[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, FOUAD I UNIVERSITY, AND THE LABORATORIES OF THE MEMPHIS CHEMICAL COMPANY]

Furo-chromones and -Coumarins. VII. Degradation of Visnagin, Khellin and Related Substances; Experiments with Chromic Acid and Hydrogen Peroxide; and a Synthesis of Eugenitin

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The action of chromic acid on visnagin yields 6-formyl-7-hydroxy-5-methoxy-2-methylchromone, the methyl ether of which gives the color reaction characteristic for 2-methylchromones having no free phenolic group. Visnagin and khellol when treated with hydrogen peroxide yield 6-hydroxy-4-methoxybenzofuran-5-carboxylic acid. Khellin yields the 7-methoxy derivative of this acid. The formyl derivative obtained from visnagin leads, through three steps, to eugenitin. The styryl derivatives obtained from visnaginone and khellinone, respectively, were converted into the coumaran-3-one derivatives by treatment with hydrogen peroxide in an alkaline medium.

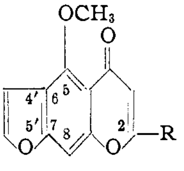
Khellin (II), visnagin (Ia) and khellol (Ib) obtained from *Ammi visnaga* (L.) are now available in quantity, and a number of degradations and similar reactions have been carried out with these three substances with the view of obtaining products which may be useful as medicinals or in further synthesis. This paper is divided into three parts. The first describes the oxidation of visnagin to the formylchromone derivative (IIIa) which is of interest because very little is known of formyl derivatives of chromones. The second part deals with the facile oxidation of visnagin, khellin and khellol with hydrogen peroxide to salicyclic acid derivatives. Oxidation of these substances with hydrogen peroxide, but under different conditions, has already been carried out by Späth and Gruber,[1a,b] who obtained 2,3-furandicarboxylic acid. The third part deals with the condensation of visnaginone and khellinone with benzaldehyde, and the transformation of the chalcones thus obtained into benzalcoumaranones.

Oxidation of Visnagin (Ia) with Chromic Acid.—This oxidation gave in good yield a substance $C_{12}H_{10}O_5$ containing one methoxyl and one hydroxyl group. It is believed to be 6-formyl-7-hydroxy-5-methoxy-2-methylchromone (IIIa). Analogous reactions leading from benzofurans to derivatives of salicylic aldehyde are already known, but the oxidation is usually carried out by the action of ozone.[2]

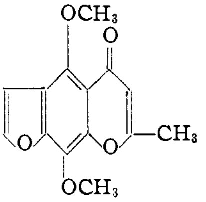
IIIa gives in alcoholic solution a wine-red color with ferric chloride, dissolves in sodium hydroxide solution with a yellow color and condenses with aromatic amines easily, to give colored anils of the type IVb. IIIa condenses readily at room temperature with hydroxylamine and other carbonyl reagents both in an acid and in an alkaline medium. It is believed that this condensation takes place with the formyl group and not the carbonyl group of the γ-pyrone ring as under similar conditions visnagin itself does not condense with these reagents. Supporting IIIa is also the fact that like salicylaldehyde it gives a green color with titanium trichloride in methanol.[3] The methyl ether IIIb which can be obtained by allowing IIIa to react with methyl iodide in the presence of acetone and potassium carbonate gives the color reaction characteristic for 2-methylchromones which have no phenolic groups.[4]

A number of derivatives of IIIa have been prepared, *viz.*, its demethylation with dilute hydrochloric acid yielded the corresponding phenolic product Va (compare the demethylation of visnagin[5]), while nitration and bromination of IIIa yielded the 8-nitro and 8-bromo compounds, respectively. Similar reactions were also carried out with 5-ethoxy-2-methylfuro-4',5',6,7-chromone (Id) and 5-methoxy-furo-4',5',6,7-chromone (Ic).

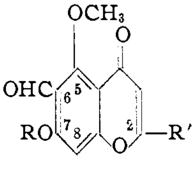
Reduction of (Va) to (VIa), followed by methylation of the latter, led to (VIb) which was proved to be identical with eugenitin, isolated by Schmid[6] from *Eugenia caryphyllata* (L.).



I



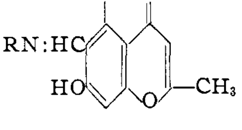
II



III

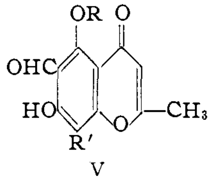
Ia, R = CH_3
Ib, R = CH_2OH
Ic, R = H
Id, R = CH_3, replace OCH_3 by OC_2H_5

IIIa, R = H, R' = CH_3
IIIb, R = R' = CH_3
IIIc, R = R' = H
IIId, R = H, R' = CH_3, replace OCH_3 by OC_2H_5



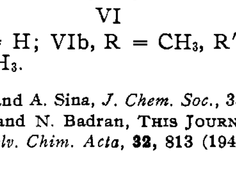
IV

IVa, R = OH
IVb, R = C_6H_5
IVc, R = NHC_6H_5



V

Va, R = R' = H
Vb, R = CH_3, R' = NO_2
Vc, R = CH_3, R' = Br
Vd, R = H, R' = NO_2



VI

VIa, R = R' = H; VIb, R = CH_3, R' = H; VIc, R = CH_3, R' = $COCH_3$.

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(1) (a) E. Späth and W. Gruber, *Ber.*, **71**, 106 (1938); (b) **74**, 1492 (1941).

(2) A. Wacek, H. O. Eppinger and A. Bézard, *ibid.*, **73**, 521 (1940).

(3) F. Weygand and E. Csendes, *ibid.*, **85**, 48 (1952).

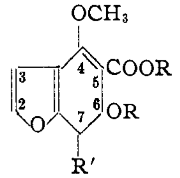
(4) A. Schönberg and A. Sina, *J. Chem. Soc.*, 3344 (1950).

(5) A. Schönberg and N. Badran, THIS JOURNAL, **73**, 2960 (1951).

(6) H. Schmid, *Helv. Chim. Acta*, **32**, 813 (1949).

Oxidation of Visnagin (Ia), Khellin (II) and Khellol (Ib) with Hydrogen Peroxide.—By the controlled oxidation of Visnagin with hydrogen peroxide we obtained 6-hydroxy-4-methoxybenzofuran-5-carboxylic acid (VIIa). The reaction Ia → VIIa did not proceed *via* visnaginone VIIIa as the latter did not yield the acid VIIa under the same experimental conditions. The substance VIIa gave a blue color with ferric chloride and contained one methoxyl group. By the action of methyl iodide in acetone in the presence of potassium carbonate, VIIa gave an ester VIIb containing no free hydroxyl groups.

A further proof for the correctness of VIIa is the fact that khellol (Ib) and 2-norvisnagin[7] (Ic) gave also VIIa under similar conditions. Khellin (II), on the other hand, yields 6-hydroxy-4,7-dimethoxybenzofuran-5-carboxylic acid (VIIc).

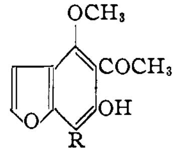


VII

VIIa, R = R′ = H
VIIb, R = CH_3, R′ = H
VIIc, R = H, R′ = OCH_3

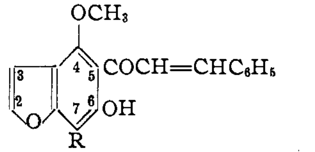
Styryl Derivatives Obtained from Visnaginone and Khellinone and their Oxidation with Hydrogen Peroxide.—Derivatives of this type have already been prepared by Schönberg and Sina.[8a,b] We have obtained 6-hydroxy-4-methoxy-5-benzalacetocoumarone (IXa) and 6-hydroxy-4,7-dimethoxy-5-benzalacetocoumarone (IXb) by allowing benzaldehyde to react with visnaginone (VIIIa) and Khellinone (VIIIb), respectively.

Geissman and Fukushima,[9] have pointed out that the oxidation of 6′-methoxychalcones of the type X with hydrogen peroxide in alkaline medium leads to the formation of benzalcoumaranones, *e.g.*, XI. The chalcones IXa and IXb may be regarded as derivatives of 6′-methoxychalcones, and so their oxidation to benzalcoumaranones may be expected. This is indeed the case and 4-methoxy-5,6,4′,5′-furano-2-benzalcoumaran-3-one (XIIa) and 4,7-dimethoxy-5,6,4′,5′-furano-2-benzalcoumaran-3-one (XIIb) were obtained. In favor of the benzalcoumaranone constitution XI is the fact that the intensely colored oxidation products gave a deep red color with sulfuric acid, had a negative ferric chloride reaction and were insoluble in alkali; similar reactions are shown by benzalcoumaranones obtained by Geissman and Fukushima.[9]



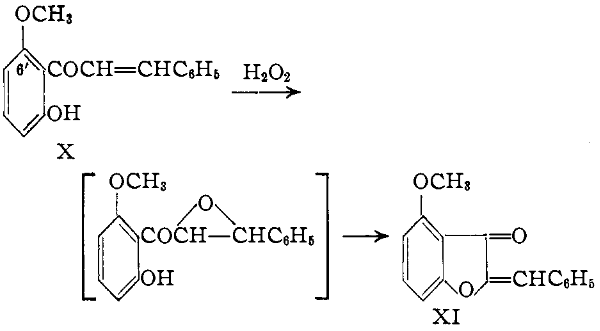
VIII

VIIIa, R = H
VIIIb, R = OCH_3



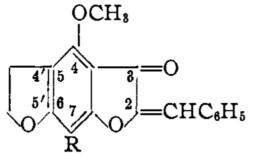
IX

IXa, R = H
IXb, R = OCH_3



X

XI



XII

XIIa, R = H
XIIb, R = OCH_3

Experimental[10]

Oxidation of Visnagin with Chromic Acid.—Two grams of visnagin (Ia) were dissolved in 60 cc. of hot 10% sulfuric acid. Forty cc. of 10% potassium dichromate solution was added by portions in such a way that the temperature maintained itself at 70–80°. A colorless precipitate appeared almost at once. The mixture was allowed to stand at room temperature for 2 hours. The white precipitate of 6-formyl-7-hydroxy-5-methoxy-2-methylchromone (IIIa) was filtered off and washed with water. After recrystallization from hot water, the substance had m.p. 189°. It dissolved in dilute sodium hydroxide solution with a yellow color and gave a wine-red ferric chloride reaction. IIIa is sparingly soluble in cold alcohol and freely soluble in chloroform. Its methyl alcoholic solution gave with a very small amount of aqueous titanium trichloride solution (15%), (iron-free, obtained from Merck, Darmstadt, Germany) a green color, yield 1.5 g.

Anal. Calcd. for $C_{12}H_{10}O_5$: C, 61.5; H, 4.3; OMe, 13.2. Found: C, 61.4; H, 4.3; OMe, 13.1.

Oxime of **6-Formyl-7-hydroxy-5-methoxy-2-methylchromone. (a) In Alkaline Medium.**—To 0.5 g. of IIIa in 5 cc. of 5% sodium hydroxide solution was added a solution of 0.34 g. of hydroxylamine hydrochloride in 5 cc. of water. The mixture was stirred and left to stand 1 hour. It was then largely diluted with water and acidified with acetic acid. The precipitated IVa crystallized from ethanol in tiny colorless crystals, m.p. about 276° (dec., with evolution of gas), was sparingly soluble in usual organic solvents and had a violet ferric chloride reaction.

Anal. Calcd. for $C_{12}H_{11}O_5N$: C, 57.8; H, 4.4. Found: C, 58.1; H, 4.5.

(b) **In Acid Medium.**—To 0.5 g. IIIa in 50 cc. of warm glacial acetic acid was added a solution of 0.34 g. of hydroxylamine hydrochloride in 1 cc. of warm water. The mixture was allowed to stand at room temperature for 6 hours and it was then diluted to 100 cc. with water. The white precipitate obtained was crystallized from ethanol and was identical with IVa.

The **phenylhydrazone IVc** was similarly prepared either from an alkaline or an acid medium and crystallized from ethanol in pale yellow prisms, m.p. about 273° (dec., with evolution of gas). Its ferric chloride reaction was negative.

Anal. Calcd. for $C_{18}H_{16}O_4N_2$: C, 66.6; H, 4.9; N, 8.6. Found: C, 66.4; H, 5.0; N, 8.5.

Anil IVb.—To one gram of IIIa dissolved in 10 cc. of 5% sodium hydroxide solution was added 0.75 g. of aniline hydrochloride dissolved in 4 cc. of water. A yellow deposit

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[7] For the nomenclature comp. A. Schönberg and G. Aziz, THIS JOURNAL, **75**, 3265 (1953).

[8] (a) A. Schönberg and A. Sina, *ibid.*, **72**, 1611 (1950); (b) **72**, 3396 (1950).

[9] T. A. Geissman and D. K. Fukushima, *ibid.*, **70**, 1686 (1948).

[10] All melting points are uncorrected. The ferric chloride reactions were carried out by dissolving the substances in 95% ethanol, and adding at room temperature a drop of an aqueous solution of ferric chloride. For the determination of melting points higher than 220°, the melting point tubes were immersed in a bath preheated to this temperature. Elemental micro-analyses were all by Drs. Weiler and Strauss, Oxford.

was gradually formed on stirring. The mixture was then diluted with water and acidified with acetic acid. IVb which was precipitated crystallized from ethanol in yellow shining needles, m.p. 179°, having a wine-red ferric chloride reaction.

Anal. Calcd. for $C_{18}H_{15}O_4N$: C, 69.9; H, 4.8; N, 4.5. Found: C, 69.5; H, 4.6; N, 4.4.

Action of IIIa on *p*-Phenylenediamine.—To 1 g. of IIIa dissolved in 40 cc. of glacial acetic acid was added a solution of 0.4 g. of *p*-phenylenediamine in 20 cc. of the same solvent. A thick orange crystalline precipitate was immediately formed which was washed with glacial acetic acid and ether, m.p. 282° (dec.).

Visnagin (Ia) and Hydroxylamine.—They did not condense under the conditions described for the formation of IVa. The colorless needles obtained had m.p. 142–144° after drying at 100° and gave no depression with an original sample of visnagin.

5,7-Dimethoxy-6-formyl-2-methylchromone (IIIb).—Two grams of IIIa was refluxed for 36 hours with acetone (50 cc.), methyl iodide (10 cc.) and anhydrous potassium carbonate (8 g.). The mixture was filtered while hot and the solid residue was washed several times with boiling acetone. On evaporation of the combined filtrate and washings, a residue was obtained which crystallized from ethanol in colorless needles, m.p. 196–198°, having a negative ferric chloride reaction. When IIIb and potassium hydroxide were pulverized together a red color was produced. With *p*-phenylenediamine in alcohol, IIIb gave a bright red crystalline product.

Anal. Calcd. for $C_{13}H_{12}O_5$: C, 62.9; H, 4.8; OMe, 25.0. Found: C, 63.2; H, 4.9; OMe, 24.5.

5,7-Dihydroxy-6-formyl-2-methylchromone (Va).—One gram of IIIa was refluxed with a mixture of concentrated hydrochloric acid and 12.5 cc. of water. The solid matter in the reaction vessel gradually turned yellow. After 75 minutes, the precipitate of Va was filtered and dried. It crystallized from toluene in pale yellow prisms, m.p. 195°, difficultly soluble in hot alcohol and having a violet ferric chloride reaction, yield 0.8 g.

Anal. Calcd. for $C_{11}H_8O_5$: C, 60.0; H, 3.6. Found: C, 59.8; H, 3.6.

5,7-Dihydroxy-6-formyl-2-methyl-8-nitrochromone (Vd).—One gram of Va was dissolved in a mixture of 10 cc. of 92% sulfuric acid and 10 cc. of nitric acid (sp. gr. 1.40) at 20°. After 10 minutes, the solution was poured in cold water and the precipitate was crystallized from glacial acetic acid. The yellow plates of Vd were very difficultly soluble in hot alcohol and gave with ferric chloride a red color, m.p. about 248° (dec.).

Anal. Calcd. for $C_{11}H_7O_7N$: C, 49.8; H, 2.7; N, 5.3. Found: C, 49.7; H, 2.9; N, 5.0.

Vd in glacial acetic acid gave with *p*-phenylenediamine in the same solvent an orange crystalline deposit, very difficultly soluble in organic solvents.

8-Bromo-6-formyl-7-hydroxy-5-methoxy-2-methylchromone (Vc).—To a solution of 1 g. of IIIa in 8 cc. of chloroform was added 0.8 g. of bromine in 25 cc. of the same solvent. After 24 hours, the pale yellow precipitate which was formed was filtered off and digested with an aqueous solution of sulfur dioxide and then with alcohol. Colorless needles of Vc obtained by crystallization from benzene had m.p. about 220° (dec.) and gave a red ferric chloride reaction.

Anal. Calcd. for $C_{12}H_9O_5Br$: C, 46.0; H, 2.9. Found: C, 46.3; H, 2.9.

With *p*-phenylenediamine in alcoholic medium, Vc gave an orange-red crystalline precipitate.

6-Formyl-7-hydroxy-5-methoxy-8-nitrochromone (Vd).—One gram of IIIa was dissolved in a warm mixture of 6 cc. of 92% sulfuric acid and 6 cc. of nitric acid (sp. gr. 1.40). The clear solution thus obtained was gently warmed for some minutes until red fumes began to appear and it was then poured in cold water. The precipitated nitro compound crystallized from glacial acetic acid in long colorless needles, m.p. 242° (dec.). Vd was soluble in dilute alkali and in sodium bicarbonate solution with a yellow color and its ferric chloride reaction was red.

Anal. Calcd. for $C_{12}H_9O_7N$: C, 51.6; H, 3.3. Found: C, 51.2; H, 3.3.

Vd was made to react with *p*-phenylenediamine as described for IIIa; the red crystalline reaction product decomposed above 290°.

6-Formyl-7-hydroxy-5-methoxychromone (IIIc).—One-half gram of 2-norvisnagin[8b] (Ic) was oxidized with chromic acid under the conditions described previously for the oxidation of visnagin. The colorless oxidation product was crystallized from benzene, m.p. 155°. IIIc gave a yellow color with dilute alkali and a red ferric chloride reaction.

Anal. Calcd. for $C_{11}H_8O_5$: C, 60.0; H, 3.6. Found: C, 60.0; H, 3.7.

IIIc dissolved in alcohol gave an orange crystalline precipitate with an alcoholic solution of *p*-phenylenediamine.

5-Ethoxy-2-methylfuro-4',5',6,7-chromone (Id).—One gram of 5-hydroxy-2-methylfuro-4',5',6,7-chromone[5] was refluxed for 24 hours with 50 cc. of dry acetone, 5 cc. of ethyl iodide and 5 g. of anhydrous potassium carbonate. After filtration, the acetone was evaporated yielding a brownish residue which after recrystallization from ethanol gave colorless needles of Id, m.p. 96°. This substance had a negative ferric chloride reaction and it gave a red color when powdered together with potassium hydroxide.[4]

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.8; H, 4.9. Found: C, 68.6; H, 4.9.

6-Formyl-7-hydroxy-5-ethoxy-2-methylchromone (IIId).—One-half gram of Id was oxidized with chromic acid as described for visnagin. The oxidation product IIId separated in colorless needles and was crystallized from ethanol, m.p. 120°. IIId had a red ferric chloride reaction and dissolved in alkali with a yellow color.

Anal. Calcd. for $C_{13}H_{12}O_5$: C, 62.9; H, 4.9. Found: C, 62.9; H, 5.0.

Reduction of 5,7-Dihydroxy-6-formyl-2-methylchromone (Va).—A mixture of granulated zinc (7 g.), water (12 cc.), concentrated hydrochloric acid (4 cc.) and mercuric chloride (0.7 g.) was shaken for 10 minutes. The solution was then decanted and (Va) (2 g.), dissolved in 40 cc. of glacial acetic acid, was added to the amalgam. The mixture was refluxed for 8 hours, while 20 cc. of concentrated hydrochloric acid was introduced dropwise. The solution, thus obtained, was cooled and poured into 200 cc. of water. The yellow precipitate which separated out, was filtered and crystallized from alcohol. The pale yellow prisms of 5,7-dihydroxy-2,6-dimethylchromone (VIa), thus obtained, had m.p. 287° (dec.) and gave a blue ferric chloride reaction. The yield was *ca.* 40% (VIa) dissolved in sodium hydroxide (4%) and in concentrated sulfuric acid with yellow coloration.

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.1; H, 4.9. Found: C, 64.4; H, 4.7.

2,6-Dimethyl-7-methoxy-5-hydroxychromone (VIb).—A mixture of (VIa) (1 g.), acetone (100 cc.), methyl iodide (7 cc.) and anhydrous potassium carbonate (7 g.) was refluxed for 12 hours and was then filtered while hot. Evaporation of the acetone solution to dryness, gave yellowish crystals of (VIb), which crystallized from ethanol (80%) in colorless prisms, m.p. 161–162°.[6] (VIb) gave a blue color with ferric chloride[6] and a green-yellow color with a drop of titanium chloride in dilute alcoholic solution.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.4; H, 5.5. Found: C, 65.2; H, 5.5.

(IVb) was further identified by its conversion to 2,6-dimethyl-7-methoxy-5-acetoxychromone (VIc) as described by Schmid.[6] (VIc) had m.p. 176° and gave no color with ferric chloride.

Anal. Calcd. for $C_{14}H_{14}O_5$: C, 64.1; H, 5.4. Found: C, 64.1; H, 5.3.

6-Hydroxy-4-methoxybenzofuran-5-carboxylic Acid (VIIa).—To a suspension of 2 g. of visnagin (Ia) in 50 cc. of 5% sodium hydroxide at 30° was added 6 cc. of 30% hydrogen peroxide, and the mixture stirred for 30 minutes; at the end of this time the Ia was completely dissolved. On acidification, VIIa separated in colorless prisms which after recrystallization from ethanol had m.p. 180° (evolution of gas). VIIa had a blue ferric chloride reaction and was soluble in sodium bicarbonate solution with effervescence, yield 1.3 g.

Anal. Calcd. for $C_{10}H_8O_5$: C, 57.7; H, 3.9; OMe, 14.9. Found: C, 57.8; H, 3.9; OMe, 14.2.

VIIIa was also obtained when khellol (Ib) or 2-norvisnagin (Ic) was oxidized under the same conditions.

Methyl (4,6-Dimethoxybenzofuran)-5-carboxylate (VIIb).—One gram of VIIa was methylated by refluxing it with 25 cc. of acetone, 3 g. of anhydrous potassium carbonate and 5 cc. of methyl iodide for 24 hours. The acetone solution was then filtered off and on its evaporation VIIb was obtained which separated from acetone in colorless crystals, m.p. 83–84°. VIIb was insoluble in alkali and gave a negative ferric chloride reaction.

Anal. Calcd. for $C_{12}H_{12}O_5$: C, 61.0; H, 5.1. Found: C, 61.3; H, 5.2.

6-Hydroxy-4,7-dimethoxybenzofuran-5-carboxylic Acid (VIIc).—When khellin (II) was oxidized with hydrogen peroxide under the same conditions as visnagin, colorless crystals of VIIc were obtained, which, when crystallized from alcohol, had m.p. 149°. VIIc gave a blue color with ferric chloride, and was soluble in sodium bicarbonate solution.

Anal. Calcd. for $C_{11}H_{10}O_6$: C, 55.4; H, 4.2. Found: C, 55.4; H, 4.3.

Condensation of Visnaginone (VIIIa) with Benzaldehyde.—To a mixture of 1 g. of (VIIIa) and 4 cc. of 30% sodium hydroxide solution was added a solution of 1 cc. of benzaldehyde in 5 cc. of alcohol. The red solution was allowed to stand for 24 hours and was then diluted with water to 100 cc. and acidified. The red crystalline precipitate of **5-benzalaceto-4-methoxy-6-hydroxybenzofuran (IXa)** crystallized from ethanol in orange needles, m.p. 106°, m.p. 106° (red melt), and gave a green ferric chloride reaction and a red color with concentrated sulfuric acid, yield 1 g.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.5; H, 4.8. Found: C, 73.3; H, 4.8.

Condensation of Khellinone (VIIIb) with Benzaldehyde.—Khellinone treated as above gave **5-benzalaceto-4,7-dimethoxy-6-hydroxybenzofuran (IXb)** which crystallized from ethanol in orange prisms, m.p. 128° (red melt), giving a brown ferric chloride reaction and a brown-red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{19}H_{16}O_5$: C, 70.4; H, 4.9. Found: C, 69.9; H, 4.8.

4-Methoxy-4′,5′,5,6-furano-2-benzal-3-coumaranone (XIIa).—To 1.5 g. of IXa dissolved in a mixture of 8 cc. of 16% sodium hydroxide solution and 20 cc. of methanol was added 3 cc. of 15% hydrogen solution. After standing 24 hours in the cold, the precipitate of XIIa was filtered off and crystallized from chloroform–acetone mixture. Yellow prisms, m.p. 189°, were obtained having a negative ferric chloride reaction and giving a blood-red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{18}H_{12}O_4$: C, 74.0; H, 4.1. Found: C, 73.9; H, 4.2.

4,7-Dimethoxy-4′,5′,5,6-furano-2-benzal-3-coumaranone (XIIb).—It was prepared from IXb by a similar procedure. XIIb crystallized from acetone in orange prisms, m.p. 186° (red melt). It gave no reaction with ferric chloride and an intense violet color with concentrated sulfuric acid.

Anal. Calcd. for $C_{19}H_{14}O_5$: C, 70.8; H, 4.4. Found: C, 70.5; H, 4.4.

CAIRO, EGYPT

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Studies Relating to the Formation and Reactions of Glycidic Esters

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A procedure for effecting the glycidic ester condensation with potassium *t*-butoxide has been developed. This method appears to offer some advantage over previous procedures. The decarboxylation of some glycidic acids has been studied. The most satisfactory method involves conversion to the β-halo-α-hydroxy acid followed by treatment with base which effects spontaneous decarboxylation of the anion. The free glycidic acids corresponding to Ia and Ic were found to be very unstable and easily isomerized into the cyclohexenylglycolic acids IXa and IXb, which do not undergo decarboxylation readily. The latter compounds add bromine, and the resulting dibromo acids are decarboxylated and dehydrobrominated readily with base to form tetrahydrobenzaldehyde and acetylcyclohexene, respectively. Prolonged heating of cyclohexenylglycolic acid with water effects an oxotropic rearrangement to 2-hydroxycyclohexylideneacetic acid (X).

The experiments described in this report were carried out for the purpose of examining some modified techniques of effecting the glycidic ester condensation and of promoting the decarboxylative decomposition to aldehydes and ketones. In the course of this study some interesting rearrangements of glycidic acids were observed and these results are also described.

We have found that potassium *t*-butoxide, which has not hitherto been given serious study as a condensing agent for the glycidic ester condensation,[1] is particularly useful for this purpose. For example, when a solution of this alkoxide in *t*-butyl alcohol was added slowly to a solution of cyclohexanone and ethyl chloroacetate in *t*-butyl alcohol at 10–15°, the glycidic ester Ia was obtained in 83% yield when the reactants were employed on an equimolar basis and in 90% yield from the ketone when the other reactants were used in 10 mole per cent. excess. The best previously reported[2] yield is 65% obtained by the classical sodium ethoxide method. Using equimolar amounts of reactants the new procedure gave an 82% yield of glycidic ester from acetophenone, a 68% yield from benzaldehyde, and a 66% yield from acetone, all of these representing some improvement over the older methods.[1] Other (mostly new) condensations carried out by the modified procedure were: cyclohexanone and *t*-butyl chloroacetate to Ib (82% yield), cyclohexanone and ethyl α-chloropropionate to Ic (86% yield), cyclohexanone and *t*-butyl α-chloropropionate to Id (64% yield), 2-propionyl-6-methoxynaphthalene and ethyl α-chloropropionate to V ($R = C_2H_5$) (71% yield), 3-phenylcyclohexanone and ethyl α-chloropropionate to VII ($R = C_2H_5$) (70% yield), and 3-phenylcyclohexanone and *t*-butyl α-chloropropionate to VII ($R = t\text{-}C_4H_9$) (61% yield).

No generally satisfactory procedure has yet been developed for the hydrolysis and decarboxylation of glycidic esters to aldehydes or ketones.[3] For example, while certain glycidic acids give good yields of the decarboxylation products simply on pyrolysis,[3] the acid obtained by hydrolysis of Ic

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[1] M. S. Newman and B. J. Magerlein, in Adams, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 413.

[2] G. Darzens and P. Lefebure, *Compt. rend.*, **142**, 714 (1906). The 68% yield recorded on p. 431 ref. 1 refers to the higher homolog Ic and not Ia.

[3] Reference 1, p. 422.