Reactions of Isocyanates with Methyl *N*-(Cyanothioformyl)anthranilate

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The triethylamine-catalyzed reactions of methyl *N*-(cyanothioformyl)anthranilate (**1**) with isocyanates result in cyclization involving the cyano group to form methyl 2-(4-imino-2-oxo-3-substituted-5-thioxoimidazolidin-1-yl)benzoates (**4**). Ring closure at the ester carbonyl to form 3-aryl-3,4-dihydro-4-oxoquinazoline-2-carbonitriles (**8**) is observed when the *S*-methyl derivative of **1** is allowed to react with aromatic amines.

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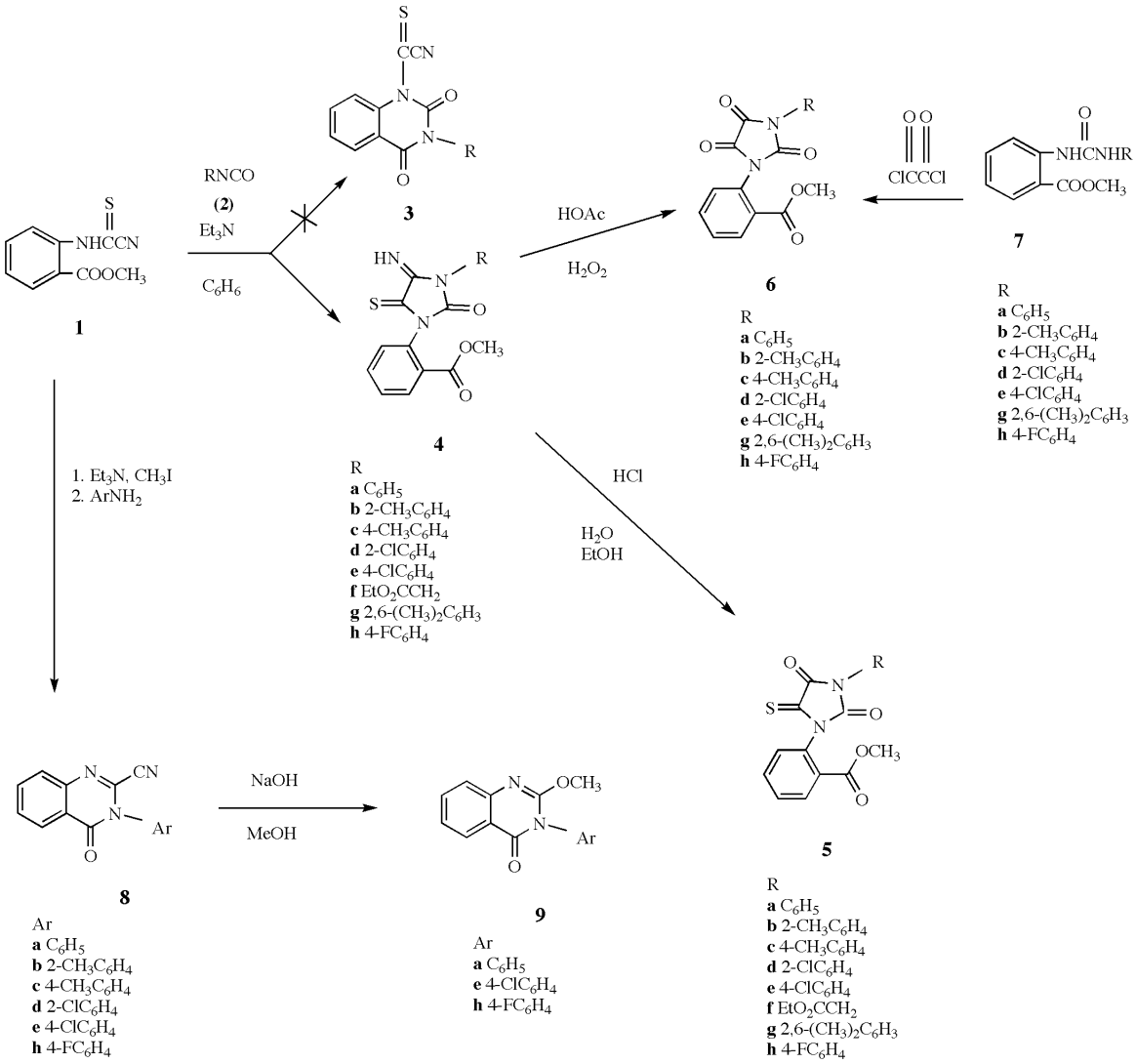
Esters of anthranilic acid react with isocyanates to yield 3-substituted 2,4(1*H*,3*H*)-quinazolinediones [1]. On the other hand, the analogous reaction between 2- or 3-aminonitriles and isocyanates is known to lead to a wide variety of heterocyclic compounds [2]. A variation of the latter reaction involving 1-cyanothioformanilide results in the formation of 1-substituted 5-imino-3-phenyl-4-thioxo-2-imidazolidinones [3]. It was of interest to investigate the behavior of methyl *N*-(cyanothioformyl)anthranilate (**1**) toward isocyanates (**2**) since in this case the reaction may in principle follow either (or both) of two pathways: after initial nucleophilic attack by the thioamide nitrogen on the isocyanate, further reaction and cyclization could involve either the ester group to form an *N*-cyanothioformylquinazolinedione (**3**), or the cyano group to form a 4-imino-5-thioxo-2-imidazolidinone (**4**). A literature method for preparation of **1** involves the reaction of methyl anthranilate with 4,5-dichloro-1,2,3-dithiazolium chloride to form an *N*-aryliminodithiazole, which is then treated with triphenylphosphine to yield **1** [4]. For our purposes **1** was prepared in analogy with cyanothioformanilide from methyl 2-isothiocyanatobenzoate [5] by treatment with potassium cyanide followed by acidification [6]. The results of the present investigation showed that when **1** is treated with an isocyanate in the presence of triethylamine the reaction proceeds following exclusively the second of the two pathways shown in Scheme 1 to form the corresponding methyl 2-(4-imino-2-oxo-3-substituted-5-thioxoimidazolidin-1-yl)benzoates (**4**) in excellent yields (Table 1). Structure **4** is consistent with an N-H band at 3210-3275 cm^{-1} and a relatively high wavenumber (1750-1790 cm^{-1}) band for the imidazolidinone carbonyl in the infrared spectra of the products (Table 1), whereas for compounds of structure **3** the carbonyl bands would be expected to appear at 1630-1730 cm^{-1} [1c]. In addition, structure **4** is supported by the presence of a 3-proton singlet at 3.7-3.8 ppm for the methyl protons of the ester group in the proton nmr spectra of the products (Table 4). Treatment of **4** with hydrochloric acid in ethanol cleaves the imino group with formation of brightly colored methyl 2-(2,4-dioxo-3-substituted-5-thioxoimidazolidin-1-yl)benzoates (**5**, Table 2). Both cleavage of the imino group and oxidation of the thiocarbonyl group of **4** were observed when hydrogen peroxide in acetic acid was used, but the methyl 2-(2,4,5-trioxo-3-substituted-imidazolidin-1-yl)benzoates (**6**, Table 2) formed as products were isolated only in moderate yields possibly due to side reactions involving hydrolysis of the ester group. However, the structure of compounds **6** is confirmed by their formation in excellent yield from the corresponding ureas (**7**), (readily obtainable from methyl anthranilate and the appropriate isocyanate) and oxalyl chloride [7]. The reaction of suitably substituted thioamides with primary amines under mild conditions is known to proceed with elimination of hydrogen sulfide and formation of amidines [8]. This reaction is often facilitated by initial conversion of the thioamides to their more reactive *S*-methyl derivatives [9]. In the present case the proximity of the thioamide and ester groups in **1** suggested the possibility that such an amidine formation could be followed by a cyclization resulting from nucleophilic attack on the ester carbonyl group. Indeed this was the observation when compounds **1** were treated first with methyl iodide, in the presence of triethylamine and then with a primary aromatic amine. The products were 3-aryl-3,4-dihydro-4-oxoquinazoline-2-carbonitriles (**8**, Table 3), as indicated by the nitrile band at 2236-2260 cm^{-1} in their infrared spectra (Table 3) and the absence of the methoxy protons signal from their proton nmr spectra (Table 6). As expected, the cyano group in compounds **8**, is readily displaced by nucleophiles [10]. Thus treatment with sodium hydroxide in methanol converts **8** to the corresponding 3-aryl-2-methoxy-4(3*H*)-quinazolinones (**9**, Table 3), as indicated by the removal of the nitrile band from the infrared spectra (Table 3) and the appearance of a three proton singlet at 3.89-3.90 ppm for the methoxy protons in the proton nmr spectra (Table 6).

Table 4 contains proton nmr spectroscopic data of compounds **4a**-**4h** in dimethyl-d_6 sulfoxide solutions. It is interesting to note that for compounds **4b** and **4d** additional signals for some resonances are seen which are attributed to rotational isomers. Since compound **4g** would also be expected to exhibit rotational isomerism, proton

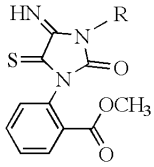
Scheme 1



nmr spectra were taken in hexadeuteriobenzene and deuteriochloroform. Unlike the dimethyl-d_6 sulfoxide spectrum, shown in Table 4, the spectra in $CDCl_3$ and C_6D_6 do show additional signals. Additional spectra taken above room temperature for compounds **4b**, **4d** and **4g** confirmed rotational isomerism. Sets of peaks converged and often coalesced as the temperature was increased. Table 5 contains proton nmr spectroscopic data for compounds **5a-5h** in dimethyl-d_6 sulfoxide solutions. In this case additional signals are seen for **5b** and **5g** but not **5d**. However spectra of **5d** taken in C_6D_6 do show additional resonances. Again spectra taken above room temperature confirmed rotational isomerism because signals converged or coalesced. This nonequivalence of protons should be attributed to restricted rotation about the *o*-substituted aryl-nitrogen bond, as a result of which compounds **4b, 4d, 4g, 5b, 5d** and **5g** exist as mixtures of rotational isomers. Table 5 contains proton nmr spectroscopic data of compounds **6a-6h** taken in dimethyl-d_6 sulfoxide. Since compounds **6b** and **6g** would be expected to exhibit rotational isomerism, spectra were also taken in deuteriochloroform. Both compounds exhibit a broad singlet for the methyl protons. However this signal splits into a doublet when the spectra are taken below room temperature thus indicating the presence of rotational isomers. As shown in Table 4, compound **4f** exhibits a doublet of doublets for the methylene protons alpha to the substituent carbonyl, probably due to the overall chirality of the molecule. Similarly, the proton nmr spectrum of compound **5f** taken in dimethyl-d_6 sulfoxide shows a singlet for the methylene protons, but when taken in deuteriochloroform a doublet of doublets is observed. There are many reports of axially twisted

Table 1

Methyl 2-(4-Imino-2-oxo-3-substituted-5-thioxoimidazolidin-1-yl)benzoates (**4**)

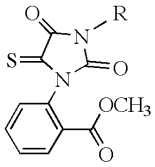


	R	Yield [a] (%)	Mp [b] (°C)	Elemental Analysis Calcd. (Found) C	H	N	IR (cm^{-1}) C=N	N-H	C=O
4a	C_6H_5	93%	140–141.5	60.17 (60.39)	3.86 (3.92)	12.38 (12.32)	1640	3235	1700,1760
4b	2-$CH_3C_6H_4$	92%	147–148	61.18 (61.12)	4.28 (4.37)	11.89 (11.95)	1665	3260	1730,1775
4c	4-$CH_3C_6H_4$	95%	166–167	61.18 (61.40)	4.28 (4.35)	11.89 (11.84)	1640	3210	1700,1750
4d	2-ClC_6H_4	76%	176-177	54.62 (54.65)	3.24 (3.44)	11.24 (11.12)	1660	3240	1720,1770
4e	4-ClC_6H_4	92%	187–189	54.62 (54.76)	3.24 (3.40)	11.24 (11.25)	1675	3270	1735,1780
4f	$EtOOCCH_2$	91%	119–120[c]	51.57 (51.38)	4.33 (4.55)	12.03 (12.23)	1668	3275	1728,1755 1773
4g	2,6-$(CH_3)_2C_6H_3$	87%	170–171.5	62.11 (62.14)	4.66 (4.76)	11.44 (11.28)	1655	3260	1722,1790
4h	4-FC_6H_4	94%	170-171	57.14 (57.01)	3.38 (3.42)	11.76 (11.82)	1660	3245	1728,1775

[a] Crude or recrystallized product with melting point within 10° of the analytically pure compound; [b] Recrystallized from ethanol; [c] Recrystallized from benzene/ligroine.

Table 2

Methyl 2-(2,4-Dioxo-3-substituted-5-thioxoimidazolidin-1-yl)benzoates (**5**) and Methyl 2-(2,4,5-Trioxo-3-substituted-imidazolidin-1-yl)benzoates (**6**)



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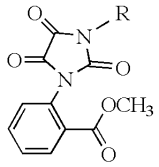

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	R	Yield [a] (%)	Mp [b] (°C)	Elemental Analysis Calcd. (Found) C	H	N	IR (cm^{-1}) C=O
5a	C_6H_5	90%	144–146	59.99 (60.08)	3.55 (3.62)	8.23 (8.23)	1760,1740
5b	2-$CH_3C_6H_4$	90%	176-177	61.01 (61.17)	3.98 (4.08)	7.90 (7.89)	1750, 1725
5c	4-$CH_3C_6H_4$	91%	156-157	61.01 (60.98)	3.98 (4.13)	7.90 (8.00)	1750, 1728
5d	2-ClC_6H_4	90%	159-161	54.48 (54.56)	2.96 (3.29)	7.47 (7.50)	1755, 1725
5e	4-ClC_6H_4	89%	172–174	54.48 (54.63)	2.96 (3.15)	7.47 (7.47)	1750, 1725
5f	$EtOOCCH_2$	90%	92-93.5	51.42 (51.61)	4.03 (4.18)	8.00 (8.22)	1770, 1755,1729
5g	2,6-$(CH_3)_2C_6H_3$	90%	176-178	61.94 (61.83)	4.38 (4.26)	7.60 (7.68)	1755, 1730

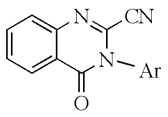
Table 2 (continued)

	R	Yield [a] (%)	Mp [b] (°C)	Elemental Analysis Calcd. (Found) C	H	N	IR (cm^{-1}) C=O
5h	4-FC_6H_4	81%	146-147	56.98)	3.09	7.82	1770, 1730
				(56.91)	(3.15)	(7.93)	
6a	C_6H_5	65%[c]	138-139	62.96	3.73	8.64	1747, 1735, 1725, 1716
		85% [d]		(62.66)	(3.64)	(8.53)	
6b	2-$CH_3C_6H_4$	63%[c]	126-127	63.90	4.17	8.28	1748, 1718
		90% [d]		(63.66)	(4.12)	(8.24)	
6c	4-$CH_3C_6H_4$	91%[d]	159.5-160.5	63.90	4.17	8.28	1747,1712, 1709
				(63.65)	(4.13)	(8.24)	
6d	2-ClC_6H_4	66%[c]	177.5-179	56.92	3.09	7.81	1747, 1725, 1715
		90% [d]		(56.64)	(3.03)	(7.69)	
6e	4-ClC_6H_4	90%[d]	159-160	56.92	3.09	7.81)	1746, 1716
				(56.62)	(3.07)	(7.71)	
6g	2,6-$(CH_3)_2C_6H_3$	85%[d]	163.5-165	64.77	4.58	7.95	1744, 1715
				(64.61)	(4.58)	(7.84)	
6h	4-FC_6H_4	91%[d]	154-155.5	59.65	3.24	8.18	1743, 1725
				(59.41)	(3.16)	(8.02)	

[a] Crude or recrystallized product with melting point within 10° of the analytically pure compound; [b] Recrystallized from ethanol; [c] Method A; [d] Method B.

Table 3

3-Aryl-3,4-dihydro-4-oxoquinazoline-2-carbonitriles (**8**) and 3-Aryl-2-methoxy-4(3*H*)-quinazolinones (**9**)



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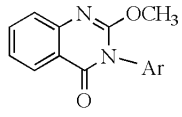

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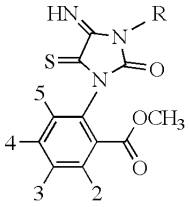
	R	Yield [a] (%)	Mp [b] (°C)	Elemental Analysis Calcd. (Found)			IR (cm^{-1}) C=O	C≡N
8a	C_6H_5	60%	196–197[c]	72.87	3.67	16.99	1690	2238
				(72.85)	(3.90)	(17.11)		
8b	2-$CH_3C_6H_4$	59%	179-180	73.55	4.24	16.08	1700	2236
				(73.42)	(4.29)	(16.04)		
8c	4-$CH_3C_6H_4$	65%	179–180.5	73.55	4.24	16.08	1695	2260
				(73.55)	(4.43)	(16.15)		
8d	2-ClC_6H_4	16%	198–200	63.96	2.86	14.92	1698	2238
				(63.80)	(2.89)	(14.83)		
8e	4-ClC_6H_4	56%	181-182	63.96	2.86	14.92	1700	2238
				(64.04)	(2.98)	(14.57)		
8h	4-FC_6H_4	69%	182-183	67.92	3.04	15.84	1705	
				(67.77)	(3.02)	(15.76)		
9a	C_6H_5	93%	135-136	71.42	4.79	11.10	1694	
				(71.32)	(4.68)	(11.01)		
9e	4-ClC_6H_4	86%	145-146.5	62.84	3.87	9.77	1694	
				(62.84)	(3.88)	(9.79)		
9h	4-FC_6H_4	95%	156-157	66.66	4.10	10.37)	1690	
				(66.56)	(4.21)	(10.21)		

[a] Crude or recrystallized product with melting point within 10°of the analytically pure compound; [b] Recrystallized from ethanol; [c] Lit [11] mp 198°C.

amides and imides exhibiting chirality due to a high rotational barrier [2g,12]. Tables 7 and 8 contain carbon-13 nmr spectra of compounds **4a**-**4h** and **5a**-**5h**. The carbon spectra of compounds **4b**, **4d**, **4g**, **5b**, **5d** and **5g** all exhibit additional resonances due to rotational isomerism. Assignments of carbon resonances was facilitated by DEPT, HMQC and HMBC experiments in addition to literature data on structurally related compounds [13].

Table 4

^{1}H-nmr Chemical Shifts (δ) of Compounds **4** in Dimethyl-d_6 Sulfoxide

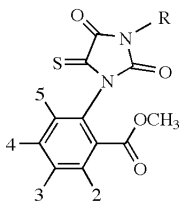


	H-5(dd)	H-4(dt)	H-3(dt)	H-2(dd)	OCH_3(s)	=NH(s)	Ar-H(m)	CH_2(dd)	CH_3(s)	OCH_2(q)	CH_3(t)
4a	8.13	7.89	7.74	7.71	3.78	9.85	7.45–7.60				
4b	8.13, 8.11[a]	7.89	7.75	7.70	3.77, 3.80[a]	9.71, 9.82[a]	7.27–7.49		2.26, 2.29[a]		
4c	8.12	7.88	7.72	7.70	3.78	9.80	7.41[b], 7.35[b]		2.37		
4d	8.11, 8.15[a]	7.88	7.75	7.71	3.75, 3.82[a]	9.86, 10.1[a]	7.54–7.73				
4e	8.13	7.89	7.73	7.68	3.78	9.93	7.65[b], 7.58[b]				
4f	8.10	7.86	7.72	7.61	3.74	9.85		4.56		4.19	1.24
4g	8.12	7.88	7.73	7.81	3.78	9.80	7.24[b], 7.32[d]		2.24[c]		
4h	8.18	7.94	7.77	7.73	3.83	9.93	7.43-7.67				

[a] Due to rotational isomers; [b] doublet; [c] six protons; [d] triplet.

Table 5

^{1}H-nmr Chemical Shifts (δ) of Compounds **5** and **6** in Dimethyl-d_6 Sulfoxide



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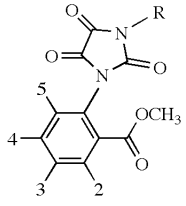

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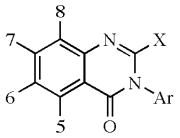
	H-5(dd)	H-4(dt)	H-3(dt)	H-2(dd)	OCH_3(s)	Ar-H(m)	CH_2(s)	CH_3(s)	OCH_2(q)	CH_3(t)
5a	8.15	7.91	7.74	7.66	3.80	7.50–7.61				
5b	8.14	7.91	7.77	7.67	3.79, 3.82[a]	7.27–7.50		2.29, 2.28[a]		
5c	8.14	7.90	7.74	7.64	3.80	7.39[b]		2.38		
5d	8.13	7.91	7.78	7.67	3.77	7.57-7.73				
5e	8.15	7.91	7.75	7.65	3.80	7.56[c],7.68[c]				
5f	8.12	7.87	7.73	7.60	3.75		4.58		4.20	1.24
5g	8.14	7.91	7.82	7.74	3.79	7.37[c], 7.27[e]		2.25, 2.28[a]		
5h	8.15	7.91	7.75	7.64	3.80	7.41-7.63				
6a	8.11	7.89	7.72	7.60	3.82	7.46-7.59				
6b	8.11	7.88	7.72	7.62	3.83	7.47-7.37		2.31		
6c	8.12	7.88	7.72	7.59	3.82	7.38[c],7.34[c]		2.37		
6d	8.11	7.88	7.73	7.59	3.81	7.57-7.70				
6e	8.11	7.88	7.74	7.58	3.82	7.67[c], 7.51[c]				
6g	8.11	7.88	7.72	7.73	3.81	7.25[c], 7.35[e]		2.27[d]		
6h	8.11	7.88	7.72	7.59	3.82	7.61-7.40				

[a] Due to rotational isomers; [b] singlet; [c] doublet; [d] six protons; [e] triplet.

Table 6
^{1}H-nmr Chemical Shifts (δ) of Compounds **8** and **9** in Dimethyl-d_6 Sulfoxide



8: X = CN
9: X = OCH_3

	H-8(dd)	H-7(dt)	H-6(dt)	H-5(dd)	CH_3(s)	Ar-H(m)
8a	7.90	8.00	7.76	8.23		7.58-7.70
8b	7.92	8.02	7.78	8.26	2.14	7.40–7.56
8c	7.88	7.99	7.75	8.22	2.42	7.53[a], 7.41[a]
8d	7.94	8.05	7.81	8.26		7.91[b], 7.70-7.84
8e	7.90	8.00	7.76	8.22		7.72[c]
8h	7.90	8.00	7.76	8.22		7.76[b], 7.47[b]
9a	7.54	7.78	7.48	8.03	3.89	7.36-7.51
9e	7.44	7.78	7.38	8.03	3.89	7.57[a], 7.54[a]
9h	7.54	7.77	7.47	8.03	3.90	7.31-7.46

[a] Doublet; [b] doublet of doublets; [c] singlet.

EXPERIMENTAL

Reagent-grade solvents were used without further purification. Tetrahydrofuran was distilled over calcium hydride. Melting points were determined in capillaries with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-33 spectrophotometer using mineral oil mulls. Proton and carbon-13 nmr spectra were obtained on Bruker AC250 and AC500 nmr spectrometers. Chemical shifts are given in ppm (δ).

Methyl *N*-(Cyanothioformyl)anthranilate (**1**).

To a solution of 7.5 g (0.115 mol) of potassium cyanide in 75 mL of water was gradually added with stirring 19.3 g (0.100 mol) of methyl 2-isothiocyanatobenzoate in 60 mL of ethanol. The resulting mixture was stirred at room temperature for one half hour. After 150 mL of water was added, the solution was acidified by dropwise addition of concentrated hydrochloric acid (Caution: Possible HCN evolution!). The resulting solid was filtered and washed several times with water to give 21.7 g (98%) of **1,** mp 121-122° C. Recrystallization from ethyl acetate gave the pure compound, mp 122-123 °C (lit [4] mp 118 °C).

Methyl 2-(4-Imino-2-oxo-3-substituted-5-thioxoimidazolidin-1-yl)benzoates (**4**).

To 0.0050 mole of methyl *N*-(cyanothioformyl)anthranilate (**1**) in 10 mL of benzene was added 0.0051 mole of the isocyanate (**2**) and 5 drops of triethylamine. An exothermic reaction took place and the solution was allowed to stand for 10 hours. Petroleum ether (bp 63-75 °C) was added to the resulting mixture and the precipitate was collected by filtration. Yields and physical properties of compounds **4** are shown in Table 1.

Methyl 2-(2,4-Dioxo-3-substituted-5-thioxoimidazolidin-1-yl)benzoates (**5**).

A solution of 0.5 g of the substituted imidazolidinone **4** in 5 mL of ethanol and 5 mL of concentrated hydrochloric acid was stirred at room temperature for one to six hours, the reaction progress being followed by thin layer chromatography. The solution was then diluted with water and the precipitated solid was collected by filtration. Yields and physical properties of compounds **5** are shown in Table 2.

Methyl 2-(2,4,5-Trioxo-3-substituted-imidazolidin-1-yl)benzoates (**6**).

Method A.

To an ice cold solution of 0.5 g of **4** in 5 mL of acetic acid was added 3 mL of 30% hydrogen peroxide and the resulting mixture was stirred at room temperature until its yellow color had essentially been discharged (1-4 h). The product was isolated by dilution with water and filtration.

Method B.

A solution of equal weights (5-10 g) of oxalyl chloride and the corresponding urea (**7**) in an adequate volume of benzene (25-50 mL) was refluxed for 1-6 h (the reaction progress being followed by thin layer chromatography). The reaction was then cooled, diluted with petroleum ether (bp 63-75° C) and filtered to give the product. Yields and physical properties of compounds **6** are shown in Table 2.

3-Aryl-3,4-dihydro-4-oxoquinazoline-2-carbonitriles (**8**).

To 0.0050 mole of methyl *N*-(cyanothioformyl)anthranilate (**1**) in 10 ml of benzene was added 0.0055 mole of triethylamine dropwise with stirring. After five minutes, 0.0055 mole of methyl iodide was added dropwise and the solution was stirred for thirty minutes, after which time 0.0050 mole of the appropriate amine was added. The resulting mixture was then refluxed for 24 hours. After cooling of the solution and removal of benzene by distillation, addition of ethanol caused precipitation of a buff solid. Yields and physical properties of compounds **8** are shown in Table 3.

3-Aryl-2-methoxy-4(3*H*)-quinazolinones (**9**).

To a solution of 30 mg of sodium hydroxide in 30 ml of methanol was added 0.38 mmole of 3-aryl-3,4-dihydro-4-oxoquinazoline-2-carbonitrile (**8**). The mixture was stirred for one hour at room temperature and then neutralized with 10% hydrochloric acid. The solvent was removed by distillation and the residue was extracted repeatedly with dichloromethane. The combined extracts were dried over magnesium sulfate, filtered and the solvent was removed by distillation to yield a solid, which was recrystallized from hexane. Yields and physical properties of compounds **9** are shown in Table 3.

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* Author to whom correspondence should be addressed.

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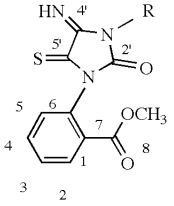
Table 7

^{13}C-nmr Chemical Shifts (δ) of Compounds **4** in Dimethyl-d_6 Sulfoxide



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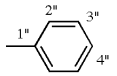
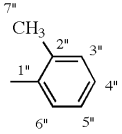
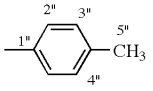
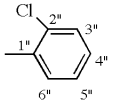
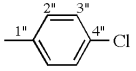
a. 

b. 

c. 

d. 

e. 

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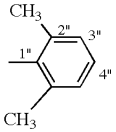
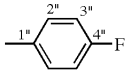
g. 

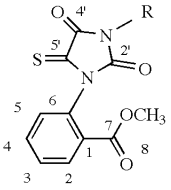
h. 

	6	5	4	3	2	1	7	8	5'	4'	2'	1''	2''	3''	4''	5''	6''	7''
4a	132.8	130.1	134.0	130.4	131.2	126.9	164.1	52.7	182.4	153.7	153.3	132.1	126.9	128.9	128.2			
4b	132.8	130.1	134.0	130.4	131.1	127.1	164.2	52.8	182.6	153.6	153.2	129.4	136.5	129.9	128.8	130.9	126.8	17.5
								52.6 [a]	182.8 [a]		153.1 [a]		136.4 [a]					17.2 [a]
4c	132.8	130.1	133.9	130.4	131.2	126.9	164.1	52.7	182.5	153.9	153.3	129.5	126.7	129.4	137.8	20.7		
4d	132.4	129.9	133.9	130.2	131.2	126.6	164.2	52.8	182.4	153.0	152.5	129.7	132.2	131.0	130.4	131.5	128.2	
	132.5 [a]	130.0 [a]	134.2 [a]			127.6 [a]		52.7 [a]	182.2 [a]		152.4 [a]	129.4 [a]	132.0 [a]	130.9 [a]	130.2 [a]		128.5 [a]	
4e	132.8	130.2	134.1	130.6	131.3	127.0	164.2	52.8	182.3	153.4	153.2	131.0	128.6	129.1	132.7			
4f	132.2	130.0	133.9	130.4	131.3	127.3	164.1	52.6	182.3	153.7	152.3	41.1	166.6	61.3	13.9			
4g	132.6	130.4	133.9	130.4	131.1	127.0	164.1	52.6	182.5	152.7	152.5	129.8	136.7	128.2	129.3	17.6		
													136.8 [a]			17.4 [a]		
4h	132.7	130.1	134.0	130.4	131.3	127.0	164.1	52.7	182.4	153.7	153.3	128.3	129.1	115.9	161.2			

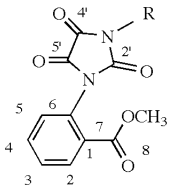
[a] Due to rotational isomers.

Table 8

^{13}C-nmr Chemical Shifts (δ) of Compounds **5** and **6** in Dimethyl-d_6 Sulfoxide



5



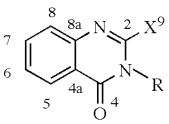
6

	6	5	4	3	2	1	7	8	5'	4'	2'	1"	2"	3"	4"	5"	6"	7'
5a	132.3	130.1	134.2	130.6	131.5	127.0	164.2	52.8	184.2	153.4	153.0	130.5	126.5	129.4	129.1			
5b	132.3	130.1	134.2	130.7	131.5	127.1	164.2	52.7	184.5	153.4	152.7	129.4	136.1	129.9	128.4	130.9	126.9	17.0
					131.3 [a]			52.8 [a]	184.2 [a]	153.1 [a]			136.3 [a]		128.1 [a]			17.5 [a]
5c	132.2	130.1	134.2	130.6	131.4	127.0	164.1	52.8	184.2	153.1	152.9	127.8	126.2	129.7	138.7	20.7		
5d	131.8	129.9	134.2	130.2	131.4	127.6	164.1	52.8	184.0	152.7	152.1	128.0	131.8	130.7	130.5	131.9	128.4	
	134.4 [a]				131.6 [a]			53.0 [a]						130.9 [a]	132.1 [a]		128.7 [a]	
5e	132.1	130.0	134.1	130.6	131.3	126.9	164.1	52.7	183.8	152.9	152.6	130.2	128.0	129.3	133.8			
5f	131.1	130.0	134.1	130.7	131.4	127.3	164.0	52.7	184.0	153.5	153.1	138.5	166.3	61.7	13.9			
5g	132.2	130.5	134.2	130.7	131.2	126.9	164.1	52.7	184.1	152.8	152.3	128.8	136.8	128.4	129.9	17.4		
													136.3 [a]	128.5 [a]		17.6 [a]		
5h	132.2	130.0	134.2	130.6	131.4	127.0	164.2	52.8	184.0	153.2	152.8	126.6	128.7	116.3	161.7			
6a	129.4	129.8	133.9	130.2	131.2	127.1	164.5	52.7	155.7	155.6	151.9	130.0	126.4	129.2	129.0			
6b	129.5	129.8	133.8	130.2	131.1	127.1	164.5	52.5	156.0	155.9	151.8	129.0	136.2	129.8	128.1	130.9	126.8	17.1
6c	129.4	129.6	133.8	130.1	131.1	127.0	164.5	52.6	155.7	155.7	152.0	127.3	126.1	129.6	138.6	20.7		
6d	129.0	129.7	133.9	130.2	131.2	127.3	164.4	52.7	155.5	155.1	151.0	127.5	131.7	130.3	130.1	131.8	128.4	
6e	128.9	129.4	133.9	130.3	131.2	127.1	164.5	52.6	155.6	155.4	151.7	129.7	128.1	129.4	133.6			
6g	129.5	130.2	133.9	130.3	131.0	127.1	164.5	52.5	155.8	155.5	151.4	127.8	136.6	128.4	129.8	17.5		
6h	129.3	129.6	133.8	130.2	131.2	127.1	164.5	52.6	155.6	155.5	151.8	126.1	128.7	116.3	161.6			

[a] Due to rotational isomers.

Table 9

^{13}C-nmr Chemical Shifts (δ) of Compounds **8** and **9** in Dimethyl-d_6 Sulfoxide



8: X = CN
9: X = OCH_3

	8a	8	7	6	5	4a	4	2	9	1"	2"	3"	4"	5"	6"	7"
8a	146.0	128.0	135.3	130.0	126.6	122.9	159.5	135.8	111.6	132.0	128.7	129.4	128.0			
8b	146.3	128.4	135.8	130.5	126.9	122.8	159.2	131.8	111.5	134.9	136.1	130.9	129.2	131.3	127.6	17.1
8c	146.1	128.0	135.2	129.9	126.6	122.9	159.6	133.2	111.6	132.1	128.4	129.9	139.9	20.9		
8d	145.8	128.4	135.9	130.6	126.8	122.5	158.6	132.8	111.0	131.7	131.1	132.5	130.2	131.2	128.8	
8e	146.0	128.0	135.3	130.0	126.5	122.8	159.4	131.7	111.5	134.9	129.5	130.7	134.6			
8h	146.0	128.0	135.3	130.0	126.6	122.9	159.6	132.1	111.6	132.0	131.2	116.4	162.7			
9a	146.7	125.4	134.7	126.7	124.5	118.7	161.7	152.4	55.5	135.1	128.4	128.9	128.4			
9e	146.7	125.4	134.7	126.6	124.5	118.7	161.6	152.1	55.5	134.1	129.0	130.4	133.1			
9h	146.7	125.4	134.7	126.6	124.4	118.7	161.8	152.4	55.5	131.3	130.6					

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