REACTION OF N,N'-DIMETHYL-1,4-BENZOQUINONEDIIMINE WITH ORGANOMETALLIC REAGENTS

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N,N'-Dimethyl-1,4-benzoquinonediimine (*III*) yields with methylmagnesium halides and methyl-lithium products of the 1,6-addition (*IV*), 1,4-addition (*V*), and reduction (*VI*). The effect of sol-vating ability of the reaction medium, of temperature and catalysis with a copper(I) salt on the competition between these reactions has been investigated.

An unusual 1,6-addition of organolithium and Grignard reagents was found for N,N'-diphenyl-1,4-benzoquinonediimine (*I*) and N-phenyl-1,4-benzoquinoneimine[1,2] (*II*). In this work we investigated the reaction of N,N'-dimethyl-1,4-benzoquinone-imine (*III*) with organometallic reagents. The above substrate was chosen in order to find out the reactivity of the quinoneimine system unaffected by steric and electronic effects of phenyl substituents.

The reaction of *III* with methyllithium yielded after hydrolysis a mixture of *p*-phenylenediamine derivatives, unstable in air and difficult to separate. Type analysis of the sample by mass spectrometry shows the presence of molecular ions corres-ponding to the addition products of one, two, and three molecules of methyllithium, and of the product of reduction; their intensity ratios were 75 : 8 : 1 : 16 respectively. N,N,N'-Trimethyl-*p*-phenylenediamine (*IV*) (1,6-addition product) and 2,5-bis-(methylamino)toluene (*V*) (1,4-addition product) were identified as products of monoaddition, while base *VI* was detected as the reduction product with the help of a gas chromatography–mass spectrometry system and by using authentic samples.
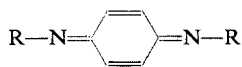
$$I, R = C_6H_5$$
$$III, R = CH_3$$
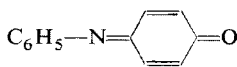
II
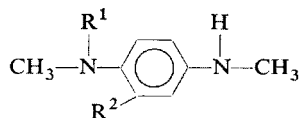
$$IV, R^1 = CH_3; R^2 = H$$
$$V, R^1 = H; R^2 = CH_3$$
$$VI, R^1 = R^2 = H$$

Similarly to previous cases, for this substrate we investigated the effect of the solvating ability of the medium and of the character of the agent used on the competition between the 1,4-addition, 1,6-addition, and reduction. Analytical liquid chromatography on silicagel with basic mobile phase seemed a suitable method for these purposes. The results are given in Table I.

In the reactions of methyllithium the yield of the 1,6-addition decreases and the yield of reduction increases if a more solvating solvent is used (ether–tetrahydrofuran). This effect becomes stronger with the addition of N,N,N',N'-tetramethylethylenediamine. The effect of the solvating ability of the solvent is less clear for reactions of the Grignard reagents.

In reactions carried out at 22°C the solvent of a high solvating ability causes a change in the composition of the reaction product similar to methyllithium; on the other hand, in the reaction carried out at a low temperature in tetrahydrofuran the 1,6-addition is strongly favoured for methylmagnesium bromide and methylmagnesium iodide. In reactions of methylmagnesium halides in ether solution the yields of the 1,6-addition decrease in the order $CH_3MgCl > CH_3MgBr > CH_3MgI$. Catalysis with a cuprous salt increases reduction; the same takes place to an even greater extent if an organocuprous reagent is used. It has been mentioned several times in the literature that the above reagents favour the most extended conjugated addition, and in some cases even reduction (*cf.* references in paper[2]). It is quite likely that reduction on the leucobase *VI* proceeds in our case as a twofold one-electron reduction. The total decrease in the yield of the reaction in strongly solvating solvents or with organocuprous reagents can probably be assigned to the one-electron reduction to the anion-radical which on hydrolysis probably gives products of oligomeric character.

The competition between the addition reaction and reduction has been studied for the reaction of benzophenone with ethylmagnesium bromide[3] and with dimethylmagnesium[4] at 25°C. It was found that similarly to our case the replacement of ether with tetrahydrofuran or the addition of N,N,N',N'-tetramethylethylenediamine decreases the total conversion and changes also the reduction/addition reaction ratio in favour of reduction. At a low temperature when according to our results an inverse ratio of the amounts of the products of the addition reaction and reduction was found, competition between the above reactions was not studied for benzophenone. The effect of strongly solvating solvents, such as tetrahydrofuran and N,N,N',N'--tetramethylethylenediamine on the competition between the addition reaction and reduction depends on the conditions of binding and on the geometry of complexes formed by these solvents and by the organometallic reagent used. For reactions of sterically hindered Grignard reagents with benzophenone, a mechanism involving electron transfer is assumed, but the 1,2 addition of methylmagnesium halide to benzophenone is probably a quasiionic reaction[5]. The competition between the addition reaction and reduction may in this case be explained as the competition of

Yields (%) of Products of the 1,6-Addition (*IV*), 1,4-Addition (*V*) and Reduction (*VI*) of the Reaction of N,N′-Dimethyl-1,4-benzoquinonediimine with Organometallic Reagents under Different Conditions

Reagent	Solvent	°C	*IV*	*V*	*VI*
CH$_3$Li	ether	22	59·0	2·9	8·6
	ether	−20	52·5	0	[b]
	ether	−40	34.6	0	4·3
	tetrahydrofuran	22	51·2	0	9·6
	tetrahydrofuran	−20	54·9	0	16·0
CH$_3$Li[a]	ether	22	58·8	4·8	12·3
	tetrahydrofuran	22	13·1	0	12·4
	tetrahydrofuran	−20	39·2	0	20·0
CH$_3$Cu.LiI	ether	22	2·6	0	45·6
	ether	−20	1·5	0	34·5
CH$_3$MgI	ether	22	31·6	0	9·2
	ether	−20	20·8	1·6	8·6
	ether	−40	11·8	0	5·9
	tetrahydrofuran	22	39·2	1·6	8·6
	tetrahydrofuran	−20	62·1	0·8	7·0
CH$_3$MgI[a]	ether	22	16·8	[b]	17·2
	tetrahydrofuran	22	30·0	0	7·6
	tetrahydrofuran	−20	72·0	0	8·6
CH$_3$MgI[c]	ether	22	18·0	[b]	15·7
	ether	−20	16·4	1·6	15·2
CH$_3$MgBr	ether	22	53·2	0	9·2
	ether	−20	28·7	0	7·2
	ether	−40	13·9	0	11·6
	tetrahydrofuran	22	5·2	0	11·2
	tetrahydrofuran	−20	82·1	1·6	5·2
CH$_3$MgBr[a]	tetrahydrofuran	22	0	0	20·8
CH$_3$MgBr[c]	ether	22	31·6	[b]	31·8
	ether	−20	27·2	0	16·7
CH$_3$MgCl	ether	22	56·0	0	8·6
	ether	−20	63·0	0	6·4
	ether	−40	53·0	0	1·2
	tetrahydrofuran	22	44·8	1·2	11·2
	tetrahydrofuran	−20	40·0	3·8	9·2
CH$_3$MgCl[c]	ether	22	18·9	0·8	76·4
	ether	−20	8·7	0	24·1

[a] Addition of 1·1 equiv. N,N,N′,N′-tetramethylethylenediamine (related to reagent); [b] traces; [c] Addition of 0·104 equiv. CuI (related to reagent).

a quasiionic reaction with a reaction of the electron-transfer type: A strong coordination bond of the solvent with the organometallic reagent makes difficult the coordination of the metal atom of the reagent with the carbonyl oxygen atom of the substrate, which is substantial for the addition reaction of the second molecule of the reagent to the carbonyl carbon atom.

In our case no quasiionic mechanism of the addition reaction (1,6 addition) can be assumed, because this mechanism could not lead to the transfer of the negatively charged organic residue of the organometallic reagent to the site of the largest negative defect on the molecule of the substrate. Even in the case of a transfer mechanism of the addition reaction, steric and binding properties of the reacting organometallic species may affect competition between the addition reaction and reduction. It is quite likely that in reactions of stable and bulky complexes of the organometallic reagent with the acceptor substrate there occurs electron transfer before the decomposition of the complex, thus reducing the probability of recombination of the radical with the anion radical formed from the substrate. The effect of the coordination of tetrahydrofuran or N,N,N',N'-tetramethylethylenediamine to the lithium salt of the anion-radical formed should act in the same direction because of its stabilization effect[6], that is, facilitate the release of the anion-radical from the reaction pathway.

The effect of the temperature cannot be interpreted unambiguously. The decrease in temperature may cause an increase in solvation of the organometallic reagent and may lead to a larger exposure of the carbanion, thus increasing its reduction capability owing to a higher donor ability. This case is similar to the use of a more basic reagent. On the other hand, an increase in temperature may facilitate an increase in the distance between the anion-radical and other components formed by the decomposition of the transition state complex. Thus, an increase in temperature may favour the formation of free anion-radicals compared to the immediately occurring competition recombination of these radicals on the original products.

The reactivity of quinoneimine *III* compared to substrates *I* and *II* investigated earlier may generally be characterized as follows: The reasons for which the electron-transfer mechanism has been suggested for the 1,6 addition of *I* and *II* holds also for *III*. However, the dependence of the addition reactions and reduction on reaction conditions still exhibits some differences compared to the substrates studied earlier. Compared to similar reactions of *I* and *II*, in reactions of *III* the participation of the 1,6 addition is much larger (the yield of the 1,4 addition attains 4·8% at utmost); the 1,6 addition-to-reduction ratio can be more affected by the solvating ability of the medium and by the character of the reagent. In our opinion, the above differences are related to the different structure of the substrates investigated. For anion radicals derived from substrates *I* and *II* one may expect steric hindrance of the nitrogen atom due to the bulkier phenyl group and differences in reactivity caused by a higher conjugation which can decrease the substitution preference.

EXPERIMENTAL

If not indicated otherwise, the melting points were determined with the Kofler block. Infrared spectra were recorded with a UR-10 spectrophotometer in KBr pellets. GLC separation was carried out on a column 100 cm long packed with 10% Carbowax 20 M on Chromaton N AW; $N_2 = 35$ kp/m^2.

The preparation of organometallic compounds and all reactions with these compounds were performed in an argon atmosphere. The tetrahydrofuran solution of methyllithium was prepared immediately before use by evaporation of the ether solution[7] followed by dissolution of the residue.

The suspension of CH_3Cu . LiI was prepared by adding 1 ml of 0·25M-CH_3Li to 49·5 mg CuI at a given temperature and by bubbling argon through the mixture during 15 min. If CuI was added to the Grignard reagents, the mixture was prepared similarly with the difference that the ratio was 4·9 mg CuI per 1 ml of 0·25M solution of reagent.

Chemicals

N,N′-*Dimethyl*-1,4-*phenylenediamine*: As commercial samples of this compounds are not sufficiently pure, the following procedure was used: To a mixture of 10·3 g (0·069 mol) of N,N′-diformyl-1,4-phenylenediamine[8] (dried at 200°C and 0·5 Torr for 6 h), 6 g (0·16 mol) of lithium aluminium hydride was added in small doses while stirring. The mixture was boiled under a reflux for 6 h, left to stand overnight, decomposed with a small amount of methanol and water (50 ml) and then treated with 100 ml of 4M-NaOH. Both the solution and coagulated aluminium salts were shaken with ether seven times, the ether solution was dried with potassium carbonate and the residue was subject to sublimation and crystallized twice from heptane. The yield was 2·6 g (27·5%) of compound, m.p. 47—50°C. The compound thus obtained was pure according to the GLC data. Its retention time at GLC and the IR spectrum are identical with the retention time or the spectrum of an authentic sample obtained by hydrolysis of N,N′-dimethyl-N,N′-ditosyl-*p*-phenylenediamine[9].

N,N,N′-Trimethyl-*p*-phenylenediamine was prepared by reduction of N′-formyl-N,N-dimethyl-*p*-phenylenediamine carried out similarly to N,N′-dimethyl-*p*-phenylenediamine. N,N′-Dimethyl-2-methyl-*p*-phenylenediamine was obtained according to the literature[10]. N,N′-Dimethyl-1,4-benzoquinonediimine was prepared by oxidation of its leucobase with silver (*I*) oxide in ether[9,11], or with lead dioxide in light petroleum[9]. The oxidation of 0·6% of the solution of leucobase in heptane with freshly prepared silver oxide in the presence of Na_2SO_4 seemed the most suitable procedure in this case. The product, m.p. 92°C, was obtained from the reaction liquid by crystallization at —75°C in a yield of 48·9% (m.p. determined in an evacuated sealed capillary. The literature[11] gives the melting point 92—93°C). The whole preparation procedure including filtration and crystallization must be carried out in an argon atmosphere. ·

Reaction of N,N′-Dimethyl-1,4-benzoquinonediimine with Methyllithium for Type Analysis

To 20 ml of a benzene solution of N,N′-dimethylbenzoquinonediimine prepared from 0·8g N,N′-dimethyl-*p*-phenylenediamine, 20 ml of tetrahydrofuran was added. The mixture was added dropwise at 22°C to 35 ml of 1 M tetrahydrofuran solution of methyllithium and left at 22°C for 2 h. After decomposition with water the organic layer was separated, the aqueous solution was shaken four times with ether, the organic layers were dried (MgSO$_4$), evaporated, and the residue was redistilled *in vacuo*. The yield was 0·4 g of the product.

Reaction of Organometallic Reagents with N,N′-Dimethyl-1,4-benzoquinonediimine

The reactions were carried out each time in two tuberculin tubes connected with a stainless steel capillary so that 1 ml of a 0·05M solution of N,N′-dimethyl-1,4-benzoquinonediimine and 1 ml of a 0·25M solution of the reagent were dozed into the first and second tube respectively. Both tubes were then thermostated to the given temperature, and the solution of the substrate was displaced to the reagent by means of argon. The reaction mixture was decomposed after 30 min with 40 ml of ethanol saturated with ammonia, and the solution thus obtained without any further treatment was subjected to analytical liquid chromatography performed on an apparatus of our own construction[12]. A UV detector (Czechoslovak Academy of Sciences, Development Works) operating at 254 nm was used for detection. Silpearl 10−30 µ (Kavalier, Votice) was used as carrier, heptane with 6·5% of ethanol and 0·1% of repurified triethylamine was the mobile phase. The results are summarized in Table I.

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Translated by L. Kopecká.