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IMIDAZO[1,5-*a*]- AND THIAZOLO[3,4-*a*]-QUINOXALINES BASED ON 3-(α-THIOCYANO-BENZYL)QUINOXALIN-2(1H)-ONE

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When 3-(α-thiocyanobenzyl-2(1H)-one is heated, competing processes of [a]-annelation of the imidazole or thiazole rings occurs with formation of imidazo[1,5-a]- and thiazolo[3,4-a]quinoxalin-4(5H)-ones.

Keywords: imidazo[1,5-*a*]quinoxalines, thiazolo[3,4-*a*]quinoxalines, quinoxalines, Kornblum reaction.

The fact that 3-(α-thiocyanobenzyl)quinoxalin-2(1H)-one (**1**) [1] has endocyclic imine, carbamoyl, and exocyclic benzylthiocyanate functional groups capable to tautomerism and also the reality of thiocyano–isothiocyano isomerism makes it possible to obtain various condensed systems based on it. We showed earlier that in acid medium, the quinoxalinone **1** is isomerized to the tricyclic 1-imino-3-phenylthiazolo[3,4-*a*]-quinoxalin-4(5H)-one (**2**) [1]. This work is devoted to realization of another direction for conversions of compound **1**: to derivatives of the tricyclic imidazo[1,5-*a*]quinoxaline system.

At the melting point of thiocyanate **1** (205°C), rapid crystallization of the melt occurs with formation of a high-melting compound that is difficultly soluble even in hot DMSO and DMF. The latter compound is not identical to compound **2**; but judging from elemental analysis and mass spectra (Table 1), it is isomeric to **2** and also to the starting quinoxaline **1**. We can explain these isomeric relationships by the ability of organic thiocyanates to be easily isomerized to isothiocyanates [2] and we can suggest the next conversions on heating compound **1**, including isomerization of thiocyanate **1** to isothiocyanate **3** and cyclization of the latter as a result of nucleophilic attack by the $N_{(4)}$ of the quinoxaline ring on the carbon atom of the isothiocyano group. Further stabilization of the zwitterion intermediate **4** formed occurs by migration of a benzyl proton to the nucleophilic centers, the $N_{(2)}$ or S atoms, with formation of the end products **5** and/or **6**.

In the $^{13}C\{^1H\}$ NMR and ^{13}C NMR spectra of the solution of the isolated product in DMSO (Table 2), the signal furthest downfield at 160.33 ppm can be assigned to the carbon atom of the dyad C=N of the imidazole ring of tautomer **5**, since the carbon atom of the N–C(=S)–N moiety in tautomer **6** usually resonates significantly further downfield (190-210 ppm) [3]. Thus we can choose between tautomeric structures **5** and **6** more likely in favor of the former. The ^1H NMR spectrum of the compound obtained in the same solvent (Table 1) does not contradict this conclusion, since the presence in the spectrum of a singlet peak at 13.72 ppm (1H) more likely suggests the presence of an SH group rather than the NH group of the thione tautomer: the latter usually appears in the 8-11 ppm region for solutions of related tautomeric systems in DMSO, while the SH group of the thiolactim tautomer usually appears near 14 ppm [4-6].

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TABLE 1. Physicochemical and Spectral Characteristics of Synthesized Compounds

Compound	Empirical formula	Found, M / Calculated, M	Found, % / Calculated, %				mp*, °C	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum (DMSO-d_6), δ, ppm (spin–spin coupling constant, *J*, Hz)	Yield, %
			C	H	N	S				
5	$C_{16}H_{11}N_3OS$	293.06015 / 293.06229	65.85 / 65.51	4.08 / 3.78	14.36 / 14.32	10.88 / 10.93	>360	1670 (C=O), 1600 (C=C), 1630 (C=N), 2680-3210 (NH, SH)	7.14-7.83 (8H, m, $5H_{Ph}$, 6-, 8-H); 10.48 (1H, d, *J* = 8.25, 9-H); 11.34 (1H, s, NH); 13.72 (1H, s, SH)	90 (A); 45 (B)
8	$C_{31}H_{21}N_5O_2S$	527.13959 / 527.14160	69.82 / 70.57	4.22 / 4.01	13.87 / 13.27	5.34 / 6.08	275-276	1610 (C=N), 1670 (C=O), 2570-3210 (NH)	7.02 (1H, s, CHCl); 7.25-7.59 (18H, m, $10H_{Ph}$, 6-, 9-H, 5'-, 8'-H); 11.39 (1H, s, NH); 12.72 (1H, s, N'H)	62 (A); 30 (B); 68 (C)
11	$C_{23}H_{17}N_3SO$		71.53 / 72.04	4.67 / 4.47	10.65 / 10.96	8.67 / 8.36	285-287	1610 (C=N), 1657 (C=O), 2600-3220 (NH)	4.74 (2H, s, CH_2); 7.17-7.52 (11H, m, $5H_{Ph}$, 6-, 8-H, 2*m*-$H_{3\text{-}Ph}$, 1*p*-$H_{3\text{-}Ph}$); 8.23 (2H, br. d, 2*o*-$H_{3\text{-}Ph}$); 8.30 (1H, d, *J* = 8.36, 9-H); 11.30 (1H, br. s, NH)	50
13	$C_{15}H_{10}N_2O_2$		71.96 / 71.99	3.66 / 4.03	11.02 / 11.19	—	276-278	1605 (C=N), 1660 (C=O), 1690 (C=O), 2680-3180 (NH)	7.45-8.08 (9H, m, $5H_{Ph}$, 5-, 8-H); 12.92 (1H, s, NH)	70
14	$C_{16}H_{10}N_2O_2S$	294.04575 / 294.04630	64.93 / 65.29	3.62 / 3.42	9.50 / 9.52	11.02 / 10.89	312-315	1675 (C=O), 2600-3220 (NH)	7.17-7.66 (8H, m, $5H_{Ph}$, 6-, 8-H); 8.90 (1H, d, *J* = 8.25, 9-H); 11.39 (1H, s, NH)	15
15	$C_{16}H_{11}N_3O$	261.08850 / 261.09021	73.82 / 73.55	4.02 / 4.24	16.19 / 16.08	—	>360	1620 (C=N), 1660 (C=O), 2650-3240 (NH)	7.33-7.38 (6H, m, 6-, 8-H, 1*p*-$H_{3\text{-}Ph}$, 2*m*-$H_{3\text{-}Ph}$); 8.31 (2H, br. d, *J* = 8.80, 2*o*-$H_{3\text{-}Ph}$); 8.32 (1H, d, *J* = 8.00, 9-H); 9.22 (1H, s, 1-H); 11.49 (1H, br. s, NH)	59 (A); 11 (C)

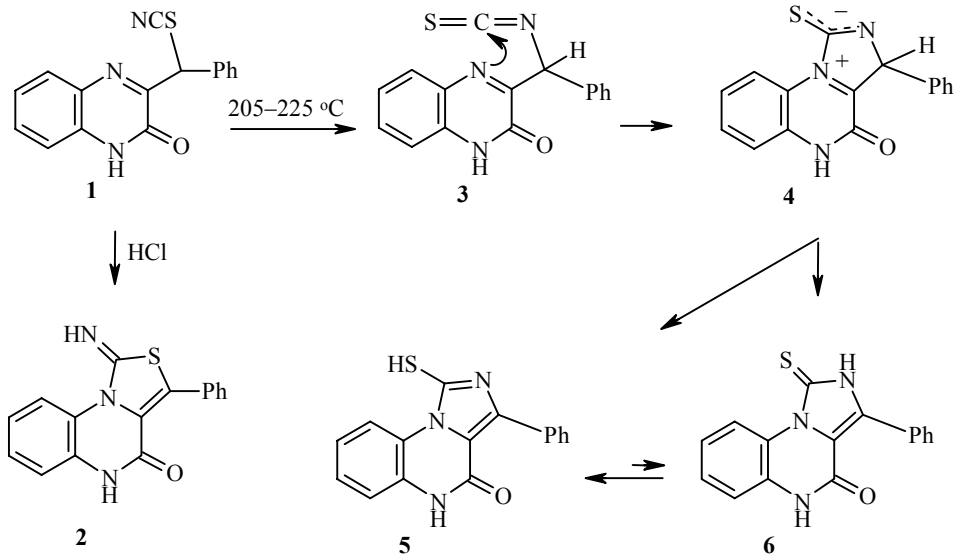
* Solvent for crystallization: DMF (**8, 11**), Ac (**13**), DMSO (**14**), MeCN–DMSO, 3:2 (**15**).

TABLE 2. ^{13}C NMR Spectra of Compounds **5** and **15** (DMSO–acetone-d_6, 10:1)

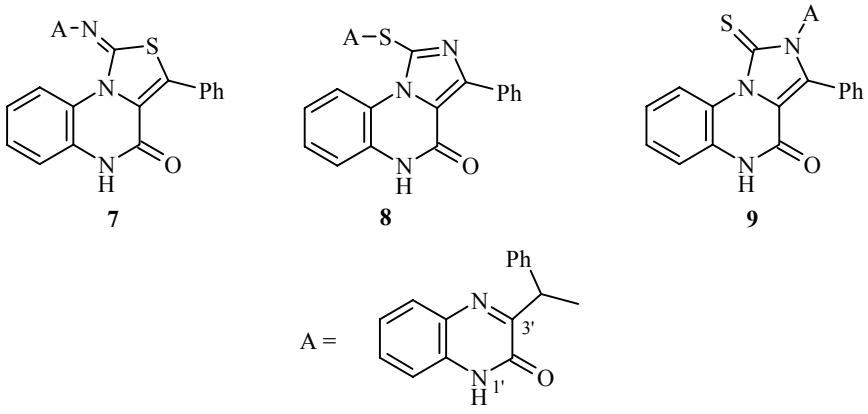
Compound	Chemical shifts, δ, ppm (spin–spin coupling constant, *J*, Hz)							
	C=O, s	C=N	$C_{(3)}$	$C_{(3a)}$	$C_{(6)}$, $C_{(9)}$	$C_{(7)}$, $C_{(8)}$	$C_{(5a)}$, $C_{(9a)}$	Ph
5	155.05	160.33 (br. s)	133.37 (s)	130.86 (s)	128,15 (dd, *J* = 162.96, 6.61); 122.49 (dd, *J* = 165.16; 8.81)	118.53 (dm, *J* = 162.52); 116.03 (dm, *J* = 158.55)	124.85 (m); 116.03 (m)	131.30 (dt, *J* = 160.75, 6.61, C_p); 130.99 (dt, *J* = 162.96, 8.15, C_o); 128.92 (dd, *J* = 160.75, 6.61, C_m); 127.71 (t, *J* = 8.81, C_i)
15	159.04	136.55 (d, *J* = 15.15)	137.14 (t, *J* = 7.63)	147.85 (t, *J* = 4.58)	131.14 (dd, *J* = 163.65; 7.63); 120.88 (dd, *J* = 163.65; 7.63)	126.73 (dd, *J* = 164.80; 7.63); 119.25 (d. br. d, *J* = 164.41; 7.63)	132.84 (t, *J* = 6.87); 120.25 (t, *J* = 3.82)	130.06 (dt, *J* = 160.98, 6.86, C_o); 131.96 (dt, *J* = 160.98, 7.63, C_p); 131.73 (dd, *J* = 160.22, 7.63, C_m); 131.73 (dd, *J* = 160.22, 7.63, C_m)

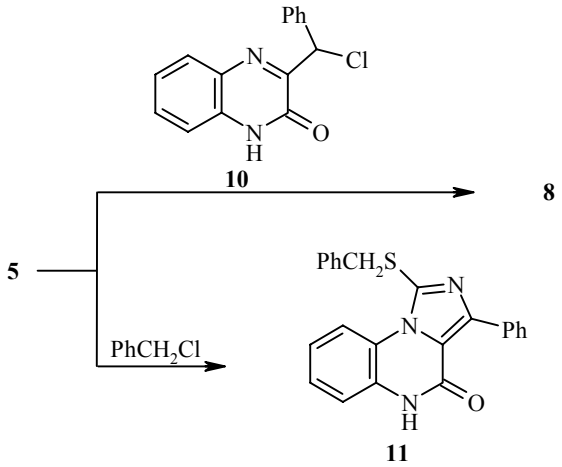
TABLE 3. ^{13}C NMR Spectra of Compound **8** (DMSO–acetone-d_6, 10:1)

Compound	Chemical shifts, δ, ppm (spin–spin coupling constant, *J*, Hz)								
	C=O	C=N	$C_{(3)}$	$C_{(3a)}$	$C_{(6)}$, $C_{(9)}$, $C_{(5')}$, $C_{(8')}$	$C_{(7)}$, $C_{(8)}$, $C_{(6')}$, $C_{(7')}$	C_{i1} or C_{i2}	PhCH	Ph
8	153.11 (d, *J* = 1.70, $C_{(2)}$); 154.07 (s, $C_{(4)}$)	157.85 (br. d, *J* = 5.30, $C_{(3')}$); 139.96 (d, *J* = 3.20, $C_{(1)}$)	142.96 (t, *J* = 4.40)	119.07 (d, *J* = 14.30)	114.94 (dd, *J* = 165.5, 7.6); 115.93 (dd, *J* = 163.1; 7.5); 121.78 (dd, *J* = 161.2; 7.0); 126.44 (dd, *J* = 160.3; 7.6)	116.40 (dm, *J* = 164.3); 122.91 (ddd, *J* = 163.9, 8.3, 1.8); 127.91 (dm, *J* = 162.5); 129.87 (dm, *J* = 153.7)	131.78 (m); 130.79 (m); 128.98 (m); 120.97 (m)	51.60 (dt, *J* = 149.11; 2.60)	128.81 (dt, *J* = 161.40; 7.10, C_o); 128.49 (dt, *J* = 159.50; 7.00, C_o); 128.05 (dd, *J* = 160.70; 7.70, C_m); 127.10 (dd, *J* = 159.50; 7.60, C_m); 127.64 (dt, *J* = 61.50; 7.70, C_p); 127.61 (dt, *J* = 160.10; 8.00, C_p); 136.35 (br. q, *J* = 7.20, C_i); 132.10 (t, *J* = 7.40, C_i)



Under relatively mild conditions (in DMF solution at 140±5°C), thiocyanate **1** undergoes a different conversion than at higher temperatures that does not amount to isomerization and cyclization with formation of compounds **2** or **5**. The major reaction product is a compound having the empirical formula $C_{31}H_{21}N_5O_2S$; according to elemental microanalysis and mass spectral determination of the molecular weight, it is composed of two moieties: $C_{15}H_{11}N_2O$ and $C_{16}H_{10}N_{13}OS$, i.e., of benzylquinoxalinyl and thiocyano- or isothiocyanobenzylquinoxalinyl, imidazoquinoxalinylthiyl or thiazoloquinoxalinyliminyl residues. Based on this, a structure of one of the possible isomeric compounds **1-3, 5, 6** may be assigned to the product obtained. The absence of absorption bands in its IR spectrum from thiocyanate and isothiocyanate groups eliminates derivatives of bicyclic compounds **1** and **3** from consideration. Since the presence of two one-proton singlets in the ^{1}H NMR spectrum corresponding to two different types of NH lactam groups and the presence of two signals from carbon atoms of the C=O group in the ^{13}C spectrum eliminates structures **5, 6** and indicates that the lactam group of the tricyclic structure remains untouched and there is an additional benzylquinoxalinone moiety, we consider structures **7-9** next.

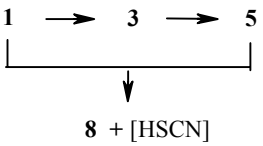




The absence of a signal for the thiocarbonyl group in the ^{13}C NMR spectrum in the 190-210 ppm region allows us to eliminate structure **9** from consideration. We cannot choose between structures **7** and **8** based on spectral data. But making a choice is quite possible based on purely chemical data. Thus as a result of thermolysis of compound **8** at 280±5°C, the imidazoquinoxaline **5** is formed in good yield, which is evidence in favor of the imidazoquinoxaline nature of the compound under study, i.e., in favor of structure **8**. And finally, unambiguous proof for such a structure for the product obtained comes from an alternate synthesis of the product: reaction of imidazoquinoxaline **5** with 3-(α-chlorobenzyl)quinoxalin-2(1H)-one (**10**) leads to formation of compound **8**, identical to the product formed from thiocyanate **1** in DMF.

Formation of specifically an S-benzylated product on benzylation of imidazo[3,4-*a*]quinoxaline **5** is also confirmed by reaction of the latter with unsubstituted benzyl chloride, which leads to the benzylthio compound **11** in high yield. The structure of product **11** is established on the basis of spectral data, like compound **8** there is a signal in its ^{13}C NMR spectrum from the carbon atom of the C=N group at 154.83 ppm and there is no signal from the ^{13}C atom of the C=S group in the 190-210 ppm region.

We can explain as follows the fact that when thiocyanate **1** is heated in DMF, instead of the expected imidazoquinoxaline **5** we obtained its derivative **8:**

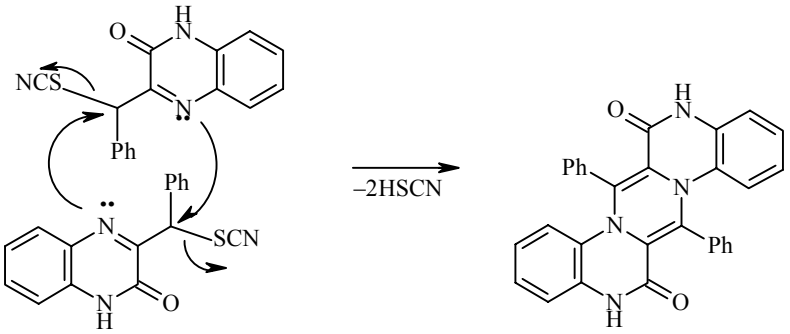


Imidazoquinoxaline **5** evidently is formed from compound **1** not only at temperatures higher than 200°C but also at 140°C (in DMF), but at this lower temperature the thiocyanate substituent in compound **1** begins to exhibit the ability to play the usually uncharacteristic [2] role of a pseudohalogen, completely analogous to the role of the chlorine atom in chloride **10** when the latter is used to obtain compound **8** from imidazoquinoxaline **5**. This is possible if the activation energy for nucleophilic substitution in thiocyanate **1** with imidazoquinoxaline **5** is appreciably lower than the activation energy for the overall process of isomerization of thiocyanate **1** to imidazoquinoxaline **5**. Finally we must note that nucleophilic substitution of the thiocyanate anion in the organic thiocyanate **1** probably is reversible, since if we heat it in DMF as described above but in the presence of potassium thiocyanate, we can detect intermediate mercapto compound **5** in the reaction mixture in addition to the starting compound **1** and the end product **8**, while if the salt is not added to the solution then we do not observe intermediate **5**. This may be a consequence of slower consumption of the indicated intermediate as a result of the occurrence of the reverse reaction **8** + $^{-}$SCN → **1** + **5**.

The thiocyanic acid obtained in the course of conversion of thiocyanate **1** to compound **8** should form salts with the latter and other nitrogen-containing heterocycles found in the reaction mixture, but alkalinization is not required in isolation of the end products. We know that thiocyanates of weak bases dissociate to an appreciable degree on heating to form free HSCN, tending toward oligomerization, the product of which is isolated as a gum.

While annelation of the thiazole ring [1] to a quinoxaline ring occurs when thiocyanate **1** is treated with acid but annelation of the imidazole ring occurs in neutral medium, in the presence of bases the reaction also is directed toward imidazoquinoxaline **5**: when compound **1** is heated in toluene in the presence of pyridine, it is specifically this compound that is formed.

We should note that in the mass spectrum of unrecrystallized product **8**, when the vaporization temperature of the sample is raised from 200 to 240°C, in addition to its molecular ion M^+ peak (*m*/*z* 527) we observe the appearance of a new peak with *m*/*z* 468.1586 of composition $C_{30}H_{20}N_4O_2$, which corresponds to twice the mass of the product of cleavage of HSCN from thiocyanate **1** (the same peak appears under these conditions in the mass spectral study of thiocyanate **1** itself). It can be considered as the molecular ion of compound **12**, formed by thermal self-condensation of unreacted starting thiocyanate **1** as a result of double nucleophilic substitution, in which the role of the electrophile is played by the thiocyanobenzyl group, and the role of the nucleophile is played by the imine nitrogen atom of the quinoxaline part of the molecule (yet another example of the thiocyano group in compound **1** behaving as a pseudohalogen).



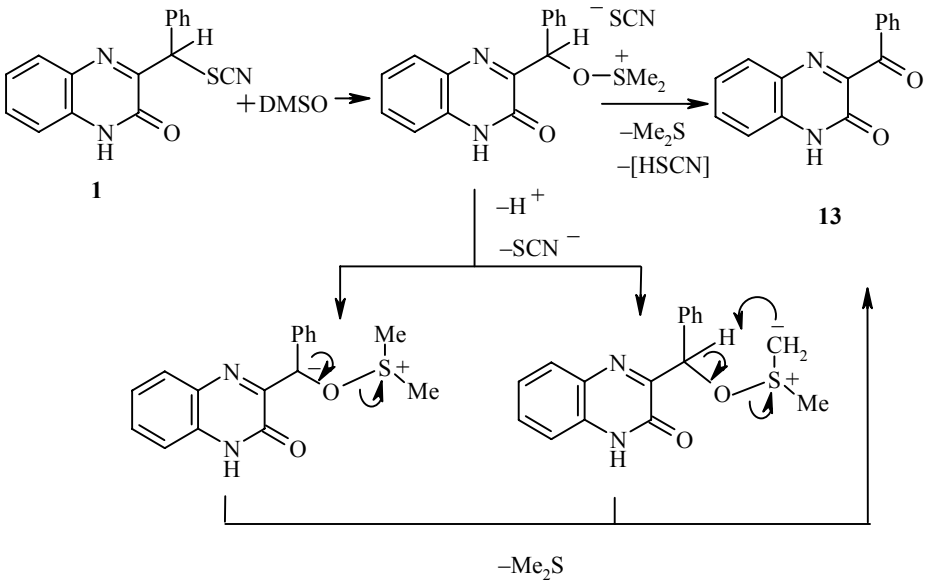
1 **12**

When thiocyanate **1** is heated in DMSO under the same conditions as for the heating in DMF considered above, the direction of the reaction is fundamentally changed. The major product in this case is 3-benzoylquinoxalin-2(1H)-one (**13**), the formation of which probably can be explained by the occurrence of a reaction analogous to Kornblum oxidation of organic halides, in which the role of the halogen is played by thiocyanate **1** and the role of the base is played by the quinoxaline moiety of the same molecule (Scheme 1).

The results of elemental analysis and spectral data (Tables 1 and 4) clearly prove the structure of the ketone **13** formed, and it is a lactam tautomer both in a 1:5 DMSO–acetone mixture (according to NMR data) and in the crystalline state (according to IR spectroscopy). The same ketone, obtained by oxidation of 3-benzylquinoxalin-2(1H)-one by chromic anhydride, had a melting point 20°C lower than the one we determined [7].

We isolate from the reaction mixture, in addition to compound **13**, two more minor tricyclic condensed products **14** and **15**, the structure of which has been established from the combined results of elemental analysis, IR and mass, and also NMR spectra (Tables 1 and 2). Their formation may be explained on the basis of the above-considered rearrangement of thiocyanate **1** to isothiocyanate **3** and isomerization of compounds **1** and **3** to the tricyclic condensed systems **2** and **5** respectively, occurring when thiocyanate **1** is heated. As an intermediate, thiazole quinoxaline **2** can lead to thiazolinoquinoxaline end product **14** both through preliminary nucleophilic addition of DMSO to the imino group with intermediate formation of compound **16**, and as a result

Scheme 1



of hydrolysis of the same imino derivative **2** by uncontrollable water impurity to the oxo derivative of heterocyclic system **17**. Taking isothiocyanate **3** as the starting point, the tricyclic imidazoquinoxaline system can lose the sulfur-containing functional group by oxidation of mercapto derivative **5** with the help of DMSO to form sulfinic acid **18**, followed by cleavage of SO_2. A similar loss of a sulfur atom under oxidation conditions by heterocyclic compounds capable of thiolactam/thiolactim tautomerism (oxidative dethionation, essentially leading to the reduction product) is known for a number of such systems when they are treated with various oxidants [8]. This assumption is completely confirmed by the fact that heating compound **5** in DMSO at 140°C indeed leads to their loss of sulfur and conversion to compound **15**.

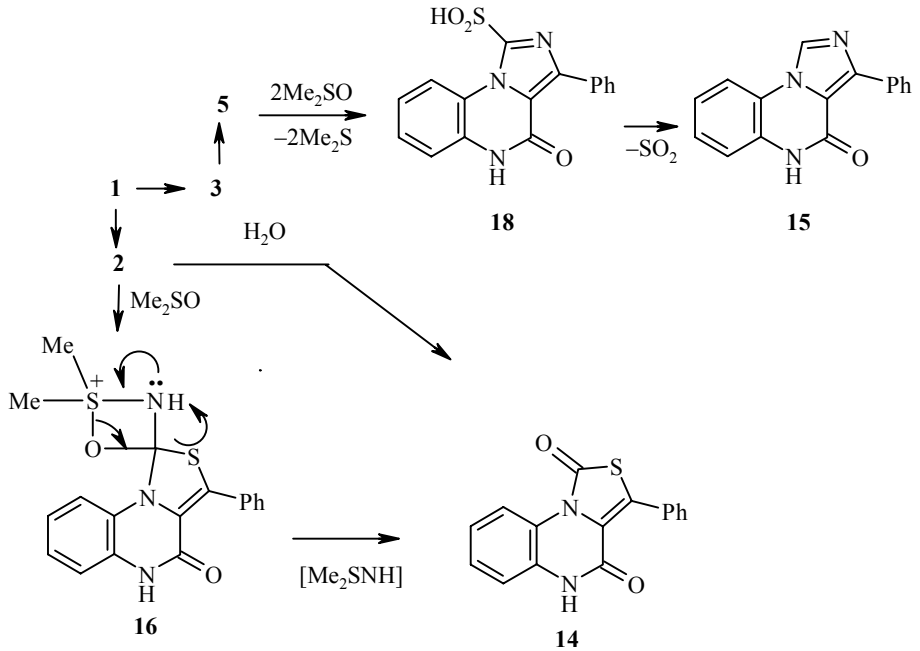


TABLE 4. ^{13}C NMR Spectrum of Benzoylquinoxaline **13** (DMSO–acetone-d_6, 10:1)

Compound	Chemical shifts, δ, ppm, (spin-spin coupling constant, *J*, Hz)					
	C=O	C=N	$C_{(5)}$, $C_{(8)}$, dd	$C_{(7)}$, $C_{(6)}$, dd	$C_{(i)}$, $C_{(i2)}$, m	Ph
13	191.79 (br. s, PhC=O); 152.77 (s, C_2)	155.74 (br. s)	131.09 (*J* = 161.10; 8.10); 123.17 (*J* = 163.40; 8.20)	128.50 (*J* = 163.40; 8.20); 115.31 (*J* = 164.00; 8.10)	130.65; 132.12	129.03 (dt, *J* = 161.9; 6.50, C_o); 133.95 (dt, *J* = 163.2; 7.20, C_p); 128.39 (dd, *J* = 163.3; 3.74, C_m); 134.02 (t, *J* = 7.11, C_i)

EXPERIMENTAL

The melting points were determined on a Boetius stage. The IR spectra were taken on a UR-20 spectrometer (vaseline mulls). ^1H NMR spectra were recorded on a Bruker MCL-250 spectrometer (250 MHz). The ^{13}C NMR spectra were taken on a Bruker WV-400 (100 MHz) spectrometer. The chemical shifts were given on a δ scale relative to DMSO-d_6. The molecular weights of the ions (electron impact) were recorded on an MX-1310 mass spectrometer with resolution *R* = 10 000. Sample injection was done using an SVP-5 direct injection system for an ion source temperature of 160°C; *U* = 60 eV.

3-(α-Thiocyanobenzyl)quinoxalin-2(1H)-one (1) was synthesized from 3-(α-chlorobenzyl)quinoxalin-2(1H)-one and potassium thiocyanate [1].

3-(α-Chlorobenzyl)-2(1H)-one (10) was obtained using the familiar procedure in [9] from the methyl ester of phenylchloropyruvic acid [10] and *o*-phenylenediamine.

When the same compound was synthesized by different methods, the match between their physical and spectral properties and also the absence of a depression of the melting point for a mixed sample established that the products were identical.

1-Mercapto-3-phenylimidazo[1,5-*a*]quinoxalin-4(5H)-one (5). A. Thiocyanate **1** (0.50 g, 1.70 mmol) was heated up to 225°C in a test tube and held at that temperature for 5 min. At 205°C, the compound melts and then crystallizes. After cooling, the crystals of product **5** were triturated with CF_3COOH (2 ml), filtered out and washed with acetone (2 × 3 ml).

B. Compound **8** (0.12 g, 0.23 mmol) was heated to 290°C in a test tube and then cooled; 5 ml of dioxane was added, it was brought to the boiling point, then product **5** was filtered out and washed with acetone (2 × 3 ml).

1-(α-2-Oxo-1,2-dihydro-3-quinoxalinyl)benzylthio-3-phenylimidazo[1,5-*a*]quinoxalin-4(5H)-one (8). A. A solution of thiocyanate **1** (2.70 g, 9.2 mmol) in DMF (20 ml) was held for 3 h at 135°C to 145°C. The crystals that precipitated on cooling were filtered out, washed with 2-propanol (2 × 5 ml), and recrystallized from DMF. To remove residues of DMF, the product **8** obtained was held for 3 h under an oil pump vacuum at 160-200°C.

B. A solution of thiocyanate **1** (0.30 g, 1.0 mmol) in a mixture of toluene (3 ml) and pyridine (0.5 ml) was refluxed for 3 h. The reaction mixture was cooled, the crystals of product **8** were filtered out and washed with 2-propanol (2 × 3 ml).

C. A solution of compound **5** (0.20 g, 0.68 mmol) and chloride **10** (0.20 g, 7.4 mmol) in DMF (15 ml) was held at 100-110°C for 1 h 30 min, cooled and held for ~16 h at room temperature. The crystals of product **8** that precipitated were filtered out and washed with acetone (2 × 5 ml).

1-Benzylthio-3-phenylimidazo[1,5-*a*]quinoxalin-4(5H)-one (11). A solution of compound **5** (0.20 g, 0.68 mmol) and benzyl chloride (1 ml) in DMF (10 ml) was held for 1 h 30 min at 100-110°C. The solution was cooled and held for ~16 h at room temperature. The crystals of product **11** that precipitated were filtered out and washed with 2-propanol (2 × 5 ml). Water was added to the filtrate, the crystals of product **11** formed were filtered out and washed with 2-propanol.

3-Phenylimidazo[1,5-*a*]quinoxalin-4(5H)-one (15). A. A solution of compound **5** (0.50 g) in DMSO (7 ml) was held for 1 h at 135-155°C, cooled and poured into water (20 ml). The crystals of product **15** that precipitated were filtered out and then washed with water and 2-propanol.

Reaction of 3-(α-Thiocyanobenzyl)quinoxalin-2(1H)-one (1) with DMSO. A solution of compound **1** (1.60 g, 5.50 mmol) [1] in DMSO (25 ml) were held for 1 h at 135-145°C. The solution was cooled and poured into 50 ml water. The crystalline mixture of reaction products was filtered out, dried, and recrystallized from a 2:3 DMSO–MeCN mixture. The mixture of compounds **14** and **15** was filtered out. The filtrate was poured into water; then crystals of 3-benzoylquinoxaline-2(1H)-one (**13**) precipitated. The crystalline mixture of compounds **14** and **15** was separated by recrystallization from DMSO; 3-phenylthiazolo[3,4-*a*]quinoxaline-1,4(5H)-dione (**14**) precipitated under these conditions, while compound **15** was precipitated from the DMSO mother liquor by water.

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