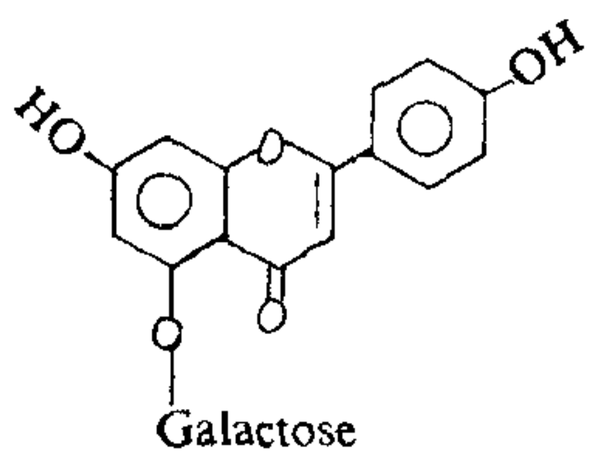
sugar linkage was deduced by comparing the properties of the aglycone with those of the glycoside. The glycoside neither gave a positive reaction with Dimorth reagent[10] nor produced any positive test with boric acid and citric acid in acetone[11, 12]. In addition to this, ethanolic solution of the glycoside in $AlCl_3$[13, 14] or $ZrOCl_2$[15] gave no specific observations under UV light, indicating that 5-OH group was not free in the glycoside. The completely methylated glycoside (Hakomori method[16]) on hydrolysis with acid (7% H_2SO_4) afforded dimethyl ether of apigenin, which responded to all the colour reactions characteristic of 5-hydroxy flavone and 2,3,4-tri-O-methyl-D-galactose (R_G value and Co-PC). The UV spectra of glycoside as well as aglycone further confirmed the galactosidation at C-5 OH (λ_{max}^{MeOH} nm, glycoside, 268, 335; + $AlCl_3$, 270, 335; aglycone; 268, 336; + $AlCl_3$, 276, 345, 380). The glycoside was hydrolysed with almond enzyme emulsin to yield apigenin (m.p., m.m.p. and Co-TLC) and D-galactose (Co-PC) indicating the presence of β-linkage.



The authors thank the Director, CDRI, Lucknow for the micro-analysis and spectral data of the glycoside and Dr J. S. Chauhan, Chemistry Department, Allahabad University for providing the authentic sample of apigenin. HOG thanks the Ministry of Health and Family Welfare, New Delhi for a fellowship.

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REACTIONS OF BENZYLPYRIDINIUM BROMIDE AND 4-NITROBENZYL-PYRIDINIUM BROMIDE WITH α,β-UNSATURATED KETONES: SYNTHESIS OF SOME NEW 1,3-DISUBSTITUTED NAPHTHALENES

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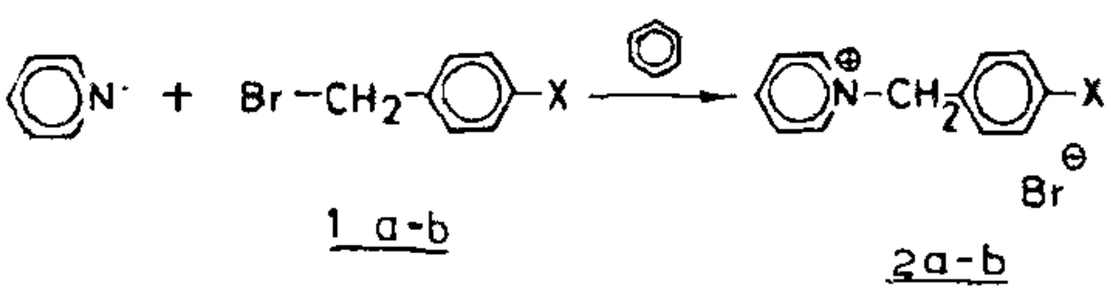
THE pyridinium salts and their ylides have been utilized in the synthesis of a wide variety of heterocyclic compound[1-12]. But little attention has been paid towards the synthesis of carbocyclic system especially leading to the naphthalene nucleus by the interaction of pyridinium ylides and α,β-unsaturated ketones[13]. With a view of exploring the domain of such a reaction, we have studied the reaction of substituted benzylpyridinium salts with different α,β-unsaturated ketones, in the presence of anhydrous $AlCl_3$ or $ZnCl_2$ in a mixture of glacial acetic acid of sodium acetate.

The experimental techniques were the same as reported earlier[2-4]. Both the pyridinium salts (2a, b) were prepared by heating benzyl bromides (1a, b) with pyridine in dry benzene[13, 14].

Preparation of 1,3 *diaryl-naphthalenes* (5a–h; 6a–g).

A mixture of benzylpyridinium bromide (2a–b) (3 mmol) and α,β-unsaturated ketones (3 mmol) was stirred at 200 C in the presence of anhydrous zinc chloride (3 g) in 10 ml glacial acetic acid for 6–9 hr under nitrogen. The reaction mixture, after being kept overnight at room temperature, was poured into ice-cold water (200 ml) to precipitate a solid. This solid mass was filtered, dried and subjected to column chromatography using neutral alumina as absorbent and chloroform as eluent. The product was recrystallized from suitable solvents (table 1) to give better yield of the title compound (5a–h; 6a–g). The NMR spectral data of naphthalenes (5a–h; 6a–g) have also been tabulated in table 1.

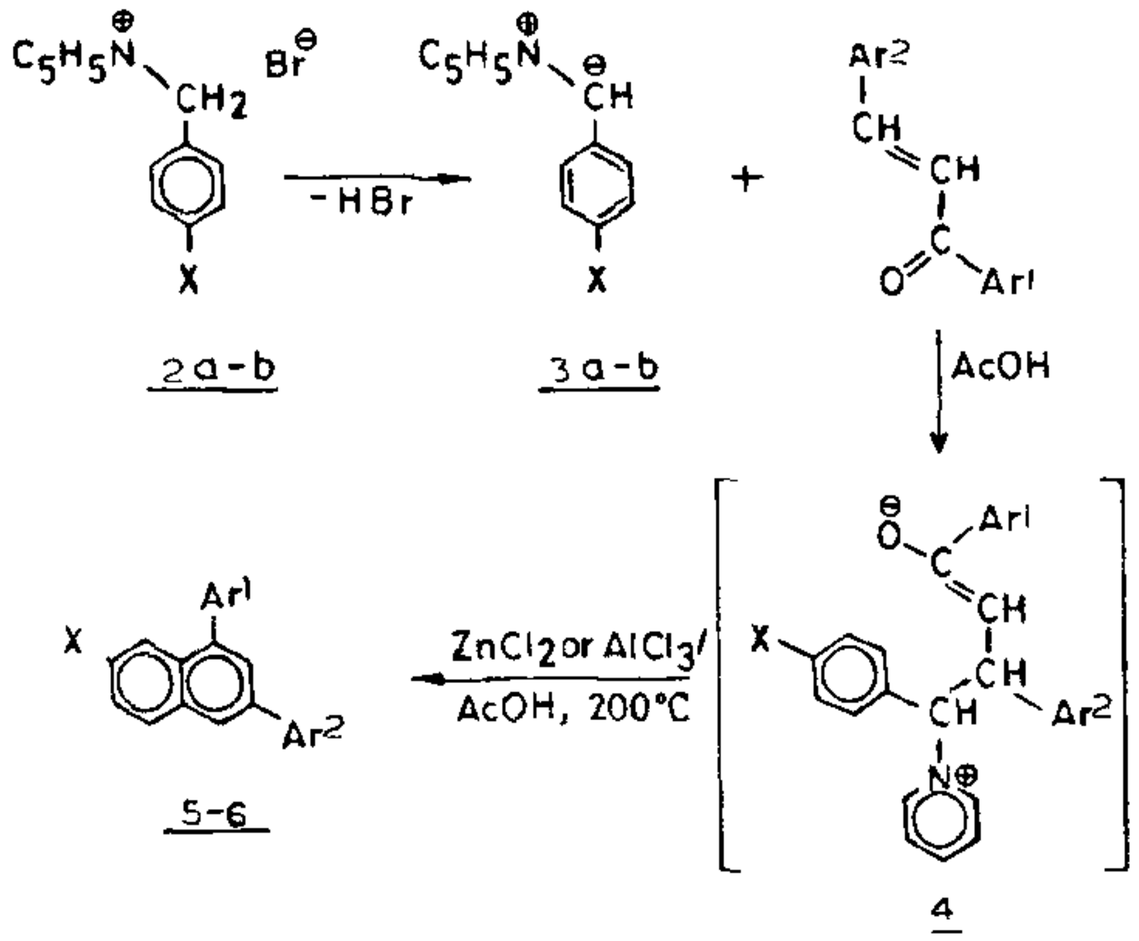
Reaction of benzyl bromide (1a) and 4-nitrobenzyl bromide (1b) with pyridine in benzene at reflux temperature gave benzylpyridinium bromide (2a) and 4-nitrobenzylpyridinium bromide (2b) (scheme 1).



Scheme 1

The structure of benzylpyridinium bromide (2a) and 4-nitrobenzylpyridinium bromide (2b) was confirmed on the basis of IR and NMR spectral data. The IR spectra of 2*a* and 2*b* showed a diagnostic absorption band of strong intensity at 3045 and 3040 cm^{-1} respectively due to C—H stretching vibration band of methylene group attached to a position adjacent to nitrogen atom. Characteristic absorption bands due to $-NO_2$ group in salt (2b) were obtained at 1515 and 1300 cm^{-1}. The NMR spectrum of salts (2a-b) showed a singlet at δ 6.30 and δ 6.38 due to the methylene and aromatic protons appeared in the range δ 6.80–9.35.

The reactions of these salts (2a–b) were carried out with a wide range of α,β-unsaturated carbonyl compounds in the presence of anhydrous $AlCl_3$ or $ZnCl_2$ with a mixture of sodium acetate and acetic acid at 200° C to afford 1,3-diaryl naphthalenes (5a–h) and 1,3-diaryl-7-nitronaphthalenes (6a–g) in 45–70% yields (scheme 2). It was, however, observed that the yields of the resulting naphthalenes were dependent upon the nature of substituents attached to pyridinium salts as well as to the α,β-unsaturated ketones. The reactivity of salt (2b) was lower than (2a) because of–I effect of NO_2 group which stabilized the carbanion formation. Hence, salt (2b) afforded lower yield of naphthalene derivatives than the salt (2a).



Scheme II

The reaction seems to proceed *via* the intermediary of a betaine type of derivative (4) which is formed by the nucleophilic attack of the ylide carbons (3a–b) presumably generated *in situ* by dehydrohalogenation of the salts (2a–b), on the β-carbon of α, β-unsaturated ketone. Betain (4), then undergoes cyclization in the presence of anhydrous $ZnCl_2$ or $AlCl_3$ used as cyclization agent to afford naphthalene derivatives (5a–h) & (6a–g).

All the compounds (5a–h; 6a–g) synthesized in the present study are new and gave satisfactory elemental analysis. The IR spectral studies of naphthalene derivatives showed a double absorption maxima in the region 1630–1620 cm^{-1} which were assigned to the stretching vibrations of carbon-carbon double bond. The strong bonds in region 900–850 cm^{-1} had diagnostic absorption of polynuclear aromatics. The nitro group of the products showed a strong symmetrical stretching bond at 1350–1330 cm^{-1}. The NMR spectra of the compound, in general, exhibited aromatic multiplet in the range δ 6.5–8.5.

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Table 1 *Physical and spectral properties of naphthalene derivatives (5a–h and 6a–g)*

Compound	X	Ar^1	Ar^2	Yield (%)	M.P. (°C)	Recrystn. solvent	IR spectra (KBr) cm^{-1} $\nu_{C=C}$	ϕ_{C-H}	ν_{C-NO_2}	H-NMR spectra ($CDCl_3$) δ ppm
5a	H	C_6H_5	C_6H_5	45	107–09 (109–10)[15]	A	1595	995	1490, 1315	—
b	H	C_6H_5	4-$CH_3OC_6H_4$	50	85–89	B	—	—	—	3.70 (s, 3H, OCH_3); 6.70–8.10 (m, 15H, ArH)
c	H	C_6H_5	3,4-$O_2CH_2C_6H_3$	58	90–92	A	1600	990	1500, 1320	6.00 (s, 2H, OCH_2O); 6.80–8.00 (m, 14H, ArH)
d	H	4-$CH_3C_6H_4$	4-CH_3–O–C_6H_4	60	118–20	B	1600	1000	1510, 1300	2.30 (s, 3H, CH_3); 3.72 (s, 3H, OCH_3) 6.65–7.95 (m, 14H, ArH)
e	H	2-$C_{10}H_7$	C_6H_5	70	180–82	A	1590	998	1580, 1325	—
f	H	2-$C_{10}H_7$	4-ClC_6H_4	65	192–94	B	1595	997	1490, 1310	—
g	H	4-ClC_6H_4	4-$NO_2C_6H_4$	50	212–14	B	1600	990	1520, 1340	—
h	H	2-$C_{10}H_7$	3-$CH_3C_6H_4$	50	92–94	A	—	—	—	2.28 (s, 3H, CH_3); 6.72–8.22 (m, 17H, ArH)[3]
6a	NO_2	C_6H_5	C_6H_5	60	92–94	A	1600	990	1495, 1330	2.45 (s, 3H, CH_3); 6.90–8.25 (m, 14H, ArH)
b	NO_2	C_6H_5	4-$CH_3OC_6H_5$	68	128–30	B	—	—	—	3.85 (s, 3H, OCH_3); 6.85–8.28 (m, 14H, ArH)
c	NO_2	C_6H_5	3,4-$O_2CH_2C_6H_3$	60	131–33	A	1590	985	1500, 1310	6.05 (s, 2H, O_2CH_2); 6.75–8.15 (m, 13H, ArH)
d	NO_2	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	66	96–98	A	1600	995	1500, 1340	2.35 (s, 3H, CH_3); 3.78 (S, 3H, OCH_3) 6.82–8.20 (m, 13H, ArH)
e	NO_2[2]	$2C_{10}H_7$	C_6H_5	60	172	A	1610	998	1520, 1335	—
f	NO_2	4-$C_6H_5C_6H_4$	C_6H_5	45	192–94	C	1605	980	1500, 1315	2.38 (s, 3H, CH_3); 6.80–8.30 (m, 16H, ArH)
g	NO_2	4-$C_6H_5C_6H_4$	C_6H_5	50	165–67	B	1595	985	1500, 1330	3.80 (s, 3H, OCH_3); 6.85–8.25 (m, 12H, ArH)

*All compounds gave satisfactory elemental analyses for C, H, N which agreed with their calculated values within the limits of experimental errors.

A = Benzene/pet. ether, B = Chloroform/Pet. ether

S = Singlet; d = doublet; m = multiplet; ν = stretching vibrations, ϕ = out-of-plane deformations of hydrogen attached to aromatic nucleus.

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WELTRICHIA (MALE *WILLIAMSONIA*) FROM THE BOREHOLE SAMPLES OF MALDA, WEST BENGAL, INDIA

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WHILE studying the bore hole samples of Malda in West Bengal, two interesting specimens of bennettalean male 'flower' at a depth of 214 m below the surface were recently found.

Drilling operation was taken up in Malda district to prove the existence of Gondwana formations below the alluvial cover and, upto 1972, four bore holes were drilled in Milki (MK-1), Mathurapur (MR-1), Bankipur (BK-1) and Ratua (RT-1) (figure 1). In the MK-1 bore hole, Gondwana sequence is met with below an alluvial cover of 92 m. Traps and intertrappeans similar to the Rajmahal area were encountered upto a depth of 410 m. The present specimens come from the intertrappean beds between volcanic flows IV and V. The associated flora at this level comprises *Taeniopteris spatulata* McClelland and *Ptilophyllum* spp.

The bore hole data suggest that Malda basin is the eastern continuation of the main Rajmahal basin with a probable fault in between, along the channel of the river Ganga. Out of 14 flows in the type area, the bottom eight flows of traps are encountered in the

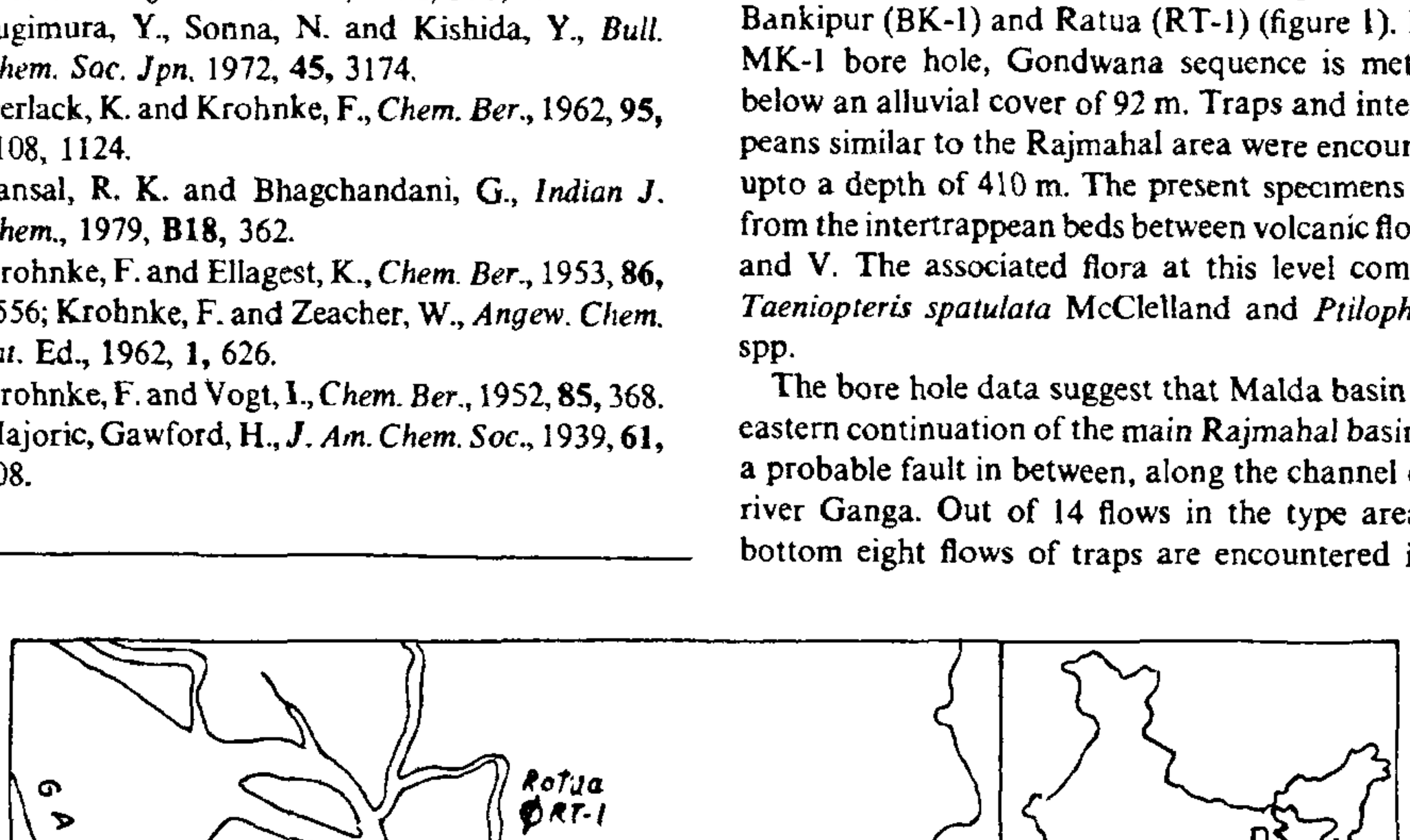

Figure 1. Showing the drilling operation in Malda district.