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1,4-ADDITION OF GRIGNARD REAGENTS AND 1,6-ADDITION OF LITHIUM ORGANOCUPRATES TO N,N-DIETHYLSORBAMIDE

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Summary: When they react with N,N-diethylsorbamide, saturated and allylic Grignard reagents give γ,δ-ethylenic amides (1,4-addition) whereas saturated and allylic lithium organocuprates give β,γ-ethylenic amides (1,6-addition).

During the course of a study on the reactivity of α,β-γ,δ-unsaturated carbonyl compounds with organometallics, we have studied the case of N,N-diethylsorbamide $CH_3-CH=CH-CH=CH-CO-N(C_2H_5)_2$; we report here the results we have obtained with Grignard reagents and with lithium organocuprates.

Three types of compounds can be formed when an organometallic RM reacts with N,N-diethylsorbamide :

$$\begin{array}{l} CH_3-CH=CH-CH=CH-CO-N(C_2H_5)_2 \\ \qquad + RM \end{array} \longrightarrow \begin{cases} \underline{1}\ CH_3-CH=CH-CH(R)-CH_2-CO-N(C_2H_5)_2 & \text{(1,4-addition)} \\ \left.\begin{array}{l} \underline{2}\ CH_3-CH(R)-CH=CH-CH_2-CO-N(C_2H_5)_2 \\ \underline{3}\ CH_3-CH(R)-CH_2-CH=CH-CO-N(C_2H_5)_2 \end{array}\right\} & \text{(1,6-addition)} \end{cases}$$

Grignard reagents: The reaction of a Grignard reagent with an α,β-ethylenic N,N-disubstituted amide gives a saturated amide (1,4-addition)(1-3):

$$R'-CH=CH-CO-NR''_2 \quad + \quad RMgX \longrightarrow R'-CH(R)-CH_2-CO-NR''_2$$

The only known example of a reaction with an α,β-γ,δ-diethylenic N,N-disubstituted amide is the reaction of C_2H_5MgBr with N,N-diethylsorbamide (4): the γ,δ-ethylenic amide 1 (R= C_2H_5) corresponding to a 1,4-addition was obtained.

We tried to carry out this type of reaction with other organomagnesium compounds (table 1): in every case we obtained the γ,δ-ethylenic amide 1 corresponding to a 1,4-addition (5). When α,β-ethylenic Grignard reagents $R-CH=CH-CH_2MgBr$ are used, the reaction proceeds with rearrangement (entries 7,8, table 1). The yield is rather low from a saturated organomagnesium compound and fairly good from allylic Grignard reagents. Untractable mixtures of products were obtained from $CH_2=CH-CH_2MgBr$/ether and C_6H_5MgBr/ether. No reaction was observed from CH_3MgI/ether, $CH_3O-CH_2-C\equiv CMgBr$/ether and $(CH_3)_3Si-CH_2MgCl$/ether (8).

Lithium organocuprates R_2CuLi: With these reagents, the only product formed is the β,γ-ethylenic amide 2 arising from a 1,6-addition; no α,β-ethylenic isomer was detected by NMR (table 2). The yield is low from a saturated lithium organocuprate and fairly good from an α,β-ethylenic lithium organocuprate; with the latter type of cuprate, the reaction

Table 1

$RMgBr + CH_3\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CO\text{-}N(C_2H_5)_2 \xrightarrow{20°C} CH_3\text{-}CH{=}CH\text{-}CH(R')\text{-}CH_2\text{-}CO\text{-}N(C_2H_5)_2$

Entry	R	Yield[a]	b.p.(°C/torr)
1	nC_3H_7	53	85/0.05
2	iC_3H_7	55	101/0.5
3	nC_4H_9	48	94/0.05
4	iC_4H_9	35	91/0.05
5	nC_5H_{11}	42	114/0.1
6	nC_7H_{15}	42	132/0.01
7	$CH_3\text{-}CH{=}CH\text{-}CH_2$	60[b]	106/0.07
8	$C_2H_5\text{-}CH{=}CH\text{-}CH_2$	80[c]	108/0.05

Table 2

$R_2CuLi + CH_3\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CO\text{-}N(C_2H_5)_2 \xrightarrow{-60°C} CH_3\text{-}CH(R')\text{-}CH{=}CH\text{-}CH_2\text{-}CO\text{-}N(C_2H_5)_2$

Entry	R	Yield[a]	b.p.(°C/torr)
9	nC_3H_7	30	88/0.05
10	nC_4H_9	40	106/0.05
11	nC_5H_{11}	35	130/0.1
12	$CH_2{=}C(CH_3)\text{-}CH_2$	55	115/0.1
13	$CH_3\text{-}CH{=}CH\text{-}CH_2$	60[b](15)	130/1.5
14	$C_2H_5\text{-}CH{=}CH\text{-}CH_2$	67[c]	125/0.1

[a] R'= R unless otherwise mentioned. [b] R'= $CH_2{=}CH\text{-}CH(CH_3)$. [c] R'= $CH_2{=}CH\text{-}CH(C_2H_5)$.

proceeds with rearrangement (entries 13, 14, table 2). The cuprate $(CH_3)_2CuLi$ proved unreactive with N,N-diethylsorbamide: the starting amide was recovered.

The 1,6-conjugate addition we have observed is similar to the 1,6-conjugate addition which occurs when lithium organocuprates are reacted with conjugated dienoates (11-13) and with 3,5-heptadiene 2-one (14) :

$$CH_3\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CO\text{-}CH_3 + R_2CuLi \longrightarrow CH_3\text{-}CH(R)\text{-}CH{=}CH\text{-}CH_2\text{-}CO\text{-}CH_3$$

All compounds obtained in this work showed satisfactory analytical data.

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