Studies on Benzoquinolines(f) and (h). Part II

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3-Hydrazino-1-methyl, 1-hydrazino-3-methylbenzo(f) quinoline (IA, IIA) and 2-hydrazino-4-methyl, 4-hydrazino-2-methylbenzo(h) quinoline (IIIA, IVA) were reported[1] to give triazines and diazepines with nitrous and formic acids. It would be interesting to study the reactions of IA—IVA with acetylacetone and ethyl acetoacetate respectively.

Reactions of alcoholic solution of IA with acetylacetone yielded IB, $C_{19}H_{19}ON_3$. A characteristic absorption band at 1730 cm^{-1} in IR spectrum indicated the presence of a carbonyl group. NMR spectrum indicated the presence of six aromatic protons at δ 7.6—8.0 ppm, one aromatic proton as singlet at δ 7.10 ppm, nine protons as three singlets for methyl groups at δ 2.50, 2.25, and 2.10 ppm and the presence of two protons of a methylene group as singlet at δ 3.25 ppm. Therefore, IB had the structure as assigned, thereby indicating the formation of an intermediate hydrazone. IB on further refluxing in glycerol in the presence of fused sodium acetate, gave a mixture of products from which a compound, IC ($C_{19}H_{17}N_3$) was isolated. In IC, absence of an absorption band at 1730 cm^{-1} and the presence of an absorption band at 1602 cm^{-1} indicated the existence of a 1,2-diazepine system in it.[2] NMR spectrum indicated the presence of six aromatic protons at δ 7.60—8.00 ppm and nine protons of three methyl groups as singlets at δ 2.95,

Table 1.

Compound number	Molecular formula	Infrared in cm^{-1}	NMR chemical shifts (δ) expressed in ppm =CH	-NH	Aromatic	$-\overset{O}{\overset{\Vert}{C}}-CH_2-$	$=\overset{\vert}{C}-CH_3$	-C-CH$_3$
IB	$C_{19}H_{19}ON_3$	1730	—	—	7.60—8.00 (6) 7.10 (1)	3.25 (2)	2.50 (3) 2.25 (3) 2.10 (3)	—
IC	$C_{19}H_{17}N_3$	1602	6.10 (1)	9.20 (1)	7.60—8.00 (6)	—	2.95 (3) 2.80 (3) 2.40 (3)	—
IIB	$C_{19}H_{19}ON_3$	1728	—	—	—	—	—	—
IIC	$C_{19}H_{17}N_3$	1605	6.05 (1)	8.80 (1)	7.60—8.00 (6)	—	3.15 (3) 2.85 (3) 2.40 (3)	—
IIIB	$C_{19}H_{19}ON_3$	1730	—	—	—	—	—	—
IIIC	$C_{19}H_{17}N_3$	—	6.10 (1)	9.15 (1)	7.60—8.00 (6)	—	2.95 (3) 2.80 (3) 2.40 (3)	—
IVB	$C_{19}H_{19}ON_3$	1725	—	—	—	—	—	—
IVC	$C_{19}H_{17}N_3$	—	6.05 (1)	8.90 (1)	7.60—8.00 (6)	—	3.10 (3) 2.85 (3) 2.40 (3)	—

Compound number	Molecular formula	Infrared in cm^{-1}	NMR chemical shifts (δ) expressed in ppm =CH	-NH	Aromatic	$-\overset{O}{\overset{\Vert}{C}}-CH_2$	H-C/H	-O\C/H	=C-CH$_3$
ID	$C_{20}H_{21}O_2N_3$	1735	—	—	—	—	—	—	—
IE	$C_{18}H_{15}ON_3$	1702 1602	—	8.8 (1)	7.60—8.00 (6)	3.10 (2)	—	—	2.60 (3) 2.50 (3)
IID	$C_{20}H_{21}O_2N_3$	1735	—	—	7.10—8.00 (7)	3.10 (2) 3.50 (2)	—	—	2.50 (6) 2.25 (3)
IIE	$C_{18}H_{15}ON_3$	1702 1590	—	8.80 (1)	7.60—8.00 (6)	3.00 (2)	—	—	2.50 (6)
IIID	$C_{20}H_{21}O_2N_3$	1735	—	—	—	—	—	—	—
IIIE	$C_{18}H_{15}ON_3$	1705 1600	—	8.90 (1)	7.60—8.00 (6)	3.10 (2)	—	—	2.55 (3) 2.40 (3)
IVD	$C_{20}H_{21}O_2N_3$	1735	—	—	—	—	—	—	—
IVE	$C_{18}H_{15}ON_3$	1705 1600	—	8.80 (1)	7.60—8.00 (6)	3.10 (2)	—	—	2.50 (3) 2.40 (3)

	Melting points	Analysis C	H	N		Melting points	Analysis C	H	N
IB	decomp.[a]	Calcd 74.75%	6.23%	13.77%	IC	114—115°C	Calcd 79.44%	5.92%	14.63%
		Found 74.54	6.08	13.52			Found 79.22	5.81	14.34
IIB	decomp.[a]	Calcd —	—	13.77	IIC	85—86	Calcd —	—	14.63
		Found —	—	13.49			Found —	—	14.28
IIIB	decomp.[a]	Calcd —	—	13.77	IIIC	103—104	Calcd —	—	14.63
		Found —	—	13.52			Found —	—	14.19
IVB	decomp.[a]	Calcd —	—	13.77	IVC	78—79	Calcd —	—	14.63
		Found —	—	13.43			Found —	—	14.29
ID	decomp.[a]	Calcd 71.64	6.26	12.53	IE	178—179	Calcd 74.74	5.19	14.53
		Found 71.34	5.97	12.37			Found 74.34	4.98	14.27
IID	decomp.[a]	Calcd —	—	12.53	IIE	122—123	Calcd —	—	14.53
		Found —	—	12.62			Found —	—	14.19
IIID	decomp.[a]	Calcd —	—	12.53	IIIE	156—157	Calcd —	—	14.53
		Found —	—	12.36			Found —	—	14.27
IVD	decomp.[a]	Calcd —	—	12.53	IVE	117—118	Calcd —	—	14.53
		Found —	—	12.73			Found —	—	14.30

a) No sharp melting point obtained.

2.80, and 2.40 ppm respectively. A signal at δ 9.20 ppm due to the –NH proton and a singlet at δ 6.10 ppm due to =CH– proton also indicated the presence of a 1,2-diazepine system.[2] The absence of a proton at position 2 of the benzoquinoline ring, the presence of an –NH proton and an absorption band at 1602 cm^{-1} would explain the fusion of a 1,2-diazepine ring with benzoquinoline system. Based on these observations, IC proved to be 10,12,13-trimethyl-8*H*-benzo(f)-[1,2]diazepino[3,4-*b*]quinoline.

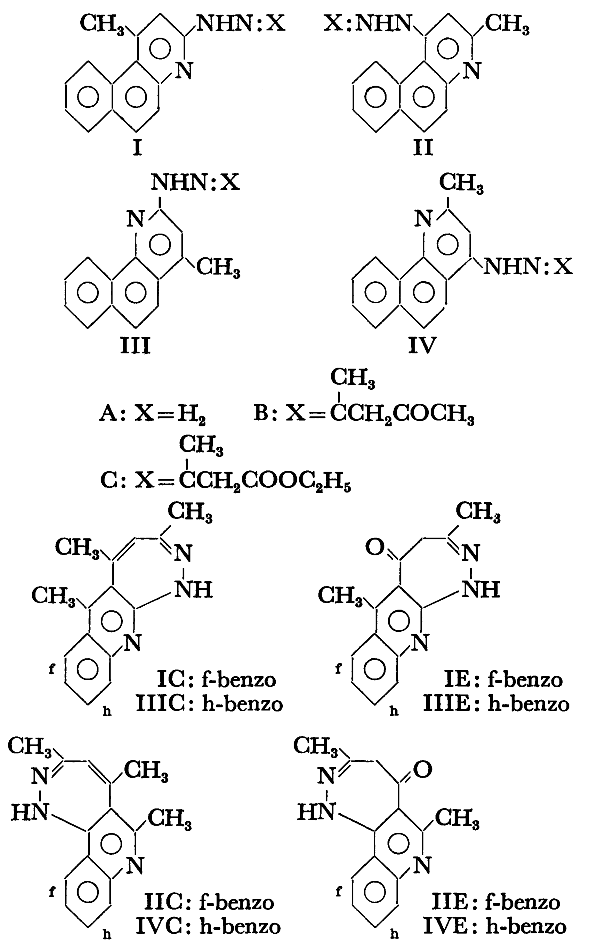

Fig. 1.

IA with ethyl acetoacetate yielded an intermediate hydrazone, ID ($C_{20}H_{21}O_2N_3$), the IR spectrum of which with an absorption band at 1735 cm^{-1} indicated the presence of an ester group. On further refluxing in glycerol in the presence of fused sodium acetate, IE ($C_{18}H_{15}ON_3$) was obtained. IR spectrum gave absorption bands at 1702 and 1602 cm^{-1} showing the presence of diazepinone moiety in it. NMR spectrum indicated the presence of six aromatic protons at δ 7.6—8.00 ppm, six protons as two singlets of methyl groups at δ 2.60 and 2.50 ppm, two protons of methylene group as singlet at δ 3.10 ppm, an –NH proton at δ 8.80 ppm and there was no proton at position 2 of the benzoquinoline ring. Thus, IE was assigned the structure to be 10,13-dimethyl-12-oxo-8*H*-11,12-dihydrobenzo(f)[1,2]diazepine[3,4-*b*]quinoline.

Similar observations were made when IIA—IVA were reacted with acetyl acetone and ethyl acetoacetate respectively (Fig. 1). The characteristic absorption bands and chemical shifts obtained in the NMR spectra of various products are compiled in Table 1. From these observations it can be concluded that cyclization of intermediates, hydrazones, occurred at position 2 in benzo(f) or at position 3 in benzo(h) quinolines to yield benzo(f) or benzo(h) quinolino-1,2-diazepine compounds.

Experimental

All the reported melting points are uncorrected. Microanalyses, IR and NMR spectra were from Central Drug Research Institute, Lucknow. IR spectra were recorded on Perkin-Elmer infrared in nujol and NMR spectra on a Varian A-60D model (using $CDCl_3$ or TFA as solvent and TMS as internal reference standard).

Acetylacetone-1-methyl-benzo(f)quinolyl-3-hydrazone(IB). To a well stirred solution of 3-hydrazino-1-methyl-benzo(f)-quinoline (IA) (8.92 g, 0.04 M) in absolute alcohol, acetylacetone (4.49 g, 0.045 M) was added dropwise and the reaction mixture was refluxed for 1 hr. It was cooled, poured into ice-cold water and kept overnight at 0°C. The solid was washed well with water and dried. After repeated crystallization from ethanol IB, 9.8 g (80%) was obtained having no sharp melting point.

Similarly, IIB from IIA, IIIB from IIIA, and IVB from IVA were prepared. These hydrazones have no sharp melting points.

*10,12,13-Trimethyl-8*H*-benzo(f)[1,2]diazepino[3,4-*b*]quinoline (IC).* IB (7.6 g, 0.025 M) was refluxed in glycerol in the presence of fused sodium acetate for 4—5 hr with occasional shaking. It was poured into ice-cold water, kept overnight at 0 °C. The solid was washed well with water and repeatedly crystallized from ethanol to give pure IC, 3.58 g (50%), mp 114—115 °C.

Similarly, IIB yielded IIC, 8,9,11-trimethyl-13*H*-benzo(f)-[1,2]diazepino[3,4-*c*]quinoline. IIIB yielded IIIC, 10,12,13-trimethyl-8*H*-benzo(h)[1,2]diazepino[3,4-*b*]quinoline.

IVB yielded IVC, 8,9,11-trimethyl-13*H*-benzo(h)[1,2]-diazepino[3,4-*c*]quinoline.

Ethyl Acetoacetate-1-methyl-benzo(f)quinolinyl-3-hydrazone (ID). To a well stirred solution of IA (8.92 g, 0.04 M) in absolute alcohol, freshly distilled ethyl acetoacetate (5.72 g, 0.045 M) was added dropwise and the reaction mixture was refluxed for 1 hr. It was cooled and poured into ice-cold water. The solid obtained was washed well with water and repeatedly crystallized from ethanol to give pure ID, 9.38 g (70%).

Similarly, IID from IIA, IIID from IIIA and IVD from IVA were prepared.

*10,13-Dimethyl-12-oxo-8*H*-11,12-dihydro-benzo(f)[1,2]diazepino-[3,4-*b*]quinoline (IE).* ID (8 g) was refluxed in glycerol in the presence of fused sodium acetate for 6—7 hr, with occasional shaking. The reaction mixture was cooled, poured into ice-cold water and kept overnight at 0 °C. The crude product was crystallized from ethanol, when a pure compound, IE (3.45 g), was obtained.

Similarly, IID yielded IIE, 8,11-dimethyl-9-oxo-13*H*-9,10-dihydro-benzo(f)[1,2]diazepino[3,4-*c*]quinoline.

IIID yielded IIIE, 10,13-dimethyl-12-oxo-8*H*-11,12-dihydro-benzo(h)[1,2]diazepino[3,4-*b*]quinoline.

IVD yielded IVE, 8,11-dimethyl-9-oxo-13*H*-9,10-dihydro-benzo(h)[1,2]dizepino[3,4-*c*]quinoline.

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References

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