INTERACTION OF SCHIFF BASES WITH INDANDIONE-1, 3

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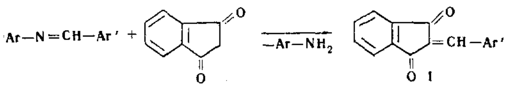
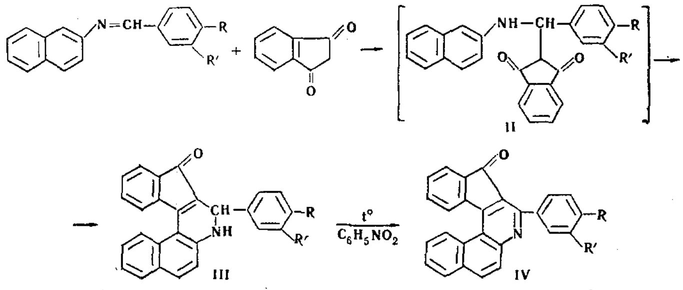
A new method was examined for the synthesis of multinuclear systems based on dihydroquinoline and quinoline, consisting of the interaction of arylidene-β-naphthylamines with indandione-1,3. The reaction of arylidene anilines with indandione-1, 3 leads to the formation of arylidenindandiones-1, 3.

The reaction of Schiff bases with cyclic β-diketones, as distinct from the reaction with methylketones [1–4, 7] and aliphatic β-diketones [5, 6] has not been studied. In the present work we studied the reaction of condensation of the azomethines with indandione-1, 3. Schiff bases were used which had been obtained from aromatic aldehydes and amines in the aniline and β-naphthylamine series.

When the reaction was conducted in alcohol or benzene in most cases arylidenindandiones-1, 3 (I) were formed.



However, the interaction between benzal-β-naphthylamine and indandione-1, 3 in alcoholic (but not in benzene) solution proceeds atypically with the formation of 2-phenyl-3, 4-(2', 3'-indenone-1')-5, 6-benzodihydroquinoline (III, R=R'=H). The reaction of this azomethine and its derivatives with indandione-1, 3 in fusion proceeds in an analogous manner.



R = H, NO_2, OCH_3, $N(CH_3)_2$, $N(C_2H_5)_2$, Cl, Br, CH_3; R' = H, NO_2, Cl

The synthesized 2-aryl-3, 4-(2'-, 3'-indenone-1')-5, 6-benzodihydroquinolines (table 1) are red or claret substances with high melting points. They do not dissolve in alcohol, benzene, and toluene, but are relatively soluble in nitrobenzene, pyridine, and dimethylformamide.

Table 1. The 5, 6-Benzodihydroquinolines, III

R	R'	Mp, °C	Empirical formula	N, %		Yield, %
				Found	Calculated	
H	H	334—336	$C_{26}H_{17}NO$	3.66	3.90	56
Cl	H	336.5—399	$C_{26}H_{16}ClNO$	3.28	3.56	62
H	Cl	331.5—333.5	$C_{26}H_{16}ClNO$	3.50	3.56	53
Br	H	345—347	$C_{26}H_{16}BrNO$	2.96	3.19	58
NO_2	H	335—337	$C_{26}H_{16}N_2O_3$	6.60	6.93	71
H	NO_2	303—305	$C_{26}H_{16}N_2O_3$	6.83	6.93	66
$N(C_2H_5)_2$	H	150—152	$C_{30}H_{26}N_2O$	6.22	6.51	50
$N(CH_3)_2$	H	199.5—201.5	$C_{28}H_{22}N_2O$	6.54	6.96	53
OCH_3	H	341—343	$C_{27}H_{19}NO_2$	3.28	3.60	37
CH_3	H	340.5—342	$C_{27}H_{19}NO$	3.49	3.75	51

Compounds III on further heating in air to 300–350° C or on boiling in nitrobenzene are converted into 2-aryl-

3, 4-(2', 3'-indenone-1')-5, 6-benzoquinolines (IV) (table 2). They are yellow in color and have lower melting points than the corresponding 2-aryl-3, 4-(2', 3'-indenone-1')-5, 6-benzodihydroquinolines, and in contrast to the latter are soluble in toluene.

Table 2. 5, 6-Benzoquinolines

R	R′	Mp, °C	Empirical formula	N, %		Yield %
				Found	Calculated	
H	H	300—301	$C_{26}H_{15}NO$	3.59	3.92	71
Cl	H	311—313	$C_{26}H_{14}ClNO$	3.31	3.58	82
H	Cl	315—317	$C_{26}H_{14}ClNO$	3.27	3.58	77
Br	H	311—313	$C_{26}H_{14}BrNO$	2.93	3.21	81
NO_2	H	347—349	$C_{26}H_{14}N_2O_3$	6.68	6.96	86
H	NO_2	262—264	$C_{26}H_{14}N_2O_3$*	6.69	6.96	82
OCH_3	H	259.5—262	$C_{27}H_{17}NO_2$	3.33	3.61	86
CH_3	H	278—280	$C_{27}H_{17}NO$	3.45	3.78	50

*Found, %: C 78.24; H 3.66. Calculated for, %: C 77.60; H 3.57.

In the IR spectra of the dihydroquinolines, III, one absorption band at 3360–3366 cm^{-1} was observed, corresponding to valency oscillations of the N—H bond. The accuracy of the structure of compound III was also confirmed by the presence of only one absorption band in the 1656 cm^{-1} region in the IR spectra of these compounds corresponding to the valency oscillations of the CO group. This provides evidence that the primary products of the reaction have not the aminoindandione structure of compound II, as the derivatives of indandione have at least two frequencies in the absorption region of the CO group.

In the IR spectra of the quinolines of compound IV there are no absorption bonds in the 3300–3500 cm^{-1} region, which indicates the presence of a tertiary amine. Compounds IV, as with all 5, 6-benzoquinolines, are stable in a medium of concentrated hydrochloric acid in the cold and on heating.

It was also established that these dihydroquinolines III, in which there is a strong electron accepter substitute (NO_2) in the phenyl radical, readily transform into quinolines IV, whereas the dihydroquinolines with the electron donor substitute OCH_3 are converted into quinolines with difficulty. If the dihydroquinolines contain a strong electron donor substitute [$N(CH_3)_2$, $N(C_2H_5)_2$] in the phenyl radical, they are unable to be oxidized to quinolines IV even on prolonged boiling.

EXPERIMENTAL

Aryllidenindandiones-1, 3. A) A mixture of 1.46 g (0.01 mole) of indandione-1, 3 and 1.81 g (0.01 mole) of benzal aniline in alcohol or benzene was heated in a water bath for 3–5 min. During this procedure a crystalline precipitate readily separated out from the hot solution. The product of the reaction was recrystallized from a mixture of alcohol and benzene (1:1). Yellow needles with a mp of 152–153° C. Yield, 2.1 g (~70%). The compound was identified by melting a mixed sample with the known benzilidenindandione-1, 3.

Benzilidenindandione-1, 3 is also formed under the same conditions during the interactions of indandione-1, 3 and benzal-p-toluidine, benzal-p-bromamiline, and benzalanestezine and benzal-p-anisidine.

In an analogous manner p-methoxylbenzilidendandione-1, 3 with a mp of 155–156° C (yield, 80%) was obtained from indandione-1, 3 and p-methoxybenzalaniline or p-methoxybenzal-β-naphthylamine, p-bromobenzolidenindandione-1, 3 with a mp of 167–170° C (yield 85%) was obtained from indandione-1, 3 and p-bromobenzalaniline or p-brombenzal-β-naphthylamine, m-nitrobenzalindandione-1, 3 with a mp of 246–248° C was obtained from indandione-1, 3 and m-nitrobenzalaniline or p-nitrobenzal-β-naphthylamine, and p-nitrobenzalindandione-1, 3 with a mp of 228–230° C (yield 85%) was obtained from indandione-1, 3 and p-nitrobenzalaniline or p-nitrobenzal-β-naphthylamine. The constants of the arylidenindandiones-1, 3 obtained in this work correspond to previously published data [8].

B) A mixture of equimolecular quantities of indandione-1, 3 and the Schiff base, formed from an aromatic aldehyde and amines in the aniline series, was heated in a sealed ampoule at 160° C for 3 min. The products obtained are the corresponding arylidenindandiones-1, 3.

2-Phenyl-3, 4-(2', 3'-indenone-1')-5, 6-benzodihydroquinoline. A solution of 1.46 g (0.01 mole) of indandione-1, 3 and 2.31 g (0.01 mole) of benzal-β-naphthylamine in 20 ml ethanol was heated in a water bath for 5 min. The red flaked crystals which separated out from the hot solution were recrystallized from nitrobenzene or pyridine. Yield, 2.26 g (63%). Mp 334–336° C, Found, %: C 87.45; H 4.51; N 3.66. Calculated for $C_{26}H_{17}NO$, %: C 86.88; H 4.73; N 3.90. Under similar conditions benzilidenindandione-1, 3 with a mp of 152–153° C separated out from the benzene solution.

2-Aryl-3, 4-(2', 3'-indenone-1')-5, 6-benzodihydroquinolines (III). A mixture of equimolecular quantities of indandione-1, 3 and arylidene-β-naphthylamine was heated in a sealed ampul at 160–170° C for 3 min. The reaction mixture began to melt, and then foamed and solidified. On cooling the solid residue was recrystallized from a mixture of nitrobenzene and toluene (or pyridine). The melting point of the compounds obtained was determined in an aluminum block by heating in air (Table 1).

2-Aryl-3, 4-(2', 3'-indenone-1')-5, 6-benzoquinolines (IV). A) 0.02 mole of 2-phenyl-3, 4-(2', 3'-indenone-1')-5, 6-benzodihydroquinoline was heated at 300–350° C for 3–5 min. During this procedure partial resinification occured. The product of the reaction was recrystallized from toluene or from a mixture of nitrobenzene and toluene.

B) 2-Aryl-3, 4-(2', 3'-indenone-1')-5, 6-benzoquinolines were also obtained by boiling the corresponding 5, 6-benzoquinolines in nitrobenzene for 2 hr.

C) 2-Aryl-3, 4-(2', 3'-indenone-1')-5, 6-benzoquinolines may also be obtained on heating a reaction mixture consisting of indandione-1, 3 and benzal-β-naphthylamine or its derivatives to 300° C.

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