

REACTION OF N-PHENYL-*p*-QUINONEIMINE WITH ORGANOMETALLIC AGENTS

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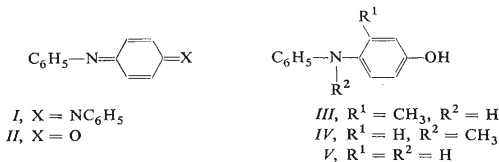
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N-Phenyl-*p*-quinoneimine yields with methyl lithium and methylmagnesium iodide products of the 1,4-addition (*III*), 1,6-addition (*IV*) and reduction (*V*), while the reaction with the organo-copper reagent gives only products of the 1,6-addition and reduction.

N,N'-Diphenyl-*p*-quinonediimine (*I*) yields with organometallic compounds products due to the 1,4-, 1,6-addition and reduction¹. Competition between these reactions is dependent on the nature of the organometallic reagent and on the medium in which the reaction takes place. The reaction is likely to have a chain character, and it certainly involves electron transfer from the organometallic compound to the substrate. 1,6-Addition occurs at the nitrogen atoms of the substrate. On the other hand, in the additions to the majority of quinones the nucleophilic group is bonded to one of the carbon atoms of the quinone ring. The unusual 1,6-addition to N,N'-diphenyl-*p*-quinonediimine was explained in terms of the electron-transfer mechanism. The highest density of free spins as well as the largest netto charge in the intermediate anion radical are probably localized on the nitrogen atoms. Both the organic free radical and the metal cation derived from the reagent will then preferentially be bonded to the nitrogen atoms of the substrate. A similar situation probably arises during the O,O-addition of the Grignard reagents to *o*-quinones described later².

We have recently extended these studies to include N-phenyl-*p*-quinoneimine (*II*), in which compared to N,N'-diphenyl-*p*-quinonediimine there is no equivalency between the carbon atoms 1 and 4 or 2 and 3 of the quinone ring. The former compound can also be regarded as a nitrogen analogue of fuchsonone, for which the 1,6-addition of the Grignard reagents has also been observed³.

From a reaction with methyl lithium performed under conditions identical with those for N,N'-diphenyl-*p*-quinonediimine, 4-hydroxy-2-methyldiphenylamine (*III*),



N-methyl-4-hydroxydiphenylamine (IV) and leucobase V were isolated in small quantities, the yields being almost the same and the main product consisting of poorly soluble materials. Since the small yields did not allow to follow competition between the individual reactions, we used a lower temperature, a different medium and different reagents. The results are summarized in Table I.

The substitution of ether for tetrahydrofuran and methylmagnesium iodide for methyllithium does not lead to any significant change. On the other hand, no 1,4-addition takes place during the reaction of the organocopper compound. The reagents of this type are known to favour the highest range addition reaction⁴⁻⁶. A similar effect was observed during reactions of the Grignard reagents with conjugated carbonyl compounds of a feebly acceptor character when a catalytic amount of a copper salt was added to the solution of the Grignard reagent^{4,7-9}. In our case the addition of a catalytic amount does not have any essential influence upon the competition between the individual reactions, which is probably connected with the different character of the substrate used. A pronounced change in the 1,6-addition to reduction ratio occurs if methyllithium is added to the mixture of the substrate and cuprous chloride at room temperature. This can be explained by the formation of a complex of cuprous chloride and the substrate, or by the fact that in this case there occurs a homolysis of the organocopper reagent at an elevated temperature, so that we have here a reaction of the substrate with the free methyl radicals.

EPR spectroscopy has revealed that on mixing of solutions of N-phenyl-*p*-quinoneimine and methylmagnesium iodide at -60°C a paramagnetic species is formed, which suggests that the reaction is at least partly of an ionradical character.

TABLE I

Course of Reactions of N-Phenyl-*p*-quinoneimine (II) with the Organometallic Compounds at -60°C

Reagent	Solvent	1,4-Addition	1,6-Addition	Reduction
		%	%	%
CH ₃ Li	THF ^a	9.8	9.3	9.8
CH ₃ Li	ether	13.6	14.1	13.9
CH ₃ MgI	ether	15.6	14.0	14.8
CH ₃ CuLiI	ether	0	30.5	28.7
CH ₃ CuLiI	THF ^a	0	28.1	57.7
CH ₃ Li + CuCl ^b	THF ^a	0	44.0	7.8
CH ₃ MgI + CuI ^c	ether	23.4	17.8	18.4

^aTetrahydrofuran; ^ba solution of methyllithium was added to the mixture of the substrate and CuCl (1 : 2) at $+25^{\circ}\text{C}$ while stirring; ^c5 mol % of CuI (referred to the reagent) was added to the solution of the Grignard reagent at -15°C and the solution was stirred for 30 min at this temperature, then cooled to -60°C and the reaction was effected.

EXPERIMENTAL

The preparation of organometallic compounds and the reactions with the compounds were carried out under argon. The products were separated by chromatography on a two-hundredfold excess of silicagel (60—120 mesh) deactivated with 12% of water in the light petroleum-ether system 85 : 15. The melting points were determined on Kofler's block and were not corrected. The IR spectra were recorded on a UR 10 spectrometer in the KBr pellets.

Chemicals: N-phenyl-*p*-quinoneimine was obtained from 4-hydroxydiphenylamine¹⁰ by oxidation with silver oxide¹¹. 2-Methyl-4-hydroxydiphenylamine was obtained as described in ref.¹², with the only difference that hydrochloride was used instead of 6-amino-3-hydroxytoluene sulphate; the product was isolated in a yield of 52% by chromatography on silicagel, m.p. 88 to 89°C. The solution of methyllithium in ether was obtained after Gilman and coworkers¹³; the tetrahydrofuran solution was obtained by evaporating the ether solution and dissolving the dry residue.

Reaction of N-Phenyl-*p*-quinoneimine with Methyllithium and Methylmagnesium Iodide

To a solution of 0.0235 mol methyllithium in 50 ml tetrahydrofuran a solution of 1.8 g (0.0098 mol) of N-phenyl-*p*-quinoneimine in 100 ml tetrahydrofuran was added at -60°C with stirring. The reaction mixture was stirred at -60°C 2 h and decomposed with water. On acidifying with acetic acid the ether layer was shaken with water and subjected to chromatography on silicagel. The identity between compounds III, IV and V and the authentic samples was established by comparing the IR spectra. The reaction of the substrate with methyllithium in ether was effected in a similar manner. The reaction with methylmagnesium iodide was carried out in ether similarly to the preceding case, with the difference that owing to the weaker activity of the reagent the mixture was allowed to attain room temperature and then decomposed. The reaction with a catalytic amount of cuprous iodide added was performed in such a way that to the solution of the Grignard reagent, the same as in the preceding case, 0.205 g (0.00106 mol) of cuprous iodide was added at -15°C, the mixture was stirred 30 min at the same temperature, cooled to -60°C and on adding the substrate treated similarly as above.

Reaction of N-Phenyl-*p*-quinoneimine with Methylcopper

To a suspension of 10.5 g (0.55 mol) of cuprous iodide in 250 ml of ether a solution of 0.0481 mol methyllithium in 45 ml of ether was added at -30°C with stirring. After stirring for 1 h the suspension was cooled to -60°C, and a solution of 1.8 g (0.0098 mol) of N-phenyl-*p*-quinoneimine in 100 ml of ether was added dropwise at this temperature. The mixture thus obtained was stirred two hours, decomposed with water when cool and treated as described above. An analogous route was employed to effect the reaction in tetrahydrofuran, with the only difference that the organocopper reagent was prepared at -40°C.

Reaction of N-Phenyl-*p*-quinoneimine with Cuprous Chloride and Methyllithium

To a solution of 1.8 g (0.0098 mol) of N-phenyl-*p*-quinoneimine in 100 ml of tetrahydrofuran 2 g (0.0202 mol) cuprous chloride was added. The suspension was stirred 15 min at room temperature, and a solution of 0.055 mol methyllithium in 50 ml ether was added during 30 min while stirring continuously. The mixture was decomposed with water after stirring for two hours at room temperature and then treated as usual.

N-Methyl-4-hydroxydiphenylamine

A mixture of 1 g of anhydrous zinc chloride, 5 g of hydroquinone and 3.5 g of N-methylaniline was heated to 180°C for 2 h. On cooling the product was extracted from the mixture with HCl (1 : 5), precipitated from the solution with a saturated solution of sodium acetate and extracted with ether. Chromatographic separation yielded 1.07 g (53%) of N-methyl-4-hydroxydiphenylamine. The compound was a liquid, and it was redistilled *in vacuo* for the purposes of analysis and recording of spectra. IR spectrum: 699 cm^{-1} , 757 cm^{-1} (monosubstituted benzene ring); 815 cm^{-1} (disubstituted benzene ring); 2800 cm^{-1} (CH_3); 3370 cm^{-1} (OH). For $\text{C}_{13}\text{H}_{13}\text{NO}$ (199.2): calculated: 78.36% C, 6.58% H, 7.03% N; found: 78.05% C, 6.66% H, 7.03% N.

REFERENCES

1. Honzl J., Metalová M.: *Tetrahedron* 25, 3641 (1969).
2. Blomberg C., Grootveld H. H., Gerner T. H., Bickelhaupt F.: *J. Organometal. Chem.* 24, 549 (1970).
3. Julian P. L., Gist W. J.: *J. Am. Chem. Soc.* 57, 2030 (1935).
4. House H. O., Fischer W. L.: *J. Org. Chem.* 33, 949 (1968).
5. Luong Thi N. T., Riviere H.: *Tetrahedron Letters* 1970, 1579.
6. Luong Thi N. T., Riviere H.: *Tetrahedron Letters* 1971, 587.
7. Kharash M. S., Reinmuth O.: *Grignard Reactions of Nonmetallic Substances*. Prentice-Hall, New York 1954.
8. House H. O., Satham R. A., Slater C. J.: *J. Org. Chem.* 31, 2667 (1966).
9. House H. O., Respass W. L., Whitesides G. M.: *J. Org. Chem.* 31, 3128 (1966).
10. Heller G.: *Ann.* 418, 265 (1919).
11. Bandrowski E.: *Monatsh.* 9, 134 (1888).
12. Burmistrov S. I., Romanovskaja L. G.: *Probl. Poluč. Poluprod. Prom. Org. Sin. Akad. Nauk SSSR, Otd. Obšč. Tech. Chim.* 1967, 158; *Chem. Abstr.* 68, 86936 (1968).
13. Gilman H., Zoelner E. A., Selby W. M.: *J. Am. Chem. Soc.* 55, 1252 (1933).

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