

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

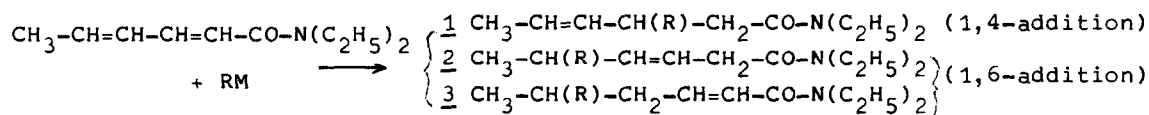
F. BARBOT, A. KADIB-ELBAN and Ph. MIGINIAC\*

Laboratoire de Chimie des Organométalliques. Groupe de Recherches  
 de Chimie Organique. Université de Poitiers. 86022 POITIERS, France.

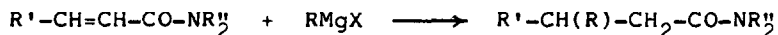
**Summary:** When they react with N,N-diethylsorbamide, saturated and allylic Grignard reagents give  $\gamma,\delta$ -ethylenic amides (1,4-addition) whereas saturated and allylic lithium organocuprates give  $\beta,\gamma$ -ethylenic amides (1,6-addition).

During the course of a study on the reactivity of  $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl compounds with organometallics, we have studied the case of N,N-diethylsorbamide  $\text{CH}_3\text{-CH=CH-CH=CH-CO-N}(\text{C}_2\text{H}_5)_2$ ; 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 :



**Grignard reagents:** The reaction of a Grignard reagent with an  $\alpha,\beta$ -ethylenic N,N-disubstituted amide gives a saturated amide (1,4-addition) (1-3):



The only known example of a reaction with an  $\alpha,\beta,\gamma,\delta$ -diethylenic N,N-disubstituted amide is the reaction of  $\text{C}_2\text{H}_5\text{MgBr}$  with N,N-diethylsorbamide (4): the  $\gamma,\delta$ -ethylenic amide 1 ( $\text{R} = \text{C}_2\text{H}_5$ ) 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  $\gamma,\delta$ -ethylenic amide 1 corresponding to a 1,4-addition (5). When  $\alpha,\beta$ -ethylenic Grignard reagents  $\text{R-CH=CH-CH}_2\text{MgBr}$  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  $\text{CH}_2=\text{CH-CH}_2\text{MgBr}$ /ether and  $\text{C}_6\text{H}_5\text{MgBr}$ /ether. No reaction was observed from  $\text{CH}_3\text{MgI}$ /ether,  $\text{CH}_3\text{O-CH}_2\text{-C}\equiv\text{CMgBr}$ /ether and  $(\text{CH}_3)_3\text{Si-CH}_2\text{MgCl}$ /ether (8).

**Lithium organocuprates  $\text{R}_2\text{CuLi}$ :** With these reagents, the only product formed is the  $\beta,\gamma$ -ethylenic amide 2 arising from a 1,6-addition; no  $\alpha,\beta$ -ethylenic isomer was detected by NMR (table 2). The yield is low from a saturated lithium organocuprate and fairly good from an  $\alpha,\beta$ -ethylenic lithium organocuprate; with the latter type of cuprate, the reaction

Table 1

Entry	R	Yield <sup>a</sup>	b.p.(°C/torr)
1	nC <sub>3</sub> H <sub>7</sub>	53	85/0.05
2	iC <sub>3</sub> H <sub>7</sub>	55	101/0.5
3	nC <sub>4</sub> H <sub>9</sub>	48	94/0.05
4	iC <sub>4</sub> H <sub>9</sub>	35	91/0.05
5	nC <sub>5</sub> H <sub>11</sub>	42	114/0.1
6	nC <sub>7</sub> H <sub>15</sub>	42	132/0.01
7	CH <sub>3</sub> -CH=CH-CH <sub>2</sub>	60 <sup>b</sup>	106/0.07
8	C <sub>2</sub> H <sub>5</sub> -CH=CH-CH <sub>2</sub>	80 <sup>c</sup>	108/0.05

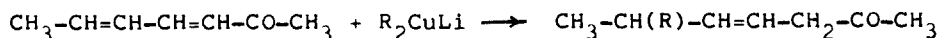
Table 2

Entry	R	Yield <sup>a</sup>	b.p.(°C/torr)
9	nC <sub>3</sub> H <sub>7</sub>	30	88/0.05
10	nC <sub>4</sub> H <sub>9</sub>	40	106/0.05
11	nC <sub>5</sub> H <sub>11</sub>	35	130/0.1
12	CH <sub>2</sub> =C(CH <sub>3</sub> )-CH <sub>2</sub>	55	115/0.1
13	CH <sub>3</sub> -CH=CH-CH <sub>2</sub>	60 <sup>b(15)</sup>	130/1.5
14	C <sub>2</sub> H <sub>5</sub> -CH=CH-CH <sub>2</sub>	67 <sup>c</sup>	125/0.1

<sup>a</sup>R' = R unless otherwise mentioned. <sup>b</sup>R' = CH<sub>2</sub>=CH-CH(CH<sub>3</sub>). <sup>c</sup>R' = CH<sub>2</sub>=CH-CH(C<sub>2</sub>H<sub>5</sub>).

proceeds with rearrangement (entries 13, 14, table 2). The cuprate (CH<sub>3</sub>)<sub>2</sub>CuLi 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) :



All compounds obtained in this work showed satisfactory analytical data.

#### References and notes

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- In a similar way, N,N-dimethylthiosorbamide CH<sub>3</sub>-CH=CH-CH=CH-CS-N(CH<sub>3</sub>)<sub>2</sub> reacts with nC<sub>4</sub>H<sub>9</sub>Li/THF, C<sub>2</sub>H<sub>5</sub>MgBr/ether (6) and CH<sub>2</sub>=CH-CH<sub>2</sub>Li/THF (7) to give 1,4-addition products.
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- In the same way, no reaction was observed with nC<sub>4</sub>H<sub>9</sub>-C≡CLi/ether, CH<sub>2</sub>=CH-CH<sub>2</sub>Al<sub>2/3</sub>Br/ether (9) and LiCH<sub>2</sub>-COOC<sub>2</sub>H<sub>5</sub>/liq. NH<sub>3</sub> (10).
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