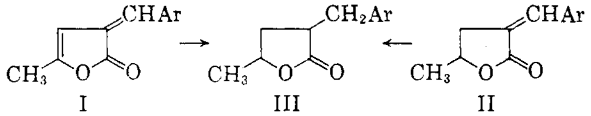
TABLE II

Hydrogenation Products, III

Cpd.	Yields from I	Yields from II	M.P.	Formula	Calcd. C	Calcd. H	Found C	Found H
IIIa	—	95	[a]	$C_{14}H_{19}NO_2$	72.07	8.21	71.28	8.25[d]
IIIb	70	97	62–64[b,c]	$C_{14}H_{18}O_4$	67.18	7.25	67.65	7.38
IIIc	41	90	68–69[c]	$C_{16}H_{22}O_4$	69.04	7.97	69.17	7.94

[a] B.p. 202–203°/4 mm. [b] B.p. 190–191°/1 mm. [c] Recrystallized from methanol. [d] Calcd.: N, 6.00. Found: N, 6.00.

certain aromatic aldehydes. Reactions of this type are known and give products of type I[5] and II.[6] In either case, 3-nitrobenzaldehyde furnished comparatively low yields of the desired condensation products, contaminated by large amounts of brown tars and resins. This fact confirm previous observations[4] regarding the influence of electron-withdrawing groups in the aromatic aldehyde on the result and yield of the reaction. Hydrogenations of either I or II led to α-benzyl-γ-valerolactones (III), the yields from II being comsiderably higher than from I.



a. Ar = $4\text{-}CH_3NC_6H_4$; b. Ar = $3,4\text{-}(CH_3O)_2C_6H_3$; c. Ar = $3,4\text{-}(C_2H_5O)_2C_6H_3$; d. Ar = $3\text{-}O_2NC_6H_4$.

The structures of type I and type II compounds have been established (a) by carbon, hydrogen analysis, (b) infrared spectra, and (c) by the fact that they lead to identical hydrogenation products of type III.

EXPERIMENTAL

Melting points are uncorrected. Microanalysis are by A. Bernhardt, Microanalytisches Laboratorium im Max-Planck-Institut, Mülheim/Ruhr, Germany.

Materials. Generally Eastman White Label products were employed without further purification.

α-(4-Dimethylaminobenzylidene)-$\Delta^{\beta,\gamma}$-angelicalactone (Ia). $\Delta^{\beta,\gamma}$-Angelicalactone[7] (0.08 mole), 4-dimethylaminobenzaldehyde (0.1 mole) and diethylamine (*ca.* 2 ml.) were heated on a water bath for 1 hr. After cooling to room temperature, the excess aldehyde was removed by shaking with sodium bisulfite solution. The remaining yellow solid was filtered and recrystallized from methanol–petroleum ether (2:1); yield 7.4 g. (40%), orange leaflets, m.p. 120–121°.

Anal. Calcd. for $C_{14}H_{15}NO_2$: N, 6.11. Found: N, 6.23.

α-(3,4-Dimethoxybenzylidene)-$\Delta^{\beta,\gamma}$-angelicalactone (Ib) was prepared similarly from veratraldehyde, but in benzene solution (initial cooling with water, then 30 min. heating on a water bath with stirring), to give yellow prisms from methanol, m.p. 118–119°, yield 40%. The compound slowly turns orange under the influence of light.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.21; H, 5.64.

α-(3,4-Diethoxybenzylidene)-$\Delta^{\beta,\gamma}$-angelicalactone (Ic) was prepared from 3,4-diethoxybenzaldehyde (no solvent, 40 min. heating on a water bath) to give yellow crystals from methanol, m.p. 100–101°, yield 43%.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 69.85; H, 6.69.

α-(3-Nitrobenzylidene)$\Delta^{\beta,\gamma}$-angelicalactone (Id) was prepared from 3-nitrobenzaldehyde (no solvent, initial cooling with ice salt, then standing overnight). The crude resinous product was dissolved in methylene chloride and chromatographed on neutral alumina. A yield of 70%, as yellow needles from methanol, m.p. 154–155°, was obtained besides much noncrystalline material.

Anal. Calcd. for $C_{12}H_9NO_4$: C, 62.34; H, 3.92; N, 6.06. Found: C, 62.12; H, 3.97; N, 6.30.

α-(4-Dimethylaminobenzylidene)-γ-valerolactone (IIa) was obtained from the aldehyde and γ-valerolactone in benzene with sodium methoxide as condensing agent (1.5 hr. stirring at room temperature; yield 69%; see ref. 4) as yellow leaflets from methanol, m.p. 130–131°.

Anal. Calcd. for $C_{14}H_{17}NO_2$: N, 6.06. Found: N, 6.11.

Similarly, the following were prepared: *α-(3,4-dimethoxybenzylidene)-γ-valerolactone* (IIb), m.p. 116° (from methanol); yield 54%.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.51; H, 6.49.

α-(3,4-Diethoxybenzylidene)-γ-valerolactone (IIc), m.p. 110–112° (from methanol); yield 40%.

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.68; H, 7.12.

α-(3-Nitrobenzylidene)-γ-valerolactone (IId), m.p. 110–112°, yellow crystals from methanol; the product was isolated in a small yield only and was separated from much resinous material by chromatography of its solution in methylene chloride on alumina.

Anal. Calcd. for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75; N, 6.01. Found: C, 61.56; H, 4.89; N, 6.20.

Hydrogenations. These were performed using an Adams catalyst in methanol in a Parr apparatus (50 p.s.i. initial pressure). The results are tabulated below.

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2-Acetyl-6-methoxycoumaran-3-one. Benzylation at the Terminal Methyl Group[1]

Wm. Ivo O'Sullivan and Charles R. Hauser

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Wheeler and co-workers[2] have synthesized a number of coumaran-3-ones by rearrangement of the

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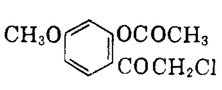
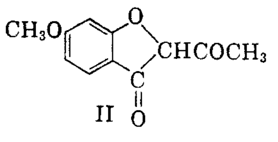
(1) Supported by the Office of Ordnance Research, U. S. Army.

appropriate *o*-acyloxy-ω-chloroacetophenone in dioxane by means of sodium hydride, which is a modification of the method of Auwers.[3] We have similarly effected the rearrangement of the *o*-acetoxy-ω-chloro-4-methoxyacetophenone (I) to form the coumaranone II in 80% yield.


I

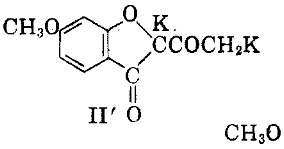

II

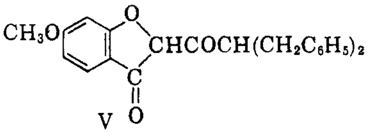
The coumaranone II was prepared for the purpose of studying the possibility of effecting condensations at its terminal methyl group similar to those realized recently[4] with certain simpler β-diketones. For example, acetylacetone was benzylated through its dipotassio salt III to form the terminal methyl derivative IV in 60% yield.[4]

$CH_3COCH(K)COCH_2K$
III

$CH_3COCH_2COCH_2CH_2C_6H_5$
IV

The coumaranone II was added to two molecular equivalents of potassium amide in liquid ammonia to form presumably the dipotassio salt II′, which was treated with one equivalent of benzyl chloride. However, none of the corresponding monobenzyl derivative could be isolated. Instead, there was obtained the copper chelate of a product which, on the basis of analysis, was the dibenzyl derivative V. A considerable amount of the starting β-diketone II was recovered as its copper chelate.


II′


V

The possible dibenzyl derivative that might have resulted from alkylation at both the methyl and methinyl groups of II through II′ could not have formed a copper chelate. Another example of dibenzylation at the terminal methyl group has recently been observed with *o*-hydroxyacetophenone.[5]

An unsuccessful attempt was made to effect the benzoylation of dipotassio salt II′ with methyl benzoate under the conditions that were found satisfactory with dipotassio salt III.[4]

EXPERIMENTAL[6]

2-Acetoxy-ω-chloro-4-methoxyacetophenone (I). A solution of resorcinol dimethyl ether and chloracetyl chloride in carbon disulfide was treated with anhydrous aluminum chloride as described previously[7] to form ω-chloro-2-hydroxy-4-methoxyacetophenone.

A mixture of 20 g. (0.086 mole) of this compound, 40 ml. of acetic anhydride, and one drop of 70% perchloric acid was kept at room temperature for 1 hr., and then stirred with water for several hours (to hydrolyse the excess acetic anhydride). The resulting precipitate was collected on a funnel and washed with water. It was recrystallized from ethanol and then from ligroin to give 23 g. (95%) of the product I (white cubes), m.p. 99–100°.

Anal. Calcd. for $C_{11}H_{11}O_4Cl$: C, 54.44; H, 4.57; Cl, 14.61. Found: C; 54.47; H, 4.58; Cl, 14.59.

2-Acetyl-6-methoxycoumaran-3-one (II). To a stirred solution of 60 g. (0.252 mole) of 2-acetoxy-ω-chloro-4-methoxyacetophenone in 500 ml. of dioxane (purified by Vogel's method)[8] was added 15 g. of a 48.5% suspension of sodium hydride in mineral oil (0.32 mole of sodium hydride). The reaction mixture, which was kept under an atmosphere of nitrogen, was brought to a temperature of 50–60°, and the stirring was continued until hydrogen ceased to evolve (3–4 hr.). After adding a small quantity of methanol to destroy the excess sodium hydride, the precipitate of the sodium salt of the product was collected and washed with ether. It was dissolved in water and the cooled solution was acidified. The resulting precipitate was collected, washed with water, and dried to give 40.5 g. (80%) of crude 2-acetyl-6-methoxycoumaran-3-one. After recrystallization once from *n*-hexane and twice from ethanol the product was obtained as orange-brown cubes, m.p. 117–118°.

Anal. Calcd. for $C_{11}H_{10}O_4$: C, 64.67; H, 4.8. Found: C, 64.53; H, 4.85.

The compound gave a green enol test with ferric chloride, and formed a green copper chelate which was washed with water, ethanol, and ether. Attempts to recrystallize the chelate from several solvents were unsuccessful. The dried chelate decomposed between 275 to 285°. Its infrared spectrum showed the following peaks: 3.4, 6.18, 6.28, 6.35, 6.53, 6.73, 6.93, 7.15, 7.4, 7.7, 7.85, 8.15, 8.5, 8.7, 9.15, 9.85, 10.6, 11.35, 12.25, 12.9, 13.15, 13.8, 14.3, 14.5μ.

Benzylation of II. To a stirred solution of 0.484 mole of potassium amide in liquid ammonia[4] was added in small portions 5 g. (0.0242 mole) of 2-acetyl-6-methoxycoumaranone (II). After stirring for 15–30 min., 3.08 g. (0.0242 mole) of benzyl chloride was added and the stirring was continued for 2 hr. An excess (2.5 g.) of solid ammonium chloride was added and the ammonia was evaporated as an equal volume of ether was added. The resulting ethereal suspension was shaken with water to dissolve the inorganic salts. The aqueous and ethereal layers were separated, the aqueous layer being discarded. The ethereal layer was extracted with a saturated aqueous solution of copper acetate to precipitate 3.3 g. of the copper chelate of the starting compound II which, after washing with water, ethanol, and ether, was identified by its infrared spectrum. The ethereal filtrate was evaporated to precipitate 2.3 g. (21%, based on benzyl chloride) of copper chelate of 2-dibenzylacetyl-6-methoxycoumaran-3-one (V) which, after recrystallization from ethanol, melted at 205–207°. Its infrared spectrum

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[6] Melting points were taken on a Fisher-Johns melting point apparatus. Infrared spectra were produced with a Perkin-Elmer, Model 21 Infrared Spectrophotometer. Elemental analyses were by Galbraith Microchemical Laboratories, Knoxville, Tenn.

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showed the following peaks: 3.3, 3.45, 6.18, 6.35, 6.55, 6.7, 6.95, 7.45, 7.75, 7.9, 8.2, 8.5, 8.7, 9.35, 12.15, 13.05, 13.4, 4.35μ (potassium bromide pellet).

Anal. Calcd. for $C_{50}H_{42}O_6Cu$: C, 71.98; H, 5.07; Cu, 7.62. Found: C, 71.80; H, 5.09; Cu, 7.52.

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The Nitration of 3-Chloro-4-iodonitrobenzene

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Halonitrobenzenes are important intermediates in the synthesis of a variety of compounds such as phenylhydrazine,[2] phenylsemicarbazide,[3] benzotriazole,[4,5] phenoxazine,[6] and anthranil.[7] In a program[8,9,10] on preparation of such compounds, the nitration of 3-chloro-4-iodonitrobenzene was undertaken for detailed investigation. Although it might give a mixture of dinitroisomers, only 1-iodo-2-chloro-4,6-dinitrobenzene[11] was isolated. It reacts with hydrazine hydrate to give 2-chloro-4,6-dinitrophenylhydrazine.[12]

EXPERIMENTAL[13]

Nitration of 3-chloro-4-iodonitrobenzene. To a suspension of 3-chloro-4-iodonitrobenzene (10 g.) in conc. sulfuric acid (42 ml., d., 1.82), fuming nitric acid (14 ml., d., 1.5) was added dropwise with vigorous shaking. When all the nitric acid was added, it was heated on a water bath for an hour and poured on crushed ice. The yellow crystalline solid was filtered and recrystallized successively from acetic acid, methanol, and ethanol to give 1-iodo-2-chloro-4,6-dinitrobenzene (7 g.) in yellow needles, m.p. 118°. Mixed melting point with an authentic sample of 1-iodo-2-chloro-4,6-dinitrobenzene remained undepressed.

Anal. Calcd. for $C_6H_2N_2O_4ClI$: $Cl + I$, 49.4. Found: $Cl + I$, 49.2.

2-Chloro-4,6-dinitrophenylhydrazine. To a cooled solution of 1-iodo-2-chloro-4,6-dinitrobenzene (1 g.) in ethanol twice the equivalent quantity of hydrazine hydrate was added. 2-Chloro-4,6-dinitrophenylhydrazine was filtered after an hour, m.p. 175° (lit.[12] m.p., 175°). After two recrystallizations from ethyl acetate, yellow needles (0.5 g.) melting at 190° were obtained.

Anal. Calcd. for $C_6H_5N_4O_4Cl$: Cl, 15.2. Found: Cl, 15.1.

The *acetyl* derivative prepared by the acetic acid–acetic anhydride method crystallized in lemon yellow needles from ethanol, m.p. 189°.

Anal. Calcd. for $C_8H_7N_4O_5Cl$: Cl, 12.9. Found: Cl, 12.7.

The *benzoyl* derivative prepared by the pyridine method crystallized in colorless needles from ethanol, m.p. 208°.

Anal. Calcd. for $C_{13}H_9N_4O_5Cl$: Cl, 10.5. Found: Cl, 10.2.

Acknowledgment. The author wishes to express his gratitude to Dr. S. S. Joshi, D.Sc., Principal, Meerut College, Meerut (India) for his keen interest during the progress of this work.

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[13] All melting points are uncorrected.

Reactions of Nitrohydroxychalcones. Oxidation by Hydrogen Peroxide in Alkaline Medium

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In earlier publications,[3] we had communicated our observations regarding the isomerization of some nitrohydroxychalcones to flavanones and the conversion of nitrohydroxychalcones to flavones. The behavior of some of these chalcones towards alkaline hydrogen peroxide oxidation is now reported. The chalcones studied were 2′,4′-dihydroxy-3′-nitrochalcone derivatives (type I) and 2′,6′-dihydroxy-3′-nitrochalcone derivatives (type II). The type I chalcones on oxidation yielded the corresponding 3,7-dihydroxy-8-nitroflavone derivatives (type III), while the type II chalcones gave 2-benzylidene-4-hydroxy-7-nitro-3(2H)-benzofuranone derivatives (type IV). The constitutions were fully supported by color tests and analytical values.

The oxidation of type I chalcones gave products that gave a yellow coloration with concentrated sulfuric acid, and with ferric chloride a pale purplish-brown color characteristic of 3-hydroxy flavones. The enhanced halochromism of the 3-hydroxyflavones with *ortho* and *para* alkoxy substitution is shown in Table I.

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