Naphthalic and bis(naphthalic) anhydrides with acetylene groups

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Cross-coupling Pd-catalyzed reactions of readily available 4-bromo-1,8-naphthalic anhydride with acetylene or its derivatives result in naphthalic and bis(naphthalic) anhydrides with acetylene groups. The temperature ranges of the cross-linking of the acetylenic groups in the synthesized compounds have been determined.

Key words: naphthalic anhydrides, bis(naphthalic) anhydrides, 4-bromo-1,8-naphthalic anhydride, acetylenes, cross-coupling Pd-catalyzed reaction.

A great number of recent investigations have been devoted to the synthesis of polymers with acetylene groups.[1—3] Polymers containing acetylene fragments in the main chains have been studied to a greater extent than macromolecules containing ethynyl[4,5] or phenylacetylene[6,7] terminal and side groups. Polyimide copolymers, for example, have been synthesized with the use of bis(3-aminophenyl) acetylene.[8]

As shown by differential scanning calorimetry (DSC)[5,7], terminal ethynyl groups react to give cross-linked polymers at 250—300 °C, whereas substituted acetylene groups react at 400—450 °C.

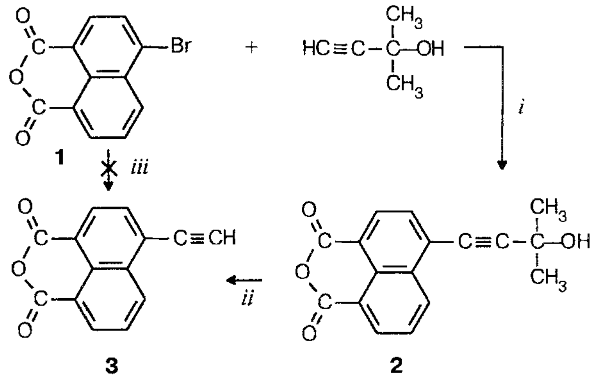
Bis(4-(3,4-dicarboxyphenoxy)phenyl)acetylene dianhydride[9] has been used in the past for the synthesis of polyimides (PI) with acetylene groups, and PI based on bis(3,4-dicarboxyphenyl)acetylene dianhydride[10] have been described recently. It should be noted, however, that this monomer is obtained as a result of a multistep synthesis and, therefore, seems to be difficult to obtain.

Within the framework of this investigation we have elaborated a simple procedure for the synthesis of naphthalic and bis(naphthalic) anhydrides[11] containing acetylene fragments. Our procedure is based on cross-coupling reactions of readily available 4-bromo-1,8-naphthalic anhydride (**1**) with acetylene and its derivatives, catalyzed by Pd complexes.[12]

4-Ethynyl-1,8-naphthalic anhydride (**3**) was synthesized as shown in Scheme 1. This compound can be, on the one hand, a blocking agent for PI, reacting with their terminal groups, or, on the other hand, it can interact with many aromatic or heteroaromatic dibromides or diiodides to form new bis(naphthalic) anhydrides.

Intermediate **2** was obtained by the reaction of anhydride **1** with 2-methyl-3-butene-2-ol in 80 % yield, using dichlorobis(triphenylphosphine)palladium ($PdCl_2(Ph_3P)_2$, 1 molar %), CuI (5 molar %) and Ph_3P (5 molar %) as catalysts in the presence of Et_3N in DMF or pyridine solution. Then, cleavage of compound **2** was carried out with alkali following the earlier described procedure.[13]

Scheme 1



i. [Pd]; *ii.* 1. KOH; 2. Ac_2O; *iii.* HC≡CH, [Pd]

Although the process is accompanied in this case by hydrolysis of anhydride, it is possible to obtain anhydride **3**, albeit in low yield (< 50 %), by heating the formed acid with acetic anhydride at 100—120 °C.

Attempts to synthesize the compound **3** by the direct interaction between anhydride **1** and acetylene in the presence of Pd catalysts resulted in the formation of bis(naphthalic) anhydride **5** (see below).

4-Phenylethynylnaphthalic anhydride (**4**), which is the product of the interaction between anhydride **1** and phenylacetylene in the presence of the same Pd catalyst (Scheme 2), appeared to be a more easily available blocking agent for PI.

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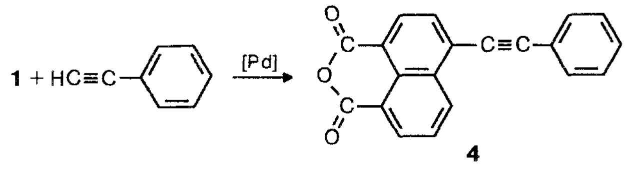
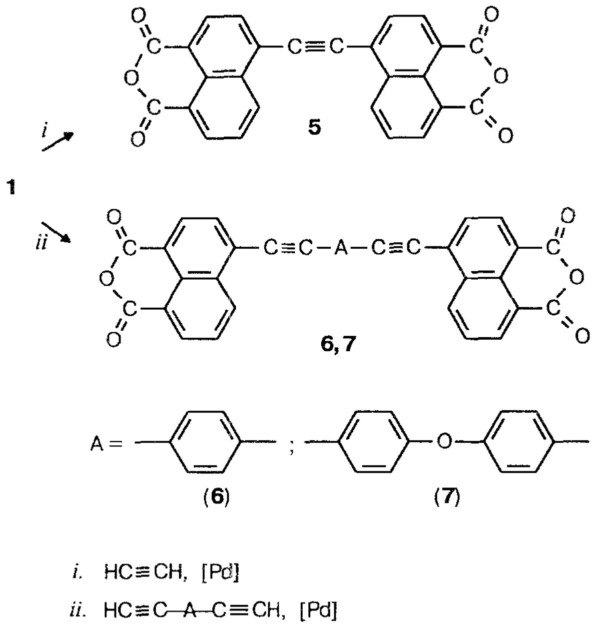
Scheme 2



Bis(naphthalic) anhydrides **5—7** were obtained according to Scheme 3.

Scheme 3



The reactions between the anhydride **1** and acetylene, *para*-diethylbenzene, or 4,4'-diethynyldiphenyl oxide were carried out in pyridine or DMF in the presence of the same catalyst.

The IR spectra of the obtained anhydrides contain intense bands at 1750 and 1770 cm^{-1} (ν C=O). A band at 2220 cm^{-1} is observed in the spectra of compounds **4**, **6**, and **7**; it belongs to the oscillations of the —C≡C— bond. The spectrum of anhydride **3** contains a rather intense band at 2240 cm^{-1}, which is characteristic of oscillations of the hydrogen atom in the —C≡CH group. A band related to the oscillations of the C≡C bond appears at 2100 cm^{-1}. In the IR spectrum of compound **5** the band characterizing the triple bond that is observed when both substituents at the —C≡C— moiety are identical is absent.

Some of the properties of naphthalic and bis(naphthalic) anhydrides containing acetylene groups are shown in Table 1.

Table 1. Properties of naphthalic and bis(naphthalic) anhydrides with acetylene groups

Compound	M.p /°C	Molecular formula	Found / Calculated (%) C	H	Thermic effects/°C endo	exo
2	172—173	$C_{17}H_{12}O_4$	71.98 72.85	4.10 4.32	—	—
3	210—211	$C_{14}H_6O_3$	74.23 75.67	3.16 2.72	160*	270*
4	224—225	$C_{20}H_{10}O_3$	80.08 80.54	3.60 3.36	221*	320*
5	**	$C_{26}H_{10}O_6$	73.69 74.64	2.43 2.49	—	460
6	**	$C_{34}H_{14}O_6$	78.98 79.38	2.35 2.99	—	415
7	327—329	$C_{40}H_{18}O_7$	78.71 78.69	2.99 2.95	320*	331*

* According to the DSC data, the other is according to the DTA data.

** Do not melt below 350 °C.

Anhydride **3** is readily soluble in organic solvents, while **4** has low solubility, but is soluble in $CHCl_3$, toluene, and amide solvents. The bis(naphthalic) anhydrides **5** and **7** are slightly soluble in *N*-methylpyrrolidone, compound **7** being soluble also in DMF. Anhydride **6** is insoluble in organic solvents.

On the DSC curve of compound **3** an exothermic peak at 270 °C is observed (Table 1), suggesting that a polymerization process involving ethynyl groups occurs.

The exothermic peaks of anhydrides **4** and **5** have similar values. The exothermic peak of compound **5** is close to the endothermic peak that corresponds to melting. In this case the rather low temperature of polymerization can be related to the increase in molecular mobility because of the nearness of the melting point, which, in turn, is due to the presence of the oxygen bridge. Rigid molecules **5** and **6** have their exothermic peaks above 400 °C. It is most likely that the same thermic effects would be observed in polymers based on the obtained monomers and, therefore, it will be possible to predict the temperature ranges of cross-linking of the polymers.

Experimental

The IR spectra were recorded on an UR-20 instrument.

The DSC curves were obtained with a DMS-2 differential scanning calorimeter at a heating rate of 8 °C/min.

The starting compounds. 2-Methyl-3-butyne-2-ol was purified by distillation, b.p. 104 °C, n_D^{20} = 1.420; phenylacetylene was distilled, b.p. 142—144 °C, n_D^{20} = 1.5325; 1,4-diethynylbenzene was recrystallized from alcohol, m.p. 94—95 °C (*cf.* Ref. 14: 95 °C); 4,4'-diethynyldiphenyl ether was recrystallized from alcohol, m.p. 74—76 °C (cf. Ref. 15: 75—76 °C); 4-bromo-1,8-naphthalic anhydride was recrystallized from toluene, m.p. 224—225 °C.

4-(2-Hydroxyprop-2-yl-ethynyl)naphthalic anhydride (**2**). 2 mL of Et_3N, 0.72 g (8.7 mmol) of 2-methyl-3-butine-2-ol, 0.050 g (0.072 mmol, *i.e.* 1 molar %) of $PdCl_2(Ph_3P)_2$, 0.10 g of Ph_3P (0.36 mmol), and 0.05 g of CuI (0.36 mmol) were added at 100 °C to a solution of 2.0 g (7.2 mmol) of anhydride **1** in 15 mL of pyridine, and the mixture was stirred at this temperature for 5 h. The volatile compounds were removed *in vacuo*, the residue was recrystallized from acetone, and yellowish brown needle crystals of anhydride **2** (80 %) were obtained. IR (ν/cm^{-1}): 1750, 1780, 2230, 3000.

4-Ethynylnaphthalic anhydride (**3**). 1.1 g (50 mmol) of compound **2** were dissolved in 10 mL of toluene, then a 10 % alcohol solution of 0.5 g KOH was added and the mixture was heated at 110 °C for 3 h. The solvents were removed in the course of the reaction with a Dean-Stark trap, and fresh portions of toluene were added (3×5 mL). A 5 % HCl solution was added to the obtained solution until a yellow precipitate fell out, which was filtered off, washed, and dried *in vacuo* and then heated with 10 mL acetic anhydride at 100 °C for 15 min. Then the acetic anhydride was removed *in vacuo*. The product obtained was recrystallized from acetone. Yield 40 %.

4-Phenylethynylnaphthalic anhydride (**4**). 5 mL of Et_3N was added to a solution of 10 g (36 mmol) of anhydride **1** in 40 mL of DMF, then 3.68 g (36 mmol) of phenylacetylene, 0.25 g (1.8 mmol) of $PdCl_2(Ph_3P)_2$ and 0.5 g of Ph_3P (1.8 mmol) were added. The mixture was heated to 100 °C, 0.34 g (1.8 mmol) of CuI was added, and the reaction solution was stirred at this temperature for 5 h. A precipitate was filtered off, and recrystallized from toluene, and anhydride **4** was obtained (84 %).

1,2-bis(4,5-Dicarboxynapht-1-yl)acetylene dianhydride (**5**). 2 mL of Et_3N was added to a solution of 2.0 g (7.2 mmol) of anhydride **1** in pyridine, then 0.05 g (0.36 mmol) of Ph_3P and 0.05 g (0.36 mmol) of CuI were added. Acetylene was passed through the reaction mixture for 5 h at a flow rate of 10—15 mL/min. The precipitate formed was filtered off, washed with water, dried *in vacuo*, and recrystallized from *N*-methylpyrrolidone to give anhydride **5**, yield 66 %.

1,4-bis(4,5-Dicarboxynaphth-1-yl-ethynyl)benzene (6) and 4,4'-bis(4,5-dicarboxynaphth-1-yl-ethynyl)diphenyloxyde (**7**) **dianhydrides** were obtained similarly to the preparation of **5** from anhydride **1** and 1,4-diethynylbenzene[14] or 4,4'-diethynyldiphenyloxide[15] in 65 and 60 % yields, respectively.

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