Synthesis of Heterocycles. Part V. (1) The Synthesis of Substituted Indenopyridines

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2-Arylmethylene-1-indanones (I) and 2-arylmethylene-1,3-indanediones (VII) react with active methylene compounds in the presence of ammonium acetate as a basic catalyst to afford substituted pyridines. The postulated routes to the formation of the reported compounds are given.

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A recent modification in the Michael reaction is the use of ammonium acetate as a basic catalyst in the reaction of α,β-unsaturated ketones with active methylene compounds to give pyridones (2), benzoquinolines and -acridines (3). The present study describes the extension of this modification to the synthesis of indenopyridines. The results of this investigation are formulated in Scheme 1 and the products obtained are given in Tables I and II.

	Y	Z
I	CH_2	
II	CH_2	H[a]
III	CH_2	CN
IV	CH_2	$CONH_2$
V	CH_2	COMe
VI	CH_2	Ph
VII	CO	
VIII	CO	H[a]
IX	CO	COMe
X	CO	Ph

Ar = a, C_6H_5 ; b, 4-$MeOC_6H_4$; c, 4-ClC_6H_4.

(a) C_3-C_4 doubly bonded

Scheme 1

Results and Discussion.

Fusion of 2-arylmethylene-1-indanone I, ethyl cyanoacetate, and an excess of ammonium acetate at 145° gave 4-aryl-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones II (55%) and 4-aryl-3-cyano-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones III (35%). The structures of compounds II and III were inferred from their analytical (Table I) and spectral data (Table II), chemical reactions, and independent synthesis. Thus, the ir spectra of II revealed the presence of a conjugated C=C (1640 cm^{-1}), cyclic lactam C=O (1665 cm^{-1}), a NH (3250 cm^{-1}), and an OH (3580 cm^{-1}) bands, characteristic of the stretching frequencies in 2-pyridone type compounds (4). No band was observed in the region 2240-2220 cm^{-1} due to a free CN group. The uv absorption pattern of II showed, in each case, three maxima in the 375-345, 275-260, and 240-225 nm regions (Table II), which is similar to the absorption pattern of 1-azafluorenes (5). The nmr spectrum of II (Ar = *p*-methoxyphenyl) for example, in deuterated chloroform showed a multiplet at δ 7.3-7.9 (10H, aromatic and NH), a singlet at δ 3.7 (3H, CH_3OAr) and a singlet at δ 2.4 (2H, CH_2) ppm. Upon shaking with deuterium oxide a new singlet appeared at δ 4.45 ppm assignable to DOH proton and the mutiplet at δ 7.4-8.1 ppm corresponding to nine protons only. For compound III, the ir spectra showed a lactam C=O (1675 cm^{-1}), a C≡N (2235 cm^{-1}), a NH (3350 cm^{-1}), and a broad OH (3600 cm^{-1}) bands. Their uv spectra in ethanol (Table II) showed two maxima in the 295-265, and 235-230 nm regions. The nmr spectrum of III (Ar = *p*-methoxyphenyl) exhibits a multiplet at δ 7.2-8.0 (9H, aromatic and NH), a singlet at δ 3.6 (3H, CH_3OAr), a doublet at δ 2.65 (1H, CHCN), a doublet at δ 2.5 (1H, CHAr) and a singlet at δ 2.35 (2H, CH_2) ppm. Further, the treatment of I with cyanoacetamide and an excess of ammonium acetate at elevated temperature afforded prodcuts that proved to be identical in every respect with the corresponding II and III prepared earlier.

Treatment of I with diethyl malonate or malondiamide and ammonium acetate at 150° for 12 hours gave in each case II (50%) and 4-aryl-3-carbamoyl-4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones IV (35%). Similar treatment of I with ethyl acetoacetate gave II (50%) and 3-acetyl-4-aryl-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2-(1*H*)-ones V (40%). The analytical and spectral data of compounds II prepared through both latter routes were in accord with the structure assigned earlier. The ir spectra of compound IV revealed the presence of a cyclic lactam C=O (1660 cm^{-1}), a primary amide C=O (1675 cm^{-1}), a NH (3320 cm^{-1}) and an OH (3570 cm^{-1}) bands. The nmr spectrum of IV (Ar = *p*-methoxyphenyl) showed a singlet at δ 2.4 (2H, CH_2), a doublet at δ 2.55 (1H, CHAr), a doublet at δ 2.95 (1H, CHCO), a singlet at δ 3.75 (3H, CH_3OAr), a singlet at δ 4.5 (2H, H_2NCO) and a multiplet at δ 7.3-7.9 (9H, aromatic and NH) ppm. However, compounds IV

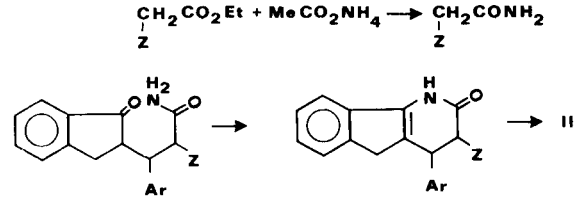
Table I

Substituted Indenopyridinones

Compound No.	Ar	Mp °C	Molecular Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found	Cl, % Calcd.	Cl, % Found
4-Aryl-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones, II											
IIa	C_6H_5	241	$C_{18}H_{13}NO$	83.38	83.31	5.05	4.99	5.40	5.31		
IIb	*p*-$MeOC_6H_4$	285	$C_{19}H_{15}NO_2$	78.87	78.80	5.23	5.26	4.84	4.91		
IIc	*p*-ClC_6H_4	232 (a)	$C_{18}H_{12}ClNO$	73.60	73.52	4.12	4.09	4.77	4.76	12.07	12.09
4-Aryl-3-cyano-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones, III											
IIIa	C_6H_5	218	$C_{19}H_{12}N_2O$	79.70	79.61	4.93	4.85	9.78	9.63		
IIIb	*p*-$MeOC_6H_4$	238	$C_{20}H_{14}N_2O_2$	75.93	75.88	5.10	5.01	8.86	8.80		
IIIc	*p*-ClC_6H_4	283	$C_{19}H_{11}ClN_2O$	71.14	71.06	4.06	4.02	8.73	8.61	11.05	10.97
4-Aryl-3-carbamoyl-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones, IV.											
IVa	C_6H_5	320	$C_{19}H_{16}N_2O_2$	74.97	74.91	5.30	5.37	9.20	9.08		
IVb	*p*-$MeOC_6H_4$	277	$C_{20}H_{18}N_2O_3$	71.83	71.89	5.43	5.36	8.38	8.27		
IVc	*p*-ClC_6H_4	325 (a)	$C_{19}H_{15}ClN_2O_2$	67.36	67.46	4.46	4.41	8.27	8.18	10.46	10.35
3-Acetyl-4-aryl-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones, V											
Va	C_6H_5	263	$C_{20}H_{17}NO_2$	79.19	79.02	5.65	5.58	4.62	4.50		
Vb	*p*-$MeOC_6H_4$	253	$C_{21}H_{19}NO_3$	75.66	75.57	5.75	5.69	4.20	4.13		
Vc	*p*-ClC_6H_4	284	$C_{20}H_{16}ClNO_2$	64.60	64.52	4.34	4.24	3.77	3.68	9.53	9.46
4-Aryl-3-phenyl-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones, VI											
VIa	C_6H_5	260 (a)	$C_{24}H_{19}NO$	85.43	85.34	5.68	5.55	4.15	4.03		
VIb	*p*-$MeOC_6H_4$	229	$C_{25}H_{21}NO_2$	81.72	81.51	5.76	5.53	3.81	3.74		
VIc	*p*-ClC_6H_4	310 (a)	$C_{24}H_{18}ClNO$	77.52	77.39	4.88	4.72	3.77	3.64	9.65	9.44
4-Aryl-5-indeno[1,2-*b*]pyridin-2(1*H*)-ones, VIII											
VIIIa	C_6H_5	251	$C_{18}H_{11}NO_2$	79.11	78.95	4.06	3.89	5.13	5.06		
VIIIb	*p*-$MeOC_6H_4$	311	$C_{19}H_{13}NO_3$	75.24	75.09	4.32	4.39	4.62	4.51		
VIIIc	*p*-ClC_6H_4	306	$C_{18}H_{10}ClNO_2$	70.26	69.98	3.28	3.41	4.55	4.45	11.52	11.47
3-Acetyl-4-aryl-3,4-dihydro-5-ketoindeno[1,2-*b*]pyridin-2(1*H*)-ones, IX											
IXa	C_6H_5	238	$C_{20}H_{15}NO_3$	75.70	75.54	4.76	4.63	4.41	4.30		
IXb	*p*-$MeOC_6H_4$	231	$C_{21}H_{17}NO_4$	72.62	72.58	4.93	4.71	4.03	3.92		
IXc	*p*-ClC_6H_4	264	$C_{20}H_{14}ClNO_3$	68.29	68.11	4.01	3.88	3.98	3.82	10.08	9.95
4-Aryl-3-phenyl-3,4-dihydro-5-ketoindeno[1,2-*b*]pyridin-2(1*H*)-ones, X											
Xa	C_6H_5	283	$C_{24}H_{17}NO_2$	82.03	81.86	4.88	4.76	3.99	3.81		
Xb	*p*-$MeOC_6H_4$	320	$C_{25}H_{19}NO_3$	78.73	78.61	5.02	4.86	3.67	3.55		
Xc	*p*-ClC_6H_4	292	$C_{24}H_{16}ClNO_2$	74.71	74.59	4.18	4.03	3.63	3.51	9.19	9.01
2-Acetoxy-4-aryl-3-phenyl-5*H*-indeno[1,2-*b*]pyridines, XI											
XIa	C_6H_5	219	$C_{26}H_{19}NO_2$	82.74	82.66	5.07	5.19	3.71	3.83		
3-Acetyl-4-aryl-2-chloro-5-ketoindeno[1,2-*b*]pyridines, XII											
XIa	C_6H_5	197	$C_{20}H_{12}ClNO_2$	71.97	72.03	3.62	3.51	4.20	4.33	10.62	10.58

(a) With decomposition

were found to convert to the corresponding II upon standing. On the other hand, the ir spectra of V showed a cyclic lactam C=O (1660 cm^{-1}), an acetyl C=O (1680 cm^{-1}), a NH (3355 cm^{-1}) and an OH (3590 cm^{-1}) bands. Their nmr spectra (Ar = *p*-methoxyphenyl) exhibited a multiplet at δ 7.1-8.0 (9H, aromatic and NH), a singlet at δ 3.6-3.7 (3H, CH_3OAr), a doublet at δ 2.85 (1H, CHCO), a doublet at δ 2.65 (1H, CHAr), a singlet at δ 2.40 (2H, CH_2), and a singlet at δ 2.10 (3H, CH_3O) ppm. Under analogous experimental conditions, I reacted with ethyl phenylacetate and ammonium acetate to give the 4-aryl-3-phenyl-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones (VI) only. The ir spectra of VI contained common bands at 1655 cm^{-1} (2-keto group), 3335 cm^{-1} (NH group) and 3580 cm^{-1} (OH group). The nmr spectrum of VI (Ar = *p*-methoxyphenyl) in deuteriochloroform revealed the presence of a multiplet in the aromatic region δ 7.2-8.2 (14H, aromatic and NH), a singlet at δ 3.7-3.8 (3H, CH_3OAr), two overlapped doublets centered at δ 2.65 (2H, 2CHAr), and a singlet at δ 2.4-2.5 (2H, CH_2) ppm. The uv data are shown in Table II.



Scheme 2

Table II

Compound	λ max (Ethanol) nm	δ (Deuteriochloroform) (multiplicity, assignment) (a)	ν (Potassium bromide) cm⁻¹ CH_3CO	H_2NCO	CO (ester)	CO (indanone)	C≡N	NH(OH)	CO (b)
		4-Aryl-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones, II							
IIa	345 (4.29), 260 (4.36), 225 (3.76)	2.45 (s, 2H, CH_2)						3240	1670
IIb	375 (4.37), 275 (4.12), 240 (3.98)	3.70 (s, 3H, CH_3O), 2.40 (s, 2H, CH_2)						3250	1665
IIc	367 (4.30), 265 (3.88), 236 (4.02)	2.43 (s, 2H, CH_2)						3245	1670
		4-Aryl-3-cyano-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones, III							
IIIa	285 (3.98), 230 (3.34)	2.60 (d, 1H, CHCN), 2.50 (d, 1H, CHAr), 2.40 (s, 2H, CH_2)					2232	3365	1670
IIIb	295 (3.79), 235 (3.64)	3.60 (s, 3H, CH_3O), 2.65 (d, 1H, CHCN), 2.50 (d, 1H, CHAr), 2.35 (s, 2H, CH_2)					2235	3350	1675
IIIc	268 (3.43), 233 (3.21)	2.63 (d, 1H, CHCN), 2.44 (d, 1H, CHAr), 2.43 (s, 2H, CH_2)					2230	3355	1670
		4-Aryl-3-carbomoyl-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones, IV							
IVa	301 (4.36), 250 (3.16)	4.45 (s, 2H, H_2NCO), 2.88 (d, 1H, CHCO), 2.50 (d, 1H, CHAr), 2.43 (s, 2H, CH_2)		1688				3288	1675
IVb	312 (4.47), 245 (3.37)	4.50 (s, 2H, H_2NCO), 3.75 (s, 3H, CH_3O), 2.95 (d, 1H, CHCO), 2.55 (d, 1H, CHAr), 2.40 (s, 2H, CH_2)		1675				3320	1660
IVc	303 (4.35), 248 (3.53)	4.48 (s, 2H, H_2NCO), 2.85 (d, 1H, CHCO), 2.63 (d, 1H, CHAr), 2.43 (s, 2H, CH_2)		1690				3200	1675
		3-Acetyl-4-aryl-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones, V							
Va	278 (4.16), 260 (4.58)	2.85 (d, 1H, CHCO), 2.55 (d, 1H, CHAr), 2.35 (s, 2H, CH_2), 2.15 (s, 3H, CH_3CO)	1688					3320	1655
Vb	283 (4.37), 275 (4.45)	3.65 (s, 3H, CH_3O), 2.85 (d, 1H, CHCO), 2.65 (d, 1H, CHAr), 2.40 (s, 2H, CH_2), 2.20 (s, 3H, CH_3CO)	1680					3355	1660
Vc	280 (4.52), 265 (3.75)	2.83 (d, 1H, CHCO), 2.50 (d, 1H, CHAr), 2.42 (s, 2H, CH_2), 2.20 (s, 3H, CH_3CO)	1690					3295	1650
		4-Aryl-3-phenyl-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)pyridin-2(1*H*)-ones, VI							
VIa	315 (4.14), 245 (4.30)	2.70 (t, 2H, 2CHAr) (c), 2.4 (s, 2H, CH_2)						3200	1670
VIb	320 (4.22), 270 (4.08)	3.75 (s, 3H, CH_3O), 2.65 (t, 2H, 2CHAr) (c), 2.50 (s, 2H, CH_2)						3335	1655
VIc	315 (4.12), 245 (4.37)	2.68 (t, 2H, 2CHAr) (c), 2.43 (s, 2H, CH_2)						3200	1640
		4-Aryl-5-ketoindeno[1,2-*b*]pyridin-2(1*H*)-ones, VIII							
VIIIa	364 (4.18), 274 (4.24), 230 (4.20)					1723		3290	1658
VIIIb	369 (4.23), 283 (4.20), 238 (4.19)	3.80 (s, 3H, CH_3O)				1720		3250	1655
VIIIc	358 (4.31), 279 (4.06), 233 (3.99)					1727		3300	1655
		3-Acetyl-4-aryl-3,4-dihydro-5-ketoindeno[1,2-*b*]pyridin-2(1*H*)-ones, XI							
IXa	284 (4.07), 263 (4.11)	2.95 (s, 1H, CHCO), 254 (s, 1H, CHAr), 2.23 (s, 3H CH_3CO)	1695			1725		3310	1660
IXb	289 (4.32), 271 (4.20)	3.75 (s, 3H, CH_3O), 2.90 (s, 1H, CHCO), 2.50 (s, 1H, CHAr), 2.20 (s, 3H, CH_3CO)	1690			1728		3295	1655
IXc	278 (4.45), 266 (4.02)	2.88 (s, 1H, CHCO), 2.55 (s, 1H, CHAr), 2.25 (s, 3H, CH_3CO)	1695			1725		3290	1655
		4-Aryl-3-phenyl-3,4-dihydro-5-ketoindeno[1,2-*b*]pyridin-2(1*H*)-ones, X							
Xa	328 (4.36), 248 (4.19)	2.75 (t, 2H, 2CHAr) (c)				1727		3290	1658
Xb	329 (4.29), 253 (4.27)	3.73 (s, 3H, CH_3O), 2.70 (t, 2H, 2CHAr) (c)				1730		3315	1655
Xc	319 (4.23), 254 (4.08)	2.66 (t, 2H, 2CHAr) (c)				1726		3295	1660
		2-Acetoxy-4-aryl-3-phenyl-5*H*-indeno[1,2-*b*]pyridines, XI							
XIa	355 (3.80), 293 (3.91), 241 (3.86)	2.85 (s, 3H, CH_3COO), 2.45 (s, 2H, CH_2)			1775				
		3-Acetyl-4-aryl-2-chloro-5-ketoindeno[1,2-*b*]pyridines, XII							
XIIa	368 (4.29), 317 (4.08), 230 (4.50)	2.25 (s, 3H, CH_3CO)	1685			1715			

(a) All compounds exhibit a multiplet signal on the 7.00-8.50 ppm region due to ArH and lactam NH (except series XI and XII) protons. (b) All compounds, except series XI and XII, showed a weak broad band in the region 3600-3500 cm^{-1} attributed to the ν OH of the lactim form. (c) Two overlapped doublets.

The above results indicate that the synthesis of the indenopyridine derivatives II *via* any of the mentioned routes proceed through one and the same intermediate. The latter is undoubtedly (A) which, after cyclization to either III, IV or V depending on the Z group, loses a HZ molecule to give II (Scheme 2).

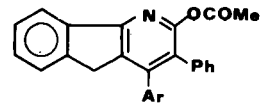
Non-isolation of II in the reaction of I with ethyl phenylacetate, that gave VI only, is attributed to the difficulty of losing a strong base like the phenyl ion (6).

On the other hand, treatment of VII (Scheme 1) with a benzene solution of ethyl cyanoacetate or cyanoacetamide in the presence of ammonium acetate afforded in each

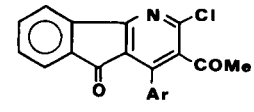
case 4-aryl-5-ketoindeno[1,2-*b*]pyridin-2(1*H*)-ones (VIII). The structures of VIII were deduced from their analytical and spectral data. The ir spectrum of each of compounds VIII showed a lactam C=O (1655 cm^{-1}), an indanone C=O (1720 cm^{-1}), a NH (3250 cm^{-1}) and an OH (3530 cm^{-1}) bands. The nmr spectrum of VIII (Ar = *p*-methoxyphenyl) for example, showed a multiplet at δ 7.3-8.2 (10H, aromatic and NH), and a singlet at δ 3.7-3.9 (3H, CH_3OAr). Further confirmation of the structure of VIII was achieved through comparison with samples prepared by the selenium dioxide oxidation of the corresponding II.

Analogous treatment of VII with ethyl acetoacetate gave VIII (40%) and 3-acetyl-4-aryl-3,4-dihydro-5-ketoindeno-[1,2-*b*]pyridin-2(1*H*)-ones IX (45%). On the other hand, boiling of VII with ethyl phenylacetate and ammonium acetate in benzene gave 4-aryl-3-phenyl-3,4-dihydro-5-ketoindeno[1,2-*b*]pyridin-2(1*H*)-ones (X) only. Both the elemental and spectral data of compounds of series IX and X were in accordance with their proposed structures (Table I and II). The nmr spectrum of IX (Ar = *p*-methoxyphenyl) exhibits a multiplet at δ 6.9-7.7 (9H, aromatic and NH), a singlet at δ 3.7-3.8 (3H, CH_3OAr), a doublet at δ 2.90 (1H, CHCO), a doublet at δ 2.50 (1H, CHAr), and a singlet at δ 2.20 (3H, CH_3CO) ppm. The nmr spectrum of X (Ar = *p*-methoxyphenyl) showed two overlapped doublets centered at δ 2.70 (2H, 2CHAr), a singlet at δ 3.6-3.8 (3H, CH_3OAr), and a multiplet at δ 7.2-7.9 (14H, aromatic and NH) ppm. The synthesis of compounds VIII-X from VII and active methylene compounds could be accounted for in a similar way to what have been proposed earlier (Scheme 2).

The existence of lactam-lactim tautomerism in the synthesized compounds listed in Scheme 1 was verified by the observation that their ir spectra showed a broad band at 3600-3500 cm^{-1} characteristic of the ν OH group. This broadness in the stretching frequency of the hydroxyl group is attributed to hydrogen bonding (7). When the spectra were carried in a dilute chloroform solution, a sharp band at 3550 cm^{-1} was observed and attributed to the ν OH of the monomer. Moreover, the phenolic character of these compounds was shown by their solubility in aqueous sodium hydroxide, their colouration with ferric chloride solution, and the formation of soluble azo dyes when coupled with benzene diazonium chloride. Furthermore, the suggested existence of the lactim form was verified when the treatment of VI with acetic anhydride and anhydrous sodium carbonate gave 2-acetoxy-4-aryl-3-phenyl-5*H*-indeno[1,2-*b*]pyridine (XI). The ir spectrum of XI showed a C=N (1620 cm^{-1}) and a conjugated ester C=O (1775 cm^{-1}) bands. No bands were observed in the regions 1650-1670, 3250-3350 and 3500-3600 cm^{-1} due to a cyclic lactam group. The nmr spectrum of XI a (Ar = phenyl) showed a multiplet at δ 7.1-7.8 (14H, aromatic), a singlet at δ 2.85 (3H, CH_3COO) and a singlet at δ 2.45 (2H, CH_2) ppm. This conversion of VI into XI is similar to the formation of 2-acetoxy quinoline derivatives from the corresponding 1,2-dihydro-2-oxoquinoline (8). Similarly, treatment of IX with phosphorus oxychloride afforded 3-acetyl-4-aryl-2-chloro-5-ketoindeno[1,2-*b*]pyridine (XII). The ir spectrum of XII showed no bands assignable to



XI



XII

lactam C=O and NH frequencies, but exhibited a C=N (1617 cm^{-1}), an acetyl C=O (1685 cm^{-1}) and indanone C=O (1715 cm^{-1}) bands. The nmr spectrum of XII (Ar = phenyl) revealed the presence of a multiplet at δ 7.3-8.1 (9H, aromatic) and a singlet at δ 2.25 (3H, CH_3CO) ppm, only.

EXPERIMENTAL

All melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by Prof. Dipl.-Ing., Dr. H. Malissa and G. Reuter, West Germany. Spectra were recorded with Pye-Unicam SP 1000 Infrared spectrophotometer (potassium bromide wafer technique), and Pye-Unicam SP 8000 visible and ultraviolet spectrophotometer (in ethanol). The ^{1}H-nmr spectra in deuteriochloroform were recorded on a Varian-T 60 A spectrometer using TMS as an internal standard.

2-Arylmethylene-1-indanones I (9), and 2-arylmethylene-1,3-indanediones VII (10) were prepared as previously reported.

4-Aryl-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones (II), and 4-Aryl-3-cyano-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones (III).

Procedure 1.

A mixture of ethyl cyanoacetate (0.1 mole), ammonium acetate (0.2 mole) and I (0.1 mole) was fused in an oil-bath at 140-150° for 12 hours. The fused mixture was cooled and poured onto ice. The crude product which precipitated was filtered and recrystallized from benzene to give II (55%) (Table I). The benzene-insoluble residue was recrystallized from ethanol to give III (35%) (Table I).

Procedure 2.

A mixture of cyanoacetamide (0.1 mole), ammonium acetate (0.1 mole) and I (0.1 mole) was fused for 6 hours then treated as above to give II and III. These compounds showed the same physical and spectral data as those of the products obtained by procedure 1 (Table I and II).

II and 4-Aryl-3-carbamoyl-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones (VI).

General Procedure.

Compound I (0.1 mole) and ammonium acetate (0.15 mole) were fused with diethyl malonate (0.1 mole) for 12 hours, or with malondiamide (0.1 mole) for 7 hours, at 140-160°. The reaction product was treated as described earlier to give in each case, II in 50% yield from benzene, and IV in 35% yield from methanol (Table I and II).

II and 3-Acetyl-4-aryl-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones (V).

General Procedure.

Compound I (0.1 mole), ethyl acetoacetate (0.1 mole), and ammonium

acetate (0.2 mole) were fused for 10 hours at 140° then poured on ice. The solid was collected, washed with water, and subjected to fractional crystallization to give II (50% yield) from benzene and V (40% yield) from ethanol (Table I and II).

4-Aryl-3-phenyl-3,4-dihydro-5*H*-indeno[1,2-*b*]pyridin-2(1*H*)-ones (VI).

General Procedure.

Ethyl phenylacetate (0.1 mole), ammonium acetate (0.2 mole), and I (0.1 mole) were fused together at 140° for 12 hours, then poured on ice. The crude product was collected, washed with water, dried and finally purified by crystallization from toluene to give VI (Table I and II) in 85% average yield.

4-Aryl-5-ketoindeno[1,2-*b*]pyridin-2(1*H*)-ones (VIII).

General Procedure.

A solution of VII (0.1 mole) in benzene (150 ml) was refluxed with ethyl cyanoacetate (0.1 mole) and ammonium acetate (0.2 mole) for 3 hours and left overnight at room temperature. Removal of the solvent under reduced pressure gave a solid residue which was washed with water and crystallized from ethanol. The products VIII (Table I and II) were obtained in alsmost quantitative yields.

Repeating the same synthesis using cyanoacetamide instead of ethyl cyanoacetate gave the same products VIII, which proved to be identical with those prepared earlier.

Oxidation of II. General.

Compound II (1 g) and selenium dioxide (0.8 g) in dioxan (10 ml) were refluxed for 4 hours. Filtration of the reaction mixture followed by removal of the solvent under reduced pressure gave a residue which ws crystallized from ethanol to afford VIII in 75-85% yield. These products showed the same analytical and spectral data as those obtained before (Table I and II).

VIII and 3-Acetyl-4-aryl-3,4-dihydro-5-ketoindeno[1,2-*b*]pyridin-2(1*H*)-ones (IX).

General Procedure.

A mixture of VII (0.1 mole), ethyl acetoacetate (0.1 mole) and ammonium acetate (0.2 mole) in benzene (150 ml) was heated for 2 hours. The solvent was removed under reduced pressure and the residue crystallized from ethanol to give VIII in 40% yield. The ethanol-insoluble solid was recrystallized from benzene-methanol to give IX in 45% yield (Table I and II).

4-Aryl-3-phenyl-3,4-dihydro-5-ketoindeno[1,2-*b*]pyridin-2(1*H*)-ones (X).

General Procedure.

Compound VII (0.1 mole) in benzene (150 ml) was refluxed with ethyl phenylacetate (0.1 mole) and ammonium acetate (0.2 mole) for 3 hours. The product which precipitated after removing the solvent was filtered and recrystallized from the appropriate solvent to give X in 78-89% yield (Table I and II).

Acylation of VI.

Compound VI (1 g) was refluxed in acetaic anhydride (25 ml) and anhydrous sodium carbonate (0.2 g) for 6 hours, cooled and poured onto ice. The crude product which precipitated was filtered and recrystallized from acetic acid to give XI in 86% yield (Table I and II).

3-Acetyl-4-aryl-2-chloro-5-ketoindeno[1,2-*b*]pyridines (XII).

Compound IX (1 g) and phosphorus oxychloride (15 ml) were refluxed for 4 hours. The reaction mixture was cooled, neutralized with aqueous sodium hydroxide and extracted with ether. Removal of ether and recrystallization of the residue from benzene gave XII in 90% yield (Tables I and II).

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