SYNTHESIS OF 2,4-SUBSTITUTED 5,6-BENZOQUINOLINES

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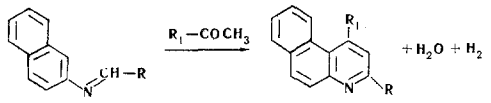
By the catalytic condensation of azomethines with aliphatic-aromatic and heterocyclic ketones, derivatives of 5,6-benzoquinoline containing thiophene or pyridine rings as substituents have been synthesized.

It is known from the literature that many compounds of the quinoline series possess various physiological activities and have found use in medicine and in agriculture [1–3]. The present work is a continuation of our investigations on the synthesis of derivatives of 5,6-benzoquinoline [4–6]. The synthesis of these compounds was effected by the catalytic condensation of arylidene-2-naphthylamines with organic compounds containing mobile hydrogen atoms.

In the present investigation, the synthesis of 5,6-benzoquinolines was performed in two ways.

1. In the presence of hydrochloric acid as catalyst, α-thienylidene-2-naphthylamine was brought into reaction with aliphatic-aromatic ketones (acetophenone, p-chloroacetophenone, p-bromoacetophenone, etc.). The reaction gave derivatives of 4-aryl-5,6-benzoquinolines with an α-thienyl radical in position 2.

2. Arylidene-2-naphthylamines were brought into reaction with α-acetylthiophene and 3-acetylpyridine. This gave 2-aryl-5,6-benzoquinolines with α-thienyl or 3-pyridyl radicals in position 4.



R and R_1 = 2-thienyl, 3-pyridyl, or aryl

The IR spectra of the compounds synthesized lacked absorption bands characteristic for the stretching vibrations of a carbonyl group; this shows the cyclic structure of the compounds obtained.

EXPERIMENTAL

The catalytic condensation of the Schiff's bases with the aliphatic-aromatic ketones was effected in the following way: 0.005 mole of a ketone and 5–10 drops of concentrated HCl were added to an ethanolic solution of 0.005 mole of a Schiff's base. The reaction mixture was heated in a sealed tube in the water bath for 0.5–2 hr. After cooling, a precipitate generally separated out which was removed and treated with ammonia. The resulting product was crystallized from a mixture of ethanol and benzene (1 : 1).

The compounds synthesized and the results of their analysis are given in the table. The contents of platinum in the platinates of these compounds corresponded to the calculated figures.

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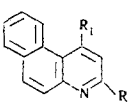

R	R_1	Mp, °C	Empirical formula	Found, %		Calculated, %		Yield, %
				N	S	N	S	
α-C_4H_3S	C_6H_5	181—182	$C_{23}H_{15}SN$	3.70	8.41	3.91	9.00	34.50
α-C_4H_3S	p-ClC_6H_4	176	$C_{23}H_{14}ClSN$	3.38	7.30	3.57	8.21	25.70
α-C_4H_3S	p-BrC_6H_4	185—186	$C_{23}H_{14}BrSN$	3.08	6.85	3.20	7.30	34.40
α-C_4H_3S	p-$CH_3OC_6H_4$	169—170	$C_{24}H_{17}OSN$	3.41	7.83	3.61	8.30	29.40
α-C_4H_3S	p-$C_2H_5OC_6H_4$	179—180	$C_{25}H_{19}OSN$	3.28	7.52	3.50	8.01	21.30
α-C_4H_3S	p-$CH_3C_6H_4$	150—151	$C_{24}H_{17}SN$	3.61	8.15	3.74	8.60	48.40
α-C_4H_3S	α-C_4H_3S	158—160	$C_{21}H_{13}S_2N$	3.84	17.60	3.90	17.72	26.60
C_6H_5	α-C_4H_3S	149—150	$C_{23}H_{15}SN$	3.83	8.70	3.91	9.40	51.70
p-ClC_6H_4	α-C_4H_3S	172—173	$C_{23}H_{14}ClSN$	3.47	7.72	3.57	8.20	13.80
p-BrC_6H_4	α-C_4H_3S	179—180	$C_{23}H_{14}BrSN$	3.33	6.80	3.20	7.35	21.40
p-$CH_3OC_6H_4$	α-C_4H_3S	147—148	$C_{24}H_{17}OSN$	3.63	8.03	3.61	8.36	25.10
p-$NO_2C_6H_4$	α-C_4H_3S	246—247	$C_{23}H_{14}O_2SN_2$	6.80	8.06	6.96	7.96	55.60
m-$NO_2C_6H_4$	α-C_4H_3S	238—239	$C_{23}H_{14}O_2SN_2$	7.07	8.10	6.96	7.96	17.80
C_6H_5	β-C_5H_4N	181—182	$C_{24}H_{16}N_2$	8.07	—	7.99	—	50.20
p-ClC_6H_4	β-C_5H_4N	173—174	$C_{24}H_{15}ClN_2$	7.39	—	7.28	—	22.90
p-BrC_6H_4	β-C_5H_4N	190—191	$C_{24}H_{15}BrN_2$	6.68	—	6.55	—	30.80
p-$CH_3OC_6H_4$	β-C_5H_4N	175—177	$C_{25}H_{18}ON_2$	7.47	—	7.36	—	32.40
p-$CH_3C_6H_4$	β-C_5H_4N	161—162	$C_{25}H_{18}N_2$	7.78	—	7.69	—	14.90
p-$NO_2C_6H_4$	β-C_5H_4N	240—241	$C_{24}H_{15}O_2N_3$	10.45	—	10.62	—	32.70
m-$NO_2C_6H_4$	β-C_5H_4N	235—237	$C_{24}H_{15}O_2N_3$	10.53	—	10.62	—	35.20
α-C_4H_3S	β-C_5H_4N	217—218	$C_{22}H_{14}SN_2$	7.73	8.45	7.83	9.00	24.60