Synthesis of polyacenequinones *via* crossed aldol condensation in pressurized hot water in the absence of added catalysts†

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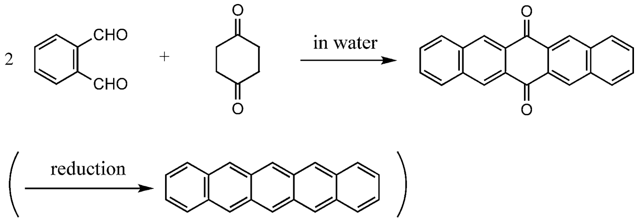
Phthalaldehyde and 1,4-cyclohexanedione react in the 2:1 molar ratio *via* a crossed aldol condensation in sub- and supercritical water to produce 6,13-pentacenequinone. The reaction conditions were optimized at 77% yield at 250 °C for 60 min with the starting molar ratio of 2:1:800 for phthalaldehyde, 1,4-cyclohexanedione and water, respectively. Whereas the initial rate of the reaction increased at higher pH, as suggested by earlier studies of the crossed aldol condensation of the two carbonyl compounds using a base catalyst in an organic solvent, the present results of successful reactions without the addition of any acid or base show the role of the increased solubility of the starting materials and the higher ion product in pressurized hot water. 6,13-Pentacenequinone was obtained as fine needles from the cooled reaction mixture just by filtration. Under similar conditions, 7,16-heptacenequinone and 5,12-naphthacenequinone were obtained in 46 and 70% isolated yields, respectively.

Introduction

Many organic reactions are carried out by the action of acid or base catalysts in organic solvents. These reactions often require work-up processes such as neutralization of the catalysts and removal of the solvents that could cause deterioration of waste water and VOC emission in the atmosphere, thus increasing the burden on the environment. Water at or near the supercritical conditions (T_C = 374.15 °C, P_C = 22.12 MPa) has various merits as alternative reaction media. Its high specific dielectric constant (ε_r) of 78 at room temperature drops continuously to about 28 at 250 °C (cf. ε_r = 28 for ethanol and 33 for methanol at 25 °C) and down to *ca.* 2 at 450 °C (cf. ε_r = 2.3 for benzene at 25 °C),[1] suggesting the higher solubility/miscibility of organic compounds in such water. The ion product of water of 10^{-14} at 25 °C increases gradually and peaks at a value three orders of magnitude greater at 243 °C under the saturated vapor pressure,[2] thereby facilitating various acid- or base-catalyzed organic reactions,[3] such as aldol condensations,[4,5] hydration–dehydration reactions,[6,7] Diels–Alder reaction,[8] retro-aldol reaction,[9] pinacol rearrangement,[10] Beckman rearrangement,[11] and Friedel–Crafts alkylation[12] in the absence of added catalysts.

In this study we focused our attention on a crossed aldol condensation of phthalaldehyde and 1,4-cyclohexanedione in the 2:1 molar ratio to produce 6,13-pentacenequinone that had been obtained in the presence of 5% potassium hydroxide in ethanol in 78% yield for 48 hr at room temperature.[13] The choice of the target compound was based on the importance of the quinone as a precursor to parent pentacene that can be obtained by chemical reduction[14] of the precursor and exhibits the highest hole mobility of $\mu = 35\ \mathrm{cm^2/V\,s}$ at room temperature comparable to amorphous silicon, when carefully purified free from the quinone.[15] Thus pentacene serves as a raw material for organic field-effect transistors,[16] solar batteries,[17] liquid crystal displays[18] and organic electroluminescence displays[19] in the area of the ever-expanding organic semiconductor industry. For these reasons we took up the synthesis of 6,13-pentacenequinone in hot pressurized water without added catalyst (Scheme 1). Preparation of higher and lower members of the linear polyacenequinone series was also studied under similar conditions.



Scheme 1 Reaction scheme for 6,13-pentacenequinone.

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† Electronic supplementary information (ESI) available: Instrumentation and identification; Tables S1–S5. Numerical data supporting Fig. 2–6 for the formation of 6,13-pentacenequinone under various conditions; the equations necessary for calculating real pH values under reaction conditions as shown in Table 1. See DOI: 10.1039/b914784p

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Experimental

1. Chemicals

Phthalaldehyde, 1,4-cyclohexanedione and 1,4-dihydroxynaphthalene of chemical purity greater than 99% were purchased from Tokyo Chemical Industry Co., Ltd. 2,3-Naphthalenedicarboxyaldehyde (98.0%) was from Sigma-Aldrich. They were used without further purification.

Ultrapure water that had a specific resistivity greater than 18.2 MΩ and TOC smaller than 20 ppb was obtained by treating tap water through a Millipore Milli-RX75 ultrapure water purification system. Other chemicals and solvents when necessary were commercially available.

2. Reaction vessel

A batch reactor (Fig. 1) made of a SUS316 1/2-inch tube (length of 170 mm, diameter of 12.7 mm, wall thickness of 2.1 mm) (Mecc Technica Co.) fitted with a SUS316 1/2-inch cap (Swagelok Co., No. SS-810-C), 1/16-inch to 1/2-inch reducing connector (Swagelok Co., No. SS-810-6-1), and a 1/16-inch plug (Swagelok Co., No. SS-100-P) had an effective inner volume of *ca.* 10 cm^3. Prior to its use in experiments, the reactor was loaded with 2% aqueous hydrogen peroxide and conditioned for 1 hr at 370 °C to remove any lubricants/oils that might remain from the manufacture of the Swagelok parts and possible catalytic metal sites on the inner wall, unless otherwise stated. The reactor was cleaned with acetone and dried prior to repeated use. The internal pressure was estimated to become 30 MPa at 400 °C with the charged 10 cm^3-water. Below the critical temperature, the pressure is subject to the gas–liquid equilibrium of water.

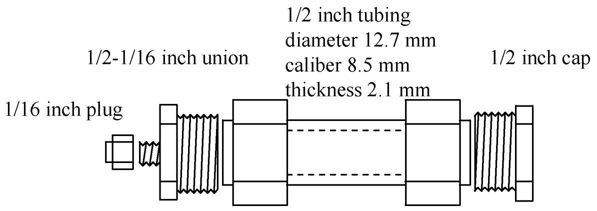

Fig. 1 Reaction vessel.

3. Typical runs

Phthalaldehyde (0.533~0.0665 g), 1,4-cyclohexanedinone (0.223~0.0278 g), and water (3.574 g) to make the molar ratio of 1 to 0.5 to 50~400 were brought into a reaction vessel and the content was purged with a stream of argon. The capped vessel was immersed in a metal salt bath (Taiatsu Techno Corp., Model TBC-B600) preheated at 230~400 ±1 °C. After a given period of time, the heating was stopped by removing the reactor from the heat bath and immersing it promptly in cold water. The reactor heat-up time was on the order of a few minutes, which was generally short compared to the reaction times employed. The solid product in the reactor was collected on a membrane filter (Millipore T050A025A) with the aid of some acetone and measured directly by weighing after being dried for more than 12 h in air. The solid products that varied in amount depending on reaction conditions were confirmed to be 6,13-pentacenequinone by means of a DTA analysis, and mass, FT-IR, and ^{1}H-NMR spectral data. They agreed nicely with those in the literature if they were available (see the ESI†). The amount of 6,13-pentacenequinone in the filtrate was negligible.

The morphology of the crystalline 6,13-pentacenequinone appeared to depend somewhat on the temperature of the reactions, as the chemical formation was followed by spontaneous crystallization. Orange-brown powdery solids were obtained from the reactions carried out at or higher than 370 °C, whereas yellow fine needles were obtained mostly from lower temperature experiments (<300 °C). Sue *et al.* found that high-temperature crystallization from water was a recommended method for production of nanocrystals of stable organic compounds[20] such as quinacridone that happens to be a nitrogen-containing pentacyclic analog of the pentacenequinone.

Similar experiments were carried out on a 2:1:400 molar mixture of 2,3-naphthalenedicarboxyaldehyde (0.0912 g), 1,4-cyclohexanedinone (0.0280 g) and water (3.633 g) to give 0.0462 g of orange powders of 7,16-heptacenequinone in 45.7% yield at 250 °C for 20 min. Their mass and FT-IR spectra agreed nicely with those of heptacenequinone in the literature.[21]

Two runs on 1:1:400 molar mixtures of phthalaldehyde (0.0654, and 0.0659 g), 1,4-dihydroxynaphthalene (0.0809 and 0.0807 g) and water (3.589 and 3.578 g) gave 0.0705 and 0.0772 g of 5,12-naphthacenequinone as orange needles in 67.0 and 72.7% yield, respectively, at 250 °C for 20 min. Their mass, ^{1}H NMR and FT-IR spectra agreed nicely with those of naphthacenequinone in the literature.[22]

4. Control experiments

With either one of the starting materials. The starting materials phthalaldehyde in 400-molar excess water and 1,4-cyclohexanedione in 800-molar excess water were separately heated for 7 min at 250 °C. No solid products ensued and therefore the organic layer was analyzed as filtrate as described below. No meaningful peak was detected by GC-MS.

Without water. For a duplicate control experiment in the absence of water, phthalaldehyde (0.0663 and 0.1352 g) and 1,4-cyclohexanedione (0.0284 and 0.0560 g) were mixed to make the molar ratio of 2 to 1 and subjected to heating at 250 °C for 20 min. Only very small amounts (0.5 mg (0.7%) and 1.5 mg (1.0%), respectively) of 6,13-pentacenequinone were obtained.

5. Runs with added acid or base catalyst

Hydrochloric acid or sodium hydroxide was added to pure water to make 10^{-3} M HCl, 10^{-4} M HCl, 10^{-4} M NaOH, 10^{-3} M NaOH solutions representing pHs of 3.0, 4.0, 10, and 11 at 25 °C, respectively.

6. Analyses of the solid product and the filtrate

Instrumentation and conditions used for GC/FID quantitative analyses, GC-MS analyses, melting point measurements, NMR spectra, FT-IR spectra are detailed in the ESI.†

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Results and discussion

1. The effect of the amount of water on the formation of 6,13-pentacenequinone

A series of experiments were performed at 250 °C for 20 min by changing the molar amount of water in the range 0~400 relative to one mole of 1,4-cyclohexanedione and two moles of phthalaldehyde as starting materials. The results are given in Table S1 (ESI†) and Fig. 2.

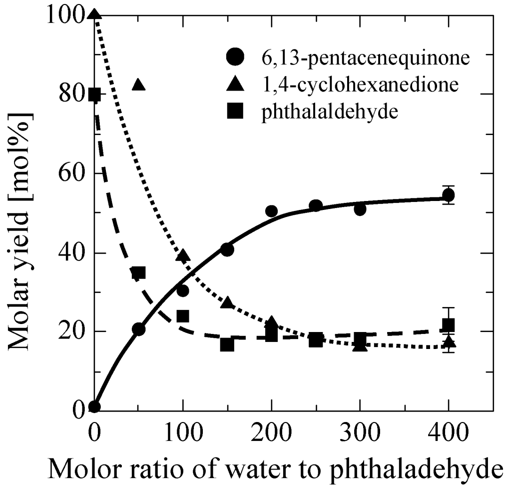

Fig. 2 Changes in the amount of the starting materials and the reaction product with the relative amount of water for the reactions fixed at 250 °C for 20 min.

Only a small amount (≦ 1% yield) of 6,13-pentacenequinone was obtained in the absence of added water. Its yield increased with increasing relative amount of water, reaching the highest yield of 66% at the water to phthalaldehyde molar ratio of 400:1. The results are interpreted in terms of the highest ion product of water at 250 °C and the catalysis of the reactions by means of latent H^+ or OH^- ion from a large excess of water. In view of the entropic barriers associated with bringing one mole of 1,4-cyclohexanedione and two moles of phthalaldehyde together and closing two additional rings in 6,13-pentacenequinone at high temperatures, the accelerating effect of the amount of water would rule out the effect of organic microdroplet in the pressurized hot water as media of the reaction.

3. The effects of reaction time

Temporal variation of the amounts of starting materials and 6,13-pentacenequinone in 100- and 400-fold excess water was examined at 250 °C. The results are given in Tables S2 and S3 (ESI†) and Figs. 3 and 4, respectively. In either case, the formation of the product quinone increased with time and the increase became slow after 30 min.

4. The effect of temperature

The molar ratio of the starting materials was fixed at 2:1:400 for phthalaldehyde:1,4-cyclohexanedione:water and the temporal decrease of the starting materials and development of the product were studied at 230~400 °C. The results summarized in Table S4 (ESI†) and Fig. 5 show that higher temperature

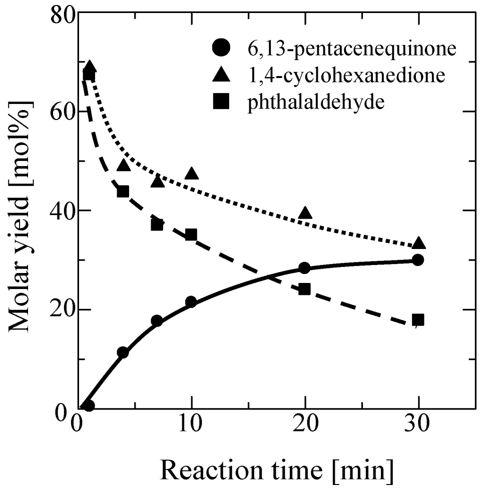

Fig. 3 Temporal variation of the amounts of the starting materials and the product quinone in 100-fold excess water at 250 °C.

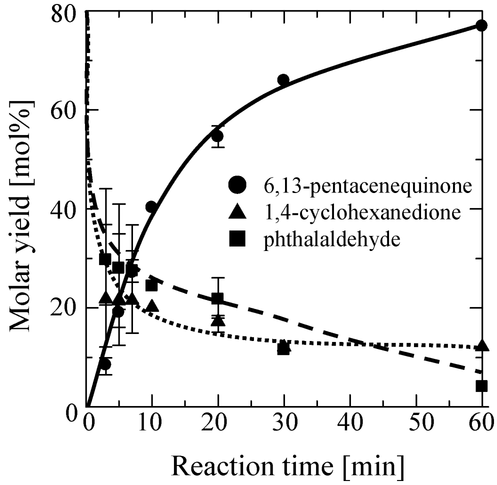

Fig. 4 Temporal variation of the amounts of the starting materials and the product quinone in 400-fold excess water at 250 °C.

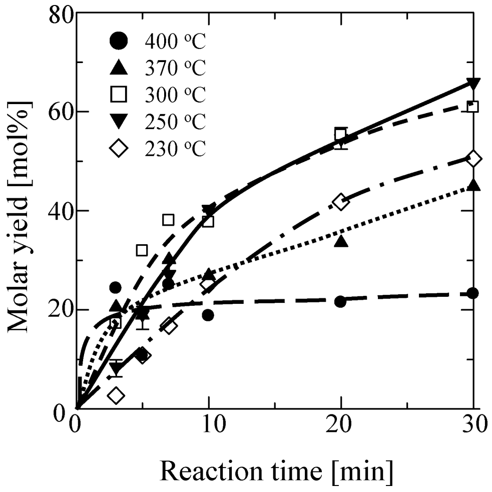

Fig. 5 Temporal variation of 6,13-pentacenequinone in 400-excess water at 230~400 °C.

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favored the product formation at *ca.* 3 min. After that, the product yield was higher for lower temperature; the highest yield of 72% was attained at 250 °C and that was followed by 45% at 230 °C. Note that the ion product of water in these temperature ranges is highest and the specific dielectric constant is close to that of ethanol at room temperature, the solvent of choice by the original preparation of potassium hydroxide-catalyzed reaction.[13] Although the dielectric constant may be more favorable at higher temperature, the starting materials would be lost by side reactions.

5. The effect of pH of water on the rates of the reaction

In order to disclose the mechanism of the two-to-one crossed aldol reaction of phthalaldehyde with 1,4-cyclohexanedione in pressurized hot water, pHs of the media were adjusted to become (pH =) 3.0, 4.0, 7.0 and 10.0 at 25 °C by prior addition of hydrochloric acid or sodium hydroxide. The product yields in 400-molar excess aqueous solution were compared at the earlier stages (3, 5, and 7 min) of the reactions at 230, 250 and 370 °C. The initial rates of the batch reactions were found to increase with reaction time, temperature, and pH as seen in Table S5 (ESI†) and Fig. 6, supporting the base catalysis of the reaction.

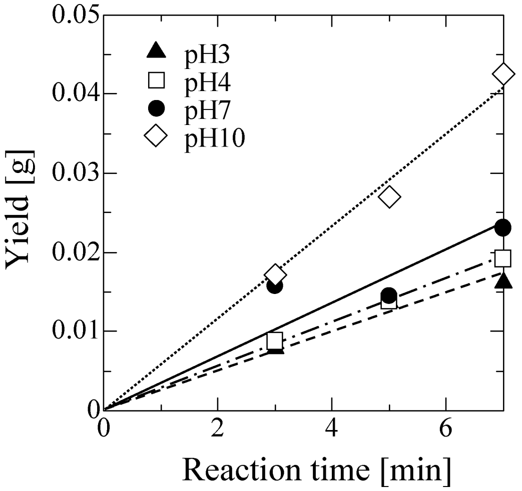
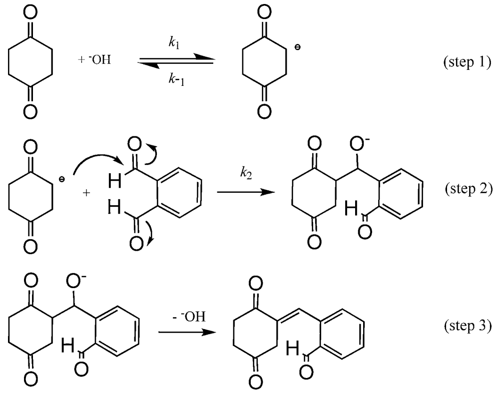


Fig. 6 Temporal variation of molar yields of 6,13-pentacenequinone under various pHs at 370 °C.



Scheme 2 The first few steps of the crossed aldol reaction.

The first two steps of a plausible path for the crossed aldol reaction are depicted in Scheme 2 that are followed by irreversible dehydration. Such processes should occur four times before forming 6,13-pentacenequinone.

The rates of such reactions are given by Eq. 1.

$$\text{Rate} = \frac{k_1 k_2[\mathrm{OH}^-][\text{dione}][\text{aldehyde}]}{k_{-1} + k_2[\text{aldehyde}]} \qquad (1)$$

When the first step is rate-determining,

$$\begin{gathered} k_2[\text{aldehyde}] \gg k_{-1} \\ \text{Rate} = k_1[\mathrm{OH}^-][\text{dione}] \end{gathered} \qquad (2)$$

When the second step is rate-determining, a case which is more likely for the crossed aldol reaction of a ketone and an aromatic aldehyde,

$$\begin{gathered} k_{-1} \gg k_2[\text{aldehyde}] \\ \text{Rate} = \frac{k_1 k_2}{k_{-1}}[\mathrm{OH}^-][\text{dione}][\text{aldehyde}] \end{gathered} \qquad (3)$$

In either case, the reaction rate is proportional to $[\mathrm{OH}^-]$. The logarithm of the initial rate R^{init} would then be given by Eq. 4, assuming that the concentration of the starting materials should not decrease very much.

$$\log R^{\text{init}} = \text{constant} + \text{pH}. \qquad (4)$$

Such a plot is given in Fig. 7.

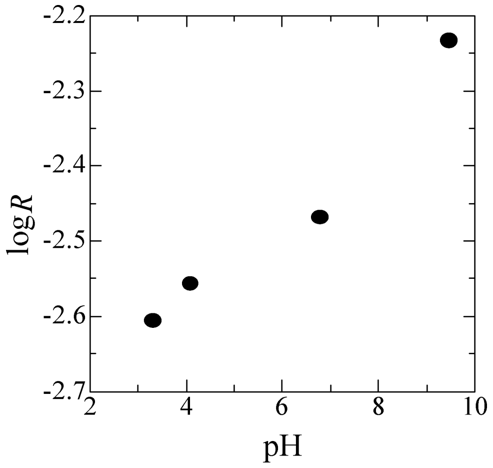


Fig. 7 Initial rates R vs. calculated pH at 370 °C.

Note that the effective pH values under reaction conditions in eq. 4 should not be the same as the nominal pH values at 25 °C. As stated in the Introduction, the ion product K_w of water is dependent on temperature. Since the ionic dissociation of water is endothermic, the K_w values increase with temperature. At higher temperature, however, the density of water decreases gradually at higher temperature and sharply at the critical point to lower the K_w values. The two competing effects produce a maximum K_w value at *ca.* 240 °C.[2] This is partly seen in the minimum of pH values for neutral water in the third line of Table 1.

When ionic species such as HCl and NaOH are present to adjust pH of the aqueous solution, their electrolytic dissociation

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Table 1 Calculated pH of pressurized hot aqueous HCl and NaOH solutions at a given temperature

pH at 25 °C	pH at 230 °C	pH at 250 °C	pH at 300 °C	pH at 370 °C
3.00	3.03	3.03	3.04	3.31
4.00	4.01	4.01	4.01	4.08
7.00	5.60	5.60	5.70	6.78
10.0	7.17	7.17	7.33	9.46

is spontaneous and complete at ambient temperature. However, since the dissociation is exothermic, it may be reversed in pressurized hot water. Furthermore, at higher concentration of the ionic species, HCl and NaOH, the activity coefficients γ different from unity must be taken into account. With the same concentration of HCl, the pH values of the acidic solution increase with temperature. Similarly, the pH values of the aqueous NaOH solutions decrease with increasing temperature. At > 300 °C, however, the effect of the lowered K_w values on pH becomes conspicuous. More quantitatively, the necessary real pH values under reaction conditions were calculated using the equations given in the ESI† and the dissociation constants from the literature.[23] These effective pH values are listed in Table 1 and used in Fig. 7.

The results summarized in Fig. 7 are in contrast with the reaction of crossed aldol condensation between acetone and benzaldehyde. Comisar and Savage reported that the reaction in water gave benzalacetone in 22% maximum yield in 8 hr at 250 °C in the absence of added acid or base and that, when the reactions were compared in 1 hr, the reactions were facilitated by 4 and 2.5 times at 1.5-point lower pH and 1.3-point higher pH, respectively. Both acid and base are effective in catalyzing the reaction and the former is more effective than the latter.[4] The Claisen-Schmidt condensation of 2-butanone with benzaldehyde was also found to be acid-catalyzed in near critical water.[24] The acid-catalyzed formation of the enols of acetone and 2-butanone appears to be contributing to the reactions, whereas the enol of 1,4-cyclohexanedione in the present study might be less effective for the condensation reaction.

6. Material balance and by-products

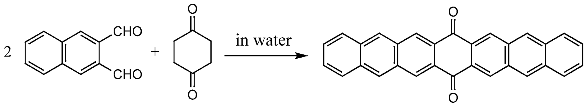
In this study, material balance was not necessarily satisfactory especially at an earlier stage of the reactions where the yield of 6,13-pentacenequinone was low. At 250 °C in 400-fold excess water (see Table S3†), for example, the sums of 1,4-cyclohexanedione and the product pentacenequinone fell less than 50% in 10 min but became nearly 90% after 60 min. Careful analyses of the GC-MS spectrum of the filtrate revealed no significant peaks corresponding to more than a few percent of the total materials. When the starting materials phthalaldehyde/400 molar-excess water and 1,4-cyclohexanedione/800 molar-excess water were separately heated for 7 min at 250 °C, neither phthalide nor self aldol products due to 1,4-cyclohexanedione, most conceivable byproducts, was detected by GC-MS.

Some loss of the materials could not be avoided due to handling of these small scales of the reactants in a large excess of water in a small reaction vessel having many screw cocks. There is a possibility of having higher yield in scale-up reaction conditions.

7. Formation of other polyacenequinones

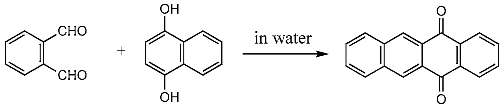
We should point out that the crossed aldol condensation in pressurized hot water in the absence of added catalysts described above is not only limited to 6,13-pentacenequinone but also has the capability of being extended to other polyacenequinones as well.

7,16-Heptacenequinone (Scheme 3) was obtained (orange powder (46%)) by replacing phthalaldehyde in the pentacenequinone synthesis (Scheme 1) with 2,3-naphthalenedicarboxyaldehyde. The quinone had been obtained by the Diels–Alder reaction of a naphto[2,3-c]furan derivative with *p*-benzoquinone in 45% yield.[21]



Scheme 3 Reaction scheme for 7,16-heptacenequinone.

5,12-Naphthacenequinone (Scheme 4) was obtained as orange needles in 70% yield by a 1:1 crossed aldol condensation of phthalaldehyde with 1,4-dihydroxynaphthalene that is tautomeric with 1,2,3,4-tetrahydronaphthalene-1,4-dione.[25] A previous method used piperidine as a base catalyst in refluxing benzene for 3–4 hr to give the naphthacenequinone in 70% yield.[22]



Scheme 4 Reaction scheme for 5,12-naphthacenequinone.

Conclusion and Future prospects

It has been established that the crossed aldol condensation of phthalaldehyde and 1,4-cyclohexanedione in the 2:1 molar ratio produces 6,13-pentacenequinone in sub- and supercritical water in the absence of any organic solvent and added catalyst. A series of experiments in this study showed unequivocally that the increased solubility of the starting carbonyl compounds by means of lowered dielectric constant and the highest ion product under saturated water vapor pressure at 250 °C of pressurized hot water are responsible for the successful condensation reaction. The environment-conscious process is further emphasized by the fact that pure 6,13-pentacenequinone was obtained as fine needles from the cooled reaction mixture just by filtration. A possible production of nanoparticles of the quinone warrants a further study using a flow reactor.[26] Polyacenequinones have their own merit of exhibiting interesting photophysical properties[27] and are precursors to parent polyacenes having interesting p-type organic semiconductor characteristic.[28]

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