BENZINDAZOLES FROM INDANETRIKETONES

III.* 1-ALKYL-5-HYDROXYBENZ[g]INDAZOLES

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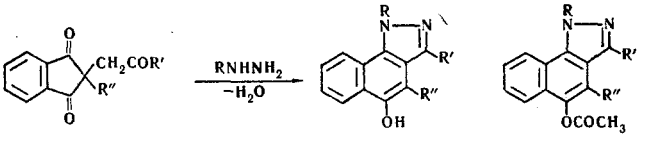
1-Alkyl-5-hydroxybenz[g]indazoles have been synthesized by the reaction of 2-acetonyl- and 2-phenacyl-2-arylindan-1, 3-diones with alkylhydrazines, accompanied by intramolecular cyclization and ring rearrangement.

It has been shown previously [1, 2] that reaction of 2-acetonyl- and 2-phenacylindan-1, 3-diones with hydrazine hydrate and phenylhydrazine affords 5-hydroxybenz[g]indazoles. The reaction is accompanied by isomerization of the five-membered ring of the indandione to the six-membered benzindazole ring.

An examination of the reaction of 2-phenacyl-2-phenylindan-1, 3-dione (Ia), 2-acetonyl-2-phenyl-1, 3-indandione (Ib), and 2-acetonyl-2-(p-methoxyphenyl)indan-1, 3-dione (Ic) with methyl- and ethylhydrazine has shown that the reaction of the triketones with alkylhydrazines is generally similar, and proceeds according to the scheme put forward previously [1, 2], to give 1-alkyl-5-hydroxybenz[g]indazoles (IIa-e). The alkylhydrazones which are presumably formed as intermediates were not isolated.

The alkylhydroxybenzindazoles are colorless, crystalline substances which are soluble in alcoholic alkalies with a yellow coloration. Acetylation affords the acetoxy derivatives IIIa-e.



I a-b II a-e III a-e

I a $R'=C_6H_5$, $R''=C_6H_5$, b $R'=CH_3$, $R''=C_6H_5$, c $R'=CH_3$, $R''=C_6H_4OCH_3$; II, III a $R=CH_3$, $R'=C_6H_5$, $R''=C_6H_5$, b $R=CH_3$, $R'=CH_3$, $R''=C_6H_5$, c $R=CH_3$, $R'=CH_3$, $R''=C_6H_4OCH_3$, d $R=C_2H_5$, $R'=CH_3$, $R''=C_6H_5$, e $R=C_2H_5$, $R'=CH_3$, $R''=C_6H_4OCH_3$

In the 3 μ region, in dichloroethane and carbon tetrachloride solution, the spectra of 1-alkyl-5-hydroxybenz[g]indazoles show bands due to stretching of the OH group at 3535-3565 cm^{-1}. This band is absent in the spectra of the 5-acetoxy derivatives, but a band appears due to the ester carbonyl near 1750 cm^{-1}.

The UV spectra of 1-alkyl-5-hydroxybenz[g]indazoles in ethanol show four absorption bands (see Table 2). They differ little from the spectra recorded in the literature for both N-substituted and N-unsubstituted benz[g]indazoles [1-4] and for 5-hydroxyindazoles [5].

*For Part II, see [2].

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TABLE 1. IR Spectra of Benzindazoles*

Compound	Medium	6μ Region, ν, cm⁻¹	νC-O, cm⁻¹	νOH, cm⁻¹
IIa	Dichloroethane	1608, 1591, 1532		3536
IIb	CCl_4	1545		3562
	Nujol	1581, 1568, 1530		Not taken
IId	Dichloroethane	Not taken		3540
IIIb	Nujol	1584, 1561, 1525	1742	
IIId	Dichloroethane	1595, 1559	1753	

*The spectra were obtained on an IKS-14 instrument.

TABLE 2. UV Spectra of Benzindazoles

Compound	λmax, nm (ε · 10⁻³)			
IIa	225 (42,0)	252 (34.4)	320 (10,1)	340 (7,8)
IIb	225 (40,0)	255 (35.2)	310 (8,8)	335 (8,0)
IIc	230 (44,0)	255 (40,0)	315 (9,0)	335 (8,0)
IId	230 (43,6)	257 (41.2)	320 (9,2)	335 (8.6)
IIe	225 (42.0)	260 (40.0)	320 (9,6)	335 (8,8)

TABLE 3. 1-Alkyl-5-hydroxybenz[g]indazoles and Their Acetoxy Derivatives

Compound	Name	Mp, °C	Molecular formula	Found, %			Calculated, %			Yield, %
				C	H	N	C	H	N	
IIa	1-Methyl-1,4-diphenyl-5-hydroxybenz[g]indazole	243	$C_{24}H_{18}ON_2$	82,22	5,20	8,11	82,26	5,18	8,00	68
IIb	1,3-Dimethyl-4-phenyl-5-hydroxybenz[g]indazole	169—170	$C_{19}H_{16}ON_2$	78,93	5,75	10,16	79,14	5,59	9,72	69
IIc	1,3-Dimethyl-4-(p-methoxyphenyl)-5-hydroxybenz[g]indazole	189—190	$C_{20}H_{18}O_2N_2$	75,41	5,46	8,74	75,48	5,70	8,81	78
IId	1-Ethyl-3-methyl-4-phenyl-5-hydroxybenz[g]indazole	167—168	$C_{20}H_{18}ON_2$	79,73	6,01	9,43	79,47	6,00	9,27	60
IIe	1-Ethyl-3-methyl-4-(p-methoxyphenyl)-5-hydroxybenz[g]indazole	179—180	$C_{21}H_{20}O_2N_2$	75,26	5,88	8,12	75,87	6,07	8,42	54
III	1-Methyl-3,4-diphenyl-5-acetoxybenz[g]indazole	175—176	$C_{26}H_{20}O_2N_2$	79,34	5,24	7,26	79,60	5,14	7,14	—
IIIb	1,3-Dimethyl-4-phenyl-5-acetoxybenz[g]indazole	157—159	$C_{21}H_{18}O_2N_2$	76,56	5,44	8,10	76,33	5,49	8,48	—
IIIc	1,3-Dimethyl-4-(p-methoxyphenyl)-5-acetoxybenz[g]indazole	182—183	$C_{22}H_{20}O_3N_2$	72,66	5,60	7,71	73,30	5,59	7,78	—
IIId	1-Ethyl-3-methyl-4-phenyl-5-acetoxybenz[g]indazole	142—143	$C_{22}H_{20}O_2N_2$	76,33	5,57	8,43	76,70	5,85	8,14	—
IIIe	1-Ethyl-3-methyl-4-(p-methoxyphenyl)-5-acetoxybenz[g]indazole	135	$C_{23}H_{22}O_3N_2$	73,48	6,25	7,69	73,75	5,92	7,48	—

EXPERIMENTAL

1-Alkyl-5-hydroxybenz[g]indazoles (IIa-e). To a solution of 0.01 mole of triketones Ia-b in 10 ml of glacial acetic acid was added 0.02 mole of the alkylhydrazine. The mixture was heated on the water bath for 30 min, and poured into water. The precipitate was filtered off and recrystallized from ethanol.

1-Alkyl-5-acetoxybenz[g]indazoles (IIIa-e). 10 ml of acetic anhydride and 8 mmole of anhydrous sodium acetate were heated with 2 mmole of IIa-e for 1 h. The mixture was poured into water, and the precipitate was filtered off and recrystallized from ethanol.

The mp's, yields, and analyses of the compounds obtained are given in Table 3.

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