Heteroelectrocyclic Reaction of 4-Azido-3-hydrazonoalkyl-quinolines to 2-Arylaminopyrazolo[4,3-*c*]quinolones [1]

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4-Azido-3-acylquinolones **4** obtained from 4-hydroxy derivatives **1** *via* tosylates **3** or chlorides **5**, reacted with arylhydrazines **6** to generate 4-azido-3-hydrazonoalkylquinolines **7**. Thermolysis of **7** gave ring closure products which were assigned to 2-arylaminopyrazolo[4,3-*c*]quinolones **10**. The thermal decomposition conditions of the azides **4** and **7** were studied by differential scanning calorimetry (DSC).

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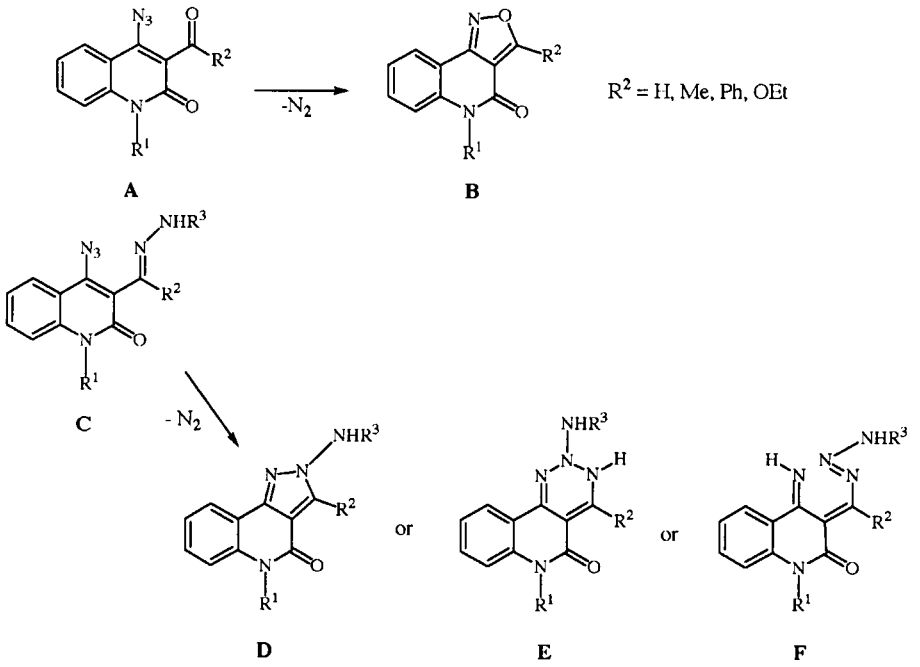
Recently we reported that 4-azidoquinolines **A** with 3-acyl substituents gave on thermolysis the corresponding isoxazolo derivatives **B** [2]. In the present work we extended this type of reaction to azidoquinolines **C** having a 3-hydrazonoalkyl group as a heteroacyl substituent. Depending on the attack of the azide either at N-1 or N-2 of the hydrazone, either 2*H*-pyrazolo[4,3-*c*]quinolones **D**, a class of compounds which has found pharmaceutical interest because of its benzodiazepine receptor affinity and as immunomodulating drugs [3], or triazino[5,4-*c*]-quinolones **E**, a hitherto unknown class of compounds, should be formed. The formation of the openchain imino-quinoline **F** is unlikely because of the reactive *ortho*-substituent.

Another point of interest was to obtain information about the thermal behavior of azidoarenes using differential scanning calorimetry (DSC). We found this method very suitable for the determination of thermal reaction conditions [4]. Additionally, data from differential scanning calorimetry give safety hints, which are important in synthetic azide chemistry.

The reaction sequence was started with 3-acyl-4-hydroxy-2-quinolones **1**, which were prepared according to literature procedures [5,6]. In a retrosynthetical view, both of the pyrazolo or triazino nitrogens of the cyclized target compounds **D/E** (Scheme 1) can be derived by substitution of the oxygen functions of the 4-hydroxy- and the 3-acyl-group of **1** by azide and hydrazine, respectively. The suitable reaction path differs mainly in the sequence of the substitution. We found that the best results were obtained by first replacing the 4-hydroxy group of **1** with an azido group to obtain **4** followed by conversion of the 3-acyl group of **4** to a hydrazono group in **7**. The reversed reaction sequence, involving as the first step, conversion

Scheme 1

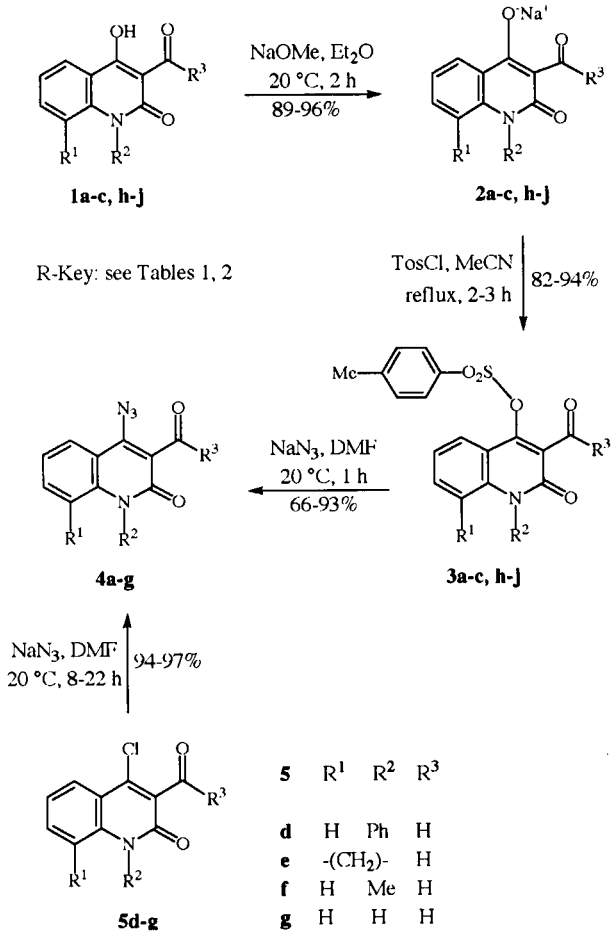


of the 3-acyl- to the hydrazono group and then replacement of the 4-hydroxy function by an azido substituent *via* **8** or **9** led to 1-substituted 1*H*-pyrazoles [8].

In order to obtain an intermediate with a reactive substituent in position 4, we tried to exchange the 4-hydroxy group of **1** for a 4-chloro substituent to obtain compounds **5a-c, h-j** (R^3 = Me, Ph). However, attempts with the usual reagents such as phosphoryl chloride, phosphorus trichloride and phosphorus pentachloride failed, also using triethylamine as a base to destroy hydrogen bonding between the 3-acyl group and the 4-hydroxy group, which we used successfully in earlier reports [2d].

Good results were afforded in the two-step reaction of 4-hydroxy-3-acetylquinolones **1a-c** *via* the sodium salts **2a-c** to give the 3-acetyl-4-tosyloxyquinolones **3a-c**. In this reaction sequence sodium salts **2a-c** were isolated as solids, dried and then reacted with tosyl chloride in dry acetonitrile to give in high yields the reactive 3-acetyl-4-tosyloxyquinolones **3a-c**. Tosylates **3a-c** gave with sodium azide at room temperature in excellent yields 3-acetyl-4-azido-2-quinolones **4a-c**. In the same manner 4-tosyloxy-3-benzoyl derivatives **3h-j** were obtained from 3-benzoyl-4-hydroxy-2-quinolones **1h-j**.

Scheme 2



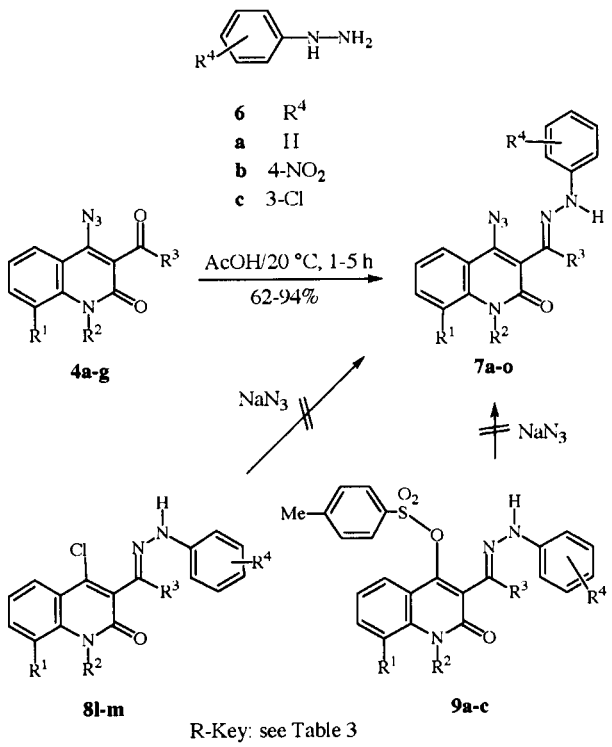
However, the reaction of **3h-j** with sodium azide gave under various conditions only product mixtures, which could not be purified. 4-Azido-3-formyl-2-quinolones **4d-g** (R^3= H) were prepared smoothly from 4-chloro-3-formyl-2-quinolones **5d-g** (R^3 = H) and sodium azide; **5d-g** were obtained in a 3-step reaction starting from 4-hydroxy-2-quinolones *via* 3-phenylaminomethylenequinoline-2,4-diones [2a,7]. The phenylaminomethylene moiety was cleaved when chlorinated with phosphorylchloride to give 4-chloro-3-dichloromethyl-2-quinolones; acidic catalyzed hydrolyzation gave regioselectively the 4-chloro-3-formyl compounds **5d-g** [2a,7,8].

Attempts to prepare 4-azido-3-acylcoumarins with the corresponding *O*-heterocyclic ring system were unsuccessful.

4-Azido-3-acyl-2-quinolones **4a-g** gave at room temperature with phenylhydrazines **6a-c** in acetic acid in good yields the corresponding hydrazones, 3-(1-arylhydrazonoalkyl)-4-azido-2-quinolones **7a-o**. The structures of these highly reactive azido-hydrazones **7** were confirmed by infrared signals of the azido group at 2120-2130 cm^1 and the lack of the ketone or aldehyde carbonyl signals. The elemental analyses showed in some cases deviation from the theoretical percentages due to the instability of the azido group, but azides **7** could be used without problems for further thermolytic decomposition experiments.

We made several attempts to obtain the hydrazonoazides **7** by the reversed reaction sequence, introducing in the first step the hydrazone and in the second step the

Scheme 3



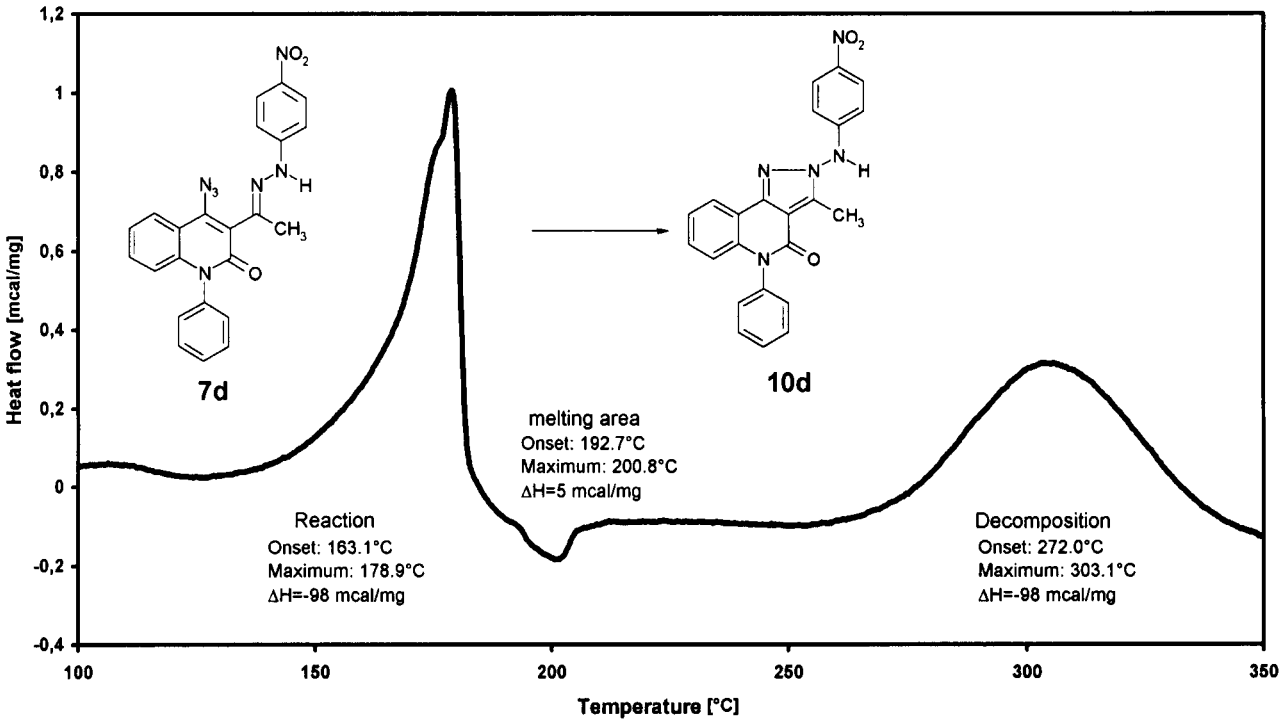


Figure 1. Differential scanning calorimetry diagram of 4-azido-3-[1-(4-nitrophenylhydrazonoethyl)-2(1*H*)-quinolone (**7d**).

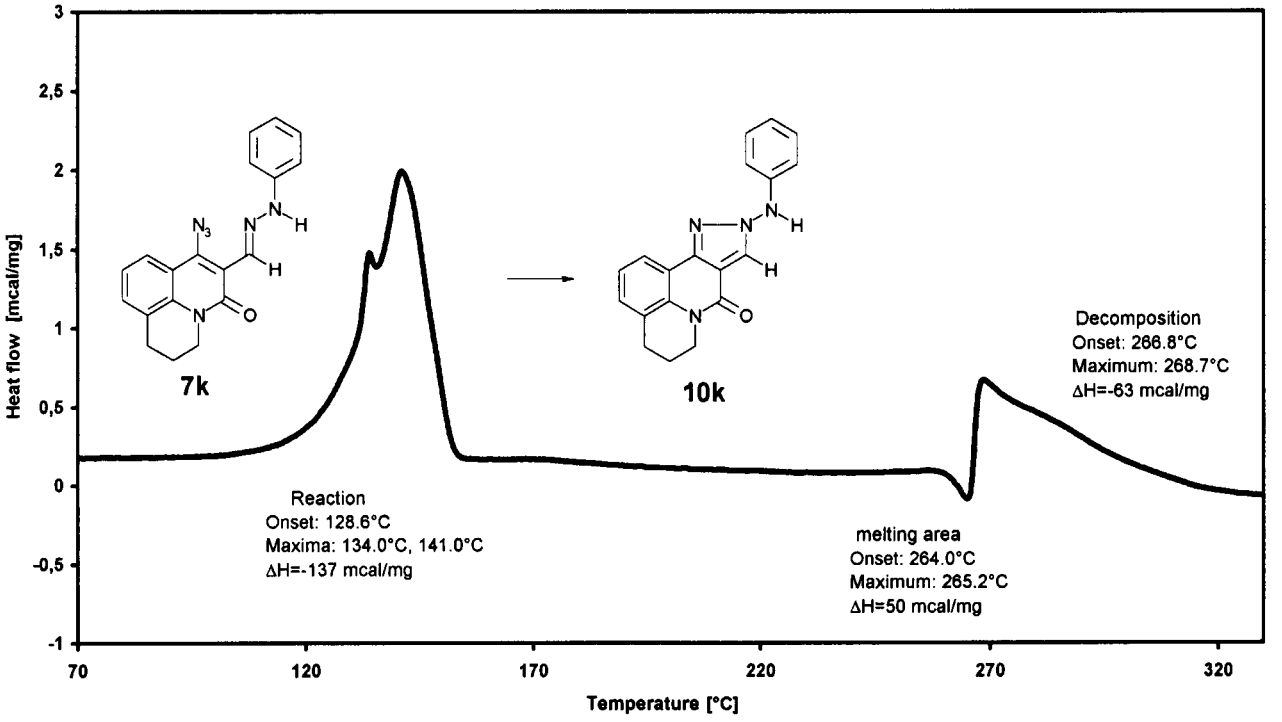


Figure 2. Differential scanning calorimetry diagram of 1-azido-2-(1-phenylhydrazonoethyl)-benzo[*ij*]quinolizin-3-one (**7k**).

Scheme 4

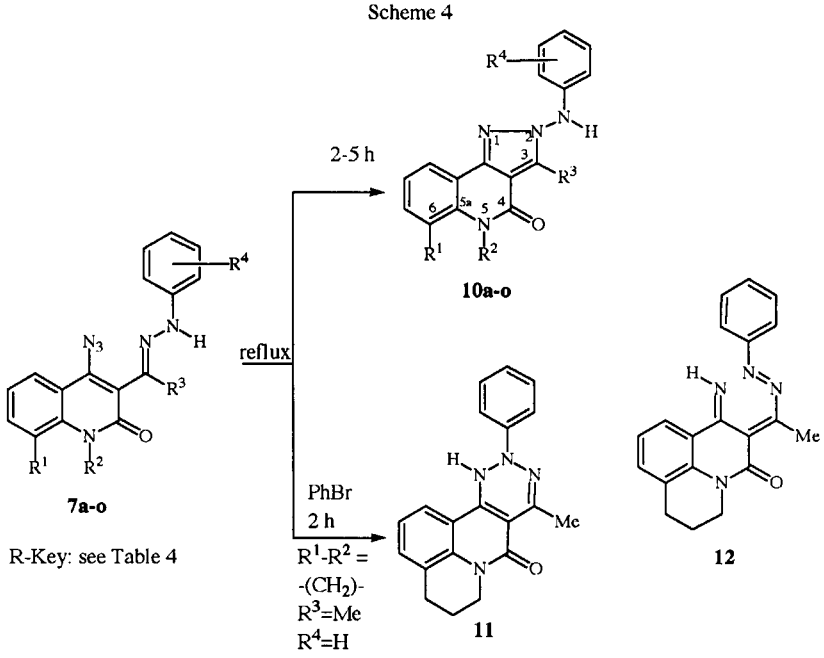


Table 1

Yields of Sodium 3-Acyl-2-oxo-1,2-dihydroquinoline-4-olates (**2a-c, h-j**); Physical, Analytical and Spectroscopic Data of 3-Acyl-4-tosyloxy-2(1*H*)-quinolones (**3a-c, h-j**)

No.	R^1	R^2	R^3	Yield of **2** (%) Yield of **3** (%) mp (°C) Recrystallization solvent	Molecular formula Molecular weight Appearance	Analysis (%) Calcd./Found C	H	N	IR [cm^{-1}] ^{1}H-NMR (δ ppm)
3a	H	Ph	Me	94 94 173-175 DMF/H_2O	$C_{24}H_{19}NO_5S$ 433.49 light brown microprisms	66.50 66.13	4.42 4.22	3.23 3.21	1700 m, 1695 s, 1630 m, 1595 m 2.50 (s, CH_3), 6.60 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.20-7.30 (m, 1 Aryl-H), 7.40-7.70 (m, 9 Aryl-H), 7.90 (dd, J = 7.0+1.5 Hz, 2 Aryl-H)
3b	-$(CH_2)_3$-		Me	96 89 99-100 xylene	$C_{21}H_{19}NO_5S$ 397.45 light brown microprisms	63.46 63.38	4.82 4.74	3.52 3.63	3050 w, 2950 w, 1700 m, 1640 s, 1590 m 2.00 (t, J = 7.0 Hz, -CH_2-), 2.45 (s, -CH_3), 2.95 (t, J = 7.0 Hz, Ar- CH_2-), 4.05 (t, J = 7.0 Hz, -N-CH_2-), 7.05-7.15 (m, 1 Aryl-H), 7.35 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.45-7.55 (m, 3 Aryl-H) 7.90 (dd, J = 7.0+1.5 Hz, H at C-10)
3c	H	Me	Me	95 82 88-88.5 ethanol	$C_{19}H_{17}NO_5S$ 371.42 light brown microprisms	61.44 61.30	4.61 4.49	3.77 4.01	3090 w, 3050 w, 1705 m, 1640 s, 1620 m, 1590 m 2.45 (s, -CO-CH_3), 3.70 (s, -N-CH_3), 7.20-7.30 (m, 1 Aryl-H), 7.50 (dd, J = 7.0+1.5 Hz, 3 Aryl-H), 7.60-7.80 (m, 2 Aryl-H), 7.90 (dd, J = 7.0+1.5 Hz, 2 Aryl-H)
3h	H	Ph	Ph	90 88 208-210 toluene	$C_{29}H_{21}NO_5S$ 495.56 light brown microprisms	70.29 69.89	4.27 4.10	2.83 2.62	1680 m, 1640 s, 1620 m, 1595 m 2.40 (s, -CH_3), 6.70 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.30-7.40 (m, 3 Aryl-H), 7.45-7.50 (m, 4 Aryl-H), 7.55-7.70 (m, 7 Aryl-H), 7.75-7.90 (m, 3 Aryl-H)
3i	-$(CH_2)_3$-		Ph	95 88 247 dec toluene	$C_{26}H_{21}NO_5S$ 459.52 light brown microprisms	67.96 67.66	4.61 4.56	3.05 3.15	1670 m, 1635 s, 1580 m, 2.05-2.15 (m, -CH_2-), 2.40 (s, -CH_3), 3.00 (m, Ar-CH_2-), 4.10 (m, -N-CH_2-), 7.25-7.35 (m, 3 Aryl-H), 7.40-7.50 (m, Aryl-H), 7.55-7.70 (m, 7Aryl-H)
3j	H	Me	Ph	89 92 199 dec toluene	$C_{24}H_{19}NO_5S$ 433.49 light brown microprisms	66.50 66.25	4.42 4.30	3.23 3.24	3060 w, 1675 m, 1640 s, 1595 m, 2.40 (s, -CH_3), 3.70 (s, N-CH_3), 7.30 (dd, J = 7.0+1.5 Hz, 2 Aryl-H), 7.40-7.50 (m, 3 Aryl-H), 7.55-7.65 (dd, J = 7.0+1.5 Hz, 2 Aryl-H), 7.70 (m, Aryl-H), 7.75-7.90 (m, Aryl-H)

Table 2

Physical, Analytical and Spectroscopic Data of 3-Acetyl-4-azido-2(1*H*)-quinolones **4a-c** and 4-Azido-3-formyl-2(1*H*)-quinolones **4d-g**

No.	R^1	R^2	R^3	Yield (%) mp (°C) Recrystallization Solvent reaction time (h)	Molecular formula Molecular Mass Appearance	Analysis (%) Calcd./Found C	H	N	IR [cm^{-1}] ^{1}H-NMR (δ ppm)	Calorimetric data: onset (°C)/peak max (°C) (ΔH, mcal/mg)
4a	H	Ph	Me	93 138 (ref [2c]: 160) ethanol (methanol) 1						cyclization 111.6/123.4 (-88)
4b	-$(CH_2)_3$-		Me	66 108 (ref [2c]: 120) ethanol (methanol) 1						cyclization 119.2/125.7 (-126)
4c	H	Me	Me	91 104 (ref [2a]: 118) ethanol (methanol) 1						cyclization 113.8/118.0 (-122)
4d	H	Ph	H	97 251 dec ethanol 19	$C_{16}H_{10}N_4O_2$ 290.28 light brown microprisms	[a]			3060 w, 2870 w, 2130 s, 1680 s,1645 s, 1600 s	cyclization 146.2/156.9 (-64), dec 214.6/255.7 (-75)
4e	-$(CH_2)_3$-		H	97 149 dec ethanol 8	$C_{13}H_{10}N_4O_2$ 254.25 brown microprisms	[a]			2940 w, 2880 w, 2130 s, 1680 s,1630 s, 1600 m, 1590 s	cyclization 137.3/141.3 (-67), mp 223.9/226.8, dec 232.9/248.0 (-84)
4f	H	Me	H	94 132 (ref [2b]: 130) ethanol (methanol) 22						cyclization 124.5/128.6 (-68), mp 217.7/220.9, dec 222.5/226.2 (-8), dec 256.1/288.3 (-53)
4g	H	H	H	68 181 DMF/H_2O 8	$C_{10}H_6N_4O_2$ 214.18	56.08 56.37	2.82 3.02	26.16 25.76	3000-2850 br, 2120 s, 1690 s,1670 s, 1610 m, 1590 m, 1530 m	cyclization 146.4/159.5 (-57), dec 263.4/272.5 (-72)

[a] Because of the ease of decomposition no exact analytical data were obtained

reactive azide group, in order to avoid decomposition and cyclization reactions of the reactive 3-acyl-4-azido-quinolones [2c]. However, all these experiments failed. When 3-arylhydrazonomethyl-4-chloro- (**8**) or 3-aryl-hydrazonomethyl-4-tosyloxy-2-quinolones (**9**) [8] were reacted with sodium azide, these compounds cyclized in all cases without introduction of the azide group at room temperature to 1-aryl-3-methyl-1*H*-pyrazolo[4,3-*c*]-quinolin-4(5*H*)-ones [8].

Thermolysis or photolysis of azides with *ortho*-acyl substituents is known to afford, in a 1,5-heteroelectrocyclic reaction *via* a pseudopericyclic process (without formation of a nitrene intermediate), the corresponding cyclization products [9,10]; this reaction is of synthetic value. To get insights into the thermal behavior of the hydrazono-azides **7**, differential scanning calorimetry experiments were performed, which should give information about reaction and decomposition temperatures and in addition about the reaction enthalpy as security hint.

A DSC experiment of the hydrazono-azide **7d** with an acetyl-hydrazone moiety (Figure 1) revealed that the first reaction starts at an onset temperature of about 163 °C; then a mp at about 193 °C is visible. The reaction enthalpy of -98 mcal/mg is an average range of azido compounds [8]. Decomposition of the so formed new compound is shown by an additional exothermic peak starting at 270 °C.

Formylhydrazono-azides such as **7k** (Figure 2) showed both a lower reaction onset temperature of *e.g.* 129 °C and a higher reaction enthalpy of *e.g.* -137 mcal/mg. After the mp at 264 °C, decomposition of the formed new compound is shown by an exothermic peak and takes place again above 270 °C.

Table 3

Physical, Analytical and Spectroscopic Data of 3-(1-Arylhydrazonoalkyl)-4-azido-2(1*H*)-quinolones **7a-o**

No.	R^1	R^2	R^3	R^4	Yield (%) mp (°C) Recrystallization Solvent	Molecular formula Molecular Weight Appearance	Analysis (%) Calcd./Found C	H	N	IR [cm^{-1}] ^{1}H-NMR (δ ppm)	Calorimetric data: onset (°C)/peak max (°C) (ΔH, mcal/mg)
7a	H	Ph	Me	H	87 94-98 dec [b]	$C_{23}H_{18}N_6O$ 394.44 organge microprisms	[a]			2110 m, 1685 w, 1630 m, 1610 m 2.20 (s, CH_3), 6.50-6.70 (m, 1 Aryl-H), 7.70-7.90 (m, 1 Aryl-H), 7.10-7.80 (m, 10 Aryl-H), 8.05 (dd, J = 7.0+15 Hz, 1 Aryl-H), 8.20 (dd, J = 7.0+1.5 Hz, H at C-8), 9.40 (s, 1 N-H)	cyclization 92.4/151.3 (-66)
7b	-$(CH_2)_3$-		Me	H	82 160-163 dec [b]	$C_{20}H_{18}N_6O$ 358.41 brown microprisms	67.03 67.41	5.06 5.46	23.45 23.08	3300 w, 3240 w, 2105 m, 1640 m, 1605 m, 1585 m 2.00 (m, -CH_2-), 2.65 (s, 3-CH_3),2.90 (m, Ar-CH_2-), 4.00 (m, N-CH_2-), 6.85-6.95 (m, 1 Aryl-H), 7.00-7.50 (m, 6 Aryl-H), 7.90 (dd, J = 7.0+1.5 Hz, H at C-9), 9.40 (s, 1 N-H)	cyclization 159.9/169.3 (-42)
7c	H	Me	Me	H	79 144-148 dec [b]	$C_{18}H_{16}N_6O$ 332.37 brown microprisms	[a]			3300 m, 2110 s, 1620 s, 1600 s 2.20 (s, CH_3), 3.65 (s, N-CH_3), 6.80 (m, 1 Aryl-H), 7.00-7.40 (m, 4 Aryl-H), 7.50-7.08 (m, 3 Aryl-H), 8.10 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 9.40 (s, 1 N-H)	cyclization 143.0/152.4 (-75)
7d	H	Ph	Me	4-NO_2	79 165-167 dec [b]	$C_{23}H_{17}N_7O_3$ 439.44 brown microprisms	[a]			3280 m, 2120 s, 1685 m, 1630 s, 1590 s 2.40 (s, CH_3), 6.60 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.25-7.45 (m, 4 Aryl-H), 7.55-7.75 (m, 4 Aryl-H), 8.05-8.25 (m, 3 Aryl-H), 10.40 (s, 1 N-H)	cyclization 163.1/178.9 (-98)
7e	-$(CH_2)_3$-		Me	4-NO_2	87 64-166 dec [b]	$C_{20}H_{17}N_7O_3$ 403.40 brown microprisms	[a]			3200-3300 m, 2930 w, 2120 s, 1620 s, 1590 s 2.00, (m, -CH_2-), 2.30 (s, Acetyl-CH_3), 2.95-3.05 (m, Ar-CH_2-), 4.05-4.15 (m, -N-CH_2-), 7.15-7.35 (m, 3 Aryl-H), 7.50 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.80 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 8.15 (dd, J = 7.0+1.5 Hz, 2 Aryl-H), 10.35 (s, 1 N-H)	cyclization 163.2/171.9 (-115)
7f	H	Me	Me	4-NO_2	87 157-159 dec [b]	$C_{18}H_{15}N_7O_3$ 377.37 brown microprisms	[a]			3200-3310 m, 2120 s,1620 s, 1590 s 2.30 (s, CH_3), 3.70 (s, N-CH_3), 7.20-7.40 (m, 3 Aryl-H), 7.60 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.65-7.80 (m, 1 Aryl-H), 8.00 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 8.15 (dd, J=7.0+1.5 Hz, 2 Aryl-H), 10.35 (s, 1 N-H)	cyclization 154.0/164.4 (-101)
7g	H	Ph	Me	3-Cl	83 154-159 dec [b]	$C_{23}H_{17}ClN_6O$ 428.88 brown microprisms	[a]			3290 m, 2120 s, 1625 s, 1610 s, 1595 s, 2.20 (s, CH_3), 6.60 (dd, J = 7.0+ 1.5 Hz, 1 Aryl-H), 6.80 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.00-7.40 (m, 6 Aryl-H), 7.50-7.70 (m, 4 Aryl-H),8.00 (dd, J = , 7.0+1.5 Hz, 1 Aryl-H), 9.70 (s, 1 N-H)	cyclization 152./166.3 (-79)
7h	-$(CH_2)_3$-Me			3-Cl	94 144-146 dec [b]	$C_{20}H_{17}ClN_6O$ 392.85 brown microprisms	[a]			3300 m, 2840-2960 w, 2120 s, 1715 w, 1615 s, 1600 s, 1590 s, 2.00 (m, -CH_2-), 2.10 (s, CH_3), 3.00 (m, Ar-CH_2-), 4.10 (m, N-CH_2-), 6.80 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.10-7.30 (m, 4 Aryl-H), 7.50 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.80 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 9.60 (s, 1 N-H)	cyclization 141.1/161.8 (-146)
7i	H	Me	Me	3-Cl	88 148-152 dec [b]	$C_{18}H_{15}ClN_6O$ 366.81 brown microprisms	[a]			3300 m, 2120 s, 1620 s, 1595 s 2.20 (s, CH_3), 3.70 (s, N-CH_3), 6.80 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.10-7.30 (m, 3 Aryl-H), 7.35-7.40 (m, 1 Aryl-H), 7.60-7.08 (m, 2 Aryl-H), 8.00 (dd, J = 7.0+1.5 Hz, H at C-8), 9.65 (s, 1 N-H)	cyclization 146.4/159.4 (-104)

Table 3 (continued)

No.	R^1	R^2	R^3	R^4	Yield (%) mp (°C) Recrystallization Solvent	Molecular formula Molecular Weight Appearance	Analysis (%) Calcd./Found C	H	N	IR [cm^{-1}] ^{1}H-NMR (δ ppm)	Calorimetric data: onset (°C)/peak max (°C) (ΔH, mcal/mg)
7j	H	Ph	H	H	85 111-113 dec cyclohexane	$C_{22}H_{16}N_6O$ 380.41 yellow microprisms	69.46 69.91	4.24 4.25	22.09 21.61	3260 m, 2125 m, 1635 s, 1600 s, 6.55 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 6.75-6.85 (m, 1 Aryl-H), 7.10 (dd, J = 7.0+1.5 Hz, 2 Aryl-H), 7.20-7.50 (m, 7 Aryl-H), 7.55-7.60 (m, 3 Aryl-H), 8.15 (dd, J = 7.0+1.5 Hz, H at C-8), 8.30 (s, N=CH-), 10.90 (s, 1 N-H)	cyclization 113.0/119.8 (-99)
7k	-$(CH_2)_3$-		H	H	64 127-129	$C_{19}H_{16}N_6O$ 344.38 microprisms	66.27 66.60	4.68 4.75	24.40 24.01	3250 m, 2130 m, 1620 s, 1605 s, 1585 s 2.00 (m, -CH_2-), 3.00 (m, Ar-CH_2-), 4.10 (m, -N-CH_2-), 6.75-6.80 (m, 1 Aryl-H), 7.05 (dd, J = 7.0+1.5 Hz, 2 Aryl-H), 7.20-7.35 (m, 3 Aryl-H), 7.40 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.90 (dd, J = 7.0+1.5 Hz, H at C-9), 8.35 (s, N=CH-), 10.90 (s, 1 N-H)	cyclization 128.6/134.0 (-137)
7l	H	Me	H	H	64 110 dec toluene	$C_{17}H_{14}N_6O$ 318.34	64.14 64.36	4.43 4.77	26.40 25.99	3280 m, 2130 s, 1620 s, 1600 s, 1560 m, 1525 m, 1495 m	
7m	H	H	H	H	92 105 dec dioxane	$C_{16}H_{12}N_6O$ 304.31	63.15 63.53	3.97 4.20	27.62 27.27	3240 w, 2120 s, 1655 s,1600 s, 1570 m, 1520 m 6.85-7.60 (m, 8 Aryl-H), 8.00 (dd, J = 7.0+1.5 Hz, H at C-5), 8.30 (s, 1 N-H), 10.85 (s, N=CH-), 11.45 (s, 1 N-H)	
7n	H	Me	H4-NO_2		62 241 dec [b]	$C_{17}H_{13}N_7O_3$ 363.34 brown microprisms	[a]			3325 m, 2120 m, 1670 s, 1640 s, 1600 s 3.70 (s, N-CH_3), 6.90 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.20-7.70 (m, 3 Aryl-H), 7.90 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 8.10 (dd, J = 7.0+1.5 Hz, H at C-8), 8.30 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 8.45 (s, N= CH-), 11.40 (s, 1 NH) ,	cyclization 99.2/121.8 (-6)
7o	H	Me	H	3-Cl	73 135-137 [b]	$C_{17}H_{13}ClN_6O$ 352.79 yellow microprisms	[a]			3265 m 2125 s, 1625 s, 1600 s, 3.70 (s, N-CH_3), 6.8-6.9 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 6.9-7.10 (m, 2 Aryl-H), 7.25-7.40 (m, 2 Aryl-H), 7.55-7.75 (m, 2 Aryl-H), 8.10 (dd, J = 7.0+1.5 Hz, H at C-8), 8.40 (s, N=CH-), 11.10 (s, 1 N-H)	cyclization 133.2/142.4 (-120)

[a] Because of the ease of decomposition no exact analytical data were obtained
[b] Because of the ease of decomposition no recrystallization was possible

These differential scanning calorimetry data allowed us to plan the synthetic thermolysis of azides of type **7**: the azides **7** were heated to its individual reaction temperatures indicated by the first exothermic reaction peak; decomposition could be avoided because the reaction temperature was held below the next exothermic peak which indicated decomposition or a further reaction (see Table 4). As example, the thermal cyclization of **7d** with an onset of the reaction temperature at 163 °C was performed in refluxing bromobenzene (bp 156 °C) for two hours until nitrogen gas evolution had stopped; in the case of **7j** with an onset of the reaction temperature at 113 °C, refluxing trichloroethylene (bp 87 °C) was used. The reason why we used thermolysis temperatures below the onset temperature was because we found that solvent effects lower the decomposition temperatures by about 20 - 40 °C [8]. Structural characterization of the thermolysis products by ir spectra revealed the lack of the azide signal at 2120 cm^{-1}; in the ^{1}H nmr spectrum the NH proton signals were shifted downfield by about 1.5 ppm.

However, these data did not allow an assignment to either the 2-arylaminopyrazolo structure **10** or to the isomeric triazino structure **11**. To elucidate the structures of the cyclized products, experiments using deuterium induced differential isotope shift ^{13}C nmr [11] were performed. A usual ^{13}C nmr spectrum of the cyclization

Table 4
Physical, Analytical and Spectroscopic Data of 2-Arylamino-pyrazolo[4,3-c]quinolin-4(5*H*)-ones **10a-o**

No.	R^1	R^2	R^3	R^4	Solvent/time (h) Yield (%) mp (°C) Recrystallization Solvent	Molecular Formula Molecular Mass Appearance	Analysis (%) Calcd./Found C	H	N	IR [cm^{-1}] ^{1}H-NMR (δ ppm) ^{13}C NMR (δ ppm)
10a	H	Ph	Me	H	bromobenzene/2 88 221-222 bromobenzene	$C_{23}H_{18}N_4O$ 366.43 light brown	75.39 75.06	4.95 4.98	15.29 14.93	3340 m, 3080 w, 1675 s, 1610 m, 1590 m 6.45-6.55 (m, 3 Aryl-H), 6.90-6.95 (m, 1 Aryl-H), 7.20-7.40 (m, 6 Aryl-H), 7.55-7.70 (m, 3 Aryl-H), 8.10 (dd, J = 7.0+1.5 Hz, H at C-9), 10.00 (s, 1 N-H)
10b	-$(CH_2)_3$-		Me	H	bromobenzene/2 66 275-277 bromobenzene	$C_{20}H_{18}N_4O$ 330.39 yellow	72.71 72.35	5.49 5.23	16.96 16.63	3200 m, 1630 s, 1600 m 2.00 (m, -CH_2-), 2.60 (s, CH_3), 2.90 (m, Ar-CH_2-), 4.10 (m, -N-CH_2-), 6.50 (dd, J = 7.0+1.5 Hz, 2 Aryl-H), 6.90-6.95 (m, 1 Aryl-H), 7.10-7.40 (m, 4 Aryl-H), 7.85 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 9.95 (s, 1 N-H)
10c	H	Me	Me	H	bromobenzene/2 81 205-207 dec ligroin	$C_{18}H_{16}N_4O$ 304.35 light brown	71.04 71.17	5.30 5.10	18.41 18.20	3300 m, 3280 m, 1650 s, 1590 s, 2.60 (s, 3-CH_3, 3.65 (s, N-CH_3), 6.60 (dd, J = 7.0+1.5 Hz, 2 Aryl-H), 6.90-6.95 (m, 1 Aryl-H), 7.20-7.35 (m, 3 Aryl-H), 7.60-7.65 (m, 2 Aryl-H), 8.05 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 9.95 (s, 1 N-H)
10d	H	Ph	Me	4-NO_2	bromobenzene/2 63 284-286 dec bromobenzene	$C_{23}H_{17}N_5O_3$ 411.42 light brown	67.15 66.88	4.16 3.88	17.02 16.74	3210 m, 3150 w, 2980-3090 w, 1645 s, 1595 s 2.65 (s, 3-CH_3), 6.55 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 6.75 (dd, J=7.0+1.5 Hz, 2 Aryl-H), 7.20-7.50 (m, 5 Aryl-H), 7.55-7.75 (m, Aryl-H), 8.15 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 8.25 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 11.10 (s, 1 N-H)
10e	-$(CH_2)_3$-		Me	4-NO_2	bromobenzene/2 62 272 dec bromobenzene	$C_{20}H_{17}N_5O_3$ 375.39 light brown	63.99 63.64	4.56 4.44	18.66 18.27	3260 m, 3080 w, 2840-2960 w, 1635 s, 1600 s 2.00 (m, -CH_2-), 2.60 (m, -CH_3), 3.00 (m, Ar-CH_2-), 4.15 (m, -N-CH_2-), 6.65 (dd, J = 7.0+1.5 Hz, 2 Aryl-H), 7.20-7.25 (m, 1 Aryl-H), 7.40 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.90 (dd, J= 7.0+1.5 Hz, Aryl-H), 8.20 (dd, J = 7.0+1.5 Hz, 2 Aryl-H), 11.00 (s, 1 N-H)
10f	H	Me	Me	4-NO_2	bromobenzene/2 76 245 dec bromobenzene	$C_{18}H_{15}N_5O_3$ 349.35 light brown	61.89 61.52	4.33 4.07	20.05 19.69	2820-3380 m, 1660 m, 1630 s, 1595 s 2.60 (s, 3-CH_3), 3.65 (s, N-CH_3), 6.65 (dd, J = 7.0+1.5 Hz, 2 Aryl-H), 7.25-7.40 (m, 1 Aryl-H), 7.50-7.70 (m, 2 Aryl-H), 8.10 (dd, J = 7.0+1.5 Hz, H at C-9), 8.20(dd, J = 7.0+1.5 Hz, 2 Aryl-H), 11.00 (s, 1 N-H)
10g	H	Ph	Me	3-Cl	bromobenzene/2 22 239-241 bromobenzene	$C_{23}H_{17}ClN_4O$ 400.87 light brown	68.91 68.61	4.27 3.96	13.98 13.60	3330 m, 1655 s, 1595 m 2.60 (s, 3-CH_3), 6.45-6.55 (m, 3 Aryl-H), 7.00 (dd, 1 Aryl-H), 7.20-7.45 (m, 5 Aryl-H), 7.55-7.75 (m, 3 Aryl-H), 8.10 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 10.30 (s, 1 N-H)
10h	-$(CH_2)_3$-		Me	3-Cl	bromobenzene/2 84 315 dec chlorobenzene	$C_{20}H_{17}ClN_4O$ 364.84 brown	65.84 65.44	4.70 4.60	15.36 15.22	3220 m, 2960 w, 1930 w, 1630 s, 1600 s 2.00 (m, -CH_2-), 2.60 (s, 3-CH_3), 2.95 (m, Ar-CH_2-), 4.15 (m, -N-CH_3-), 6.45-6.50 (m, 2 Aryl-H), 6.95 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 7.15-7.40 (m, 2 Aryl-H), 7.90 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 8.25 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 10.20 (s, 1 Aryl-H)
10i	H	Me	Me	3-Cl	bromobenzene/2 86 263 dec chlorobenzene	$C_{18}H_{15}ClN_4O$ 338.80 brown	63.81 63.50	4.46 3.96	16.54 16.14	3200 m, 1630 s, 1595 s, 2.65 (s, 3-CH_3), 3.65 (s, N-CH_3), 6.50 (dd, J = 7.0+1.5 Hz, 2 Aryl-H), 6.95 (dd, J=7.0+1.5 Hz, 1 Aryl-H), 7.20-7.40 (m, 2 Aryl-H), 7.50-7.70 (m, 2 Aryl-H), 8.05 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 10.20 (s, 1 N-H)

Table 4 (continued)

No.	R^1	R^2	R^3	R^4	Solvent/time (h) Yield (%) mp (°C) Recrystallization Solvent	Molecular Formula Molecular Mass Appearance	Analysis (%) Calcd./Found C	H	N	IR [cm^{-1}] ^{1}H-NMR (δ ppm) ^{13}C NMR (δ ppm)
10j	H	Ph	H	H	trichloroethylene/2 85 166 dec cyclohexane	$C_{22}H_{16}N_4O$ 352.40 yellow microprisms	74.98 74.65	4.58 4.38	15.90 15.56	3180-3280 w, 1670 m, 1615 w, 1600 m 6.50-6.60 (m, Aryl-H), 6.95-7.00 (m, 1 Aryl-H), 7.20-7.45 (m, 6 Aryl-H), 7.55-7.70 (m, 3 Aryl-H), 8.10 (dd, J = 7.0+1.5 Hz, H at C-9), 8.90 (s, 1 pyrazol-H)
10k	-$(CH_2)_3$-		H	H	DMF/5 71 280 dec acetone	$C_{19}H_{16}N_4O$ 316.37 yellow microprisms	72.14 71.76	5.10 5.18	17.71 17.71	3190 m, 3120 m, 3085 s, 2960 m, 2880 m, 1710 w, 1625 s 2.00 (m, -CH_2-), 2.90 (m, Ar-CH_2-), 4.15 (m, -N-CH_2-), 6.50 (dd, J = 7.0+1.5 Hz, 2 Aryl-H), 6.90-6.95 (m, 1 Aryl-H), 7.10-7.40 (m, 4 Aryl-H), 7.90 (dd, J = 7.0+1.5 Hz, H at C-10), 8.80 (s, H at C-1 and C-3), 10.10 (s, 1 N-H)
10l	H	Me	H	H	bromobenzene/2 69 248 toluene	$C_{17}H_{14}N_4O$ 290.33 pale yellow microprisms	70.33 70.02	4.86 4.92	19.30 19.49	3300-3150 br, 3125 w, 3070 w, 1630 s, 1605 s, 1590 s, 1500 m 3.70 (s, -CH_3), 6.50-7.70 (m, 8 Aryl-H), 8.10 (dd, J = 7.0+1.5 Hz, H at C-5 and C-6), 8.80 (s, 1 N-H), 10.15 (s, H at C-3) 29.1 (CH_3), 110.8 (C-3a), 111.7, 113.3 and 114.9 (C2 and C-6 of phenyl), 116.0 (C-6), 121.1, 122.4, 129.1, 129.5, 129.9, 137.5 (C-1 of phenyl), 139.0 (C-3), 145.9 (C-9b), 147.5 (C-5a), 157.8 (C-4)
10m	H	H	H	H	bromobenzene/2 85 281 dec DMF	$C_{16}H_{12}N_4O$ 276.30 pale yellow microprisms	69.55 69.71	4.38 4.45	20.28 20.24	3220-3130 br, 3020 m, 1650 s, 1600 s, 1560 m 6.55 (dd, J = 7.0+1.5 Hz, H at C-6 and C-7), 6.85-7.00 (m, H at C-8), 7.15-7.50 (m, 5 Aryl-H), 7.95 (dd, J = 7.0+1.5 Hz, H at C-8 and C-9), 8.75 (s, 1 N-H), 10.15 (s, -CH=N), 11.25 (s, 1 N-H) [a] 111.2 (C-3a), 113.3 (113.4) (C-2 and C-6 of phenyl), 113.6, 116.2 (116.3) (C-6), 121.2, 122.2, 122.4, 129.2, 129.6, 131.8, 137.7 (137.8) (C-1 of phenyl), 147.0 (C-9b), 147.3 (147.4) (C-5a), 158.5 (158.6) (C-4)
10n	H	Me	H	4-NO_2	toluene/2 97 268 dec bromobenzene	$C_{17}H_{13}N_5O_3$ 335.33 brown microprisms	60.89 60.63	3.91 3.56	20.89 20.53	3200 m, 1630 s, 1620 sh, 1600 m 2.00 (s, -CH_3), 6.75 (dd, J = 7.0+1.5 Hz, 2 Aryl-H), 9.00 (s, 1 N-H), 10.00 (s, 1 O-H)
10o	H	Me	H	3-Cl	chlorobenzene/2 68 198-200 bromobenzene	$C_{17}H_{13}ClN_4O$ 324.77 brown microprisms	62.87 62.47	4.03 3.91	17.25 16.87	3200 m, 3070 m, 1635 s, 1595 s, 3.70 (s, N-CH_3), 6.65 (d, J = 6.0 Hz, 2 Aryl-H), 7.00 (dd, J=7.0+1.5 Hz, 1 Aryl-H), 7.25-7.40 (m, 2 Aryl-H), 7.60-7.70 (m, 2 Aryl-H), 8.10 (dd, J = 7.0+1.5 Hz, 1 Aryl-H), 8.90 (s, H at C-3), 10.50 (s, 1 N-H)

[a] in brackets ^{13}C nmr signals with deuterium induced shifts are shown

product **10/11** was recorded in this method as the first step. Then deuterium oxide/water (1:1) was added to the solution to exchange all NH protons in the molecule. From this deuterium oxide/water solution again a ^{13}C nmr was recorded: this caused a shift in all carbon signals neighbored to atoms with NH protons. Overlaying both spectra indicated the carbons neighbored to NH with doubled signals. As example, 2-phenylamino-pyrazolo[4,3-*c*]-quinolin-4-one (**10m**) showed in this experiment doubled signals not only for carbons C-4, C-5a and C-6 of the quinoline nucleus, but also for C-1, C-2 and C-6 of the 2-phenylamino substituent, which confirmed the structure of **10**, because the triazine-proton of structure **11** should not have any influence on the phenyl substituent.

When we thermolyzed the hydrazono-azide **7b**, we were able to isolate an intermediate cyclization product, which we assume to have the triazino stucture **11**. We observed, in a sample of the freshly prepared compound, in the ^{1}H nmr spectrum a NH signal of 9.3 ppm, which vanished after some hours and a new NH signal at 9.95 ppm

appeared. The structure of the endproduct was then assigned to **10b** by spectral and microanalytical data. Also in the solid state, a slow isomerization of **11** to **10b** took place, and we were not able to get unequivocal ^{13}C nmr data. We interpreted these findings in such a way that the primary cyclization leads to triazines **11** in a kinetically controlled step, and then **11** rearranges to the thermodynamically more stable arylaminopyrazole **10b**. A further isomeric structure **12b**, having a phenylazo- and an imino moiety, can be excluded because of two reasons: the arylaminopyrazoles **10b** and the triazine **11** are only slightly yellowish in color, which does not fit to the chromophoric system of **12**. The second reason is that mechanistically the formation of amines from azides proceeds *via* a triplet nitrogen reaction only without reactive *ortho*-substituents [9]. A possible mechanism for the formation of **10** and **11** starts with an electrocyclization of N1 of the azide at the more basic NH of the hydrazone to give the unstable triazine **11**, followed by ring opening (maybe with **12** as the intermediate) and recyclization to the more stable arylaminopyrazole **10b**.

Summarizing the results, hetarylazides with *ortho*-acyl substituents such as azidoquinolines **7** have been shown again to give excellent starting materials for the construction of *N*-containing heterocycles, although effort is required to find the suitable reaction sequence. Differential scanning calorimetry was used successfully as a tool for the synthetic chemist in thermolytic reactions because it gives both hints for suitable reaction temperatures and the stability of the reaction product before the reaction itself is performed.

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 25-500 °C, with a heating rate of 2-10 °C/minute, and 1.5-5 mg compound in sealed aluminium crucibles (11 bar). Infrared spectra were taken as potassium bromide pellets on a Perkin-Elmer 298 spectrophotometer. The ^1H nmr spectra were recorded on a Varian Gemini 200 (200 MHz) or a Bruker AM 360 instrument (360 MHz). Chemical shifts are reported in ppm from internal tetramethylsilane standard and are given in δ-units. The solvent for NMR spectra was deuteriodimethylsulfoxide unless otherwise stated. ^{13}C nmr spectra were recorded on a Bruker AM 360 instrument (90 MHz). Microanalyses were performed on a Fisons elemental analyzer, Mod. EA1108 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 60 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-Acetyl-4-hydroxy-2(1*H*)-quinolones (**1a-c**) were obtained from the corresponding anilines and diethyl malonate in a two step reaction according to literature procedures [5]. 3-Benzoyl-4-hydroxy-2(1*H*)-quinolones (**1h-j**) were obtained from 4-benzoyloxyquinolones by a Fries rearrangement according to literature procedures [6]. 4-Chloro-3-formyl-2(1*H*)-quinolones (**5d-g**) were obtained from 4-chloro-3-dichloromethyl-2-quinolones according to literature procedures [7]. 3-Arylhydrazonomethyl-4-chloro-2(1*H*)-quinolones **8l-m** and 3-arylhydrazonomethyl-4-(4-methylphenylsulfonyloxy)-2(1*H*)-quinolones **9a-c** were prepared according to literature procedures [8].

General Procedure for the Synthesis of Sodium 3-Acyl-2-oxo-1,2-dihydroquinoline-4-olates (**2a-c, h-j**).

A solution of the corresponding 3-acyl-4-hydroxy-2(1*H*)-quinolones (**1a-c, h-j**) (0.010 mol) in dry diethylether (50 ml) was combined with a small excess of sodium methanolate, obtained from sodium (0.011 mol) in methanol (5 ml). The reaction mixture was stirred at 20 °C for 1 hour, the resulting precipitate filtered by suction and dried at room temperature. The yields are given in Table 1.

General Procedure for the Synthesis of 3-Acyl-4-(4-methylphenylsulfonyloxy)-2(1*H*)-quinolones (**3a-c, h-j**).

A suspension of the corresponding powdered sodium salt of **2a-c, h-j** (0.008 mol) and a small excess of tosyl chloride (0.009 mol) in dry acetonitrile (20 ml) was heated under reflux with intensive stirring for 3 hours. After cooling to 20 °C the reaction mixture was poured into ice water (150 ml), the resulting precipitate filtered, washed with water (200 ml) and dried at room temperature. Experimental, analytical and spectral data are given in Table 1.

General Procedure for the Synthesis of 3-Acetyl-4-azido-2(1*H*)-quinolones **4a-c** and 4-Azido-3-formyl-2(1*H*)-quinolones **4d-g**.

A solution of the corresponding 3-acetyl-4-tosyloxy-2(1*H*)-quinolone **3a-c** or 4-chloro-3-formyl-2(1*H*)quinolone **5d-g** (0.010 mol) in dimethylformamide (30 ml) was combined with a small excess of sodium azide (0.011 mol) and stirred at room temperature for the periods given in Table 2. Then the reaction mixture was poured into ice/water (250 ml), the obtained precipitate filtered by suction and dried at room temperature. Experimental, analytical and spectral data are given in Table 2. Azidoquinolones **4a-c** and **4f** we have been described already in earlier reports [2a-c] without having the possibility to obtain DSC experiments. These data are listed now in Table 2.

General Procedure for the Synthesis of 3-(1-Arylhydrazonoalkyl)-4-azido-2(1*H*)-quinolones **7a-o**.

A suspension of 3-acyl-4-azido-2(1*H*)-quinolones **4a-g** (0.002 mol) in glacial acetic acid (10 ml) was combined with a small excess of the corresponding arylhydrazine **6a-c** (0.0022 mol) and stirred at 20 °C for 4-5 hours. Then the reaction mixture was poured onto ice/water (100 ml), the resulting precipitate filtered by suction and washed with water. Experimental, analytical, spectral and calorimetric data are given in Table 3.

General Procedure for the Synthesis of 2-Arylamino-pyrazolo[4,3-*c*]quinolin-4(5*H*)-ones **10a-o**.

A suspension of the corresponding 3-(1-arylhydrazonoalkyl)-4-azido-2(1*H*)-quinolone **7a-o** (0.002 mol) in the solvent listed in Table 4 (15 ml) was heated under reflux for the periods listed in

Table 4. After cooling to room temperature the solvent was removed under reduced pressure and the resulting oil treated with cyclohexane to obtain a microcrystalline precipitate. The product was filtered by suction, dried at room temperature and recrystallized from the solvent given in Table 4. Experimental, analytical and spectral data are given in Table 4.

9-Methyl-11-phenyl-5,6,11,12-tetrahydro-4*H*-benzo[*ij*][1,2,3]triazino[4,5-*b*]quinolizin-8-one (**11**).

A suspension of 1-azido-2-(1-phenylhydrazonoethyl)-6,7-tetrahydro-5*H*-benzo[*ij*]quinolizin-3-one (**7b**) (0.56 g, 1.6 mmol) in bromobenzene (20 ml) was heated under reflux for 2 hours. After cooling to room temperature the solvent was removed under reduced pressure and the resulting oil treated with cyclohexane to obtain a microcrystalline precipitate. The product was filtered by suction, dried at room temperature and recrystallized from bromobenzene. The yield was 0.35 g (66 %), light brown prisms, mp 270-275 °C dec; ir: 3240 w, 1630 s, 1600 s cm^{-1}; ^1H nmr: δ 2.0 (m, CH_2), 2.60 (s, CH_3), 2.90 (m, 2 H, Ar-CH_2), 3.95 (m, 2 H, N-CH_2), 6.70 (t, 1 H, Ar-H), 6.95-7.40 (m, 6 H, Ar-H), 7.85 (dd, J = 7.0+1.5 Hz, 1 H, Ar-H), 9.30 (s, 1 H, N-H). Triazine **11** was expected to be stable at room temperature. But it was found that it isomerized slowly to give after some hours **10b**.

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REFERENCES AND NOTES

[1] Organic Azides in Heterocyclic Synthesis, Part 27; Part 26: W. Stadlbauer, W. Fiala, M. Fischer and G. Hojas, *J. Heterocycic. Chem.*, in press.

[2a] P. Roschger and W. Stadlbauer, *Lieb. Ann. Chem.*, 821 (1990); [b] P. Roschger and W. Stadlbauer, *Lieb. Ann. Chem.*, 401 (1991); [c] W. Steinschifter, W. Fiala and W. Stadlbauer, *J. Heterocyclic Chem.*, **31**, 1647 (1994); [d] W. Stadlbauer, S. Prattes and W. Fiala, *J. Heterocyclic Chem.*, **35**, 627 (1998).

[3a] L. Checchi, F. Melani, G. Palazzino, G. Filacchioni and C. Martini, *Farmaco Ed. Sci.*, **40**, 509 (1985); [b] F. Melani, L. Checchi, G. Palazzino, G. Filacchioni, C. Martini, E. Penacchi and A. Lucacchini, *J. Med. Chem.*, **29**, 291 (1986); [c] L. Ismaili, B. Refouvelet, J. F. Robert, *J. Heterocyclic Chem.*, **36**, 719 (1999).

[4] Th. Kappe and W. Stadlbauer, *Molecules*, **1**, 255 (1996).

[5] P. Roschger, W. Fiala and W. Stadlbauer, *J. Heterocyclic Chem.*, **29**, 225 (1992).

[6] Th. Kappe and B. Schnell, *J. Heterocyclic Chem.*, **33**, 663 (1996).

[7a] W. Fiala and W. Stadlbauer, *J. Prakt. Chem.*, **335**, 128 (1993); [b] W. Fiala, dissertation, Karl-Franzens University of Graz (Austria), 1993.

[8] G. Hojas, dissertation, Karl-Franzens University of Graz (Austria), 1999.

[9a] P. A. S. Smith, in "Azides and Nitrenes", E. F. V. Scriven, ed., Academic Press, Orlando, Florida, 1984; [b] E. F. V. Scriven, K. Turnbull, *Chem. Rev.*, **88**, 297 (1988).

[10] V. A. Bakulev, C. O. Kappe and A. Padwa, in "Organic Synthesis: Theory and Applications", Vol. **3**, 149, T. Hudlicky, ed., JAI Press Inc., Greenwich/USA - London, 1996.

[11a] P. E. Pfeffer, K. M. Valentine and F. W. Parrish, *J. Am. Chem. Soc.*, **101**, 1265 (1978); [b] J. Reuben, *J. Am. Chem. Soc.*, **106**, 6180 (1984).