TABLE I

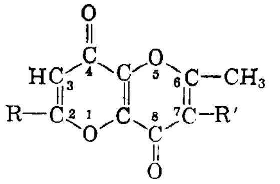
Hydroxyacylated Pyrones

	Pyrone Used	Lactone Used	M.P.	% Yield	Empirical Formula	Calculated (Found) Carbon	Hydrogen	Chlorine
Ia[a]	Kojic acid	γ-Butyrolactone	159–160	56.5	$C_{10}H_{12}O_6$	52.63 52.27	5.30 5.14	
Ib[b]	2-Hydroxymethyl-5-methoxy-4-pyrone	γ-Butyrolactone	164–165	61	$C_{11}H_{14}O_6$	54.54 54.37	5.82 5.58	
Ic[c]	Coumarin	γ-Butyrolactone	69–70	40	$C_{13}H_{12}O_4$	67.23 66.89	5.20 5.01	
Id[d]	Kojic acid	β-Propiolactone	154.5	62	$C_9H_{10}O_6$	50.47 50.31	4.70 4.49	
Ie[e]	α-Chloro-α-deoxy kojic acid	β-Propiolactone	158	78	$C_9H_9ClO_5$	46.46 46.19	3.89 3.67	15.24 15.03
If[f]	2-Hydroxymethyl-5-methoxy-4-pyrone	β-Propiolactone	150	32	$C_{10}H_{12}O_6$	52.63 52.19	5.30 4.88	
Ig[g]	Kojic acid	γ-Valerolactone	155–156	54	$C_{11}H_{14}O_6$	54.54 54.32	5.82 5.62	

[a] Ia = 2-Hydroxymethyl-5-hydroxy-6-(γ-hydroxybutyryl)-4-pyrone. [b] Ib = 2-Hydroxymethyl-5-methoxy-6-(γ-hydroxybutyryl)-4-pyrone. [c] Ic = 3-(γ-Hydroxybutyryl)-coumarin. [d] Id = 2-Hydroxymethyl-5-hydroxy-6-(β-hydroxypropionyl)-4-pyrone. [e] Ie = 2-Chloromethyl-5-hydroxy-6-(β-hydroxypropionyl)-4-pyrone. [f] If = 2-Hydroxymethyl-5-methoxy-6-(β-hydroxypropionyl)-4-pyrone. [g] Ig = 2-Hydroxymethyl-5-hydroxy-6-(γ-hydroxyvaleryl)-4-pyrone.

TABLE II

Pyrano[3,2-b]pyran-6-methyl-4,8-diones from Members of Ia–g Series



No.	Pyrone Used	Pyranopyran Product M.P.	R	R′	Empirical Formula	Calculated (Found) Carbon	Hydrogen	Chloride
IIa	Ia	126–127	Acetoxymethyl	Acetoxyethyl	$C_{16}H_{16}O_7$	59.99 55.49	5.03 4.84	
IIb	Id	91	Acetoxymethyl	Acetoxymethyl	$C_{15}H_{14}O_8$	55.90 55.69	4.37 4.19	
IIc	Ie	93–94	Chloromethyl	Acetoxymethyl	$C_{13}H_{11}ClO_6$	52.27 52.50	3.71 3.94	11.87 11.69
IId	Ig	102–104	Acetoxymethyl	2-Acetoxypropyl	$C_{17}H_{18}O_8$	58.28 58.44	5.17 5.29	

the 2,4-dinitrophenylhydrazone by dissolving it in 100 ml. of boiling ethanol to which 1 g. of 2,4-dinitrophenylhydrazine was added. The solution was boiled for 5 min. and filtered. The brown compound was recrystallized once from ethanol to give a m.p. of 195–196°.

Anal. Calcd. for $C_{16}H_{17}N_5O_8$: N, 17.27. Found: N, 17.48.

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Preparation of 3-Keto-9-methyl-$\Delta^{4,6}$- and 3-Keto-4,9-dimethyl-$\Delta^{4,6}$-hexahydronaphthalenes

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We required 3-keto-9-methyl-$\Delta^{4,6}$-hexahydronaphthalene (IIa) and 3-keto-4,9-dimethyl-$\Delta^{4,6}$-hexahydronaphthalene (IIb) for synthetic projects in the field of terpenoids. These compounds were previously prepared[1-3] in varying yields by bromination of 3-keto-9-methyl-Δ^4-octahydronaphthalene (Ia) and 3-keto-4,9-dimethyl-Δ^4-octa-

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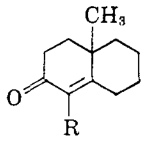
[1] (a) F. D. Gunstone and R. M. Heggie, *J. Chem. Soc.*, 1437 (1952); (b) F. D. Gunstone and A. P. Tulloch, *J. Chem. Soc.*, 1130 (1955).

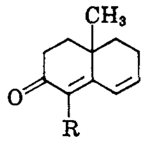
[2] M. Yanagita, S. Inayama, M. Hirakura, and F. Seki, *J. Org. Chem.*, **23**, 690 (1958).

[3] T. Harukawa, *J. Pharm. Soc. Japan*, **75**, 521 (1955).

hydronaphthalene (Ib) followed by dehydrobromination.



Ia. R = H
b. R = CH_3



IIa. R = H
b. R = CH_3

We now record the preparation of the dienones IIa and IIb by one-step chloranil dehydrogenation of the unsaturated ketones Ia and Ib, respectively.[4–9]

EXPERIMENTAL[10]

3-Keto-9-methyl-Δ^{4,6}-hexahydronaphthalene (IIa). A solution of 5 g. of Ia, 0.025 g. of *p*-toluenesulfonic acid, and 15 g. of chloranil in 360 ml. of *t*-butyl alcohol was heated at reflux for 3 hr. with stirring. The mixture was cooled and filtered, and the solvent was removed from the filtrate under diminished pressure. A chloroform solution of the residue was washed successively with water, 5% aqueous sodium hydroxide, and water. Removal of the chloroform and fractionation of the residue afforded 2.7 g. (55%) of the dienone (IIa) b.p. 110° (1 mm.), n_D^{26} 1.5625, $\lambda_{max}^{ethanol}$ 280 mμ log ϵ 4.29 [reported[1b] b.p. 80–86° (0.25 mm.), n_D^{18} 1.5630, $\lambda_{max}^{ethanol}$ 281 mμ log ϵ 4.22. It gave a 2,4-dinitrophenylhydrazone, m.p. 198° (reported[1b] m.p. 187–190°; 194–195°[2]), in almost quantitative yield.

3-Keto-4,9-dimethyl-Δ^{4,6}-hexahydronaphthalene (IIb). Using a solution of 6 g. of Ib, 0.025 g. of *p*-toluenesulfonic acid and 16.5 g. of chloranil in 360 ml. of *t*-butyl alcohol and following the same procedure as for IIa, except that the solution was refluxed for 10 hr., gave 2.69 g. (45%) of the dienone (IIb), b.p. 105° (1 mm.), n_D^{24} 1.5580, $\lambda_{max}^{ethanol}$ 288 mμ log ϵ 4.22 [reported b.p. 106–108° (1 mm.), n_D^{20} 1.5590[1a]; b.p. 110–111° (3 mm.), $\lambda_{max}^{ethanol}$ 288 mμ log ϵ 4.29[2]]. Its 2,4-dinitrophenylhydrazone melted at 214° (reported[1a] m.p. 216°; m.p. 212–214°[2]) after crystallization from acetic acid.

Use of xylene[4] or *t*-butyl alcohol without *p*-toluenesulfonic acid[4,6–9] as solvents in the dehydrogenation experiments impaired the yield of the products. Oxidation of Ia with manganese dioxide[11] in benzene resulted in poorer yield (20%) of the dienone (IIa).

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Reactions of Vanillin and Its Derived Compounds. XXXI.[1] New Derivatives of Vanillic Acid[2]

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During the course of our studies on the esters, amides, hydrazides, ethers, and other derivatives of vanillic acid,[3] we had the occasion to prepare a number of derivatives of vanillic acid and intermediates which were never reported. The preparation, properties, and ultraviolet absorption spectra of these compounds are reported in the present paper.

EXPERIMENTAL[4]

Carbobenzyloxyvanillic acid. A solution of 90 g. (0.53 mole) of vanillic acid in 1000 ml. of 4.5% sodium hydroxide solution was treated slowly with vigorous stirring at room temperature with 100 g. (0.59 mole) of carbobenzyloxy chloride. After addition was complete, the clear solution was stirred for 1 hr., filtered, and acidified with dilute hydrochloric acid. The white granular precipitate was filtered, washed with water, and air dried to yield 145 g. (91%) of crude carbobenzyloxyvanillic acid. Recrystallization from dilute acetone yielded colorless crystals melting at 130–131°.

Anal. Calcd. for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67. Found: C, 63.78; H, 4.77.

2,4,5-Trichlorophenyl carbobenzyloxyvanillate. A mixture of 120 g. of carbobenzyloxyvanillic acid and 300 cc. of thionyl chloride was boiled under reflux for 1 hr. The excess thionyl chloride was removed under reduced pressure, and the residue was boiled with petroleum ether (b.p. 65–110°) and cooled. The supernatent liquid was decanted, and the residual oil was warmed under reduced pressure to yield 113 g. (89%) of carbobenzyloxyvanilloyl chloride as an almost colorless viscous oil.

A mixture of 96 g. (0.3 mole) of carbobenzyloxyvanilloyl chloride, 60 g. (0.3 mole) of 2,4,5-trichlorophenol, 110 ml. of pyridine, and 800 ml. of dry ether was boiled under reflux 4 hr. The ether and pyridine were distilled under reduced pressure, and the solid residue was stirred into water. The precipitate was filtered, washed with water and warm ethanol, and air dried to give 115 g. (80%) of crude 2,4,5-trichlorophenyl carbobenzyloxyvanillate. Recrystallization from ethanol and then from petroleum ether (b.p. 65–110°) yielded white powdery crystals melting at 138–139°.

Anal. Calcd. for $C_{22}H_{15}O_6Cl_3$: C, 54.85; H, 3.14. Found: C, 55.15; H, 3.27.

2-Methoxy-4-methylphenyl carbobenzyloxyvanillate. This

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(1) For paper XXX of this series, see *J. Org. Chem.*, 26, 2553 (1961).

(2) This paper represents a portion of the results obtained in the research program sponsored by the Sulphite Pulp Manufacturers' Research League and conducted for the League by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the League to publish these results.

(3) For a complete bibliography of these papers see I. A. Pearl, *Am. Perfumer Essent. Oil Rev.*, 65, No. 1, 25 (1950) and *J. Chem. Ed.*, 35, 502 (1958).

(4) All melting points are uncorrected. Ultraviolet spectral data are for solutions in 95% ethanol (concentration, 0.02 g. per l.). Analyses and ultraviolet absorption spectra were determined by the Analytical Department of The Institute of Paper Chemistry.