523. *Some Chroman and* 1 : 2-*Benzopyran Derivatives.*

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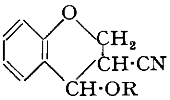
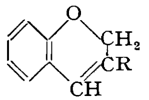
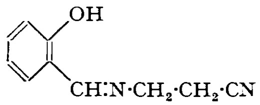
3-Cyanochroman-4-ol and 3-cyano-1 : 2-benzopyran have been prepared by condensation of acrylonitrile with salicylaldehyde in an aqueous alkaline medium. Some derivatives of these substances are described.

We undertook an investigation of the reaction between salicylaldehyde and acrylonitrile as a model experiment to obtain information about the possibility of using acrylonitrile for the preparation of chroman derivatives which might prove useful intermediates for the synthesis of certain naturally occurring substances. Since this work was begun Bachman and Levine (*J. Amer. Chem. Soc.*, 1948, **70**, 599) have published an account of their work on this reaction, and although further work is in progress it seems desirable to publish some of our results at this stage.

Like these authors, we found that there is very little reaction between salicylaldehyde and acrylonitrile when the two substances are heated together with basic catalysts such as sodium or sodium methoxide, and the use of salicylonitrile, which is not chelated like the aldehyde, provided no more promising route to the desired compounds. Nevertheless, assuming that chelation is at any rate one important factor in preventing combination, we investigated the reaction in aqueous alkaline solution and have developed methods by which 3-cyanochroman-4-ol (I; R = H) and 3-cyano-1 : 2-benzopyran (II; R = CN) can be prepared in reasonable quantities. Bachman and Levine obtained very small yields of these substances, and the m. p. of their substance (I; R = H) was some 11—12° lower than that of our product. (It is of course possible that *cis–trans*-isomerism is responsible for this difference.) We have also isolated a substance which appears to be β-(*o*-hydroxybenzylideneamino)propionitrile (III). This has evidently been formed by condensation of salicylaldehyde with β-aminopropionitrile formed from acrylonitrile and ammonia. An alkaline solution of acrylonitrile smells of ammonia when


(I.)


(II.)


(III.)

warmed; (III) is formed in larger yield if ammonia is added to the reaction mixture and it separates when the solution no longer contains free alkali.

1 : 2-Benzopyran-3-carboxylic acid (II; R = CO_2H) can be obtained by hydrolysis of either (I; R = H) or (II; R = CN), and when (I; R = H) is heated with sodium acetate and acetic anhydride it is converted into a mixture of (II; R = CN) and 4-acetoxy-3-cyanochroman (I; R = Ac). (I; R = H) is not dehydrated by boiling it with phosphoric oxide in benzene or by distilling it *in vacuo*, which may indicate that the 4-OH and the 3-H are *cis* to one another.

EXPERIMENTAL.

3-*Cyanochroman*-4-*ol*.—Salicyladehyde (40 g.), acrylonitrile (40 c.c.), and water (30 c.c.) were mechanically stirred and treated, during 5 hours, with sodium hydroxide (12 g.) in water (120 c.c.) as the mixture boiled under reflux. Stirring was continued for a further hour and, on cooling, 3-cyanochroman-4-ol (8·5 g.) separated. It crystallised from alcohol as colourless plates, m. p. 153° (Found : C, 68·9; H, 5·1; N, 8·0. Calc. for $C_{10}H_9O_2N$: C, 68·6; H, 5·1; N, 8·0%). Extraction of the aqueous solution with ether afforded a little more 3-cyanochroman-4-ol, and salicylaldehyde (about 20 g.) was recovered. When kept, the aqueous solution sometimes deposited a small quantity of pale yellow needles, m. p. 74—75°.

β-(o-*Hydroxybenzylideneamino*)*propionitrile*.—Salicylaldehyde (12 g.), water (50 c.c.), potassium hydroxide (6 g.), and ammonia (10 c.c.; *d* 0·88) were mixed and slowly treated with acrylonitrile (10 g.) with shaking. After ½ hour, the mixture was heated on a steam-bath for ½ hour, and when it was then kept for several days crystals separated. Recrystallisation from alcohol afforded the *nitrile* as pale yellow needles, m. p. 74—75° (1·0 g.), identical (mixed m. p.) with the compound, m. p. 74—75° (above) (Found : C, 68·9; H, 5·8; N, 16·2. $C_{10}H_{10}ON_2$ requires C, 68·9; H, 5·7; N, 16·1%). This substance dissolves in sodium hydroxide to give a yellow solution and is decomposed by dilute acid with formation of salicylaldehyde (recognised by conversion into the phenylhydrazone). It becomes deep orange on exposure to light but this does not appear to involve appreciable decomposition.

3-*Cyano*-1 : 2-*benzopyran*.—Salicylaldehyde (40 g.), acrylonitrile (40 c.c.), and water (100 c.c.) were treated very slowly during 48 hours with sodium hydroxide (6 g.) in water (120 c.c.); the mixture was gently boiled. After a further 24 hours the solution was extracted with ether, and the ether washed with sodium hydroxide and then water. After drying (Na_2SO_4) and evaporation, 3-cyano-1 : 2-benzopyran (10 g.) remained. It crystallised from light petroleum (b. p. 40—60°) as colourless prisms, m. p. 50° (Found : C, 76·3; H, 4·7; N, 8·7. Calc. for $C_{10}H_7ON$: C, 76·4; H, 4·5; N, 8·9%). Bachman and Levine give m. p. 48—49°. Salicylaldehyde (17 g.) was recovered.

1 : 2-*Benzopyran*-3-*carboxylic Acid*.—3-Cyanochroman-4-ol (or 3-cyano-1 : 2-benzopyran) was refluxed with 10% aqueous sodium hydroxide until evolution of ammonia ceased (about 30 minutes). Acidification then gave a good yield of 1 : 2-*benzopyran*-3-*carboxylic acid*, which crystallised from alcohol as slightly yellow prisms, m. p. 190° (Found: C, 68·3; H, 4·6. $C_{10}H_8O_3$ requires C, 68·2; H, 4·5%). The *methyl* ester was obtained when this acid or 3-cyanochroman-4-ol was boiled with methyl-alcoholic hydrogen chloride for 1½ hours. It separated from methyl alcohol as colourless plates, m. p. 57° (Found : C, 69·6; H, 5·2. $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·2%).

Action of Acetic Anhydride on (I; R = H).—3-Cyanochroman-4-ol (3 g.), sodium acetate (3 g.), and acetic anhydride (15 c.c.) were boiled for 2 hours. On addition of water the product slowly solidified. Recrystallisation from a little alcohol gave 4-*acetoxy*-3-*cyanochroman* (0·9 g.), which was obtained as nearly colourless needles on recrystallisation from light petroleum (b. p. 80—100°) (Found : C, 65·9; H, 5·2. $C_{12}H_{11}O_3N$ requires C, 66·3; H, 5·1%). Addition of water to the alcoholic mother-liquor precipitated an oil which solidified. After drying, this was extracted with cold light petroleum (b. p. 40—60°), and 3-cyano-1 : 2-benzopyran (1·4 g.) was obtained on evaporation. When 4-acetoxy-3-cyanochroman (0·3 g.) was dissolved in a solution containing potassium hydroxide (0·3 g.), alcohol (2 c.c.), and water (2 c.c.), and the solution was kept at room temperature for one hour, 3-cyanochroman-4-ol (identified by mixed m. p.) was obtained on dilution with water.

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