

THE REDUCTION OF β -SUBSTITUTED DIMETHOXYNAPHTHALENES WITH Li IN HMPA

Wojciech Kotlarek

Agricultural Academy, Institute of General Chemistry, Wrocław

ul. Norwida 25, Poland

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Solutions of alkali metals in HMPA /Hexamethylenephosphotriamide - abbreviated HMPT in the French literature/, have recently found application in the reduction of various unsaturated systems, e. g. α, β -unsaturated ketones ^{1/}, α, β -unsaturated acids ^{2/}, saturated ketones ^{3/} and unconjugated and even tetrasubstituted C=C bonds ^{4/}. The reduction of α, β -unsaturated ketones and acids has been carried out under conditions which selectively reduce only one function. For simple benzene derivatives the site of reduction can be predicted easily and depends on the presence or absence of a proton donor /ROH/. Without the proton donor one obtains, for example, phenol from anisole ^{5/} and a mixture of naphthalene and β -naphthol from 2 - methoxynaphthalene ^{6/}. Thus, only the C - O bond is split and the aromatic ring is not attacked. In the presence of alcohol the ring is reduced and the products are the same as those obtained from the Birch reduction in liquid ammonia ^{7/}.

A totally different situation may exist in the case of polysubstituted naphthalene derivatives. For this reason we thought that it would be interesting to apply the reduction with metals in HMPA to various dialkoxynaphthalenes. In these compounds two -OR groups can complicate the reaction course, particularly in unsymmetrically substituted dialkoxynaphthalenes. A study of the reaction to determine conditions permitting selective reduction in cases

where many susceptible groups are present in the molecule appeared to be advisable prior to applying this method to more complicated systems, steroids for example.

Initially we turned our attention to the simplest dialkoxynaphthalenes containing two equivalent -OR groups at the β positions of the naphthalene ring. This arrangement of the substituents was expected to ensure a relatively simple course for the reduction. Reduction of 2,6 - dimethoxy - /I/ and 2,7 - dimethoxynaphthalene /II/ with sodium in liquid ammonia yielded, respectively, 1,4,5,8 - tetrahydro - 2,6 - dimethoxynaphthalene ^{8/} and 1,4,5,8 - tetrahydro - 2,7 - dimethoxynaphthalene ^{9a - e/}. A third compound, 2,3 - dimethoxynaphthalene /III/ was also tested. Because of the ortho relation of the groups one to another, the reduction of compound /III/ with sodium in liquid ammonia yields a mixture containing products of a reductive removal of one or two methoxyl groups ^{10/}.

All compounds were reduced with lithium in HMPA in two ways:

A/ - without a proton donor,

B/ - with a proton donor /EtOH/

A/ A THF solution of the compound to be reduced was added to a solution of lithium in HMPA - THF /5 : 4/ and the reaction mixture was stirred for 6 hours at 20 - 25°C. The HMPA was decomposed with 2N HCl at 5°C.

B/ As in A except that the addition of the compound to be reduced was followed by a slow addition of anhydrous EtOH.

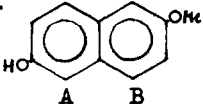
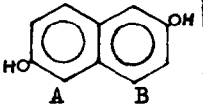
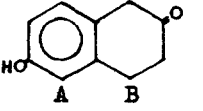
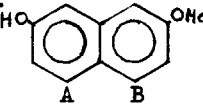
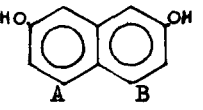
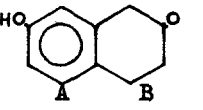
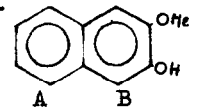
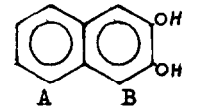
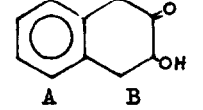
Multicomponent mixtures were obtained in every case. Pure compounds were identified by comparison of tlc mobilities, melting points, and ir and uv spectra with authentic samples and by preparation of suitable derivatives. Qualitative and quantitative results are presented in the Table.

The experiments demonstrate that without alcohol "reductive cleavage" of the type: naphth. \int O - Me and naphth. - O \int Me is the major reaction. In the presence of alcohol reduction of the ring prevails preceded, however, by an attack at one of the two methoxyl groups. These reactions give distinctly different product mixtures than those from reduction with sodium in liquid ammonia.

Experiments currently under way are aimed at finding conditions permitting

the Birch - type reduction, to the exclusion of other reactions. We are also currently engaged in the reduction of other dialkoxynaphthalenes /1,4 -, 1,5 -, 1,6 -, 1,7 -/ with lithium in HMPA.

T a b l e

Compound reduced	Products obtained %/					
	A /without EtOH/		B /with EtOH/			
2,6-dimethoxy-naphthalene /I/	 A 30	 B 20	β -naphthol A 20	B <5	 A <5	β -tetralone B 45 trace 10
2,7-dimethoxy-naphthalene /II/	 A 25	 B 20	β -naphthol A 45	B 25 <5	 A <5	β -tetralone B 40 trace 10
2,3-dimethoxy-naphthalene /III/	 A 20	 B 15	β -naphthol A 35	B 20 10	 A <5	β -tetralone B 45 trace 10

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