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SYNTHESIS OF BENZOCHROMENES AND RELATED COMPOUNDS

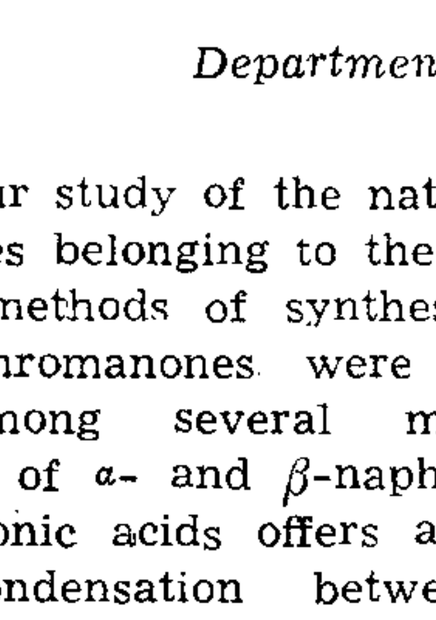
Part I. 5 : 6 and 7 : 8 Benzochromanones and Benzocoumarins

A. S. R. ANJANEYULU, L. RAMACHANDRA ROW, C. SRI KRISHNA AND C. SRINIVASULU

Department of Chemistry, Andhra University, Waltair

DURING our study of the naturally occurring fungicides belonging to the class of benzochromenes, methods of syntheses of 5 : 6 and 7 : 8 benzochromanones were critically examined. Among several methods,[1-8] the condensation of α- and β-naphthols with substituted crotonic acids offers a facile method. Such a condensation between polyhydric phenols and crotonic acids was already effected using $SbCl_3$, $ZnCl_2$ or $SnCl_2$,[3,4] P_2O_5,[5] polyphosphoric acid[6] or $AlCl_3$.[7] Alternatively, the phenolic esters of crotonic acids were subjected to Fries migration using $AlCl_3$[7] or HF[8] to yield the chromanones.

In the current investigation, α- and β-naphthols were condensed with β : β-dimethyl acrylic acid and crotonic acid in presence of $SbCl_3$, $ZnCl_2$ and polyphosphoric acid to secure 7 : 8 and 5 : 6 benzochromanones (I, II). The optimum conditions with $SbCl_3$ and $ZnCl_2$ were found to be heating at 140–50° for 1–2 hr., while with polyphosphoric acid, heating on a water-bath for 1 hr. would be sufficient. The latter reagent caused exclusive formation of benzochromanones (I, II) in good yields (upto 70%). But, $SbCl_3$ and $ZnCl_2$ furnished them only in low yields (12–30%). The results are summarised in Table I.



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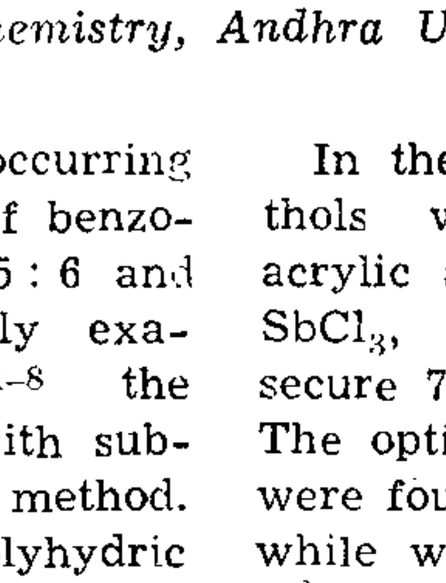

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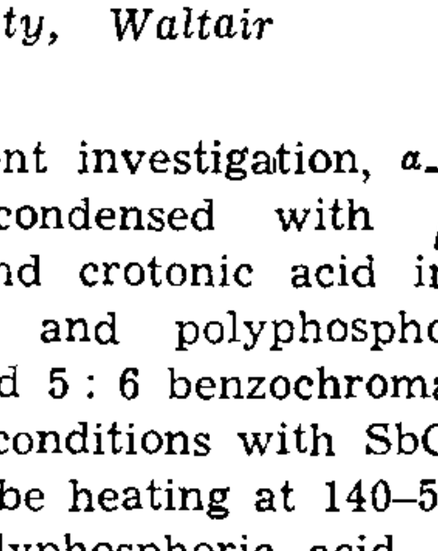
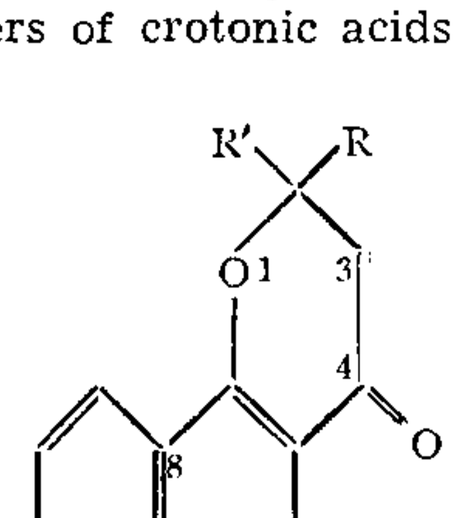


III



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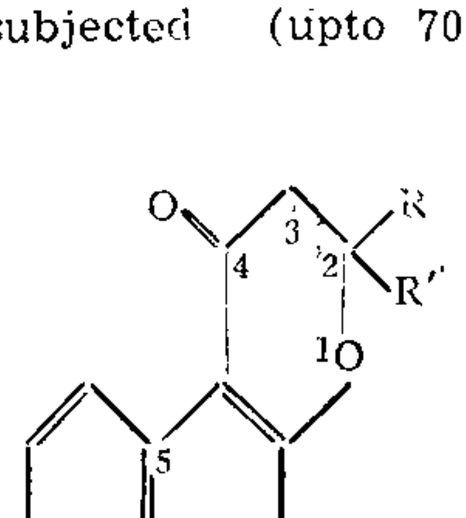
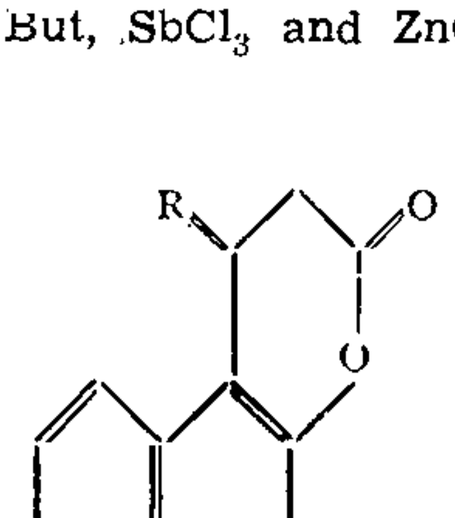


V



IV

TABLE I*

Sl. No.	Compound	M.P. or B.P.	I.R.-CO ν in cm.$^{-1}$	Mol. Form.	Required C	Required H	Found C	Found H
	A. 7 : 8-Benzo series :							
1	2 : 2-dimethyl chromanone[7]	136–40°/ 0·8 mm.	1680	$C_{15}H_{14}O_2$	79·62	6·24	79·29	5·90
	2 : 4-d.n.p.[7] ..	281–82°	..	$C_{21}H_{18}O_5N_4$	62·07	4·46	62·37	4·64
2	2-methyl chromanone ..	164–68° 0·7 mm.	1680	$C_{14}H_{12}O_2$	79·23	5·70	78·94	5·86
	2 : 4-d.n.p. ..	288–89°	..	$C_{20}H_{16}O_5N_4$	61·22	4·11	61·10	4·12
3	3 : 4-dihydro 4 phenyl coumarin	110–11°	1770	$C_{19}H_{14}O_2$	83·19	5·14	82·81	5·37
4	4-phenyl coumarin ..	125–26°	1730	$C_{19}H_{12}O_2$	83·81	4·44	83·83	4·03
5	3 : 4-dihydro 4-(*p*-methoxy) phenyl coumarin	127–28°	1770	$C_{20}H_{16}O_3$	79·83	5·30	78·68	5·25
6	4-(*p*-methoxy) phenyl coumarin	160°	1730	$C_{20}H_{14}O_3$	79·46	4·67	79·07	4·89
	B. 5 : 6-Benzoseries :							
1	2 : 2-dimethyl chromanone[7]†	160–64°/ 1·5 mm.	1670	$C_{15}H_{14}O_2$	79·62	6·24	79·14	6·34
	2 : 4-d.n.p.[7] ..	257–58°	..	$C_{21}H_{18}O_5N_4$	62·07	4·46	61·84	4·31
2	2-methyl chromanone[8] ..	75–76°	1675	$C_{14}H_{12}O_2$	79·23	5·70	79·07	5·91
	2 : 4-d.n.p.[8] ..	260–62°	..	$C_{20}H_{16}O_5N_4$	61·22	4·11	60·98	3·85
3	3 : 4-dihydro 4-methyl coumarin	153–54°	1770	$C_{14}H_{12}O_2$	79·23	5·70	78·89	5·82
4	4-methyl coumarin[9] ..	180–81°	1730	$C_{14}H_{10}O_2$	79·98	4·79	79·53	5·14
5	3 : 4-dihydro 4-phenyl coumarin[11]	114–15°	1790	$C_{19}H_{14}O_2$	83·19	5·14	82·89	5·22
6	4-phenyl coumarin ..	157–58°	1735	$C_{19}H_{12}O_2$	83·81	4·44	84·09	4·58
7	3 : 4-dihydro 4-(*p*-metnoxy) phenyl coumarin	110°	1760	$C_{20}H_{16}O_3$	78·93	5·30	79·02	5·49
8	4-(*p*-methoxy) phenyl coumarin	115–16°	1730	$C_{20}H_{14}O_3$	79·46	4·67	79·21	4·44

* All the compounds described above are purified by column chromatography over alumina or silica gel and then snbjected to vacuum distillation or crystallisation from suitable solvents.

† Livingstone *et al.*[4] recorded the m.p. 81° for 5 : 6-benzo 2 : 2-dimethyl chromanone (II, R = R′ = Me) obtained by Friedel and Craft's method. But, in our hands the benzochromanone was obtained as colourless liquid B.P. 160–64°/1·5 mm. whose 2 : 4-d.n.p. agreed with the m.p. recorded by Livingstone *et al.* To resolve this difference, their synthesis was repeated with scrupulous adherence to their experimental conditions. Only a liquid benzochromanone was again secured which gave a 2 : 4-d.n.p. identical with that obtained earlier using polyphosphoric acid or $SbCl_3$.

In the condensation between β-naphthol and crotanic acid the 2-methyl 5 : 6-benzochromanone (II, R = H, R′ = Me) was accompanied by a minor product (III, R = Me) when $SbCl_3$ or $ZnCl_2$ was used, while polyphosphoric acid gave exclusively the benzochromanone (II, R = H, R′ = Me). The minor compound (III, R = Me; m.p. 153–54°; ν 1770 cm.$^{-1}$) exhibits green fluorescence in concentrated H_2SO_4 and dissolves in 10% aqueous NaOH with bluish-violet fluorescence. It was proved to be a 3 : 4-dihydro coumarin which on dehydrogenation with 30% Pd-C gave 4-methyl 5 : 6-benzocoumarin (IV, R = Me) identical with an authentic sample prepared following the method of Seshadri *et al.*[9]

This formation of 4-methyl 5 : 6-benzo 3 : 4-dihydro coumarin (III, R = Me) led us to investigate the condensation between α- and β-naphthols with cinnamic acid and its *p*-methoxy derivative. Miyano and Mitsuii[3] recorded the formation of the corresponding coumarin with phloroglucinol and cinnamic acid; but with resorcinol only a cinnamoyl ester was obtained. Buu-Hoi *et al.*[10] prepared 3 : 4-dihydro 7 : 8-benzo 4-phenyl coumarin (V, R = C_6H_5) by condensing α-naphthol and cinnamic acid in presence of concentrated H_2SO_4 by refluxing in tetralin solution. In the present study, α- and β-naphthols were condensed with cinnamic acid and its *p*-methoxy derivative using $SbCl_3$, $ZnCl_2$ at 140–50° and HOAc-H_2SO_4 (1 : 1) at refluxing temperature. In all the three reagents, the 3 : 4-dihydro-4-phenyl benzocoumarins (III, V R = C_6H_5) were formed exclusively. These could be dehydrogenated with 30% Pd-C to

yield the 4-phenyl benzocoumarins (IV, VI $R = C_6H_5$). With *p*-methoxy cinnamic acid, however, β-naphthol yielded a coumarin (IV, $R = C_6H_4OMe$) (lactone C = O, 1730 cm.$^{-1}$, m.p. 115°, brilliant fluorescence in concentrated H_2SO_4) instead of a dihydro coumarin (III, $R = C_6H_4OMe$). This point was confirmed by hydrogenating it and securing the 5 : 6-benzo 4-*p*-methoxyphenyl 3 : 4-dihydro coumarin (III, $R = C_6H_4OMe$) (lactone C = O ν 1760 cm.$^{-1}$, m.p. 116°). The mixed m.p. (90–94°) of these two compounds (III and IV, $R = C_6H_4OMe$) was also depressed. It is rather difficult to explain this difference in the condensation between α- and β-naphthols and *p*-methoxy cinnamic acid.

Thus, cinnamic acids yield coumarins while substituted crotonic acids yield a mixture of chromanones and coumarins with both phenols and naphthols. This variation in their reactivity may be explained on the basis of resonance in these molecules where the β-carbon is comparatively less reactive in cinnamic acids compared to the β-carbon in crotonic acids.

Experimental

A typical procedure is given below for the synthesis of benzochromanones.

7 : 8-Benzo 2 : 2-Dimethyl Chromanone.—(I, $R = R' = Me$) (*a*) Using $SbCl_3$.—A mixture of α-naphthol (7·2 g., 2 moles), β : β-dimethyl acrylic acid (5 g., 2 moles) and freshly distilled $SbCl_3$ (5·7 g., 1 mole) was heated in an oil-bath at 140–50° for 1 hr. The mixture was cooled and extracted with ether. The ether extract was washed with dilute HCl (1 : 1), water, cold 5% aqueous NaOH and finally with water. It was then dried and evaporated. The brown liquid was distilled under vacuum at 136–40°/0·8 mm. to get the chromanone as pale yellow viscous liquid (yield 3·45 g.).

(*b*) The above synthesis was repeated using $ZnCl_2$ instead of $SbCl_3$ (yield 2·1 g.).

(c) Using Polyphosphoric Acid.—Polyphosphoric acid was prepared by mixing P_2O_5 (8 parts by weight, 40 g.) with syrupy ortho phosphoric acid (85%, 5 parts by volume, 25 ml.) and stirred at 85° for half-an-hour before use.

A mixture of α-naphthol (7·2 g., 1 mole) β : β-dimethyl acrylic acid (5 g., 1 mole) and the above phosphoric acid was heated at 95° for 1 hr. on a water-bath. Working up the reaction mixture as above gave the chromanone (4·6 g.).

5 : 6-Benzo 3 : 4-Dihydro 4-Phenyl Coumarin.—(III, $R = C_6H_5$) (*a*) Using concentrated H_2SO_4.—A mixture of β-naphthol (12 g.), cinnamic acid (12·4 g), glacial acetic acid (35 ml.) and concentrated H_2SO_4 (15 ml.) was refluxed for 1 hr. The mixture was poured into ice-cold water and working up in the usual way, gave the benzo coumarin which crystallised from ethanol (charcoal) as colourless prisms (5·6 g.) m.p. 114–15°.

(*b*) With $SbCl_3$ or $ZnCl_2$, experimental conditions are similar to those followed for benzochromanones.

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