Tetrahedron. Vol. 24, pp. 949 to 957 Pergamon Press 1968. Printed in Great Britain

SYNTHESIS OF CHROMANS AND BENZOPYRYLIUM SALTS INVOLVING HYDRIDE TRANSFER*

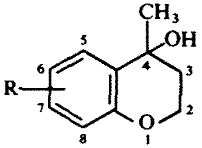
B. D. TILAK and Z. MULJIANI
National Chemical Laboratory, Poona 8, India

(*Received in UK* 9 *May* 1967; *accepted for publication* 5 *June* 1967)

Abstract—Synthesis of chromans and benzopyrylium salts by acid catalysed disproportionation of Δ^3-chromenes and dehydration of 4-chromanols is reported. The disproportion of Δ^3-chromenes involves intermolecular hydride transfer which was found to be non-stereospecific in the case of 3,4-dimethyl-Δ^3-chromene. Thus the latter on acid treatment gave a 50:50 mixture of *cis*- and *trans*-3,4-dimethylchroman.

THE cyclization of 2-arylmercaptoethyl alkyl ketones with acids to give thiachromans and thiapyrylium salts[1-3] and that of 2-arylaminoethyl alkyl ketones to give derivatives of quinoline and tetrahydroquinoline[4] has been reported. The above synthesis involves acid induced disproportionation of Δ^3-thiachromenes and 1,2-dihydroquinolines which are formed as intermediates. The disproportionation of these dihydro derivatives involves intermolecular hydride transfer. The present paper which describes an extension of the above work, deals with the study of dehydration of 4-methyl-4-chromanols and their derivatives in the presence of perchloric acid. A reference to early studies on the present work was also made in a previous communication.[1]

Interaction of phenol and substituted phenols with propiolactone in aqueous alkaline solution gave 2-phenoxypropionic acids[5] which on cyclization with polyphosphoric acid (PPA) gave 4-chromanones.[6] The latter on interaction with MeMgI gave 4-methyl-4-chromanols[6] (I–IV).



I, R = H; II, R = 6-Me; III, R = 6-OMe; IV, R = 7-OMe

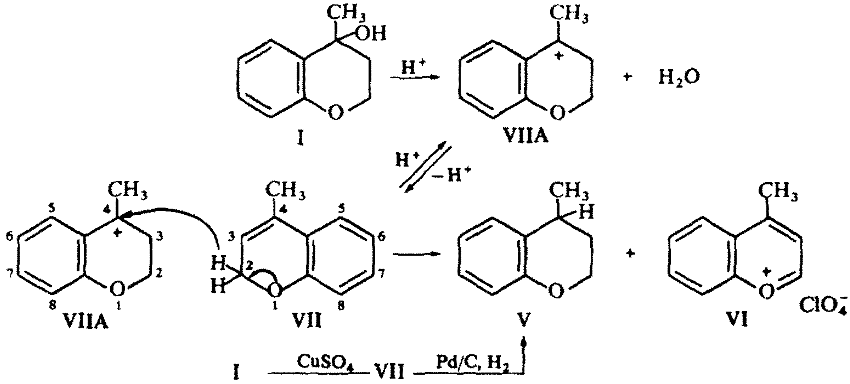
Dehydration of 4-methyl-4-chromanol (I) with perchloric acid gave a mixture of 4-methylchroman (V) and 4-methyl-1-benzopyrylium perchlorate (VI). 4-Methyl-Δ^3-chromene (VII), obtained by dehydration of I with anhydrous copper sulphate,[6] also yielded V and VI on treatment with perchloric acid. The chroman V was also prepared by catalytic hydrogenation of VII. Although some instances of formation of pyrylium salts by the action of mineral acids on chromenes in the absence of oxidizing agents have been reported earlier,[6a] the formation of these salts is attributed to air oxidation. The simultaneous formation of chromans in these reactions which also

---

[*] NCL Communication Number 1050.

appears likely as will be seen from the present paper has, however, not been reported.

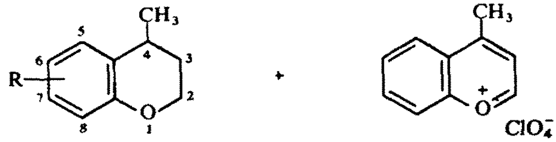
The following sequence of reactions and their mechanism is suggested as a most likely explanation to account for the simultaneous formation of chromans and pyrylium salts by acid treatment of 4-chromanols and Δ^3-chromenes:-



The disproportionation of VII involves intermolecular transfer of C-2 hydrogen atom as hydride to the carbonium ion [C-4 position in VIIA (cf. Ref. 1–4)]. 4-Methyl-1-benzopyrylium perchlorate (VI), isolated under very carefully controlled experimental conditions, was extremely unstable and changed rapidly to an unidentified red dye.

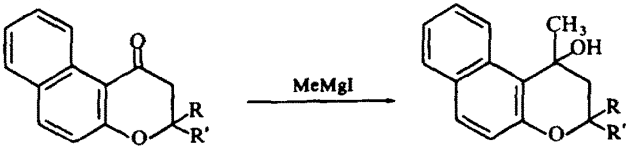
Dissolution of the red dye in perchloric acid gave a yellow colored solution which gave a UV spectrum identical with VI (in perchloric acid). As against corresponding dyes derived from 4-methylthianaphthalenium perchlorates[1–3] which could be isolated and identified, the above red dye derived from VI could not be isolated in an analytically pure form.

The substituted 4-methyl-4-chromanols (II, III and IV) on treatment with perchloric acid likewise gave the corresponding chromans VIII, X and XII and the 1-benzopyrylium perchlorates (IX, XI and XIII) respectively. Compound IX was too unstable for isolation but its formation was shown by the UV spectrum of the perchloric acid solution of the reaction mixture after removal of the chroman VIII. Whereas IX was extremely unstable and XI decomposed within a few hours, 7-methoxy-4-methylbenzopyrylium perchlorate (XIII) was much more stable presumably because of the stabilization of the cation by the 7-OMe group.



II → VIII; R = 6-Me + IX; R = 6-Me
III → X; R = 6-OMe + XI; R = 6-OMe
IV → XII; R = 7-OMe + XIII; R = 7-OMe

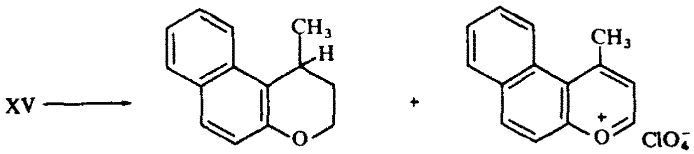
4-Methyl-5,6-benzo-4-chromanols listed below were prepared from the corresponding 5,6-benzo-4-chromanones.[7–9]



XIV; R, R' = H
XVI; R = H; R' = Me
XVIII; R, R' = Me

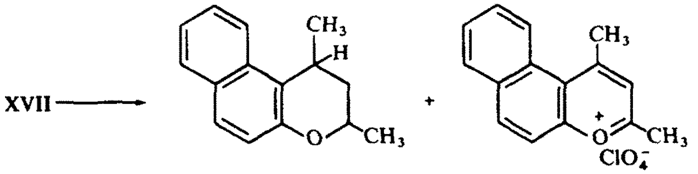
XV; R, R' = H
XVII; R = H; R' = Me
XIX; R, R' = Me

Treatment of XV with perchloric acid gave 4-methyl-5,6-benzochroman[10] (XX) and 4-methylnaphtho-[2,1-b] pyrylium perchlorate (XXI)·



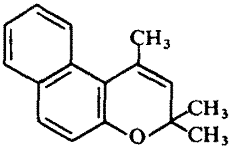
XX XXI

Compound XVII, on treatment with perchloric acid, similarly gave 2,4-dimethyl-5,6-benzochroman (XXII) and 2,4-dimethylnaphtho-[2,1-b]-pyrylium perchlorate (XXIII).



XXII XXIII

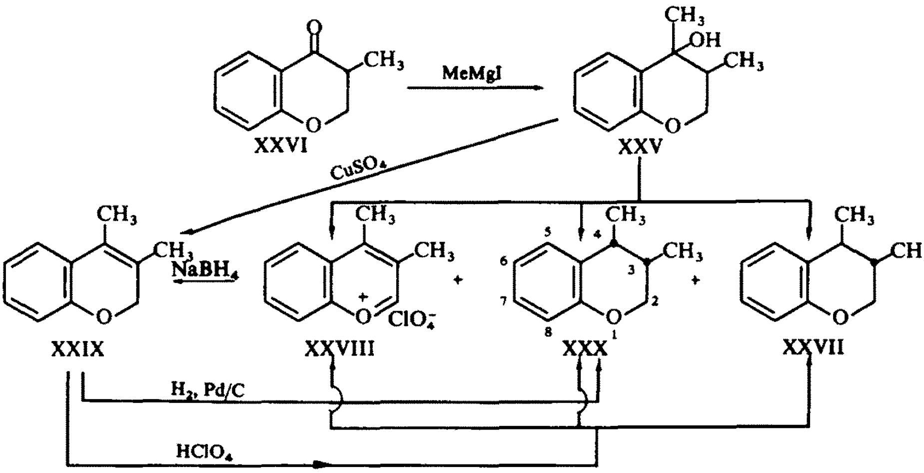
When XIX was treated with perchloric acid, 2,2,4-trimethylnaphtho-(2,1-b)-pyran[9] (XXIV) was the only product formed there being no possibility of hydride transfer.



XXIV

With the view to study the stereochemistry of chromans obtained by hydride transfer, 3,4-dimethyl-4-chromanol (XXV) [prepared by interaction of 3-methyl-4-chromanone (XXVI)[11] with MeMgI] was treated with perchloric acid. As expected the reaction yielded 3,4-dimethylchroman (shown to be a 50: 50 mixture of *cis*-XXX and *trans*-XXVII 3,4-dimethylchromans) and 3,4-dimethylbenzopyrylium perchlorate (XXVIII).

Dehydration of XXV by heating with anhydrous copper sulphate gave 3,4-dimethyl-Δ^3-chromene (XXIX) which was also obtained by reduction of XXVIII with sodium borohydride. The structure of XXIX was confirmed by its UV and NMR spectra. Catalytic hydrogenation of XXIX yielded 3,4-dimethylchroman (XXX). NMR spectrum of the latter reveals it to be nearly pure (ca. 90%) *cis*-XXX. When XXIX was treated with perchloric acid it yielded XXVIII and a 50:50 mixture of *cis*-3,4-dimethylchroman (XXX) and *trans*-3,4-dimethylchroman (XXVII). Thus treatment of both XXV and XXIX with perchloric acid gave a 50:50 mixture of *cis*-XXX and *trans*-XXVII-3,4-dimethylchromans along with XXVIII.



NMR spectrum of *cis*-3,4-dimethylchroman (XXX) obtained by catalytic hydrogenation of XXIX was as follows (soln in CCl_4, the position of the protons are indicated in ppm and J values in c/s):

(a) Two methyl doublets at 0·97 and 1·17 ($J = 7$); (b) The benzylic methine proton at C_4 showed two pairs of overlapping quartets centered at 2·9 ($JH_{4,3} = 6$); The coupling constant 6 for C_4 and C_3 protons confirmed their *cis* orientation; (c) A complex band for C_3-H centered at 2·15; (d) A band for O—CH_2-protons centered at 3·9; (e) Four aromatic protons centered at 6·9.

NMR spectrum of the mixture of *cis*- and *trans*-dimethylchromans obtained by treatment of XXV and XXIX with perchloric acid showed:

(a) Four pairs of Me doublets at 0·97, 1·17, 0·91 and 1·27. Of these, the two pairs at 0·97 and 1·17 belong to the *cis*-isomer XXX as seen from the NMR spectrum of XXX obtained by catalytic hydrogenation of XXIX. The other pair at 0·91 and 1·27 [a small amount of which is also discernible in the catalytic reduction product XXX] is due to the *trans* isomer XXVII. Integration showed the ratio of the two isomers to be 50:50.

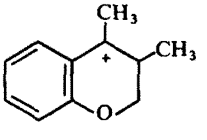
(b) The band for C_4 proton in this mixture was too complex for analysis. The C_3 and C_4 protons show as a complex band from 2–3.

(c) A complex band for O—CH_2 protons centered at 3·85.

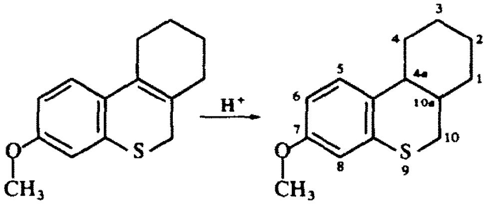
(d) Four aromatic protons centered at 6·8.

The NMR data agreed with the following VPC analysis:

Using a 50 ft SE-30 (Golay) column, (Col. temp 125°, H_2 flow-rate 375 ml/min), XXX, obtained by catalytic hydrogenation of XXIX, gave a peak with retention time of 9 min 36′ showing 90% of *cis* isomer and 10% of *trans* isomer with a retention time 8 min 15′. The product obtained by acid catalysed disproportionation of XXIX on the other hand under similar conditions gave two peaks with retention time 9 min 36′ and 8 min 15′ corresponding to 50% of each of the isomers XXX and XXVIII respectively.



XXIXA



XXXI XXXII

The lack of sterospecificity in the intermolecular transfer of hydride from the 2-position in one molecule of XXIX to the 4-position of its protonated derivative XXIXA may be due to the similar thermodynamic stability of the *cis* and *trans* end products XXX and XXVII (cf. the nearly equal thermodynamic stability of *cis*- and *trans*-octohydrophenanthrene[12]). The acid catalysed disproportionation of XXIX however differs from the acid catalysed disproportionation of 7-methoxy-9-thia-1,2,3,4,9,10-hexahydrophenanthrene (XXXI) where hydride transfer gives predominantly *cis*-7-methoxy-9-thia-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (XXXII) (yield, 77%).[13] In order to throw further light on the stereochemistry involved in the hydride transfer in the acid treatment of Δ^3-chromenes, it is proposed to study the disproportionation of the oxa-analogue of XXXI.

EXPERIMENTAL

General method for the syntheses of 4-methyl-4-chromanols (I–IV). Phenols were condensed with propiolactone to give β-phenoxy acids.[5] The latter were cyclized with PPA at 60–70° for 1½–2 hr to give the relevant chromanones in 75–85% yield. The chromanones were treated at 0° with MeMgI, the Grignard complex being decomposed with NH_4Cl soln to yield I–IV.

5,6-*Benzo-4-chromanone* XIV. β-2-Naphthoxypropionitrile was prepared by the condensation of β-naphthol with acrylonitrile using Et_3N as a catalyst.[7] Cyclization of the condensation product by interaction with 85% H_2SO_4 gave XIV.[7]

2-*Methyl-5,6-benzo-4-chromanone* (XVI). β-Naphthyl crotonate[14] on cyclization with HF gave XVI.[8] The chromanone was preferably purified by chromatography over neutral alumina instead of distillation as reported, m.p. 72–73° (lit.,[8] m.p. 73–74°).

2,2-*Dimethyl-5,6-benzo-4-chromanone* (XVIII). The compound could not be obtained by the method reported.[9] It was prepared by the following procedure:

β-Methylcrotonic acid chloride (8·6 g) was refluxed with β-naphthol (10·5 g) in dry benzene (50 ml) in the presence of Mg turnings to give the β-naphthyl ester (15·7 g) m.p. 54–56° (yield, 96%). The latter (22·3 g) was treated with HF (60–70 ml) at room temp for 2 hr. The acid was removed by passing a stream of N_2. The reaction mixture was dissolved in ether and the ether extract washed 4–5 times with 1·5% NaOH aq and then with saturated brine till free of alkali. The crude chromanone (18·6 g) was chromatographed over neutral alumina (400 g) using pet. ether (b.p. 60–80°). The product (11·3 g) on further purification by 3 crystallizations from pet. ether (b.p. 40–60°) gave pure XVIII as white cubes (6 g), m.p. 79–81° (lit.,[9] m.p. 81°).

TABLE 1. SYNTHESIS OF 4-METHYLCHROMANS FROM CHROMANOLS AND Δ^3-CHROMENES (VII AND XXXII) BY TREATMENT WITH PERCHLORIC ACID AND CATALYTIC REDUCTION WHERE INDICATED

Starting compd.	Chroman	Percentage yield	m.p./b.p. (temp of air bath)	Appearance	Analysis %				UV spectrum in EtOH λ_{max} in mμ (log ε)
					Found		Required		
					C	H	C	H	
II	VIII	34·4	105–15°/5 mm	Colourless liquid	81·3	8·9	81·5	8·6	281 (3·49) 289 (3·27)
III	X	28	100–25°/2 mm	Colourless liquid	74·3	7·9	74·1	7·9	294 (3·54)
IV	XII	35	90–95°/0·7 mm	Colourless liquid	73·7	8·0	74·1	7·9	282 (3·50) 288 (3·46)
VII	V	27	75–85°/4 mm	Colourless liquid	81·5	8·0	81·0	8·1	275 (3·40) 283 (3·37)
VII	V (Cat. redn.)	80	80–90°/5 mm	Colourless liquid	80·6	8·1	81·0	8·1	274 (3·35) 283 (3·32)
XV	XX	30	135–50°/2·5 mm m.p. 61–62°	White solid	84·8	6·8	84·8	7·1	233 (4·86) 257 (3·45) 266 (3·62) 277 (3·70) 288 (3·58) 319 (3·31) 333·5 (3·40)
XVII	XXII	36	140–60°/0·5 mm m.p. 76°	White solid	85·2	7·8	84·9	7·8	232 (4·88) 288 (3·56) 276 (3·68) 267 (3·60) 332 (3·33) 318 (3·28)
XXIX	XXX + XXVII	46	81–83°/3 mm	Colourless liquid	81·7	8·3	81·4	8·7	278 (3·42) 285 (3·38)
XXIX	XXX (Cat. redn.)	66	100–5°/5 mm	Colourless liquid	81·7	8·7	81·4	8·7	275 (3·39) 283 (3·37)

TABLE 2. SYNTHESIS OF BENZOPYRYLIUM AND NAPHTHOPYRYLIUM PERCHLORATES BY TREATING CHROMANOLS WITH PERCHLORIC ACID

Starting compound	Perchlorate	Percentage yield	m.p.	Appearance	Analysis %						UV spectrum (solvent) λ_{max} in mμ (log ε)
					Found			Required			
					C	H	Cl	C	H	Cl	
I	VI	2	—	Yellow solid	—	—	15·0	-	—	14·5	(70% $HClO_4$) 317 (4·10) 240 (4·51)
III	XI	21	156–7°	Yellow solid	—	—	12·9	—	—	13·1	(70% $HClO_4$) 245 (4·27) 258 (4·13) 325 (4·05) 269–70 (3·54)
IV	XIII	28	182–83°	Buff colored needles	48·6	4·4	12·3	48·0	4·0	12·9	(70% $HClO_4$) 248 (4·27) 372 (3·94)
XV	XXI	29	235°	Golden yellow needles	57·2	3·4	12·8	57·1	3·7	12·1	ACOH (1% $HClO_4$) 282 (4·25) 399 (4·08)
XVII	XXIII	31	231°	Golden yellow flakes	58·4	4·1	11·3	58·3	4·2	11·5	ACOH (1% $HClO_4$) 286·5 (4·67) 396 (4·54)
XXV	XXVIII	12	160–62°	Pale yellow needles	51·2	4·7	14·0	51·0	4·2	13·7	(70% $HClO_4$) 243 (4·37) 328 (4·10)

4-*Methyl-5,6-benzo-4-chromanol* (XV) was prepared as reported earlier (lit.,[6] m.p. 124°).

2,4-*Dimethyl-5,6-benzo-4-chromanol* (XVII). A soln of XVI (5·89 g) in ether was added dropwise at 0° to 2 equivts of MeMgI in ether. The reaction was allowed to come to room temp gradually and then refluxed for 1 hr. The Grignard complex was decomposed with 20% NH_4Cl aq and the ether layer washed with 2% $Na_2S_2O_3$ aq and saturated brine. Removal of ether gave XVII as a white solid (5·56 g; 88%). On crystallization from EtOH it gave white needles, m.p. 134–135°. (Found: C, 78·7; H, 6·8; $C_{15}H_{16}O$ requires: C, 78·9; H, 7·1%.)

2,2,4-*Trimethyl-5,6-benzo-4-chromanol* (XIX) was prepared from XVIII (5·65 g) as above to yield crude XIX (4·42 g). The latter on several crystallizations from EtOH gave white needles m.p. 161–163° (2·6 g, 43%). (Found: C, 79·2; H, 7·8; $C_{16}H_{18}O$ requires: C, 79·3; H, 7·4%.)

2,2,4-*Trimethyl-5,6-benzo-* Δ^3-*chromene* (XXIV). A soln of XIX (0·6 g) in benzene (7 ml) was stirred with 60% perchloric acid (1 ml) for 15 min at room temp. The benzene layer was washed with $NaHCO_3$ aq. Removal of benzene and distillation of the product gave a pale yellow liquid (0·53 g), b.p. 120–140° (air bath)/0·2 mm. On redistillation, a white solid was obtained which after 3 crystallizations from pet. ether (b.p. 40–60°) gave XXIV as colourless cubes, m.p. 81–82°. (Found: C, 86·2; H, 7·4; $C_{16}H_{16}O$ requires: C, 85·7; H, 7·1%.) UV spectrum in alcohol λ_{max} (log ε) $-$347 (3·64), 313 (3·60), 301 (3·64), 244 (4·74). The NMR spectrum in CCl_4 confirmed the structure XXIV (positions of protons in ppm: 1·4 for 2,2-dimethyl; 2·36 for 4-methyl, 5·37 for C_3-proton, multiplet at 6·67–8·15 for aromatic protons).

3-*Methylchromanone* (XXVI) was prepared by treating the Na salt of *o*-hydroxypropiophenone with formaldehyde as reported.[11] However the experimental conditions have not been described. By adopting the following procedure XXVI was obtained in yields varying from 27–50%: *o*-Hydroxypropiophenone (6 g) was dissolved in the required quantity of NaOH in water (40 ml) at 50°. Aqueous (37–41%) formaldehyde (5 ml) was added and the mixture heated at 50° for 75 min. After keeping at room temp for 2 hr, the mixture was extracted with ether. Work up gave a liquid which on fractional distillation gave a fraction distilling between 112–126°/3 mm. The latter on redistillation gave XXVI b.p. 113–115°/3 mm. (Found: C, 74·2; H; 6·5. $C_{10}H_{10}O_2$ requires: C, 74·1; H, 6·2%.)

3,4-*Dimethyl-4-chromanol* (XXV) was prepared as described above. The chromanone XXVI (8·23 g) gave XXV as a colourless viscous oil (8·79 g). The latter showed absence of a carbonyl band in IR and was used as such in subsequent reactions.

3,4-*Dimethyl-* Δ^3-chromene (XXIX). A soln of XXV (6 g) in dry benzene (250 ml) was refluxed with anhy $CuSO_4$ (3 g). Water formed in the reaction was removed azeotropically. The benzene soln on work up gave a liquid which on distillation gave XXIX (4·98 g;, 92%) b.p. 102–107°/3–4 mm. (Found: C, 82·8; H, 7·7; $C_{11}H_{12}O$ requires: C, 82·5; H, 7·6%.) UV spectrum in EtOH λ_{max} and log ε): 307–308 (3·65), 266 (3·74).

cis-3,4-*Dimethylchroman* (XXX). A soln of XXIX (0·3 g) in AcOEt (10 ml) and 10% Pd–C (150 mg) was treated under stirring with H_2 at atm press, till H_2 absorption ceased. Removal of solvent and distillation of the residue gave XXX as a colourless oil (0·20 g) b.p. 106° (bath temp)/5 mm.

4-*Methylchroman* (V). A soln of VII prepared from I as reported[6] (0·25 g) in AcOEt, and 30% Pd–C (50 mg) was treated with H_2 until absorption ceased. Removal of solvent and distillation of the residue gave V as a colourless liquid (0·16 g) b.p. 80–90° (air bath)/5 mm.

General procedure for treatment of 4-*methylchromanols, benzochromanols or* Δ^3-*chromenes with* 60% *perchloric acid*. The chromanols and benzochromanols were treated with 60% aqueous perchloric acid (5–10 ml per gm of the compound), at 60–70° for 2 hr, except in the case of IV which was treated with 70% aqueous perchloric acid at room temp for 2 hr. The reaction mixture was extracted with pet. ether (b.p. 60–80°). The solvent extract was washed with $NaHCO_3$ aq and water. After drying (Na_2SO_4) the solvent was removed and the residual liquid distilled in vacuum whereby the chromans were obtained as colourless liquids. The perchloric acid soln left after extraction with pet. ether was cooled in an ice bath and ether gradually added under agitation until the mixture was saturated with ether. The reaction mixture gave the relevant perchlorates which separated out in a few cases as crystalline solids. In the case of chromanols I, II and III, the above perchloric acid treatment gave dark violet solns from which very small quantities of colored compounds were isolated which however have not been examined fully so far.

4-*Methylbenzopyrylium perchlorate* (VI). The chromanol I (0·50 g) was gradually added to aqueous 70% perchloric acid (2·5 ml) at $-15°$. The reaction mixture was kept for 1 hr at -13 to $-15°$, with occasional stirring. Chilled ether was added very gradually keeping the temp below $-10°$. After adding ether to saturation point, the mixture was allowed to stand for a few min and then filtered in an atmosphere of N_2 and washed with dry ether. The crystalline VI was immediately analysed and its NMR spectrum in trifluoroacetic acid also immediately taken. The perchlorate (yield, 16 mg) had no sharp m.p. It shrinks at 95° and melts at 105–110°. (Position of protons in ppm: 3·36 for 4-methyl; 8·16–8·8 for four aromatic protons and C_3 proton; 9·59 a doublet for C_2 proton.)

6-Methoxy-4-methylbenzopyrylium perchlorate (XI). Chromanol III (0·5 g) was gradually added to 70% aqueous perchloric acid (2·5 ml) cooled in an ice-salt bath. The reaction mixture was then kept at room temp for 1 hr, after which it was again cooled in an ice–salt bath and ether added to saturation point. The yellow ppt obtained was immediately filtered and washed with ether. The crystalline XI (0·15 g) was immediately analysed and its NMR spectrum recorded in trifluoroacetic acid. (position of protons in ppm: 3·26 for 4-Me; 4·16 for 6-OMe; 7·67–8·26 for three aromatic protons and C_3 proton; 9·36 a doublet for C_2 proton.)

7-Methoxy-4-methylbenzopyrylium perchlorate (XIII). The chromanol IV (4·6 g) on treatment with 70% aqueous perchloric acid (12 ml) at room temp for 2 hr gave, on saturation with ether, XIII (1·72 g). The NMR spectrum in trifluoroacetic acid showed the following characteristics: (position of protons in ppm: 3·2 for 4-Me; 4·27 for 7-OMe; 7·67–8·7 for three aromatic protons and C_3 proton; 9·2 a doublet for C_2 proton.)

The physical constants, properties, yields and elementary analysis of 4-methylchromans (prepared by perchloric acid treatment of the relevant chromanols and Δ^3-chromenes) are recorded in Table 1. The data on catalytic hydrogenation of VII and XXIX is also reported in this Table.

The physical constants, properties and elementary analysis of 4-methylbenzopyrylium salts (obtained by perchloric acid treatment of 4-methylchromanols) are recorded in Table 2.

Acknowledgements—This research was supported in part by a grant from the Petroleum Research Fund administered by American Chemical Society. Grateful acknowledgement is hereby made to the donors of the Fund. We are also grateful to the Council of Scientific and Industrial Research for supporting the work, to Dr. T. S. Gore for microanalyses and to Dr. R. B. Mitra for VPC analysis.

REFERENCES

[1] B. D. Tilak and V. M. Vaidya, *Tetrahedron Letters* 487 (1963).

[2] B. D. Tilak, H. S. Desai, C. V. Deshpande, S. K. Jain and V. M. Vaidya, *Tetrahedron* **22**, 7 (1966).

[3] B. D. Tilak and S. K. Jain, unpublished work.

[4] B. D. Tilak, T. Ravindranathan and K. N. Subbaswami, *Tetrahedron Letters* 1959 (1966).

[5] T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert, W. L. Beears and Marie G. Prendergast, *J. Am. Chem. Soc.* **71**, 661 (1949).

[6] J. Colonge and A. Guyot, *Bull. Soc. Chim. Fr*, 325 (1958).

[a] W. Baker, *J. Chem. Soc.* 1595 (1929); W. H. Perkin (Jr), J. N. Ray and R. Robinson, *Ibid.* 1504 (1928); Y. Ashahina and M. Inubuse, *Ber. Dtsch. Chem. bes.* **61**, 1646 (1928).

[7] G. Baryant Bachman and H. A. Levine, *J. Am. Chem. Soc.* **69**, 2341 (1947).

[8] Otto Dann, Gerda Volz and Otto Huber, *Liebig Ann* **587**, 16 (1954).

[9] R. Livingstone, D. Miller and R. B. Watson, *J. Chem. Soc.* 2422 (1958).

[10] Issei Iwai and Junya Ide, *Chem. Pharm. Bull.* **10**, 926 (1962).

[11] P. Dare and L. Verlicchi, *Experentia* **16**, 301 (1960).

[12] Z. G. Hajas, K. J. Doebel and M. W. Goldberg, *J. Org. Chem.* **29**, 2527 (1964).

[13] B. D. Tilak, R. B. Mitra and Z. Muljiani, unpublished work.

[14] Aleksandr Spasov Ber *Dtsch. Chem. bes.* **75B**, 779–80 (1942).