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REACTIONS WITH LITHIUM DIMETHYLCUPRATE AND LITHIUM DIMETHYLAURATE

SOLVENT EFFECTS ON THE CONJUGATE ADDITION.

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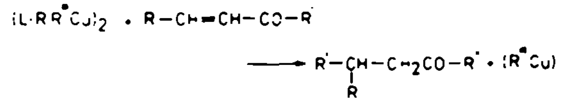
Abstract—The reaction of lithium dimethylcuprate with *E*-4-phenyl-3-buten-2-one in different solvents has been investigated. Fast conjugate addition occurs in hydrocarbons, dichloromethane and diethylether, while the reaction is retarded in better coordinating solvents.

In highly polar solvents such as DMF or DMSO, no conjugate addition is observed. Dichloromethane-d_2 was chosen as a convenient solvent for NMR investigations of cuprates. The reaction of lithium dimethylaurate with different enones gave no conjugate addition products, but base induced self-condensation of enones.

In earlier investigations we have studied the asymmetric induction in the conjugate addition of mixed chiral diorganocuprates to prochiral α,β-unsaturated carbonyl compounds.[1-5] Enantiomeric excess of up to 23% has been obtained:



$$(Li{\cdot}RR^*Cu)_2 + R{-}CH{=}CH{-}CO{-}R' \longrightarrow R'{-}\underset{\displaystyle R}{\underset{|}{C}}H{-}CH_2CO{-}R' + (R^*Cu)$$

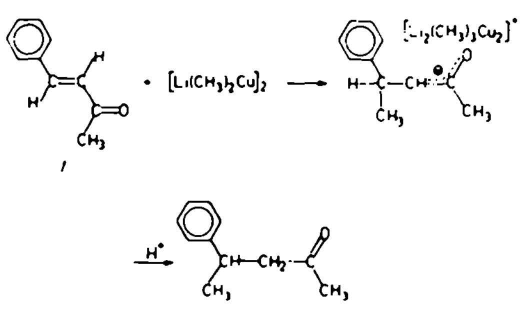
In order to improve the asymmetric induction, more knowledge about the structures of the cuprates involved and the mechanism(s) of the conjugate addition of these is needed. Several hypotheses have been presented.[6-10]

Organogold(I) compounds are known to give oxidative addition to alkyl halides, forming relatively stable trialkylgold(III)-phosphine compounds. Organic products are formed by reductive elimination of R-R from the $R_3Au(III)L$ species.[11] The reaction between lithium diorganocuprates and alkyl halides and tosylates is thought to proceed via a nucleophilic attack of copper on the halide, with the intermediate formation of a copper(III) species, followed by reductive elimination, giving the C–C bond:[12-14]

$$Li^+R_2Cu^- + {>}C{-}X \longrightarrow \left[R_2Cu{-}C{\lessgtr}\right] \longrightarrow R{-}C{\lessgtr} + LiRXCu$$

Cu(III) species have also been suggested as intermediates in the conjugate addition of cuprates to enones.[6-9] It is, however, quite reasonable to assume the operation of different mechanisms depending on the reaction conditions, e.g. the choice of solvent or substrate. An alternative mechanism, 1,2-addition of the cuprate to the enone C=C bond, has been suggested.[10]

In the present investigation we have studied the influence of the solvent on the reactivity of the cuprate in the conjugate addition and on competing reactions. The aim has also been to find suitable solvents for future NMR investigations of conjugate additions. Furthermore, we have explored some possible analogies between Cu(I) and Au(I) reactions by studying the reaction between lithium dimethylaurate and some enones. The reaction between lithium dimethylcuprate and *E*-4-phenyl-3-buten-2-one, **1**, was carried out in various solvents. The results are summarized in Table 1:



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Lithium dimethylcuprate was prepared in a small volume of toluene at 0°, giving a white suspension. The solvent under investigation was then added to the lithium dimethylcuprate, which is sparingly soluble in hexane, toluene and dichloromethane. On addition of any of the following solvents, diethyl ether, tetrahydrofuran (THF), pyridine, acetonitrile, N,N-dimethylformamide (DMF), and dimethylsulfoxide (DMSO), the white suspension dissolved. However, $LiMe_2Cu$ probably reacted with DMF and DMSO.

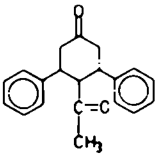
The cuprate was assumed to be dimeric[15,16] and the substrate, compound **1**, was used in an equimolar amount. The reactions were run at 0° and followed by GLC analysis. The expected product, 4-phenyl-2-pentanone, **2**, was formed quantitatively within less than a minute in hexane, toluene, diethylether, or dichloromethane. In THF the reaction was considerably slower, a comparable yield being obtained only after 1 hr.

In pyridine or acetonitrile the slow formation of **2** was accompanied by the formation of a dimer 4-acetyl-3,5-diphenylcyclohexanone, **3**, of **1**.[1] Traces of 5-acetyl-4,6-diphenyl-2-heptanone, **4**, were observed when THF, pyridine, or acetonitrile were used as solvents. In acetonitrile, *E* - 3 - hydroxy - 3 - methyl - 5 - phenyl - 4 -

Table 1. Addition of lithium dimethylcuprate to E-4-phenyl-3-butene-2-one, 1, in various solvents at 0°. The ratio of $(LiMe_2Cu)_2$-substrate was 1 : 1. The yields were measured by GLC with benzylphenylether as internal standard. The observed products were 4-phenyl-2-pentanone, 2, 4-acetyl-3,5-diphenylcyclohexanone, 3, 5-acetyl-4,6-diphenyl-2-heptanone, 4, and E-3-hydroxy-3-methyl-5-phenyl-4-penterenitrile, 5. The solubility of the organocopper species is indicated as i = insoluble, ms = moderately soluble and s = soluble

Solvent	Solubility		Reaction	Yield of products, %				
	CH_3Cu	$Li(CH_3)_2Cu$	time, min	1	2	3	4	5
Hexane	i	i	1	0	>98			
Toluene	i	ms	1	0	>98			
Diethyl ether	i	s	1	0	>98			
Dichloromethane	i	ms	1	0	>98			
THF	s	s	1	64	35		1	
			10	14	82		4	
			60	3	90		7	
Pyridine	s	s	1	78	17	4	1	
			10	60	28	8	4	
			60	58	28	9	5	
Acetonitrile	i	s	1	43	28	3	2	24
			10	11	50	7	7	25
			60	6	54	7	8	25
DMF	s	s	60	5	0	mixture of products		
DMSO	s	s	1	>98	0			
			10	30	0	mixture of products		
			60	10	0			

pentenenitrile, 5 was also formed:



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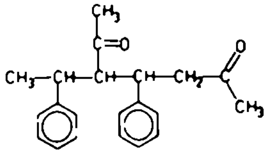

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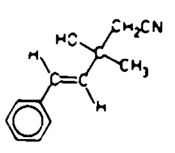

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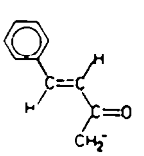

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The addition of lithium diphenylcuprate to 1 in pyridine at 0° afforded the conjugate addition product 4,4-diphenyl-2-butanone in quantitative yield after 3 hr, while a complex mixture of products was obtained in DMF solution.

^{1}H and ^{13}C NMR spectra of lithium dimethylcuprate and lithium diphenylcuprate, present in dichloromethane-d_2 and pyridine-d_5 solutions were recorded. Considerable differences in chemical shifts were observed on changing the solvent (*cf* Tables 2 and 3).

Lithium dimethylaurate, $LiMe_2Au$, was prepared from methylgold(I)-triphenylphosphine and MeLi in diethylether at 0°.[17] Addition of 4-phenyl-3-buten-2-one or 2-cyclohexenone to the solution of $LiMe_2Au$ at 0° gave a light yellow precipitate, while the remaining solutions turned yellow. The substrate enones could not be detected by GLC. The precipitate was an organogold species not further characterized. With 2-cyclohexenone several products of higher molecular weight were formed, while with 1 the dimer 3 was the main product. After addition of methyl E-3-phenylpropenoate to $LiMe_2Au$ the starting material was recovered unchanged.

DISCUSSION

The reaction between $LiMe_2Cu$ and 1 is very fast in solvents such as hexane, toluene, and diethylether, as has earlier been observed in some cases,[18] and is also rapid in dichloromethane in spite of the limited solubility of the cuprate in these solvents. This indicates a high reactivity of the "naked" cuprate towards the enone in these solvents. The conjugate addition is sufficiently fast in dichloromethane that any competitive substitution reaction with the solvent does not interfere.

The small amount of toluene present from the preparation of $LiMe_2Cu$ does not seem to alter the effect of the solvents under investigation. In the more polar and coordinating solvents such as THF, pyridine and acetonitrile, the conjugate addition is substantially slower. It has been proposed that such solvents are coordinated to the Li atom in the cuprate. The activating effect of Li coordination to the CO oxygen of the substrate could thus be hampered by complexation between Li and solvent molecules.[3,6,10,18,19] Competing reactions occur when the conjugate addition is slow. The for-

Table 2. ^1H and ^{13}C NMR spectra for methyllithium, lithium dimethylcuprate and lithium dimethylaurate in various solvents. Chemical shifts are relative to TMS as internal standard

	Solvent	Temp. °C	Chemical shifts, δ ppm ^1H	^{13}C
CH_3Li^a	diethylether	-60	-1.9	-13.2
	tetrahydrofuran	-80	-2.1	-16.2
	diethylamine	-80	-2.1	-12.2
$Li(CH_3)_2Cu$	diethylether	-67	-1.11^b	-9.6^c
	dichloromethane-d_2	-50	-0.96	-8.7
	pyridine-d_5	0	0.13	-8.5
$Li(CH_3)_2Au^d$	diethylether		-0.18	

[a] ref 23, [b] ref 15, 16, [c] ref 19, [d] ref 17.

Table 3. ^1H and ^{13}C NMR spectra for phenyllithium, lithium diphenylcuprate, lithium ditolylcuprate, and phenylcopper in various solvents. Chemical shifts are relative to TMS as internal standard

	Solvent	Temp. °C	Chemical shifts, δ ppm, ^1H / ^{13}C 1	2,6	3,5	4
PhLi	diethylether			8.024	7.025	6.958^a
			171.7	141.4	126.1	125.4^b
$LiPh_2Cu$	dichloromethane-d_2	-50		8.1	7.2	7.1
			162.3	142.2	128.4	126.8
	pyridine-d_5	0		8.57 (d,2H)	7.21 (d,2H)	7.10 (t,1H)
			173.6	141.8	125.9	122.7
$Li(4\text{-}tol)_2Cu$	benzene-d_6			8.20 (d,2H)	7.0 (d,2H)^c	
PhCu	chloroform-d	-30		7.90 (d,2H)	7.25 (m,3H)	
			137.2	144.4	127.5	131.3^d

[a] ref 26, [b] ref 27, [c] ref 25, [d] ref 28.

mation of by-products 3 and 5 is probably induced by the cuprate acting as a base.[18] An enolate anion 6 of the substrate 1 is generated and performs a Michael addition to a second molecule of 1, followed by ring closure to 3 in a second Michael addition.[1] The formation of 5 is obviously initiated by proton abstraction from acetonitrile, followed by attack by the anion on 1.

Product 4, observed in reactions run in THF, pyridine, or acetonitrile is probably formed *via* attack of primarily formed enolate 6 on another molecule of 1. We have previously observed this type of attack in the reaction between lithium diorganocuprates and methyl *E*-butenoate in THF.[20] This reaction might be synthetically interesting.[21]

The single product 3 identified from the reactions between $LiMe_2Au$ and different enones indicates that $LiMe_2Au$ in analogy with $LiMe_2Cu$ can act as a base abstracting α-protons from the enones. Unlike $LiMe_2Cu$, however, $LiMe_2Au$ shows no reactivity towards the β-C of the enone.

The low reactivity of $LiMe_2Cu$ in conjugate additions in solvents more polar than diethylether could be rationalized as due to stronger coordination of solvent molecules, THF, or pyridine, to the cuprate. At present little is known about the structure of $LiMe_2Cu$ in solvents other than diethylether. NMR studies,[15,16,19] a liquid phase X-ray investigation,[15] and molecular weight measurements[15] indicate a dimeric cluster structure, $Li_2Me_4Cu_2$, in diethylether. $LiMe_2Au$ is more stable than its Cu analog, and its structure has been studied using ^1H NMR and Rahman spectroscopy[17,22] with diethylether as solvent. Spectra indicate a monomeric, solvent-separated ion pair with the dimethylaurate ion having a linear structure.[22] There is little or no tendency towards further association to Au(I). However, addition of pyridine yields crystals of lithium dimethyl-bis(pyridine)-aurate(I).[17] The crystals probably have pyridine coordinated to Li, giving the composition $Li(py)_2(Me_2Au)$.[22]

Our NMR data (Table 2) indicate that the electronic surroundings of the Me groups in $LiMe_2Cu$ are relatively similar in diethylether and dichloromethane. ^1H and ^{13}C chemical shifts undergo only small changes. However, pyridine causes a downfield shift of *ca* 1 ppm of the Me protons. This deshielding effect is larger than the solvent effects observed for MeLi[23] (Table 2) and is contrary to the expected shielding effect of an aromatic solvent. The proton shift for $LiMe_2Cu$ in pyridine is close to that observed for $LiMe_2Au$ in diethylether.[17]

The downfield shift is hardly consistent with a structure of the ion pair type, $Li(py)_2(Me_2Cu)$. This structure is expected to show an upfield shift in its ^1H and ^{13}C absorptions due to an increased electron density on the Me_2Cu group.[24]

A comparison of the NMR proton chemical shifts for $LiPh_2Cu$ (Table 3) in dichloromethane with those for lithium di(4-tolyl)cuprate, $Li(4\text{-}tol)_2Cu$, in benzene[25] shows only small differences in the shifts for the *ortho* protons, suggesting similar structures. $Li(4\text{-}tol)_2Cu$ probably has a dimeric cluster structure with the 4-tolyl group bridging Li and Cu in a 2e–3c bond.[25] It is not unreasonable to assume a similar dimeric cluster structure, $Li_2Ph_4Cu_2$, for lithium diphenylcuprate in nonpolar solvents.

The rather small shift differences observed in the C_4 and H_4 absorptions on going from PhLi[26,27] to $LiPh_2Cu$ to PhCu[28] in various solvents seem to indicate that a change in metal–carbon bonding or coordination of solvent molecules has rather small effects on the ring current or π-electron densities (*cf* benzene chemical shift at 128.7 ppm).[24]

However, the downfield shift for C_1 in $LiPh_2Cu$ on changing from dichloromethane to pyridine, 11.3 ppm, indicates a change in magnetic anisotropy for the C_1–metal bond. This downfield shift can be related to an increased ionic character in the C_1-metal bond in the more polar solvent, as indicated by a comparison with PhLi and PhCu (Table 3). The polymeric PhCu has its C_1 absorption at 137.2 ppm. The C–Cu–C 2e–3C bond can be assumed to be largely covalent, while the C_1–Li bond in PhLi has been interpreted to have a large ratio of ionic character (C_1 at 171.7 ppm).[26,27]

Pyridine is known to be a good coordinating solvent for Cu(I) compounds.[29] Addition of pyridine to cuprates changes the ionic character of the C–metal bonds and the nucleophilicity of Cu.

It is thus concluded that the reduced reactivity of lithium diorganocuprates towards enones in polar, coordinating solvents at least in part is due to structural changes in the cuprate clusters, caused by coordination of solvent molecules. Exchange between clusters of different composition could also be anticipated. The lack of ^{13}C-Li and ^{13}C–Cu couplings could indicate fast exchange reactions, but is likely an effect of the large quadrupole moment of Cu on relaxation.[30]

EXPERIMENTAL

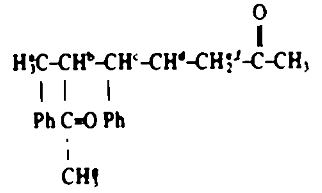
Organometallic reactions were carried out under dry, O_2 free N_2. All solvents were dried before use. Diethylether, toluene and THF were distilled from sodium benzophenone ketyl; hexane was distilled from K. Pyridine, DMF and CH_2Cl_2 were dried dynamically with molecular sieves 4Å, and acetonitrile with molecular sieves 3Å. Commercially available DMSO (< 0.01% H_2O) was used. Commercial MeLi in diethylether was used after titration.[31]

NMR spectra were recorded on a Bruker WH 270 MHz spectrometer (67.89 MHz ^{13}C), gas chromatograms on an HP 5880 chromatograph using OV 101, HPLC chromatograms on a Waters 6000, and mass spectra on an AEI MS 902.

General procedure for reactions between lithium dimethylcuprate and E*-4-phenyl-3-buten-2-one in various solvent mixtures.* MeLi (16 mmol) in diethylether was transferred *via* syringe to a reaction flask fitted with a septum and magnetic stirring bar. The diethylether was evaporated and dry toluene (20 ml) was added. Lithium dimethylcuprate was prepared by addition of the MeLi in toluene to a slurry of 8 mmol of Cu(I) I in 5 ml toluene at 0°. After the addition of one equiv of MeLi a yellow ppt formed, which turned into a white slurry after the addition of the second equiv of MeLi. After stirring for 30 min the dry solvent under investigation was added to the cuprate. The volume of the solvent was chosen to give a total volume of 70 ml. *E*-4-Phenyl-3-buten-2-one (4 mmol) and benzylphenylether (2 mmol, internal standard for GLC) dissolved in 10 ml of the dry solvent were added to lithium dimethylcuprate. The total volume was 80 ml and the ratio of toluene to dry solvent 25 : 55. The reaction was kept at 0°. A brown to orange colour appeared immediately on addition of the substrate and rapidly changed to yellow. In some cases a yellow ppt formed, possibly MeCu. When DMF or DMSO was used as solvents the yellow colour of the soln darkened after some time. Small samples were withdrawn from the mixture after 1, 10 and 60 min, hydrolysed with a satd NH_4Cl/NH_3 aq, and analysed by GLC. The mixture was hydrolysed after 3 hr, and the products recovered by extraction.[2,32] The reactions between lithium diphenylcuprate and *E*-4-phenyl-3-buten-2-one in pyridine and in DMF were carried out analogously. The reaction in pyridine gave a quantitative yield of 4,4-diphenyl-2-butanone after 3 hr. The reaction in DMF gave a complex product mixture that could not be identified.

Isolation and characterisation of products from addition of $LiMe_2Cu$, $LiPh_2Cu$, *and* $LiMe_2Au$ *to enones.* Compound 2 was isolated after distillation and the NMR spectrum compared with that of an authentic sample.[33] The dimer 3 was isolated by preparative TLC as described earlier,[1] or by HPLC (hexane. EtOAc 4 : 1) m.p. 99–100°. The NMR was compared to that of an authentic sample.[1]

Compound 4, was separated by kugelrohr destillation followed by flash chromatography (EtOAc–hexane 1:3, silica gel), m.p. 80–82°. Abs. mass 308.185. IR (KBr) 1700 cm^{-1}.M ^1H NMR (270 MHz, $CDCl_3$): δ 7.22 (10 H, m), 3.73 (1H, ddd, $J_{cd} = 4.5$, $J_{de} = 3.2$, $J_{df} = 11$, H_d), 3.28 (1H, dd, $J_{gem} = 17.5$, $J_{df} = 11$, H_f), 3.10 (1H, dd, $J_{bc} = 10.5$, $J_{cd} = 4.5$, H_c), 3.01 (1H, qd, $J_{bc} = 10.5$, $J_{ab} = 6.7$, H_b), 2.88 (1H, dd, $J_{gem} = 17.5$, $J_{de} = 3.2$, H_e), 2.10 (3H, s), 1.35 (3H, d, $J_{ab} = 6.7$, H_a), 1.12 (3H, s, H_g). H_g is shielded due to its position between two aromatic π-systems.



$$H_3^aC-\underset{Ph}{\underset{|}{CH^b}}-\underset{\underset{CH_3^g}{\underset{|}{C=O}}}{\underset{|}{CH^c}}-\underset{Ph}{\underset{|}{CH^d}}-CH_2^{e,f}-\overset{O}{\overset{\|}{C}}-CH_3$$

E-5[34] was isolated by HPLC (hexane: EtOAc 4 : 1, silica gel), ^1H NMR (270 MHz, $CDCl_3$): δ 7.37 (5 H, m), 6.77 (1 H, d, *J* 10 Hz), 6.33 (1 H, d, *J* 10 Hz), 2.66 (2H, s), 2.29 (1 H, broad s), 1.55 (3 H, s).

4,4-Diphenyl-2-butanone was isolated after kugelrohr distillation. Its NMR spectrum was in agreement with the published spectrum.[35]

General procedure for the preparation of NMR-samples of $LiMe_2Cu$ *and* $LiPh_2Cu$. MeLi or PhLi (1 mmol) in diethyl ether was added to CuI (0.52 mmol, recrystallized) at 0°. The ether was evaporated by a stream of N_2, the solvent under investigation was added, and the sample was transferred to an NMR tube. In some cases the tube was sealed, in others special tubes fitted with a glass stopper were used. The solns sometimes contained traces of diethyl ether. No attempt was made to remove the LiI (1 eq) formed in the preparation of $LiMe_2Cu$ or $LiPh_2Cu$, except in one case. No differences in the spectra could be observed.

General procedure for the reactions between lithium dimethylaurate and enones in diethylether. Methylgold(I)triphenylphosphine[36] was prepared from MeLi and triphenylphosphine gold(I) chloride[37] in diethylether at 0°. Lithium dimethylaurate was prepared by adding MeLi (1.0 mmol) in diethylether to a slurry of methylgold(I)-triphenylphosphine (1.06 mmol) in diethyl ether (10 ml) at 0°. The solid phase dissolved upon addition of MeLi, giving a colourless, clear soln of lithium dimethylaurate,[38] which was stirred for 30 min before addition of the enone (1.0 mmol) dissolved in diethyl ether (5 ml). Some minutes after the addition of the substrate, the soln turned yellow and a light yellow ppt formed. After stirring for 2 hr at 0°, the reaction was quenched by pouring the mixture into 0.5% H_2SO_4. The layers were separated, the ether phase washed twice with water and dried and the ether evaporated. The crude mixtures were analysed by GLC and NMR, which showed the absence of conjugate addition products. With 2-cyclohexenone as the substrate no residual starting material was observed, while several products of higher molecular weight had been formed. With *E*-4-phenyl-3-buten-2-one no starting material was left. The dimer 3 was the main product together with an unidentified product of higher molecular weight. After addition of methyl *E*-3-phenylpropenoate to $LiMe_2Au$ the starting material was recovered unchanged (> 95%) after 2 hr.

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