Reactions of quinazolinium salts with quaternary heterocyclic salts yielding 3-hetarylquinolines

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A novel type of transformations of the pyrimidine ring under the action of C-nucleophiles was found and a new method was developed for the synthesis of 3-hetarylquinolines from quinazoline derivatives and quaternary heterocyclic salts. An independent synthesis was carried out and transformations of one of the probable intermediates were studied. By-products were isolated. The effects of the nature of the heterocycle and substituents on the course of the ring transformation reaction were found, and the mechanism of the reaction was suggested.

Key words: quinazolinium salts, quaternary heterocyclic salts, ring transformation reaction, quinoline derivatives.

Quinazoline derivatives can be considered both as pyrimidine derivatives, for which nucleophilic addition at positions 2, 4, and 6 and ring transformations are typical,[1,2] and as condensed diazine systems that are similar in electron deficiency to *symm*-triazine derivatives.[3—5]

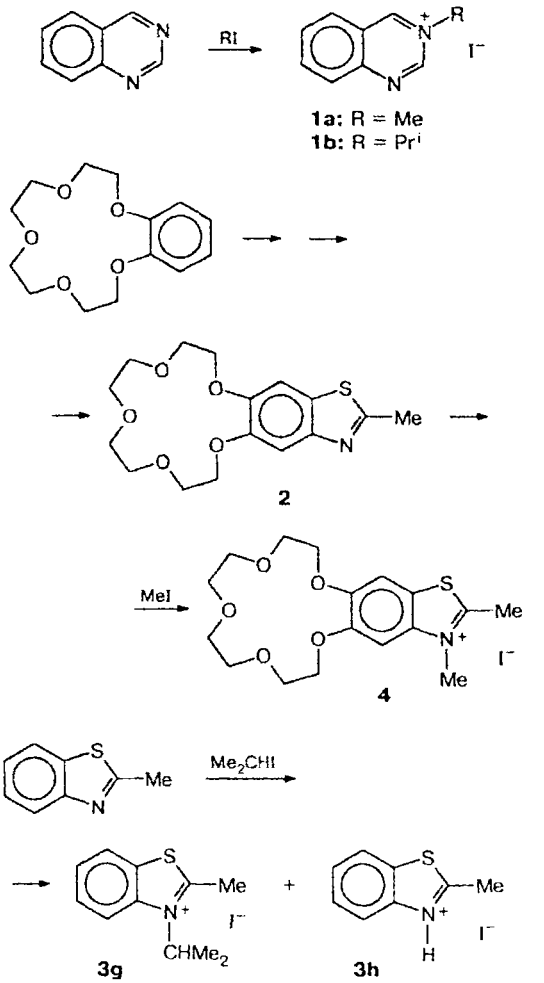
It is known[6,7] that quinazoline derivatives exhibit high reactivity toward C-nucleophiles. Previously,[8,9] it was found that quinazoline and its derivatives react with quaternary heterocyclic salts in an Ac_2O medium to form carbocyanine and styryl dyes. The reaction of 3-methylquinazolinium iodide with quaternary salts of some 2(4)-methyl derivatives of heterocyclic bases in pyridine resulted in ring transformation of the quinazoline bicycle to form 3-hetarylquinolines.[10]

It was of interest to find the regularities of the reactions of quinazolinium salts with quaternary heterocyclic salts under the action of basic reagents, which can provide information on the mechanism of the reaction of ring transformation of the quinazoline bicycle.

N-Metylquinazolinium iodide, which was required for this reaction, was prepared by quaternization of quinazoline with methyl iodide.[9] The resulting salt was a mixture of 3-methylquinazolinium iodide (**1a**) and 1-methylquinazolinium iodide (the latter does not react with C-nucleophiles[9,11]) in a ratio of 5 : 1. *N*-Methylquinazolinium iodide was used without separation,[6,9] and therefore, for the procedures under consideration, the yields are given with respect to 3-methylquinazolinium iodide (**1a**) introduced into the reaction.

3-Isopropylquinazolinium iodide (**1b**) was prepared by heating quinazoline with isopropyl iodide in a sealed tube (Scheme 1) and did not contain an admixture of 1-isopropylquinazolinium iodide. Apparently, steric hindrance at the N(1) atom due to the presence of the

Scheme 1



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benzene ring prevents the formation of the quaternary salt that bears the bulky isopropyl moiety at N(1) of the heterocycle.

Quaternary heterocyclic salts **3a—f**, **5**, and **6** were prepared by heating of 2-methylbenzothiazole, 2-methylbenzoxazole, 2-methylquinoline, 2-methylnaphtho-[1,2-*d*]thiazole, 2-methyl-5-methoxybenzothiazole, 2-methyl-5-phenylbenzothiazole, 4-methylquinoline, and 2-methyl-5-phenylthiazole, respectively, with MeI in a sealed tube. New quaternary salt **4** was prepared similarly from crown-containing benzothiazole **2**, which, in turn, has been synthesized in four steps from benzo-15-crown-5 according to known procedures.[12,13] According to the data of ^{1}H NMR spectroscopy, heating of 2-methylbenzothiazole with PrⁱI in a sealed tube afforded a mixture of 3-isopropyl-2-methylbenzothiazolium iodide (**3g**) and unreactive 2-methylbenzothiazolium iodide (**3h**) in a ratio of 1 : 1.85, which was used without separation. The yield of 3-(2-benzothiazolyl)quinoline (**7a**) with respect to iodide **3g**, which was introduced into the reaction, is given in the Experimental section.

It was found that boiling of 3-alkylquinazolinium iodide (**1a,b**) with an excess of the quaternary heterocyclic salt (**3a—g** or **4—6**) in Py gave 3-hetarylquinolines (**7a—f** and **8—10**) in yields of up to 63% (Scheme 2, Table 1).

The use of quinoline instead of Py as a base did not lead to an increase in the yield of compound **7**, while in the presence of strong bases, such as piperidine, 3-hetarylquinolines were not formed at all.

The above-mentioned data allow definite conclusions about the mechanism of ring transformation of quinazolinium salts into 3-hetarylquinolines (Scheme 3). Previously,[9] we have suggested the mechanism of formation of trimethine dyes from quinazoline derivatives and quaternary heterocyclic salts in a medium of Ac_2O or Et_3N, which involves the stage of formation of the 1 : 1 adduct at position 2 of the quinazoline bicycle with one molecule of C-nucleophile. In our case, when we changed the **1a** : **3a** reagent ratio from 1 : 1 to 1.0 : 8.3, the yield of 3-(2-benzothiazolyl)quinoline **7a** was increased also only slightly. This corresponds more closely to the suggestion that the reaction proceeds through the 1 : 1 adduct.

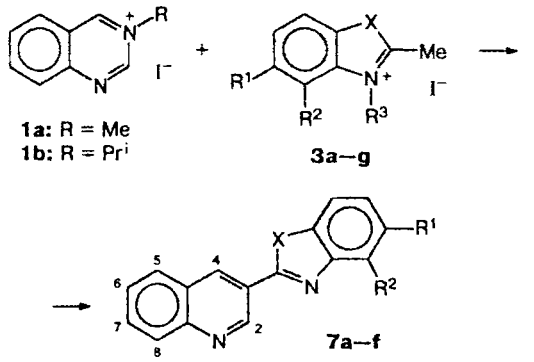
1a : **3a**, mol/mol	2 : 1	1 : 1	1 : 2	1 : 4	1.0 : 8.3
Yield of **7a** (%)	24	40	49	50	49

The use of 3-isopropylquinazolinium iodide (**1b**) instead of compound **1a** did not change substantially the yield of **7a**, which is evidence in favor of the fact that ring transformation proceeded predominantly through a product of addition of anhydrobase of salt **3a** at position 2, which is sterically more accessible than position 4.

We suggest that under the action of pyridine, quaternary salt **3** gave anhydrobase **11**. As a result of the nucleophilic attack of the enamine carbon atom, compound **11** was added to position 2 of the quinazoline bicycle to form adduct **12**. Then adduct **12** underwent cleavage to form, apparently, compound **13**. Its successive cyclization, which was accompanied by elimination of alkylamine, gave quaternary salt **14**. At the final stage, *N*-dealkylation occurred to form 3-hetarylquinoline **7**.

With the aim of studying the mechanism of the reaction of ring transformation of the pyrimidine ring of

Scheme 2



3, 7: R^1 = H (**a—c, g**), MeO (**e**), Ph (**f**), R^2 = H (**a—c, e—g**), $R^1 + R^2 = C_4H_4$ (**d**); X = S (**a, d—g**), O (**b**), CH=CH (**c**); **3**: R^3 = Me (**a—c, d—f**), Pr^i (**g**)

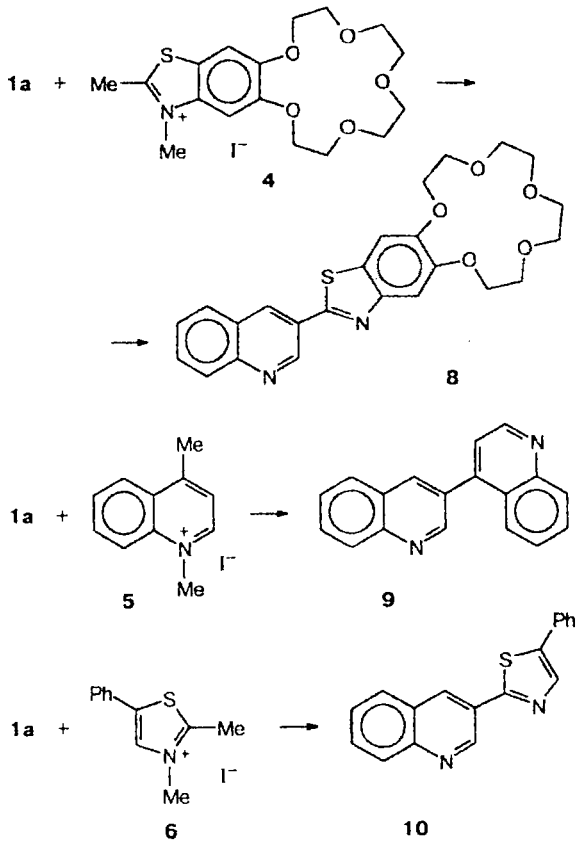
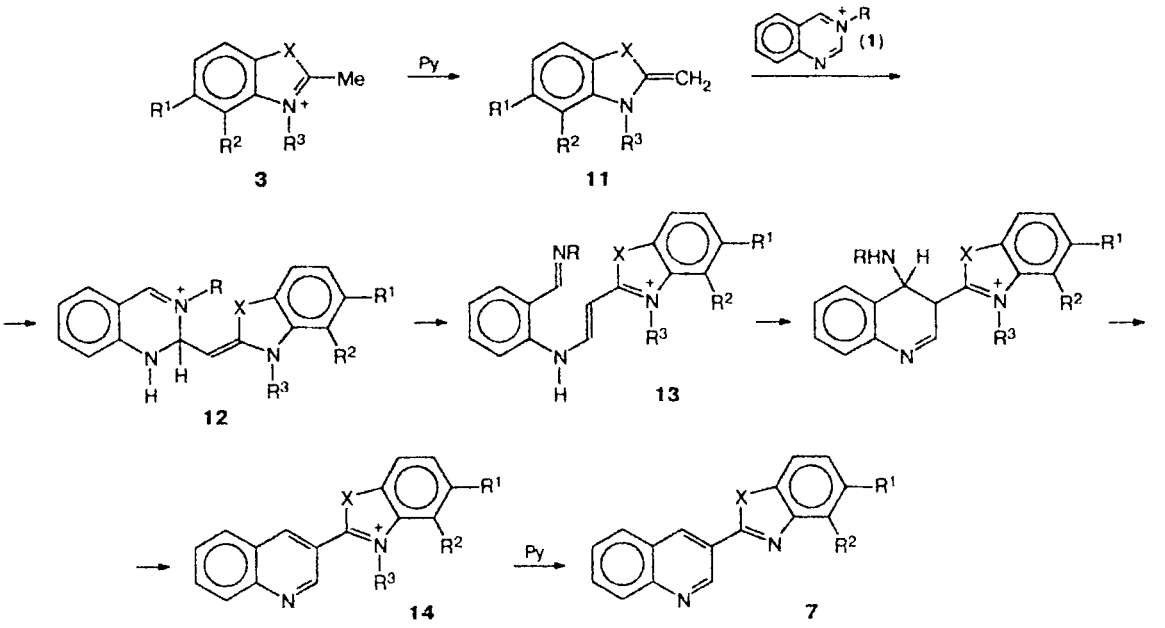


Table 1. Characteristics of hetarylquinolines **7a—f** and **8—10** synthesized from **1a,b**, **3a—g**, and **4—6**

Starting compounds	Hetaryl-quinoline	M.p./°C (from EtOH)	Yield (%)	Found / Calculated (%)			Molecular formula
				C	H	N	
1a, **3a**	**7a**	199—200[a]	50	—	—	—	$C_{16}H_{10}N_2S$
1b, **3a**	**7a**	199—200[a]	55	—	—	—	$C_{16}H_{10}N_2S$
1a, **3g**	**7a**	199—200[a]	28	—	—	—	$C_{16}H_{10}N_2S$
1a, **3b**	**7b**	178—179[a]	5	—	—	—	$C_{16}H_{10}N_2O$
1a, **3c**	**7c**	173—174[b]	20	—	—	—	$C_{18}H_{12}N_2$
1a, **3d**	**7d**	175—177	25	76.64 76.90	3.94 3.87	8.63 8.97	$C_{20}H_{12}N_2S$
1a, **3e**	**7e**	173—174	32	69.42 69.84	4.27 4.14	9.34 9.58	$C_{17}H_{12}N_2OS$
1a, **3f**	**7f**	169—171	55	78.05 78.08	4.23 4.17	7.85 8.28	$C_{22}H_{14}N_2S$
1a, **4**	**8**	183—185	39	60.32 60.11	5.31 5.68	—	$C_{24}H_{24}N_2O_5S \cdot 1.5H_2O$
1a, **5**	**9**	102—103[c]	19	84.06 84.35	4.77 4.72	10.63 10.93	$C_{18}H_{12}N_2$
1a, **6**	**10**	109—111	63	74.53 74.97	4.25 4.19	9.42 9.71	$C_{18}H_{12}N_2S$

[a] *Cf.* Ref. 14. [b] *Cf.* Ref. 15. [c] *Cf.* Ref. 16.

Scheme 3

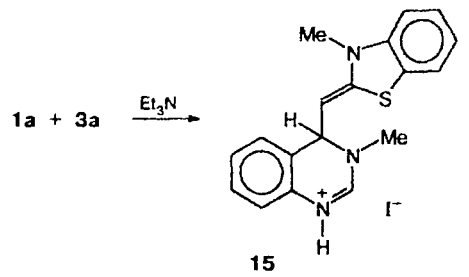


salt **1a** in detail, we attempted to isolate the by-products and to study the possible intermediates.

Previously,[9] we have found that compounds analogous to adduct **15** were formed in the reaction of the quaternary heterocyclic salt with 3-methylquinazolinium iodide (**1a**) under the action of Et_3N in MeCN followed by cleavage of the pyrimidine fragment in an Ac_2O medium to form a trimethine dye. It should be suggested that compound **15**, which was obtained in 74% yield (Scheme 4) as a result of the addition of anhydrobase of quaternary salt **3a** at position 4 of the quinazoline bicycle, is one of the possible intermediates in the synthesis of 3-(2-benzothiazolyl)quinoline (**7a**).

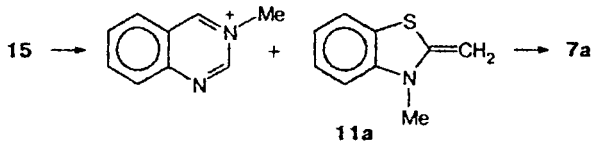
Actually, boiling of adduct **15** in pyridine gave, while in low yield (18%), compound **7a** (Scheme 5). Apparently, the low yield of **7a** is due to the fact that dissocia-

Scheme 4



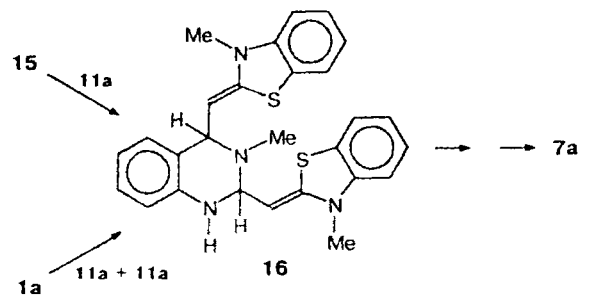
tion of adduct **15** into the quinazolinium cation and anhydrobase **11a** followed by ring transformation according to Scheme 3 through an intermediate product of addition at position 2 (of type **12**) is necessary for the reaction to occur.

Scheme 5



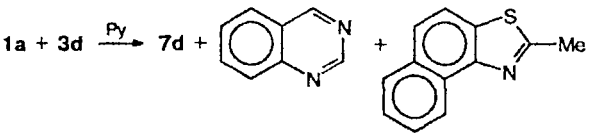
On the other hand, boiling of a mixture of equimolar amounts of compounds **15** and **3a** in pyridine afforded **7a** in 60% yield, which is indicative of the possible addition of the second molecule of anhydrobase **11a** to form adduct **16** (Scheme 6). This agrees also with the fact that the maximum yield of **7a** in the reaction of **1a** with **3a** was observed at a **1a** : **3a** ratio of 1 : 2, and when this ratio was further increased, no increase in the yield of **7a** was observed. Consequently, although the suggested mechanism of ring transformation of the quinazoline bicycle (Scheme 3) is, apparently, the major one, it is not the unique pathway of formation of hetarylquinolines **7**.

Scheme 6



Chromatographic analysis of the products of the reaction of **1a** with **3d** revealed the presence of 2-methylnaphtho[1,2-*d*]thiazole and quinazoline resulting from *N*-dealkylation of the initial compounds (Scheme 7) in low yields (~2%) along with 3-hetarylquinoline **7d**. The presence of these compounds in the reaction mixture is proof of the possibility of *N*-dealkylation under the reaction conditions, which is the final stage of the ring transformation reaction of the quinazoline bicycle.

Scheme 7



The presence of the bulky *N*-substituent in quaternary salt **3g** hampers efficient *N*-dealkylation resulting in a substantial decrease in the yield of **7a** (to 28%). The efficiency of *N*-dealkylation is also affected by steric hindrances owing to the substituent in the *ortho* position with respect to the nitrogen atom of quaternary salt **14**. Thus, benzannelation of thiazolium and benzothiazolium salts led to a successive increase in the yield of 3-hetarylquinolines (63%, 50%, and 25% for **10**, **7a**, and **7d**, respectively).

It was of interest to study the effect of the nature of the heterocycle and substituents in this heterocycle on the yield of 3-hetarylquinolines **7**—**10**. The highest yields of 3-hetarylquinolines (to 63%) were observed when quaternary salts **3** and **6** based on thiazole derivatives were used (see Table 1). Salts **3c** and **5** that contain the electron-deficient pyridine ring gave isomeric diquinolyls in lower yields (~20%). We succeeded in obtaining 3-(2-benzoxazolyl)quinoline (**7b**) only in 5% yield, which is, apparently, associated with the instability of the oxazole ring of salt **3b** toward cleavage under the action of nucleophiles. Apparently, the introduction of electron-donating groups into the benzene ring of benzothiazole leads to a decrease in the *CH*-acidity of the methyl group of quaternary salt **3**, which is responsible for the lower stationary concentration of anhydrobase **11** and, correspondingly, for the decrease in the yield of 3-hetarylquinolines **7e** and **8**.

It is known that crown-containing compounds are capable of binding metal ions efficiently and selectively.[17] On the other hand, di- and polyhetaryls belong to a promising class of organic luminophores.[18]

In this connection, using compound **8** as an example, we have developed the procedure for introducing the crown fragment into 3-hetarylquinoline. This procedure enables one to prepare fluoroionophores of a novel type, which are not reported in the literature.[19]

The structures of compounds **7a**—**f** and **8**—**10** were established by ^{1}H NMR spectroscopy and mass spectrometry. The structures of **7a**—**c** were also confirmed by comparing their physicochemical characteristics with

Table 2. Mass spectra of hetarylquinolines **7a—f** and **8—10**

Compound	m/z (I_{rel} (%))*
7a	262 (100), 261 (38), 156 (39), 128 (30), 127 (34), 97 (26), 82 (34), 81 (27), 70 (41), 69 (54), 68 (32)
7b	246 (100), 245 (93), 244 (63), 220 (48), 190 (36), 144 (45), 128 (40), 127 (48), 123 (45), 101 (49), 100 (31)
7c	256 (100), 255 (91), 254 (60), 230 (38), 154 (73), 129 (72), 128 (80), 127 (41), 114 (41), 102 (42), 101 (59)
7d	312 (100), 311 (86), 158 (69), 153 (58), 127 (66), 115 (49), 114 (86), 113 (60), 76 (53), 75 (53), 63 (44)
7e	292 (100), 291 (59), 277 (42), 249 (54), 248 (44), 155 (18), 146 (20), 123 (19), 95 (54), 69 (44), 63 (18)
7f	338 (100), 337 (66), 152 (29), 139 (34), 127 (41), 101 (36), 77 (80), 76 (47), 75 (38), 69 (28), 63 (26)
8	452 (75), 321 (28), 320 (100), 305 (22), 294 (23), 293 (14), 265 (14), 264 (33), 236 (10), 160 (12), 153 (15)
9	256 (100), 255 (96), 254 (25), 227 (26), 128 (16), 101 (17), 77 (16), 76 (25), 75 (21), 74 (16), 63 (16)
10	288 (100), 287 (86), 134 (94), 133 (82), 127 (86), 109 (77), 108 (88), 90 (78), 89 (95), 69 (88), 63 (83)

* The peaks of the molecular ion and the ten most intense peaks are given.

Table 3. ^{1}H NMR spectra of hetarylquinolines **7a—f** and **8—10** ($CDCl_3$—CCl_4, 1 : 1)

Compound	δ (*J*/Hz)
7a[a]	7.51 (m, 1 H, H-5′); 7.59 (m, 1 H, H-6′); 7.71 and 7.87 (both m, 2 H, H-6, H-7); 8.11 (d, 1 H, H-5); 8.13 (d, 1 H, H-7′); 8.18 (d, 1 H, H-4′, $J_{4',5'}$ = 7.6); 8.20 (d, 1 H, H-8, $J_{8,7}$ = 7.9); 9.01 (d, 1 H, H-4, *J* = 2.1); 9.57 (d, 1 H, H-2, *J* = 2.1)
7b	7.43 (m, 2 H, H-5′, H-6′); 7.66 (m, 2 H), 7.84 (m, 2 H), 7.99 (dd, 1 H, *J* = 8.1), 8.21 (d, 1 H, *J* = 8.4) (H-6, H-7, H-4′, H-7′, H-5, H-8); 9.02 (d, 1 H, H-4, *J* = 2.0); 9.76 (d, 1 H, H-2, *J* = 2.0)
7c[a]	7.66 and 7.82 (both m, 4 H, H-6, H-6′, H-7, H-7′); 8.03 (d, 1 H, H-5′, *J* = 8.2); 8.10 (d, 1 H, H-5, *J* = 8.2); 8.15 (m, 2 H, H-8, H-8′); 8.34 (d, 1 H, H-3′, *J* = 8.5); 8.53 (d, 1 H, H-4′, *J* = 8.5); 9.16 (s, 1 H, H-4); 9.81 (s, 1 H, H-2)
7d	7.62 (m, 2 H, H-5′, H-6′); 7.73 and 7.79 (both m, 2 H, H-6, H-7); 7.84 (d, 1 H, *J* = 8.8), 7.96 (m, 3 H) (H-8′, H-5, H-7′, H-9′); 8.18 (d, 1 H, H-8, *J* = 8.4); 8.84 (d, 1 H, H-4, *J* = 1.9); 8.97 (d, 1 H, H-4′, *J* = 8.2); 9.71 (d, 1 H, H-2, *J* = 1.9)
7e	3.95 (s, 3 H, OMe); 7.11 (dd, 1 H, H-6′, *J* = 8.8, *J* = 2.4); 7.65 and 7.81 (both m, 2 H, H-6, H-7); 7.65 (d, 1 H, H-4′, *J* = 2.4); 7.83 (d, 1 H, H-7′, *J* = 8.8); 7.98 (d, 1 H, H-5, *J* = 8.1); 8.19 (d, 1 H, H-8, *J* = 8.4); 8.80 (d, 1 H, H-4, *J* = 2.2); 9.6 (d, 1 H, H-2, *J* = 2.2)
7f	7.39 (m, 1 H, Ph); 7.49 (m, 2 H, Ph); 7.63 and 7.81 (both m, 2 H, H-6, H-7); 7.68—7.71 (m, 3 H, Ph, H-6′); 7.97 (d, 1 H, H-5, *J* = 8.1); 8.01 (d, 1 H, H-7′, *J* = 8.3); 8.18 (d, 1 H, H-8, *J* = 8.4); 8.35 (d, 1 H, H-4′, *J* = 1.3); 8.82 (d, 1 H, H-4, *J* = 2.1); 9.64 (d, 1 H, H-2, *J* = 2.1)
8	3.78 (m, 8 H, 4 CH_2O); 3.99 (m, 4 H, 2 CH_2O); 4.24 (m, 4 H, 2 CH_2O); 7.33 and 7.56 (both s, 2 H, H-4′, H-7′); 7.61 and 7.77 (both m, 2 H, H-6, H-7); 7.93 (d, 1 H, H-5, *J* = 8.0); 8.15 (d, 1 H, H-8, *J* = 8.4); 8.69 (br.s, 1 H, H-4); 9.56 (d, 1 H, H-2, *J* = 2.0)
9	7.45 (d, 1 H, H-3′, $J_{3',2'}$ = 8.1); 7.55 (m, 1 H, H-6′); 7.66 (m, 1 H, H-6); 7.74—7.94 (m, 4 H, H-7′, H-7, H-5′, H-5); 8.23 (both d, 2 H, H-8′, H-8); 8.32 (d, 1 H, H-4); 9.03 (d, 1 H, H-2′, $J_{2',3'}$ = 8.1); 9.08 (d, 1 H, H-2)
10	7.36—7.49 (m, 3 H, Ph); 7.59 and 7.76 (both m, 2 H, H-6, H-7); 7.65 (m, 2 H, Ph); 7.92 (dd, 1 H, H-5, *J* = 8.1, *J* = 1.4); 8.09 (s, 1 H, H-4′); 8.15 (d, 1 H, H-8, *J* = 8.0); 8.67 (d, 1 H, H-4, *J* = 2.3); 9.50 (d, 1 H, H-2, *J* = 2.3)

[a] In DMSO-d_6.

those reported previously. The data of elemental analysis of the copounds obtained correspond to the structures suggested (see Tables 1—3).

We used the COSY and NOESY spectra for assigning signals in the ^{1}H NMR spectra of 3-hetarylquinolines. In the ^{1}H NMR spectra of compounds **7a—f** and **8—10** in a 1 : 1 $CDCl_3$: CCl_4 mixture, the protons of the pyridine ring of the quinoline bicycle occur as doublets at δ 9.1—9.8 (H-2) and 8.3—9.0 (H-4) with the spin-spin coupling constants J_{meta} = 1.9—2.3 Hz. The signals of the protons of the benzene fragment are observed in the region of δ 7.6—8.2.

Under the action of electron impact, 3-hetarylquinolines **7a—f** and **8—10** formed stable molecular ions and $[M-H]^+$ ions, whose decomposition occurred rather selectively to form several major fragment ions, including those corresponding to the quinoline residue.

It should be noted that the melting point of diquinolyl **9** (102—103 °C) determined by us is substantially higher than the value reported in the literature[16] (83—84 °C). Apparently, the authors[16] dealt with the insufficiently pure compound or mistakenly assigned the structure of 3-(4-quinolyl)quinoline to the compound under consideration.

The reaction under study belongs to the previously unknown type of transformations of the pyrimidine ring under the action of C-nucleophiles, in the course of which the C atom is incorporated instead of the N atom to form the pyridine ring. Only several examples of the synthesis of 3-substituted hetarylquinolines were reported in the literature.[14—16] The reaction discovered by us is a new procedure for the synthesis of difficultly accessible 3-hetarylquinolines, and it demonstrates a new approach to the synthesis of organic luminophores based on di- and polyhetaryls.

Experimental

The ^{1}H NMR spectra were recorded on Bruker AC-200p and Bruker AMX-400 spectrometers with Me_4Si as the internal standard. A 1 : 1 $CDCl_3$: CCl_4 mixture and DMSO-d_6 were used as solvents. The chemical shifts were measured with an accuracy of 0.01 ppm. The spin-spin coupling constants were measured with an accuracy of 0.1 Hz.

The mass spectra were obtained on a Varian MAT-311A instrument (the energy of ionizing electrons was 70 eV) with direct introduction of the sample into the ionization zone. The course of the reactions was monitored by TLC on DC-Alufolien Kieselgel 60 F_{254} plates.

3-Isopropylquinazolinium iodide (1b). A mixture of quinazoline (2.6 g, 20 mmol) and Pr^{i}I (2.5 mL, 25 mmol) was heated in a sealed tube at 90 °C for 13 h. The resulting product was successively washed with hot benzene and acetone. The yield of **1b** was 3.78 g (63%), m.p. 202—204 °C (with decomp.). ^{1}H NMR (DMSO-d_6), δ: 1.84 (d, 6 H, 2 Me, J = 6.6 Hz); 5.28 (m, 1 H, NCH); 8.27 and 8.61 (both m, 2 H, H-6, H-7); 8.45 (d, 1 H, J = 8.4 Hz), 8.69 (d, 1 H, J = 8.3 Hz) (H-5, H-8); 9.92 (d, 1 H, H-4, J = 1.4 Hz); 10.71 (d, 1 H, H-2, J = 1.4 Hz). Found (%): C, 43.84; H, 4.27; N, 9.14. $C_{11}H_{13}IN_2$. Calculated (%): C, 44.00; H, 4.37; N, 9.33.

2-Methyl-3-isopropylbenzothiazolium iodide (3g) and 2-methylbenzothiazolium iodide (3h). A mixture of 2-methylbenzothiazole (2.98 g, 20 mmol) and Pr^{i}I (2.5 mL, 25 mmol) was heated in a sealed tube at 135 °C for 80 h. The resulting product was successively washed with hot benzene and acetone. The yield of the mixture of **3g** and **3h** was 4.78 g. ^{1}H NMR of **3g** (DMSO-d_6), δ: 1.85 (d, 6 H, 2 Me, J = 6.9 Hz); 3.33 (s, 3 H, Me); 5.49 (m, 1 H, NCH); 7.88 and 7.93 (both m, 2 H, H-5, H-6); 8.55 (d, 1 H, J = 8.0 Hz), 8.60 (d, 1 H, J = 8.4 Hz) (H-4, H-7). ^{1}H NMR of **3h** (DMSO-d_6), δ: 2.90 (s, 3 H, Me); 7.49 and 7.57 (both m, 2 H, H-5, H-6); 8.00 (d, 1 H, J = 8.1), 8.13 (d, 1 H, J = 8.1 Hz) (H-4, H-7). The ratio **3g** : **3h** = 1 : 1.85.

2,3-Dimethyl-5,6,8,9,11,12,14,15-octahydro-1,4,7,10,13-pentaoxacyclopentadecino[2,3-*f*]benzothiazolium iodide (4). A mixture of crown-containing benzothiazole **2** [12,13] (0.71 g, 2.1 mmol) and Pr^{i}I (0.65 mL, 10 mmol) was heated in a sealed tube at 90 °C for 60 h. The precipitate was filtered off and washed with benzene. The yield of **4** was 0.80 g (76%), m.p. 186—189 °C (with decomp.). ^{1}H NMR (DMSO-d_6), δ: 3.17 (s, 3 H, Me); 3.73 (m, 8 H, 4 OCH_2); 3.94 (m, 4 H, 2 OCH_2); 4.24 (m, 5 H, NMe, OCH_2); 4.36 (m, 2 H, OCH_2); 7.87 and 8.00 (both s, 2 H, H-4, H-7). Found (%): C, 40.76; H, 4.73; N, 2.82. $C_{17}H_{24}INO_5S \cdot H_2O$. Calculated (%): C, 40.88; H, 5.25; N, 2.81.

Synthesis of 3-hetarylquinolines 7a—f, 9, and 10 (general procedure). A mixture of 3-alkylquinazolinium iodide (**1a,b**) (1 mmol), quaternary heterocyclic salt **3a—g**, **5**, or **6** (2 mmol), and dry Py (5 mL) was refluxed for 5 h (**7a,d—f** and **10**), 9 h (**7c** and **9**), or 22 h (**7b**). The reaction mixture was concentrated *in vacuo*, and the dry residue was repeatedly extracted with hot benzene. The extract was concentrated *in vacuo*. The residue was chromatographed on silica gel (Kieselgel 60, 0.063—0.100 mm, Merck) (a 6 : 1 benzene : AcOEt mixture (**7a,d,e**), a 5 : 1 benzene : AcOEt mixture (**7b**), a 6 : 1 heptane : AcOEt mixture (**7f**), or AcOEt (**7c** and **9**) were used as the eluents). Compound **10** was isolated by flash chromatography on a dry column packed with silica gel (Kieselgel 60, 5—40 μm, Merck); gradient elution with a successive change from benzene to a 1 : 1 benzene : AcOEt mixture was used.

3-(5,6,8,9,11,12,14,15-Octahydro-1,4,7,10,13-pentaoxacyclopentadecino[2,3-*f*]benzothiazol-2-yl)quinoline (8). A mixture of *N*-methylquinazolinium iodide (0.13 g, 0.48 mmol), compound **4** (0.40 g, 0.80 mmol), and dry Py (5 mL) was refluxed for 5 h. The reaction mixture was concentrated *in vacuo*. The dry residue was extracted with hot AcOEt. The extract was concentrated *in vacuo*. The residue was chromatographed on silica gel (Kieselgel 60, 63—100 μm, Merck); a 1 : 1.5 : 0.1 AcOEt : EtOH : MeOH mixture was used for elution. Compound **8** was obtained in a yield of 0.075 g.

3-Methyl-4-[(3-methyl-3*H*-benzothiazol-2-ylidene)methyl]-3,4-dihydroquinazolinium iodide (15). A mixture of *N*-methylquinazolinium iodide (**1a**) (0.99 g, 3.6 mmol), 2,3-dimethylbenzothiazolium iodide (**3a**) (0.91 g, 3.1 mmol), Et_3N (0.42 mL, 3 mmol), and MeCN (9 mL) was kept at ~20 °C for 1 day. The reaction mixture was cooled. The precipitate was filtered off and washed with MeCN. The yield of **15** was 0.97 g (74%), m.p. 186—189 °C (with decomp.). ^{1}H NMR (DMSO-d_6), δ: 3.28 and 3.36 (both s, 6 H, 2 NMe); 4.92 (d, 1 H, α-H, J = 10.0 Hz); 5.63 (d, 1 H, H-4, J = 10.0 Hz); 7.01 (m, 1 H, H-5′); 7.08 (d, 1 H, H-7′, J = 8.0 Hz); 7.19 (d, 1 H, H-5, J = 8.0 Hz); 7.27—7.36 (m, 3 H, H-7, H-8, H-6′); 7.45 (m, 1 H, H-6); 7.53 (d, 1 H, H-4′, J = 7.7 Hz); 8.53 (s, 1 H, H-2); 12.2 (br.s, 1 H, NH). Found (%): C, 49.97; H, 4.07; N, 9.44. $C_{18}H_{18}IN_3S$. Calculated (%): C, 49.66; H, 4.17; N, 9.65.

3-(2-Benzothiazolyl)quinoline (4a). ***A.*** A solution of compound **15** (0.44 g, 1 mmol) in dry Py (5 mL) was refluxed for 5 h. The reaction mixture was concentrated. The residue was repeatedly extracted with boiling benzene. The extracts were combined and concentrated *in vacuo*. The dry residue was extracted with a 2 : 1 hexane : benzene mixture. The extracts were concentrated *in vacuo*. The resulting product was purified chromatographically according to the general procedure. The yield of **7a** was 0.047 g (18%).

B. A mixture of compound **15** (0.22 g, 0.5 mmol), **3a** (0.15 g, 0.5 mmol), and dry Py (5 mL) was refluxed for 5 h. The reaction mixture was treated according to the general procedure. The yield of **7a** was 0.078 g (60%).

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