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Influence of Triphenylphosphine Complexes on Condensation of Acetylenes with Aryl Halides

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ABSTRACT

Efficient organic luminophores displaying a blue luminescence were obtained by the interaction of 4-iodonaphthalic anhydrides or the corresponding naphthalimides with phenylacetylene in the presence of triethylamine and using bis(triphenyl phosphine)palladium dichloride copper iodide systems as catalysts. © 1997 Elsevier Science Ltd

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INTRODUCTION

Among the organic luminophores that are widely used in various fields of science and technology, naphthalic acid derivatives exhibit all the necessary optical characteristics and are readily available from a synthetic point of view. Naphthalic anhydride shows weak luminescence under UV light in hydrocarbon solvents, and the luminescence intensity increases when an electron-donor substituent conjugated with the electron-acceptor anhydride moiety is introduced into the naphthalene ring. In addition to electron-donor substituted derivatives, luminescent derivatives of naphthalic anhydride also include aromatic or heterocyclic substituted variants with well-developed

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system of conjugated bonds by varying the substituents, it is possible to obtain compounds which are intensely fluorescent over a wide wavelength range (450–600 nm). One such group of luminophores are the phenylethylnaphthalic acid derivatives.

An important reaction of aromatic and heteroaromatic halogen derivatives, offering broad ways of synthesis of many unsaturated compounds, is the substitution of the halogen atom by various groups, including acetylenic moieties. Such substitution can be performed in two main ways, namely, (i) aryl halides are condensed with copper acetylenides (equation 1), which need to be obtained in advance from acetylenic compounds with a terminal triple bond:

$$Ar - I + CuC \equiv CR \rightarrow ArC \equiv CR + CuI \qquad (1)$$

and, (ii) terminal acetylenes are introduced directly into the reaction with iodides (equation 2):

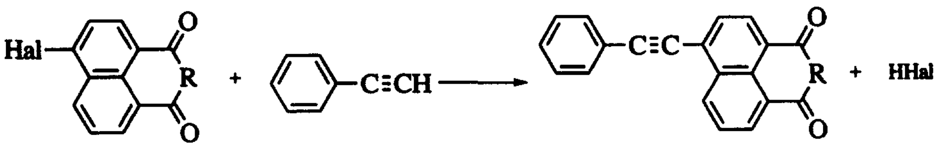
$$ArI + HC \equiv CR \;\rightarrow\; cat.base\; ArC \equiv CR + HI \qquad (2)$$

In both variants the condensation is a direct introduction of the acetylenic substituent into the aromatic ring, i.e. combination of the pre-synthesized structures in the molecule of the final product. Thus they differ substantially from the majority of other methods of preparation of aromatic acetylenic compounds, in which a substituent (present in the ring) is converted into the acetylenic group. The catalytic reaction offers many advantages compared with the acetylenide synthesis because there is no need to prepare and use dry copper-containing acetylenides as reagents [1].

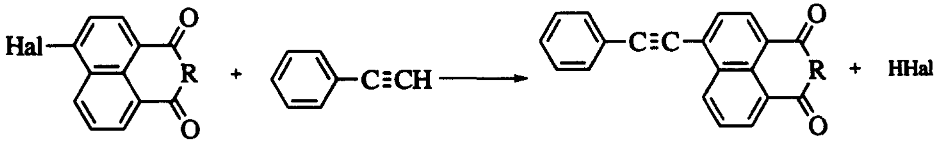
Two main types of catalytic systems are now known in which condensation of aryl iodides with terminal acetylenes takes place. In systems of the first type, Cu(I) compounds are used as catalysts (usually CuI). The reaction is carried out in the presence of a base (mostly K_2CO_3) in pyridine or dimethylformamide at 85–155°C [2, 3]. In systems of the second type, palladium complexes $Pd[(C_6H_5)_3P]_2X$ ($X = (C_6H_5)_3P$, $OCOCH_3$, Cl, I), are used as catalysts [4, 5, 6]. The bases, which also act as solvents, are amines (e.g. diethylamine, piperidine or triethylamine) or a solvent such as dimethyl formamide (in which case a base is additionally introduced).

RESULTS AND DISCUSSION

With respect to the above, it seemed of interest to study the reaction of phenylacetylene with halogen–naphthalic anhydrides or their corresponding imides (equation 3):



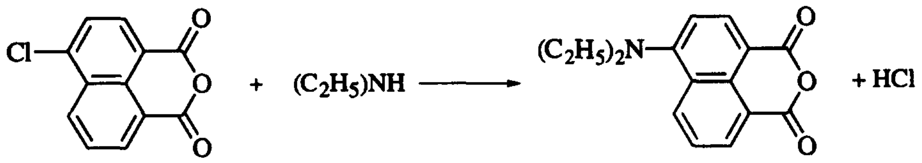
R = O, N - Alk, N - Ar; Hal = I, Br, Cl



R = O, N - Alk, N - Ar; Hal = I, Br, Cl

$$R = O, N - Alk, N - Ar; \quad Hal = I, Br, Cl. \tag{3}$$

However, the use of more basic secondary amines as solvents is not possible in this case because the halogeno-naphthalic anhydrides can react with them (e.g. as with diethylamine, equation 4):



As a result, 4-diethylaminonaphthalic anhydride is formed, which is intensely luminescent in the yellow–green spectral range [7]. Another disadvantage of the use of dimethylformamide as solvent is the possibility of 4-dimethylamino-naphthalic anhydride formation [8]. Therefore we chose triethylamine as a more suitable less basic solvent for the acetylenic condensation, which then favoured the unambiguous formation of the desired products.

TABLE 1
Effect of the Nature of the Halogen Substituent on the Yield of Phenylethynilnaphthalic Anhydride using $Pd[(C_6H_5)_3P]_2Cl_2$–CuI as Catalyst

Hal	*Yield (%)*	*Reaction time (h)*
Cl	2.3	5
Br	27.6	5
I	81.2	5

In nucleophilic substitution reactions, when halogeno-naphthalic anhydrides react with secondary amines, the nature of the halogen substituent has practically no effect upon the reaction activity, due to the strong electron-accepting properties of the anhydride moiety. However, when halogeno-naphthalic anhydrides react with phenylacetylene, the most reactive derivative is the iodo compound, and the chloro derivative has only minimal reactivity (Table 1).

Influence of the catalysts on the acetylenic condensation

We have studied the influence of the most widely used catalysts on the course of the acetylenic condensation. CuI, $PdCl_2$, $Pd[(C_6H_5)_3P]_2Cl_2$ and $Pd[(C_6H_5)_3P]_2Cl_2$ CuI systems were used. From Table 2, it is clear that the reaction practically does not proceed without a catalyst during the first 5 h. Palladium-containing catalysts were somewhat more active than copper iodide, and the use of triphenylphosphine–palladium dichloride afforded nearly three times higher yields of phenylethylnaphthalic anhydride. The catalytic action of the Pd complex is enhanced by the addition of CuI, which probably facilitates substitution of the halogen phenylacetylenic group.

A similar reaction course was observed when the corresponding iodo-naphthalimides were used, since when the central oxygen atom in the anhydride group is replaced by the more electronegative nitrogen, no substantial change in the electron density distribution in the system occurs. This is confirmed by quantum-chemical calculations carried out using the PPP method accounting for configurational interaction to the redistribution of electron density on individual atoms and fragments of the molecule.

Efficient organic luminophores displaying blue luminescence were obtained by the interaction of 4-iodonaphthalic anhydride, or of corresponding naphthalimides, in triethylamine medium and using a triphenylphosphine palladium dichloride–copper iodide system as catalyst. Table 3 shows the

TABLE 2
Effect of Catalysts on the Yield of 4-Phenyl-ethynilnaphthalic Anhydride

Catalyst	*Yield (%)*	*Reaction time (h)*
—	0.5	5
CuI	13.3	5
$PdCl_2$	17.3	5
$Pd[(C_6H_5)_3P]_2Cl_2$	49.8	5
$Pd[(C_6H_5)_3P]_2Cl_2$–CuI	26.7	1
$Pd[(C_6H_5)_3P]_2Cl_2$–CuI	52.2	2
$Pd[(C_6H_5)_3P]_2Cl_2$–CuI	61.9	3
$Pd[(C_6H_5)_3P]_2Cl_2$–CuI	76.1	4
$Pd[(C_6H_5)_3P]_2Cl_2$–CuI	81.2	5

spectral luminescent characteristics of the luminophores. It can be seen that the absolute quantum yield of photoluminescence for the synthesized compounds is 0.55–0.66, i.e. they may be considered to be efficient optical whitening agents for polymer materials and (when an imide group is present) for synthetic fibers. Table 4 contains yields, melting points, elementary analysis and IR data of the synthesized compounds.

EXPERIMENTAL

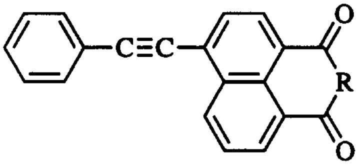
Synthesis of 4-phenylethenaphthalic anhydride (1)

2.6 g (0.008 mol) 4-iodonaphthalic anhydride, 0.13 g (0.00018 mol) bis(triphenyl posphine)palladium dichloride, 0.05 g (0.00026 mol) cuprous iodide and 1.3 ml (0.012 mol) phenylacetylene were refluxed in 65 ml triethylamine for 6 h under a nitrogen stream. When the reaction was complete, triethylamine was steam distilled off. The resultant precipitate was collected, dried and purified chromatographically on aluminium oxide (using benzene as eluent). The yield was 2.42 g; 86.5% based on the 4-iodonapathalic anhydride used.

Compounds **2**, **3** and **4** were similarly prepared, using the appropriate 4-iodo-naphthalimides. The amount of the 4-halogeno-naphthalic anhydride and catalysts, and the time of reaction, were changed in order to study the influence of the halogen atom and of the catalysts on the yield. The correlation between the 4-halogeno-naphthalic anhydride and catalysts was the same in these experiments (as in the synthesis of compound **1**) at various reaction times (Tables 1 and 2). The reactions were monitored by

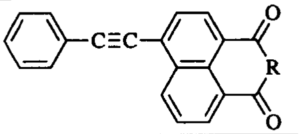
TABLE 3

Spectral-luminescent Characteristics of the Synthesized Compounds



	$\lambda_{max.\ abs.}$ (nm)	$\lambda_{max.\ lum.}$ (nm)	η
R			
O	390	470	0.55
N–C_6H_5	383	460	0.55
N–CH_2–CH_2OH	387	465	0.65
N–$CH_2CH_2CH_2OCH_3$	385	465	0.65

TABLE 4
Yields, Melting Points, Elementary Analysis and IR Data of the Synthesized Compounds

N	 R	*Yield % (g)*	*T$_{mp}$, (°C)*	*Elementary analysis results*							*Data of IR spectroscopy (cm^{-1})*
				Experimental values				*Calculated values*			
				(%)			*Formula*	*(%)*			
				C	*H*	*N*		*N*	*H*	*N*	
1	O	86.5 (2.42)	233–234	80.37	3.27	—	$C_{20}H_{10}O_3$	80.54	3.34	—	1530 (C=C) 1740–1780 (C=O) 2200 (C C)
2	C_6H_5–N	84.0 (2.51)	215–216	83.30	4.17	3.65	$C_{26}H_{15}NO_2$	83.65	4.02	3.75	1320 (C–N) 1590 (C=C) 1750–1790 (C=O) 2200 (C C)
3	$HOCH_2CH_2$–N	83.0 (2.15)	148–149	77.26	4.31	4.20	$C_{22}H_{15}NO_3$	77.42	4.40	4.11	1360 (C–N) 1590 (C=C) 1670–1700 (C=O) 2200 (C C) 2970 (C–H) 3560 (OH)
4	$H_3CO_2(CH_2)_3$–N	86.0 (2.54)	204–205	77.91	5.20	3.68	$C_{24}H_{19}NO_3$	78.05	5.15	3.79	1190 (C–O) 1340 (C–N) 1590 (C=C) 1660–1670 (C=O) 2200 (C C)

4-iodonaphthalic anhydride decomposition, and by the formation of phenylethynilnaphthalic anhydride using a Hewlett-Packard 5890-II chromatograph with a quartz capillary column of 25 m length and 0.32 mm diameter with HP-1 (a methylsilicone elastomer) as a stationary phase, under column temperature scanning from 170 to 230°C (4°C per minute, carrier gas helium, volume of the introduced probe 1×10^{-6} liter, partition coefficient of the probe 1/80, evaporator temperature 290°C, flame ionization detector temperature 300°C).

Electronic absorbtion spectra were obtained using a 'Specord M40', luminescent analysis on a 'CD L-2' and IR spectra on a UR-20 spectrophotometer (KBr).

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