cooled in ice and treated carefully with solid sodium carbonate and water. The solid separated was recrystallised from ethanol to get colourless crystals, m.p. 84–85°C (lit. value 84°C; yield 53%). The analytical values for C and H agreed with the calculated value within the limits of experimental accuracy. i.r. ν_{max}^{KBr} cm^{-1} 1675 aldehydic C=O); 1600 (arom. C=C); 2875–2975 (weak aldehydic C–H). nmr ($CDCl_3$) δ : 4·05 (3H, s, $-OCH_3$); 7·1–8·1 (6H, complex m, arom. protons); 9·2 (1H, broad bifurcated singlet, $-\overset{H}{\overset{|}{C}}=O$).

2-phenyl-4- (2-methoxynaphthalidene)- 5-oxazolone(II): 2-methoxy-1-naphthaldehyde (5 g), hippuric acid (4·8 g), fused sodium acetate (3·2 g) acetic anhydride (75 ml) were heated over water bath for two hours at 60–70°C. The yellow azlactone formed was collected, washed with a little alcohol and recrystallised from alcohol into bright yellow needles m.p. 177°C–178°C; lit. (3) m.p. 178–179°C, yield (50%). The elemental analysis for C, H, and N agreed with the calculated values within the limits of experimental accuracy. u.v. $\lambda_{max}^{CHCl_3}$ nm (ϵ) 419 (9976), 300 (10,400) nmr ($CDCl_3$) δ : 4·0 (3H, s, $-OCH_3$); 7·3–8·1 (11H, complex multiplet in two groups, arom. protons); 8·2 (1H, vinylic proton fused with aromatic proton signals). i.r. ν_{max}^{KBr} cm^{-1} 1805 (C=O); 1670 (C=N); 1600; 1575; 1525 (arom. C=C).

α-Benzamido-β-(2-methoxynaphthyl)-acrylic acid (I): 2-phenyl-4-(2-methoxy naphthylidene)-5-oxazolone (II) (3·0 g), Ba $(OH)_2$, 2 H_2O (5·7 g), water (100 ml) and alcohol (20 ml) were mixed and the mixture was refluxed for 8 hours. The mixture was filtered hot and the filtrate was acidified with dil. HCl. The solid separated on cooling was washed with water and recrystallised from ethanol to get (I) m.p. 198–200°C. yield 62%. The compound on heating with acetic anhydride gave back (II) as yellow crystalline needles m.p. and the mixed m.p. with authentic sample, 166–167°C. The analytical values for C, H, and N agreed with the calculated values within the limits of experimental accuracy. UV λ_{max}^{EtOH} nm 255 (E = 74,030); 310 (E = 15,730): 342 (E = 11,100). IR ν_{max}^{KBr} cm^{-1} 3550–3250 (m, br); 2950 (w); 1725 (s); 1640 (s); 1600 (w): 1525 (s): 1475 (s): 1400 (w): 1350 (w). 1275 (s); 1195 (w); 1160 (w); 1125 (w); 1100 (m); 1030 (m); 925 (w); 815 (s); 750 (s). NMR ($CDCl_3$) δ : 4·05 (s) (3H, $-OCH_3$); 4·8 (br. s.) (1H, N=H): 7·2–8·2 (complicated m) (11H, arom. protons): 8·6 (ill-defined s) (1H, vinylic proton).

Mass spectrum. : *m/e* 347 (M^+, 1%); 303 (M–CO_2, 4%); 270 (M–C_6H_5, 1%); 226 (M–H and $-C_6H_5CONH$, 8%): 211 (M–H, $-C_6H_5CONH$ and $-CH_3$, 8·5%); 197 (M-COOH and $-C_6H_5CO$, 12%); 182 (M–COOH and C_6H_5CONH, 40%); 167 (M COOH, $-C_6H_5CONH$ and CH_3, 32·5%); 105 ($C_6H_5CO^{7+}$, 100%); 77 ($C_6H_5^{7+}$, 54%).

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N-ACYLATION AND N-BENZYLATION OF FUSED BENZOPYRANO-BENZODIAZEPINONES UNDER PHASE TRANSFER CATALYSIS CONDITIONS

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Benzodiazepines exhibit varying physiological properties such as psychopharmocological activity, anti-anxiety and sedative[1,2]. The diazepines when N-acylated or N-alkylated, their physiological activity was enhanced[3,4]. The present communication deals with the synthesis of a few fused benzopyrano-benzodiazepinones and their N-acyl or N-benzyl products under phase transfer catalysis (PTC) conditions.

Recently Fitton *et al.* reported the synthesis of 5a, 11-Dihydro[1]benzopyrano [2, 3-*b*][1, 5] benzodiazepin-13(6H)-ones (II*a–b*)[5] by reacting equimolar quantities of chromone-3-carboxaldehydes (I*a–b*)[6] and *o*-phenylenediamine in chloroform and oxidation of II*a–b* to [1] benzopyrano [2, 3 *b*] [1, 5] benzodiazepin-13 (6H)-ones (III*a–b*] with chloranil. In the present investigation, we report the condensation of chromone-3-carboxaldehydes (I*a–d*) with *o*-phenylenediamine under different conditions. Coloured products were separated as soon as I*a–d* were mixed with *o*-phenylenediamine in acetic acid and characterised as dihydro compounds II*a d*. These dihydro compounds II*a–d* were also obtained by condensing I*a–d* with o-phenylenediamine in methanol. Keeping the dihydro compounds II*a–d* alone in acetic acid or allowing the reaction mixture of I*a–d* and *o*-phenylenediamine in acetic acid

TABLE I

Product	R	R_1	M.P. in °C	Yield %	Molecular formula**	IR ν_{max}^{KBr} cm^{-1}
IIa	H	..	208 (209 lit.)[5]	95	$C_{16}H_{12}N_2O_2$	..
IIb	CH_3	..	221 (222 lit.)[5]	78	$C_{17}H_{14}N_2O_2$	..
IIc*	Cl	..	225 (decomp.)	98	$C_{16}H_{11}N_2O_2Cl$	..
IId*	Br	..	198–200	93	$C_{16}H_{11}N_2O_2Br$	..
IIIa	H	..	271 (271 lit.)[5]	55	$C_{16}H_{10}N_2O_2$	3350 (NH)
IIIb	CH_3	..	262 (264 lit.)[5]	60	$C_{17}H_{12}N_2O_2$	3260 (NH)
IIIc*	Cl	..	265	58	$C_{16}H_9N_2O_2Cl$	3275 (NH)
IIId*	Br	..	268	48	$C_{16}H_9N_2O_2Br$	3280 (NH)
IVa*	CH_3	COPh	185	84	$C_{24}H_{18}N_2O_3$	1720 (COPh)
IVb*	CH_3	$COCH_3$	231 (decomp.)	68	$C_{19}H_{16}N_2O_3$	1710 ($COCH_3$)
IVc*	CH_3	CH_2Ph	192	72	$C_{24}H_{20}N_2O_2$	..
IVd*	Cl	COPh	185	80	$C_{23}H_{15}N_2O_3Cl$	1715 (COPh)
IVe*	Cl	$COCH_3$	196	73	$C_{18}H_{13}N_2O_3Cl$	1690 ($COCH_3$)
IVf*	Cl	CH_2Ph	224 (decomp.)	64	$C_{23}H_{17}N_2O_2Cl$	..
IVg*	Br	COPh	182	81	$C_{23}H_{15}N_2O_3Br$	1690 (COPh)
IVh*	Br	$COCH_3$	178	76	$C_{18}H_{13}N_2O_3Br$	1690 ($COCH_3$)
IVi*	Br	CH_2Ph	216 (decomp.)	87	$C_{23}H_{17}N_2O_2Br$	..

* These compounds were synthesised for the first time by us.

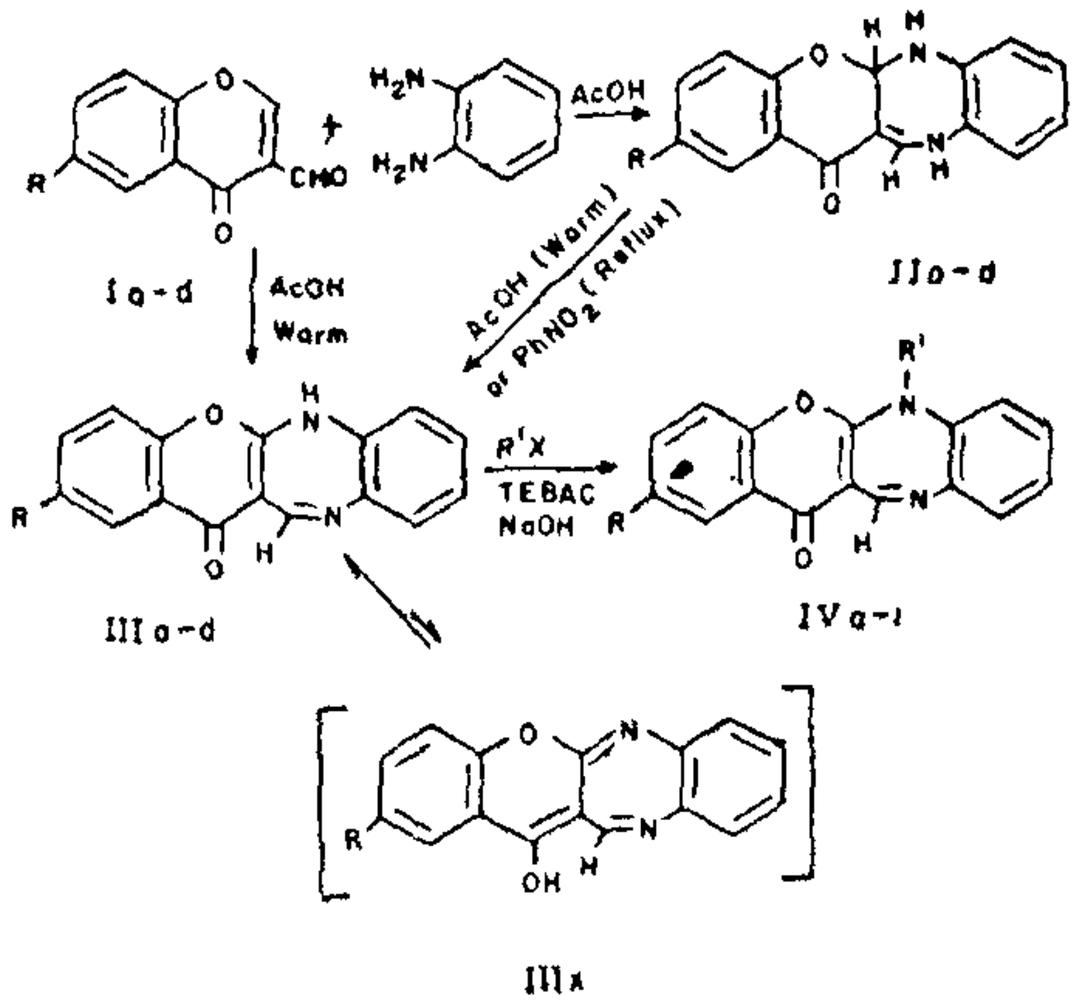
** The microanalysis for all compounds were in agreement with the calculated values (C ±0·4, H ±0·35, N ±0·25).

on hot water bath—the oxidized products—benzodiazepinones IIIa–d were formed. The direct formation of oxidized products IIIa–d may be due to aerial oxidation. To establish this, the condensation of Ia with *o*-phenylenediamine was carried out under nitrogen atmosphere, when only dihydro compound IIa and no benzodiazepinone IIIa was obtained. Further, when the reaction was carried out by passing oxygen through the reaction mixture IIIa resulted in a shorter duration and in good yields. The oxidation of the dihydro compounds IIa–d was also effected using nitrobenzene. The analytical and spectral data of IIa–d and IIIa–d are given in Table I.

The yields of N-acyl and N-benzyl products of IIIb–d—under Schotten-Baumann reaction conditions—were found to be very poor. Therefore the N-acylation and N-benzylation were carried out under phase transfer catalysis[7] (PTC) conditions using triethylbenzyl ammonium chloride (TEBAC) as a catalyst and varying the concentration of alkali (10%, 20% and 30% sodium hydroxide). The same reaction was carried out using tributyl benzyl ammonium chloride (TBBAC) as a catalyst also. However no improvement in the yields was noticed. It has been observed that when TEBAC and 20% sodium hydroxide were used, the yields of N substituted products IVa–i were found to be maximum.

The benzopyrano-benzodiazepinone IIIa–d gave greenish colouration with alcoholic ferric chloride, while the N-substituted products did not, indicating the presence of a small amount of enol tautomer IIIx.

The structures of N-acyl and N-benzyl compounds IVa–i were confirmed by the following spectral data. In the IR spectra of IIIa–d, a band around 3325 cm^{-1} (–NH) is present whereas it is significantly absent



in the N-substituted compounds IV*a–i*. In the IR spectra of IV*a–i* in addition to the band around 1640 cm^{-1} (chromone carbonyl) another band around 1700 cm^{-1} (ester carbonyl) is present. The NMR spectra of III*b–d* recorded in DMSO-D_6 exhibit a signal around 12.6δ due to (−NH) while this signal disappeared in IV*a–i*. The UV data of these compounds (IV*a–i*) are found to be similar to those of parent diazepinones (III*b–d*)[8].

Experimental

*Preparation of dihydrobenzopyrano-benzodiazepinones (II*a–d*)*

Method A.—Chromone-3-carboxaldehydes (I*a–d*) (0·005 mol) were separately mixed with o-phenylenediamine (0·005 mol) in acetic acid (30 ml). The coloured products II*a–d*, separated immediately, were filtered and recrystallised from chloroform-acetone mixture as orange red needles.

Method B.—Orthophenylenediamine (0·005 mol) was separately refluxed with the chromone-3-carboxaldehydes (I*a–d*) (0·005 mol) in methanol for three hours. The coloured products II*a–d* separated during reflux were filtered and recrystallised from chloroform-acetone mixture as orange red needles.

*Preparation of benzopyrano-benzodiazepinones (III*a–d*)*

Method A.—Chromone-3-carboxaldehydes (I*a–d*) (0·005 mol) in acetic acid (15 ml) were added separately to a solution of *o*-phenylenediamine (0·005 mol) in acetic acid (15 ml) at room temperature. The coloured products were separated out immediately. The reaction was allowed to continue on water bath until a clear solution obtained. The solution was cooled and poured into cold water. Neutralization of the above reaction mixture with ammonia solution gave III*a–d*, and were recrystallised from a mixture of benzene-chloroform as shining crystals.

Method B.—The dihydro compounds II*a–d* (0·005 mol) were separately dissolved in nitrobenzene (15 ml) and refluxed for 30 minutes. The excess of nitrobenzene was removed by steam distillation. The residual mixture was cooled. The products III*a–d* separated were filtered and recrystallisation from chloroform-benzene mixture furnished shining crystals. The compounds were found to be identical with those obtained directly from acetic acid.

*Preparation of N-acyl and N-benzyl compounds (IV*a–i*)*

A solution of benzopyrano-benzodiazepinone (III*b*) (0·005 mol) and triethylbenzyl ammonium chloride (TEBAC) (0·002 mol) in benzene was added to aqueous sodium hydroxide solution (40 ml, 20%), and benzoyl chloride (0·005 mol) in benzene (10 ml) was added dropwise over a period of 30 minutes. Then the reaction mixture was stirred well for two hours. The benzene layer was separated, washed with water and dried over anhydrous sodium sulphate. Removal of the solvent yielded IV*a* and was recrystallised from benzene-petroleum ether mixture as colourless crystals.

Similarly benzodiazepinones (III*b–d*) when reacted separately with benzoyl chloride, acetyl chloride and benzyl chloride yielded respective N-substituted products IV*b–i*.

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CHLOROSULPHONIC ACID AS DIFFERENTIATING TITRANT IN NON-AQUEOUS MEDIUM

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Chlorosulphonic acid has been used as a titrant in acetic acid and acetic acid-methyl ethyl ketone media for the determination of number of individual bases[1–4]. The acid has certain advantages over perchloric acid[3]. However, no attempt has been made to use the acid as a differentiating titrant. The present work has been undertaken to study the use of chlorosulphonic acid as differentiating titrant. Differentiation of *n*-butylamine from aniline, N-methylaniline and N, N-dimethylaniline was investigated.

Materials and Methods

All the chemicals used were of analytical grade. The purity of the samples was checked by comparing the measured densities with those reported in the