is not, or that the two species are adducts of different cuprates, e.g. Me_2CuLi and Me_3Cu_2Li. However, this is contradicted by the fact that the equilibrium between these cuprates can only be detected in the absence of LiI17).

An explanation for the other two questions requires a copper allenolate structure that is unsymmetrical with regard to the allenic system. An interaction between the π-system of the allenolate and unoccupied orbitals of the copper atom as suggested in structure **4** would explain the observation of two methyl resonances for the Me_2CuLi adduct to methyl tetrolate. The protonation of **4**, presumably occurring from the side occupied by the copper atom, would result in the formation of the cis-addition product. A way to establish whether π-interactions as in **4** are important for the behavior of the cuprate adducts examined in this work could be the determination of the ^{13}C-^{13}C coupling constants of the allenic system which should be significantly different from those of model systems without such interactions. Further work concerning this point is in progress.



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To summarize the results of this work, it is concluded from comparison of the ^{13}C NMR chemical shifts of the adducts of lithium dimethylcuprate to acetylenic esters **1a-c** with those of model compounds that these adducts possess copper allenolate rather than vinyl cuprate structures. There are two different, rapidly interconverting copper allenolates observed in diethyl ether in the presence of lithium iodide; one of them disappears if LiI-free cuprate is used. In contrast to this, only one intermediate is found in THF in the presence of lithium iodide. Possible explanations for this behavior, basing on the steric properties of the adducts, are given. In order to explain the high cis stereoselectivity of the protonation of the adducts, an interaction between the π-system of the allenolate and the copper atom is suggested.

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