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The Synthesis of Phenyl Acetylene Phenols for Development of New Explosives

Nikoloz Chikhradze¹, Merab Nadirashvili¹, Sergo Khomeriki¹,
Iasha Varshanidze¹

¹ G. Tsulukidze Mining Institute, 7 E. Mindeli str., Tbilisi 0186, Georgia

chikhradze@mining.org.ge

Abstract. The purpose of this research is to produce derivatives of simple phenols as “raw material” for the synthesis of new phenolic explosives. A big number of valuable products is synthesized from phenol and its homologues including well-known explosives - picric acid, methyl picrate, cresolite, etc. In general, a structural modification of well-known explosives’ molecules is the most important among the methods for the synthesis of new explosives. This method can be used in certain modifications. For example, the synthesis of methyl picrate is possible not only to replace picric acid’s hydroxyl with methoxyl, but with nitration of anisole as well, i. e., by the reciprocating synthesis. Thus, to produce the new analogues of well-known phenolic explosives, the preliminary modification of simple phenols’ molecules and further nitration, presumably by a formation of dinitro derivatives may be performed. The alkylation of phenol, anisole and m – cresol by the secondary phenyl acetylene alcohols in the presence of concentrated phosphoric acid was carried out. Para-substituted alkynyl phenols with high yields were developed. The chemical transformations were carried out by a participation of their molecules’ active centres. The corresponding ethers, esters and saturated isologues have been synthesized. The article describes the conditions of a synthesis of 14 new phenyl acetylenes’ substances that may be used as substrates in a nitration reaction.

1. Introduction

In order to obtain new alkynyl phenols, it must be carried out alkylation of simple phenols by phenyl acetylene alcohols in the presence of concentrated phosphoric acid.

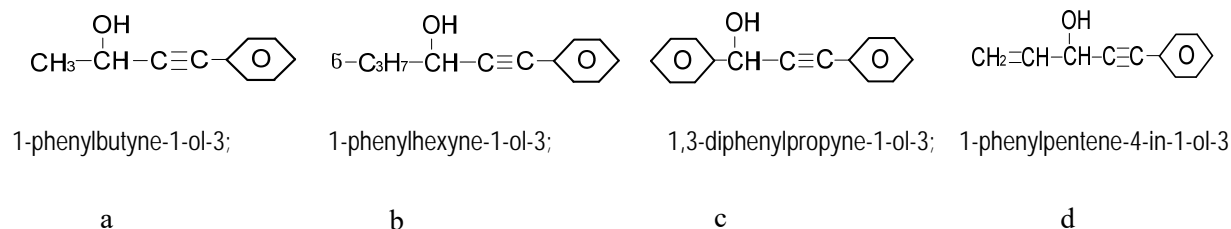
Tertiary phenyl acetylene alcohols lead to formation of p-substituted phenols. These products and their derivatives – ethers, esters, benzoates, as well as, Si- and Ge-containing varieties [3, 5] were formed with high yields [1, 4].

Anomalous course of a reaction has been observed in the case of primary 1-phenylpropyne-1-ol-3: instead of phenyl acetylene phenols, ketophenols have been formed [2].

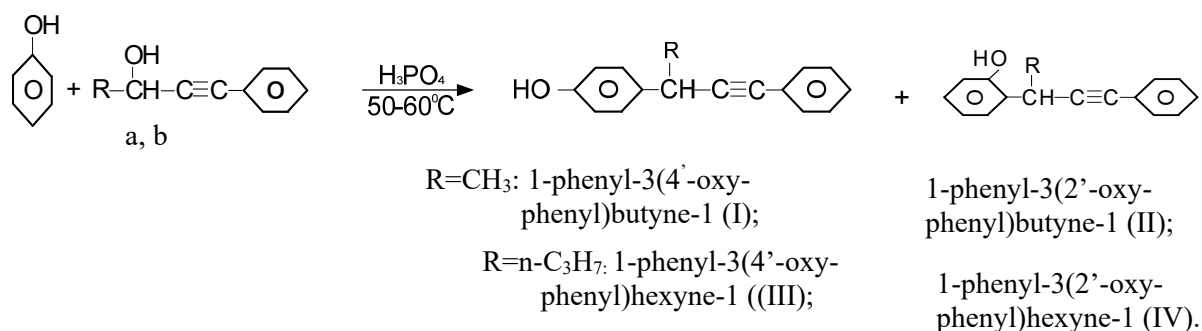
2. Synthesis

For investigation of influence of alcohols structural modification on alkylation process, we have synthesized several secondary phenyl acetylene alcohols:



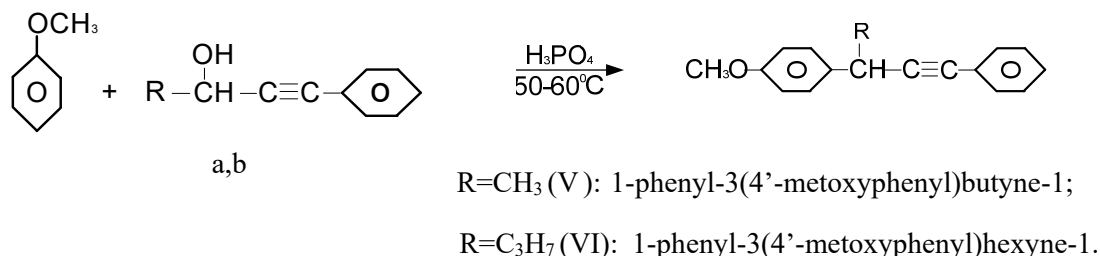


Alkylation of phenol by a- and b-alcohols leads to formation of o- and p- substituted alkynyl phenols:



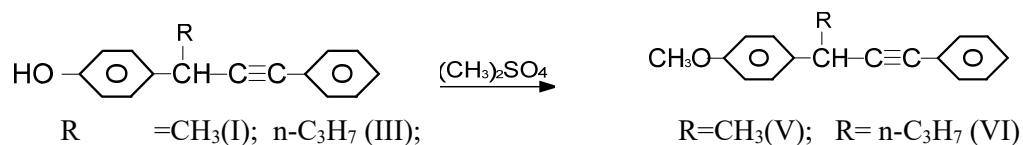
In the case of a-alcohol, correlation of para/orto is 3/2 in the case of b-alcohol – 4/1. Such difference may be explained by steric factor.

Alkylation of anisole by a- and b-alcohols leads to formation of the corresponding p-alkynyl anisole:

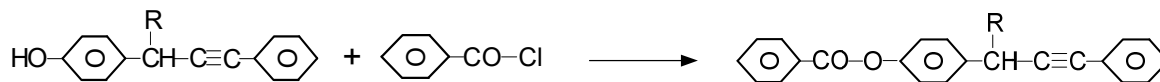


Choice of anisole, as a substrate of alkylation, is conditioned, at first, by simplicity of its molecule, which excludes side-reactions, such as etherification, cyclo-addition of o-isomer etc. Furthermore, it appears possibility to receive phenyl acetylene anisoles by counter synthesis, that is one of the important methods to establish of alkylates' structure.

Really, the alkynyl anisoles V, VI have been synthesized by methylation of I and III:



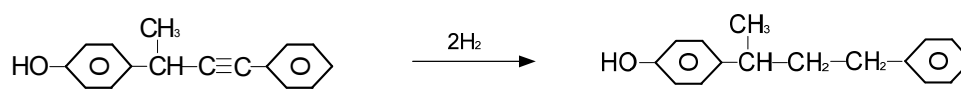
Besides methylation, other chemical conversions of alkynyl phenols have been carried out by participation their active centres. Corresponding benzoates and saturated isolog have been obtained:



R=CH₃(I); n-C₃H₇ (III);

R=CH₃(VII): 1-phenyl-3(4'-benzoiloxyphenyl)butyne-1;

R=n-C₃H₇(VIII): 1-phenyl-3(4'-benzoiloxyphenyl)hexyne-1.

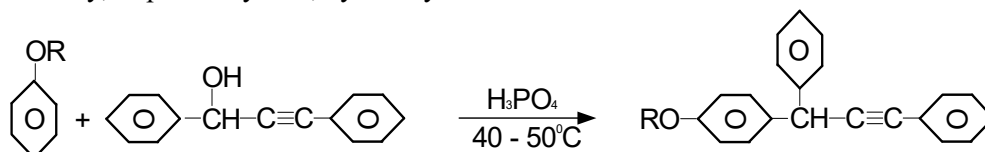


Reney-Ni

I

IX: 1-phenyl-3(4'-oxyphenyl)butan

To change alcohols' saturated radicals by phenyl group must increase stabilization of intermediate carbocation. So, alkylation of phenol and anisole by c-alcohol courses in soft conditions and leads, exclusively, to para-alkylates, by 80% yield:

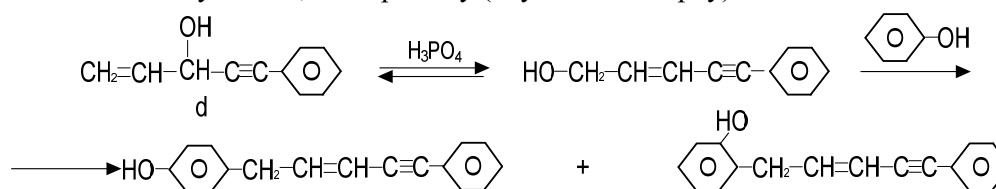


R=H (X): 1,3-diphenyl-3(4'-oxyphenyl)propyne-1;

R=CH₃ (XI): 1,3-diphenyl-3(4'-methoxyphenyl)propyne-1;

Such course of reaction has been expected, because mentioned changing has an influence not only on electronic factor, but - steric too. To rise of last one from a-alcohol to b -, caused increase the part of p - isomer from 3/2 to 4/1. The subsequent increasing (c -alcohol case) has exclusively led to p-isomer.

As to alkylation by d -alcohol, its molecule consists of allyl and phenyl acetylene fragments simultaneously, because of, in acid area it suffers allyl regrouping and to phenolic substrate's molecule entries not secondary radical, but - primary (allyl anionothrophy):

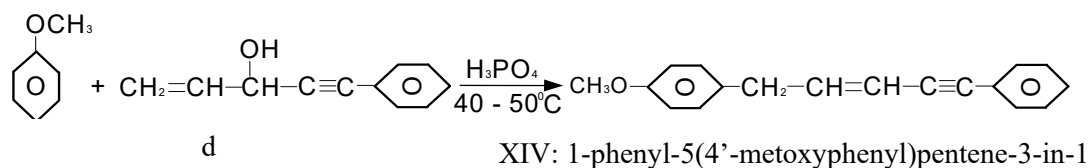


XII: 1-phenyl-5(4'-oxyphenyl)pentene-3-in-

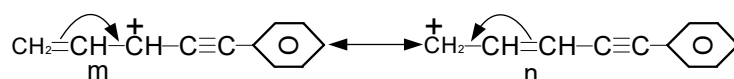
XIII: 1-phenyl-5(2'-oxyphenyl)pentene-3-in-1;

In this case, correlation of para/orto isomers is also 3/2.

Anisole, in the same reaction, gives p -substituted product:



It is notable that alkylation of phenols by d-alcohol courses quite easy: reactions finish for 20-25 min. at room temperature. This may be explained by mesomeric effect, which makes allyl carbocation steady system:



n – carbocation's substitution in benzene ring is conditioned by: 1. its less steric obstacle, than m – carbocation, and 2. Formation of conjugated π - electronic steady system, including ethylene, acetylene and phenyl components. So, formation of XII-XIV compounds may be explained in full accordance with theory.

The structure of synthesized phenyl acetylene phenols has been established by IR and NMR spectral data, also by other physical and chemical methods of investigation (table 1).

Table 1. Constants of I-XIV compounds

№	B.p., °C (mm) M.p., °C	n_D^{20}	d_4^{20}	MR_D		R_f (Al_2O_3 C ₆ H ₆ : CH ₃ OH 30:1)	Found, %		Formula	Calculated, %	
				Found	Calculated		C	H		C	H
I	-	1.5835	1.0292	67.99	68.67	0.60	85.81	6.07	C ₁₆ H ₁₄ O	86.48	6.30
II	-	1.5940	1.0579	68.88	68.67	0.72	86.42	6.13	C ₁₆ H ₁₄ O	86.48	6.30
III	72-73	-	-	-	0.49	0.49	86.28	7.69	C ₁₈ H ₁₈ O	86.40	7.20
IV	-	1.5800	1.0638	78.20	77.97	0.74	85.17	7.81	C ₁₈ H ₁₈ O	86.40	7.20
V	169-170 (1)	1.5886	1.0648	74.46	73.58	-	85.84	6.80	C ₁₇ H ₁₆ O	86.10	6.48
VI	183-184 (1)	1.5752	1.0436	83.73	82.87	0.81	86.06	7.79	C ₁₉ H ₂₀ O	86.36	7.58
VII	69-71	-	-	-	-	-	85.03	5.21	C ₂₃ H ₁₈ O ₂	84.66	5.52
VIII	120-121	-	-	-	-	-	84.24	5.87	C ₂₅ H ₂₂ O ₂	84.74	6.21
IX	167-168 (1)	1.5700	1.0604	69.91	70.41	-	85.30	7.40	C ₁₆ H ₁₈ O	84.95	7.96
X	78-80	-	-	-	-	0.26	88.00	6.24	C ₂₁ H ₂₇ O	88.72	5.97
XI	215-216 (1)	1.6262	1.1149	94.65	95.05	0.52	88.52	5.83	C ₂₂ H ₂₉ O	88.59	6.04
XII	-	1.5890	1.0910	72.35	72.85	0.52	86.96	5.24	C ₁₇ H ₁₄ O	87.18	5.98
XIII	-	1.6020	1.0994	73.30	72.85	0.68	86.74	6.14	C ₁₇ H ₁₄ O	87.18	5.98
XIV	-	1.5700	1.0336	78.70	77.75	0.66	86.72	6.11	C ₁₈ H ₁₆ O	87.09	6.45

3. Conclusions

Several phenyl acetylene alkynyl phenols have been synthesized by the method of catalytic alkylation of simple phenols. These compounds, also products of their transformation may be considered as possibility to develop new explosives. Besides, compound III possesses the plant growth stimulant property, and more, than well-known heteroauxin.

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