Thermolysis of 3-Azidophenalen-1-ones to Naphtho[8,1-ab]carbazolones and Naphtho[8,1-ab]-8a-azonia-9-λ²-azafluoren-7-ones [1]

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3-Azido-1-phenalenones **4** with aryl- or hetarylsubstituents in position 2 cyclized by thermolysis to give naphtho[8,1-ab]carbazolones **5** or naphtho[8,1-ab]-8a-azonia-9-λ²-azafluorenones **7**. Reduction of the azides **4** gave the corresponding amino derivatives **9**. The thermolysis conditions were studied by differential scanning calorimetry.

When we studied thermolysis reactions of azidoarenes [2,3] with *ortho*-aryl and hetaryl substituents we found that differential scanning calorimetry [4] provided us with important data about the reaction sequence, *e.g.* the reaction temperature, subsequent rearrangement and decomposition temperatures, and safety precautions in exothermic processes before the synthesis had been started, whereas in conventional synthesis projects these data can be obtained only by large expense of time and material.

The differential scanning calorimetry method was used till now mainly in material science, in polymer and biopolymer chemistry and for pharmaceutical purposes. An important field which is scarely investigated, is the investigation of organic reactions by observing kinetic data by differential scanning calorimetry. Of special interest for synthetic organic chemists is the fact that all differential scanning calorimetry information can be obtained from 2-5 mg of substance, an amount which is usually not enough to obtain ¹H nmr spectra. A literature survey covering the last 3 years revealed that only a few applications dealing with synthetic organic chemistry could be found in the literature [5].

For new azide thermolyses we studied 3-azido-1-phenalenones with reactive *ortho*-substituents such as aryl or hetaryl substituents in position 2. The synthesis of 3-azido-2-phenyl-1-phenalenone (**4a**) started from 3-hydroxy-2-phenyl-1-phenalenone (**2a**) which we prepared from naphtho[1,8-*cd*]-pyran-1,3-dione (**1**) and phenylmalonate using zinc chloride as the catalyst, because the known [6] procedures for **2** gave us only a poor 16% yield. The chlorination of **2a** to 3-chloro-2-phenyl-1-phenalenone **3a** was achieved by reaction with phosphoryl chloride in dimethylformamide using an adopted literature method [7]. The azide **4a** was obtained from the chloro compound **3a** by reaction with a threefold excess of sodium azide at 80° in dimethylformamide.

The differential scanning calorimetry plot of **4a** revealed that an exothermic reaction started at about 120° (Figure 1). Actually, in a synthetic experiment the azido group of **4a** decomposed quantitatively on heating in refluxing dimethylformamide (bp 153°) with loss of nitrogen and formed in 70% yield the naphtho[8,1-*ab*]carbazolone **5**.
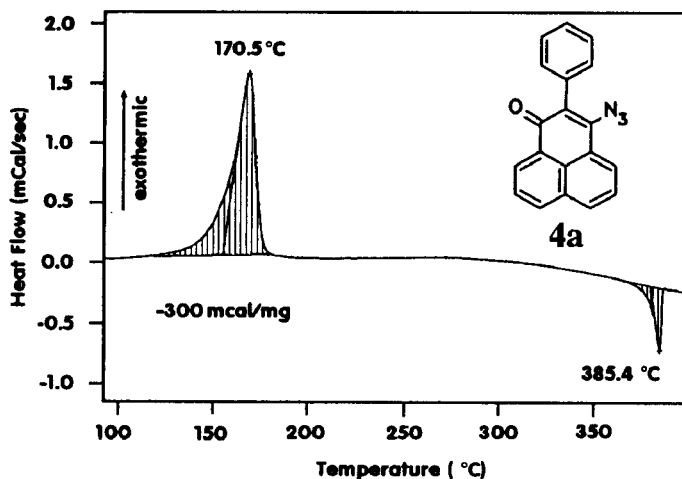

Figure 1. Differential scanning calorimetry plot of **4a**.
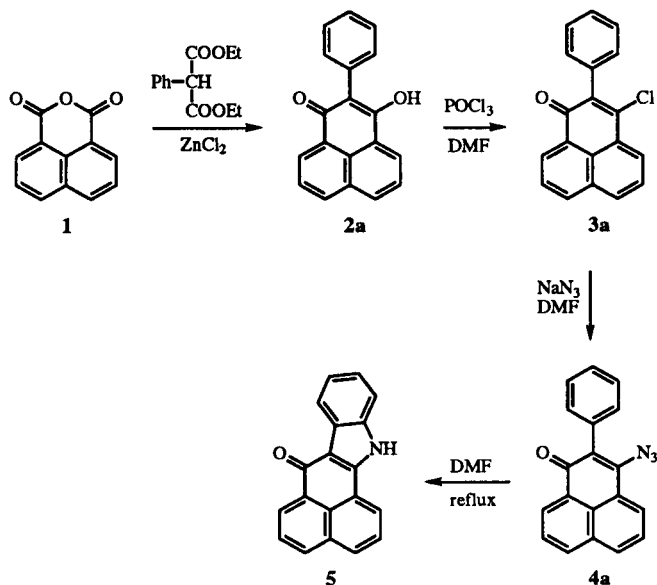
The differential scanning calorimetry diagram shows also that higher temperatures bear no danger of decomposition; only at about 380° the melting range of the cyclization product **5** can be observed.

Another aspect where the differential scanning calorimetry was very helpful for the purification of **4a** is the knowledge of the temperature range where no decomposition takes place. It is in most cases a problem to get pure azido samples because of their easy decomposition. Calorimetric data help here in the selection of the recrystallization solvent.

The hetaryl substituted phenalenones **2b** and **2c** with 2-pyridyl- and 2-quinolinyl substituents in position 2 were obtained according to a literature procedure [8] from naphtho[1,8-*cd*]-pyran-1,3-dione (**1**) and 2-methylpyridine (**6a**) or 2-methylquinoline (**6b**), respectively. Chlorination with phosphoryl chloride in dimethylformamide gave 3-chloro-2-(2-pyridinyl)phenalen-1-one (**3b**) and 3-chloro-2-(2-quinolinyl)phenalen-1-one (**3c**).

Reaction of **3b** with sodium azide gave the azido derivative **4b**, but the temperature had to be kept below 50° to prevent undesireable decomposition. Calorimetric analysis of the azide **4b** showed an exothermic reaction starting at
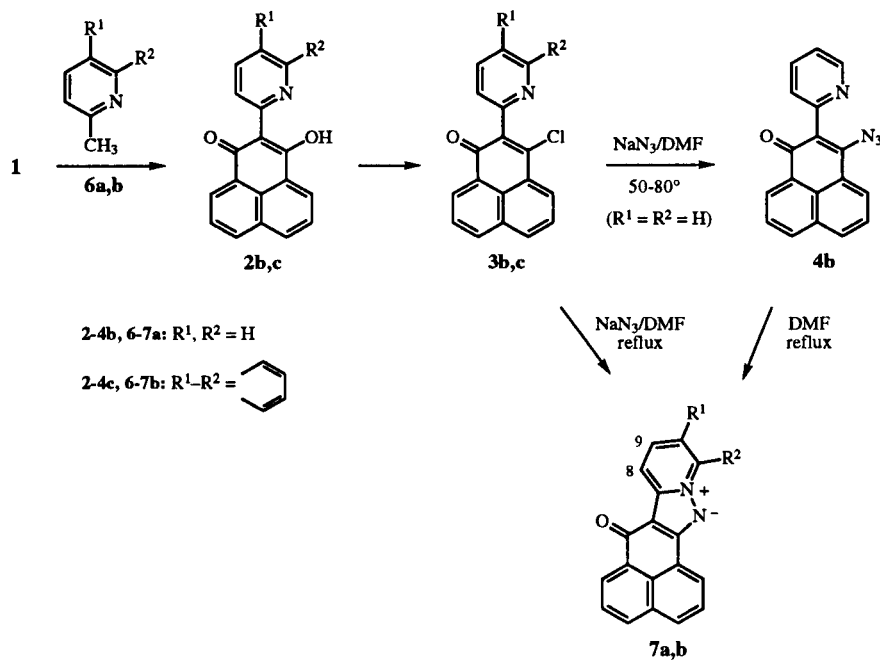
Scheme 1

the naphtho[8,1-*ab*]-8a-azonia-9-λ²-azafluoren-7-one according to the structural assignment described below.

When we attempted to synthesize the 2-quinolinyl azide **4c** from the chloro derivative **3c**, in all experiments, even already at 0°, partial formation of the ring closure product **7b** was observed by tlc. It was not possible to obtain the azide **4c** in a pure form, and therefore for preparative uses a one pot reaction from the chloro derivative **3c** and excess sodium azide in refluxing dimethyl formamide was carried out to yield benzo[*i*]naphtho[8,1-*ab*]-8a-azonia-9-λ²-azafluoren-7-one (**7b**).

The analysis of impure azide **4c** by differential scanning calorimetry showed an exothermic reaction starting not before 90° but with a baseline with a slow increase over the whole range before the reaction peak. So in this case no clear prediction for the stability and isolation of **4c** could be obtained. An interesting aspect is the reaction enthalpy of organic azides: whereas usually exothermic reaction heats are in the range of 50-100 mcal/mg [4], azides **4** range between 200 and 300 mcal/mg, a hint on the thermolability of organic azides.

The structure of **7a** and **7b** was assigned by ¹H nmr spectroscopy experiments using the H,H-COSY method (two dimensional homonuclear H,H-correlated nmr spectroscopy). The two dimensional nmr diagram of **7b** showed a coupling of the multiplet of H-9 at δ 7.79-7.81 ppm with the multiplet of H-8 at δ 8.33-8.35 ppm, which proved, that the ring closure had taken place at the pyridyl or quinoline nitrogen, respectively, and not at the carbon at position 3.

about 100°, followed by an endothermic peak at about 200°, the melting point of the cyclized compound. Following the calorimetric hints, the azide **4b** was thermolyzed in refluxing dimethylformamide to give the cyclization product **7a**. Product **7a** was also obtained in a one pot reaction starting from the chloro compound **3b** and excess sodium azide involving as the first step, the substitution reaction to the azide followed subsequently by cyclization without isolation of azide **4b**. The structure of **7a** was assigned to

Scheme 2

2-4b, 6-7a: R¹, R² = H

2-4c, 6-7b: R¹–R² =

Azido compounds are well known as intermediates for amino compounds [9]. Hydrogenation of 3-azido-2-phenyl-1-phenalenone **4a** in dimethylformamide/ethanol at room temperature using palladium on charcoal as catalyst gave 3-amino-2-phenyl-1-phenalenone **9a** in moderate yields. Attempts, to obtain the corresponding amine **9b** from 3-azido-2-(2-pyridyl)-1-phenalenone **4b** by catalytic hydrogenation, failed because of decomposition. When we used the reaction sequence *via* the phosphazene **8b**, however, we obtained **9b** in good yields. This reaction sequence was also sucessful with **4a**, which yielded **9a** in good yields.

Scheme 3

8,9	X
a	CH
b	N
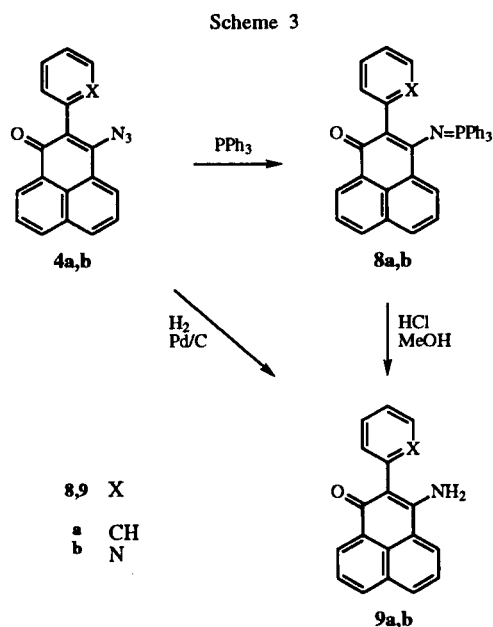
EXPERIMENTAL

Melting points were determined on a Gallenkamp Melting Point Apparatus, Model MFB-595 in open capillary tubes. Calorimetric data were obtained on a Rheometric Scientific DSC-Plus instrument with the differential scanning calorimetry software V5.42. The differential scanning calorimetry plots were recorded between 25-400°, with a heating rate of 2-10°/min, and 1.5-3 mg compound in sealed aluminium crucibles (11 bar). The ^{1}H nmr spectra were recorded on a Bruker AM 360 instrument (360 MHz). The solvent for nmr spectra was deuterichloroform. Chemical shifts are reported in ppm from internal tetramethylsilane standard and are given in δ-units. Infrared spectra were taken on a Perkin-Elmer 298 spectrophotometer or a Galaxy Series FTIR 7000 in potassium bromide pellets. Elemental analyses were performed on a Fisons elemental analyzer, Model EA 1108 and are within ±0.4 of the theoretical percentages. All reactions were monitored by thin layer chromatography carried out on 0.2 mm silica gel F-254 (Merck) plates using uv light (254 and 366 nm) for detection. Common reagent-grade chemicals are either commercially available and were used without further purification or prepared by standard literature procedures.

3-Hydroxy-2-phenylphenalen-1-one (**2a**).

A mixture of naphtho[1,8-*bc*]pyran-1,3-dione (**1**) (30.0 g, 0.15 mole), diethyl phenylmalonate (37.7 ml, 0.15 mole) and freshly melted anhydrous zinc chloride (20.64 g, 0.15 mole) was heated for 6 hours to 240°. During this time the formation of ethanol and carbon dioxide was observed. The black solid obtained was treated with water (100 ml), crushed and filtered. The crude product was stirred with 1 *N* sodium hydroxide solution (300 ml) for 15 minutes, filtered, and the filtrate acidified with diluted hydrochloric acid. A yellow precipitate was formed, filtered by suction after 1 hour and washed with water. Then the product was dissolved again in 1 *N* sodium hydroxide solution (300 ml) and the solution extracted with toluene (2 x 200 ml). The alkaline solution was heated to 100° to convert excess naphthalic anhydride to the free acid, cooled, brought to *p*H = 6.5 with diluted hydrochloric acid, washed with water and dried; the yield was 13.4 g (33%), orange crystals, mp 217-218° (ethanol); lit mp 214-16° [6].

3-Hydroxy-2-(2-pyridinyl)-phenalen-1-one (**2b**) and 3-hydroxy-2-(2-quinolinyl)phenalen-1-one (**2c**)

These compounds were prepared from naphtho[1,8-*bc*]pyran-1,3-dione (**1**) and 2-methylpyridine (**6a**) or 2-methylquinoline (**6b**), respectively according to ref [8].

3-Chloro-2-phenylphenalen-1-one (**3a**).

Dimethyl formamide (2.8 ml, 40 mmoles) was added to phosphoryl chloride (3.5 ml, 40 mmoles), stirred for 20 minutes and then added at 15-20° to a solution of **2a** (6.86 g, 30 mmoles) in dimethylformamide (100 ml). The mixture was stirred for 12 hours and then poured on ice, stirred for 1 hour and filtered by suction; the yield was 3.4 g (49%), yellow powder, mp 144° (hexane); ir: 1630 s, 1620 m, 1570 s cm^{-1}.
Anal. Calcd. for $C_{19}H_{11}ClO$: C, 78.49; H, 3.81; Cl, 12.19. Found: C, 78.42; H, 3.93; Cl, 11.95.

3-Chloro-2-(2-pyridinyl)phenalen-1-one (**3b**).

This compound was prepared from **2b** (8.0 g, 30 mmoles) according to the procedure described for **3a**. After treatment with ice, the mixture was brought to *p*H = 4-6 with 1 *N* sodium hydroxide solution, filtered by suction and recrystallized from ethanol; the yield was 5.53 g (65%), brown crystals, mp 187° (ethanol); ir: 1680 s, 1665 s, 1640 s, 1620 s, 1550 m cm^{-1}.
Anal. Calcd. for $C_{18}H_{10}ClNO$: C, 74.11; H, 3.45; N, 4.80; Cl, 12.15. Found: C, 74.26; H, 3.58; N, 4.79, Cl, 12.26.

3-Chloro-2-(2-quinolinyl)phenalen-1-one (**3c**).

This compound was prepared from **2c** (10.0 g, 30 mmoles) according to the procedure described for **3a**; the yield was 9.70 g (92%), green powder, mp 254-256° (ethanol); ir: 3050 w, 1630 s, 1620 w, 1600 m, 1580 s cm^{-1}.
Anal. Calcd. for $C_{22}H_{12}ClNO$: C, 77.31; H, 3.34; N, 4.10; Cl, 10.37. Found: C, 77.40; H, 3.58; N, 4.07; Cl, 10.23.

3-Azido-2-phenylphenalen-1-one (**4a**).

To a stirred solution of **3a** (4.0 g, 14 mmoles) in dimethylformamide (140 ml), sodium azide (2.72 g, 42 mmoles) was added slowly. Then the mixture was heated to 80° for 12 hours, poured into water (500 ml) and the precipitate filtered by suction; the yield was 3.72 g (91%), yellow powder, mp 168-

169° dec (ethanol); calorimetric data for thermolysis: onset 156.3°, peak 170.6°, ΔH -300 mcal/mg; ir: 2090 s (N_3), 1630 s, 1610 w, 1575 s cm^{-1}.

Anal. Calcd. for $C_{19}H_{11}N_3O$: C, 76.76; H, 3.73; N, 14.13. Found: C, 76.45; H, 3.94; N, 13.67. A more satisfactory elemental analysis could not be obtained because of easy decomposition of the azido compound.

3-Azido-2-(2-pyridinyl)phenalen-1-one (4b).

This compound was prepared from 3b (3.50 g, 12 mmoles) in dimethyl formamide (120 ml) and sodium azide (2.73 g, 42 mmoles) at 50° following the procedure for 4a; the yield was 3.34 g (93%), brown powder, mp 145-146° dec (ethanol); calorimetric data for thermolysis: onset 148.2°, peak 155.3°, ΔH -172 mcal/mg; ir: 2920 w, 2110 s (N_3), 1630 s, 1615 w, 1590 s, 1570 s cm^{-1}.

Anal. Calcd. for $C_{18}H_{10}N_4O$: C, 72.48; H, 3.38; N, 18.78. Found: C, 74.34; H, 3.98; N, 15.67. A correct elemental analysis could not be obtained because of easy decomposition of the azido compound.

12H-Naphtho[8,1-ab]carbazol-7-one (5).

A solution of 4a (1.0 g, 3.4 mmoles) in dimethylformamide (40 ml) was heated to reflux for 30 minutes, cooled, poured into water (150 ml) and filtered by suction. The yield was 0.63 g (70%), orange red powder, mp 382-387° (xylene); ir: 3280-3000 m, 1630 s, 1610 s, 1570 s cm^{-1}.

Anal. Calcd. for $C_{19}H_{11}NO$: C, 84.74; H, 4.12; N, 5.20. Found: C, 84.68; H, 4.25; N, 5.05.

Naphtho[8,1-ab]-8a-azonia-9-λ^2-azafluoren-7-one (7a).

Method A.

A solution of the azide 4b (0.50 g, 1.6 mmoles) in dimethylformamide (20 ml) was heated to reflux for 30 minutes, cooled, poured into water (100 ml) and filtered by suction; the yield was 0.33 g (70%).

Method B.

To a solution of chloro compound 3b (0.50 g, 1.7 mmoles) in dimethylformamide (20 ml), sodium azide (0.65 g, 10 mmoles) was added slowly. Then the mixture was heated under reflux for 30 minutes, cooled, poured into water (100 ml) and filtered by suction. The yield was 0.32 g (69%), brown powder, mp 213-215° (ethanol); ir: 3600-3200 w, 3080-3020 w, 1660 w, 1640 s, 1580 s cm^{-1}.

Anal. Calcd. for $C_{18}H_{10}N_2O$: C, 79.99; H, 3.73; N, 10.36. Found: C, 79.68; H, 4.06; N, 9.98.

Benzo[i]naphtho[8,1-ab]-8a-azonia-9-λ^2-azafluoren-7-one (7b).

This compound was prepared from 3c (0.50 g, 1.5 mmoles) in dimethylformamide (30 ml) and sodium azide (0.48 g, 7.4 mmoles) following method B described for 7a. The yield was 0.35 g (75%), brown crystals, mp 264-265.5° (ethanol); ir: 1640 s, 1610 s, 1580 m, 1550 s cm^{-1}; ^{1}H nmr: δ 7.51-7.59 (m, H at C-11), 7.63-7.71 (m, H at C-5), 7.71-7.73 (m, H at C-2), 7.79-7.81 (m, H at C-9, H at C-12), 7.82-7.89 (m, H at C-10), 8.0-8.02 (m, H at C-6), 8.11-8.13 (m, H at C-1), 8.33-8.35 (m, H at C-8), 8.64-8.71 (m, H at C-3, H at C-4), 8.72-8.80 (m, H at C-13).

Anal. Calcd. for $C_{22}H_{12}N_2O$: C, 82.49; H, 3.78; N, 8.74. Found: C, 82.61; H, 3.86; N, 8.64.

2-Phenyl-3-(triphenylphosphoranylideneamino)phenalen-1-one (8a).

Triphenylphosphane (3.36 g, 12.8 mmoles) was added to a solution of 4a (3.50 g, 11.8 mmoles) in toluene (60 ml) under stirring. Then the solution was heated for 45 minutes to 80°, the solvent removed *in vacuo* and the solid residue digested with cyclohexane (100 ml) to remove excess triphenylphosphane. The crude product was recrystallized from ethanol and after standing at 4° for 12 hours filtered by suction; the yield was 4.6 g (75%), orange powder, mp 169-170° (ethanol); ir: 3080-3000 w, 1625 s, 1610 s, 1570 s cm^{-1}.

Anal. Calcd. for $C_{32}H_{27}NOP$: C, 83.60; H, 4.93; N, 2.63. Found: C, 83.43; H, 4.75; N, 2.64.

2-(2-Pyridinyl)-3-(triphenylphosphoranylideneamino)phenalen-1-one (8b).

A solution of 4b (4.00 g, 13.4 mmoles) was reacted and worked up as described for 8a. The yield was 5.48 g (77%), orange powder, mp 182-184° (ethanol/water); ir: 3040 w, 1630 s, 1605 s, 1580 m cm^{-1}.

Anal. Calcd. for $C_{36}H_{25}N_2OP$: C, 81.19; H, 4.73; N, 5.26. Found: C, 80.97; H, 4.62; N, 5.11.

3-Amino-2-phenylphenalen-1-one (9a).

Method A.

A solution of the phosphazene 8a (2.46 g, 4.6 mmoles) in 0.5 N hydrochloric acid (45 ml) and methanol (2.7 ml) was heated under reflux for 60 minutes. After cooling the precipitated triphenylphosphanoxide was removed by filtration and the filtrate brought to $pH = 10$ with 2 N sodium hydroxide solution. A yellow precipitate was formed, which was filtered by suction. The yield was 1.05 g (84%), orange prisms, mp 216° (ethanol/water).

Method B.

A solution of the azide 4a (0.90 g, 3 mmoles) in dimethylformamide (40 ml) was diluted with ethanol (50 ml) and then palladium/charcoal (10%) (0.1 g) was added. This mixture was hydrogenated at room temperature for 5 hours, then the catalyst was filtered and the product precipitated by addition of water. The yield was 0.48 g (58%), orange prisms, mp 217° (toluene); ir: 3430 w, 3310 m, 3260-3000 m, 1640 m, 1630 m, 1600 s.

Anal. Calcd. for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.00; H, 4.93; N, 4.79.

3-Amino-2-(2-pyridinyl)phenalen-1-one (9b).

A solution of the phosphazene 8b (5.00 g, 9.4 mmoles) was reacted and worked up as described for 8a (method A). The yield was 2.12 g (83%), orange crystals, mp 236-239° (toluene); ir: 3380-3200 m, 1630 s, 1600 w, 1590 s cm^{-1}.

Anal. Calcd. for $C_{18}H_{12}N_2O$: C, 79.40; H, 4.44; N,10.29. Found: C, 79.66; H, 4.62; N, 10.04.

Acknowledgments.

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