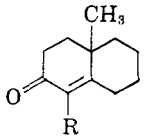
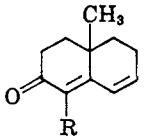
hydronaphthalene (Ib) followed by dehydrobromination.



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-$\Delta^{4,6}$-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°[9]), in almost quantitative yield.

3-Keto-4,9-dimethyl-$\Delta^{4,6}$-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[9]]. Its 2,4-dinitrophenylhydrazone melted at 214° (reported[1a] m.p. 216°; m.p. 212–214°[9]) 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

(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.

compound was prepared in an analogous manner from carbobenzyloxyvanilloyl chloride and creosole in 91% yield. Recrystallization from ethanol yielded white powdery crystals melting at 135°.

Anal. Calcd. for $C_{24}H_{22}O_7$: C, 68.24; H, 5.25. Found: C, 68.32; H, 5.34.

2,4,5-Trichlorophenyl carbethoxyvanillate. This compound was prepared by the general method outlined for phenyl vanillate in the past[5] and was obtained as white crystals from ethanol melting at 133°.

Anal. Calcd. for $C_{17}H_{13}O_6Cl_3$: C, 48.64; H, 3.12. Found: C, 48.66; H, 3.22.

2,4,5-Trichlorophenyl vanillate. A mixture of 2,4,5-trichlorophenyl carbethoxyvanillate and excess acetone and ammonium hydroxide was stirred at room temperature for 5 hr., diluted with water, and acidified with dilute sulfuric acid. The oil which separated solidified when the acetone was removed under reduced pressure. The solid was recrystallized from petroleum ether (b.p. 65–110°) to give white crystals, m.p. 104–105°, λ_{max} 222 mμ, ε 25660; λ_{max} 246 mμ, ε 8610; λ_{max} 272 mμ, ε 10250; λ_{max} 294 mμ, ε 9200.

Anal. Calcd. for $C_{14}H_9O_4Cl_3$: C, 48.38; H, 2.61. Found: C, 48.56; H, 2.47.

Ethyl carboxymethylvanillate. Ethyl vanillate[6] (294 g., 1.5 moles) was melted and treated with 145 g. (1.53 moles) of chloroacetic acid and 600 ml. of anhydrous acetone. With vigorous stirring 420 g. (3.04 moles) of anhydrous potassium carbonate was added, and a vigorous reaction took place with the separation of potassium chloroacetate. The mixture was boiled under reflux with mercury-sealed stirring for 1.5 hr. and allowed to stand at 20° for 16 hr. The solidified mass was diluted with 3 l. of water, stirred vigorously, cautiously acidified with excess dilute sulfuric acid, and extracted with ether. The ether was dried and distilled, and the residue was recrystallized from methyl ethyl ketone to give colorless crystals, m.p. 135–136°.

Anal. Calcd. for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55. Found: C, 57.06; H, 5.67.

Ethyl carboxymethylvanillate was also prepared by boiling under reflux a mixture of 1 mole potassium ethyl vanillate, 1 mole sodium chloroacetate, and toluene. The mixture was mixed with water, and the water layer was removed and acidified to yield the desired product.

Carboxymethylvanillic acid. Ethyl carboxymethylvanillate was hydrolyzed by warming with dilute sodium hydroxide solution, and the alkaline solution was acidified strongly with dilute sulfuric acid. The precipitate was recrystallized from methyl ethyl ketone to yield colorless crystals, m.p. 256–257°, λ_{max} 218 mμ, ε 17280; λ_{max} 256 mμ, ε 11020; λ_{max} 290 mμ, ε 5050.

Anal. Calcd. for $C_{10}H_{10}O_6$: C, 53.10; H, 4.46. Found: C, 53.07; H, 4.55.

Methyl carboxymethylvanillate. This compound was prepared from methyl vanillate[6] by reaction with chloroacetic acid and potassium carbonate in anhydrous acetone as described for the ethyl ester and was obtained as colorless crystals from ethyl acetate, m.p. 143–144°, λ_{max} 220 mμ, ε 18350; λ_{max} 258 mμ, ε 11720; λ_{max} 292 mμ, ε 5910.

Anal. Calcd. for $C_{11}H_{12}O_6$: C, 55.00; H, 5.04. Found: C, 54.93; H, 5.04.

Carbomethoxymethylvanillic acid. Short boiling of the crude carboxymethylvanillic acid above with anhydrous methanol in the presence of a little hydrochloric acid followed by dilution with water and recrystallization of the precipitate from methanol yielded colorless crystals, m.p. 175–176°, λ_{max} 218 mμ, ε 16500; λ_{max} 256 mμ, ε 10570; λ_{max} 290 mμ, ε 4640.

Anal. Calcd. for $C_{11}H_{12}O_6$: C, 55.00; H, 5.04. Found: C, 54.97; H, 5.12.

Ethyl methoxymethylvanillate. A solution of 400 g. (2.04 moles) of ethyl vanillate in 1500 ml. of anhydrous ether was treated with a solution of 75 g. (1.92 moles) of potassium dissolved in 1000 ml. of absolute ethanol. The white precipitate of potassium ethyl vanillate was filtered, washed thoroughly with ether, and air dried.

A mixture of 117 g. (0.5 mole) of potassium ethyl vanillate, 53 g. (0.73 mole) of chloromethyl ether, and 1000 ml. of anhydrous ether was boiled under reflux with mercury-sealed stirring for 6 hr. and allowed to cool. The mixture was extracted with dilute sodium hydroxide and then with water, and the ether was dried with sodium sulfate and distilled. The residue (44 g.) was distilled under reduced pressure to give ethyl methoxymethylvanillate as a colorless oil boiling at 202° at 1 mm. which solidified upon cooling to crystals, m.p. 65–67°. The melting point remained unchanged upon recrystallization from petroleum ether (b.p. 30–60°). The ultraviolet absorption spectrum had the following maxima: λ_{max} 217 mμ, ε 16480; λ_{max} 255 mμ, ε 11290; λ_{max} 292 mμ, ε 5280.

Anal. Calcd. for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.02; H, 6.71.

Methoxymethylvanillic acid. The above ethyl methoxymethylvanillate was boiled with ethanolic sodium hydroxide, and the alkaline solution was diluted with water and exactly neutralized with dilute hydrochloric acid. The precipitate was filtered, washed with water, and recrystallized from ethanol to yield methoxymethylvanillic acid as fine white crystals, m.p. 157–158°, λ_{max} 216 mμ, ε 16120; λ_{max} 252 mμ, ε 10540; λ_{max} 290 mμ, ε 4810.

Anal. Calcd. for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.60; H, 5.74.

N-Ethyl methoxymethylvanillamide. A mixture of 5 g. of ethyl methoxymethylvanillate and 150 ml. of 33% aqueous ethylamine solution was warmed to effect solution and allowed to stand 72 hr. at 20°. The mixture was concentrated under reduced pressure on the water bath to yield a yellow oil which solidified upon cooling. The solid was stirred with benzene and filtered. The filtrate was stirred into petroleum ether (b.p. 30–60°), and the resulting precipitate was recrystallized from petroleum ether to yield *N*-ethyl methoxymethylvanillamide as colorless crystals, m.p. 80°, λ_{max} 216 mμ, ε 20950; λ_{max} 252 mμ, ε 10770; λ_{max} 288 mμ, ε 4690.

Anal. Calcd. for $C_{12}H_{17}O_4N$: C, 60.24; H, 7.16. Found: C, 60.03; H, 7.11.

The benzene-insoluble material in this preparation proved to be the monohydrate of *N*-ethyl methoxymethylvanillamide. It was recrystallized from benzene to yield colorless crystals, m.p. 123°, λ_{max} 213 mμ, ε 18770; λ_{max} 245 mμ, ε 9500; λ_{max} 285 mμ, ε 3770.

Anal. Calcd. for $C_{12}H_{19}O_5N$: C, 56.02; H, 7.44. Found: C, 56.09; H, 7.44.

Isobutyl 5-chlorovanillate. This compound was prepared from 5-chlorovanillic acid[6] and isobutyl alcohol in the presence of sulfuric acid as described earlier[5] and was obtained as colorless needles from petroleum ether (b.p. 65–110°) m. p. 93–94°.

Anal. Calcd. for $C_{12}H_{15}O_4Cl$: C, 55.71; H, 5.84. Found: C, 55.75; H, 5.93.

sec-Butyl 5-chlorovanillate. This compound was prepared in a similar manner from sec-butyl alcohol and was obtained as white granular crystals from petroleum ether (b.p. 65–110°), m.p. 92–93°.

Anal. Calcd. for $C_{12}H_{15}O_4Cl$: C, 55.71; H, 5.84. Found: C, 55.67; H, 5.86.

n-Octyl 5-chlorovanillate. A mixture of 55 g. of 5-chlorovanillic acid, 150 g. of *n*-octyl alcohol, 1.5 g. of sulfuric acid, and 250 ml. of benzene was boiled under reflux and a water-separatory head until no more water was collected. The clear solution was distilled under reduced pressure to remove benzene and excess octanol. The residue was stirred into water, and the resulting mixture neutralized with a slurry of sodium bicarbonate. The solid was filtered and recrystallized from petroleum ether (b.p. 65–110°) to yield 85 g. of *n*-octyl 5-chlorovanillate as tiny white platelets, m.p. 90–91°.

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Anal. Calcd. for $C_{16}H_{23}O_4Cl$: C, 61.04; H, 7.36. Found: C, 61.03; H, 7.36.

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Rates of Hydrolysis of *cis*- and *trans*-3- and 4-Substituted Ethyl Cinnamates

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In an earlier investigation of the transmission of electronic effects by the cyclopropane ring[2] several *m*- and *p*-substituted *trans*-ethyl 2-phenylcyclopropanecarboxylates were prepared, and their rates of alkaline hydrolysis were measured. Several *cis* esters were subsequently obtained, and their hydrolysis rates were measured.

The *cis* esters hydrolyze about one-tenth as rapidly as the *trans* esters, as would be expected on steric grounds. However, the Hammett *rho* value for these esters is 1.014,[3] whereas, for the *trans* esters *rho* is 0.812.[2,3] This unexpected result, which may be the result of a field effect between the phenyl group and the carbethoxy group in the *cis* esters, prompted an investigation of whether similar behavior would occur in the cinnamate series. Several *cis*- and *trans*-ethyl cinnamates have now been prepared, and the rates of alkaline hydrolysis have been measured. In this series *cis* esters hydrolyze slightly slower than the *trans* esters and *rho* is also smaller. Thus, for the *trans* cinnamates *rho* is 1.314[4] and for the *cis* cinnamates, 1.122. The rates of reaction of the esters are summarized in Table I.

From the various data available (Table II) there appears to be an increasing influence of *m*- and *p*-substituents on the reactivity of the carbethoxy group in the order $-CH_2CH_2-$, $-CH(CH_2)-CH-$, $-CH=CH-$, $-C\equiv C-$, as measured by the *rho* value for ester hydrolysis. Data for the ionization constants fall in a considerably different order, only a portion of which can be attributed to solvent and temperature differences in the various studies.[5]

Recent information[6] suggests that the Hammett *rho* value of the original equation may not be an accurate measure of the transmitting ability of various groups, because of variability in the value of *sigma* for substituents capable of resonance interaction with the reaction site. A definite separation of the possible influencing factors is not possible at this time.

The ultraviolet absorption maxima of the *trans*-cinnamates are consistently at longer wave lengths and of higher ϵ_{max} than those of the corresponding *cis* esters (Table III), as has been found previously for the chloro- and dichlorocinnamic acids.[7] This is consistent with the notion of a superior conjugating system in the *trans* compounds.

TABLE I

RATES OF ALKALINE HYDROLYSIS OF *cis*- AND *trans*-ETHYL CINNAMATES IN 87.8% ETHANOL AT 30°

Substituent	*cis*-Series, $k \times 10^{3a}$	*trans*-Series, $k \times 10^{3a,b}$
4-OCH_3	0.55	0.79 (0.74)
3,4-CH_2O_2	0.78	1.09 (1.02)
Unsubstituted	1.07	1.90 (1.77)
4-Cl	2.10	3.98 (3.58)
3-Cl	2.69	6.03 (5.69)
3,4-Cl_2	4.53	8.97 —
3-NO_2	—	14.97 (13.30)
4-NO_2	—	19.08 (17.25)

[a] Liter mole^{-1} sec.$^{-1}$ Each value is the average of two or more determinations. [b] Values in parentheses are those of Kindler, ref. 4.

TABLE II

COMPARISON OF *RHO* VALUES

Series	Ester Hydrolysis (30°)	K_i (25°)
β-Phenylpropionic	0.489[a]	0.212
trans-2-Phenylcyclopropane	0.812[b]	0.182[c]
cis-2-Phenylcyclopropane	1.014[b]	—
cis-Cinnamic	1.122 ± 0.040 (0.9998)[b]	0.643[d]
trans-Cinnamic	1.314 ± 0.023 (0.9991)[b]	0.466[a]
Phenylpropiolic	1.91[e]	0.41,[f] 0.81,[g] 0.69[h]

[a] Ref. 4. [b] This work, ref. 2, 3. Figures in parentheses are correlation coefficients. [c] E. N. Trachtenberg and G. Odian, *J. Am. Chem. Soc.*, **80**, 4018 (1958). [d] Calculated from data of W. A. Roth and R. Stoermer, *Ber.*, **46**, 260 (1913). [e] At 20° J. D. Roberts and R. A. Carboni, *J. Am. Chem. Soc.*, **77**, 5554 (1955). [f] Ref. e; measured in 50% ethanol rather than in pure water as were the others. [g] M. S. Newman and S. H. Merrill, *J. Am. Chem. Soc.*, **77**, 5552 (1955); measured in 35% dioxane. [h] I. Benghiat and E. I. Becker, *J. Org. Chem.*, **23**, 885 (1958); measured in 50% ethanol at 24°.

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